

Name	Type/population equivalent
<i>Industrial wastewater treatment plants</i>	
Company 1	Galvanising plant
Company 2	Tannery/PE120 75.000
Company 3	Fruit concentrate comp./PE120 160.0
Company 4	Abattoir
Company 5	Poultry abattoir
Company 6	Tannery/PE120 180.000
Company 7	Conductor board comp.
Company 8	Tannery/PE120 90.000
<i>Municipal wastewater treatment plants</i>	
Wastewater treatment plant 1	30.000
Wastewater treatment plant 2	32.000
Wastewater treatment plant 3	12.000
Wastewater treatment plant 4	35.000
Wastewater treatment plant 5	11.000
Sum wastewater treatment plants <1.000 PE	15.000

Full-size table

Industrial companies in the study area had onsite wastewater treatment according to the best available technology. They included a galvanising industry, a conductor board company, tanneries, abattoirs and a fruit concentrate company. Wastewater treatment of the three tanneries (C2, C6, and C8) includes biological treatment with nitrification and denitrification, sludge retention time >20 days and temperature in the activated sludge tank >20 °C. Municipal wastewater treatment plants feature single staged activated sludge process, three of them with anaerobic sludge digestion, two of them with simultaneous aerobic digestion. Population equivalents range between 11,000 and 35,000. Additionally, 10 municipal wastewater treatment plants with a population equivalent between 1000 and 10,000, as well as, 60 municipal wastewater treatment plants with a population equivalent below 1000 are situated in the Austrian part of the river basin. As they, all together, treat only negligible amounts of the disposed wastewater, they were not part of the sampling programme (see Table 1).

Table 2 gives information on the sampled dischargers and on the different sampling dates. River water samples were taken on monthly basis. The sampling frequency was increased when the industries were not in operation during holidays. An initial screening of all point source dischargers at the beginning of the study identified these dischargers as being potentially responsible for foaming. To assure the results of the first screening, all 13 dischargers were occasionally sampled again to consider varying boundary conditions (including production processes of the dischargers and physical conditions of the river). Consequently, the monitoring programme could be reduced to nine emitters including the tanning industry (WWTP1, WWTP2, WWTP4, WWTP5, C2, C3, C6, C7, and C8).

Table 2.

Listing of the sampling interval and dates at the surface water sampling sites (SP), the wastewater treatment plants (WWTP) and the companies (C).

*Additional daily samples were sent by mail for weekly composite samples; grey

setting means company holidays.

	SP1- S	WWTP1*	WWTP2*	WWTP3	WWTP4*	WWTP5*	C1	(
18.11.2005	x	x	x	x	x	x	x	>
30.11.2005	x	-	-	-	-	x	-	>
14.12.2005	-	x	x	x	x	x	x	>
29.12.2005	x	-	-	-	-	-	-	█
04.01.2006	x	-	-	-	-	-	-	>
10.01.2006	x	x	x	x	x	x	x	>
31.01.2006	x	-	-	-	-	x	-	>
21.02.2006	x	x	x	x	x	x	x	>
07.03.2006	x	-	-	-	-	x	-	>
05.04.2006	x	-	-	-	-	x	-	>
19.04.2006	x	-	-	-	-	x	-	>
10.05.2006	x	-	-	-	-	x	-	>
20.06.2006	x	-	-	-	-	x	-	>
26.07.2006	x	-	-	-	-	x	x	-
09.08.2006	x	x	x	x	x	x	x	█
23.08.2006	x	-	-	-	-	x	-	>
19.09.2006	x	-	-	-	-	x	-	>
19.10.2006	x	-	-	-	-	x	-	-

3.2. Field measurements

Physical parameters, i.e. dissolved oxygen, oxygen saturation, conductivity, temperature and pH were measured onsite at all surface water sampling sites.

To achieve detailed information on the river's water chemistry and potential diffuse pollution sources, an online monitoring station was applied close to the sampling station 4 (SP4), a point on the river where wastewater effluents from all industries and WWTPs have entered the river (Winkler et al., 2007).

An online webcam, as well as, pictures taken during the sampling campaign provided information on the different foaming situations in the river. Based on those pictures, a seven-stage "foam index" (FI) was developed (Table 3). In case of the occurrence of foaming conditions, which could not exactly be related to a certain foam index, intermediate stages were created (e.g. 0.5, 1.5, 2.5, ...). Foam index is presented as the immission parameter to assess the amount of foam on the surface of the river. The index does not quantify the foam, but allows a semi-quantitative differentiation between the varying foaming conditions (see Table 3).

Table 3.

Summary of the seven-staged foam index (FI).

<i>FI</i>	Situation	Description
0	No foam	None
1	Minimum foam	Sporadic small bubbles
2	Little foam	Bubbles accumulate to small areas
3	Moderate foam	Small foam areas, no single bubbles
4	Much foam	Flat foam areas, partly accumulating to compact foam lumps
5	Plenty of foam	Large flat foam areas and/or compact foam lumps partly large
6	Heavy foam	Ample compact foam lumps, large foam areas partly large are

Full-size table

Foam index was determined regularly at the four weirs along the river stretch (weirs are displayed in Fig. 1) during the monitoring programme. The responsible agency of the Federal State Government, allocated pictures of weirs 3 and 4 from 10/2004 until 09/2006, which were taken before the monitoring started. Thus, for the four weirs different data sets were available. Foam index of weirs 1 and 2 was surveyed onsite on nearly all sampling dates ($n = 16$). At weirs 3 and 4, the foam index was determined for 75 days (pictures provided by Federal State Government plus pictures during monitoring programme). Additionally, for weir 4 a daily foam index was available due to the online webcam, which took pictures at intervals of 15 min. Thus, the daily foam index is a "mean" value.

