Doctoral Thesis

FOAM FORMATION ON STREAMS
AN AUSTRIAN CASE STUDY

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Dissertation

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Kurzfassung

Schaum auf Oberflächengewässern ist ein weltweit beobachtetes Phänomen, auch wenn in Ländern wie Österreich, die über eine gut funktionierende Abwasserreinigung verfügen, das Auftreten von „Schaumbergen“ eliminiert werden konnte. Die Schaumentwicklung auf einem grenzüberschreitenden Fluss kurz nach der österreichisch-ungarischen Grenze führte dennoch zu massiven politischen Streitigkeiten zwischen den Ländern, des weiteren war die Ursache für den Schaum völlig unklar, da sämtliche Kläranlagen im Einzugsgebiet am Stand der Technik betrieben wurden.

Die nachfolgenden Untersuchungen erwiesen sich als schwierig, da weder Emissions- noch Immissionskriterien für Schaum existierten und dementsprechend auch keine standardisierten Parameter zur emissions- oder immissionsseitigen Schaumquantifizierung verfügbar waren. Aus diesem Grund wurden in einem ersten Schritt der Schaumindex zur Beschreibung von Schaum im Gewässer sowie das Schaumpotential zur Quantifizierung von Schaum in Emissionen entwickelt.

Schaumindex und Schaumpotential wurden in einem Schaummodellansatz miteinander verknüpft, um die Schaumentwicklung im Gewässer in Abhängigkeit von emittiertem Schaum und dem Durchfluss vorhersagen zu können. Mit Hilfe dieses Modells konnten mögliche Maßnahmen zur Schaumreduktion evaluiert werden.

Das Monitoring im Einzugsgebiet identifizierte drei Lederfabriken mit hohen Schaumpotentialemissionen, obwohl alle Betriebskläranlagen am Stand der Technik betrieben wurden. Der Schaum im gereinigten Abwasser war vermutlich das Resultat einer Mischung von pflanzlichen Gerbstoffen und Saponinen, die im Gerbprozess eingesetzt und aufgrund ihrer schlechten Abbaubarkeit im Zuge der Abwasserreinigung nicht oder nur unvollständig entfernt werden konnten.

Berechnungen mit Hilfe des Schaummodellansatzes demonstrierten, dass eine Reduktion der Schaumpotentialemission in den Lederfabriken um ca. 75% eine deutliche geringere Schaumentwicklung im Fließgewässer zur Folge hätte. Diese Reduktion erforderte zum einen die Implementierung eines neuen Stands der Technik, zum anderen die Änderung der Emissionsverordnung für Gerbereiabwässer, welche um den Parameter Oberflächenspannung und die entsprechenden Grenzwerte erweitert wurde.

Abstract

The formation of foam on surface waters is a worldwide phenomenon, although its massive occurrence due to untreated wastewater discharge has been eliminated in countries with well-developed wastewater treatment such as Austria. Thus, the presence of foam on a transboundary lowland river on the Hungarian side of the Austrian-Hungarian border caused massive strain to the political relationship between the two countries. The reason for the foam formation was unclear, as all wastewater treatment plants in the catchment were operating according to the best available technique (BAT).

No legal requirements concerning foam on surface waters or in effluents were available and no standardised parameters existed to measure either instream foam formation or foam in effluents. This caused several challenges to the subsequent investigations.

In a first step, methods to quantify the foam on the river as well as in the effluents of treatment plants had to be developed. The resulting parameters are the foam index that describes the instream foam formation and the foam potential that quantifies the amount of foam emitted by wastewater treatment plants. Both parameters were linked in a foam model approach that estimates the instream foam formation depending on the foam emitted by effluents as well as the river discharge. Possible measures to reduce the foam formation could be evaluated by applying the developed foam model approach.

The monitoring of the wastewater treatment plants in the catchment identified that the emissions from three tanneries which, despite treating the wastewater according to BAT, had high foam potential. Their foaming effluent is most likely caused by vegetable tanning agents and saponins, which are applied in the tanning process and characterized by low biodegradability. The application of the foam model approach highlighted that the foam potential of the tanneries' effluent must be cut by about 75% to reduce the instream foam formation to an acceptable level. This reduction required the implementation of a new BAT for the tanneries' wastewater treatment as well as the adaptation of the Emission Directive on Tannery Wastewater. Surface tension was applied as a new parameter together with limit values to decrease the foam emissions of the leather industry.

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Mein Mann Christian hat vielfältig zum Gelingen dieser Arbeit beigetragen. In erster Linie hat er vor mir promoviert und mir dadurch den nötigen Ansporn gegeben, es ihm gleichzutun ☺. Abgesehen davon waren auch sein Interesse und Verständnis nicht nur für meine Dissertation, sondern meine Arbeit insgesamt wesentlich für meinen beruflichen Werdegang. Schlussendlich sind der Rückhalt und die Anerkennung in der eigenen Familie weit mehr wert als jeder akademische Titel.

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Introduction

1 Background

The quality of surface waters is sensitive to anthropogenic influences (urban, industrial and agricultural activities, increasing consumption of water resources) as well as natural processes (changes in precipitation inputs, erosion, weathering of crustal materials), which can degrade surface waters and impair their use for drinking, industrial, agricultural, recreation or other purposes (Simeonov et al., 2003).

The continuous degradation of the aquatic ecosystems has been acknowledged by politicians, and legislation has been adopted to prevent further deterioration of surface water quality (Carstensen, 2007). In this regard, the EU Water Framework Directive, which is state of the art in the European Union, requests that surface waters achieve good chemical and ecological state by 2015. However, at present the pollution of surface waters by foam and hence the regulation of instream foam formation is not included in the Directive (Water Framework Directive 2000760/EC, 2000).

The presence of foam "mountains" on rivers and streams due to untreated wastewater discharge is a feature of the past in countries such as Austria where highly developed wastewater treatment is applied (see Figure 1). Nevertheless, the occurrence of foam on surface waters has been reported several times (Fisenko, 2004; Madrange et al., 1992), although the amount of available literature is scarce. Wegner and Hamburger (2002) investigated the presence of stable foam beneath the Rhine Fall, which resulted in considerable public concern and fears of potentially harmful effects of this foam. The findings of Wilson et al. (1995) proved that foam is associated with pollution and the presence of foam reduces public preference to use water for recreational purposes or as a drinking water resource. The visibility of foam is associated with making it more eye-catching and noticeable than other, "hidden" chemical pollution.

The formation of foam can have natural as well as anthropogenic sources. In this context, it is either linked to industrial effluents from paper and leather industries (Madrange L. et al., 1992) and effluents of waste water treatment plants (Defrain and Schulze-Rettmer, 1989) or to algal blooms (Lu et al., 2006; Shi et al., 2005), plant derived surfactants and release of dissolved organic substances during phytoplankton blooms or in the presence of kelp beds (Bärlocher et al., 1988; Bätje and Michealis, 1986; Craig et al., 1989; Desroy and Denis, 2004; Eberlein et al., 1985; Maynard, 1968; Seuront et al., 2006; Velimirov, 1982).

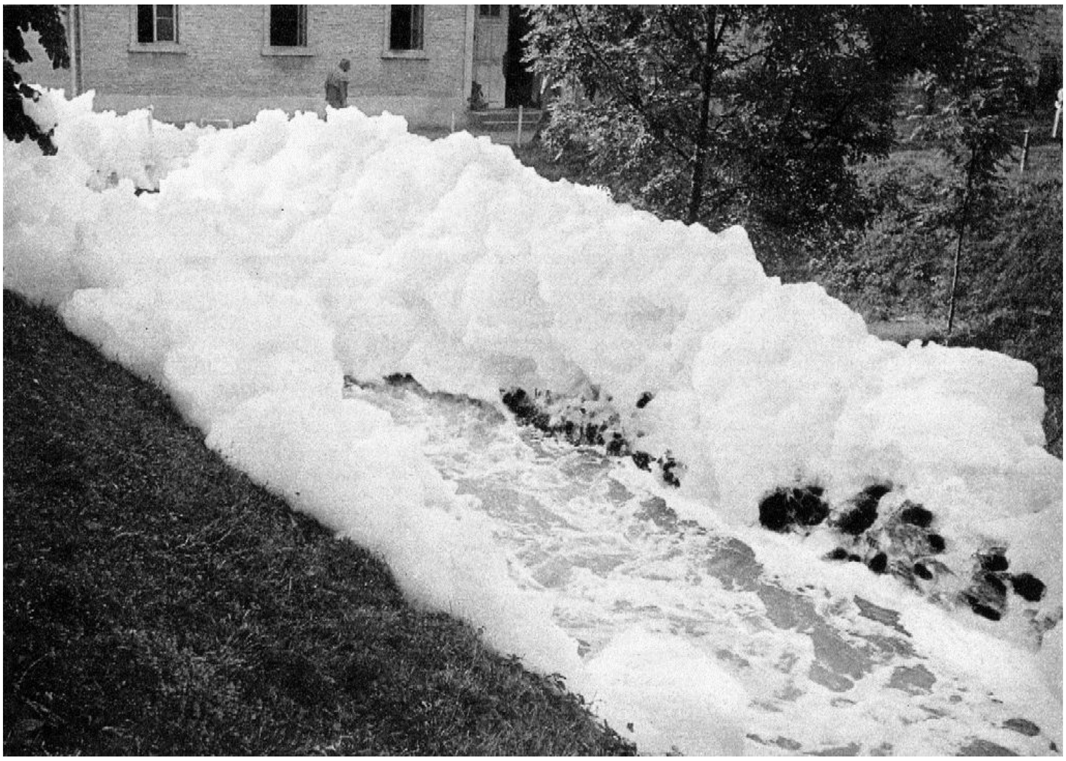


Figure 1: „Foam mountains“ on a river due to the discharge of untreated wastewater.

The list of literature above confirms that scientific research deals with the existence of foam in the aquatic environment, but techniques for its quantitative determination or measures for its elimination are not the focus of the mentioned studies. A reason for this might be the lack of legal standards for instream foam formation as well as its emission into rivers and lakes.

Thus, identification of foam causing substances, their origin and elimination, methods for quantification as well as the handling of the legal aspects are new challenges to be met, in order to solve foam formation problems.

2 Research question

The presence of foam below weirs in a lowland river in Austria and in the border region to Hungary and the associated protest by Hungarian locals led to causal research being conducted by Vienna University of Technology. The main task of the study was to find the reason for the foam formation and develop foam abatement measures.

Implementation of measures within a catchment requires a detailed knowledge of the processes taking place within the catchment as well as a sound understanding of the relationship between emitted loads into the rivers and the resulting instream concentrations. A clear understanding of the cause-effect relationship between emissions and the resulting instream concentrations is the prerequisite for the development of a model linking the emissions with instream concentrations. By means of the developed model the (cost-)efficiency of possible measures can be evaluated.

This kind of procedure is well-known in the scientific community and has been applied several times to solve water quality problems. Still, the issue of foam formation is different and hampers the application of this approach. The challenges appear as follows:

- Currently no well-defined foam parameters exist. As the foaming potential of emissions as well as foam formation on surface waters is most likely not the result of one single substance, sum parameters for the emission of foam as well as for the resulting instream foam formation had to be designed.
- In a second step those newly developed parameters had to be linked to predict the instream foam formation under certain discharge conditions, as the occurrence of foam changes with varying discharge.
- The implementation of measures requires a limit of foam formation on the river. As no legal standards for instream foam formation exist, a new threshold had to be defined.
- In order to keep the newly defined threshold in the river, the foam emissions from point sources need to be regulated. Hence, the Emission Directive is adapted and novel limit values are introduced.

3 Case study Area

The investigated river has its source in a crystalline low mountain range, flows through the south-eastern part of Austria and discharges into the Danube in central Hungary. The Austrian part of the river basin (Figure 2) covers an area of about 980 km², the climate is characterised by moderate precipitation (784 mm/a), which results in seasonal low discharge conditions (low flow during investigation period was around 2 m³/s or 63 mm/a based on the river basin area, average flow is around 6 m³/s or 189 mm/a based on the river basin area). The land use within the basin is dominated by agriculture (arable land 34%, grassland 17%) and forestry (45%). Urban areas cover 4% of the catchment. Spatial distribution of different land use types result in a short upper river section, which is almost unaffected by human impact, while the largest part of it is characterised by high agricultural, municipal and industrial exploitation.

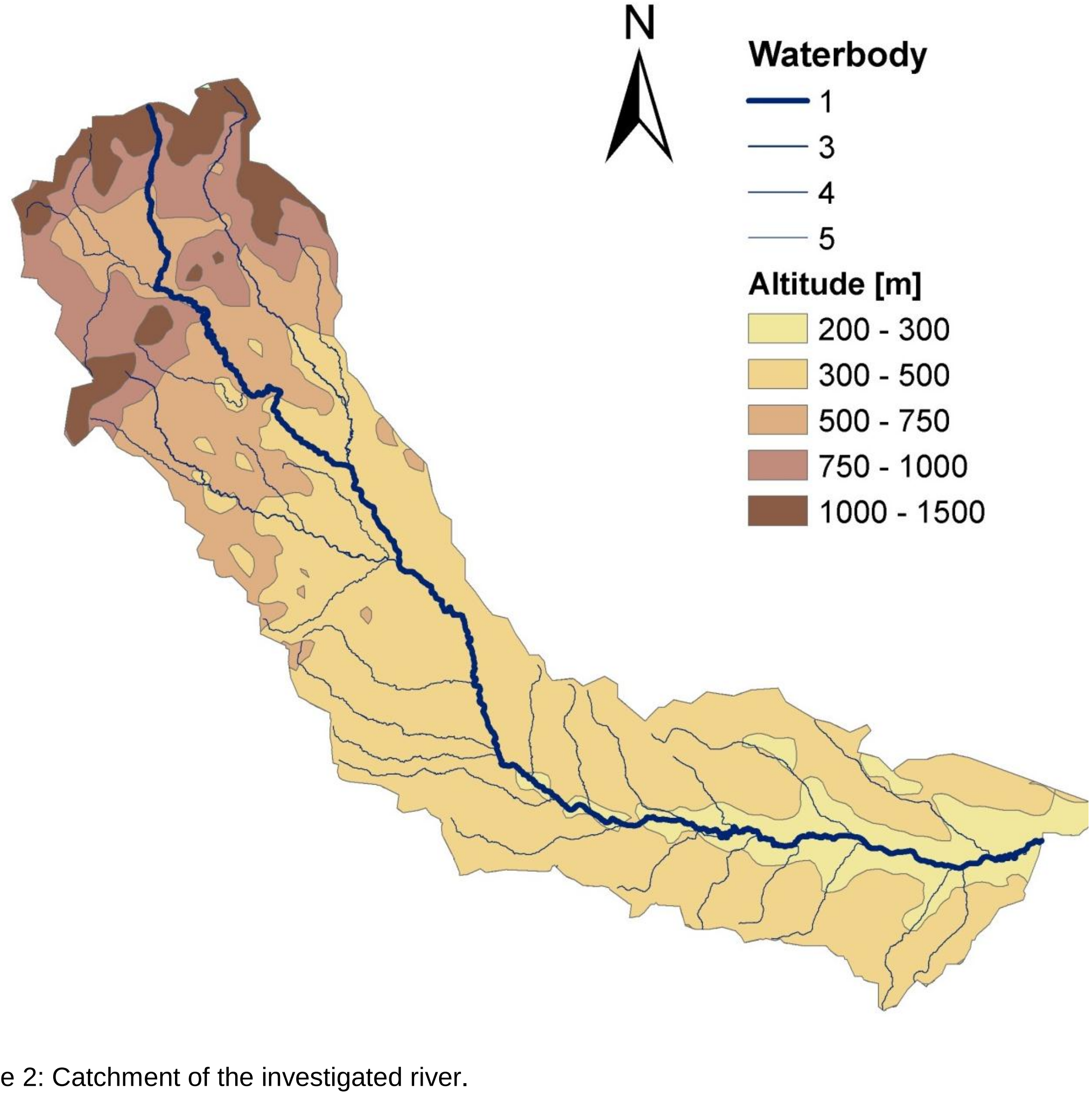


Figure 2: Catchment of the investigated river.

Further pressures are weirs and backwaters as well as flushing driven by the power industry. Due to the point source and diffuse pollution as well as the morphological deficits the whole river is at risk of failing to reach the target of ”good ecological status” defined by the EU-WFD.

4 Structure of PhD

This thesis is structured such that the main research themes that were investigated are presented in chapters as standalone documents in the manner in which they have been accepted, prepared or submitted for publication in various journals.

The first chapter called “Foam in the aquatic environment” is a literature review on foam in freshwater ecosystems as well as in the marine environment. Alongside with some basic considerations on the formation of foam, on methods to measure foam formation and on the legal aspects of foam on surface waters, the ecological importance of foam in the aquatic environment is discussed.

The second chapter named “Measurement of instream foam formation and quantification of foam in effluents” presents the developed methods to quantify instream foam formation and foam emissions, proves their accuracy and shows their possible applications.

In the third chapter the cause-effect relationship between the emitted foam and the instream foam formation is investigated and the development of a model approach to assess the instream foam formation is discussed.

Finally, chapter 4 highlights the changes made to the Emission Directive of tannery wastewaters to avoid further foam formation, which include the introduction of a novel foam parameter along with newly developed limit values depending on the river discharge.

The conclusions recapitulate the main objective of the study and summarise the main findings.

Foam in the aquatic environment

1 Introduction

Since the implementation of biodegradable detergents and the proper operation of wastewater treatment plants, it has been believed that the occurrence of foam on surface waters was eliminated in Austria and other countries with a well-developed waste water treatment infrastructure. But still, the formation of foam in freshwater ecosystems such as rivers and lakes has been reported several times. In this context foam is linked to point source emissions (Defrain and Schulze-Rettmer, 1989; Madrange et al., 1992; 2009a) as well as natural occurring surfactants derived from algae and plants (Harrington, 1997; Lu et al., 2006; Shi et al., 2005; Wegner and Hamburger, 2002). Considerable literature is available on the occurrence of “sea foam” in marine ecosystems (Bärlocher et al., 1988; Bätje and Michealis, 1986; Craig et al., 1989; Desroy and Denis, 2004; Eberlein et al., 1985; Maynard, 1968; Seuront et al., 2006; Velimirov, 1982).

Nevertheless information on foam in the aquatic environment is limited and sometimes out-dated compared to the existing literature on the foams linked to various industry-branches, e.g. food industry (Dale et al., 1999; Piazza et al.; Vanrell et al., 2007), fire-fighting-industry (Figueredo and Sabadini, 2003; Tafreshi and Marzo, 1999), cement-industry (Pedersen et al., 2007), cosmetic- and detergent-industry (Buzzacchi et al., 2006; Regismond et al., 1998; Zhang et al., 2004). Other sources of information are investigations on foam in wastewater treatment processes due to the occurrence of filamentous bacteria (Blackall et al., 1991; Blackall and Marshall, 1989; Hladikova et al., 2002; Lánský et al., 2005; Lemmer et al., 2005; Petrovski et al., 2010; Torregrossa et al., 2005).

Today quality and pollution of surface water is a not only an issue for scientists, but also policymakers, politicians and the public in general. Although foam can be used in environmental remediation processes, e.g. in aquifers (Vikingstad, 2006), in water science foam is known to be the polluter, not the pollution remover. The public exhibits considerable interest in foams and usually associates them with detergents or some form of pollution (Mills et al., 1996; Pojasek and Zajicek, 1978). A psychological investigation demonstrated that the public associated the presence of foam on surface waters with pollution which results in a reduced preference to use the water for recreational purposes or as drinking water sources (Wilson et al., 1995). A good example on how foam can provoke public concern is the formation of foam on an Austrian river close to the border with Hungary that resulted in an impaired political relationship due to massive protests from Hungarian locals. A research study related the foam to the effluent of three tanning factories, although their wastewater treatment complied with best available technology and met the legal requirements (Ruzicka et al., 2009a). As a result of the public concern, the Austrian emission directive for tanneries was adapted and the implementation of quaternary chemical treatment became a requirement to prevent instream foam formation.

This example highlights the increasing public awareness in terms of water pollution. Certainly, the visibility of foam addresses the ecological ‘‘conscience” of people more than ‘‘hidden” chemical pollution. In fact, foam is not necessarily associated with pollution, but can occur naturally in very pristine environments, e.g. humic waters from rainforests. The increasing environmental awareness and regulatory pressures demand a better understanding of the composition, origin and significance of foam (Napolitano and Richmond, 1995). In consequence, a literature review was carried out to identify existing information on foam itself, reasons for its formation and its behaviour in the aquatic environment. This paper will also deal with methods to measure foam formation, the existing legislation as well as with the importance and dangers of foam formation from an ecological perspective.

