Micropollutant removal with ozone in wastewater treatment plants

1. Trace organic contaminants within the water cycle

Micropollutants are increasingly being detected at low levels in water systems around the world. Also known as contaminants of emerging concern (CECs), this ever-evolving class of pollutants refers to a wide range of different chemicals that include pharmaceuticals and personal care products (PPCPs), pesticides, endocrine disrupting chemicals (EDCs), per-and polyfluoro-alkyl substances (PFAS), and many more. Evidence has linked numerous discrete micropollutant categories, and a combined cocktail of multiple categories, to negative impacts on human health and the aquatic environment.

Figure 1: sources that contribute to micropollutants detected in water bodies.

Addressing the unique challenges of micropollutant removal, which are resistant to removal in traditional wastewater treatment, requires advanced treatment processes for targeting these contaminants at parts per billion concentration levels. One of the most evaluated and now utilized treatment technologies is ozone. Ozone is a pure oxidation/disinfection solution for treating trace contaminants, delivering robust oxidation and disinfection of many micropollutant categories including PPCPs, EDCs, pathogens, pesticides, biocides, cosmetics, trace organic compounds, and others.

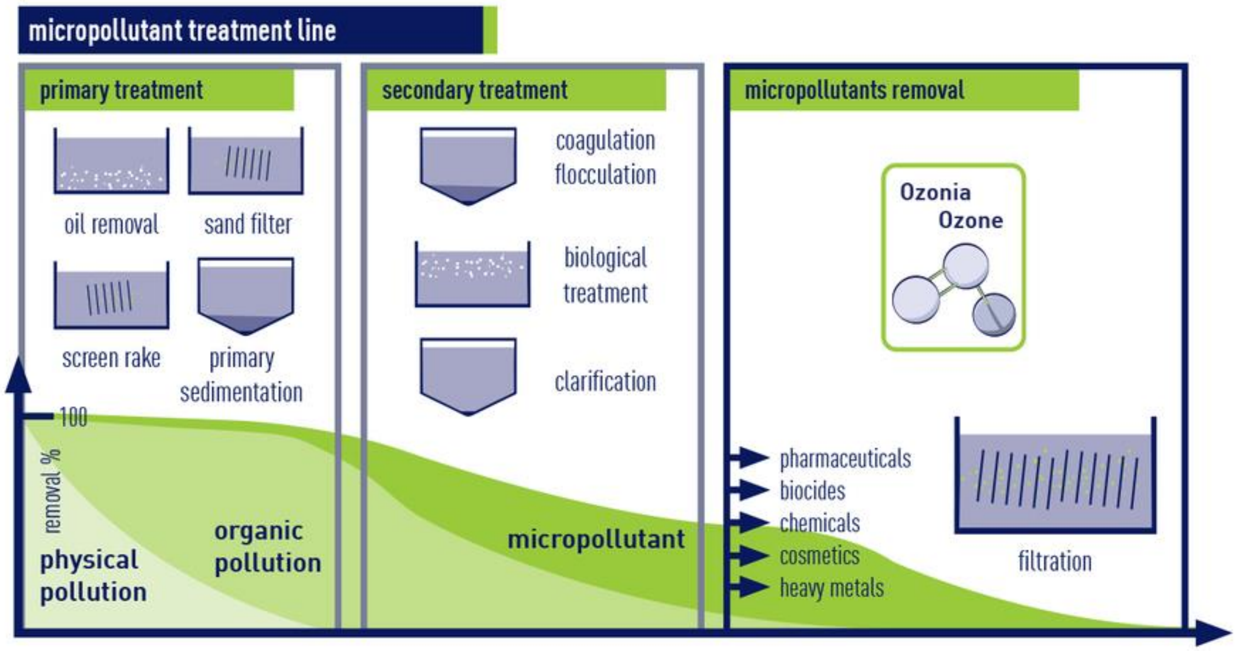

Figure 2: Fate of micropollutants across a WWTP

Ozone can be integrated at many points in a multi-treatment flowsheet and functions as a complementary technology to both filtration and carbon adsorption for targeting very low micropollutant concentrations. Ozone is generated on site, reducing shipping and handling safety concerns, and it reverts simply to oxygen over time, reducing by product formation.

