Bank filtration: a suitable process for the removal of iodinated X-ray contrast media?

S. Schittko, A. Putschew* and M. Jekel

Technical University Berlin; Institute for Environmental Engineering; Department of Water Quality Control; Sekr. KF 4; Strasse des 17. Juni 135; 10623 Berlin, Germany (E-mail: anke.putschew@tu-berlin.de)

* Corresponding author

Abstract After bank filtration, effluent influenced surface waters are often used as raw drinking water. It is known that high concentrations of iodinated X-ray contrast media are detectable in such surface waters and thus, more knowledge about the behaviour of the contrast media during bank filtration is necessary and the subject of investigations in this study. The adsorbable organic iodine (AOI), four widely used iodinated X-ray contrast media and four possible transformation products were quantified in an influenced lake, five groundwater wells and a drinking water well.

Under anoxic conditions the AOI as well as the concentration of the contrast media are decreased by bank filtration, whereby the AOI is decreased by 64% and the contrast media concentration can be reduced up to 95%, depending on the compound. In the raw drinking water the following average concentrations were determined: Iopromid < 20 ng/L, Diatrizoate 166 ng/L, Iopamidol 166 ng/L and Iohexol 34 ng/L. Instationary conditions during the sampling period indicate that, at least under anoxic conditions, a large part of the contrast media and transformation products, which are still iodinated, may be associated to colloids and/or humic material.

Keywords AOI; bank filtration; colloids; humic material; iodinated X-ray contrast media; iopromide

Introduction Iodinated X-ray contrast media, which are triiodinated benzene derivatives, are applied in large quantities in hospitals and practical surgeries. The world wide consumption of iodinated contrast media is about 3,500 t/a. The compounds are applied to humans to visualize organs and vessels, which otherwise do not absorb X-rays. As requested for the application, the compounds are designed to be very polar and persistent. After some hours of application the contrast media are excreted unmetabolized. With the public sewage the compounds are transported to municipal waste water treatment plants. Very often, iodinated X-ray contrast media contribute to a large extent to the adsorbable organic halogen (AOX) content of waste water treatment plant effluents (Gartiser et al., 1996). Oleksy-Frenzel et al. (1995, 2000) has developed a method for the differentiation of the AOX into AOCI, AOBr and AOI. Based on the AOI it is recognized that waste water treatment plants are not able to remove the compounds (Oleksy-Frenzel et al., 1995). Single compound analysis confirmed the persistence of iodinated compounds during waste water treatment (Ternes and Hirsch, 2000) and indicates that adsorption of the compounds in the aquatic environment can be excluded. Effluents of waste water treatment plants can be highly contaminated with iodinated compounds, e.g. up to 20 μg/L of Iopromide (Putschew et al., 2001). Even in surface waters widely used contrast media, like Iopromide, Diatrizoate and Iohexol are detectable with concentrations in the mg/L range (Putschew et al., 2000, 2001; Ternes and Hirsch, 2000). Furthermore, the iodinated compounds can be leached into ground water aquifers, where they have already been detected (Ternes and Hirsch, 2000; Putschew et al., 2000, 2001) with concentrations in the upper ng/L range. Although the iodinated X-ray contrast media show no toxicological effects (Steger-Hartmann et al., 1999), there is an ongoing
concern about the compounds in the aquatic environment, especially in raw drinking water. For this reason the potential of ozonation and advanced oxidation processes for the oxidation of the compounds and other pharmaceuticals were studied (Huber et al., 2003; Ternes et al., 2003). The removal efficiencies are poor for the ionic contrast media (Diatrizoate) and higher (up to 80%) for the non ionic contrast media (Iopromide). Oxidation products were not investigated in the studies cited above. In case of ozonation the concentration of the iodinated compounds are reduced, but the AOI remains nearly constant (Schumacher et al., 2003) and several iodinated transformation products are detectable via selective detection of organic bound iodine (Putschew and Jekel, 2003a, 2003b).

It is assumed that the AOI contamination of the aquatic environment is due to the presence of iodinated X-ray contrast media, although a large part of the AOI cannot be explained by the iodinated compounds (Putschew et al., 2000; Putschew and Jekel, 2001), e.g., in bank filtered water just 3 to 25% of the AOI were identified. All studies performed up to now indicate that the iodinated compounds must be transformed in the aquatic environment, under the assumption that the AOI represents the iodinated contrast media. Because bank filtered water is very often used as raw drinking water, the occurrence and the behaviour of the iodinated X-ray contrast media were examined at a bank filtration site, which is influenced by waste water. In particular the behaviour of the compounds was investigated, because it is possible that “unwanted” transformation products are produced, which can occur in the raw drinking water as well.