2 Foam characteristics

2.1 Foam formation

Foam is a dispersion of a gas in a liquid or solid separated by thin liquid films or lamellae (Heard et al., 2008; Holmberg et al., 2003). A pure liquid cannot foam unless a surface active material is present. A gas bubble introduced below the surface of a pure liquid will burst immediately as soon as the liquid drains away. In fact, purity of water can be estimated from the bubble persistence time when shaking the water sample in a closed container. A bubble persistence time of even one second is an indication of the presence of surface active impurities (Pugh, 1996). Consequently, foams are always formed from mixtures, where one component must be surface active. A measure of the surface activity is the decrease in surface tension upon adding the surface active component to a pure liquid (Holmberg et al., 2003). Surface-active foaming materials include particles, polymers, specific absorbed cations or anions from organic salts etc., most of them cause foaming at extremely low concentrations (Pugh, 1996).

A second precondition for foam formation is a source of gas bubbles (Heard et al., 2008) that must be injected at a higher rate than the rate at which the liquid between the bubbles can drain away (Napolitano and Cicerone, 1999). In aquatic ecosystems mechanical impact is needed to introduce air bubbles into the water (Poremba, 1991), which can be caused by cascades or hydraulic structures such as weirs, dams, spillways and discharge pipes, due to stormy conditions and the pounding of waves, in areas of strong currents or in areas, where fresh and salt water mixes (Craig et al., 1989; Ettema et al., 1989; Fisenko, 2004).

2.2 Surface active compounds

Surface active components or surfactants have a great influence on the surface or interfacial properties in a solution. A surfactant is a molecule that has a hydrophobic hydrocarbon chain and a hydrophilic head group. The surfactant can be anionic, cationic or zwitterionic. Above the critical micelle concentration (cmc) the surfactant molecules aggregate in micelles. The micelles have an ordered structure that is dependent on the hydrophilic and hydrophobic properties of the surfactant (Vikingstad, 2006).

According to literature several surface active compounds can cause foam in the aquatic environment. Natural foams are usually linked to humic and fulvic acid substances (Ettema et al., 1989; Napolitano and Richmond, 1995), fine colloidal particles (Ettema et al., 1989), lipids and proteins originating from aquatic or terrestrial plants leaching from soil by precipitations events (Napolitano and Richmond, 1995), saponins representing a family of plant glycosides (Pojasek and Zajicek, 1978; Wegner and Hamburger, 2002), the exudation or decomposition products of phytoplankton containing carbohydrates and proteins (Bätje and Michealis, 1986; Eberlein et al., 1985; Seuront et al., 2006) and the natural reservoir of organic matter occurring in sediments (Napolitano and Richmond, 1995). Man-made foam is linked to phosphates from farm fertilizers (Ettema et al., 1989) and organic and inorganic (detergents) pollution discharged by point sources especially from the paper and leather industry (Ettema et al., 1989; Fisenko, 2004; Madrange et al., 1992; Ruzicka et al., 2009a). In summary, the literature provides a wide range of foam causing substances, which have been investigated to greater and lesser extents. Considering the fact that foam formation is a sum effect of all surface-active compounds present in the water, in most cases not one single substance, but a mixture of various components is responsible for foam (Wegner and Hamburger, 2002).

2.3 Surface Microlayer (SML)

In marine and freshwater ecosystems, the air–water boundary, known as the surface microlayer (SML), constitutes an important interface between the troposphere and the underlying water (Hörtnagl et al., 2010). It is a vehicle for the transport of inorganic and organic materials between the atmosphere and the water column (Napolitano and Cicerone, 1999). Substances and particles temporarily or permanently incompatible with purely aquatic or atmospheric ecosystems, e.g. natural oils, organic acids and proteins will accumulate in this zone near the air-water interface. SMLs may also include components derived from human activities, such as petroleum compounds, synthetic surfactants, long-chain alcohols, synthetic pesticides and herbicides (Napolitano and Richmond, 1995; Parker and Barsom, 1970). These materials accumulate in the SML by adsorbing onto bubbles as they rise through the water column (Harden and Williams, 1989). At the water surface the bubbles may burst ejecting aerosol droplets into the air. Under certain conditions emerging bubbles may not burst instantly, but accumulate on the water surface producing foam. The aqueous foam phase contains the surface-active substances accumulated in the SML. Assuming that a typical foam consists of 90% air and that the mean thickness of the SML is about 50 µm, one litre of foam water would represent 2 m² of SML (Napolitano and Cicerone, 1999). Foam may also be produced by the compression of the SML generated by wind or as a result of breaking waves at the shoreline (Bärlocher et al., 1988; Eisenreich et al., 1978; Harden and Williams, 1989).

2.4 Foam stability

Due to their high interfacial energy foams are thermodynamically unstable. The instability has been classified into two types, which are (1) unstable or transient foams with lifetime of seconds and (2) metastable or so called permanent foams with lifetimes measured in hours to days (Pugh, 1996). Collapsing foams are the result of the bubble coalescence defined as joining together of two bubbles in a fluid to form one larger bubble. It can be described as a three-step process: bubble approach and creation of a thin film, film drainage and film rupture. In pure water no stable film is formed and coalescence takes only a few milliseconds, whereas surfactants stabilise bubbles against coalescence leading to foam lifetimes from seconds to days (Henry, 2010).

The most obvious force acting on foam is gravity causing drainage of the liquid between the air bubbles. Drainage can be reduced by either increasing the viscosity of the bulk liquid or by adding particles (Heard et al., 2008; Holmberg et al., 2003; Pugh, 1996). Such systems give very stable foams (Holmberg et al., 2003; Wegner and Hamburger, 2002). The influence of solid particles on the formation and stability of foam is dependent on the surfactant type, the particle size and concentration. Hydrophilic particles present in the aqueous phase of the foam films are able to enhance foam stability by slowing down the film drainage. On the other hand, hydrophobic particles entering the air-water surfaces of the foam can cause destabilisation via the bridging-dewetting mechanism (Binks, 2002). According to Pugh (1996) partially hydrophobic particles can cause an increase or decrease in foam stability. Small particles, if not fully wetted, may become attached to the interface and give some mechanical stability to the lamella. If completely dispersed, they may cause an increase in bulk viscosity and stabilise foams. On the other hand, larger particles having a higher degree of hydrophobicity (coal dust, sulphur, non-wetting quartz) may cause destabilisation. In wastewater treatment plants, the stability of foams is often associated with hydrophobic particles such as bacteria cells (Blackall and Marshall, 1989; Heard et al., 2008; Petrovski et al., 2010) Particles can show a second stabilizing mechanism by being surface active themselves and having a high affinity for the liquid-air interface. Eisenreich et al. (1978) found surface-active proteinaceous matter as well as small Si, Ca and Fe particles to be responsible for foam stability.

Addition of salt is another factor promoting foam stability. Craig et al. (1993) found that bubble coalescence was inhibited by some salts, whereas others had no effect. According to Holmberg et al. (2003) salt increases the surfactant critical packing parameter (CPP), which indicates how close surfactants are packed together at the air-water surface. Thus an increase in CPP will result in closely packed surfactants, in an increased surface elasticity and viscosity and thus lead to high foaming ability and foam stability. Henry (2010) argued that electrolytes inhibit bubble coalescence in water, but the inhibition is ion specific. Her experiments on thin film drainage in electrolyte solutions showed that electrolytes affect both film drainage rate and film rupture thickness. According to her results, electrolyte coalescence inhibition is a nonequilibrium effect that acts upon the dynamic film drainage process, through ion specific interfacial partitioning.

Pugh (1996) describes the increase of foam stability due to a mixture of surfactants, e.g. a mixture of tannin and heptanoic acid in aqueous solution, whereas much lower foam stability is observed from the two constituents separately.

In summary, bubble coalescence is the result of bubble approach, film drainage and finally film rupture. Foam stability can be increased by adding various substances, such as particles, salts or a mixture of surfactants.

3 Methods to quantify foam formation

Literature on foam formation and stability mainly originates from the wastewater sector and in sectors dealing with foams in industry (Blackall et al., 1991; Blackall and Marshall, 1989; Heard et al., 2008; Hladikova et al., 2002; Paris, 2004; Vikingstad et al., 2005). Table 1 provides an overview of several methods used to measure foam.

Table 1: Overview on methods to measure foam

method	measured parameters	cited in
aeration	Foam generation, Foam stability	Blackall and Marshall (1989)
Alka Seltzer	Bubble size and stability, foam height	Paris (2004)
aeration	Scum index	Hladikova (2002)
mixing	Height of foam column as function of time	Vikingstad et al.
handshaking	Foam height, foam stability	Madrange et al. (1992)
shaking	Foaming factor	Ruzicka et al. (2009)
webcam	Foam index	Ruzicka et al. (2009)

In the wastewater sector, tests on foam stability are related to the occurrence of bulking sludge. The most cited method was developed by Blackall and Marshall (1989). They designed a foaming apparatus consisting of a glass cylinder and a sintered glass disc with a maximum pore size of 40-90 µm. In the cylinder 50 ml of sample are aerated with compressed air (200 ml/min) via the glass disc. Foam generation and stability are recorded and assessed according to a classification system rated in terms of foam volume, bubble size, speed of formation and time taken for the foam to collapse after aeration ceased.

Heard et al. (2008) slightly modified the method of Blackall and Marshall (1989) and applied 20 ml of sample which is aerated with an air flow rate of 100 ml/min. They use the time at which bubbles collapse as a measure of foam stability.

The Alka-Seltzer test was developed by Ho und Jenkins and modified by Kopplow und Barjenbruch (Paris, 2004). This test uses two tablets of Alka-Seltzer (Alka-Seltzer® classic, Bayer, is a drug containing sodium bicarbonate amongst others) which are added to a beaker with 250 ml of sample. Dissolution of the tablets creates bubbles that lead to foam formation. Size and stability of the bubbles are noted and the height of foam is measured at intervals of one, three and five minutes after complete dissolution of the tablet, in order to calculate the “foam value” (Kopplow and Barjenbruch, 2002).

The scum index (SI) is a method to estimate foaming severity and was primarily proposed by Pretorius and Laubscher (1987) and modified by Hladikova (2002). The first step is the determination of the concentration of suspended solids in the mixed liquor. Then two litres of mixed liqor are aerated in a laboratory cylinder with a flow rate of 480 ml/min via a sintered silica sand diffusor. After an aeration time of four hours, the dry mass of recovered scum is determined. The scum index is calculated by dividing the mass of suspended solids initially present by the mass of the stored scum, multiplied by 100%.

Vikingstad et al. (2005) applied foam tests to assess foam stability in the oil-water-interface. Foam tests were made by mixing air into the surfactant solution. Air was dispersed into the 300 ml test solution with a pedal connected to a mixer at a speed of 2000 rounds per minute for 5 min. The mixer was a polymix obtained from Kinematica, type RW20 S12. In all the experiments the height of the foam column above the liquid phase was measured as a function of time after mixing ceased.

Limited information exists on the foaming capacity of effluent from wastewater treatment plants. Madrange et al. (1992) proposed a method to determine the foaming capacity of industrial effluents. 250 ml of sample were handshaken for five minutes and the height of the resulting foam was measured with an accuracy of 0.2 cm. Foam stability, defined as the time until the foam cover breaks, was measured.

Ruzicka et al. (2009a) introduced the foaming factor and the foam potential to estimate the capability of an effluent to cause foam in the receiving river. The foaming factor is derived by shaking 250 ml of effluent in Erlenmeyer flasks with baffles on a laboratory Shaker (Type Ceromat-U) for three minutes at a speed of 300 rpm. Samples are diluted with dilution media (in this case unpolluted river water), until no more foam appears. The dilution factor, at which minimal foam occurred, is defined as the “foaming factor”. For the calculation of the “foam potential”, the foaming factor of an effluent is multiplied with the discharge of the effluent. The calculated foam potential of an effluent is defined as the volume of river water which can potentially become foamed by the effluent’s discharge, if laboratory conditions are applied.

The study of Ruzicka et al. (2009a) also developed a seven-stage “foam index” (FI) based on webcam pictures of a river weir, where foam occurred. This parameter was developed to characterise instream foam formation and 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. Ruzicka et al. (2009) successfully correlate the resulting “foam index” in the river to the emitted “foam potential” of the major point sources in the catchment.

As a result, all methods to quantify foam (apart from the foam index) are strongly dependent on the introduction of a gas source into the liquid, which is provided by (i) aerating, (ii) mixing or (iii) shaking the sample. As most of the methods originate from the wastewater sector as a result of the bulking sludge problems, a uniform approach would be beneficial and should be developed to make future investigations comparable.

4 Legal aspects of foam formation

The need to act against degradation of aquatic ecosystems has been acknowledged by politicians and legislation has been adopted to stop further deterioration and to restore aquatic ecosystems to a healthy state (Carstensen, 2007). Examples of legislation in Europe are the European Water Framework Directive and the Regulation for Water Pollution Control in Switzerland; in the USA the US Clean Water Act is the leading standard. In all these legislations the regulation of foam is an almost neglected topic.

4.1 Regulation of instream foam formation

The Clean Water Act (CWA) establishes the basic structure for regulating discharges of pollutants into the waters of the United States and regulates quality standards for surface waters. It proclaims that “all surface waters should be free of scum in unsightly amounts”. The phrase “unsightly” is not defined any further and its interpretation is subject to the evaluator (Federal Water Pollution Control Act, 2002).

In the European Union the European Water Framework Directive (EU WFD) provides the legal standard. It applies the definition of ‘‘good chemical and ecological status” for river water bodies, which means only a minor deviation from the reference (natural) status. The chemical status is regulated by environmental quality standards for priority substances, which contain also foam related parameters such as tensides (e.g. nonylphenols). Thus an indirect criterion for foam exists by the regulation of tensioactive compounds, although specific regulation on formation of foam in surface waters is not available (Water Framework Directive 2000760/EC, 2000). The Austrian state monitoring network is administered according to the requirements of the EU WFD and so far does not include any monitoring of foam formation (Bundesministerium für Land- und Forstwirtschaft, 2006).

The Regulation for Water Pollution Control in Switzerland states that “treated wastewater discharge must not lead to foam formation after advanced mixing in the river with exception from rainfalls”. The evaluation of instream foam formation adopts a three-step scale, i.e. “no foam”, “minor to medium foam” and “lots of foam”. It is a visual survey and the resulting rating is based on comparison with pictures (Gewässerschutzverordnung Schweiz, 1998).

4.2 Regulation of foam emitted by point sources

In terms of point source pollution, the regulation of foam is weaker than with regards to instream foam formation. In the CWA, regulation of foam from point-sources is not available (Federal Water Pollution Control Act, 2002). In the EU, the emissions from municipal wastewater treatment plants are regulated in a daughter-directive of the EU-WFD, the Urban Wastewater Treatment Directive, and this does not include any parameters regarding foam (Council Directive 91/271/EEC concerning urban wastewater treatment, 1991). In Austria, the Directive on emissions from municipal wastewater treatment plants lacks regulation on foam emissions, although emission criteria for foam related parameters such as tensioactive compounds, e.g. the sum parameter for anionic and non-ionic surfactants exist (Bundesministerium für Land- und Forstwirtschaft, 1991). Another directive indirectly dealing with foam is the Directive on emissions from tanneries, which includes the parameter “surface tension” in the effluent to avoid foam formation in the river (Bundesministerium für Land- und Forstwirtschaft, 2007). The Swiss Regulation for Water Pollution Control has no emission based legislation for foam, but does include the assessment of instream foam formation below point sources (Gewässerschutzverordnung Schweiz, 1998).

In summary, the regulation of foam in the aquatic environment has been neglected entirely, although the occurrence of foam is often prominent in the media and is frequently cited as a reason for public concern. In consequence, proper legislation is necessary for instream foam formation as well as for foam originating from point sources. In this context, the regulation of a sum parameter representing foam formation such as surface tension or foam potential would offer the greatest feasibility.

5 Foam formation in wastewater systems

As foam on surface waters is often linked to point source emissions (Defrain and Schulze-Rettmer, 1989; Madrange et al., 1992; Ruzicka et al., 2009a) and a considerable amount of literature exists on this subject, foam formation in wastewater systems is discussed in this section. The formation of stable foam which reduces oxygen transfer, decreases the quality of the effluent and therefore increases maintenance costs, is a widely observed phenomenon in wastewater treatment plants and was first noted in 1969 (Heard et al., 2008). It is a common feature of activated sludge systems around the world and considerable effort has been directed to enhance understanding of the microbial ecology of foaming (Petrovski et al., 2010). Microscopic examination of foams has identified a wide range of bacteria, with the filamentous bacteria Microthrix parvicella and actinomycetes among the most common (Blackall et al., 1991; Heard et al., 2008). The results of Lemmer et al. (2005) highlighted that bacteria assembled in foam comprise morphotypes beside Microthrix parvicella and nocardioform actinomycetes, which belong to a variety of species, genera and bacteria groups. Lemmer et al. (2005) argues that the immense number of species prevent the recommendation of specific troubleshooting measures.

Heard et al. (2008) indicated that bacteria can enhance the persistence of foams, but cannot in themselves cause foaming in the absence of a surfactant. Their findings are of importance, as much of the current literature suggests that foaming in wastewater treatment plants is caused directly by the presence of bacteria (Heard et al., 2008). Nonetheless, the earlier investigations of Blackall and Marshall (1989) highlighted that both surfactants and cells were necessary for stable foam formation, since only unstable foams were formed in the absence of bacteria, and no foams were formed in the absence of a surfactant. Interestingly, the surfactant needed to initialize foam formation must not be a synthetic surfactant from the influent of the treatment plants, but may be a biotenside, e.g. glycolipids produced by various sludge bacteria such as actinomycetes, Pseudomonas or Acinetobacter species (Lemmer et al., 2005).

Foam stability seems to be dependent on a large biomass of filamentous, hydrophobic organisms such as Microthrix parvicella or actinomycetes (Blackall et al., 1991; Blackall and Marshall, 1989; Heard et al., 2008; Lemmer et al., 2005). According to Petrovski et al. (2010) foam is generated by a selective enrichment of these hydrophobic bacteria by a process of flotation, that requires three components: (i) gas bubbles surrounded by liquid films, generated by the aeration system, (ii) surfactants which reduce the surface tensions and thus prevent liquid drainage from gas bubble walls and (iii) small hydrophobic particles (bacterial cells) responsible for the long term stabilisation. With insufficient hydrophobic cells, but in the presence of the other two, large amounts of unstable foam will be generated. These findings strongly support the investigations of Blackall and Marshall (1989). Furthermore, the authors demonstrated that the non-hydrophobic Bacillus subtilis might be an important contributor to stable foams due to the production of the powerful surfactant surfactin, supporting the biotenside theory of Lemmer et al. (2005).

In the experiments of Blackall and Marshall (1989) the prevention of stable foams has been achieved by the addition of colloidal, hydrophilic clay particles. Although a variety of hydrophilic materials was tested, only a 2:1 lattice clay, montmorillonite, was able to inhibit stable foams. The authors postulate that a salt-dependent, reversible bacteria-montmorillonite complex is formed, which confers hydrophilicity to the otherwise hydrophobic actinomycetes. This property prevents cells from entering and stabilising the foam phase. Other measures to fight stable foams include spraying with water to destroy the foam (Lemmer et al., 2005) or dosing with chemical agents such as polymers (Hwang and Tanaka, 1998).

In conclusion, the widely observed appearance of stable foams on wastewater treatment plants results from the occurrence of surfactants or biotensides in the mixed liquor, whereas the hydrophobic bacterial cells are responsible for the long-term stabilisation. Because of the high diversity of filamentous bacteria the effective control of foam in wastewater treatment plants is hard to achieve.

6 Relevance of foam on surface waters

6.1 Enrichment of foams in lakes and rivers

Foams occurring on rivers, lakes and in the sea are basically collections of materials normally present in the SML (Napolitano and Richmond, 1995). Similar to the foam fractionation techniques used in industry or in wastewater treatment, the formation of foam on surface waters induces the transfer and concentration of surface-active substances from the SML into the foam (Johnson et al., 1989). Depending on the type of aquatic environment various components are enriched in the resulting foam. Fisenko (2004) hypothesized that nature “uses” this “foam fractionation and flotation technique” as a process for self-purification. In his study he demonstrated the self-restoration of the Etobicoke river after a toxic waste spill. Within three months the river was self-purified which he attributed to the production of large amounts of foam enriched in substances degrading water quality, such as cyanide and heavy metals.

Some information is available regarding the enrichment of certain substances in foams of various rivers and lakes. The existing information deals with the accumulation of nutrients, lipids, heavy metals, hydrocarbon and pesticides in “freshwater foam” (Baier et al., 1974; Eisenreich et al., 1978; Johnson et al., 1989; Napolitano and Richmond, 1995; Parker and Barsom, 1970; Pojasek and Zajicek, 1978). The enrichment is calculated via the fractionation or enrichment ratio, which is defined as the concentration of a parameter in the foam divided by its concentration in the underlying water.

