# The mobilisation of polycyclic aromatic hydrocarbons (PAHs) from the coal-tar lining of water pipes

M. Maier*†§, D. Maier‡§ and B. J. Lloyd†, †*University of Surrey, School of Engineering in the Environment, Centre for Environmental Health Engineering, Guildford GU2 5XH, Surrey, UK;* ‡*University of Karlsruhe, Faculty for Chemical Engineering, Engler-Bunte-Institute, Richard Willstätter Allee 5, 76131 Karlsruhe, Germany;* §*Stadtwerke Karlsrule, Daxlander Strasse 72, 76185 Karlsruhe, Germany*

ABSTRACT: The use of coal-tar as an internal lining for corrosion protection of water pipes was a common procedure from the 19th century up to the mid-1970s. It is reported that these coatings can lead to elevated concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in the distributed drinking water. The aim of the project was to investigate the processes and mechanisms responsible for the occurrence of these substances in drinking water distribution systems.

The results achieved in that research project showed that the occurrence of PAHs in a drinking water distribution system was linked to the presence of chlorine and chlorine dioxide used for common disinfection practice. In laboratory experiments it could be shown that the coal-tar surface represents a substrate for the growth of biofilms which exhibits protective effects. Generally, hostile environmental conditions for microbiological activity of the biofilm such as disinfection, stagnation periods and anaerobic conditions could be identified as important factors which favour the occurrence of PAHs in drinking water. Immediately after stagnation periods an increase of PAH concentrations was observed. Moreover, it was clearly shown that disturbances in the hydraulic regime such as water hammers, operation of valves and rapid increases in flow velocity can result in enhanced PAH concentrations by the destabilisation of the biofilm matrix or high shear forces affecting the pipe walls resulting in the release of particles highly contaminated with PAHs which may be responsible for the contamination of the drinking water.

## INTRODUCTION

The use of coal-tar was a very common procedure for corrosion protection of cast iron and steel water mains. Although the installation of new coal-tar lined pipes ceased in Europe in the mid-1970s, cases of the violation of the EC-Guideline value for carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) in drinking water have been reported world-wide [1–6]. In some cases the water supply had to be interrupted for a certain period and the customers were supplied with drinking water from mobile water tanks. The requirement for further research in that area was asked by the World Health Organisation (WHO) because the total exchange of these coal-tar coated pipes is not possible [7].

The development of the PAH concentrations during disinfection processes in different water supply zones during a monitoring programme showed that PAH concentrations exceeding the EC-Guideline value for PAHs were detected only in zones were chlorinated drinking water was distributed.

The influence of different factors as microbial biofilms on the internal pipe walls, the sloughing of biofilm and/or release of particles from the encrustation, the dissolving effect of trilialomethanes, and perturbations of the hydraulic regime in the mobilisation process was investigated in laboratory experi-

ments as well as in a pipe rig and in field investigations. The overall objective of the research programme was to investigate the principal mechanisms for the occurrence of PAHs in water distribution systems which were unknown up to the present and to recommend operational procedures to optimise water distribution and treatment whilst minimising the mobilisation of PAHs.

## MATERIALS AND METHODS

### Analytical methods

The analysis of PAHs comprised the detection of fluorene, fluoranthene, phenanthrene, anthracene, pyrene, chrysene, benz[a]anthracene, dibenz[a]hlanthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene according to the DIN 38 407–178 standard using HPLC technique (HP 1090) whereas the volatile hydrocarbons (VOC) were detected with a gas-chromatographic method according to DIN 38 407, part 4 with a GC HP 5890.

The physico-chemical parameters were determined using a WTW OXI-96- (dissolved oxygen), a LF 91-KLE 1/T- (conductivity), a TESTO 252/04 and a WTW pH96–97T device (pH-value).The determination of the free residual chlorine concentration was carried out according to the regulations of the DIN

*Correspondence: E-mail: matthias.maier@karlsruhe.de

38 408-G4 (Aldos-Alcon Test 310), the turbidity was measured according to the ISO 7027:1990 with a nephelometric method using a Hach 2110 P turbidity meter.

A Cadas 100 photometer was used for the determination of the following components: dissolved iron, test kits LCK 521 and LCK 321; manganese, LCW 032; and nitrate, LCK 339. The quality of the rapid screening tests were examined by parallel determinations using ion chromatography (Dionex 100) according to DIN 38 405-D19.

## Field investigations

As a result of an extensive monitoring programme comprising the investigation of 22 water supply zones with a length 834 km where 50% of the pipes were laid prior to 1972 further field investigations were carried out in a selected water supply zone which provided the possibility of changing the water source fed into the system from chlorinated water (water A) to a water which needed no disinfection (water B). The effect of the use of chlorine and chlorine dioxide was studied during five experiments where the dosage of free residual chlorine of the disinfectant ranged from 0.025 mg/L to 0.3 mg/L. The disinfection periods ranged from 11 days to 444 days.

## Pipe rig experiments

The experimental pipe rig (Fig. 1) consisted of cast-iron coal-tar lined pipes in three sections with a length of approximately 10 meters each. The pipes of the first section (Ø100, operation 1968–95) were obtained from an area where unchlorinated water was distributed (water B). A thick formation of a $CaCO_3$–rust layer complex was present on the internal coal-tar lining. The pipes installed for the second section (Ø100, operation 1963–95) were dismantled from the water distribution system which was used for the field investigations (water A)

which showed a thin encrustation on the internal surface. The pipes of third section (Ø150) were in storage since the year of their production in 1968 and were used as a reference for 'new' pipes. The internal surface of the coal tar coating was relatively undamaged.

