Ozone Wastewater Treatment

OXIDIZING MICROPOLLUTANTS IN WATER CIRCULATION

WEDECO

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Pharmaceutical substances in water circulation

The elimination of micropollutants from our water is a challenge more facilities are having to address. While conventional treatment processes don't remove them completely, oxidation with ozone is proving to be one of the most efficient methods of treatment.

Pharmaceuticals help many people and animals when fighting diseases, staying healthy, or improving quality of life. Nonetheless, a large proportion of pharmaceutical agents end up in the environment via waste from bodily excretion.

Although they do not constitute an immediate hazard, it is the long-term dangers that are becoming even more significant. The effects of micropollutants and pharmaceutical substances in surface waters have already been proven in numerous large-scale studies. These effects lead to negative changes within the ecosystem.

Micropollutants in water circulation

- Persistent substances
- Only biodegradable to a limited extent
- Have a negative effect on organisms
- Cause endocrine system disturbances
- Can spread rapidly in water supplies

Problem I: Persistence

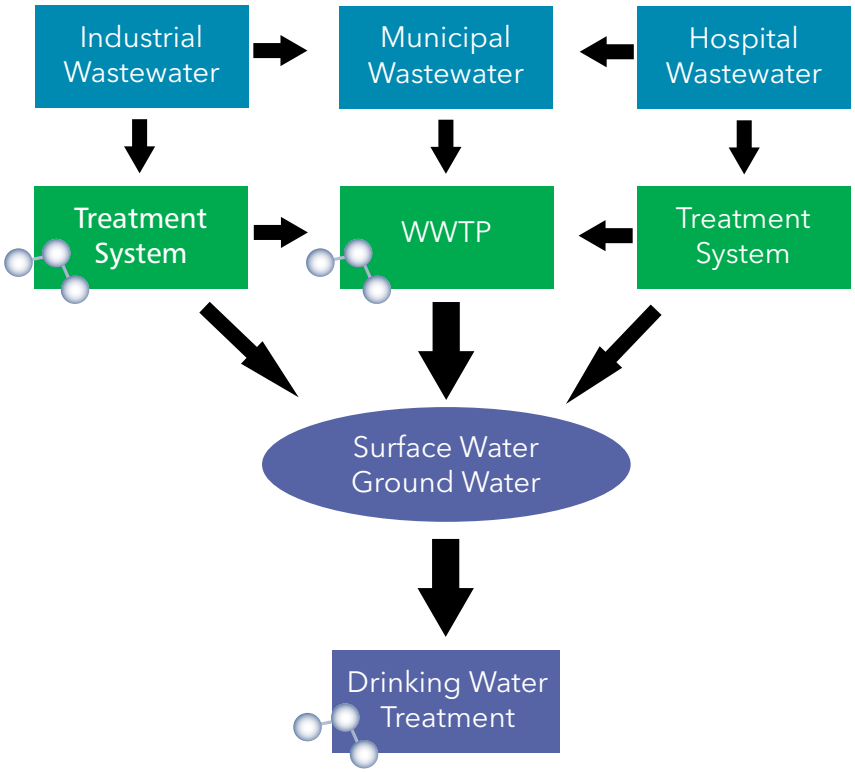
Not all approved substances in the area of pharmacy, agriculture and industry, as well as those commonly consumed are completely biodegradable. This means they cannot be fully removed with conventional treatment technologies. As a result, the number of contaminants in our water circulation is creeping upward (bioaccumulation). This means a constant rise in water pollutants and further negative effects on the aquatic environment in the future, unless appropriate measures are taken.

Problem II: Endocrine effect

Some micropollutants (e.g. ethinylestradiol) have an effect on the hormonal system of humans and animals. These so-called endocrine disrupting compounds (EDCs) have an impact even at low concentrations and have been classified as areas of concern. In connection with negative environmental influences on living creatures, EDCs are currently being considered to be linked to:

- Observations of negative effects on the reproduction of certain kinds of fish (including the feminization of male fish).
- The decrease of fertility in humans and animals due to reduced sperm quality.
- The increase of certain types of cancer which could be related to hormonal system disturbance.

Influx paths



The main influx paths of endocrine disruptive substances in wastewaters.
= possibility of treatment with ozone.