6.1.1 Metals

The analysis of wind-generated lake foam (Lake Mendota, Wisconsin) highlighted an enrichment with metals as compared to the underlying water (Eisenreich et al., 1978). Table 2 provides an overview on the fractionation ratios for several metals (total) in Lake Mendota compared to other studies cited in Eisenreich et al. (1978) as well as a study for foam below the Niagara Falls (Johnson et al., 1989). Although the fractionation ratios show huge variations, an enrichment of the foam with metals is obvious. Differences in metal fractionation ratios between various studies are most likely to result from the use of different collection techniques and bulk water concentrations than foam accumulation mechanisms (Eisenreich et al., 1978).

Table 2: Fractionation ratios for heavy metals in „freshwater foams“ - modified from Eisenreich et al., 1978, (enrichment ratios are calculated by dividing the concentration of a parameter in the foam by its concentration in the underlying water).

Metal (total)	**Fractionation Ratio (average)**			
	Lake Mendota Eisenreich et al., 1978	Delaware Bay Szekielda et al., 1972	Lake Michigan Elzerman, 1976	Niagara Falls Johnson et al., 1989
Zn	293	~10,000	14	80
Cd	544		67	20
Pb	1,110	~10,000	271	
Cu	448	~10,000	98	300
Fe	240			

The observed metal enrichment in foam of Lake Mendota is caused by metal scavenging by surface-active or particulate material in surface films, bubble adsorption and atmospheric deposition. Furthermore, a significant portion of the dissolved metal was complexed by organic matter or associated with colloidal material accumulated in the foam (Eisenreich et al., 1978).

Pojasek and Zajicek (1978) analysed the metal carrying capacity of natural SMLs and foams of several streams using iron and manganese as indicator metals (both dissolved). They found fractionation ratios varying between 10 and 40 for manganese and 30 to 74 for iron depending on the pre-analyses treatment applied. Half of the metals were strongly bound to organic terrestrial decomposition products; the rest were present as inorganic species or weakly bound organic complexes.

6.1.2 Carbon and nutrients

Parker and Barsom (1970) investigated the SML of three freshwater habitats in the vicinity of St. Louis. Total nitrogen and orthophosphate showed a two- to threefold concentration in the SML compared to the underlying water. Unfortunately, no absolute numbers are available for this study.

In Niagara Falls the fractionation ratio for DOC is about 8 (Johnson et al., 1989) compared to an average ratio of 40 for DOC and 48 for TOC in the foam of Lake Mendota (Eisenreich et al., 1978). The ratio for organic nitrogen was 95 in Lake Mendota, indicating the presence of large quantities of proteinaceous matter. About 80% of the total phosphorus occurred in dissolved form and was evenly distributed between dissolved reactive phosphorus (DRP) and dissolved organic phosphorus (DOP) with average ratios of 11 and 84, respectively (Eisenreich et al., 1978).

6.1.3 Lipids and hydrocarbons

Lipids are one of the major organic constituents of SMLs and foams because of their hydrophobicity, a low relative density and low vapour pressure (Napolitano and Cicerone, 1999). The lipid concentrations of foam samples from rivers in eastern Tennessee show some variation, but were higher than in the underlying water with fractionation ratios spanning two orders of magnitude. According to the authors, the varying concentrations between the streams could be attributed to differences in the particle load of the foam, foam age and the extent of colonization by microbes (Napolitano and Richmond, 1995). Fractionation ratios of foam below the Niagara falls ranged from 15 for total fatty acids to 370 for total sterol depending on the degree of polarity (Johnson et al., 1989).

Napolitano and Richmond (1995) regenerated foam in the laboratory to measure the enrichment under controlled conditions (8l of stream water plus 200ml of corresponding foam). The resulting fractionation ratios for phospholipids and hydrocarbons were much lower than those found in the field. These findings suggest that high concentrations of lipids in natural foams are not a direct consequence of the foam formation, but indicate a secondary enrichment of lipids in the foam after its formation due to microbial growth or entrapment of suspended solids.

Natural hydrocarbons typically account for only a small proportion of the total lipids (typically <5%). The presence of hydrocarbons at 20% to 30% in river foams in eastern Tennessee and at 10% to 15% in foam below the Niagara Falls indicates oil contamination (Johnson et al., 1989; Napolitano and Richmond, 1995).

Eisenreich et al. (1978) reported high concentrations of chlorinated hydrocarbons, such as dieldrin and DDT-group pesticides (4-360 ng/l) in foam of Lake Mendota compared to the underlying water (<1ng/l). Total DDT (sum of DDT, DDE, DDD) in the foam ranged from 75 to 767 ng/l. Although the resulting fractionation ratios are significantly high, they are subject to some uncertainty due to very low levels in the underlying water.

6.1.4 Polychlorinated biphenyl (PCB)

Polychlorinated biphenyls are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings. Due to PCB's toxicity and classification as a persistent organic pollutant, PCB production was banned by the Stockholm Convention on Persistent Organic Pollutants in 2001. In Lake Mendota the PCBs were detected in the foam samples with fractionation ratios in the range of 100 to 1000, which is far higher than in the river foam in eastern Tennessee with ratios between 5 to 9 (Eisenreich et al., 1978; Napolitano and Richmond, 1995).

In summary, various substances enriched in the SML will be transferred into and concentrated in the foam. The presence of a substance in foam does not necessarily mean that it causes foam. Often substances, e.g. metals are complexed and concentrated in the foam, even though other surface-active compounds are responsible for the foam formation. The effect of the enriched substances on the aquatic environment will be discussed in section 6.3

6.2 Occurrence and composition of sea foam

The occurrence of sea foam is a widely known phenomenon around the world (Bätje and Michealis, 1986; Craig et al., 1989; Eberlein et al., 1985; Kesaulya et al., 2008; Seuront et al., 2006). According to Baier et al. (1974) stable sea foams usually include a major silica component, which can be associated with diatom remnants. Bätje and Michaelis (1986) report unusual amounts of sea foam in the North Sea in 1978 caused by a bloom of the planktonic algae Phaeocystis pouchetii. During mass production of this organism the water turns reddish-brown and great amounts of carbohydrates and proteins are released by the mucilaginous cell colonies at the peak of the bloom and during the breakdown. Through wave action this solution is whisked and washed ashore, where layers of foam cover the beaches up to several meters. In Guzman et al. (1990) a severe bloom of Cochlodinium catenatum in the eastern Pacific is reported to be responsible for copious amounts of viscous foams and mucus in the water column.

According to Velimirov (1980) many seaweeds exude water-soluble mucilage, which provides enough surface-active agents to induce foam formation. A further important contributor to foam formation are broken phytoplankton cells, which release organic matter causing foam. Velimirov’s (1980) analysis of sea foam collected near kelp beds at Oudekraal (South Africa) demonstrated that total protein was the dominant component (21% of the total freeze-dried weight), followed by total lipids (6.1%) and carbohydrates (2.4%). Within the protein fraction the trichloroacetic-acid (TCA)-precipitated protein was the most common (15%), which is an easily metabolizable protein available for consumers (Velimirov, 1980). In a further study, Velimirov (1982) investigated the amount of individual sugar and lipid components in foam near kelp beds. The results indicate a dominance of aldoses and deoxy sugars with β-mannose (32% of total carbohydrates) being the prevalent component followed by β-glucose (19%) and β-galactose (16%). The most important lipid class is represented by triglycerides, which amount to more than 50% of total lipids. Amongst the remaining lipid classes the free fatty acids (22%) and polar lipids (7%) seem worth mentioning. In contrast to foams from rivers and streams the hydrocarbons were only present in trace concentrations or totally absent from foam.

Sea foam collected at two sites in New Brunswick was studied by Bärlöcher et al. (1988). The authors found phenols to be the major constituent, whereas approximately 13% of the organic carbon content was present in amino acids and carbohydrates. Protein concentration was two to four times higher than that of carbohydrates. Up to 75% of the organic carbon content remained unidentified and could partly be accounted for by lipids. Subsequent investigations by Craig et al. (1989) showed a strong correlation between organic carbon in the sea foam and phenolics. As phenolics are more common in higher plants than in marine algae, the authors argue that vascular plants detritus is the dominant source of the observed sea foam. Their results confirm findings from an earlier study by Coffey (1986), who determined stable C isotope ratios of sea foam and concluded that local Spartina marshes and terrestrial plants are the major contributors of sea foam carbon.

In summary, sea foam results mainly from the enrichment of surface-active substances exuded by (i) phytoplankton blooms, (ii) seaweed or (iii) even terrestrial plants in the SML. The enriched material is whisked into foam by the action of waves and washed ashore, where unaestethic foam layers accumulate.

6.3 Ecological importance of foam

Due to its composition and capacity to accumulate various components, the literature suggests foam has an ecological relevance.

6.3.1 Toxicity of foam

SMLs and foams are subject to concentrations of materials transported by bubbles. Dissolved and particulate materials adsorbed on a bubble surface are forced into intimate contact as the bubble rises resulting in surface coagulation. This process provides a mechanism for the conversion of dissolved and colloidal materials into particulate form and can produce aggregates rich in surface-active toxins. Foams enriched with those surface-active aggregates represent regions in which organisms experience accelerated rates of accumulated toxic material (Johnson et al., 1989). According to Napolitano and Richmond (1995) various pollutants might be concentrated in the SML. As a consequence, the neustonic organisms (representing the biocoenosis of the SML) could be exposed to far higher concentrations of contaminants in the SML and the resulting foam than those in subsurface waters.

Sea foam collected in New Brunswick was shown to have a toxic effect on the amphipod Corophium volutator (macroinvertebrate) which was attributed to either the phenolic content of the foam or the levels of heavy metals and pesticides (Craig et al., 1989). Eberlein et al. (1985) report that sea foam produced by a Phaeocystis pouchetii bloom contained acrylic acid which is known to be an antibiotic. Guzman et al. (1990) highlight the suffocation of scleractinian corals by mucilagic substances causing sea foam in the eastern Pacific during a bloom of dinoflagellates. Their results indicate that the production of the polysaccharides may be an indirect mechanism of mortality. Harmful effects caused by an external coating of marine birds with a proteinaceous foam derived from a red tide bloom is reported by Jessup et al. (2009). Although this red tide bloom was ostensibly non-toxic, the seabird feathers dipped in the foam lost their normal water repellence and became soaked resulting in feather fouling, reduced mobility and hypothermia.

The breaking of foam bubbles carrying surface-active pollutants produce aerosols, which become widely distributed and may cause an increased risk of human exposure to toxins and pathogens (Johnson et al., 1989; Maynard, 1968). Eisenreich et al. (1978) suggested that foam was both a sink for inorganic and organic material and a source of chemical input to the atmosphere by bubble breaking and wind-suspension processes. Furthermore the authors highlighted the crucial role of foam in the transfer of toxic pollutants into the food web, as bacteria and plankton abundant in the foam are ingested by fish and waterfowl are commonly observed to feed on foam.

Finally, the enrichment of metals, such as Zn, Pb, Cu, Fe, Mn and chlorinated hydrocarbons can cause an environmental problem, if these foams are transported to drinking water supplies (Harden and Williams, 1989).

6.3.2 Foam as food resource

The enrichment of foam with various substances is not only a threat to the aquatic biocoenosis, but also represents a potential food resource for organisms either living in the sea or at the shoreline (Bärlocher et al., 1988; Craig et al., 1989; Velimirov, 1980, 1982).

The calorific content for freshly formed marine foam near Kelp beds is reported to be 15 kJ/g ash-free dry weight, which demonstrates the importance of foam as potential energy source for the marine environment Velimirov (1980). According to the author the mucilage excreted by the kelp provides enough surface-active agents to induce foam formation and to improve the foam stability. Long lasting foams are a prerequisite for sufficient movement of the foam to various sites in and around the kelp beds, enabling the energy pool to be available to the consumer chain. Although mucilage consisting mainly of the sugar mannitol, which is likely to be an important component of the foam, none of the foam samples investigated by Velimirov (1982) contained quantifiable amounts of this sugar type. One explanation for the lack of mannitol could be the presence of heterotrophic organisms in the foam, which rapidly utilize the released sugar.

Bärlöcher et al. (1988) and Craig et al. (1989)investigated the capacity of sea foam to serve as a food source for the amphipod Corophium volutator. In laboratory experiments they proved that C. volutator has a wide variety of enzymes to digest sea foam. The released sugars and amino acids could potentially satisfy 70% of the nutritional requirements of the amphipod. However, the large spectrum of fatty acids in foam samples, suggest that sea foam concentrates and distributes essential dietary components which most consumers are unable to synthesize (Velimirov, 1982).

River foam collected from five western North American rivers contained the Bradford-reactive soil protein (BRSP), a glycoprotein of soil and of arbuscular mycorrhizal fungal origin, which was also present in alluvial soils (Harner et al., 2004). Laboratory experiments proved that the protein can be leached and washed from the soil and accumulate in the foam due to its hydrophobic properties. The authors speculate that BRSP might act as a nutrient source for aquatic food webs by contributing carbon and nitrogen from terrestrial sources to water via erosion and leaching of floodplain soils containing the protein.

6.3.3 Foam as habitat

Foam is not only a food resource for organisms, but also acts as an important habitat for various species. Regardless of their source, coastal bio foams have been described as enclosing marine metazoan fauna of several taxa and larvae, e.g. polychaete, mussel and crustacean (Castilla et al., 2007). Eberlein (1985) reported massive occurrences of saprophytic bacteria on sea foam collected in the German Bight. Wilson (1959) demonstrated that sea foam contained 25% solid matter, much of which consisted of bacteria and diatoms. Velimirov (1980) found high densities of bacteria in foam with significantly higher bacterial densities in old foam than in fresh foam.

Relatively large amounts of phospholipids measured in river foams indicate that bacteria, protozoa and/or algae are major contributors to organic matter in foams (Napolitano and Richmond, 1995).

In studies dealing with aquatic hyphomycetes, also known as amphibious fungi, foam samples show that hyphomycetes' spores are stored in foams in a viable, ungerminated state for considerable periods of time (Harrington, 1997; Pascoal et al., 2005)

The most comprehensive investigation on foam as habitat was a study by Maynard (1968) who collected foam from various aquatic habitats (freshwater and marine) and found heavy concentrations of diatoms, lesser numbers of dinoflagellates and green and blue-green algae. An outstanding fact derived from her study was that the majority of species present in foam was either benthic (attached to sediments) or periphytic (attached to plants – aufwuchs) rather than planktonic (free floating in the water column). She considered foam to be an important habitat which has been ignored previously.

6.3.4 Other roles of foam in the environment

Ettema et al. (1989) discussed the role of foam in the initiation of ice covers. The observations reported indicate that small and medium rivers convey chemicals resulting either from the decay of organic substances or from manmade pollution that generate foam. The resulting foam possibly causes ice covers to form more rapidly than in streams without foam formation and at water temperatures above freezing temperature. This is particularly likely in small rivers where complete ice-cover reduces air supply resulting in decreasing oxygen concentrations. However, the importance of foam as an ice-cover initiation mechanism diminishes with increasing size and width of a river, as wind fetch increases leading to foam dispersal.

Apart from the physical effects, foam is known to ensure egg retention and larval development in organisms (Castilla et al., 2007). According to the authors, foam nests enhance the fertilization success and the retention of eggs and larvae in freshwater nest-building fish, tropical aquatic frogs and tunicates.

In summary, the formation of foam either in freshwater systems or as sea foam is not imperatively disadvantageous for the environment. Although foams may show toxic effects depending on the substances enriched within, they also can serve as a food resource and as a habitat for organisms.

7 Conclusions

This review on foam in the aquatic environment has highlighted that minor amounts of information are available in literature, and that most studies dealing with that subject are at least twenty to thirty years old.

Several significant references on surface microlayers (SML) in freshwater and marine ecosystems were identified. SML represent the air-water boundary where surface-active components accumulate. As a consequence of the SML, the introduction of air and other gases into the water by turbulences, cascades etc. will lead to foam formation. In the presence of organic (living or dead organisms) and inorganic (silt, sand) particles very stable foams can occur.

Foam formation is observed in nearly every aquatic environment, such as rivers, lakes and oceans. Although the majority of studies show that foam is the product of natural processes and factors, the public tends to associate foam formation with manmade pollution. Public concern is likely to be enhanced due to the visibility of foam, which lead to it being more obvious than “hidden” chemical pollution.

Surface-active components causing foam include the degradation products of organic material (e.g. humic substances), lipids and proteins originating from aquatic plants or the terrestrial environment, and exudation or decomposition products of phytoplankton. Manmade foam is often the result of point source pollution (particularly from industry) or diffuse pollution originating mainly from agriculture.

There is no regulation regarding instream foam formation in the United States, nor the EU or Switzerland. Although emissions from point sources are strictly governed in general, the foam causing potential of point sources is not regulated. Methods to assess foaming and foam stability are found mainly in the wastewater sector. In wastewater treatment plants stable foam is mainly observed as a result of filamentous bacteria such as Microthrix parvicella or nocardioform actinomycetes which occur in the water. The role of the bacteria in foam formation is on the one hand the production of surface-active biotensides, and on the other hand the stabilisation of foam due to their hydrophobicity.

Apart from the aesthetic aspects of foam, foam formation involves several other ecological aspects. Due to its enrichment capacity, carbon, nutrients, metals, hydrocarbons and even pesticides accumulate in foam. According to Napolitano and Richmond (1995) foams are relatively isolated microenvironments, in which the inhabiting organisms are exposed to higher concentrations of contaminants. Toxic effects of foam were demonstrated for the amphipod Corophium volutator and the transfer of toxic substances from foam into organisms via the food web seems to be a potential danger. The break of foam bubbles carrying surface-active pollutants may even cause an increased risk of human exposure to toxins and pathogens.

Foam is also believed to be an important food resource and a site of nutrient recycling which transfers energy to the consumer level. Some literature is available on the importance of foam as a habitat, especially for benthic and periphytic organisms.

The review of the existing literature demonstrated both the crucial role of foam with regards to pollution and the ecological aspects of foam in the aquatic environment. Considering this, it is even more surprising that information on foam in the aquatic environment is still scarce and that this topic appears to have been ignored over the last decade.

Measurement of instream foam formation and quantification of foam in effluents

1 Introduction

Foam consists of a mix of a foamer (e.g. surfactant), water and gas, where the gas is introduced into the liquid by mechanical impact (Poremba, 1991; Vikingstad, 2006). In aquatic ecosystems this force can be induced by cascades or artificial constructions such as weirs and dams, due to the pounding of waves, in areas of strong currents or in areas, where fresh and salt water mixes (Craig et al., 1989).

Today, the quality and pollution of surface water is an issue of serious environmental concern worldwide (Ouyang et al., 2006; Singh et al., 2005). In this context, foam formation – both natural and anthropogenic - is a more effective eye-catcher than “hidden” chemical pollution and results in significant public awareness, regardless of its source (Wegner and Hamburger, 2002; Winkler et al., 2008). Wilson et al. (1995) demonstrated that the public associated the presence of foam on surface waters with pollution which results in a reduced preference to use the water for recreational purposes or as drinking water sources. In the literature, the appearance of foam is mostly seen as natural phenomenon and only a few authors deal with it in relation to anthropogenic pollution (Defrain and Schulze-Rettmer, 1989; Madrange et al., 1992; Ruzicka et al., 2009a).

A detailed review on foam in the aquatic environment is given in Schilling and Zessner (2011). The collection of cited literature confirms that scientific research deals with the existence of foam in the aquatic environment and a sound knowledge base exists on reasons for its occurrence. Nevertheless, only poor information is available on techniques for its quantitative determination outside of the wastewater sector, where foam appears as consequence of bulking sludge. Reasons for the lack of proper determination methods are most probably the result of the poor or non-existent legal standards for instream foam formation as well as for its emission via point sources (Schilling and Zessner, 2011).

In 2006, the presence of foam on a river close to the Austrian-Hungarian border resulted in massive public debate and became a strain to the Austrian-Hungarian relationship. The implementation of foam abatement measures on a catchment scale requires a detailed knowledge on the processes taking place within the catchment as well as a sound understanding of the relationship between emitted foam into the river and the resulting instream foam formation. This approach implies appropriate and well defined determinants, in order to measure the emitted and resulting instream foam. Although certain parameters, such as surface tension, characterise surface-active substances that could cause foam, no appropriate foam parameters regarding its quantification existed so far. Thus, one of the major tasks of a subsequent study was the development of adequate foam measurement techniques to quantify the foam in effluents as well as in the river.

At the end of the study, the foam on the river could be linked to the effluent of three tanning factories, although their wastewater treatment complied with best available technology and met the legal requirements. A model was developed to predict the foam formation on the river depending on the river discharge and the foam emitted by the tanneries (Ruzicka et al., 2009a). Based on this model, measures were investigated to reduce the foam emitted by the industry and resulted in the implementation of quaternary treatment at all tanneries. To evaluate those measures, the monitoring of instream foam formation is still ongoing.

