Risk assessment approaches for ecosystem responses to a point source of pollution on receiving waters

M. Cotman\textsuperscript{1} & J. Zagorc-Končan\textsuperscript{2}

\textsuperscript{1}National Institute of Chemistry, Slovenia
\textsuperscript{2}Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

Abstract

The European Water Framework Directive (WFD) requires the identification of significant human pressures and impacts on water bodies. An important component in protecting the ecological quality of watercourses is the regulation of point discharges. New ecotoxicological approaches for the assessment of the influence of the point source of pollution on the receiving water are presented. The limitations of a substance-specific assessment make it impossible to satisfactorily assess effluents on the basis of their environmental hazard. The new strategy starts with the investigation of effluents (chemical analyses, toxicological and biodegradation studies, toxicity identification evaluation-TIE). Then the harmful substances from the effluents are traced in the receiving stream and the impact of these substances on the stream is determined in river water and sediments. In a case study this strategy was used for impact assessment of tannery and municipal wastewater on the river Ljubljanica. We investigated the impact of pollution by the tannery and municipal effluents upon the receiving water and sediments. At the highest measured river flow the concentrations of pollutants in the river were not significantly changed as a result of the impact of the point source of pollution. At average and critical river flows the concentrations of pollutants at the sampling site near the outflow of effluents were higher, but at a site distant from the source of pollution, the concentration decreased due to different physical, chemical and biological processes in the river (biodegradation, precipitation). River water was non-toxic in acute and chronic toxicity tests with \textit{Daphnia magna}. Sediments have the ability to accumulate organic and inorganic toxic compounds. Increased amounts of chromium and aluminium in river sediments were found at the sampling site far from the source of pollution. From the results of our work it is evident that the limitation of effluent alone is not enough, and that for good river management it is essential to consider the receiving stream as well.

Keywords: municipal wastewater, point source of pollution, river water, sediment, tannery wastewater, toxicity tests.
1 Introduction

The new EC-Water Framework Directive (WFD [13]) has the objective of providing integrated catchments-oriented water quality protection for all European waters, with the purpose of attaining good quality status by the year 2015. The water quality evaluation for surface water relies predominantly on biological parameters (such as flora and fauna) aided however, by hydromorphological (such as flow and substrate conditions) and physico-chemical quality components (such as temperature, oxygen or nutrient conditions), and on identification of specific pollutants (such as metals or synthetic organic compounds). A good chemical quality status is provided when the environmental quality standards are met for all pollutants. The WFD defines new strategies against water pollution as a consequence of release from point and diffuse sources. A new aspect of the EC water policy is a combined approach, including both limitations on pollutant releases at the source resulting from promulgation of emission limit values, as well as the establishment of environmental quality standards. Releases of pollutants, especially from point sources, must meet both requirements Jirka et al. [4].

Effective environmental management of discharges from industrial wastewater treatment plants must include environmental hazard or impact assessments, as well as technical and economic evaluations of various procedures for pollution reduction, such as dilution, effluent treatment, or implementation of cleaner technologies. The environmental impact is determined by the composition of the effluent and the discharged quantities on the one hand, and by the dilution and specific characteristic of the receiving water on the other, and both local effects and possible contributions to more widespread, general pollution must be taken into account, according to different authors (Nyholm et al. [7]; Nyholm [8]).

The harmful substances from effluents are traced in the receiving stream and the impact of these substances to the stream and the organisms on the stream are determined. The impacts of contaminants on receiving waters depend on a number of physical, chemical and biological characteristics of the receiving stream. Freshwater sediments integrate harmful substances from effluents over time, so investigation of sediments as well as river water is necessary.

2 Materials and methods

2.1 Description of sampling sites

The methodology for impact assessment of discharges was used in a study of the quality of the river Ljubljanica at Vrhnika. The study area is presented on Figure 1.