The pipe rig was connected to a trunk main where unchlorinated water was distributed. The water was fed into a loop manifold in order to guarantee equal supply volume to every water pipe integrated into each section. As shown in Fig. 1, before the inlet of the water into the loop a dosage point M1 for the application of different additives was installed. Four of these ten 19 mm water taps (Mx) were selected for periodic water sampling after the water had travelled through the pipes (M4, M7, M10). The control sample point (M0) was installed before the water passed the loop.

The pipe rig was operated with different flow velocities and different additives like the disinfectants chlorine and chlorine dioxide as well as sodium sulfite, hydrochloric acid, and chloroform. The production of steady state hydraulic conditions gave the possibility to study the effect of the changes in the water quality due to the dosage of the additives shown in Table 1 as well as the influence of changes in the general hydraulic conditions.

## Biofilm experiments

In Preparation of the Biofilm experiments stainless steel slides (175 × 20 × 1.5 mm) were coated with that material according to procedures reported in the literature which was applied when dipping the water mains [8]. Therefore the slides were heated and coal-tar was applied (100 °C) of 0.2–0.3 mm thickness using a spatula. The material for coating stainless steel slides was obtained by scraping it from water pipes which were in storage the last decades. Together with blank stainless steel control slides they were inserted in a stainless steel water test
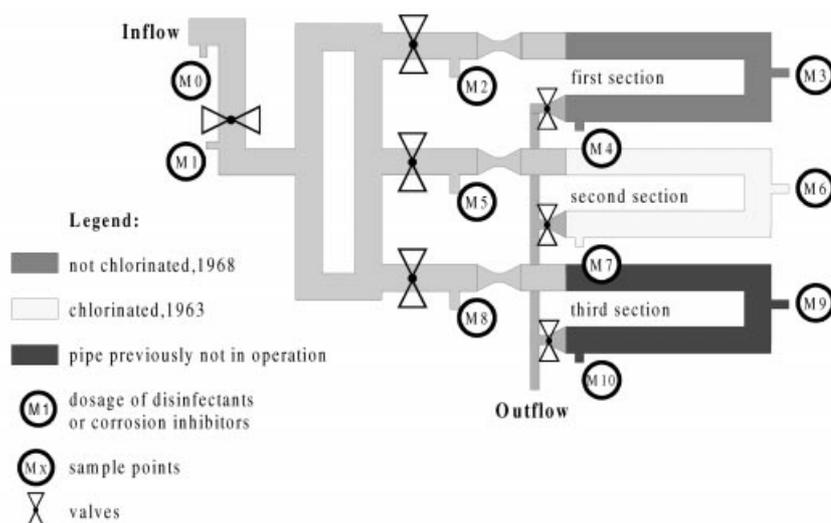


**Fig. 1** Schematic diagram of the pipe rig.

| Phase no. | Duration (days) | Flow velocity (m/s) | Dosage (mg/L) |
|---|---|---|---|
| 1 | 63 | 0.1 | none |
| 2 | 28 | 0.1 | 0.3 chlorine |
| 3 | 34 | 0 | none |
| 4 | 48 | 0.1 | none |
| 5 | 5 | 0.01 | none |
| 6 | 45 | 0.002 | none |
| 7 | 36 | 0 | none |
| 8 | 34 | 0.01 | none |
| 9 | 37 | 0.01 | 0.3 free res. chlorine |
| 10 | 60 | 0.01 | none |
| 11 | 30 | 0.01 | 40 mg/L $Na_2SO_3$ |
| 12 | 69 | 0.01 | none |
| 13 | 39 | 0.01 | 0.4 chlorine dioxide |
| 14 | 53 | 0.01 | 0.2 chlorine dioxide |
| 15 | 28 | 0.01 | none |
| 16 | 22 | 0.01 | 0.3 chlorine |
| 17 | 7 h | 0 | chlorine |
| 18 | 5 | 0.01 | chlorine |
| 19 | 1 | water hammer | none |
| 20 | 3 | 0.01 | chlorine |
| 21 | 30 | 0.01 | 1.2 chlorine |
| 22 | 1 | 0.01 | none |
| 23 | 4 | cutting pipe samples | – |
| 24 | 14 | 0.01 | none |
| 25 | 7 | 0.01 | hydrochloric acid to pH = 5 |
| 26 | 7 | 0.01 | hydrochloric acid to pH = 4 |
| 27 | 21 | 0.01 | hydrochloric acid to pH = 3 |
| 28 | 84 | 0.01 | none |
| 29 | 9 | 0.01 | 0.9 chloroform |
| 30 | 5 | 0.01 | none |

**Table 1** Pipe rig experiments—operational phases of the pipe rig

basin (800 × 350 × 400 mm) which was continuously supplied with drinking water (Q = 20 1/h, temperature 13 °C) in order to colonise the surfaces with a biofilm. The main carbon source for the supply of micro-organisms with nutrients was the coal-tar on the slides and the drinking water fed into the basin.

For the determination of the microbiological parameters of the biofilm grown on the slides the biomass was removed with a sponge rubbing in different directions to reach also crevices and depressions in the coal-tar coating. After this procedure the sponge was washed with 25 mL of sterile filtered and auto-claved water. The cell number was determined using this suspension [9]. The HPC on R2A agar was determined after Reasoner & Geldreich [10]. The total cell number was examined by an epifluorescence technique following a proposal of Hobbie *et al.* [11]. The number of PAH degrading bacteria was determined after Stieber *et al.* [12] with an MPN-technique. The determination of the total number of the heterotrophic bacteria is based on the most probable number method (MPN) after [13,14] in sterile microtitre plates (Nunclon Delta, Nunc, Denmark).

The stainless steel slides used for biofilm experiments were examined with the epifluorescence microscopy technique. Therefore these slides were removed from the water tank and treated with acridine orange (0.1 g/L Merck, Darmstadt, Germany). After a reaction time of 15 min the dye was removed with a tissue and the samples were dried in the darkness. Immersion oil (Leitz, Wetzlar, Germany) had to be added on the coal-tar surface. The dry sample had to be examined within 10 min because of the dissolving effect of the immersion oil which resulted in a considerable self-fluorescence. Therefore a method was applied where photographs of 10 areas of the slide were made. Considering the dimensions of the areas as well as the magnification of the objective and the colour print an evaluation of these photographs was made.