As no legal quantitative immission threshold for foam exists, the "not accepted degree of foam formation" at a level of $FI = 3.5$ was introduced, which was the limit, when protests from Hungary arose during the monitoring.

3.3. Laboratory measurements

Classical chemical parameters (i.e. chemical oxygen demand, total and dissolved organic carbon, total and dissolved nitrogen and phosphorus parameters, chloride and sodium) of the water samples and the samples of the dischargers were analysed in the laboratory. Samples were cooled during transport and processed within 24 h after the sampling to avoid degrading processes.

Additionally, five industrial and four municipal wastewater treatment plants (C2, 3, 6, 7, 8 and WWTP1, 2, 4, 5) sent daily composite samples for analysis. They were mixed into weekly composite samples for further chemical analysis, as well as, for foam tests described in the following. Surface tension was analysed as sum parameter for surface active compounds in the river water, as well as in the dischargers' samples. To achieve more information on the foam's origin, various surfactants (e.g. Quaternary Ammonium Compounds – QUACs, Nonylphenols – NPs, Nonylphenoxyethoxylates – NPEOs, Linear Alkylbenzolsulfonates – LAS) were analysed in the river and also in the samples provided by the wastewater treatment plants on two sampling dates. In addition, a qualitative screening of foam samples of the river and the effluents of the wastewater treatment plants was conducted once to identify single substances potentially causing foam.

The parameters "foaming factor" and "foam potential" were developed to characterize the amount of foam emitted. Effluents of all dischargers, as well as, the surface water samples were subject to standardised foaming tests, which were developed during the study. The intention of this test was to detect, (i) foam on the sample and, (ii) the dilution of the sample at which no more foam could be observed. Effluents (250 ml) were shaken in Erlenmeyer flasks with baffels on a laboratory Shaker (Type Ceromat-U) for the duration of 3 min at a speed of 300 rpm. After shaking, the foam size and the time it took for the foam cover to break were measured. In the case of foam occurrence the sample was diluted with river water up to a point where no more foam was produced. The dilution factor, at which minimal foam occurred, was defined as the "foaming factor".

For the calculation of the "foam potential" of an effluent, the foaming factor of this

effluent was multiplied with the discharge of the effluent.

$$FP_{\text{effl.x}} = FF_{\text{effl.x}} * Q_{\text{effl.x}}$$

FP = foam potential of effluent x (m^3/s); FF = foaming factor of effluent x ;

Q = discharge of effluent x (m^3/s).

That means, if for example, an effluent with a discharge of $0,02 \text{ m}^3/\text{s}$ and a foaming factor 50 was discharged into the river water (which is the diluting media), $1 \text{ m}^3/\text{s}$ (according to laboratory conditions) of the river water would show minimal foaming, if adequate turbulence was introduced. Thus, the foam potential of an effluent was defined as the volume of river water which can potentially get foamed by the effluent's discharge. Laboratory measurements of this nature underestimate the actual foam potential given in the natural environment, as a river passing through a weir or cascade would make a lot more turbulence.

3.4. Methodological approach for model development

The prerequisite to assess and to set management measures in a river basin is the identification of the cause–effect relationship between the emissions and the immissions. In this study, the assessment is provided by a model (see Results and discussion), which was developed for the foaming situation at weir 4, as the best data set for the foam index and river discharge was obtained at this weir. As the model is specific for the investigated river and the local situation, it might not be applicable for other rivers.

The statistical significance of the regressions, which were basis of the model, was checked by an F -test. The test statistic F , which is obtained by dividing the explained variance by the unexplained variance, is distributed according to an F distribution. A value higher than the critical value $F_{k-1;n-k}$ indicates that, (i) the null hypothesis has to be rejected, (ii) the probability is small that the relationship found happened by chance, and (iii) p is less than the critical level of significance. The p -value is the probability of being wrong in concluding that there is an association between the dependent and independent variables. Level of significance for the F -test was 0.01, which is highly significant. For the regression equations the coefficient of determination, the F -value and p are provided.

The model performance was estimated using the Nash–Sutcliffe-Coefficient (Nash and Sutcliffe, 1970). The efficiency of the model R^2 is given as:

$$R^2 = \frac{F_0^2 - F^2}{F_0^2} \quad (1)$$

where F_0^2 is the initial variance and F^2 is the residual variance. The Nash–Sutcliffe-Coefficient can reach values between -1 and 1 . In case of -1 no accordance between observed and calculated FI can be found, whereas, a total match between observed and calculated FI is indicated by 1 .

4. Results and discussion

4.1. Emission monitoring

The relative fractions of the loads of different parameters from the dischargers are displayed in Fig. 2. They are subsumed in three branches, i.e. the municipal dischargers (WWTPs), the leather Industry (Tanneries) and the remaining Industry. Whereas the municipal WWTPs are the main contributors to the discharge of wastewater in the river (around 80% of point sources), the other parameters, i.e. COD, TOC, Chloride and foam potential are dominated by the tanneries (70–90%). Contribution of the other industry-branches is low.