2. Removal of micropollutants within a wastewater treatment plant

The most effective way to reduce micropollutants in water bodies and drinking water is by eliminating or reducing their discharge at the source. This requires producers of water borne contaminants to effectively remove residual chemicals at the source, such as industrial factories and contaminated sites. However, many contaminants do not have a concentrated source to target for point-of-origin removal, and the next logical opportunity for removal occurs at combined collection points such as wastewater treatment plants (WWTPs).

In 2014, Switzerland demonstrated world leadership in addressing micropollutants by revising the country's Water Protection Ordinance to require additional treatment at certain large or critical wastewater treatment plants for removing these substances. Switzerland's actions were influenced in part by the United Nations (UN) Sustainable Development Goals (SDGs). Set in 2015, the 17 SDGs are the driving push behind the UN's 2030 Agenda for Sustainable Development, adopted by all UN member states. Measures to combat micropollutants are included with Switzerland's efforts to meet SDG 6: Ensure availability and sustainable management of water and sanitation for all.

ARA Neugut in Switzerland – the first full-scale reference demonstrates success

At the same year the Switzerland micropollutant regulation entered into force, ARA Neugut became the first micropollutant treatment reference in Switzerland.

Several relevant designs and solutions were provided from ARA Neugut for treatment optimization of this first full-scale plant:

- Ozone dosage optimization conducted onsite resulted in a significant decrease of specific dosage from 0.5–0.8 g O3 abs. / g DOC in design phase to 0.4 +/- 10% g O3 abs. / g DOC in current operation.
- A smart control system based on delta UV254nm measurement in between inlet and outlet ozonation stage, in combination with water flowrate and a smart algorithm, aims to optimize ozone dosage for treatment removal efficiency of 82%, thus achieving elimination without overconsumption of ozone. In Switzerland, regulation ask for 80% average removal rate of 12 substances considered as indicators.
- Ozone dose splitting was also implemented to further optimize the ozone dose by splitting the dosage and adding half in the first and half in the third chamber of the ozonation reactor.

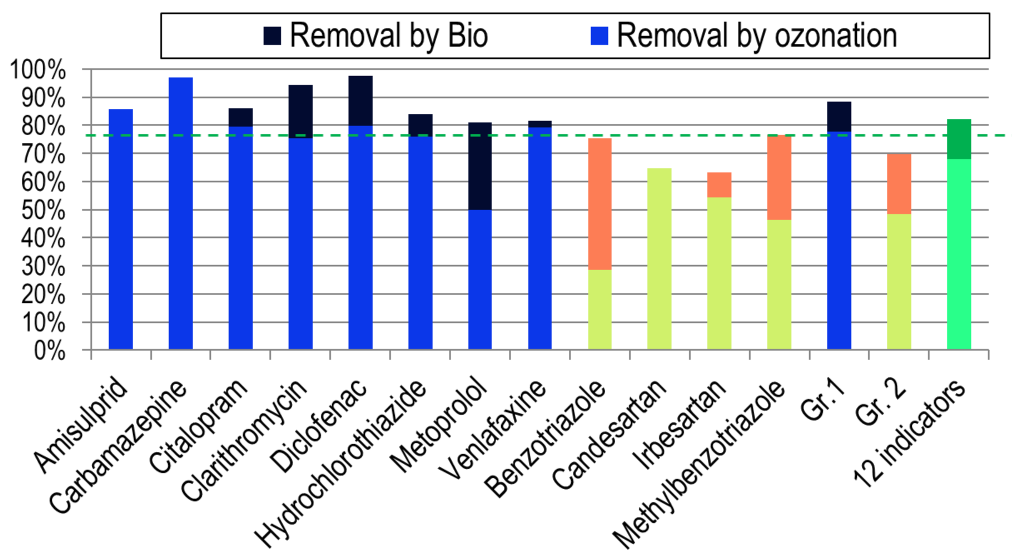

Figure 3: percent removal by ozonation (light), biology (dark) and the total plant with an average of 0.21 g O3 / g DOC per entry chamber for 82% elimination the micropollutants. Removal by group and total in the three columns on the right - Source: ARA Neugut

All in all, a significant operating cost reduction has been conducted with saving in energy and liquid oxygen of more than 30% compared to the original design estimates.