Tannery wastewaters were sampled at the output of the physico-chemical pretreatment systems. Municipal wastewaters were sampled at the outflow of the wastewater treatment plant, which has only a mechanical phase. The effluents from the industrial pretreatment system and from the municipal wastewater...
treatment plant were discharged close together into the receiving stream, so that separate impacts could not be distinguished. The river Ljubljanica is one of the largest tributaries of the Sava, which itself is the largest Slovenian river. The impact of both industrial and municipal effluents on the river Ljubljanica was investigated at the control sampling site and two sampling sites downstream from the outfall. The average yearly flow of the Ljubljanica in Vrhnika is 24.8 m$^3$/s; the lowest thirty-year flow is 2.55 m$^3$/s. The upstream sampling site (SITE 1) was at the source of Ljubljanica where both river water and control sediment were sampled. The sampling site downstream (SITE 2) was 3000 m below the upstream site, and 200 m below the outflow of pretreated tannery wastewater and municipal wastewater. The sampling site downstream (SITE 3) was 3700 m distant from site 2.

![Diagram of the study area](image)

**Figure 1:** The study area.

### 2.2 Chemical and toxicity analyses

Wastewaters and river water were chemically investigated before toxicity assay. The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were measured immediately after sampling. Phosphate, nitrite and nitrate were determined by chemically suppressed ion chromatography (DIONEX 4000 I) in the filtered samples using a 0.2$\mu$m filter. Total phosphorus was determined spectrophotometrically after mineralization with persulphate. Organic nitrogen and ammonia were measured by the macro Kjeldahl method. Analyses of metals were performed by ICP-AES (Thermo Jarrell Ash) in whole samples. Toxicity was estimated by standard non-benthic bioassay organisms as recommended for the *Daphnia magna* mobility inhibition test and the *Vibrio fischeri* bioluminescence inhibition test. The chronic toxicity test using *Daphnia magna*
reproduction inhibition was performed with river water samples. All analyses were performed according to the standard procedures in Standard Methods for the Examination of Water and Wastewater [11].

3 Results and discussion

The environmental impact of wastewaters is highly case specific and depends on the composition of the effluent, including its temporal variability, and on the volumes discharged. Frequent sampling of industrial wastewater is necessary due to varying production conditions. The tannery wastewater was sampled ten times and the municipal wastewater four times during the year. The results for the pollution load in industrial effluent and municipal effluent are presented in Table 1. The pollution loads were calculated from the highest concentration of each parameter and the highest measured daily flow of wastewater.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Pollution load of tannery effluent</th>
<th>Pollution load of municipal effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, kg day(^{-1})</td>
<td>6720</td>
<td>672</td>
</tr>
<tr>
<td>BOD(_5), kg day(^{-1})</td>
<td>4352</td>
<td>345</td>
</tr>
<tr>
<td>Tot. susp. solids, kg day(^{-1})</td>
<td>2231</td>
<td>256</td>
</tr>
<tr>
<td>Al, kg day(^{-1})</td>
<td>29.9</td>
<td>*</td>
</tr>
<tr>
<td>Cr, kg day(^{-1})</td>
<td>8.85</td>
<td>1.1</td>
</tr>
<tr>
<td>S(^2-), kg day(^{-1})</td>
<td>6.8</td>
<td>*</td>
</tr>
<tr>
<td>SO(_4^{2-}), kg day(^{-1})</td>
<td>3048</td>
<td>22.3</td>
</tr>
<tr>
<td>Cl(^-), kg day(^{-1})</td>
<td>6325</td>
<td>106</td>
</tr>
<tr>
<td>NH(_4^+)-N, kg day(^{-1})</td>
<td>214</td>
<td>82</td>
</tr>
<tr>
<td>N(_{org}), kg day(^{-1})</td>
<td>232</td>
<td>95</td>
</tr>
<tr>
<td>P(_{tot}), kg day(^{-1})</td>
<td>11.8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*concentrations of pollutants were under the detection limits so the pollution load could not be calculated.

