**Research Institute:**

PTS München
Hess-Str. 134
80797 München

Internet: www.ptspaper.de

**Head of the research institute:**

Dr. Frank Miletzky

**Project leader:**

Dr. Hans-Jürgen Öller
Tel: 089 / 12146-465
Fax: 089 / 12146-36
E-mail: hans-juergen.oeller@ptspaper.de

**Research area: General aims**

Environmental technology // Water

**Key words:**

Paper mill effluents, additives, limit value, monitoring, duckweed growth inhibition test

**TITLE:**

## Avoidance of increased duckweed toxicity values by targeted selection of papermaking additives

### Background/Problem area

Based on the request of the Federal Ministry for the Environment, the working group for the revision of Annex 28 Waste Water Ordinance included the duckweed growth inhibition test in the new Annex 28. This test was proposed as a result of a project funded by the German Federal Environment Agency due to its adequate sensitivity and minimum cross-sensitivity. The test result is expressed as inverse dilution factor $D_w$ and the proposed limit value in the new Annex 28 so far is $D_w = 8$. The majority of paper mill wastewater samples were tested by the authorities of Nordrhein-Westfalen and of Bayern. $D_w$ values were inconspicuous in the majority of samples, amounting to 1 or 2. However, there were isolated cases with measured $D_w$ values of up to 8, and values of up to 24 were found in more recent data. These increased values occurred exclusively in paper recycling mills. Their exact causes or further attendant circumstances could not be clarified so far. Basically there are several possible causes for higher $D_w$ values in wastewater samples: substances which enter the system with recovered fibres, biochemical degradation processes within the biological wastewater treatment plant, certain papermaking additives or a synergistic effect of aforesaid causes.

### Objectives/Research results

The main goal of this project is to investigate whether typical papermaking additives which are used in recovered fibre processing paper mills might contribute to increased $D_w$ values in biologically treated wastewaters. A simple evaluation scheme will be developed in order to support the paper mills at the selection of additives with no or with negligible effects on the duckweed toxicity.

Four recovered paper and one virgin fibre (as reference site) processing paper mills from Bavaria were selected as project partners. Each paper mill has performed a pre-selection of a maximum of twenty additives which might be interesting for the duckweed growth inhibition test. The total applied amount of each additive and toxicological information in the material safety data sheets were defined as selection criteria.

The additives of this pre-selection were classified according their purpose, e. g. retention aid, colorants, defoamers, biocides etc. In a second step the active ingredient of each additive class is compared and assorted if possible in order to decrease the total number of duckweed growth inhibition tests. Latest results show that biological non-treated wastewater has much higher $D_w$ values than biological fully treated effluents, so an influence from the applied additives cannot be excluded.

The additives were investigated in 6 different dilution steps corresponding to approximately 10 g/l to approximately 1 mg/l. In order to assess the toxicity of the additives, the dilutions were divided into 3 toxicity-levels. The $D_w$ values of the tested additives range from ≤ 96 up to one fixatives with 1,048,576. From the chosen additives, retention aids, biocides and colorants have continuously middle to high $D_w$ values ($D_w$ = 65,536 to = 524,288). Altogether, the group of tested defoamers show a low to a middle toxicity-level. Two of three investigated wastewater treatment chemicals have a $D_w \leq 96$, the third however has $D_w$ = 524,288. The toxicity of single tested process and functional chemicals, like wet strength resins or cleaners, vary from $D_w \leq 96$ to 131,072.

For the purpose of getting more realistic details, 9 additives were further investigated, using an aerobic degradation method, called Zahn-Wellens-Test (ZWT), before repeating the duckweed growth inhibition test with the biologically treated sample. This selection was chosen because of their results in the growth inhibition test, their different retention factor and their purpose. Apart from four additives (the fixatives, a wastewater treatment aid, a wet-strenght agent and a biocide), all the others showed a remarkable decrease to a low toxicity-level in their $D_w$ value after biological treatment. Due to that, the six remaining additives can be classified as “biologically degradable” and so five of them as not harmful anymore towards *Lemna minor*. Despite a good elimination during ZWT a wet-strength agents remains at the same toxicity level as without aerobic treatment which was $D_w$ = 131,072.

Comparing duckweed toxicity levels of the additives with their other toxicity parameters like daphnia magna, algae etc. their toxic concentrations are in a quite similar range. So, no special concern will rise due to the introduction of the duckweed growth inhibition test and in the face of application of typical papermaking additives.

### Application/Economic benefits

The inclusion of the duckweed growth inhibition test in Annex 28 of the Waste Water Ordinance is a novelty for the paper, paperboard and board manufacturing industry. It is therefore all the more important to define and stipulate a target value for $D_w$ that can be complied with by means of state-of-the-art technology. This will ensure the safe compliance of directly discharging paper mills with the minimum requirements of the Ordinance. The results of this project will contribute to an avoidance of increased $D_w$ values due to critical additives. In view of the all-pervasive economic pressure on the paper sector, it is imperative to avoid any costs incurred by the non-compliance with limit values, e.g. penalties for multiple transgressions according to the four-out-of-five rule.

**Period of time:** 01.02.13 - 31.01.14.

### Remarks

The research project Bayern - IGF - 1211-0005 was being funded by the Bavarian Ministry of Economic Affairs and Media, Energy and Technology.