3. Latest trends and the near future

3.1. Combination ozone & Granular Activated Carbon

In recent years, a combination of both technologies (ozone and activated carbon) has emerged as a more complete solution due to their complementary removal mechanisms. As a matter of fact, this combination is synergistic, providing more than only the best of each technology. Ozone reduces the chemical loading for absorption on the GAC, thus increasing the filtration media's useful life and/or reducing the amount of media required. While GAC filtration reduces the ozone dosage required and can reduce ozonation by-products. Currently, process combinations (ozonation + GAC-filter) are used at two full-scale WWTPs (Altenrhein – CH; Weißenburg in Bayern - DE).

Altenrhein WWTP (CH) is located on the border between Switzerland, Germany and Austria, directly nearby Lake Constance, a source of potable water production for more than 5 million people in Germany and Switzerland. Therefore, the lake is carefully monitored and protected to limit human activity impacts, and as shown below, the municipality of Altenrhein decided to implement the combination ozone + granular activated carbon (GAC) to the existing WWTP.

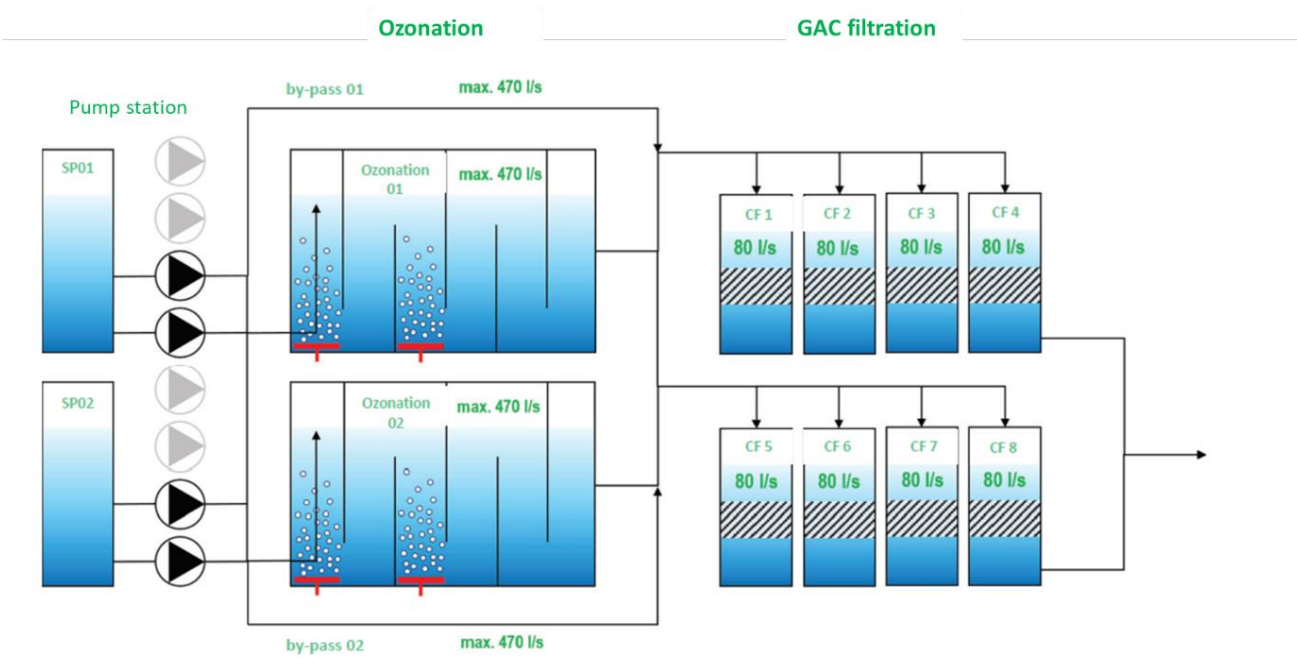

Figure 4: Treatment process for micropollutants removal in Altenrhein WWTP [source: AVA Altenrhein]