In addition to that Scanning Electron Micrographs (SEM) of the colonised coal-tar surface of the slides were made at the Laboratory for Electron Microscopy (Laboratorium für Elektronenmikroskopie) of the University of Karlsruhe, Karlsruhe, Germany. The device was a Cambridge Scientific Instruments, model S4–10, accelerating voltage 30 kV.

For the determination of the influence of the biofilm on the slides on the leaching of PAHs from the coal-tar coating batch experiments were carried out using brown flasks with a volume of 2 L. After running the water for 2 min the flasks were filled with nonchlorinated drinking water. One slide was inserted into the flask for 24 h which caused a surface/volume-ratio $A/V = 1.75$/m. The water was stirred by a magnetic stirrer (Variomag Mono) with a fish (Teflon, $\varnothing 4 \times 20$ mm) during the experiment. The experiments were carried out at a constant temperature of 15 °C in a fridge or in a water-bath with equipment for magnetic stirring (Fritz Grössner GmbH). The flasks were closed only with an aluminium foil to avoid a oxygen deficit in the flask. To prevent photooxidation of the PAHs all experiments were carried out in darkness.

The reactor experiments were carried out using a circular Reactor (Biosurface, Rotating Annular Reactor, Model 920LG, Bozeman, Montana). This system allowed the installation of 12 stainless steel slides 175 mm × 17.5 mm in size with a thickness of 1.5 mm. The water volume in the reactor was 1.2 L The slides had a surface of 367.5 cm² which results in a surface/volume ratio of 30.6/m. These slides were coated one-side and could be removed without draining the reactor system. The reactor was operated with a rotation velocity of 100 r.p.m. and a flow rate of $Q = 1.5$ L/h (Prominent-Pump gamma/4).

The encrustation of coal-tar lined pipes of the pipe rig which were previously in use for a period of more than 30 years was analysed for the content of PAHs and the biofilm was examined using Scanning Electron Microscopy (SEM) at the Max-Planck Institute for Material Research, Stuttgart, Germany, in association with the IWW Mülheim/Germany. The sublimation technique for dehydration on biofilm samples was proposed by Griebe & Flemming [15]. The samples were coated with a layer of gold using a cation bombardment method before the SEM micrographs were taken using a Joel 6400/JSM with a JXA microprobe.

## RESULTS

### Field investigations

The use of different concentrations of chlorine and chlorine dioxide as disinfectants in the selected water supply zone confirmed the observation that the occurrence of PAHs in distribution systems is clearly linked to the dosage of chlorine or chlorine dioxide. The dependence was reproducible on every occasion in 15 experiments, and PAH-free drinking water could be achieved when the disinfection was stopped.

The development of the PAH concentrations during the dosage of chlorine showed that within one week after the dosage of chlorine started at the 231st day the PAH concentrations increased from below the detection limit up to 227 ng/L. The average PAH concentrations amounted to 229 ng/L with a variation from 227 ng/L during the start phase and 357 ng/L on the last day of the experiment. Two days after the end of the chlorine dosage at the 247th day the PAH concentrations showed a reduction of 88 ng/L. This reduction was 206 ng/L 10 days after the chlorination had ceased. PAH-free conditions were obtained after 14 days.

A comparable development of the PAH concentration was observed during the dosage of chlorine dioxide (Fig. 2), where even one day after the start of the disinfection at the 379th day elevated PAH concentrations of 93 ng/L were detected, although during the previous phase comprising 115 days without disinfection no PAHs could be observed. During this disinfection period of 11 days the PAH concentrations increased up to 626 ng/L with an average value of 313 ng/L.
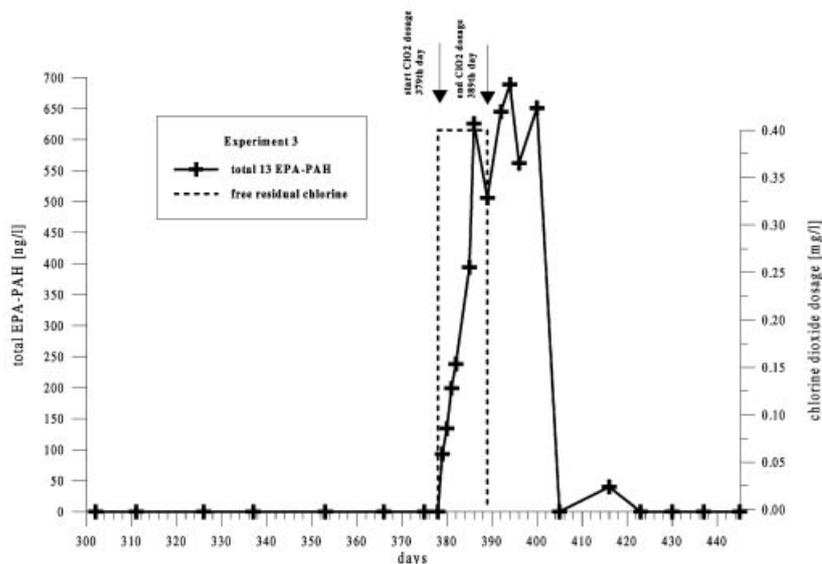


**Fig. 2** Field experiments—development of the PAH concentrations during the chlorine dioxide period.

The level of the PAHs resulting from the chlorine dioxide dosage was higher than that achieved using chlorine. The impact of the disinfection period with chlorine dioxide was much more sustained than with chlorine because elevated PAH concentrations occurred after the cessation of the disinfection period in the range of 650 ng/L for 10 days. The maximum value achieved during this experiment was 689 ng/L.

