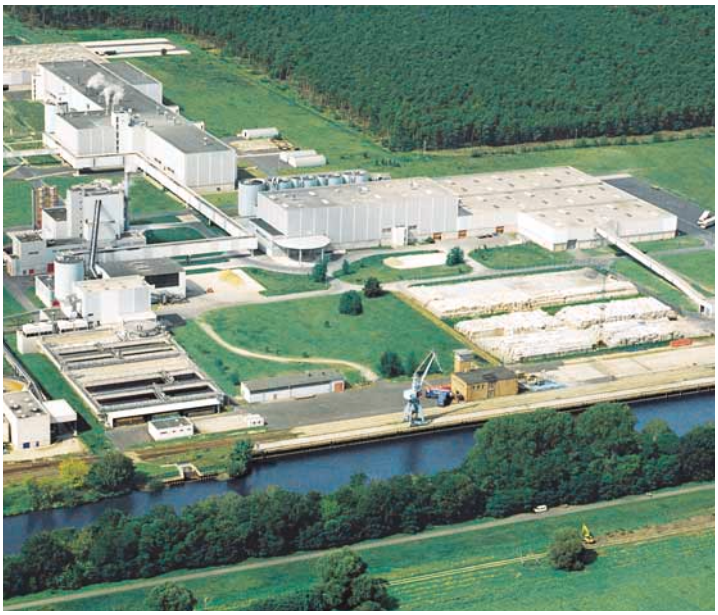

Figure 1: A birdseye view on the Schwedt plant

Figure 2: The paper production machine was commisioned in 1993

Laboratory and online TOC measurement in paper production

The environmental management statement of the UPM-Kymmene paper mill in Schwedt, Germany addressed the subject of TOC analysis in 2002. An issue was the introduction and installation of a TOC online monitoring programme to improve analytical monitoring and to assure stable plant operation, especially with respect to the biological aspects of wastewater treatment.

After carrying out TOC analyses for several months in online- and laboratory processes, it was possible to replace chemical oxygen demand (COD) measurements by TOC analyses. COD analysis is less definitive and no longer up to date due to its use of toxic chemicals.

The UPM-Kymmene plant in Schwedt – technology of paper production

The UPM-Kymmene paper mill in Schwedt is one of 22 plants belonging to the Finnish company. The Schwedt plant was founded in 1991 and has 300 employees. Collected wastepaper is used exclusively as raw material for paper production. 285.000 tonnes of newsprint paper is produced annually. UPM-Kymmene has introduced a management system for quality-, environmental- and safety control that includes the development, manufacture and sales of newsprint paper. The company complies with the regulations of ISO 9001 (2000), ISO 14001 (1996) / EMAS II and OHSAS 18001 (1999).

The plant is divided into several technical units:

- **Wastepaper plant**
  100 % wastepaper is the only raw material that is purified and treated in the deinking plant in several steps (dissolution, pre-sorting, pre-flotation, fine sorting, dispersal, post-flotation and thickening)

- **Paper production equipment**
  The Voith AG PM 11 paper production machine was commisioned in 1993. The working range is 8.50 m and the production rate is currently 1650 m/min.

- **Power- and steam plant:**
  The nominal steam capacity is 111.5 t/h. Steam is generated in three boilers (WSK, HD- and secondary boiler). The turbine capacity of the counter-pressure turbine is 8.14 MW. In the fluidised bed boiler, up to 240,000 t/p.a. of solid fuel is burnt (e.g. fibrous materials, wood shavings)

- **Wastewater treatment plant (ARA), consisting of three stages:**
  1. chemical-mechanical cleanup with disk filters and screw press
  2. chemical-mechanical cleanup in a micro-flotation tank
  3. biological cleanup in an aeration tank.