The purpose of this paper is to present the developed methods for assessment of emitted foam as well as instream foam, and to present and discuss some results to demonstrate their accuracy and applicability.

2 Material & Methods

The “foam potential” in combination with an appropriate measurement technique was developed to quantify the foam in effluents. The method was not applicable to determine the instream foam formation, as the “foam potential” of the river water was below the limit of quantification. In consequence, a second statistic called the “foam index” was introduced as parameter to assess the instream foam formation.

2.1 Foam in effluents – foaming factor and foam potential

Several methods, e.g. stirring, mixing and aeration were tested to measure the foam of effluents from industrial and municipal wastewater treatment plants. Finally, a standardised foaming test based on shaking was developed to detect (i) foam on the sample and (ii) the dilution of the sample, at which no foam occurred. 250 ml of effluent were shaken in Erlenmeyer flasks with baffles on a laboratory Shaker (Type

Ceromat-U) for three minutes at a speed of 300 rpm. After shaking, the foam height and the foam stability were measured. Foam stability was defined as the time it takes for the foam cover to break.

In the case of foam occurrence, the sample was diluted with dilution media (tap water, deionised water or unpolluted river water), until no more foam is produced. The dilution steps are chosen as follows: 0, 2, 5, 10, 25, 50, 100, 150 and 200. The dilution factor, at which minimal foam occurs, is defined as the “foaming factor”. If minimal foam occurs at dilution factor 100, the foaming factor is 100 and means that the initial sample is ten times more diluted than in case of foaming factor of 10. If minimal foaming occurs on an undiluted sample, the foaming factor is determined as 1. In case of no foam on the undiluted sample, the foaming factor is set to 0.5.

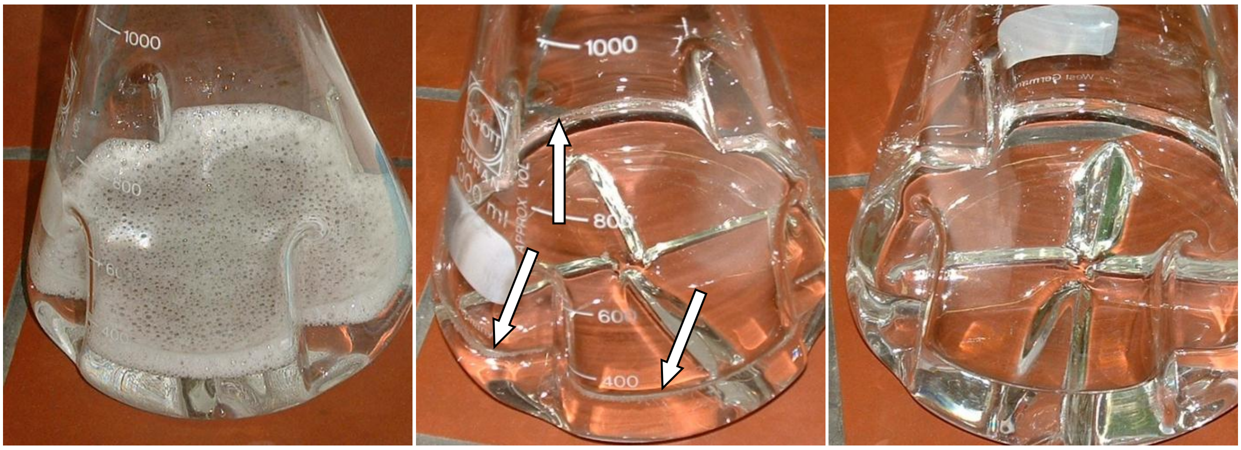
Figure 3 provides an overview on various foaming conditions in a sample, starting with a closed foam cover along with minimal foam and no foam.

The foaming factor of an effluent is multiplied with the discharge of the effluent to calculate the “foam potential” of an effluent:

Formula 1:

$$\mathrm{FP}_{\mathrm{effl.x}} = \mathrm{FF}_{\mathrm{effl.x}} \times \mathrm{Q}_{\mathrm{effl.x}}$$

with: FP = Foam potential of effluent x [m³/s], FF = Foaming factor of effluent x, Q = Discharge of effluent x [m³/s]



closed foam cover minimal foam no foam

Figure 3: Overview on various foaming conditions in a sample. Arrows indicate foam formation.

According to Formula 1, an effluent with a discharge of 0.02 m³/s and a foaming factor of 50 has a foam potential of 1 m³/s. That means, discharging this effluent into a river (in this case the diluting media) would cause a minimal foaming in 1 m³/s of the river water in case of turbulence according to laboratory conditions. Consequently, the foam potential of an effluent is defined as the flow rate of river water which will potentially foam due to an effluent's discharge.

For river water, the foaming factor of the river is multiplied by the discharge of the river. The resulting foam potential equals the amount of river water that will potentially foam, if turbulence is introduced. As the foaming factor of the river samples was below the limit of detection, the method was not applicable for river water.

Laboratory measurements of this nature underestimate the actual foam potential given in nature, as the introduced turbulence by shaking is a lot lower than in the environment, where turbulence can be induced by cascades, weirs and dams.

2.2 Surface Tension

Foams are always formed from mixtures, whereas pure liquids never foam (Holmberg et al., 2003). Thus the presence of surface-active substances in the water is a prerequisite for the formation of foam (Pugh, 1996). Surface tension is a measure to assess the amount of surface-active components present in a liquid (Vikingstad, 2006). It is defined as the work needed to augment the surface area of a liquid (Bletterie et al., 2009). Pure water has a surface tension of 72.74 mN/m at 20°C, which will decrease, as soon as surface-active substances are added.

Surface tension was measured with a KRÜSS Easy Dyne K20 tensiometer according to the DIN EN 14370 (2004). Surface tension readings were made by the means of the Wilhelmy plate method named after the German chemist Ludwig Wilhelmy (Haefele, 2006). This involves dipping a thin platinum plate into the liquid being measured. The liquid is raised until the contact between the surface or interface and the plate is registered and the force recorded on the balance is noted.

2.3 Instream foam formation

2.3.1 Austrian foam index

The site of problematic foam formation is located in Hungary shortly after the border with Austria. The Austrian Federal State Monitoring agency in cooperation with the Hungarian State Monitoring agency provided pictures of the site for a one year period (10/2004 to 11/2005, 75 pictures in total). They served as basis for the development of a seven-stage “foam index” (FI) classifying the foam conditions from 0 to 6 (see Table 3). Additionally, intermediate stages were created (e.g. 0.5, 1.5, 2.5 etc.) to determine foaming conditions, which could not exactly be related to a certain foam index.

Table 3: Seven stage foam index.

FI	Situation	Description
0	no foam	None
1	minimum foam	Sporadic small bubbles
2	little foam	Bubbles accumulate to small areas, nearly no single bubbles
3	moderate foam	Small foam areas
4	much foam	Flat foam areas, partly accumulating to compact foam lumps
5	plenty of foam	Large flat areas and/or compact foam lumps, partly large areas of accumulated or frozen foam
6	heavy foam	Ample compact foam lumps, large foam areas, partly large areas of accumulated or frozen foam

Figure 4 highlights the various foam index situations at the weir in Hungary.

FI 1 FI 3 FI 5

Figure 4: Overview on various foam index situations.

Additionally, an online webcam was installed at the Hungarian weir to determine the instream foam formation on a daily basis. Pictures taken with a 15 minutes resolution were transferred via UMTS and stored within a database. The final value of the daily FI is not the mathematical average of FI of single images, but is determined based on a set of single pictures assessed by expert judgment.

The FI represents a 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.

2.3.2 Hungarian foam index

At the end of 2009, a local Hungarian environmental organisation started an assessment of the foam situation according to their own foam index, which is based on a scale from 1 to 10. In contrast to the Austrian approach, the Hungarian assessment includes only one situation or picture per day. To eliminate the influence of the different scales, the Hungarian FI was adjusted to the Austrian scale according to Formula 2:

Formula 2: $$\mathrm{FI}_{\mathrm{AUT}} = \frac{\mathrm{FI}_{\mathrm{HU}} \times 6}{10},$$

With $\mathrm{FI}_{\mathrm{AUT}}$ = foam index Austria, $\mathrm{FI}_{\mathrm{HU}}$ = foam index Hungary, 6 = highest Austrian FI, 10 = highest Hungarian FI

In a second step, the resulting FI was rounded, in order to fit into the ordinal scaled Austrian foam index categories. Furthermore, the Delta between the two FI was calculated according to Formula 3:

Formula 3: $$\mathrm{Delta} = \mathrm{FI}_{\mathrm{AUT}} - \mathrm{FI}_{\mathrm{HU}},$$

with $\mathrm{FI}_{\mathrm{AUT}}$ = foam index Austria, $\mathrm{FI}_{\mathrm{HU}}$ = foam index Hungary

The Delta was calculated to compare the two FI determining methods and to check the plausibility of the Austrian FI. In total, the Delta was calculated for 416 datasets.

2.4 River Monitoring

The river affected by foam formation was extensively investigated over a one year monitoring programme (November 2005 to October 2006), which included a close network of surface water sampling points (R1-R5) as well as the sampling of five municipal and eight industrial wastewater treatment plants (WWTP) along the river stretch (see Figure 5). Tannery 1 is located between R1 and R2, tannery 2 discharges between R2 and R3 and tannery 3 is based between R3 and R4.

Figure 5: Foam formation along the river stretch at sampling sites R1 to R5.

Surface water samples and effluents of waste water treatment plants were subject to foam tests and the foaming factor as well as surface tension was determined (see 2.1 and 2.2). Foam index (see 2.3.1) was assessed regularly via the webcam and at the three weirs along the river stretch during the field trips. As the webcam continues to provide images, data on foam index is available for the period 2006 to 2011. Detailed information on the catchment, the sampling frequency as well as physical-chemical parameters analysed can be found in Ruzicka et al. (2009a).

2.4.1 Foam index model

Based on the monitoring of the foam index and the foam potential, a simple statistical model (see Formula 4) was developed to describe the cause-effect relationship between the instream foam formation and the emitted foam. Details on the model can be found in (Ruzicka et al., 2009a).

Formula 4: $$\mathrm{FI} = \left(\frac{11.3}{\mathrm{Q}}\right)^{1.28} - \left(0.06 + 10.42 \times \mathrm{e}^{-2.04 \times \mathrm{FP}}\right)$$

with FI = Foam index, Q = discharge and FP = foam potential

2.4.2 Flow adjusted Foam index ($\mathrm{FI}_{\mathrm{FA}}$)

To eliminate the influence of discharge on the FI, the flow adjusted FI was calculated according to the relationship between discharge and FI derived in Ruzicka et al., 2009 (see Formula 5). The discharge was set to an average discharge of 4.9 m^3/s.

Formula 5: $$\mathrm{FI} = \left(\frac{11.3}{\mathrm{Q}}\right)^{1.28}$$

with FI = Foam index, Q = discharge

3 Results and discussion

3.1 Foam in effluents

The foaming factor and the surface tension were determined for several effluent samples. To evaluate the applicability of the foaming factor as a foam parameter, it was correlated with the surface tension (Figure 6). This clearly shows that a low foaming factor (meaning low foam on the sample) is consistent with values for surface tension close to pure water. As surface tension is a measure for the presence of surface active compounds (Vikingstad, 2006), it decreases with increasing foaming factor. Thus a foaming factor of 100 indicates an average surface tension of 50 mN/m.

The good correlation (F = 479, $p<0.0001$) between the two statistics gives evidence that the foaming factor is an appropriate sum parameter to assess the presence of surface-active substances, although it has certain limitations. The two encircled samples highlight foaming factors of 1 associated with very low surface tension of about 30 mN/m. As the low foaming factor would indicate a rather high surface tension of about 70 mN/m, both samples were subject to a biodegradation test with municipal sludge and 48 hours aeration. The degraded samples were again taken to the foam test, which resulted in considerably higher foaming factors of 65 indicated by the arrow in Figure 6.

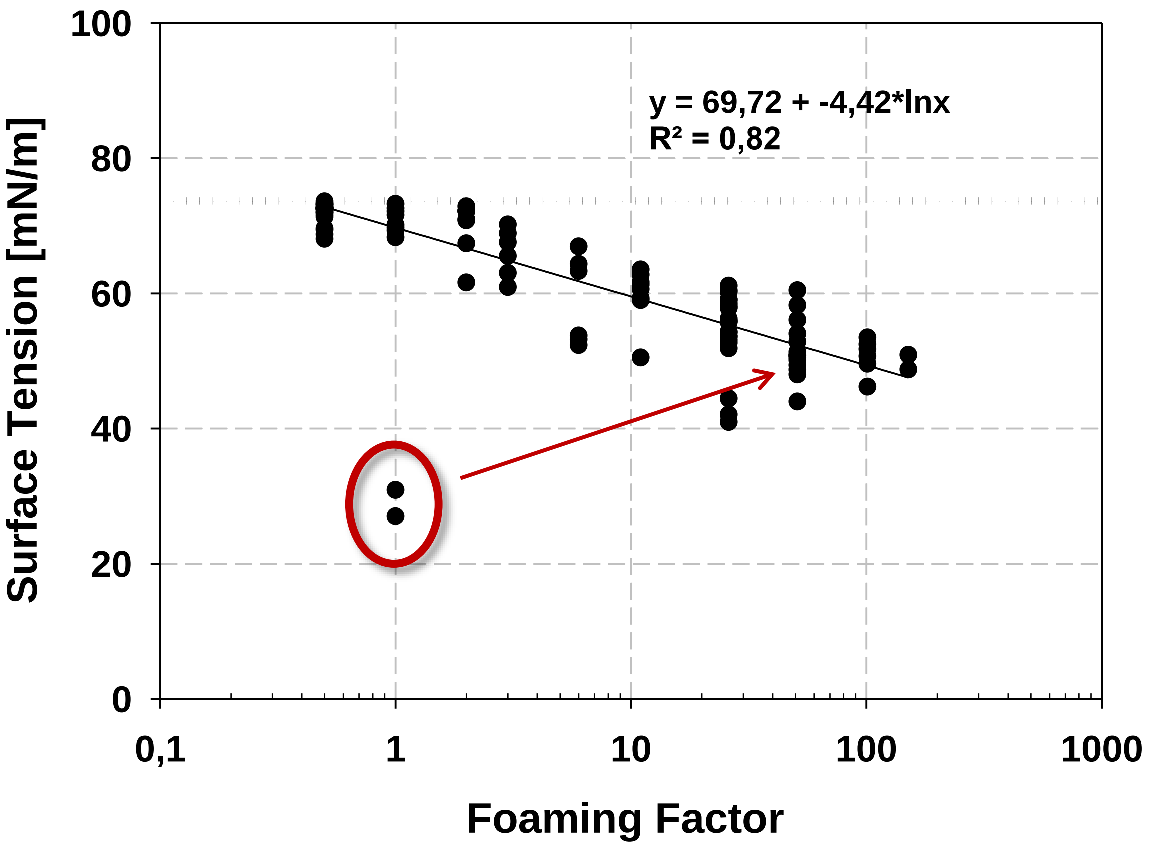


Figure 6: Correlation between Foaming Factor and surface tension (dotted line indicates the surface tension of pure water).

In this case anti-foaming agents have been applied to these two samples. Defoamers are only effective if they show lower surface tension than the medium in which they are used. This is because they have to replace the foam producing surfactants at the air/water boundary layer (Lacasse and Baumann, 2004). As a result, no foam occurs, although the surface tension of the liquid is low. After degradation of the anti-foaming agents, the original surface active substances (which are hardly degradable) emerge again and result in increasing foaming factors. This example demonstrates that the foaming factor of a sample can be reduced temporarily by adding anti-foaming agents, but will increase again as soon as the added substances are biodegraded. In reality, the degradation of the defoamers will happen in the river and foam will occur several kilometres downstream of the point source emission.

Although surface tension seems to be a more reliable parameter in this special case to detect surface-active substances, the foaming factor was finally chosen as the foam emission parameter. The reason was that the foaming factor allows the calculation of the foam potential, which is directly linked to the instream foam formation (foam potential is defined as the flow rate that could potentially foam due to an effluent’s discharge).

Furthermore it is a useful tool to characterise the type of effluent in terms of its foaming potential. Figure 7 highlights the percentages of certain foaming factor classes depending on the type of wastewater. Highest foaming factors occur in the effluent of tanning industries, whereas tannery 1 shows the lowest foaming factors of the three with about 80% in class 10-25 and only 5% with a foaming factor of 50. In tannery 2, about 50% show a foaming factor of 50 or higher compared to more than 90% in tannery 3. The application of cleansing agents is the reason for the foam in the effluent of the metal industry with about 50% in class 10-25 and 15% with even higher foaming factor classes as well as foam stability of more than one minute in about 50% of the cases (see Figure 7), although the effluent is subject to a physical-chemical treatment. The same company discharges part of its effluent into WWTP 4 for further treatment. This indirect discharge causes considerable foam with about 85% in foaming factor class 2-5 and 10% in the class 10-25. All the other municipal wastewater treatment plants feature very little foam formation in their effluents.

The difference in foaming factor classes in the tanneries is probably caused by the type of tanning agents used in the tanning process. Tannery 1 applies a mixture of chromium, synthetic and vegetable tanning agents. Tannery 2 and 3 abandoned chromium tanning completely and adopted a mixture of synthetic and vegetable tanning substances. The most frequently applied vegetable tanning agents in the investigated tanneries are the pods of the Tara tree (Caesalpinia spinosa), which is one of the most frequently used hydrolysable tannins (Bhat et al., 1998). It is used in the retanning process in concentrations depending on the amount of leathers produced. Corresponding to the mass of leather produced, tannery 1 applies about 5 t/d, tannery 2 8 t/d and tannery 3 12 t/d of Tara. Representatives of the genus Caesalpinia, to which Tara belongs, were reported to contain saponins characterized by high surface-activity and the potential to foam (Badami et al., 2004).

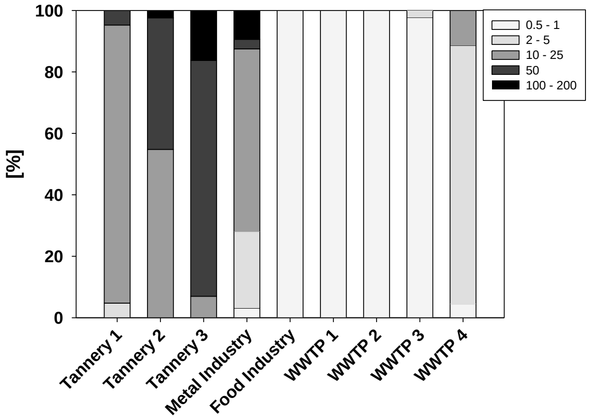


Figure 7: Percentages of certain foaming factor classes depending on the type of wastewater.

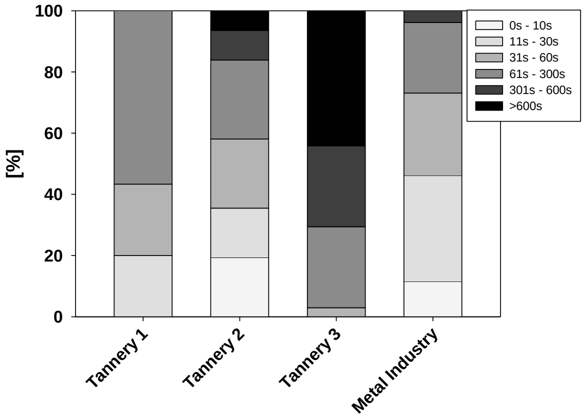


Figure 8: Percentages of foam stability classes depending on the type of wastewater.

Furthermore vegetable tannins have special chemical structure. They are water soluble polyphenols with the ability to precipitate proteins such as gelatin from solution, which is the reason for their use in the tanning of animal skins. To ensure full penetration and reaction of tannins with skin collagen, they are usually used in excess. The resulting wastewater shows poor biodegradability due to the toxic effects of tannins on microorganisms (He et al., 2007). Complexes between polyphenols (tannins) and proteins are not only known to form foam (Wu et al., 2007), but tannins are also used to produce rigid foams to absorb metal ions (Tondi et al., 2009).

Thus it was hypothesized that the vegetable tannins cause the higher foaming factor in the effluent due to their chemical structure and binding properties as well as their low biodegradability in the wastewater treatment plant. Consequently, the percentage of high foam classes increases with the amount of Tara applied from tannery 1 to tannery 3.

In Figure 8 the foam stability of various effluents is subsumed into certain stability classes and given in percentages for the most foaming effluents. It is obvious that the foam stability at the three tanneries increases with the higher usage of vegetable tanning agents. In consequence, tannery 3 with the highest foaming factors also produces the most stable foam with stabilities of more than 10 minutes in about 40% of the cases. In contrast, foam stability in tannery 1 varies between 10 seconds and one minute, as less vegetable tannins are used and chromium, which is causing no foam at all, is partly applied.