Sources of drinking water, such as ground water or surface water have different micropollutant concentrations depending on the degree to which they intermix with the influx paths.

The main influx paths or "hot spots" of persistent micropollutants in surface waters are municipal wastewater treatment plants, drainage from the pharmaceutical industry, animal breeding grounds and medical centers.

Further indirect influx paths result from the improper disposal of unused pharmaceuticals, agricultural application of animal excrements and sewage sludge.

High concentrations of endocrine disruptive substances get into our ground water and surface water via the wastewater treatment process.

The special agent: ozone

The effects of endocrine substances and persistent micropollutants on our ecosystem mean that more extensive treatment is necessary. Many wastewater treatment plants are not able to sufficiently eliminate these pollutants with their existing technologies.

Numerous pilot tests using ozone as an additional treatment step indicate ozone is an effective solution for eliminating persistent pollutants. This means that micropollutants present in water can be sufficiently removed with environmentally friendly and economically feasible doses of ozone.

How does ozone work?

Ozone reacts quickly with micropollutants containing accessible amino groups, double bonds, or aromatic systems. Alongside these pollutant-specific attributes, the efficiency of the reactions also depends on the pH value and on dissolved organic carbon (DOC). The extent to which a pollutant can be eliminated can be estimated by looking at its reaction rate constants with ozone.

Pollutants with reaction constants of > 105 M-1·s-1 can be assumed to react very quickly with ozone. For comparison: The colorant indigo (which is used for the quantitative detection of ozone among other things) shows a constant of ~107 M-1·s-1 and hydrogen sulfide of ~3x104 M-1·s-1 for the reaction with ozone.

The varying reaction constants result mainly from the different points of action of the ozone on the molecules.

- For example, 17α ethinylestradiol is affected at the phenol group.
- In the case of carbamazepine, ozone reacts with a double bond.
- Diclofenac and sulfamethoxazole have functional amino groups which can be oxidized by ozone. Bezafibrate and Ibuprofen have no such functional groups and therefore react considerably more slowly with ozone [Schuhmacher].

The table below shows the reaction rate constants of the reactions of various pharmaceuticals with ozone.

Ozone dissolution:
As soon as ozone is introduced into water, any hazardous pollutants present are effectively degraded through oxidation.

Pharmaceutical	k = [M-1·s-1]
Ethinylestradiol	~3.0 x 106
Bezafibrate	~0.6 x 103
Carbamazepine	~0.3 x 106
Diclofenac	~1.0 x 106
Ibuprofen	~9.6 x 103
Sulfamethoxazole	~2.5 x 106

Source: Project Poseidon, EAWAG, Huber et al.

Pharmaceuticals and their effect

In this example, a total of over 2,700 different agents are used in human medicine and over 600 agents in animal medicine. The table shows the pollutants with the highest concentrations in surface water and their effect.