Operation of this new treatment process started August 2019 and after 2 years of operation the main outcomes are impressive demonstrating the synergistic benefits:

- Very low operational costs
- Broad and higher removal rate of micropollutants due to the complementary specificity of each technology
- Higher resilience of the combination versus ozone or AC alone
- Increase GAC lifetime (measured with the local pilot operated 3 years ahead of full scale)

From initially designed at 0.3 mg O_3/g DOC, the ozone dosage has been continuously optimized and decreased down to ~0.1 mg O_3/g DOC. Even with these low doses, the average removal rates of the 12 micropollutant indicators tracked in Switzerland are still far above the minimal requirement of 80%: Since the start of 2021, the average removal rate of each analytical campaign are above 90%.

3.2. Ozone injection into activated sludge

Targeting these trace organic compounds for removal at the end of the WW treatment process is increasingly common; however, it is nevertheless possible to eliminate them at the heart of the treatment plant, namely the biology. The application of a low dose of ozone directly to activated sludge is an interesting alternative to a strictly tertiary or quaternary solution.

Initiated in 2018, the **MUDP** project in Braedstrup (DK) demonstrated that micropollutants can be removed up to nearly 80% from the wastewater with direct injection of ozone into sludge. Nevertheless, as illustrated in the table below, an additional treatment step such as tertiary ozonation or polishing by AC may still be required to consistently meet a required performance specification, e.g., the 80% removal rate of the Swiss regulation:

Average removal of the selected list of 36 micropollutants (%)	**1st phase** Mixed liquor 4.0 mg/L O_3 and tertiary 7.2 mg/L O_3	**2nd phase** Mixed liquor 7.2 mg/L O_3 and tertiary 4.0 mg/L O_3
Conventional Biology	63	65
O_3 in aeration tank	78	79
Tertiary O_3 (multiple point ozonation)	93	83

Table 1: Micropollutants removal rates at different treatment stages, with two ozone dosages at multiple points [source: https://mpozone.com]

Beside the micropollutants removal, injection of ozone into sludge at these low dosage rates (4 to 7 mg/l), also brought to light the beneficial side-effect on activated sludge settling. The SVI (Sludge Volume Index) was significantly decreased from around 160 ml.g-1 when injection of ozone started during the first evaluation phase, down to 80 ml.g-1, and even to 60 ml.g-1 at the end of the second evaluation phase.

Promising mitigation of bromate formation:

A concern which emerges in some cases when ozonation of micropollutants is foreseen is the risk of bromate formation. Decades of experience, with hundreds of projects, resulted in various strategies to mitigate bromates formation. Nevertheless, bromide concentrations >100-400 µg/L are considered as presenting a risk of formation of more than 10 µg/L of bromates (guideline value recommended by World Health Organization for drinking water production) during ozonation.

Therefore, being able to ensure a final bromate concentration of less than 5 µg/L after ozonation, by applying several mitigation methods, is a must. A new study was undertaken to assess direct sludge injection impact on bromate formation, and the results can be summarized as follows:

1. traditional ozone application to treated effluent from a secondary clarifier, the formation follows the usual expectations trends: above 200 µg/L bromide concentration within the water and with an ozone dosage higher than 5 mg/l, bromates are formed up to 10 µg/L.
2. Conversely, with >10 mg/l ozone dosage in sludge with bromide concentration up to 740 µg/L did not produce a measurable bromate concentration.