The company belonging to the metal industry implemented several measures including the more frequent replacement of their active carbon filter to reduce the foaming factor of its effluent (see Figure 9). Whereas the foaming factor varies between 50 and 150 in calendar week 48 to 14, the replacement of the active carbon filter reduces the factor to 1 in week 15 due to retention of foam causing substances in the filter. A fast reloading of the filter is observed in the following two weeks resulting in a foaming factor of 25. Between week 19 and 21 internal pipe installation was carried out to discharge heavily foaming wastewater streams into the municipal wastewater treatment plant (WWTP 4). After a certain adaption time these changes resulted in a decreasing foaming factor, which consequently stabilized around 10. The direction of the foaming partial flow into the wastewater treatment plant did not increase the foaming factor of this effluent, which implies that the foam causing substances in the wastewater were fully degraded within the treatment plant.

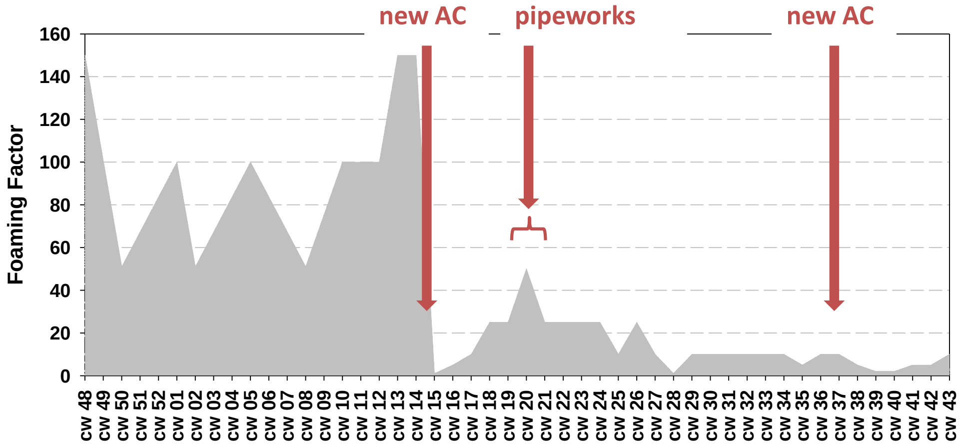


Figure 9: Foaming Factor of the effluent (metal industry) given for the calendar weeks in 2005 and 2006, AC = active carbon filter.

3.2 Instream foam formation

Five sites were sampled regularly along the affected river stretch, whereas foam formation increased steadily from site R2 to R5 (see 2.4). R1 served as reference site without any influence from municipal or industrial discharge. Foam observed there was defined as natural foam formation. All samples collected along the river stretch were subject to surface tension measurements and foam tests. The foaming factor of the samples was always 0.5, as no foam formation was observed during the tests.

Surface tension also showed no trend along the river stretch although an increase in surface active substances and consequently a decrease in surface tension would be expected as a consequence of increasing foam formation along the river stretch. Hence, the foaming factor and the surface tension are inadequate parameter to differentiate between the foaming conditions on the river, as the instream foam formation was below the limit of quantification of both parameters.

In consequence, the foam on the river was evaluated by applying the foam index (FI), which is determined daily based on the assessment of the webcam pictures since March 2006. Figure 10 highlights the relative fractions of foam index classes at four sampling sites (R2-R5, x-axis indicates the flow direction).

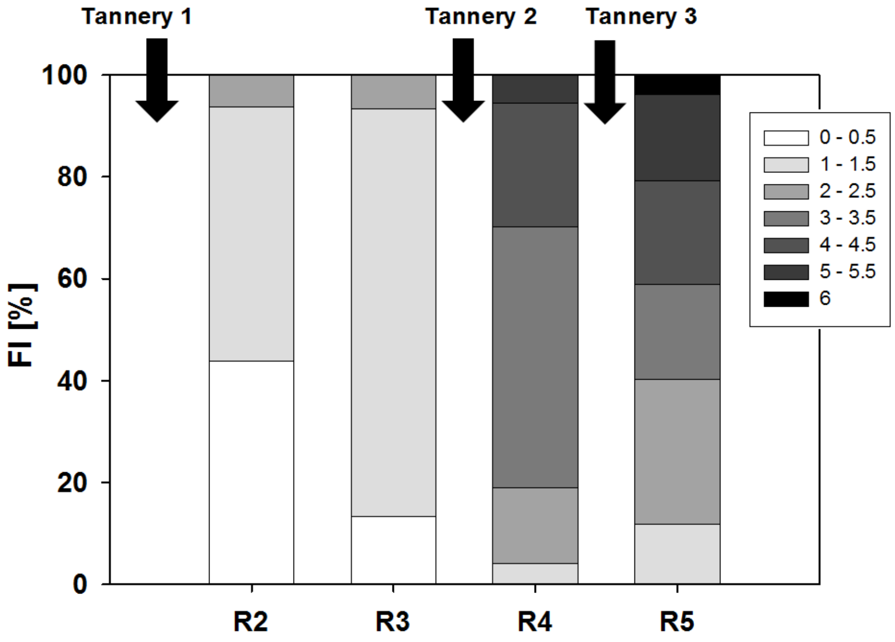


Figure 10: Fraction of the FI classes at the sampling sites R2 to R5 (x-axis indicated the flow direction of the river).

Obviously, the maximum foam index is not higher than 2 to 2.5 at sites R1 and R2, but elevates with the increasing amount of discharged effluent from the tanneries up to 5 – 5.5 at site R3 and even 6 at site R4. Thus, the FI seems to be valuable parameter to identify the raising foam formation along the river.

As mentioned before, the foam index is a statistic based on expert judgment, which involves a subjective perception of the person assessing the FI. To evaluate the influence of the subjective observation, the Delta between the Austrian FI and the adjusted Hungarian FI (see 2.3.2) was calculated. Figure 11 provides an overview on the percentage of each Delta category on the total number of data (n=416). About 30% of the Hungarian data are equal to Austrian data. 72% of the Hungarian FI show only a minor deviation between +0.5 and -0.5, whereas 90% vary between +1 and -1. The higher percentage of positive Delta categories indicates that the Austrian FI tends to be higher than the Hungarian FI. A possible reason could be the difference in the resolution of the FI determination. Whereas the Hungarian FI is based on only one image per day, the Austrian FI results from the assessment of several pictures per day (15 minutes resolution of the webcam).
The high agreement found between the two independent data sets proved the applicability of the foam index as a measure for instream foam formation, although the assessment method is not clearly objective.

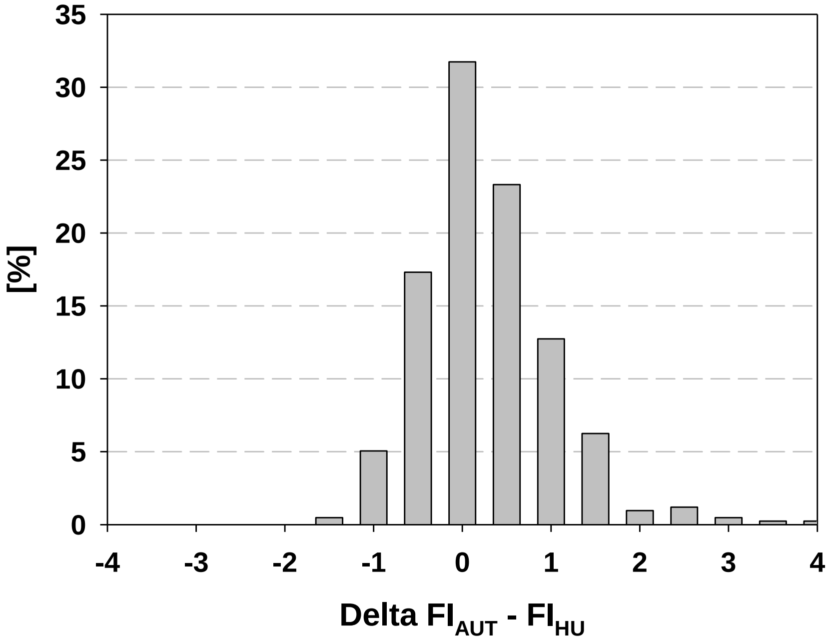


Figure 11: Percentage of delta categories between Austrian and Hungarian FI.

By the means of the foam index it is possible to differentiate between the foam occurring on the stream at a spatial and temporal scale. The spatial variability of the FI has been shown in Figure 10 as well as in Ruzicka et al. (2009a). With increasing point sources emitting foam into the river, the FI rises constantly along the river stretch. The temporal variability of the FI is given in Figure 12, where the frequency of undershooting the FI is plotted for the years 2006 and 2009 to 2010 (2007 and 2008 are similar to 2006 and not shown to provide clarity). The line at FI 3.5 indicates the ‘‘not accepted degree of foam formation”, which was introduced in 2006, as no legal instream criterion existed for foam. By definition the “not accepted degree of foam formation” is the FI, at which protests from Hungarian locals arose (Ruzicka et al., 2009a). In 2006, about 50% of the FI exceeded “the not accepted degree of foam formation”. In contrast, 100% met or fell below that limit in 2009, whereas 90% of the FI values undershoot the critical FI of 3.5 in 2010.

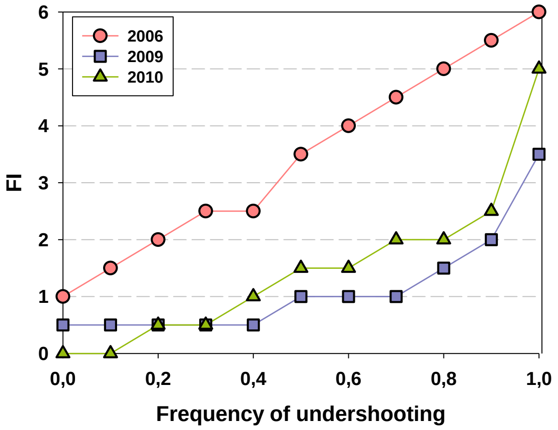


Figure 12: Frequency of undershooting a certain foam index (FI) from 2006 and 2009 to 2010. The line at FI 3.5 indicates the “not accepted degree of foam formation”.

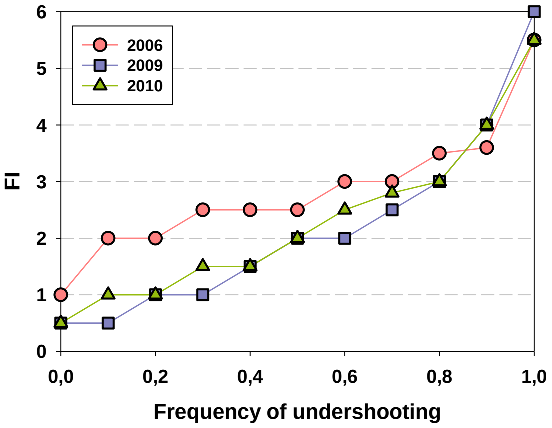


Figure 13: Frequency of undershooting a certain foam index (FI_{FA}) from 2006 and 2009 to 2010. FI_{FA} was adjusted by discharge.

The FI is influenced by two main parameters, which are the discharge of the river and the emitted foam potential. As the discharge varied considerably over the years (Table 4) and was rather high in 2009, the FI was adjusted by the discharge and the frequency of undershooting was calculated again.

Table 4: Mean annual discharge (MQ) in the years 2006 and 2008 to 2010.

	2006	2008	2009	2010
MQ [m³/s]	5,2	4,5	11,7	7,5

The flow adjusted FI_{FA} (Foam Index flow adjusted) highlighted in Figure 13 is not affected by the discharge, thus any variations between the years are the consequence of varying emissions of foam potential from the point sources. Similar to Figure 12 the FI in 2006 is the highest of all years (Figure 13). 2009 was characterised by the economic crisis, which led to a distinct decrease in leather production and resulted in considerably less effluent of treated wastewater and consequently in lower foam emissions by the tanning factories. In 2010, one of the three tanning factories (tannery 3) started the operation of a quaternary treatment to reduce the foam in the effluent. In consequence, the foam formation in 2009 and 2010 has similarly declined relative to 2006, although the trend of the FI is still slightly lower in 2009.

3.3 Link between foam in effluents and instream foam formation

To evaluate the influence of the emitted foam potential, the expected FI for each year was calculated by the means of the foam index model (see Formula 4) with the measured discharge and the foam potential as input parameters. As foam potential data was only available for 2006, it had to be estimated for the other years. For 2009, the foam potential emissions were cut by 60%, as the economic crisis resulted in reduced operation and consequently lower emissions in all factories. In 2010, emissions similar to 2006 were again adopted for tannery 1 and 2, but were reduced for tannery 3 by about 70% due to the newly installed quaternary treatment.

In a second step, the deviation between the observed and the expected FI (deviation = observed FI – expected FI) was computed for each day of the year. A positive deviating FI means the expected FI is lower than the observed, whereas a negative deviating FI indicates that the expected FI is higher than the observed FI. If the model for foam formation is able to reproduce the FI properly, the average deviating FI should show values close to zero (see boxplots in Figure 14). Accordingly, the average deviating FI (dashed line in Figure 14) in 2006, 2009 and 2010 is close to 0, which means the observed and expected FI are similar with a maximum deviation of about 2 in both directions. The variance of the deviating FI is smallest in 2006, as the input parameters were available to calculate the expected FI. Thus the existing variations are mainly the result of model inaccuracy. As the model was calibrated for the year 2006, which had a considerably lower discharge than 2009 and 2010, these two years show higher variability in the deviating FI than 2006.

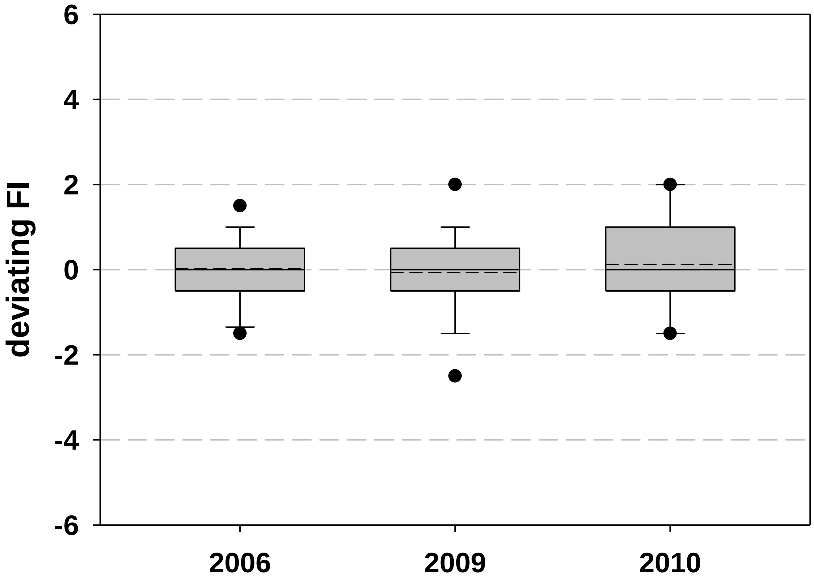


Figure 14: Boxplots of the deviating FI in the years 2006 and 2009 to 2010.

4 Conclusions

In conclusion, the parameter foaming factor is a practicable tool (i) to detect surface active components in an effluent, (ii) to differentiate between the foaming conditions of various types of effluents and finally (iii) to evaluate measures to reduce the foam. The foam index seems to be a reliable and practicable tool to differentiate between varying foaming conditions on a river on spatial as well as temporal scale. Although the introduced foam index is only valid for the investigated river, it can be effortlessly adapted to other surface waters. The installation of a webcam and online transfer of images can be easily managed nowadays and provides good insight into foam formation on a river.

Currently, image interpretation software is under development to provide an objective assessment of the FI. The resulting automated evaluation of the foam index allows several areas of applications such as surveillance. In the case of the investigated river it will be implemented into an online monitoring tool displaying not only the physical and chemical parameters and discharge, but also the foam index situation online.

Cause and effect relationship between foam formation and treated wastewater effluents in a transboundary river

1 Introduction

Rivers play a major role in receiving or carrying industrial and municipal wastewater, manure discharges and runoff from agricultural fields, roadways and streets, which are responsible for river pollution. As rivers constitute main water resources in inland areas for drinking, irrigation, industrial and recreational purposes (Vega et al., 1998), the deterioration of surface water quality with toxic chemicals and eutrophication of rivers due to excessive nutrients deposition is of great environmental concern (Ouyang et al., 2006). Compared to these water quality issues, the formation of foam on rivers is at present an overlooked subject in scientific discussions. Whereas some literature is available on the occurrence of foam in the marine environment (Bärlocher et al., 1988; Bätje and Michealis, 1986; Craig et al., 1989; Eberlein et al., 1985) and foam formation on wastewater treatment plants (Defrain and Schulze-Rettmer, 1989; Hladikova et al., 2002; Lánský et al., 2005; Torregrossa et al., 2005; Westlund et al., 1998), information on foam in freshwater ecosystems is rare (Fisenko, 2004; Madrange et al., 1992; Wegner and Hamburger, 2002).

The massive occurrence of foam on rivers was supposed to be eliminated after the introduction of biodegradable contents in detergents and the biological treatment of wastewater in wastewater treatment plants. Nevertheless, the formation of foam remains an increasingly relevant topic in freshwater ecosystems. Certainly, the visibility of foam addresses the people’s ecological “conscience” more than “hidden” chemical pollution. Production of foam can be caused by multiple factors of different origins. Anthropogenic sources are e.g. industrial effluents containing tannins, polyamides, amino acids and lipids as well as effluents of municipal wastewater treatment plants (Defrain and Schulze-Rettmer, 1989; Madrange et al., 1992). Natural foams can be created by algal blooms causing massive release of dissolved organic carbon as well as carbohydrates, proteins and humic substances originating from higher plants, plankton and microorganisms (Madrange et al., 1992; Madrange L. et al., 1992; Wegner and Hamburger, 2002). These compounds possess a surface active character, which causes a reduction of surface tension and therefore create favourable conditions for foaming. Turbulence of a river, as well as, the existence of cascades, bed drops and weirs on the river bed may also promote foam formation by introducing air bubbles into the water.

Regulation of in-stream foam by-laws is a difficult and an improper topic in many countries. For example, in the United States the US Clean Water Act proclaims that “all surface waters should be free of scum in amounts that are unsightly” (Federal Water Pollution Control Act, 2002). The Regulation for Water Pollution Control in Switzerland states that “treated wastewater discharge must not lead to foam formation after advanced mixing in the river with exception from rainfalls” (Gewässerschutzverordnung Schweiz, 1998). The EU Water Framework Directive (EU WFD) claims the “good chemical and ecological status” for river water bodies, which means only a minor deviation from the reference (natural) status. The chemical status is regulated by environmental quality standards for priority substances, which contain also foam related parameters such as tensides (e.g. nonylphenols). Thus an indirect criterion for foam exists by the regulation of tensioactive compounds. However, neither in the United States nor in Europe are there explicit emission or instream criteria, let alone thresholds for foaming (Water Framework Directive 2000760/EC, 2000; Defrain and Schulze-Rettmer, 1989). Instead of regulating foam by an instream criterion, at present the “allowed” amount of foam on a river is subject to the aesthetic of the beholder, while the emission of foam lies in the responsibility of the operators of wastewater treatment plants. In Austria, the only existing restrictions for wastewater treatment plants regarding foam are emission criteria for foam related parameters such as tensioactive compounds, e.g. the sum parameter for anionic and non-ionic surfactants (Bundesministerium für Land- und Forstwirtschaft, 1991). As foam formation on wastewater treatment plants is a widely observed phenomenon, the common solutions are sprinkling of foam with water and, in particular, the application of anti-foaming agents. Such measures minimize the foaming effect temporary, but do not eliminate the reasons, i.e. the surface active compounds. Biodegradability of anti-foaming agents leads to the recovery of foam and displaces the foaming problem from the wastewater treatment plants to the receiving waters (Defrain and Schulze-Rettmer, 1989).

Thus, identification of foam causing substances, their origin and elimination, as well as, the handling of the legal aspects and the public concern are new challenges to be met in order to solve foam formation problems.

Occurrence of foam below weirs in a lowland river in Austria and at the border region to Hungary and the associated protest by Hungarian locals, led to a causal research within the river basin. The suspect of environmental pollution by industry associated with foam formation in Hungary affected the political relationship between the neighbouring countries profoundly. Thus a fast and effective solution was required.

The challenge of river basin wide approaches lies in understanding the effects of emissions on the in-stream river quality. Only if this cause and effect relationship is well known and understood, could the development and implementation of useful and cost-effective measures be made possible. Thus, the paper is mainly focused on the development of a model to quantify the impact of emitted foam causing substances on the in-stream foam formation. The methods used and the results that were achieved, as well as a brief discussion of the investigated measures is given in the following pages.