In every experiment the pattern of the development of the PAH concentrations could be divided into three phases: firstly, a very rapid increase phase immediately after the dosage of a disinfectant started, secondly a stabilisation phase where the PAH concentrations reached values of more than 200 ng/L and a phase of slowly decreasing PAH concentrations within a period of two weeks after the chlorination had ceased.

Moreover, further experiments showed clearly, that the concentration of the free residual chlorine is linked to the level of the PAHs found in the drinking water. Lower PAH concentrations could be produced by the reduction of the dosage of the free residual chlorine from 0.12 mg/L down to unchlorinated water in four steps. After every single reduction (0.12/0.06/0.04/0.025/0 mg/L) of the chlorine dosage the average PAH concentrations could be reduced from values of 395 ng/L to 273 ng/L after the first reduction of the chlorine dosage to 74 ng/L in the third step and 59 ng/L in the fourth step until PAH-free conditions could be achieved nine days after the chlorination ceased. This dependence could also be proved by a period using different steps of increasing concentrations of free residual chlorine.

The PAH profile was characteristic in every experiment: The predominant PAHs were phenanthrene which represented about 40% of the PAHs investigated, followed by fluorene and fluoranthene showing 20–30%. Fluoranthene and phenanthrene were the only PAHs which reached values of 80–100% of the total PAH concentration in a few samples. Pyrene occurred in more than half of the water samples taken and represented about 5–10% of the total PAH concentration. Anthracene, chrysene and benz[a]anthracene occurred only sporadically in minor concentrations.

### Pipe rig investigations

The dependence of the occurrence of the PAHs from the dosage of chlorine and chlorine dioxide could be verified during all pipe rig experiments. The PAH profiles observed were comparable to that achieved during the field investigations.

Additional experiments using sodium sulfite ($Na_2SO_3$) as an oxygen reducing agent in the pipe rig showed, that elevated PAH concentrations could be observed immediately after the oxygen concentrations decreased to values which produced conditions hostile to the aerobic microbial activity of the biofilm on the pipe walls. After the dosage of $Na_2SO_3$ commenced at the 392nd day, the concentrations of dissolved oxygen at the sample point M7 decreased rapidly down to values of 0.5 mg/L within the next two days (Fig. 3). Afterwards, the oxygen concentrations decreased continuously and produced an oxygen-free environment after 23 days in all three pipe line sections. During that period of anaerobic conditions enhanced PAH concentrations were detected at all sampling points in the system. PAHs could not be detected until the oxygen-free conditions were reached. The maximum PAH concentration during that period was 240 ng/L at M7, the lowest concentration was observed at M4 exhibiting 80 ng/L. The dosage ended at the 421st day. Associated with the decreasing oxygen concentrations causing the mobilisation of PAHs an increase of the turbidity and the iron concentrations was observed during that period. The increase was not as high as during the stagnation periods, but a significant enhancement was noticeable. The turbidity and the iron concentrations
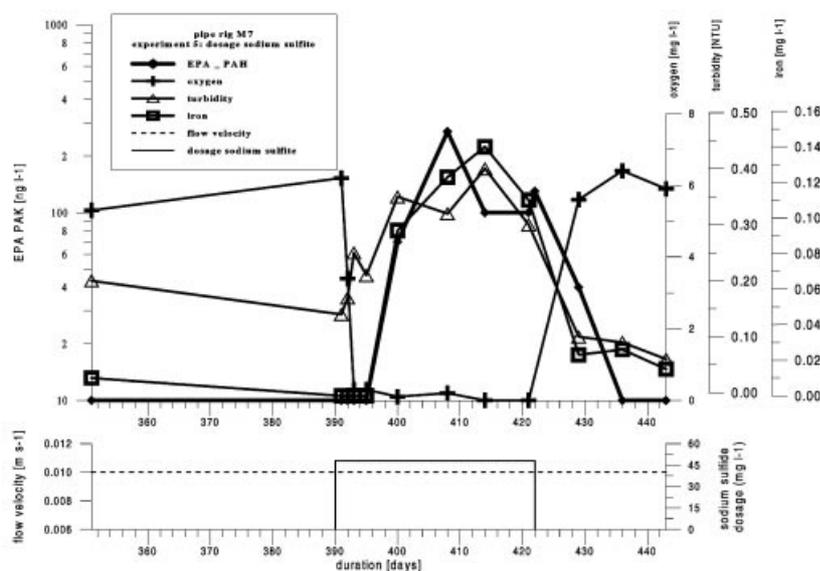


**Fig. 3** Pipe rig investigations—dosage of sodium sulfite, sample point M7—effect on the PAHs, oxygen, iron concentrations and turbidity.

reached values which were approximately seven times higher than that found under normal conditions.

The rapid decrease of the pH value from pH 7 to pH 3 in three steps by the dosage of hydrochloric acid resulted in a mobilisation of PAHs. A pH value of 5 for 7 days resulted in slightly elevated PAH concentrations. A pH value of 4 for a period of 7 days resulted in an further increase of the PAH concentrations. The highest concentrations were observed at M4 with 115 ng/L when the pH value was reduced to 3. The results clearly indicate, that the sudden production of conditions hazardous to biofilm leads to elevated PAH concentrations. The PAH concentrations started to decrease when the pH value reached a neutral value. PAH free water was analysed at M7 one day after the dosage of hydrochloric acid ceased. In both cases significantly enhanced turbidity values and iron concentrations were observed.

The presence of chloroform as a trihalomethane in a concentration up to 3700 µg/L had no effect on the mobilisation of PAHs. This compound was selected because it occurs as a disinfection by-product during the chlorination and it acts as a good solvent for coal-tar. The results clearly indicate, that the dosage of chloroform was not able to promote an increase of the PAH concentrations at M4 and M7 because all determinations made were below the detection limit. This is also valid for M10 with the exception of one sample in which a total PAH concentration of phenanthrene (11 ng/L at a detection limit of 10 ng/L) was found. This concentration can be regarded to be insignificant as an effect due to the dosage of chloroform.