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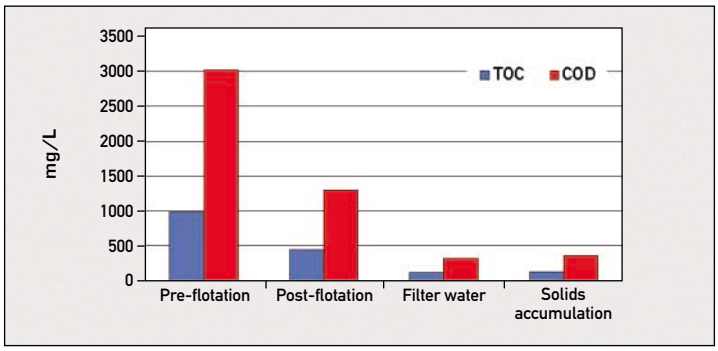

Figure 4: TOC and COD values of different types of water

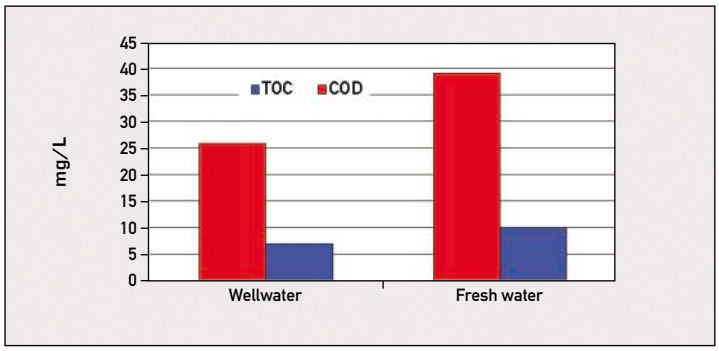

Figure 5: TOC and COD values of different types of water

The specific fresh water use is approximately 10 L/kg paper. Each year, a wastewater volume of approximately 3.5 million per m^3 is produced.

The wastewater treatment process is currently expanded with an anaerobic treatment stage (with two IC reactors). This precedes the aerobic stage which consists of 4 sequential aeration tanks and 4 parallel secondary sedimentation tanks. For a secure operation of the expanded ARA, it is particularly important to introduce TOC analysis, as the anaerobically formed reduced compounds – especially sulphur compounds in their HS^-, H_2S and SO_3^{2-} – form can be detected as well via the COD method and the desired results concerning the wastewater pollution levels would therefore not be accurate.

Figure 7: Location of the TOC-4100 online analyzer (on the right: The next generation: TOC-4110)

Why TOC analysis in the paper industry?

The COD and total nitrogen monitoring parameters (sum of ammonium-, nitrite- and nitrate [inorganic] species) which are established in wastewater regulations are, based on their ecological and industrial hygiene characteristics and their poor automation potential, no longer up to date and should be replaced in the near future by TOC- and TN_b analyses. A complete replacement of the COD method by TOC is possible without any problems when TOC minimum requirements,

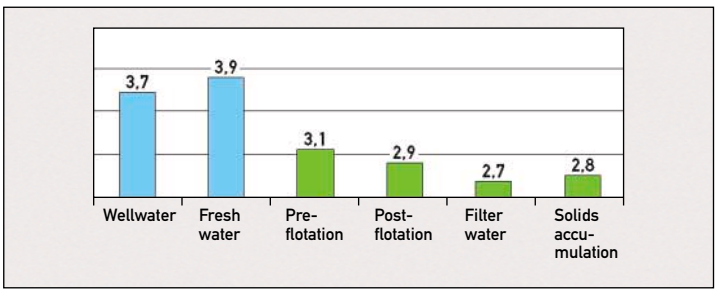

Figure 6: COD/TOC ratio in different types of water

based on a COD/TOC ratio according to industry specific TOC analyses, will be implemented. The implementation of polluter surveillance would even be more straightforward and more correct.

Shortcomings of the COD determination are that in addition to organic carbon compounds, also:

- bromide
- peroxide (H_2O_2/HO_2^-)
- dithionite, sulphite und sulphide
- copper I-, manganese II- and iron II compounds are measured.

Other shortcomings are:

- use of toxic chromium- and mercury compounds
- use of silver sulphate and concentrated sulphuric acid
- occurrence of matrix effects: high chloride- and particle concentrations interfere with COD determinations.
- analysis time is approximately 15 times longer using COD analysis.

For these reasons, UPM-Kymmene decided in 2002 on a general implementation of laboratory and online TOC measurements, as described in their environmental management statement.

From the dissolution of wastepaper to the process waters used in paper production

Figure 3 shows the laboratory setup with the TOC-V basic instrument ($TOC\text{-}V_{CPH}$), the SSM-5000A solid-state autosampler module and the data evaluation unit. Figures 4, 5 and 6 show the total process water analysis with respect to the determination of the sum of organic, soluble compounds in the technological set-up – from the dissolution of wastepaper up to the paper production equipment.