1.1 Study Site

The investigated river has its source in a crystalline low mountain range, flows through the south-eastern part of Austria and discharges into the Danube in central Hungary. The Austrian part of the river basin (Figure 15) covers an area of about 980 km², the climate is characterised by moderate precipitation (784 mm/a), which results in seasonal low discharge conditions (low flow during investigation period was around 2 m³/s or 63 mm/a based on the river basin area, average flow is around 6 m³/s or 189 mm/a based on the river basin area). The land use within the basin is dominated by agriculture (arable land 34%, grassland 17%) and forestry (45%). Urban areas cover 4% of the catchment. Spatial distribution of different land use types result in a short upper river section, which is almost unaffected by human impact, while the largest part of it is characterised by high agricultural, municipal and industrial exploitation. Further pressures are weirs and backwaters as well as flushing driven by the power industry. Due to the point source and diffuse pollution as well as the morphological deficits the whole river is in risk to miss the good ecological status according to the EU-WFD.

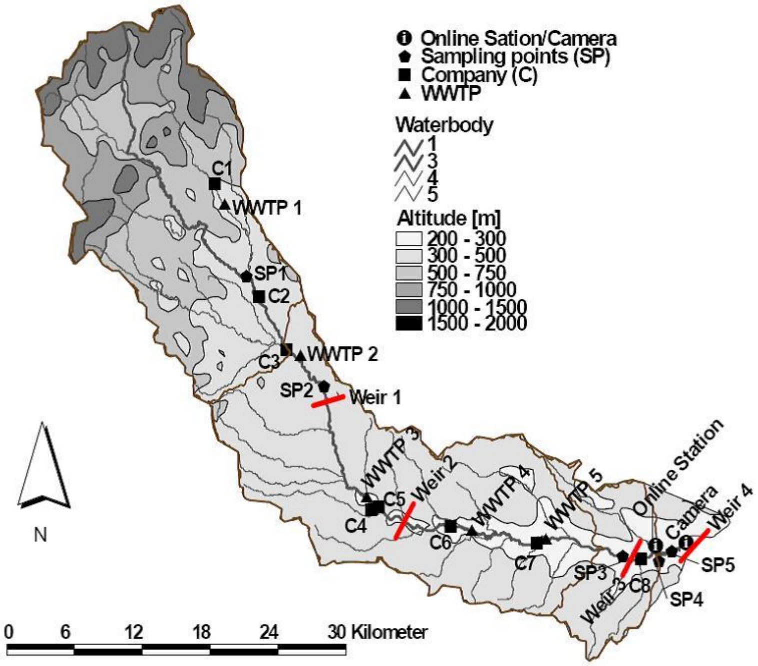


Figure 15: Austrian river basin of the investigated river, location of sampling points (SP), municipal wastewater treatment plants (WWTP), industrial companies (C), online station and online camera are displayed.

2 Material & Methods

2.1 Sampling sites

To locate the origin of foam, a river basin wide approach was chosen to gain information on the river’s chemistry, the quality and composition of the different point source discharges and the incoming diffuse loads. This resulted in the design of a one year monitoring programme, which included a close network of surface water sampling points (SP1-5), as well as, the sampling of five municipal and eight industrial wastewater treatment plants (WWTP) along the river stretch (Figure 15 and Table 5). Sampling site 1 served as the reference site with low anthropogenic impact to investigate the “natural” chemical and foaming conditions, whereas, sampling sites 2, 3 and 4 were chosen to assess the impact of various dischargers along the river. As foam forms after passing a weir, all sampling sites were located shortly after a weir. The characteristics of the weirs, e.g. height and broadness, affect the energy impact on the water, the amount of introduced air and thus the volume of created foam. Therefore it was important to choose sampling sites at similar weirs to observe foam formation. 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, 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, ten municipal wastewater treatment plants with a population equivalent between 1,000 and 10,000, as well as, sixty municipal wastewater treatment plants with a population equivalent below 1,000 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 program (see Table 5).

Table 5: Summary of sampled industrial companies and wastewater treatment plants in the Austrian part of the river basin.

Name	Type/Population Equivalent	Discharge limit [m³/d]	Abbreviation
industrial wastewater treatment plants			
Company 1	galvanising plant	22	C1
Company 2	tannery / PE_{120} 75.000	1500	C2
Company 3	fruit concentrate comp. / PE_{120} 160.000	1200	C3
Company 4	abattoir	103	C4
Company 5	poultry abattoir	210	C5
Company 6	tannery / PE_{120} 180.000	2500	C6
Company 7	conductor board comp.	398	C7
Company 8	tannery / PE_{120} 90.000	1400	C8
municipal wastewater treatment plants			
Wastewater treatmentplant 1	30.000	6000	WWTP 1
Wastewater treatmentplant 2	32.000	17280	WWTP 2
Wastewater treatmentplant 3	12.000	1650	WWTP 3
Wastewater treatmentplant 4	35.000	10000	WWTP 4
Wastewater treatmentplant 5	11.000	1760	WWTP 5
Sum Wastewater treatment-plants < 1.000 PE	15.000	5000	

Table 6 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 thirteen 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, C8).

Table 6: 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.

	SP1-5	**WWTP1***	**WWTP2***	**WWTP3**	**WWTP4***	**WWTP5***	**C1**	**C2***	**C3***	**C4**	**C5**	**C6***	**C7***	**C8***
18.11.2005	x	x	x	x	x	x	x	x	x	x	x	x	x	x
30.11.2005	x					x		x				x	x	x
14.12.2005	x	x	x	x	x	x	x	x	x	x	x	x	x	x
29.12.2005	x							▨				▨		▨
04.01.2006	x							x				x	x	x
10.01.2006	x	x	x	x	x	x	x	x	x	x	x	x	x	x
31.01.2006	x					x		x				x	x	x
21.02.2006	x	x	x	x	x	x	x	x	x	x	x	x	x	x
07.03.2006	x					x		x				x	x	x
05.04.2006	x					x		x				x	x	x
19.04.2006	x					x		x				x	x	x
10.05.2006	x					x		x				x	x	x
20.06.2006	x					x		x				x	x	x
26.07.2006	x					x		x				x	x	▨
09.08.2006	x	x	x	x	x	x	x	▨	x	x	x	▨	x	x
23.08.2006	x					x		x				x	x	x
19.09.2006	x					x		x				x	x	x
19.10.2006	x					x						x	x	x

2.2 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 7). 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 etc.). Foam index is presented as the instream 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.

Table 7: Overview on the seven-staged foam index (FI).

FI	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 areas of accumulated or frozen foam
6	heavy foam	ample compact foam lumps, large foam areas partly large areas of accumulated or frozen foam

Foam index was determined regularly at the four weirs along the river stretch (weirs are displayed in Figure 15) during the monitoring programme. The responsible agency of the Federal State Government, allocated pictures of weir 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 weir 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 minutes. Thus, the daily foam index is a “mean” value.

As no legal quantitative instream 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.

2.3 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 hours 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, Nonylphenolethoxylates - 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. 250 ml of effluent were shaken in Erlenmeyer flasks with baffles on a laboratory Shaker (Type Ceromat-U) for the duration of three minutes 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.

Formula 6: $$\mathrm{FP}_{\mathrm{effl.x}} = \mathrm{FF}_{\mathrm{effl.x}} \times \mathrm{Q}_{\mathrm{effl.x}}$$

With FP = Foam potential of effluent x [m³/s], FF = Foaming factor of effluent x, Q = Discharge of effluent x [m³/s]

That means, if for example, an effluent with a discharge of 0.02 m³/s and a foaming factor 50 was discharged into the river water (which is the diluting media), 1 m³/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.

2.4 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 instream concentrations. In this study, the assessment is provided by a model (see Results & 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:

Formula 7:
$$R^2 = \frac{F_0^2 - F^2}{F_0^2}$$

With F_0^2 = initial variance, F^2 = 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.

3 Results and Discussion

3.1 Emission monitoring

The relative fractions of the loads of different parameters from the dischargers are displayed in Figure 16. 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.

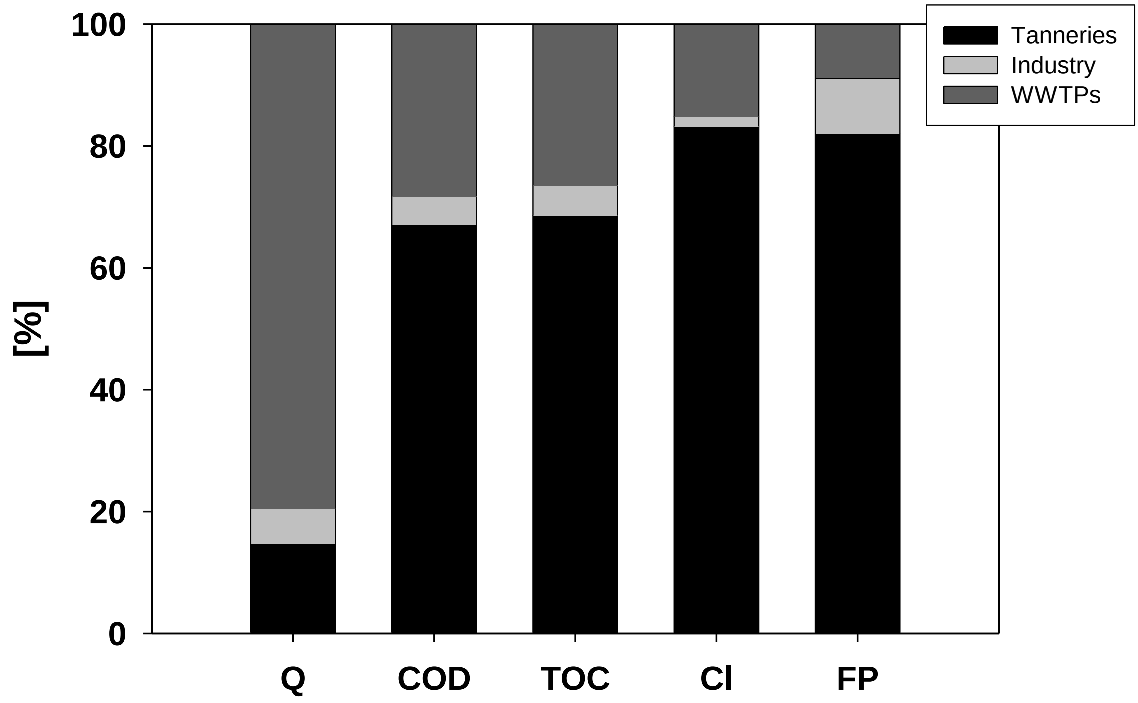


Figure 16: Relative fraction of different industrial branches on effluent’s discharge (Q), chemical oxygen demand (=COD), total organic carbon (=TOC), chloride (=Cl) and foam potential (=FP).

Although there was no reason to believe that the analysed tensides’ 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 Figure 17, 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 Figure 17 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.

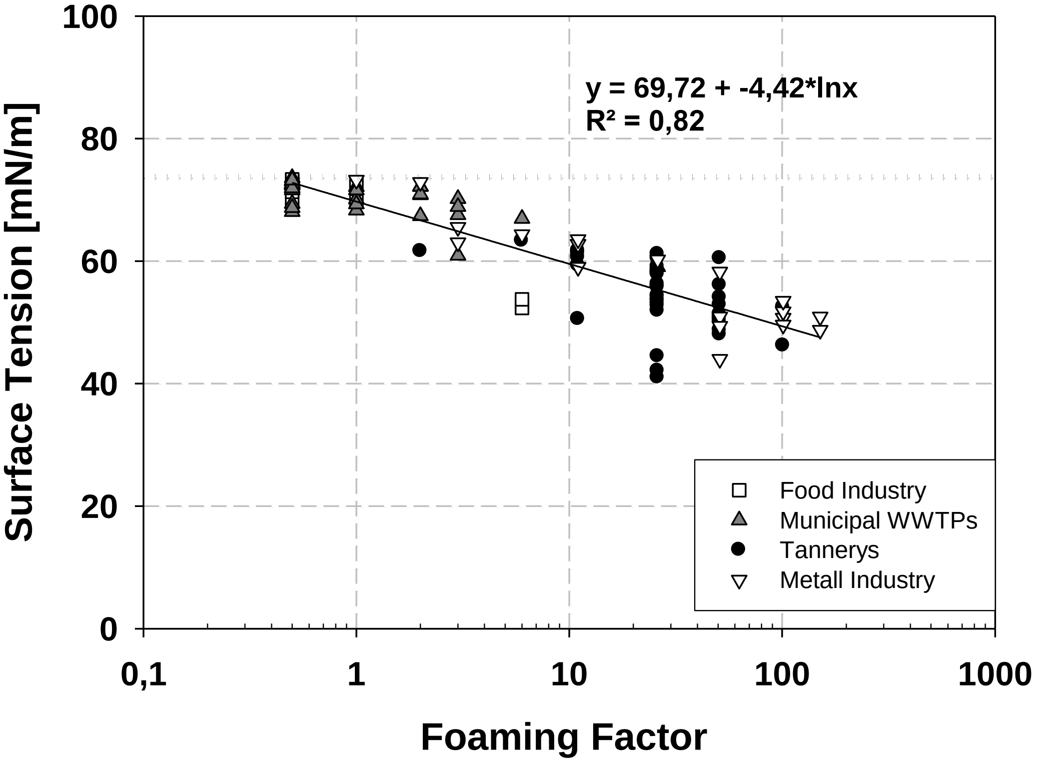


Figure 17: Regression model for surface tension and foaming factor of the sampled dischargers (dotted line indicates the surface tension of distilled water).

However, Figure 17 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.

3.2 In-stream monitoring

In-stream monitoring of foam formation shortly resulted in three statements, (i) continuous foam formation could be observed only in part of the river, but not on the whole river stretch, (ii) foam formation on the river, especially in the border region between Austria and Hungary, is a recurrent, but not a permanent phenomenon and (iii) foam occurs only short after weirs or similar constructions promoting turbulence and introducing air into the water.

Figure 18 displays the relative fractions of foam index classes at the four weirs (4a means pictures taken by hand, weir 4b means daily webcam pictures). The companies and municipal WWTPs, which discharge into the river are also displayed (x-axis indicates the flow direction).

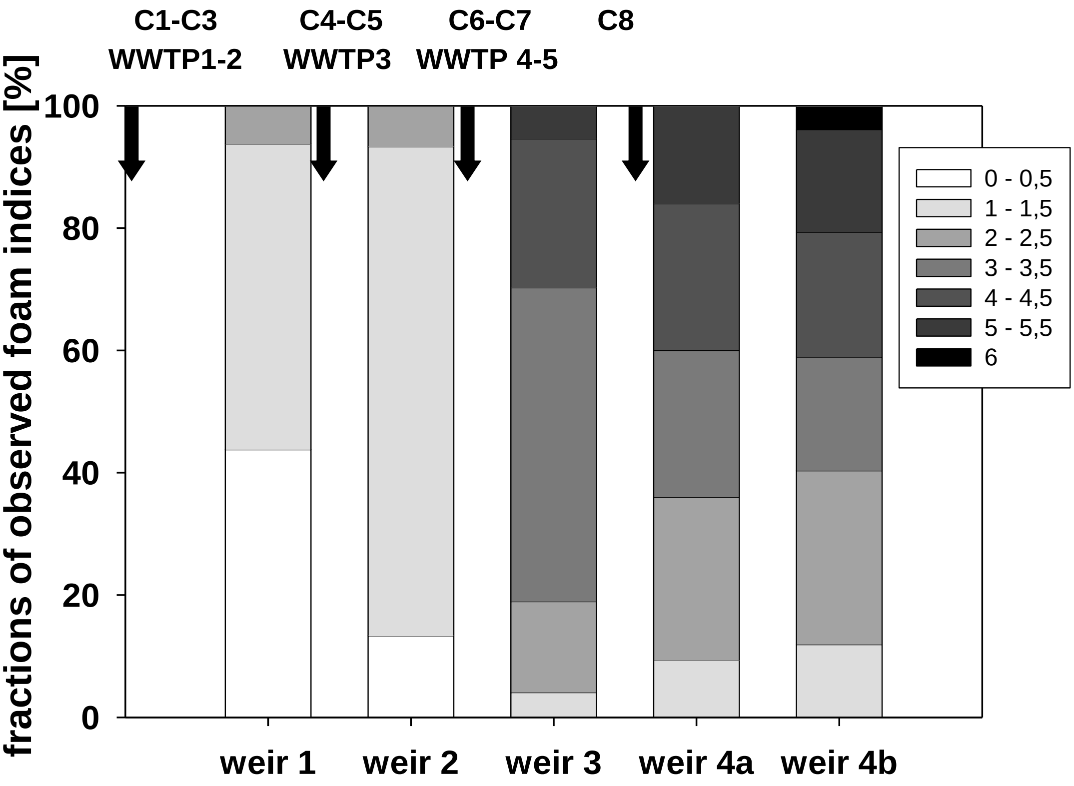


Figure 18: Relative fraction of foam index classes at the four weirs (weir4a means pictures taken by photograph, weir 4b means daily webcam pictures). Additionally municipal and industrial dischargers along the river stretch are displayed.

Obviously, the maximum foam index is not higher than 2 to 2.5 at weir 1 and 2. After the inflow of the companies C6, C7 and C8 and WWTP 4 and WWTP 5, the maximum foam index increases up to 5 – 5.5 at weirs 3 and 4a. Due to the high-resolution data of the webcam foam index 6 is displayed in weir 4b. Besides this, high foam index classes of above 3.5 occurred at weirs 3 and 4 for up to 40 % of the investigation period.

3.3 Cause-effect relationship of foam formation

Spatial distribution of foam formation as shown in Figure 18 as well as analyses of the foaming tests (Figure 16) allowed the identification of three tanneries (C3, C6 and C8) as the main foam causing emitters.

The sum of their calculated foam potential emissions was about 2 m^3/s and around 80 % of the total emitted foam potential into the investigated river basin (Figure 16). The sum of their emitted foam potential is comparable to the river's discharge at low flow conditions, which indicates that under laboratory conditions used for the determination of the foam potential, the river water volume at low flow conditions could be foamed by the emissions of the three tanneries. The actual foam potential of an effluent is higher than under laboratory conditions, because shaking the sample during the foaming tests could not introduce the same amount of energy as in the river itself. Evidence for that was that no foam occurred on the river samples during the foam tests. The calculated foam potential is therefore an underestimation of an effluents capability to produce foam on the river.

Beside foam potential emission, dilution by river discharge was identified as the second main influencing factor on foam formation. Figure 19 highlights the regression between river discharge and foam index at weir 4 ($R^2 = 0.58$, $F = 370$, $p < 0.0001$,). Foam index tends to increase with decreasing river discharge and vice versa. The trend is obvious, but nevertheless the spectrum of occurring foam indices fluctuates broadly with varying discharges. At high discharges (above 6 m^3/s) foam index ranges between 1 and 3, at low discharge (below 3 m^3/s) foam index spans between 1.5 and 6. This oscillation has several reasons. On the one hand foam index determination is quite difficult at high 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.

The variability of foam indices at low discharge conditions is caused by the varying foam potential emissions of the three tanneries. Figure 20 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.

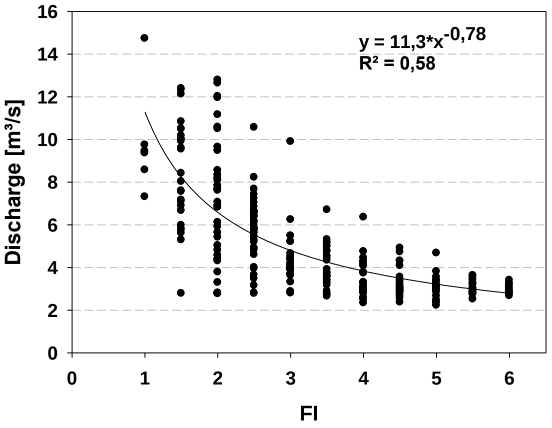


Figure 19: Regression model for river discharge and foam index (FI) at weir 4.

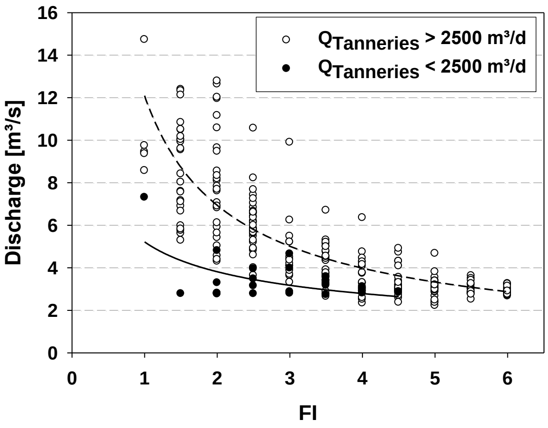


Figure 20: Regression model for river discharge and foam index (FI) depending on the discharge condition of the tanneries at weir 4.