The development of the PAH concentrations during a stagnation period after the reduction of the flow velocity revealed that quiescent water accompanied by anaerobic conditions in the system, is able to cause elevated PAH values. Further investigations indicated that even stagnation periods of only 7 h ('night stagnation') of the water in the pipe rig resulted in such enhanced PAH concentrations.

The stepwise reduction of the flow velocity of the unchlorinated water shown in Fig. 4 from 0.1 m/s (127th to 174th day) passing a short period of 0.01 m/s (175th day to 179th day) and down to 0.002 m/s (180th to 224th day) revealed, that changes in the hydraulic conditions may have an effect on the occurrence of PAHs in the distribution system, but that a slow flow velocity alone does not necessarily produce elevated concentrations of PAHs. The contact time of the water with the coal-tar lining was increased during that period from 100 s at 0.1 m/s to 5000 s at a flow velocity of 0.002 m/s which was not able to enhance the PAH concentrations in the water sampled in any of the three sections during the first 39 days. Only a change in the hydraulic regime in the pipes was able to increase PAHs concentrations during the reduction of the flow velocity from 0.1 m/s to 0.01 m/s in all three sections.

On the first day of the stagnation period (225th day) no PAHs were detected whereas after one day of stagnation, a slight enhancement of the PAH was observed at M4 and M7; M10 seemed to be unaffected during the following 24 h. Two days after the reduction of the flow velocity to zero, the stagnation resulted in extremely high PAH concentrations at all sampling points. The maximum value was reached at M10 with 135 000 ng/L, followed by M7 exhibiting a total PAH concentration of 129 000 ng/L and M4 with 55 800 ng/L. The development of the PAH concentrations was similar to that in the disinfection experiments and to those found during the field investigations. It was also characterised by a rapid enhancement of the PAHs in the beginning followed by a plateau phase after a certain time. After the end of the stagnation period at the 260th day the PAHs decreased at a much slower rate than the increase which had been recorded at the beginning.
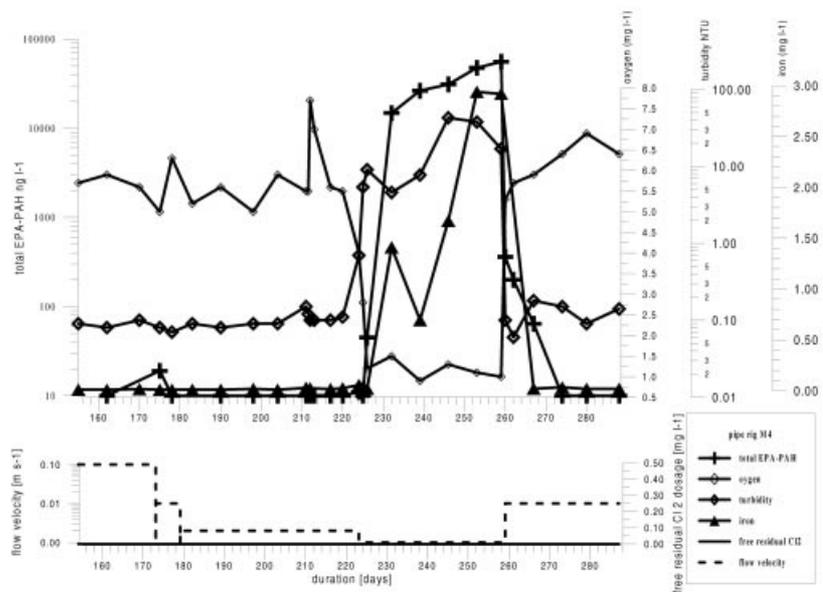


**Fig. 4** Pipe rig experiments—stepwise reduction of the flow velocity from 0.1 m/s to 0.002 m/s and stagnation of non-chlorinated water—development of the PAHs, oxygen, turbidity, iron.

The increase of the PAH concentrations was clearly associated with an increase of the turbidity values immediately after the stagnation commenced. Iron and manganese showed a distinct increase, whereas the oxygen and nitrate concentrations decreased below the detection limit.

The effect of water hammers in water distribution systems was also investigated. Therefore the pressure in the pipes was decreased to atmospheric level followed by opening a valve connected to the system very quickly which caused pressure waves ranging from 4.5 to 7 bar. The experiment was repeated four times. It could be clearly shown, that the occurrence of pressure waves produced PAH concentrations far higher than the EC-guideline value of 200 ng/L. Further, with the exception of anthracene, all 13 EPA-PAHs analysed could be detected in the pipe rig during the experiment (Fig. 5). The maximum concentrations reached values of 1123 ng/L. Benzo[a]pyrene occurred in a concentration of 68 ng/L. The removal of the turbidity using a filtration process resulted in a complete reduction of the PAH concentrations in two of the pipe line sections. The examination of the turbidity showed, that the major amount of the turbidity-particles consisted of iron, magnesium and calcium, elements which were found in the rust-layer of the internal pipe walls. The iron particles may be mainly produced by the iron bacterium *Gallionella* which was found using SEM micrographs from the rust layer of the pipes. Biofilm on the internal walls of the pipes can exhibit a sink for such particles due to its protective characteristics. The PAHs adsorbed onto these particles can lead to elevated concentrations in drinking water if mobilised by the processes named above. The analysis of the encrustation showed, that the rust-layer is highly contaminated with PAHs values up

4260 000 ng/L (Table 2). The predominant PAHs found in the water samples were the same as analysed in major concentrations in the turbidity particles of the water hammer experiment as well as in the rust-layer. The examination of the percentage of the PAHs adsorbed onto particles during all pipe rig experiments revealed that up to 75% of the PAHs measured were adsorbed onto particles and could be removed by a filtration process. If these particles from this rust layer are mobilised due to the attack of perturbations in the hydraulic regime (changes in flow direction, water hammers) or as a result of a decrease in the microbiological activity due to the presence of a biocide, a contamination of the drinking water is very likely.