The results of these experiments are illustrated in the graph below:

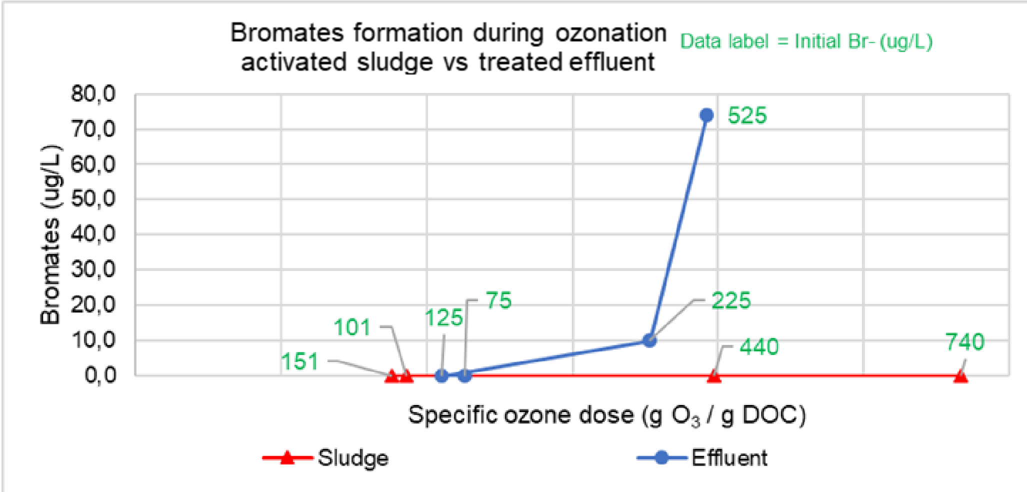

Figure 5: laboratory study of bromate formation during ozonation of treated water from secondary clarifier (Effluent) or activated sludge (Sludge) from water collected at Neugut WWTP [source: SUEZ – Water Technologies & Solutions - Duebendorf (CH)]

Removing micropollutants with ozone is a well-known process at tertiary or quaternary treatment stage of a WWTP. Doing the same by direct injection of ozone into activated sludge is a new possibility, offering high removal rates of common micropollutants at a similar or slightly higher ozone dosage range than the usual one when applied in wastewater from secondary clarifier.

As we have now learned, two main benefits can be added to that:

1. Significant decrease of the SVI which contributes to bioprocess improvement and reduction of the operational cost of the WWTP
2. Dramatic reduction in bromate formation, as effluent bromate concentration was shown to be below detection levels regardless of initial bromide concentration up to even 740 µg/L.

Therefore, direct injection of ozone in activated sludge should be considered as a serious alternative solution for micropollutants treatment. Depending on the targeted compounds and the achievable removal rate, a final polishing treatment, such as tertiary or quaternary ozonation or AC, may still be required.

4. Key process considerations for design and implementation of an ozone treatment at WWTP

With now a dozen of WWTPs in EU, equipped with a quaternary ozonation for the removal of micropollutants, initial process considerations have been adjusted:

- Systematic coupling of ozone with downstream bio-filtration (usually sand filter or better GAC filter) to ensure the removal of transformation products
- Sizing range of ozone dosage for an 80% removal rate of the 12 Swiss indicators, is nowadays usually decreased at design stage targeting 0.3-0.7 g ozone abs. / g DOC compared to initially designed values of ~0.5-1 g ozone abs. / g DOC
- With the implementation of an online UV 254 nm control system, ozone dosage can be further optimized. In ARA Neugut, optimization went to 0.4 g ozone abs. / g DOC, compared to first figures used for plant sizing while achieving a removal rate of constant 82%
- Splitting ozone dosage in at least two injection point in the contacting system allows significant reduction of OPEX costs and aids in successful mitigation or no significant formation of bromate.

5. The treatment costs of ozone at tertiary/quaternary stage

Cost of micropollutant treatment is sensitive because it comes in addition to the existing OPEX of a WWTP. In Switzerland, cost assessments regarding this quaternary treatment were provided in several studies from public organizations.