3.4 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 Figure 19. 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 (Formula 8) depicts the deviation of the actual observed FI from the calculated FI (calculated by using the regression's equation in Figure 19).

Formula 8: $$\Delta\mathrm{FI} = \mathrm{FI}_{\mathrm{calc.}} - \mathrm{FI}_{\mathrm{obs.}}$$

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 Figure 21, displaying the regression between ΔFI and emitted foam potential ($R^2 = 0.30$, F = 57, $p < 0.0001$).

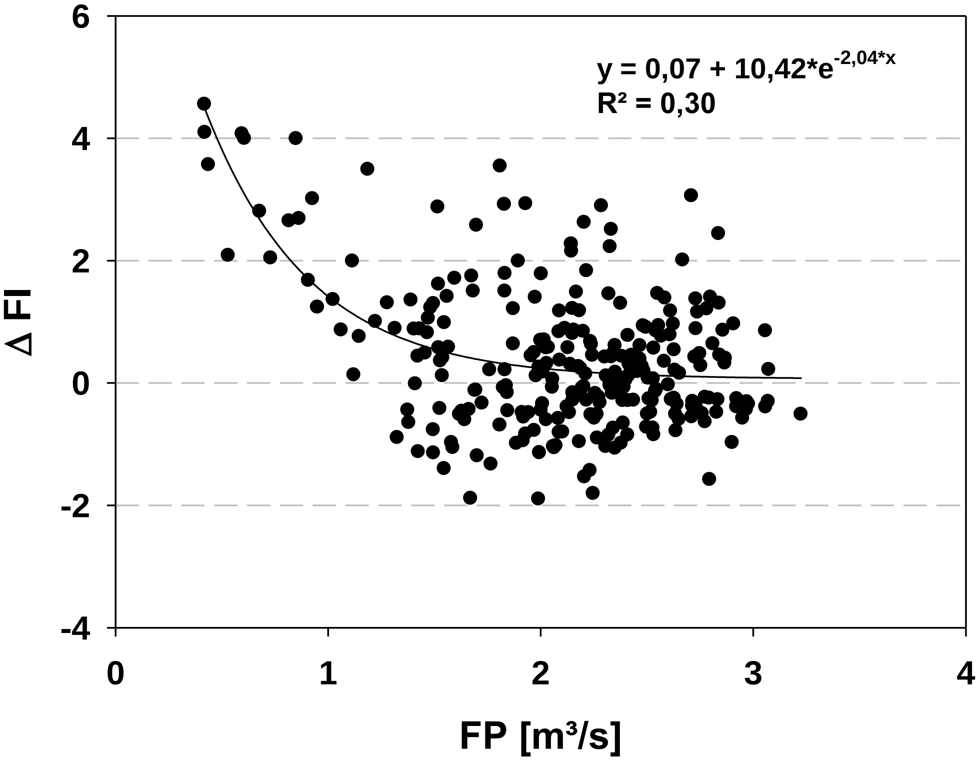


Figure 21: Regression model for ΔFI and foam potential (FP).

The regression indicates that emission of a foam potential below 2 m³/s leads to a positive ΔFI, which means less foaming compared to calculated foaming conditions. Above a foam potential of 2 m³/s, many other factors (e.g. dilution, diffuse pollution, anti-foaming agents) seem to influence the corresponding ∆FI. Thus, only a reduction of foam potential below 2 m³/s could show a quantitative effect on ∆FI and foam formation.

Combining the two regressions' equations in Figure 5 and Figure 7 resulted in the model approach for foam index calculation under varying river discharge and foam potential emission conditions (Formula 9 to Formula 11).

Formula 9: $$\mathrm{Q} = 11.3 \times \mathrm{FI}^{-0.78}$$

With Q = discharge, FI = foam index

Formula 10: $$\Delta\mathrm{FI} = 0.06 + 10.42 \times \mathrm{e}^{-2.04\times\mathrm{FP}}$$

With ∆FI = Delta FI, FP = foam potential

Formula 11: $$\mathrm{FI} = (\frac{11.3}{\mathrm{Q}})^{1.28} - (0.06 + 10.42 \times \mathrm{e}^{-2.04\times\mathrm{FP}})$$

With FI = foam index, Q = discharge, FP = foam potential

Figure 22 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.

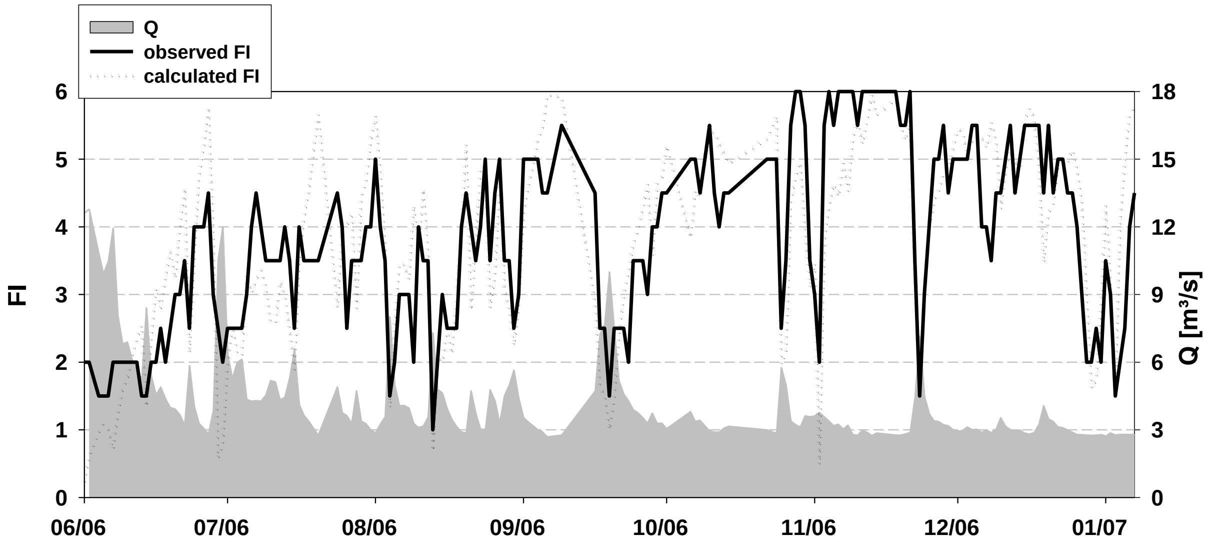


Figure 22: Observed and calculated FI at weir 4 as well as runoff discharge with daily resolution.

The achieved model approach allowed evaluating the effectiveness of measures to reduce the emission of foam potential in respect to foam formation on the river. It was used to calculate the frequency of undershooting for a certain FI considering the reduction of foam potential emission and the discharge of the river. Input data for river discharge was a long time series from 1991 to 2007, input data for foam potential was the mean foam potential observed during the monitoring, as well as, five different reduction stages of the mean value (minus 35 %, minus 50 %, minus 60 %, minus 70 % and minus 80 %). In Figure 23, the frequency of undershooting the calculated FI is displayed for the emission of the mean foam potential and the five reduction stages. It is obvious that an elimination of 70% of foam potential (dotted line) would assure a foam index lower 3.5 with 95% probability. Based on the current mean emission of foam potential the “not accepted degree” of foam formation is exceeded in around 60 % of the cases.

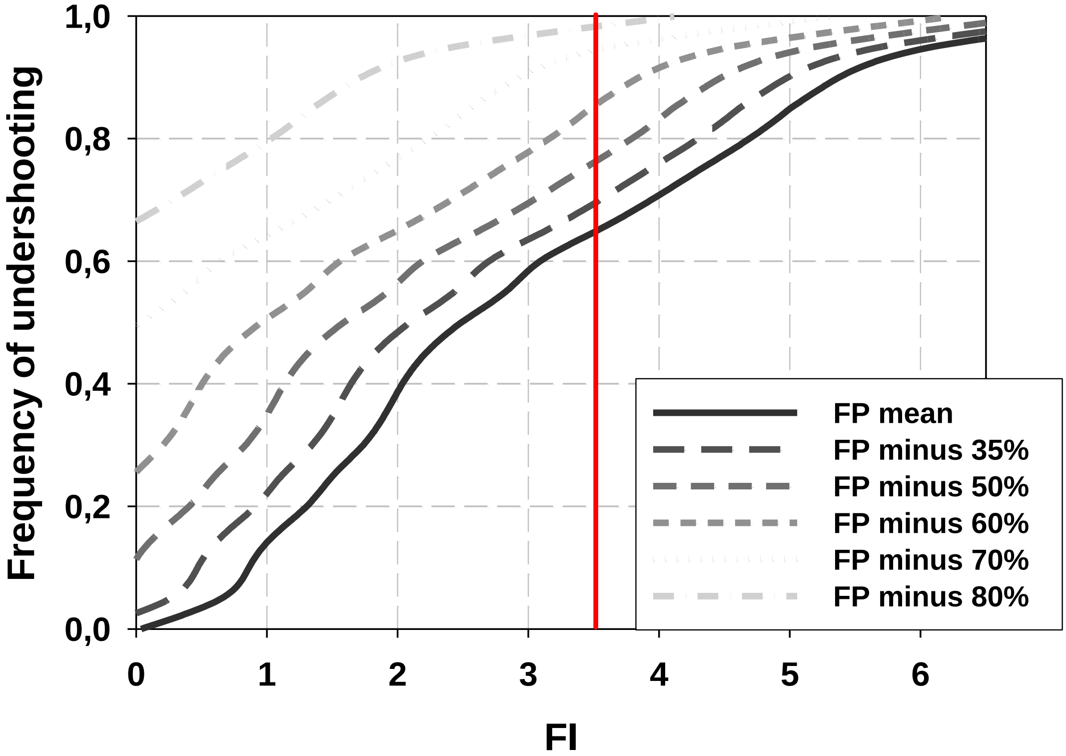


Figure 23: Frequency of undershooting a foam index depending on the different reduction stages of foam potential emission at weir 4 (the line indicates the limit for the “not accepted degree of foam formation”).

As the monitored tanneries operate their wastewater treatment plants with the best available technology (biological treatment with nitrification and denitrification, sludge retention time >20 days, temperature in the activated sludge tank > 20°C). Foam formation on the investigated river is not the result of none compliance with legal standards. Cleaning efficiency is however not sufficient to remove the surface active compounds resulting in emission of foam potential. However, analysis of tensides, as well as, qualitative screening could not identify potential foam causing substances. Thus, it was assumed that vegetable tanning agents could play a role in foam formation due to their high molecular structure and the associated poor biodegradability during the purification process. Further research is needed to gain more information on their behaviour.

As the adjustment of the production process to other chemicals is a long and complicated process in the leather industry, the implementation of end of pipe measures seemed the only fast and effective way to reduce foam formation anyway.

To evaluate proper management strategies, several end of pipe measures for the tanneries such as post treatment of tannery effluents at a municipal WWTP, precipitation and flocculation, adsorption and ozone treatment with additional biological post-treatment were tested, for which, ozonation turned out to be an appropriate way to reduce foam potential emissions. Discussion on the implementation of ozonation, as well as, other alternatives for post treatment is on-going.

Measurements concerning the morphology of the river such as the removal of weirs to avoid foam formation were also part of the discussion in the beginning of the investigations. The foam potential emissions of the tanneries could be clearly linked to foam formation on the river during this study and the implementation of tertiary treatment on the tanneries' waste water treatment plants could be an effective, as well as, a politically desired measure to reduce foaming.

4 Conclusions

Foam formation on rivers is a neglected research topic but it is becoming increasingly important due to public concern in recent days. Its occurrence generally doesn't need to originate from insufficient treatment of the classic wastewater compounds as it was in past decades, but as a consequence of the presence of numerous chemicals in effluents of industrial wastewater treatment plants as well as the intensive use of a river as receiving water for the effluents of several industries. For the investigated case no concrete statements could be made about the fate of potential foam forming chemicals during treatment, the efficiency of their removal and their behaviour in the aquatic environment.

About foam formation on rivers and foam causing substances, little literature is available and restriction of foam is difficult due to the lack of legal standards. Nevertheless, as a result of the work presented, it was possible to detect the origin of foam formation, to quantify the influence of different emitters on foam formation in the investigated river and to provide a set of tools (laboratory tests and modelling) to evaluate and compare the efficiency of measures for foam abatement.

As no clear parameter for in-stream foam formation or emission of foam exists to date, indices had to be developed during the study. The foam index is introduced as the instream parameter for foam formation. It allows a semi-quantitative differentiation between the varying foaming conditions. Description of the single foam indices is only valid for the studied river but the idea to classify different foaming conditions could be applied to other rivers. The foam potential is presented as the parameter to quantify foam emissions of a discharger. As the underlying foaming factor is clearly related to surface tension, the foam potential seems to be a valuable foam emission parameter, particularly, if the foam causing substances are unknown.

The resulting model approach provides the calculation of foam indices under varying foam potential emissions and discharge conditions. Although the model is developed for the specific local situation, via the adaption of foam index and the knowledge about the main influencing factors for foam formation, a similar model approach as the one presented in this paper could be designed for other rivers. Thus, it is a useful tool to evaluate the development and implementation of measures reducing foam. According to the model’s results a foam index <3.5 (which is the “not accepted” degree of foam formation) would be assured by the elimination of 70% of the foam potential with 95% probability. Investigations concerning foam-abatement measures identified ozonation as an appropriate way to reduce foam potential emissions.

Adapting the Austrian emission directive for tanning industries as consequence of foam formation on surface waters

1 Introduction

Since 2005, the formation of foam on a transboundary river short after the Austrian-Hungarian border has massively affected Austria's political relationship with Hungary. Occurrence of foam happens only short after weirs and both amount and frequency of foam performance vary from day to day. The Austrian part of the river catchment with a size of almost 1000 km² features intensive agriculture as well as several point source emissions from municipal and industrial wastewater treatment plants. The climate is characterised by moderate precipitation (784 mm/a), which results in seasonal low discharge conditions with a low flow of around 2 m³/s or 63 mm/a based on the river basin area in the year 2006 (Ruzicka et al., 2009a).

A subsequent one year monitoring programme resulted in the development of a model approach linking the foam mainly to the discharge conditions of the river as well as the emissions of three tanneries located within the Austrian river basin, although all of them are equipped with wastewater treatment technology according to the best available technology (Ruzicka et al., 2009a).

Within the EU, industrial emissions are regulated via the Integrated Pollution and Prevention Control Directive (IPPC). The Directive entered in force in September 1996 and was newly codified in 2008 to achieve integrated prevention and control of pollution in order to secure a high level of protection of the environment (96/61/EC, 1996; 2008/1/EC, 2008). It exclusively affects industrial installations and covers the following six main categories of industrial activities: energy, production and processing of metals, mineral industry, chemical industry, waste management, and other activities such as pulp and paper, tanning, and certain agricultural activities (O'Malley, 1999). The Directive includes emission limit values for polluting substances likely to be emitted from the installation concerned in significant quantities (2008/1/EC, 2008). Consequently, the requirements of the IPPC had to be implemented into the law of the member states. In Austria the emissions from the tanning industry are regulated in the Directive on wastewater emissions for tanneries, which was adopted in 1999. Apart from sum parameters such as COD, the directive does not limit the emission of parameters linked to foam formation, e.g. tensides (Bundesministerium für Land- und Forstwirtschaft, 1999).

Although the foam formation on the river could be linked to the tanneries' emissions, the identification of a single substance responsible for the foam was not possible. Most probably the foam was the result of various substances, such as vegetable tanning agents, saponins and other protein fractions that are not properly degraded during the wastewater treatment process (Schilling et al., submitted). Thus Ruzicka et al. (2009a) introduced a sum parameter called foam potential to quantify the foam emitted by the tanneries. The foam potential is calculated by multiplying the foaming factor with the discharge of an effluent. The foaming factor is determined in standardized foam tests and equals the dilution factor at which minimal foam occurs. The instream foam formation is defined by the seven-stage foam index, which was developed based on webcam pictures of the foam (Ruzicka et al., 2009a). The application of a model highlighted that an elimination of 70% of foam potential on catchment scale would assure an accepted degree of foam formation with 95% probability (Ruzicka et al., 2009b).

In compliance with the EU Water Framework Directive, the standard approach to eliminate instream water quality problems, such as foam, involves the determination of instream limit values and consequently the development of measures to meet these values. As no standardized parameter for instream foam formation existed and the political and medial pressure required a fast solution, the Austrian Federal Ministry for Environment adopted the well-established emission based approach. It includes the determination of emission limit values for foam causing substances, which must (i) be able to meet with technical means and (ii) improve the instream water quality.

As all tanneries treated their wastewater according to the thitherto best available technique (BAT, biological treatment with nitrification and denitrification, sludge retention time >20 days and temperature in the activated sludge tank >20°C), the implementation of possible abatement measures at the source of the foam formation required the adaptation of the Directive on wastewater emissions for tanneries. A new BAT had to be defined and presupposed the according changes in the Directive. Since neither foaming factor, nor foam potential are accredited parameters, surface tension is introduced to substitute the foam potential as sum parameter for foam formation. This paper deals with the introduction of surface tension as regulated parameter into the new Directive on wastewater emissions for tanneries as well as the development of adequate limit values, in order to regulate foam emissions. Furthermore the technical implementation (ozonation on laboratory scale and pilot plant installation with a combination of flotation, neutralisation, sedimentation and filtration) to reach the new thresholds is presented and the effect of the reduction in foam emissions is demonstrated.

2 Materials & Methods

2.1 Foaming factor and foam potential

As no emission criteria for foam exist, the parameters “foaming factor” and “foam potential” were introduced to characterize the amount of emitted foam. A standardised foam test was applied to detect the dilution of the sample, at which no more foam could be observed. The dilution factor, at which minimal foam occurred, was defined as “foaming factor”.

The obtained foaming factor of this effluent was multiplied with the effluents’ discharge to calculate the foam potential of the effluent. That means, if e.g. an effluent with a discharge of 0.02 m^3/s and a foaming factor 50 was discharged into the river water (which is the diluting media), 1 m^3/s (according to laboratory conditions) of the river water would show minimal foaming, if adequate turbulence was introduced. Foam potential of an effluent was defined as the volume of river water, which will potentially foam due to the discharge of the particular effluent (Ruzicka et al., 2009b).

2.2 Foam index

A webcam was installed at the Hungarian weir, where foam occurred. Based on the webcam pictures, the seven-stage foam index (FI) was developed to characterize the instream foam formation. The FI represents a 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 (Ruzicka et al., 2009a).

2.3 Foam model approach

Based on the monitoring programme, a simple statistical model (see Formula 12) was developed to describe the cause-effect relationship between the instream foam formation and the emitted foam. Major input data for the model are discharge and foam potential. Details on the model can be found in (Ruzicka et al., 2009a)

Formula 12: $$\mathrm{FI} = \left(\frac{11{,}3}{\mathrm{Q}}\right)^{1.28} - \left(0.06 + 10.42\mathrm{e}^{-2.04*\mathrm{FP}}\right),$$

With FI = Foam index, Q = discharge and FP = foam potential

2.4 Surface Tension

The surface tension is defined as the work needed to augment the surface area of a liquid (Bletterie et al., 2009). Surface tension of pure water is 72.74 mN/m at 20°C. In the presence of surface-active components, e.g. tensides, the surface tension starts to decrease.

Surface tension was measured with a KRÜSS Easy Dyne K20 tensiometer according to the DIN EN 14370 (2004). Surface tension readings were made by the means of the Wilhelmy plate method named after the German chemist Ludwig Wilhelmy (Haefele, 2006). This involves dipping a thin platinum plate into the liquid being measured. The liquid is raised until the contact between the surface or interface and the plate is registered and the force recorded on the balance is noted (Schilling et al., submitted).

2.5 Ozonation

All ozonation experiments were run with aerobically treated effluent of the three tanneries. Ozonation was carried out in a transparent PVC column (height 124 cm, diameter 10 cm) with a water volume of 4-7 litre. Ozone was produced by a Fischer OZ 500 generator. Oxygen was supplied by an Oxygen generator (Lenntech, ATF-8). The ozone generation was fixed to 3 g/h, while ozonation time was varied to provide ozone dosages up to 200 mg/l. Depending on the treated wastewater this corresponds to a specific ozone consumption of 0.25-0.70 g O_3/g COD_{in}. A similar specific ozone consumption (0.33 g O_3/g COD_{in}) was applied in (Kaindl and Liechti, 2008), as well as in (Jochimsen and Jekel, 1997). Ozone concentrations were determined in the feed-gas and in the off-gas by titration with the potassium-iodidemethod (DIN, 1993). Subsequent biodegradation was carried out via four Sequencing Batch Reactors (SBR; A, B, C, D) in parallel (Bletterie et al., 2009).