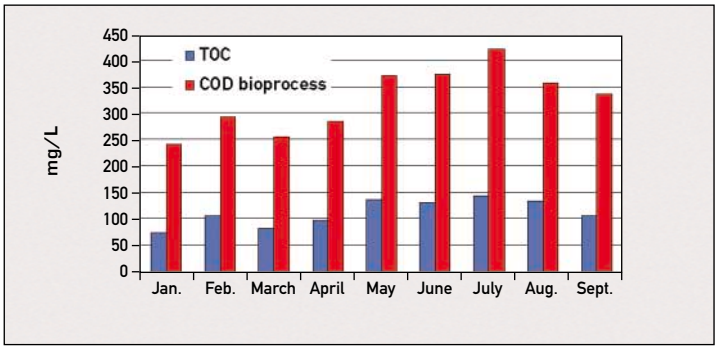

Figure 8: TOC and COD values bioprocess ARA

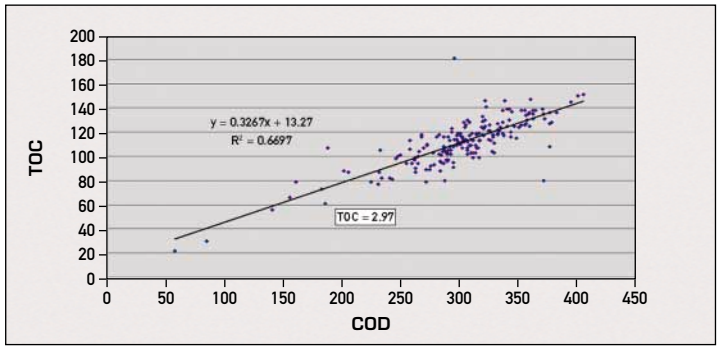

Figure 9: TOC/COD ratio ARA process 2002

Figure 4 shows the TOC/COD pollution in the pre-flotation, post-flotation (AP plant), the filter water and the paper production equipment cycle.

The reduction in concentration of the organic carbon compounds during the technological cleanup stages in wastepaper treatment up to paper production is evident.

Figure 5 shows the low organic pollution levels in wellwater and fresh water. The COD/TOC ratios are displayed in Figure 6.

The significantly higher ratio of well- and fresh water is of interest. This is due to the oxidisablility of manganese- and iron compounds which are detected in significant concentrations in these types of waters. The COD/TOC ratios of process waters are, in general, quite close to the theoretical, stoichiometric factor of 2.67 (2 oxygen to 1 carbon –> O_2 to C)

The various steps in wastewater cleanup

Figure 7 shows the TOC-4100 online analyser. The location was selected in such a way that the equipment in the ARA building can be operated safely at room temperature. In addition, care was taken that the pathways from the sampling location to the TOC-4100 analyzer – from influx and outlet of the wastewater to the biological treatment stage – were not too long and that all further necessary connections were available.

It is clear that some special precautions are needed for the safe operation of the analysis setup:
- cross-section of the sample introduction
- pre-pressure of the sample introduction
- acid rinsing of the sample pretreatment zones in the TOC-4100 analyser.

As wastewater contains compounds that are easily degradable and the temperature and the pH value are in a favourable range for bacterial growth (32 °C/pH 7.5), an acid rinse stage was included. This stage prevents the formation of biofilms which can interfere with the sampling procedure and can provide erroneous results.

The analytical reproducibility and sampling procedures were further improved by the inclusion of an overflow stage. Before the introduction of this constant-pressure sampling stage, the influx of samples was dependent on technological controlled exchange of the bio-inflow pressure after cooling and interfered with the automated sampling procedure.

In Figures 8 and 9, the COD/TOC concentration ratios are shown for various monthly average values and their ratio factors.

Conclusions

The latest changes in the draft for wastewater regulation and the wastewater taxation law indicate that the parameter for chemical oxygen demand (COD) should be replaced by TOC analysis in environmental regulations.

A factor of 3.3 for the conversion of COD to TOC has been proposed in the present drafts. This factor does not reflect the actual COD/TOC ratios in the investigated wastewater. The currently planned changes in Appendix 28 of the wastewater taxation law (for paper, carton and cardboard) have therefore been postponed due to the differing conversion factors. Otherwise several plants needing to comply with the wastewater regulation would be disadvantaged, resulting in an increase of the wastewater tax and a reduction of the limiting values.

Figure 3: The TOC systems on duty