### Background/Problem area
To remain globally competitive, paper mills must modernize or enlarge their production facilities again and again. In many cases, this results also in increased wastewater volumes and pollutant concentrations into the downstream wastewater treatment plant (wwtp). These wastewaters contain different shares of compounds contributing to the persistent COD which cannot be degraded by the biological stage of the existing wwtp, even if the latter has been enlarged. Mills are usually not allowed to discharge higher organic loads. The implementation of advanced, modern, integrated treatment technologies is additionally enforced by the EU directive 96/61/EG of 24/09/1996, in which “integrated pollution prevention and control (IPPC directive)” is stipulated.

Ozone treatment with subsequent low load biological stage is already successfully used for the advanced treatment of biologically treated effluents in paper mills using recovered paper as main raw material. Furthermore vast experience is available from numerous research projects. A few studies dealt with effluents from special productions (from the production of wood-free specialty paper with integrated processing of cotton linter, or from kraft pulp production), some of them with special aims. Consequently comprehensive studies are still necessary to investigate the effects of ozone treatment on effluents from paper mills mainly using virgin fibres.

### Objectives/Research results
The project aims to assess the effects and determine the criteria for efficient advanced ozone treatment of effluents from paper mills using no recovered paper or only to a minor extent. Besides evaluating the influence of ozone on wastewater properties, this includes the determination of the ozone dosage and retention time required.

Samples from biologically treated effluents of two pulp mills and of three integrated pulp and paper mills have been subjected to continuous ozone trials. An ozone dosage of 0.7 g O₃/g COD₀ reduced the COD by more than 40 % in systems with COD₀ between 230 (mill B) and 400 mg/l (mill A) prior to ozone treatment. The BOD₅ could be increased from below detection limit up to 49 mg/l by 0.7 g O₃/g COD₀, which means an increase in biodegradability, measured as BOD₅/COD ratio, from 0.01 up to 0.23. The enhanced biodegradability of the ozone treated wastewater could also be shown in aerobic degradation tests. Where the COD in the original sample was only reduced by 13 % in the relevant period, the COD of ozonized water was reduced by up to 53 % in the same period (mill C).

In effluents from mills A and D the AOX was at detection limit, even before subjecting the water to ozone trials. In mill B and C the AOX could be reduced from values between 690 and 1,340 µg/l to 300 µg/l by 0.8 g O₃/g CSB₀. In mill E the AOX was reduced from values between 100 and 150 µg/l to 50 µg/l. 0.7 g O₃/g CSB₀ reduced the colour at 436 nm significantly from 25 m⁻¹ (mill C), 14 – 17 m⁻¹ (mill A, B and E), and 9 m⁻¹ (mill D), respectively, to 2 – 5 m⁻¹. Biological tests showed that the biologically treated wastewater was not toxic, neither before nor after ozone treatment or further biological treatment. The COD/DOC ratio of the effluent prior to ozone treatment differed between 3.2 and 3.9 for the tested mills, varied from sampling to sampling within the mills and was decreased by ozone treatment to a minimum of 1.7. LC-OCD analysis showed that in samples from all mills ozone treatment leads to a decrease in humics as well as in the aromaticity and molecularity of humics. Building blocks arise.

### Application/Economic benefits
Enlargement of wwtp by an ozone stage and low load biological stage can avoid exceeding the limit values in the effluent from the wwtp and thus the charges thereby incurred. A significant COD reduction in the effluent can additionally result in a lower monitoring value which means savings in waste water charges.

SME of different sectors would benefit from the broader use of ozone technology by opening up a new sales market in the paper sector. These include small or medium-sized planning and engineering offices, numerous SME suppliers of ozone plant manufacturers, for example producers of liquid oxygen tanks or compressors with compressed-air conditioning, pipelines, injectors, reaction vessels, ozone analysers, ozone destructors, pumps, fittings or cooling aggregates. Further beneficiaries are SME of the measurement and control technology sector, for example companies supplying analysers and sensors for the monitoring and control of new treatment stages and integrating them into the existing process control system.

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### Remarks
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