### Effect of a biofilm on coal-tar coated slides

The examination of the biofilm removed from the coal-tar coated slides of the water tank after a residence time of 4, 8, 26 and 32 weeks for the total cell number, the HPC on R2A agar, and the total number of heterotrophic bacteria showed clearly that a significantly higher number of bacteria can grow on the coal-tar compared with stainless steel control slides. PAH degrading bacteria reached values of $2 \times 10^2$ cells/cm$^2$ with a maximum at $7.7 \times 10^2$ cells/cm$^2$. None of these PAH degrading bacteria could be observed on the control slides during the whole experiment. The percentage of the PAH degrading bacteria showed a significant increase in relation to the cells grown on R2A. After 4 weeks the proportion of the PAH degrading bacteria amounted to 1/1000 of the number of heterotrophic bacteria grown on R2A agar, whereas the percentage reached a value of 1/3 after 32 weeks. This result
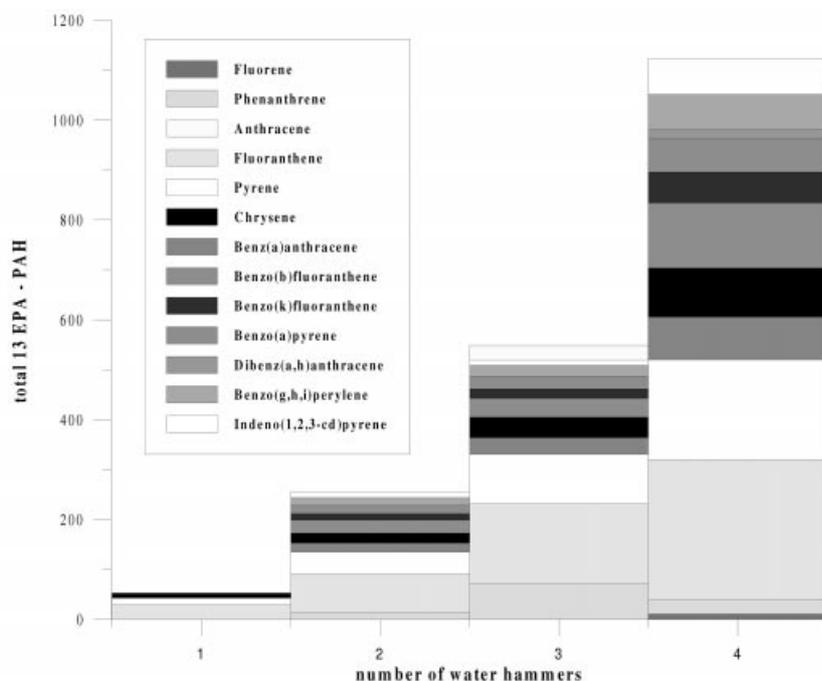


**Fig. 5** Water hammer—effect of the number of water hammers on the occurrence of PAHs at sample point M4 of the pipe rig (concentrations in ng/L).

**Table 2** PAH concentrations of the encrustation of the pipes installed in the pipe rig

| Polycyclic aromatic hydrocarbons (ng/kg) | DL | Pipe number | | |
|---|---|---|---|---|
| | | M4 | M7 | M10 |
| Fluorene | 10 | * | * | * |
| Phenanthrene | 10 | 50 000 | 160 000 | 700 000 |
| Anthracene | 10 | 14 000 | 36 000 | 640 000 |
| Fluoranthene | 10 | 106 000 | 640 000 | 1 100 000 |
| Pyrene | 10 | 56 000 | 440 000 | 670 000 |
| Benzo(a)anthracene | 10 | 16 000 | 300 000 | 370 000 |
| Chrysene | 10 | 20 000 | 300 000 | 280 000 |
| Benzo(b)fluoranthene† | 10 | 13 000 | 220 000 | 170 000 |
| Benzo(k)fluoranthene† | 10 | 5000 | 12 000 | 80 000 |
| Benzo(a)pyrene† | 10 | 10 000 | 192 000 | 130 000 |
| Dibenz(ah)anthracene | 10 | nd | 26 000 | 10 000 |
| Benzo(ghi)perylene† | 10 | 7000 | 128 000 | 60 000 |
| Indeno(1,2,3-cd)pyrene† | 10 | nd | 122 000 | 50 000 |
| Six indicator PAHs EC-guideline | – | 141 000 | 1 314 000 | 1 590 000 |
| Total EPA PAHs | – | 297 000 | 2 576 000 | 4 260 000 |

* Sample volume not sufficient for determination.
† Six indicator PAHs of EC-Guideline (1980).

indicates, that for the group of PAH degrading bacteria no limitation of the available nutrients or oxygen under conditions prevalent in drinking water distribution systems occurred. Moreover, it could be proved that coal-tar is a sufficient substrate for the formation of a biofilm where PAH degrading bacteria can be found.

The cell counts using epifluorescence microscopy confirmed the observation that the coal-tar coated slides were highly colonised by micro-organisms. The examination showed a colonisation of the slides with single cells in the first two weeks. The first colonies on the coal-tar surface were observed during the third week, followed by a formation of larger colonies during the next weeks up to values of $1.5 \times 10^6$ cells/cm$^2$. Probably as a result of an increase of the EPS-production, the cell colonies grew in a perpendicular direction to the surface of the slides from the 7th week onwards (Fig. 6). Due to the multilayered biofilm system a cell count was not possible after the sixth week. Very complex formations of cell colonies could be observed until the 29th week, which grew further after the end of the experiment. The biofilm consisted at this time of cell colonies which may be embedded in EPS and noncolonised spots within this biofilm. Single cells as observed in the first weeks were scarcely found. In contrast, the stainless steel



**Fig. 6** Biofilm experiments—coal-tar coated slide after 7 weeks in the water basin, magnification ×900.

control slides were only sparsely colonised mostly by single cells during the whole period of the experiment.

