

Fig. 2. Relative fraction of different industrial branches on effluent's discharge (Q), chemical oxygen demand (=COD), total organic carbon (=TOC), chloride (=Cl) and foam potential (=FP).

Although there was no reason to believe that the analysed tenside concentrations were responsible for massive foaming, high foaming factors, as well as, high foam potentials were observed particularly for the tanneries. This indicates that foam results not from the analysed surfactants but from other surface active compounds used in the tanning process. These substances are either not degraded during the biological treatment in the wastewater treatment plant, or are even produced as degradation by-products. A qualitative screening of the effluents was not suitable to identify single substances beside surfactants in amounts causing foam. Thus, a sum parameter for foam causing substances was required. In Fig. 3, the dischargers are subsumed in different branches and appear in different grey scales and symbols. The dotted line indicates surface tension of the river water, which is around 72 mN/m. From Fig. 3 it can be concluded that (i) the lower the surface tension, the higher the foaming factor of the sample, (ii) high foaming factors were found at the tanneries and the metal industries, although the analysed surfactants gave no indication for foaming and (iii) municipal WWTPs show mostly surface tensions in the range of 70 mN/m, which is close to that of the river water and does not lead to foam formation under laboratory conditions. The encircled symbols show the effect of applied anti-foaming agents, which influence the correlation between surface tension and foaming factor. As surface tension of anti-foaming agents must be lower than that of the media in which they are used, their application leads to a decrease in the surface tension and the foaming factor at the same time. Nevertheless, Fig. 3 highlights a reliable regression between foaming factor and the surface tension of effluents, because the presence of surface active compounds reduce the surface tension of a solution (Vikingstad, 2006), and foam can occur. Consequently, surface tension as well as the corresponding foaming factor was chosen as sum parameter for foam causing substances, while foam potential (which is calculated out of the foaming factor) is introduced as emission parameter and represents the potential volume of river water that may be foamed by the effluent of the dischargers.

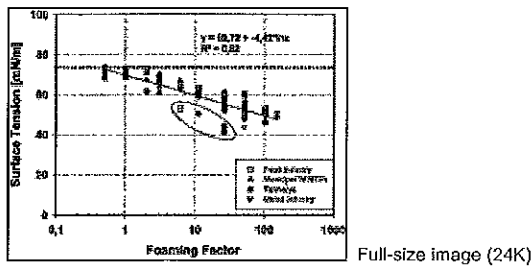
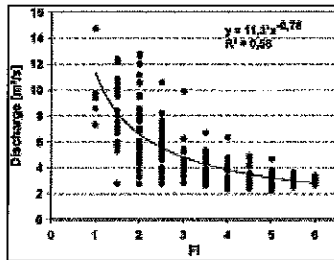


Fig. 3. Regression model for surface tension and foaming factor of the sampled dischargers (dotted line indicates the surface tension of distilled water). Encircled points indicate application of anti-foaming agents.

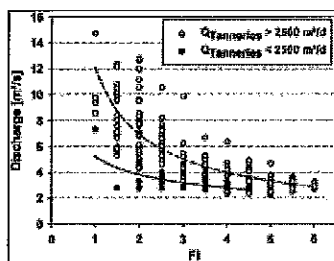
discharges due to high turbulence and diffuse pollution sources such as agricultural runoff, which may contain particulate organic matter producing foam (Wegner and Hamburger, 2002). In consequence, high discharge can occasionally result in a higher foam index than it would be expected because of the high dilution of point source emissions. On the other hand, by means of water extraction by agriculture or retaining of the water due to different reservoirs along the river stretch, the river discharge reduces to a minimum temporarily, so that little or no turbulence is created. If river discharge is that low, no foam will occur due to the lack of energy input by turbulence, although dilution is low and the foam index is expectedly high. This aspect is in accordance with the experience gained from the foaming test with river samples during this study.



Full-size image (21K)

Fig. 5. Regression model for river discharge and foam index (FI) at weir 4.