The physico-chemically pretreated tannery wastewater contained very high concentrations of organic and inorganic substances. The loads of organic pollution (COD, BOD) and suspended solids were ten times higher for industrial than for municipal wastewater. Although the concentration of COD and BOD\(_5\) varied between different samplings, their ratio remained the same in the range of 0.60 - 0.71, average 0.65. The same ratio was confirmed in the biodegradation study of Cotman and Zagorč-Končan [1]. The physico-chemical pretreatment system at the tannery using precipitation and flocculation with Al-sulfate and an anionic polyelectrolyte was insufficient. The addition of Al-sulfate is not optimal as excess aluminum, whose harmful properties have been previously
investigated, is discharged into the river Ljubljanica. With this system chromium is also unsatisfactorily removed, so that a quantity of total chromium was discharged into the river. The most toxic form of chromium, Cr(VI), was not present due to the reducing character of tannery wastewater Milacic et al. [5]. An additional load of chromium in municipal wastewater was leached from the tannery wastes dump. The industrial wastewater also contained high concentrations of sulfide, sulfate and chloride. The loads of nutrients were approximately twice as high in the industrial than in the municipal wastewater.

Chemical analyses of wastewater were complemented with toxicological analyses. The results of the toxicity test with *Daphnia magna* were in good agreement with the results of chemical analyses. The most toxic samples were those that contained the greatest organic pollution load and the highest concentrations of chromium. These substances besides in addition to ammonia and organic nitrogen were the probable reason for the toxicity of tannery wastewater. The municipal effluent contained higher amounts of organic pollutants and nutrients. An additional load of chromium in municipal wastewater was leached from the tannery waste dump. Possible reasons for the toxicity to *Daphnia magna* of municipal wastewater were chromium and ammonia. Detailed results of whole effluent toxicity were published elsewhere Tišler et al. [12].

Toxicity identification and evaluation methods (TIE) have proven very useful in characterizing, identifying and confirming toxic substances in environmental samples (Fiehen et al. [3]; Reemtsma and Jekel [10]). We identified key toxic components in pre-treated tannery wastewater by fractionation of the samples through chemical and physical means (filtration, air stripping, adsorption on activated carbon and zeolite treatment). The goal of each fractionation step was to reduce the toxicity due to a specific group of chemicals and compare the results to the toxicity present in the unaltered sample. Short-term toxicity tests with the invertebrate *Daphnia magna* and the bacterial luminescence inhibition test with *Vibrio fischeri* were used in combination with chemical analyses. During the TIE fractionation, a portion of sample was pressure-filtered. Treated samples contained less organic pollutants and metals, and were less toxic, especially to *Daphnia magna*. For the removal of ammonia a second portion of sample was air-stripped at different pH levels. We removed 84% of ammonia at pH 11; the toxicity to both organisms decreased but ammonia did not have a decisive effect on the toxicity of tannery wastewater when the organic load was still present. The most successful procedure for toxicity removal was adsorption on powdered activated carbon (PAC). We removed organic pollutants detected as COD, organic nitrogen compounds and part of the metals. The zeolite treatment was a little less successful for removing ammonia than air stripping. The details of TIE identification in tannery wastewater were published elsewhere (Cotman et al. [2]).

The impact of both industrial and municipal effluents on the river Ljubljanica was investigated at the control sampling site and two sampling sites downstream from the outfall under different river flow conditions. The temperature of river water was not increased due to discharges. The saturation with oxygen in river
water was mostly dependent on the river flow during the different seasons of the year. The excessive growth of algae and macrophytes in spring caused the river water to be oversaturated with oxygen, especially at both sampling sites downstream. At critical low flow conditions (5.37 m³/s) at the end of summer, oxygen saturation was 34% at both downstream sites.

Figure 2: The concentration of COD and chloride in the river Ljublajnica under different river flow conditions.

Both specific and non-specific harmful substances from the effluents were investigated in the river water. As examples, the concentrations of COD (non-specific pollution) and chloride (specific pollution from the tannery) in river water at various river flow conditions are presented in Figure 2. The concentrations of pollutants in the river water depend mainly on river flow. At the highest flow the concentrations of pollutants in the river were not significantly changed due to discharge of industrial and municipal effluents. At the average river flow higher concentrations of pollutants were noticed at site 2, but at site 3 the concentrations decreased due to different physical, chemical and...
biological processes in the river (biodegradation, precipitation). At the critical river flow trends were the same, except for organic pollution that did not decrease at sampling site 3 due to the impact of non-point sources, which was only evident under the low flow conditions.