### SEM micrographs of the biofilm

Further investigations of the biofilm on the coal-tar coated slides using SEM micrographs were made. The slides were examined after a residence time of 12 weeks in the water tank. These SEM micrographs revealed, that there is a great variation of organisms which colonised the coal-tar tar surface from sparsely distributed single cells to accumulations of cells in microcolonies. On one micrograph a testate amoeba was discovered grazing the cells grown on the coal-tar surface.

### Batch experiments

Coal-tar coated slides were removed from the water tank after a residence time of 14, 17, 19, 25 and 26 weeks. After this first leaching experiment the biofilm was removed from the coal-tar surface and the leaching experiment was repeated a second time. All slides showed colonisation with a biofilm which was developed corresponding to the residence time of the slide in the tank.

For the first time it could be shown that the biofilm grown on such a coal-tar surface has a protective effect because significantly higher PAH-concentrations could be detected after the removal of the biofilm from the slides. The relative change in PAH concentration for selected slides is depicted in Fig. 7 (positive numbers = increase, negative numbers = decrease). The PAH concentrations of the slides covered with a biofilm ranged between 170 and 1400 ng/L, whereas after the removal of the biofilm higher PAH concentrations between 610 and 6100 ng/L were detected. More than 80% of the PAH concentrations of the water samples taken after removing the biofilm were extremely higher than in the first water sample using the slides which were covered with a biofilm grown in low nutrient drinking water. The statistical evaluation of the data using the *t*-test for dependent samples confirmed the significance of this effect.

Further batch experiments using chlorinated water clearly indicated, that the exposure of the coal-tar coated slides to chlorinated water resulted in enhanced PAH concentrations in most of the samples within the next two experiments. The maximum concentration occurred during the chlorination experiments with 9700 ng/L.

### Biofilm reactor experiments

The reactor was operated with nonchlorinated drinking water for the first 11 days. This phase was followed by a chlorination period with a chlorine dosage of free residual chlorine of 0.3 mg/L from the 12th to the 23rd day. One day after the chlorination started the PAH concentrations increased to 500 ng/L. During the whole chlorination period the PAH concentrations reached values of 350–450 ng/L. After the chlorination ceased, a decrease of the PAH concentrations during the next three weeks to values of 100–150 ng/L could be observed.

The development of the PAH concentrations in that experiment was in an unequivocal agreement with the results of field investigations carried out by Maier [16] in real distribution systems (Fig. 2): the chlorination of coal-tar coated surfaces lead to a rapid increase in the PAH concentrations which reached a stable value and decreased slowly after the end of the chlorination period. This increase may be a result of the destabilisation of the biofilm matrix due to the disinfectant which results in enhanced PAH concentrations.

### Investigation of coal-tar coated pipes from a pipe rig for biofilm colonisation

In addition to the laboratory experiments, the colonisation of the internal pipe walls of the pipe rig was examined. For this purpose, pipes from a pilot scale pipe rig were dismantled and pieces of each pipe were cut down. Generally, the water content of the encrustation ranged from 24 to 55% showing a HPC on R2A from $5 \times 10^7$ to $2 \times 10^8$ cells/g. The microscopic examination showed areas where the encrustation was of a regular shape colonised by single rod-shaped bacteria and brownish-black particles which exhibited a structure typical for bacteria
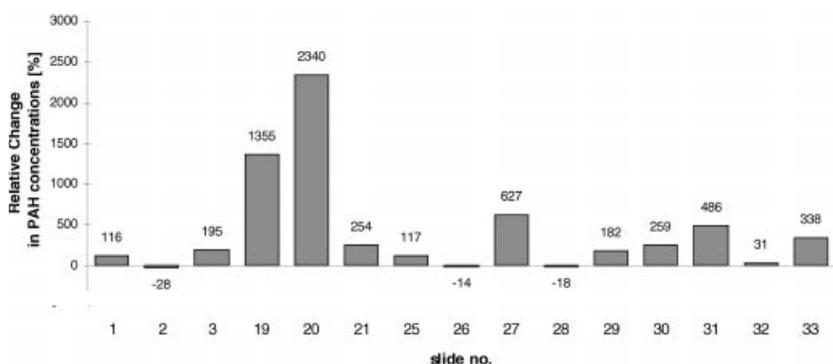


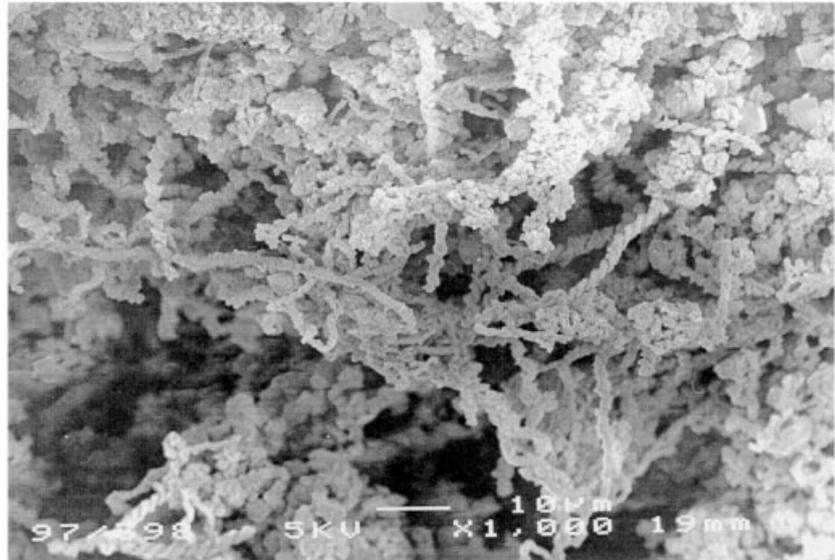**Fig. 7** Batch experiments—relative change in the PAH concentrations after removing the biofilm.