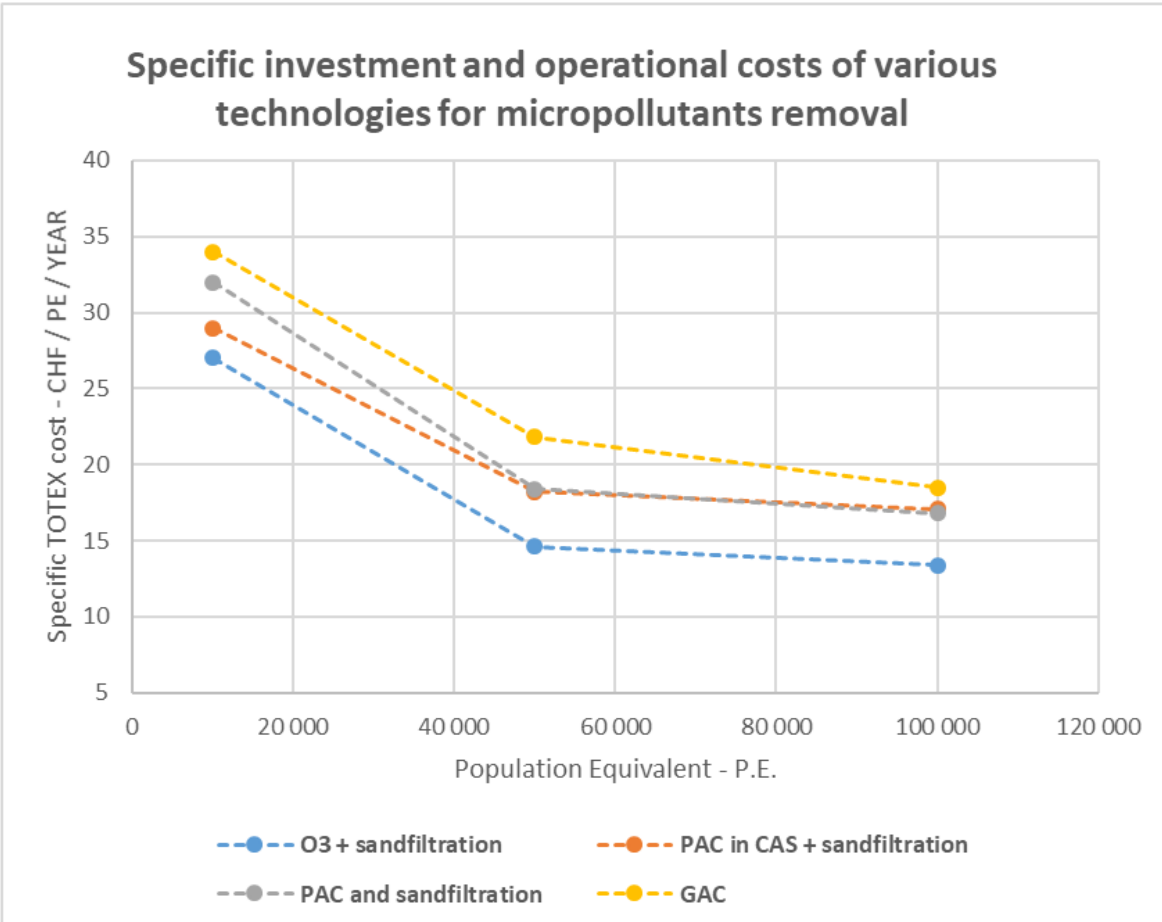

Figure 6: Empirical annualized gross specific costs of micropollutants removal technologies [source: Hunziker Betatech – Luzern 14.03.2019]

Compared to other technologies, ozone solutions require generally the lowest investment costs (CAPEX) and present the lowest operating costs (OPEX). At ARA Neugut for example, with the latest optimizations, operating costs of micropollutant treatment by ozonation is approaching only 1 €/pe/y for this 150,000 pe WWTP.

6. Carbon footprint of micropollutant removal processes

In Switzerland, WWTPs are responsible for approximately 1% of the greenhouse gas (GHG) emissions and micropollutants treatment only represent a fraction of this. Nevertheless, any additional emissions must be reduced to a minimum and numerous studies have now been published reviewing the GHG impacts for micropollutant removal. One example is shown below conducted by VSA (CH) and KWB, that demonstrates ozone is the technology with the lowest Carbon Footprint. This, taking into consideration the electrical mix of Switzerland.

