INTRODUCTION

Recycling of polluted water is limited in principle by possible contamination by persistent substances, pathogens, odors and/or colors that cannot be degraded in municipal sewage works using established treatment technology. In areas with scarce groundwater resources, though, it may be rational to treat waste from municipal sewage works to allow the water to be used, for example, for irrigation purposes. Similarly, if the waste is discharged into recreational waters, standards applicable to germ reduction in the treated wastewater must be met.

Substances that are scarcely or non-biodegradable are referred to as persistent substances. These may be of various anthropogenic origins. The main compounds/areas of origin discussed in this connection include industrial chemicals (e.g., nonylphenol, organotin compounds, PCB, phthalates), pesticides (e.g., DDT, Gammexane), medicines and cosmetics. Public debate currently is focused on what are called endocrine substances.

The term endocrine denotes substances that affect the hormone system [Seibert, 1996]. A summary of these compounds is given in Figure 1. Negative effects on the hormone system of fish in surface water have been reported [Schlumpf and Lichtensteiger, 1996]. Effects such as reduced fertility of fish are observed, in particular, in the areas influenced by sewage treatment plant outfalls. Possible effects on humans still are the subject of controversy. Aspects under discussion include general reduction of fertility, impaired development of sexual organs in young males, and greater incidence of tumors.

There are various pathways for the compounds under discussion. Our water cycle merits special attention. Substances that enter the water cycle via wastewater ultimately will, if clarification is inadequate, make their way into the potable water. Figure 2 shows two main pathways that can lead to pollution of our potable water resources (surface water/ground water). A number of anthropogenic substances enter the water cycle via municipal and industrial waste water and landfill leachate which cannot be degraded by the natural clarification mechanisms. Established treatment techniques used in sewage works (biology, filtration, flocculation/precipitation, etc.) permit a large degree of treatment to specified discharge values. The persistent substances referred to above are not regularly/systematically dealt with, however.

| EU BathingWaters Directive (76/160/EC) | Total coliforms | 500 CFU/100 mL; E.coli: 100 CFU/100 mL |
| WHO Guidelines (1989) | Fecal coliforms | 1000 CFU/100 mL |
| California Title 22 (1993) | Total coliform | 2.2 MPN/100 mL |
Figure 2: Main pathways into potable water for scarcely biodegradable compounds.

The presence of pharmaceuticals in natural and drinking water has been reported in the literature [Ternes et al., 1999]. Sewage treatment plants were pointed out as the major source of the discharge of pharmaceuticals to the environment.

All over the world many different research groups are active on this topic e.g.:

- **In Europe**: A cluster of research projects named PHARMA has been launched combining three ongoing research projects (ERAMIS, POSEIDON, REMPHARMAWATER) focusing on the residues of pharmaceuticals in water, wastewater and manure.

- **In Australia**: The IWA World Water Congress in Melbourne in 2002 “Workshop on Endocrine Disruptors”.

- **In the USA**: A recent study by the Toxic Substances Hydrology Program of the U.S. Geological Survey (USGS) shows that a broad range of chemicals found in rivers at low concentrations downstream from wastewater treatment plants.
COMBINATION OF OZONE AND UV TECHNIQUES FOR MORE EFFICIENT TREATMENT

In the case of discharge from municipal sewage works, which is heavily polluted by an increased proportion of industrial discharges, the use of ozone can enable more efficient treatment for persistent substances and disinfection. The levels of difficult to biodegrade substances can be reduced by an oxidation process (ozone or ozone/UV) and the oxidized byproducts are more biodegradable. Consequently, such post-treatment of effluents of sewage treatment works could help to make the residues remaining after ozone/UV treatment more accessible for the natural clarification mechanisms (receiving water, soil filtration). An “activated” natural treatment process of this kind contributes to keeping our potable water resources virtually free from such compounds.

Besides the persistent substances, these discharges typically are characterized by slight coloration, leading to reduced transmission in the UV-c range. The ozonation step will improve the transmission, making an optimized UV treatment for final disinfection possible. See Figure 3 for the major effects of treatments by ozone, ozone/UV and UV.

<table>
<thead>
<tr>
<th>TREATMENT STEP</th>
<th>OZONE</th>
<th>OZONE/UV</th>
<th>UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect</td>
<td>Oxidation</td>
<td>Continuing oxidation</td>
<td>Disinfection</td>
</tr>
<tr>
<td>Parameters</td>
<td>Disinfection</td>
<td>(radical reactions)</td>
<td>Bacteria</td>
</tr>
<tr>
<td>Persistent substances</td>
<td>Persistent substances</td>
<td>Viruses</td>
<td></td>
</tr>
<tr>
<td>Colors</td>
<td>Colors</td>
<td>Odors</td>
<td>Bacteria, viruses, parasites</td>
</tr>
<tr>
<td>Odors</td>
<td>Odors</td>
<td>Bacteria</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. Principal effects of ozone and/or UV treatment.

OZONE/UV PILOT TRIALS AT THE MSP IN BRAUNSCHWEIG, GERMANY

Pilot tests were conducted at the municipal sewage treatment plant (MSP) in Braunschweig (near Berlin). This treatment plant is designed for a 385,000 population-equivalent and is composed of different treatment steps with mechanical pretreatment and biological treatment for reduction of levels of carbon, nitrogen and phosphorus. Under normal conditions the flow rate is approximately 60,000 m³/d (15.8 mgd).