Methods
Samples
Grab samples of surface water influenced by a municipal waste water treatment plant effluent, ground water of a bank filtration transect and water from a drinking water well are analyzed. The water samples are obtained from the Berlin Water Works. All samples were filtered through 0.45 µm cellulose nitrate membranes (Satorius, Göttingen, Germany). If not analysed immediately the samples were stored in the dark at 4°C.

Standards/chemicals
Four iodinated contrast agents and four possible metabolites (purity > 99%) were used. The structures and abbreviations used are given in Figure 1. The iodinated contrast agents are from Schering AG (Berlin), except Iopamidol which was purchased from Promochem (Wesel, Germany) and the possible metabolites are from Prof. Sovak (University of California, San Diego, USA).

The methanol and acetonitrile used was gradient grade (Baker). Formic acid (purity > 98%) was purchased from Fluka (Deisenhofen, Germany). Ultra pure water was produced from deionized water by treatment in an Elga purification system (Ubstadt-Weiher, Germany).

Enrichment
Sample extraction was performed with an AutoTrace SPE Workstation (Zymark, Idstein, Germany). Disposable 3 ml LiChrolut EN (200 mg; Merck, Darmstadt) and Envi-Carb (250 mg; Supelco) cartridges were used for the sequential extraction. Before use the EN cartridges were first cleaned with ultra pure water and than activated with 9 ml methanol and 9 ml ultra pure water (pH 3.5). The Envi-Carb cartridges were treated similarly but with ultra pure water adjusted to pH 2. The samples, adjusted to pH 3.5, were first percolated with a flow rate of 10 ml/min through the LiChrolut EN material and the filtrates were collected. After adjustment to pH 2 the filtrates were percolated (10 ml/min) through the Envi-Carb material. After extraction the cartridges were dried for ca. 1 min with a stream of...
nitrogen. The compounds adsorbed on the EN material were eluted with 6 ml methanol. The Envi-Carb cartridges were eluted against extraction direction with a mixture (8 ml) of acetonitrile, ultra pure water (1:1/v:v) and a trace ammonium acetate.

The methanol extracts were concentrated to a final volume of 0.5 ml using a TurboVab II (Zymark, Idstein, Germany). The Envi-Carb extracts were concentrated to a final volume of ca. 1 ml in an automatic SpeedVac concentrator (AS 160, Savant). The concentrated extracts were combined. Under a gentle nitrogen stream the solvent was evaporated. For analysis the samples were dissolved in 0.5 ml of eluent A (see below).

**Liquid chromatography (LC)**

LC separation was carried out using a HP system (Hewlett-Packard series 1100, Waldbronn, Germany) comprising a vacuum solvent degassing unit, a binary high-pressure gradient pump and an automatic sample injector. The separation was performed on a reversed phase column (Phenomenex®: Luna 3 µm C18(2); 150 × 2 mm). A linear gradient, at a flow rate of 0.25 ml/min, was used. The solvents were A: 100% ultra pure water and B: 100% methanol both with 0.5% formic acid. The linear gradient elution program was as follows: from 1% B to 5% B in 10 min, to 25% B after 25 min; to 1% B after 27 min, which was then held for 5 min. The column oven was set to 45°C and the injection volume was 10 µl.

**Mass spectrometry (MS)**

The LC was coupled with an orthogonal Z-spray-electrospray interface to a mass spectrometer (Quattro-LC; Micromass, Manchester, UK). Drying gas (900 L/h) and nebulizing gas (85 L/h) was nitrogen generated from pressurized air (Whatman, Haverhill, USA). The desolvation temperature was 280°C and the source temperature 120°C.

Positive-ion electrospray ionization (PI-ESI) was used. The capillary voltage was 3.4 kV. The compounds were detected in the selected reaction monitoring (SRM) mode. Argon 5.0 (Messer Griesheim, Germany) was used as collision gas. The pressure in the collision cell was 1.3 × 10⁻³ mbar. The recorded product ions were determined by infusion experiments. The cone voltage was 30 volts and for Iopromide 40 volts. For more details and informations about the quantification see Putschew et al. (2001). In a difference to the cited method formic acid (see above) was used instead of trifluoracetic acid, resulting in a higher sensitivity. The limit of detection (LOD) and quantification (LOQ) was determined using spiked (0.001–5 µg/ml, 12 standards) uncontaminated surface water. The LOQ are as follows: Iopromide, Iohexol, Iopamidol, no. 6, no. 5: 20 ng/L; Diatrizoate: 50 ng/L, no7, no. 3: 100 ng/L.
Adsorbable organic iodine (AOI)

For the determination of the AOI samples are acidified to pH 2 and then enriched on activated carbon. By combustion of the activated carbon the adsorbed organo iodine is reduced to iodide, trapped in water and then analysed by ion chromatography. A detailed description of the procedure is given by Oleksy-Frenzel et al. (1995, 2000).