The variability of foam indices at low discharge conditions is caused by the varying foam potential emissions of the three tanneries. Fig. 6 gives the same regression depending on the discharging conditions of the tanneries caused by different operation conditions. The displayed picture indicates that the observed foam index for specific river discharges is significantly lower during company holidays than during normal production process. Thus reduced emissions of the tanneries clearly influence the foaming conditions in the river.



Full-size image (25K)

Fig. 6. Regression model for river discharge and foam index (FI) depending on the discharge condition of the tanneries at weir 4.

4.4. Model development

Setting measurements and estimating their influence on foam formation required further information, e.g. (i) the extent to which the foam potential emission has to be decreased in order to reduce the foam index and, (ii) which foam index could be achieved due to a certain reduction in foam potential emission. To correlate the three influencing factors – foam index, foam potential and river discharge – two regression equations were combined. The first regression between discharge and FI was already discussed and is shown in Fig. 5. The second regression was accomplished by correlating foam potential and ΔFI , which is supported by the finding that the foam index not only depends on river discharge

but also on the foam potential emission from industry. ΔFI (Eq. (1)) depicts the deviation of the actual observed FI from the calculated FI (calculated by using the regression's equation in Fig. 5).

$$\Delta FI = \text{calculated } FI - \text{observed } FI \tag{2}$$

A positive ΔFI indicates that for a specific river discharge the observed FI is smaller than the calculated FI , whereas a negative ΔFI displays an increase in the observed FI compared to the calculated FI for a specific river discharge. This deviation should correlate with the emitted foam potential, which is clearly highlighted in Fig. 7, displaying the regression between ΔFI and emitted foam potential ($R^2 = 0.30$, $F = 57$, $p < 0.0001$). The regression indicates that emission of a foam potential below $2 \text{ m}^3/\text{s}$ leads to a positive ΔFI , which means less foaming compared to calculated foaming conditions. Above a foam potential of $2 \text{ m}^3/\text{s}$, many other factors (e.g. dilution, diffuse pollution, anti foaming agents) seem to influence the corresponding ΔFI . Thus, only a reduction of foam potential below $2 \text{ m}^3/\text{s}$ could show a quantitative effect on ΔFI and foam formation.

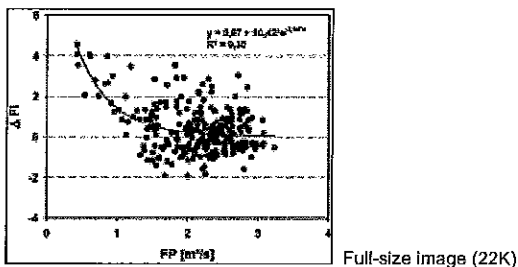


Fig. 7. Regression model for ΔFI and foam potential (FP).

Combining the two regressions' equations in Fig. 5 and Fig. 7 resulted in the model approach for foam index calculation under varying river discharge and foam potential emission conditions (Eqs. (3), (4) and (5)).

$$Q = 11.3 \cdot FI^{0.78} \tag{3}$$

$$\Delta FI = 0.06 + 10.42 \cdot e^{-2.04 \cdot FP} \tag{4}$$

$$FI = (11.3/Q)^{1.28} - (0.06 + 10.42 \cdot e^{-2.04 \cdot FP}) \tag{5}$$

Fig. 8 presents the observed foam index versus the calculated foam index. The achieved Nash Sutcliffe Coefficient was 0.62 (during the investigation period), thus the obtained model approach is a useful tool for further assessment of the efficiency of measurements.

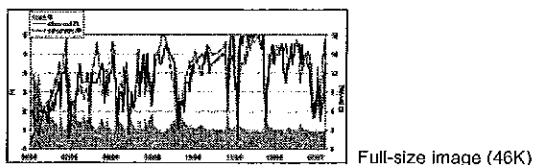


Fig. 8. Observed and calculated FI at weir 4 as well as runoff discharge with daily resolution.