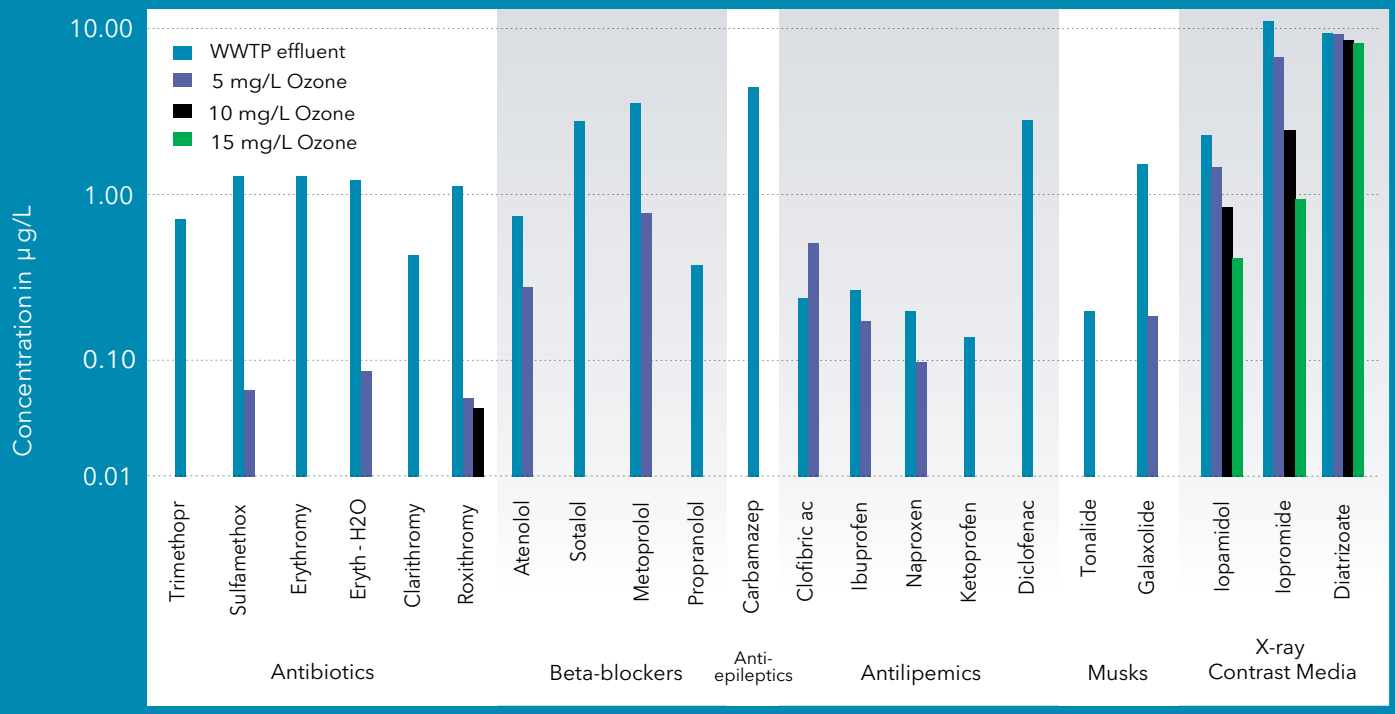
Active Ingredients	Pharmaceutical	Disposal [kg/year]	Concentration [µg/L]	Effect	Reaction
		Total disposal in 2001	Highest concentration measured in surface waters	Effects on various water organisms	Reaction in the environment (poorly degradable)
Antibiotics	Sulfamethoxazole	53,600	1	X	X
	Erythromycin	19,199	1.7		X
	Trimethoprim	11,427	0.2		X
	Clarithromycin	7,159	0.003	X	
Pain Killers	Diclofenac	85,801	2	X	X
	Ibuprofen	344,885	1.5	X	
	Phenazone	24,843	0.95	X	X
	Propyphenazone	28,140	0.31		X
Antiepileptics	Carbamazepine	87,605	6.1	X	X
Antilipemics	Bezafibrate	33,476	3.1	X	
	Clofibric acid	2	1.1		X
Beta-blockers	Atenolol	13,594	0.22		X
Antirheumatic	Indometacin	3,721	0.7		X
Hormones	Estradiol	1,098	0.0006	X	
	Ethinylestradiol	48	0.002	X	
X-ray contrast media	Iomeprol	83,377	0.89		
	Iopamidol	42,994	2.8		
	Iopromide	64,056	8.5		
	Diatrizoate	60,687	15.8		
Cytostatics	Cyclophosphamide	385	0.1		X
	Ifosfamide	170	0.18		X

Source: MUNLV 2008

Terms and definitions

Micropollution: Pollution by substances in relatively low concentrations, which are persistent against conventional treatment.

Endocrine Disrupting Compounds (EDC): Pollutants with undesired effects on the hormonal system of humans and animals. These effects can be caused by pharmaceuticals or even other substances.



The graphic shows the results achieved at the wastewater treatment plant in Brunswick with an ozone dosage of 5 to 15 mg/L. They illustrate the high degrees of degradation (not shown = under the detection limit) which can be attained with the use of ozone.