Results and discussion

To gain more information about the occurrence of iodinated X-ray contrast media in groundwater and to improve the knowledge about the behaviour of these compounds during bank filtration the amounts of adsorbable organic iodine (AOI) and selected iodinated X-ray contrast media were quantified in a partly closed water cycle influenced by effluent in Berlin (Figure 2). The effluent of a tertiary wastewater treatment plant, receiving hospital wastewater, is conducted via a receiving channel into a recreational lake. Close to the lake a waterwork is located producing drinking water from bank filtered lake water. The distance between the lakefront and the drinking water wells is about 100 m. The quality of the bank filtered water was examined via monitoring wells concerning AOI and X-ray contrast media. The depth of the monitoring wells varies between 20 m and 23 m, except well 3311 which is just 2 to 4 m deep. Well 3304, located behind the drinking water well (W13) provides background values. In the deep wells the concentration of the oxygen is < 0.5 mg/L (Wischnack, 2000). Over one year the lake and the transect were sampled monthly and all data were statistically evaluated using box plots.

Figure 3 shows the box plots of the AOI. The annual average AOI in the lake is 9.6 µg/L.
A decreased AOI is observed in the first observation well (3311) which is located in the lake, but very close to the lakeside. Here the annual average AOI is reduced by 25% to 6.9 µg/L. A further reduction by 50% is recognized in well 3301. In the following two wells a slight AOI increase is observed, up to 4.2 µg/L in well 3303. The AOI of the raw drinking water is 2 µg/L and thus decreased by 50% compared to the two wells (3302, 3303) located before the raw drinking water well. The background AOI (3304) is < 0.5 µg/L. The lowest AOI measured in the lake is 4.3 µg/L and the highest value is 14.7 µg/L. The varying values are caused here by different lake water input flows. The observed AOI reduction at the beginning of the bank filtration (lake to 3301: 63%) is caused probably by dehalogenation. Adsorption is excluded because in the soil/sand of well 3311 no AOI could be detected. Although there are no additional data to exclude dilution, an earlier investigation of Fritz et al. (1998) showed that boron and EDTA is nearly constant during the first part of the bank filtration passage. The wastewater indicators suppose a non diluted flow in the first part of the bank filtration (lake to 3302). On that base the observed decreased AOI amount is a result of reductive dehalogenation. It is known that the contrast media are partly deiodinated under anaerobic conditions (Wischnack, 2000; Drewes et al., 2001), and this reaction is presumable responsible for the decreased AOI observed here. The lower AOI of the raw drinking water is most probably caused by dilution with back groundwater, whereby the dilution is around 50%.

Beside AOI analysis selected iodinated X-ray contrast media (Iopromide, Diatrizoate, Iohexol, Iopamidol) were quantified in the same system. Figure 4a shows the box plots of Iopromide. In the lake the average amount of Iopromide is 860 ng/L. In well 3311 the Iopromide concentration is 219 ng/L and thus, compared to the lake, reduced by 75%. Compared to the lake the concentration of well 3301 is reduced by 95% to 39 ng/L. In well 3302 the concentration of Iopromide is 37 ng/L, respectively 45 ng/L in well 3303. In the raw drinking water the average Iopromide concentration is < 20 ng/L and nearly half as high as in well 3303. The average concentration of Diatrizoate in the lake is 960 ng/L (Figure 4b). Decreased values are determined in the first (3311, 464 ng/L) and in the second well (3301, 300 ng/L). The reduction from the lake to well 3301 is 69%. An increased Diatrizoate concentration is recognized in well 3302 (632 ng/L) and the concentration of well 3303 (298 ng/L) is again comparable with the concentration found in well 3301. The average concentration of Diatrizoate in raw drinking water is 166 ng/L and compared to well 3303 is reduced by 50%.

A similar behaviour as described for Iopromide and Diatrizoate is recognized for...
Iopamidol and Iohexol. In case of Iohexol the groundwater concentrations are often very close to the limit of quantification (LOQ, see Methods) and thus the data base for the box plots is too small.

In general the concentration of the iodinated X-ray contrast media is decreased in the first part of the bank filtration (lake to 3301) as found for the AOI. Adsorption (see Introduction) as well as dilution can be excluded. Degradation and/or transformation are the reasons for the reduced concentrations. As already indicated by the AOI, the concentration of the X-ray contrast media in the raw drinking water is diluted with back groundwater up to 50%.