**Fig. 8** Biofilm rxperiments—SEM-micrograph exposed to coal-tar, characteristic products of iron-oxidising bacteria, magnification ×830.

releasing iron-compounds such as *Gallionella*. This observation was confirmed using SEM-micrographs (Fig. 8).

### DISCUSSION

Based on the results of the experiments presented above the following principal mobilisation processes (Fig. 9) were proposed:

The occurrence of PAHs in drinking water distribution systems may be determined by complex processes but the major factors which were found to influence the mobilisation of PAHs are as follows:

Firstly, the presence of a hostile environment for micro-organisms such as the presence of a disinfectant or when the oxygen supply is interrupted due to stagnant water. In these cases the biofilm on the internal pipe walls and in the water channels of the rust layer may be destabilised which results in a release of particles into the water containing a high amount of PAHs.

Secondly, rapid disturbances in the hydraulic regime (for example water hammer, rapid increase in flow velocity, change in the flow direction) can attack the biofilm matrix as well as deposits and particles on the pipe walls by mechanical shear forces. This may also result in the release of particles into the water bulk which can contaminate the drinking water. These particles embedded in the biofilm matrix are directly in contact with the coal-tar lining which may result in adsorption of PAHs on the surface of the particles. If hostile microbiological conditions occur, these particles will be released into the water.

Thirdly, spots were found in the pipe rig where no rust layer was present. The SEM micrographs showed that these spots were highly colonised by micro-organisms. A concentration gradient between the drinking water and the coal-tar leads to a diffusion of PAHs from the coal-tar lining into the water until the area is covered with a biofilm showing protective characteristics.

The main mechanism which is supposed to lead to enhanced PAH concentrations is the release of particles into the water
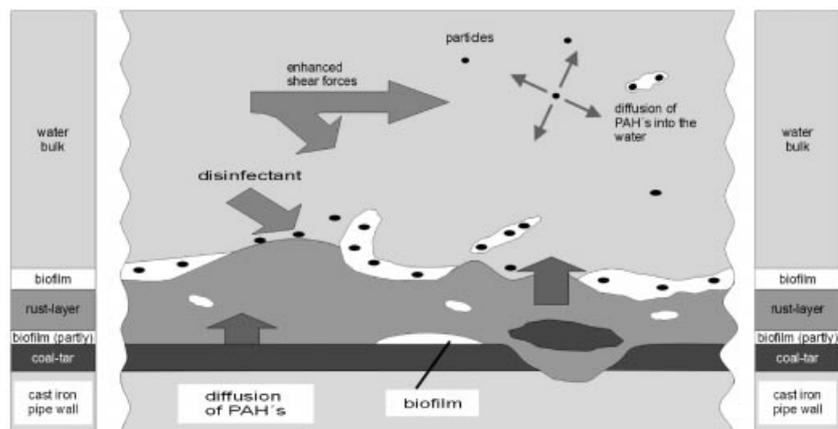


**Fig. 9** Proposed 'mobilisation mechanism' in the pipe environment to account for PAHs presence in the drinking water.

which contain a high amount of PAHs adsorbed on their surfaces. Due to the enhanced iron concentrations during the periods of elevated PAH concentrations the origin of a certain amount of these particles can be the result of iron oxidising bacteria *(Gallionella)*. If these particles are present in the water bulk a contamination of the drinking water by diffusion of the PAHs into the water is very likely.

It is the first time that the principal processes leading to elevated PAH concentrations from coal-tar lined water mains are investigated in laboratory experiments, in a pilot-scale pipe rig and in a real distribution system [16,17]. The mobilisation processes presented above are in correspondence with the little number of publications on the occurrence of elevated PAH concentrations, for example the observation of Crane *et al.* [5] who found that particles from deposits in coal-tar lined water mains exhibit high PAH concentrations. The presence of biofilms and iron oxidising bacteria in drinking water distribution systems was described by Ridgway & Olson [18] using SEM-micrographs. Moreover, the results are confirmed by the fact, that differences in PAH-levels were observed in water supply when the disinfectant was changed from gaseous chlorine to chlorine dioxide [19].

Further research should be carried out in the area of the composition of the biofilm/rust-layer system to determine the contribution of the different components to the mobilisation of PAHs. The characterisation of the microbiological and chemical conditions at the transition area of the pipe wall to the water phase as well as the composition of the particles, their size and adsorptive characteristics is necessary.

## CONCLUSIONS

Based on the findings reported here the following recommendations are made:

The dosage of a disinfectant should be orientated to the necessity of its application. Concentrations of chlorine as a disinfectant between 0.3 mg/L and 0.025 mg/L chlorine resulted in enhanced PAH concentrations. The use of chlorine dioxide lead to the highest PAH concentrations observed in the field. Therefore, drinking water distribution should be carried out without a disinfection if possible. Alternative disinfection methods without a free residual, like UV-radiation, should be considered.

Changes in the hydraulic regime and water hammers should be avoided due to the mobilisation of particles containing high amounts of PAHs which are able to contaminate the drinking water and exhibit a potential for further contamination when transported to other parts of the distribution system. As shown in the pipe rig experiments, this may occur if the difference in water pressure is more than 3 bar.

The residence time of the drinking water in coal-tar lined pipes must be reduced to a minimum. Stagnation periods of more than 7 h are able to lead to elevated PAH concentrations.

Night stagnation periods exceeding this length of time should be avoided during the operation of distribution systems.

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