MSP Braunschweig is a potential end user of the EU-project (POSEIDON). During this project the Johannes Gutenberg University, Mainz (ESWE Institute) conducted an analytical monitoring program for different persistent substances at the treatment plant. WEDECO, as an additional potential industrial end user, conducted pilot tests to investigate the treatment effect of the ozone/UV technique on the effluent of the MSP (Braunschweig). This pilot plant is composed of an ozone generator (100 g/h), two diffuser/bubble columns and a UV-reactor, and was installed at the facilities in Braunschweig. The pilot trials were conducted in September/October 2001 and May/June 2002.

The values of the raw water parameters are typical for this type of effluent in Germany. TOC (23 mg/L) and COD (30 mg/L) levels stayed nearly constant during the ozone treatment. A slight reduction of COD levels, however, could be detected. The low BOD level (2.8 mg/L) increased to approximately 5 mg/L. After ozone treatment, a certain increase of the BOD level usually is observed. The average of the total reduction of AOX level was 50%.

Ozone treatment impacts UV transmittance, SAC 254 nm and SAC 436 nm significantly. Both absorption coefficients
decreased, and as a result, the UV transmittance clearly was improved from 59.2% to 84.1%. Consequently, the ozone treatment step leads to better conditions (higher transmittance) for the UV disinfection step.

The analytical monitoring of persistent and endocrine substances was completed by ESWE Institute. More than 50 parameters were monitored. The monitored substances include antibiotics, beta blockers, neutral drugs, acid drugs, estrogens, musk scents and radiographic contrast agents. More than 30 of the monitored pharmaceuticals and personal care products were measured in the effluent of the wastewater treatment plant.

The concentration of the single substances varied between 0.5 g/L and 10 g/L in the effluent of the municipal wastewater treatment plant. The applied ozone doses during the pilot trials varied between 5 mg/L and 15 mg/L. The preliminary results show a positive treatment effect by ozonation (e.g., levels of Estrone and 17α-Ethinylestradiol treated with 5 mg ozone/L were reduced by more than 90%). For a part of the monitored organic molecules (e.g., contrast agents) the ozone reaction is obstructed and an “advanced oxidation” combining ozone and UV is likely to achieve better treatment results.

TREATMENT COSTS
On the basis of the pilot studies and our experience, the calculation for costs of a large scale installation (based on 10 g O3/m³, 60,000 m³/d, 600 kg O3/d) approximately amounts to the following:

UV < Euro 0.01/m³ for disinfection;

UV/Ozone < Euro 0.05/m³ for combination of disinfection and degradation.

In comparison to the membrane technique, the costs for an AOP process are significant lower. Optimization of the advanced treatment and the possibility of a further biodegradation of the oxidized substances will be the subject of future R & D projects (see Figure 4).

TREATMENT TECHNIQUES FOR PERSISTENT SUBSTANCES/ENDOCRINE DISRUPTERS
For removing persistent substances in effluents of municipal waste water treatment plants the following techniques may be considered:

Membrane (filtration)

Activated carbon (adsorption)

AOP (oxidation)

Table 2 gives a brief overview which are the main items to be compared.

1. Treatment efficiency
According to current available data, all three techniques are able to reduce levels of different persistent substances. Since knowledge is still limited, more detailed research must be conducted.

2. Available technique and operation
At the moment there are more detailed design and operation data available for AOPs than for granular activated carbon (GAC) and membrane techniques.

3. Costs
Costs for the ozone/UV AOP process (see Figure 4) are significantly lower.

PRINCIPLE COMMENTS
During membrane and GAC treatment the persistent substances are extracted from the effluent and enriched. For this reason, the exhausted carbon and the concentrate from membrane treatment, require a further treatment (recycling or discharging).

Ozone/UV AOP is an on-site treatment, in which the relevant substances will be oxidized and removed directly during the treatment process. However, the possible risk of by-product formation has to be considered.

Within an economical use of ozone/UV AOP, it is not possible to mineralize all persistent substances. The goal of this treatment is to reduce the toxicity of the substances and to increase their biodegradability. This effect might be used either by a subsequent biofilter or by natural biological treatment resources.
Table 2. Treatment techniques for persistent substances

<table>
<thead>
<tr>
<th></th>
<th>MEMBRANE</th>
<th>GAC</th>
<th>OZONE/UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>treatment efficiency</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>available treatment operation</td>
<td>0</td>
<td>+ / 0</td>
<td>+</td>
</tr>
<tr>
<td>cost</td>
<td>-</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>remarks</td>
<td>accumulation of persistent substances</td>
<td>adsorption of persistent substances</td>
<td>risk assessment for by-products</td>
</tr>
</tbody>
</table>

CONCLUSIONS
The combined application of ozone and UV leads to more efficient treatment results regarding disinfection and degradation of toxic compounds. This combination may meet future water clarification and recycling standards economically.

The preliminary results of the pilot trials at MSP Braunschweig show a positive treatment effect on persistent and endocrine substances [e.g., Betablockers, Antibiotics, Antiphlogistic lipid regulators, Estrone (natural estrogen) and musk fragrances]:

- fast reaction kinetics
- reduction rates >90%
- ozone dosage of 5-10 mg/L
- relatively simple design even for high flow rates
- construction and operation costs are approximately 0.05 Euro/m³

References