In difference to the AOI, very high concentrations of X-ray contrast media are determined in the groundwater in October, November and December. The data of these months are ignored in the box plots. The highest concentrations were determined in October, and continuously decreased concentrations were determined in November and December (Figure 5). Furthermore transformation products, no. 7 and no. 3 could be detected and were quantified as transformations products in these samples. The concentration of no. 7 goes up to 1 µg/L, whereas the concentration of no. 5 is just in the lower ng/L range.

The obtained high data in October, November and December are not easy to interpret. It is known that under toxic conditions, as found above the loamy clay layer (Figure 1), the AOI is persistent (AOI 12 µg/L, Wischnack, 2000; Drewes et al., 2001) and high concentrations of X-ray contrast media should be present. In principle it is possible that highly contaminated groundwater can flow through holes in the loamy clay layer, into the deep aquifer. But this effect cannot explain the high concentrations of X-ray contrast media, because the AOI profile does not show higher values in these months (Figure 6).

![Figure 5](https://iwaponline.com/wst/article-pdf/50/5/261/420171/261.pdf)

**Figure 5** Iopromide concentration determined in different groundwater wells (March 2001 to January 2002)

![Figure 6](https://iwaponline.com/wst/article-pdf/50/5/261/420171/261.pdf)

**Figure 6** AOI determined in different groundwater wells (March 2001 to January 2002)
Another explanation for the high values is that most probably due to changed physical, chemical or microbiological parameters the amount of X-ray contrast media which can be analyzed as single compounds was higher compared to the month before. This assumption is supported by the fact that only less than 10% of the AOI could be identified as contrast media in March to September, while in October to December nearly 100% of the AOI can be explained by the contrast media and the detected metabolites (Table 1).

At this point it should be mentioned that during the sampling period in 2001 well 3311 was dry in November and December and thus the water flow from the lake to the groundwater wells was disturbed. We assume that this has caused the changed parameters leading to a higher amount of analyzable X-ray contrast media. Furthermore, the hydrodynamics of the system is very complex. The drinking water wells located near the sampling points are used irregularly and intensively and thus no stable hydrodynamic conditions are present. We assume that the iodinated compounds are associated to the colloid phase and/or humic fraction and are released by any reason, here caused by a instability of the system. The assumption is supported by Heumann et al. (2000) who showed that the molecular size composition of organic matter carrying iodine is not stable. They show in laboratory experiments that the molecular size distribution of organic iodine changed over time.

The results of the October to December samples clearly indicate that the AOI represents the iodinated X-ray contrast media and transformation products (see Table 1) which are still iodinated. Thus, even in the March to September samples the AOI represents X-ray contrast media and the iodinated transformation products whereby a large part of the AOI is not amenable for single compound analysis. By LC ICP-MS analysis, conducted to trace unknown iodinated compounds, some unknown compounds could be detected. But a first estimation indicates that the concentration of these compounds is very low in the extracts of the March to September samples and just slightly higher in the October and November samples.

Conclusions

Iodinated X-ray contrast media and transformation products, which are still iodinated, are detectable by the group parameter AOI. By anoxic bank filtration the AOI amount is decreased. The observed decreased AOI amount of about 63% from the lake to 3301 is caused by transformation, mainly by partial deiodination. The low AOI of the raw drinking water is most probably caused by dilution with back groundwater (up to 50%).

The behavior of the single compounds can be summarized as follows. The concentrations of the X-ray contrast media, which are amenable for single compound analysis, are reduced by anoxic bank filtration. The reduction is caused by transformation (partly deiodination) and mainly by the formation of non analyzable associates. At least under anoxic conditions a large part of the contrast media and transformation products may be associated to colloids and/or humic material and can be released. The reason for the release is not known up to now, but caused here by unstable conditions.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>AOI and percentage of the AOI (calc.) which is represented by the iodinated X-ray contrast media and transformation products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Lake</strong></td>
</tr>
<tr>
<td>Aug.</td>
<td>14</td>
</tr>
<tr>
<td>Sep.</td>
<td>15</td>
</tr>
<tr>
<td>Oct.</td>
<td>12</td>
</tr>
<tr>
<td>Nov.</td>
<td>9</td>
</tr>
</tbody>
</table>
Acknowledgements
The authors are grateful to the Berliner Water Works for providing samples, to Schering AG (Berlin) and Prof. Dr. Sovak for the standard compounds. A special thank goes to Elke Profft for doing most of the lab work. The DFG is thanked for the financial support (PU 199 1-1/2-1).

References