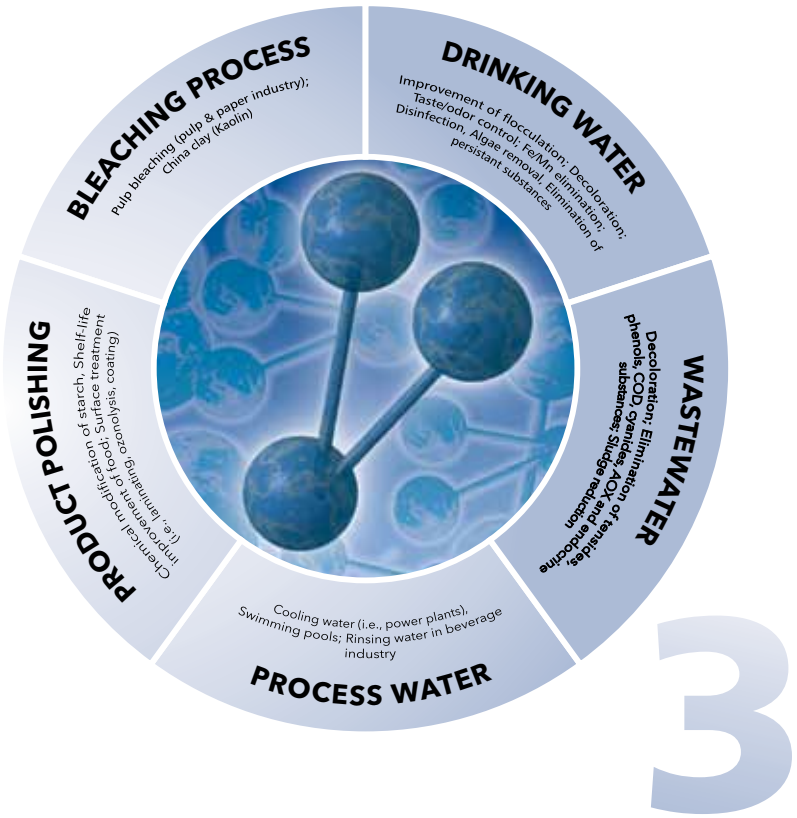
Successful pilot tests with ozone

WEDECO ozone systems have already been used for several national and international projects for micropollutant reduction:

- Project Poseidon
  Braunschweig Wastewater Treatment Plant
  January 2001 – June 2004
  (Project No. EVK1-CT-2000-00047)
- National Project of Switzerland Strategy MicroPoll
  Wueri Wastewater Treatment Plant in Regensdorf
  July 2007 – October 2008
- PILOTOX Project at the Technical University of Berlin
  Berlin Ruhleben Wastewater Treatment Plant
  December 2004 – July 2005
- Project Poseidon
  EAWAG Zurich/Opfikon Wastewater Treatment
- Research Project at the University of Stuttgart Busnau
  Wastewater Treatment Plant
  December 2003 – May 2005
- KomOzon Project at the Technical University of Vienna
  Vienna Wastewater Treatment Plant
  2007 – 2009

WEDECO ozone plant at the Wueri wastewater treatment plant in Regensdorf, Switzerland.

Ozone in use



Ozone is one of the most powerful commercially available oxidants and is commonly used for municipal water and wastewater treatment. In addition to its oxidizing capabilities, it is an environmentally friendly method of treatment. Pollutants, colored substances, odors and microorganisms are directly destroyed by oxidation, without creating harmful chlorinated by-products or significant residues.

By decomposing to oxygen as it reacts, ozone provides a cost-effective and environmentally friendly alternative to oxidation with chlorine, absorption (activated carbon) or separation processes (reverse osmosis).

Advantages of ozone:

- Ozone eliminates bacteria, viruses and most other organic and inorganic contaminants.
- Ozone can significantly reduce levels of dangerous chemicals, such as chlorine.
- Ozone acts as a microflocculant aiding in the removal of minerals such as iron and manganese.
- Ozone leaves neither chlorinated by-products nor unpleasant chemical tastes or odors.
- Ozone is generated on site and on demand from air/oxygen and power.
- No storage and handling of chemicals.

The oxidative action of ozone

Ozone reacts quickly with a large number of compounds. In doing so, these compounds are attacked either directly by the ozone molecule or indirectly by the intermediately occurring hydroxyl radicals. Preferably the ozone is completely consumed in this reaction process, releasing only oxygen. In case of remaining ozone in the off-gas, these residues are converted to oxygen by a residual ozone destructor.

By combining ozone with UV or peroxide, advanced oxidation processes are formed which are able to reduce even the most persistent substances. These advanced oxidation processes (AOP) help to render other, previously nondegradable, water pollutants harmless.

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1) The tissue in plants that brings water upward from the roots;
2) a leading global water technology company.

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