The additional conformation that a point source of pollution is dominant on the study area is the shape of the curve (hyperbolic function of flow), of COD concentration versus river flow (Figure 3), as is known from the literature (Novotny [6]). The point source discharges are considered steady state, which implies that they are more or less constant for an extended period of time. Assuming that loads from different point sources are steady over time, the water quality at a specific receiving water cross section depends primarily on the flow and consequent dilution. For conservative pollutants, their concentration depends strictly on dilution: for real constituents, their reaction and their dependence on various processes and parameters, such as temperature, may cause distortions.

![Figure 3: Concentration of COD in river water at sampling site 2 for different river flow conditions.](image)

Due to the toxicity of the whole effluent, acute and chronic toxicity tests with *Daphnia magna* were made with river water. The “Step Principle” was used (Newman et al. [9]). If river water samples were not toxic in the acute tests, the chronic test were performed. In the acute toxicity tests of 24 and 48 hours duration with samples of river water the results were negative. With the same organism the chronic toxicity tests (i.e. reproduction inhibition) with the river water sampled at the lowest river flow (critical condition) were then made. All three samples were nontoxic.

Sediments have the ability to accumulate organic and inorganic toxic compounds. The concentrations of dangerous substances in sediments are not so river flow dependent as in the river water. For this reason concentrations of pollution were determined in river sediments and are presented in Table 2.

In river sediment at the downstream sampling sites higher concentrations of organic pollutants (COD), organic nitrogen and total phosphorus were found.
The impact of effluents on metal concentrations in sediments was evident, but on the contrary, the impact of effluents on the metal concentrations in river water was not significant. The highest amounts of metals were found in sediments at the sampling site far away of the source of pollution (Site 3) due to transport of fine particles.

### Table 2: Chemical analyses of sediments.

<table>
<thead>
<tr>
<th></th>
<th>I. sampling</th>
<th>II. sampling</th>
<th>III. sampling</th>
<th>IV. sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>S2</td>
<td>S1</td>
<td>S2</td>
<td>S1</td>
</tr>
<tr>
<td>Flow, m³s⁻¹</td>
<td>19.5</td>
<td>14.3</td>
<td>4255</td>
<td>14.9</td>
</tr>
<tr>
<td>Irrigation loss, %</td>
<td>1.6</td>
<td>7.2</td>
<td>1.3</td>
<td>8.8</td>
</tr>
<tr>
<td>COD, mgg⁻¹dw</td>
<td>14</td>
<td>69</td>
<td>13</td>
<td>85</td>
</tr>
<tr>
<td>Nₜₖₑᵱ, mgg⁻¹dw</td>
<td>0.4</td>
<td>1.0</td>
<td>0.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Pₜₒₜₑ, mgg⁻¹dw</td>
<td>0.3</td>
<td>0.5</td>
<td>8</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr, µg g⁻¹dw</td>
<td>*</td>
<td>*</td>
<td>71</td>
<td>377</td>
</tr>
<tr>
<td>Al, µg g⁻¹dw</td>
<td>*</td>
<td>*</td>
<td>1400</td>
<td>2700</td>
</tr>
</tbody>
</table>

### 4 Conclusions

In our study we present an evaluation strategy for impact assessment of tannery and municipal wastewater on the receiving river. Tannery wastewater is a complex mixture of biogenic matter from hides and a large variety of organic chemicals added during the tanning process. The physico-chemically pretreated tannery wastewater contained very high concentrations of organic and inorganic substances. With the existing treatment system chromium was not satisfactorily removed from wastewater. There were high concentrations of sulfide and sulfate. The results of the toxicity test with *Daphnia magna* were in good agreement with the results of chemical analyses. The most toxic samples were those that contained the greatest organic pollutant load, with the highest concentrations of COD, BOD₅, oil and grease and the highest concentrations of chromium. These substances, as well as ammonia and organic nitrogen, were the probable reason for the toxicity of tannery wastewater. The municipal effluent contained higher amounts of organic pollutants and nutrients. An additional load of chromium in municipal wastewater was leached from the tannery wastes dump. Possible reasons for the toxicity to *Daphnia magna* of municipal wastewater were chromium and ammonia.

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The ecotoxicological approaches for the assessment of point source of pollution on receiving water presents the case study for implementation of the Water Framework Directive and its aim of consistent improvement of water quality.

**References**