When coal is used as source material for activated carbon production, Ozone carbon Footprint is from 2 to 6 times less than GAC or Powdered Activated Carbon (PAC).

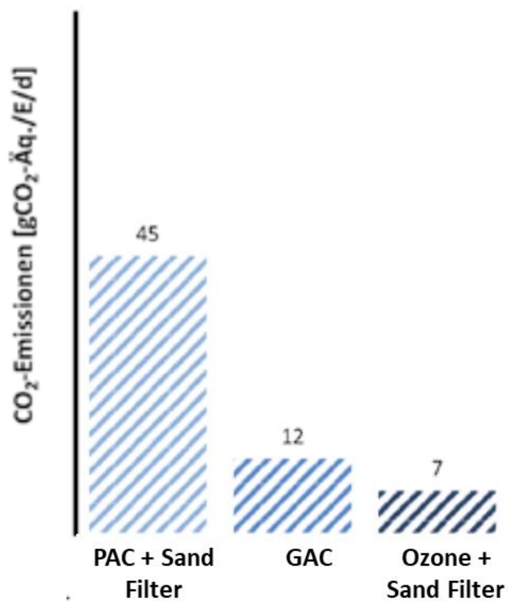

Figure 7: Carbon Footprint of Ozone and carbon solutions for micropollutants removal [source: AQUA & GAS N°2 – 2020]

Other studies and models have shown similar results, but also highlight a strong regional dependency based on the CO2 intensity of the region's electricity production. It is clear that with the progressive decarbonization of electricity production, the carbon footprint of ozone will further decrease, making it broadly the more environmentally friendly technology for micropollutants removal.

REFERENCES:

Benefits of ozonation before activated carbon adsorption for the removal of organic micropollutants from wastewater effluents – R. Guillossou, J. Le Roux, S. Brosillon, R. Mailler, E. Vuillet, C. Morlay, F. Nauleau, V. Rocher, J. Gaspéri

Simultaneous ozone and granular activated carbon for advanced treatment of micropollutants in municipal wastewater effluent - Hooman Vatankhaha, Stephanie M. Rileyc, Conner Murraya, Oscar Quineonesc,K. Xerxes Steirerb, Eric R.V. Dickensonc, Christopher Bellona

Swiss Federal Law – water protection from 24th of January 1991 (update from 2021 first of January) - Modification from March 21st 2014

Ozone + GAC: a performing process – Christoph Egli 2021 – AVA Altenrhein

Altenrhein WWTP information - https://www.ava-altenrhein.ch/

General information & Maps - https://micropoll.ch/

Financement et fonds pour les eaux usées – OFEV / BAFU

Evaluation of tertiary treatments for the reduction of refractory micropollutants in wastewater - S. Besnault, S. Martin Ruel, S. Baig, B. Heiniger, M. Esperanza, H.Budzinski, Cecile Miege, Marina Coquery, P. Dauthuille - HAL Id: hal-01379454

Synergetic biological and chemical ozone oxidation for micropollutants removal from wastewater - ASTEE 96th Annual Conference – June 6 to 9, 2017 -Adriana Gonzalez Ospina, Bruno Domenjoud, Emmanuelle Vulliet, Sylvie Baig

Application of Ozone on Activated Sludge: Micropollutant Removal and Sludge Quality - Mireia Marce, Oscar Palacios,Arantxa Bartolomé,Josep Caixach,Sylvie Baig &Santiago Esplugas – Ozone: Science & Engineering

Application of multiple point ozone injection and Powder Activated Carbon (PAC) -https://mpozone.com/

Carbon Footprint of micropollutants treatment solutions – AQUA & GAS N°2 - 2020

Options and limitations for bromate control during ozonation of wastewater – F. Soltermann, Christian Abegglen, Manfred Tschui, Sandro Stahel, Urs Von Gunten

Assessment of ozonation process – recommendation - VSA, 2017, adaptations 2021 (version 2) – Micropoll VSA CH

Contact us

If you would to learn more about how SUEZ can provide solutions for your wastewater needs, please visit: www.suezwatertechnologies.com/contact-us