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**Research area: General aims**

Environmental technology // Water

**Key words:**

COD, TOC, waste water, discharge limits

**Title:****Conduction of paper grade dependent COD-TOC-ratios as pre-condition for the replacement of the parameter COD in waste water legislation****Background/Problem area**

The EU IPPC (integrated prevention and pollution control) guideline requires an adoption of environmental laws in the EU member states. In Germany especially the waste water legislation has been revised. In 57 appendices of the text of law the discharge values of different industrial sectors are regulated. It was decided in December 2006 to amend appendices no. 28 (paper & board production) and no. 40 (metal processing and converting) as pilot cases. One of the planned major changes are the replacement of the parameter COD by TOC and replacement of  $N_{\text{total}}$ , inorganic by  $TN_b$  (= total nitrogen bound, including organic N compounds).

The actual limit value for COD discharge is 3 kg COD/t<sub>paper</sub> gross production for most paper grades. It will be not possible to assess new TOC-limit values just by applying a fixed COD-TOC ratio to convert the actual COD limit. TOC is already analysed in some paper mills parallel to COD for some years. The available COD and TOC data demonstrate that the COD-TOC ratio varies from 2.3 to 4.2, depending on the produced paper grade. Even within the different paper grades there is a wide range of measured factors. A too high COD-TOC ratio for the conversion of COD limit into new TOC limit value would lead to an unjustified tightening of discharge limits.

The today's nitrogen limit value is 10 mg N/l for the sum of  $NH_4^+$ ,  $NO_3^-$  and  $NO_2^-$ . Almost no experience is available on  $TN_b$  discharge figures of paper mills. The few data show that  $TN_b$  consists of at least 50 % organic N compounds. Hence  $TN_b$  values are at least two times higher than  $N_{\text{total}}$ , inorganic values. Therefore a new discharge value for  $TN_b$  has to be defined.

**Objectives/Research results**

The objective is the determination of reliable COD-TOC ratios (incl. their margin of deviation) of biologically treated waste waters from the production of different paper grades. This is the prerequisite to derive new TOC limit values in the amended appendix no. 28. Additionally a proposal for a limit value referring N compounds based on  $TN_b$  shall be developed.

It was decided to investigate three mills from each paper grade which are: un-sized wood free papers (p.), sized wood free p., specialty p., coated wood free p., wood containing p., p. from recovered paper (with and without de-inked pulp). In addition to TOC limit values to be deduced from COD-TOC ratios, the new limits must also base on the analysed TOC concentration, production capacity and waste water volumes. This necessity is due to the varying COD-TOC ratios even within one single paper grade. This additional evaluation is supported by numerous TOC online values, as the majority of the investigated mills are operating an TOC online analyser.

The measured COD-TOC ratios range from 1.4 (recovered paper with deinking) to 4.9 (sized wood free paper). In the latter paper grade even higher ratios up to 7.0 were measured in case of a higher content of suspended solids. Referring the new specific TOC load limits expressed as "kg TOC/t<sub>paper</sub> gross production" a complete evaluation of all laboratory and online values has to be performed before publication date. The results will be discussed within the project committee and within paper mill experts before submitting a proposal to the working group appendix 28. The available results so far demonstrate that the load limits which were proposed by the authorities might be too stringent

The analysed  $TN_b$  concentrations range from less than 2.0 (coated wood free, size wood free and specialty paper) to 27 mg/l (recovered paper with deinking). The  $TN_b$  usually consist of at least 50 % organic N compounds, in most cases 80 % or more. Organic N compounds are dominating the  $TN_b$  over the full range of analysed values. High  $TN_b$  concentrations indicate a higher usage of N-containing additives in the manufacturing process. Recommended  $TN_b$  limit values may reach at least 20 mg N/l or more.

**Application/Economic benefits**

The amendment of appendix 28 affect primarily paper & board mills, but also companies which construct waste water treatment plants, consulting bureaus and manufacturers of monitoring and control systems. If wrong COD-TOC ratios will be applied and more stringent limits will result, paper & board mills might lose the possibility to lower the waste water fee. Hence additional costs of several ten thousands of Euros will emerge which has to be avoided especially for small paper & board mills.

**Project period: 01.11.2007 – 31.10.2009**

**Remarks**

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