2.6 Pilot plant installation

The pilot plant is a combination of dissolved air flotation, neutralisation, sedimentation and filtration. It has a capacity of 4-6 m^3/h, which amounts to about 5% of the totally discharged wastewater.

In a first step, aluminiumsulfate and a polymer is added to the effluent of the secondary clarifier to activate flocculation and precipitation. During the dissolved air flotation, the generated air bubbles attach to the flocks as well as the precipitate and transport them to the surface causing foam. The flotation tailings are removed from the surface and the resulting clear water phase is lifted to a pH of 7-8 by adding lime milk.

The resulting precipitate settles in a sedimentation tank, while the supernatant is subject to a zeolite-filtration and finally passes an activated carbon filtration.

3 Results & Discussion

The Directive on wastewater emissions for tanneries had to be amended by a parameter representing the foam causing substances, in order to limit the foam emitted by the tanning factories. Although Ruzicka et al. (2009a) demonstrated that the foaming factor was a useful tool to quantify the foam emitted by an effluent, it is not an accredited parameter. As no other parameter, such as COD or TOC showed any correlations with the foaming factor, another well-known and accepted parameter had to be found to regulate the emitted foam. In this regard, the surface tension indicating the presence of surface-active substances seemed to be a sufficient alternative. Figure 24 plots the error bars (mean ± standard deviation) of surface tension for varying foaming factors of several effluents ($n = 88$) and highlights a good correlation between the two parameters with an R^2 of 0.99 ($p < 0.0001$). In case of low foaming factors about 5, the surface tension amounts to 71 mN/m, that is close to the surface tension of pure water. In contrast, foaming factors of 100 are correlated with surface tension of 51 mN/m.

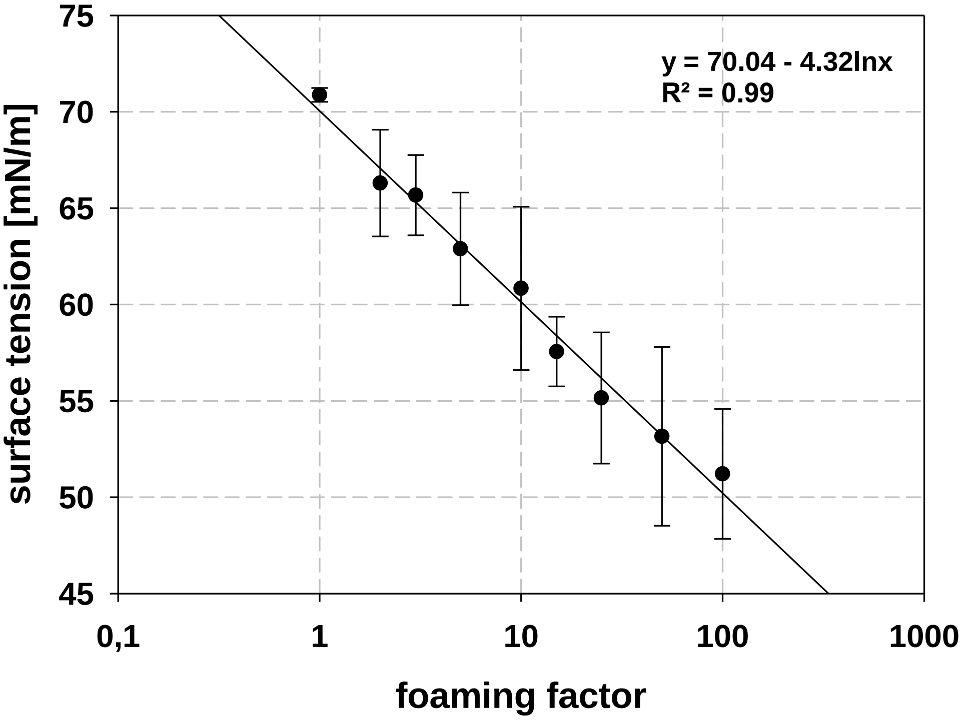


Figure 24: Correlation between surface tension and foaming factor of several effluents.

As soon as surface tension was chosen as parameter to regulate foam emissions, adequate emission standards had to be defined. Thus the possible reduction of the surface tension by technical means had to be investigated. In 2009, Bletterie et al. have already demonstrated that the surface tension of an effluent can be considerably decreased by ozonation as a post treatment step.

Figure 25 highlights the results of laboratory scale experiments to analyse the correlation between surface tension and ozone consumption. Instead of plotting a linear regression line, the lower spectrum of each correlation is indicated by a continuous line, to also include very low levels of surface tension for the determination of the limit values. The lowest surface tension values without ozonation shows tannery 1 with 50 mN/m, whereas it amounts to 55 mN/m in tannery 2 and 63 mN/m in tannery 3, respectively.

A surface tension of 60 mN/m can be achieved at tannery 1 and 2 with an ozone consumption of 130 mg/l and 100 mg/l respectively, whereas a consumption of 100 mg/l is sufficient to accomplish a surface tension of 65 mN/m in tannery 3. In contrast, in tannery 1 and 2 an ozone consumption of 190 mg/l and 175 mg/l is necessary to reach 65 mN/m. The differences in the initial values for surface tension as well as the ozone consumption to reach a certain surface tension value originate from the varying composition of the tannery wastewater due to differing tanning agents used in the production processes (Schilling et al., submitted).

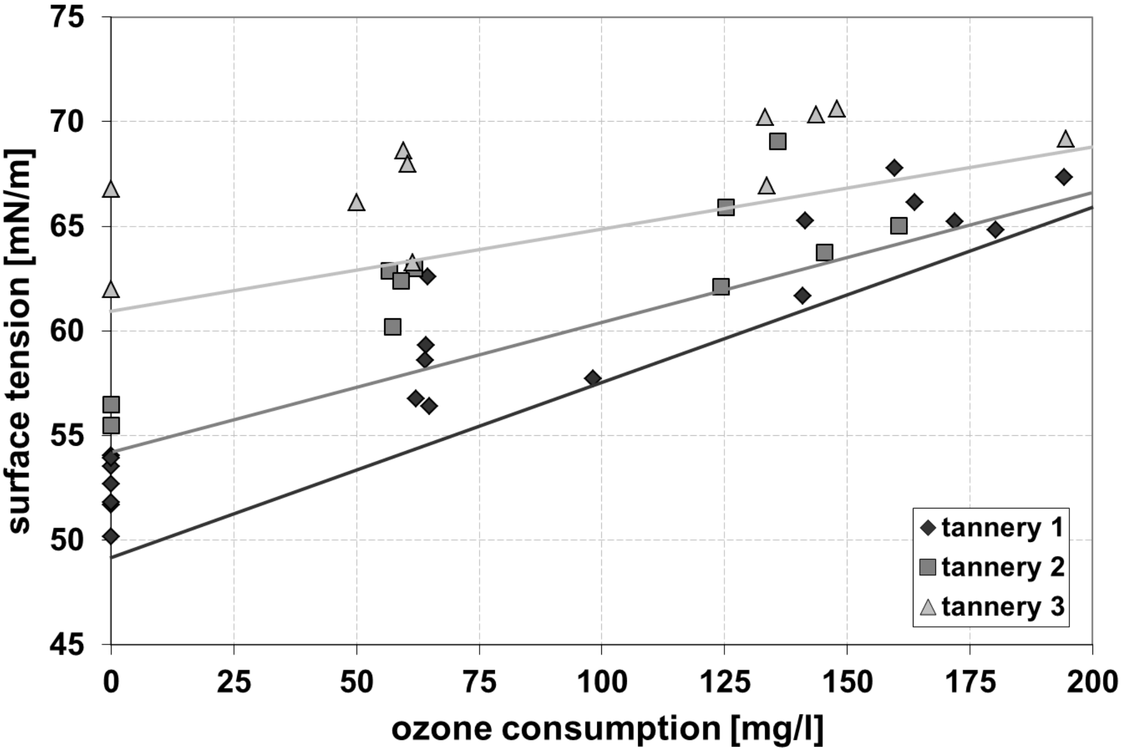


Figure 25: correlation between surface tension and ozone consumption for tannery 1, 2 and 3. The lines indicate the lower spectrum of the correlation; slightly modified from Bletterie et al. (2009).

The conducted lab scale experiments proved that an increase in surface tension up to 65mN/m in all tanneries was possible by technical means. In a further step, the effect of this increased surface tension and consequently reduced foam potential of the effluents discharged by the tanneries on the instream foam formation had to be assessed, in order to determine proper limit values. For this purpose a foam model approach linking instream foam formation with discharge and emitted foam was applied (see 2.3). As no legally binding criteria existed for instream foam formation in Austria so far, a foam index of 3.5 was suggested as threshold for the “not accepted degree of foam formation” (Ruzicka et al., 2009a).

The instream foam formation and consequently the foam index are highly dependent on the river discharge due to dilution effects. In Figure 26 the frequency of undershooting a foam index observed in 2006 is plotted for high and medium (> 4.6 m³/s) as well as medium and low (< 4.6 m³/s) discharge conditions. In case of discharges above 4.6 m³/s, 90% of the observed FI do not exceed the not accepted degree of foam formation at a FI of 3.5 due to dilution effects. In contrast, 80% of FI data overshoot the threshold during discharges below 4.6 m³/s.

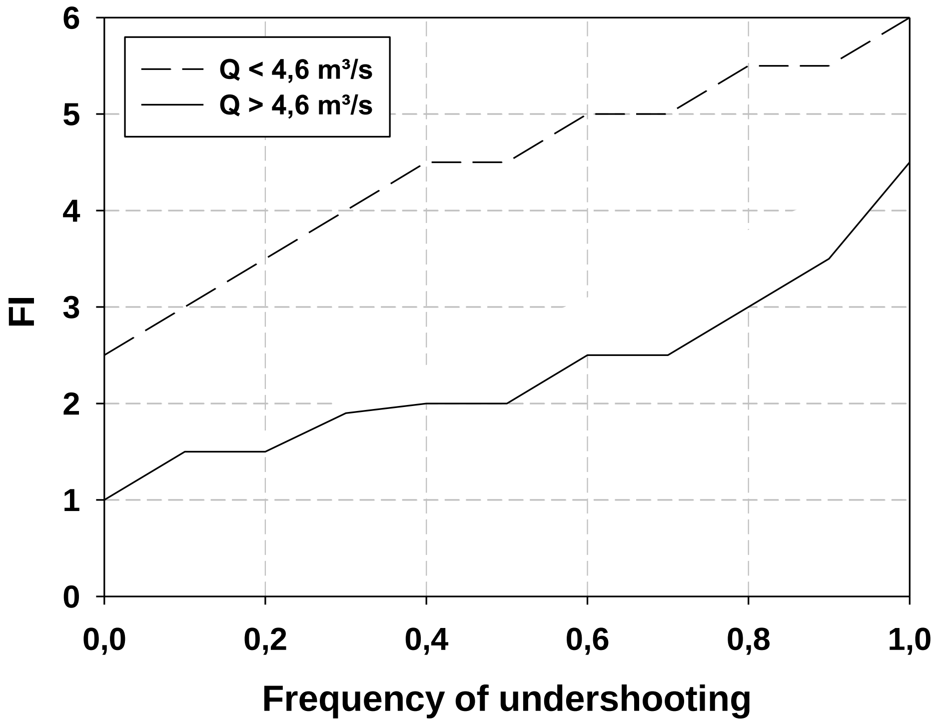


Figure 26: Frequency of undershooting the FI in the year 2006 plotted according to the discharge of the river. The red line indicates the threshold for the not accepted degree of foam formation at FI 3.5.

By applying a foam model approach (see 2.3), the effect of an emission limit value of 65mN/m at all tanneries could be evaluated. For this purpose, the foaming factor correlating with a surface tension of 65mN/m was derived from Figure 24. The resulting foaming factor of 3 was used to calculate the foam potential of the tanneries' effluents by multiplying it with the designed discharge of the tanneries. The calculated foam potential was applied to the foam model approach, by which means the foam index was computed for a discharge series of 25 years. Finally, the frequency of undershooting the calculated FI was determined for high and low discharges.

Figure 27 demonstrates that in case of high discharges (Q > 4.6 m³/s), the calculated foam index is constantly zero. During low discharge conditions, the computed FI undershoots the not accepted degree of foam formation with a frequency of 95%.

As the compliance with an emission limit value of 65mN/m requires rather high ozone dosages especially in tannery 1 and 2 (more than 175mg/l O_3, see Figure 25), the foam model approach was again applied to calculate the FI in case of a lower limit value of 60mN/m correlating with a foaming factor of 10.

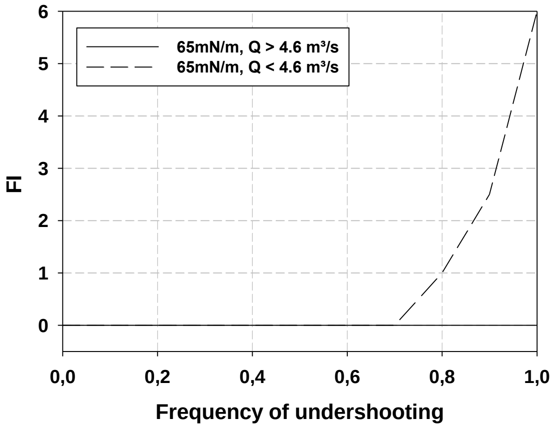


Figure 27: Frequency of undershooting the calculated FI applying a limit value of 65mN/m. The red line indicates the threshold for the not accepted degree of foam formation at FI 3.5.

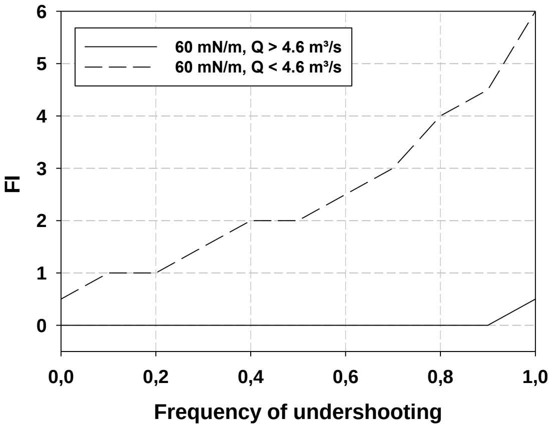


Figure 28: Frequency of undershooting the FI applying a limit value of 60mN/m. The red line indicates the threshold for the not accepted degree of foam formation at FI 3.5.

Figure 28 highlights that the estimated FI is lower than 0.5 at high discharges with a frequency of 90%, whereas the not accepted degree of foam formation is exceeded by 25% in case of low flow conditions.

In consequence, two limit values for surface tension were defined depending on the discharge of the river to ensure a significant reduction of instream foam formation in a cost-efficient manner. Emission standards for tannery effluents during average and high flow conditions are set to 60 mN/m. The definition of those conditions implies a dilution of the designed discharge of all tanneries with river water of ≥75, which occurs at a river discharge of 4.6 m³/s. Below a river discharge of 4.6 m³/s corresponding with a dilution of the tanneries' designed discharge <75, the threshold of 65 mN/m was determined.

According to the foam model approach, an emission standard of 60mN/m ensures a low foam index with high probability at medium and high discharges. In case of low flow conditions, the limit value of 65 mN/m must be applied, which provides a foam index below the "not accepted degree of foam formation" in approximately 95% of the days. As the probability is based on a model developed for the year 2006, a variation in probability according to changing conditions in following years seems possible. Nevertheless, a major reduction in instream foam formation is expected as consequence of the new technically feasible emission standards.

Although the laboratory scale experiments proved that ozonation was an appropriate method to reduce the foaming factor and consequently the surface tension, the tanneries preferred a different style of quaternary treatment. The pilot plant installed at tannery 1 is a combination of dissolved air flotation, neutralisation, sedimentation and filtration (Knoppek, 2010).

Figure 29 demonstrates the change in surface tension of the wastewater at the different stages of the pilot plant installation. The inflow (IF) into the pilot plant (which is the outflow of the existing wastewater treatment plant) shows an average surface tension of 51 mN/m, which increases to 58 mN/m in the outflow of the flotation step (OF flotation). Due to the flotation step a considerable amount of surface-active substances seems to be removed from the wastewater, which is also represented in the low surface tension value of the flotation tailings with 47 mN/m.

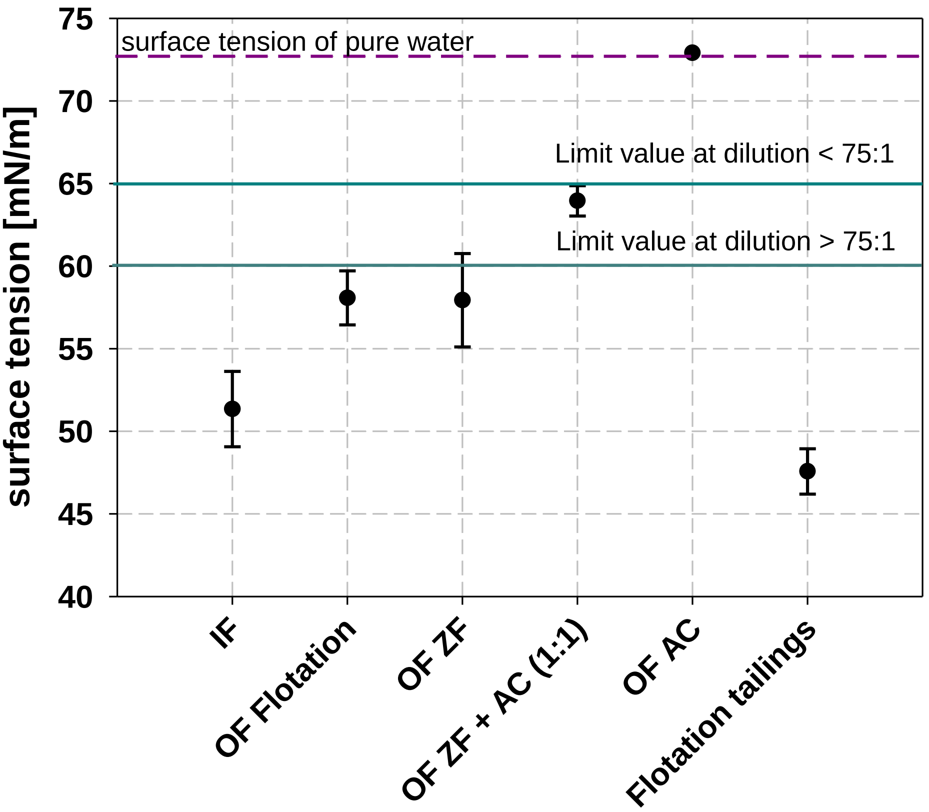


Figure 29: Error bars of surface tension in the different stages of the pilot plant. IF = inflow, OF = outflow, ZF = zeolite filtration, AC = activated carbon; straight lines show the limit values of surface tension at different dilutions; intermittent line indicates surface tension of pure water at 20°C

Zeolite filtration does not have an effect on the surface tension, as the outflow (OF ZF) equals the outflow of the filtration in terms of surface tension. By directing 50% of the wastewater over active carbon after the zeolite filtration step, the surface tension in the wastewater amounts to 64 mN/m (OF ZF + AC 1:1), which is above the limit value at a dilution higher than 75:1. The treatment of 100% of the wastewater with activated carbon after the zeolite filtration results in surface tension values of 72 mN/m, which is close to that of pure water. That means the tanneries are able to achieve limit values for surface tension by applying a combination of flotation and active carbon filter, but they have to direct a considerable amount of wastewater over the activated carbon filtration to keep the second limit value of 65 mN/m at a dilution lower than 75:1.

4 Conclusions

The formation of foam on a transboundary river in Austria short after the Austrian-Hungarian border resulted in a massive transnational conflict between the two states. A one-year monitoring programme linked the instream foam mainly to the effluent of three tanning factories in the catchment of the river. In compliance with the EU Water Framework Directive, the situation would have required the determination of instream limit values for foam formation. In a further step, measures to keep the instream standards would have been implemented. This approach was no applicable due to several reasons, one of them being the enormous political pressure to find a fast solution for the problem. Furthermore no standardized instream parameter for foam existed. Surface tension was no feasible alternative, as it did not change significantly along the river stretch.

Thus, an emission based approach was chosen to solve the foam formation problem. As all tanneries treated their wastewater according to the thitherto best available technique (BAT), the implementation of possible abatement measures at the source of the foam formation required the adaptation of the Directive on wastewater emissions for tanneries. The Directive had to be amended by a parameter representing the foam causing substances, appropriate emission standards and a new BAT to reach those standards. Consequently, surface tension was introduced as sum parameter for surface-active substances. As instream foam formation is highly influenced by the river discharge, two limit values depending on the dilution of the designed discharge of all tanneries with river water were defined to provide the cost-efficiency of the foam-abatement measures. In case of a dilution ≥ 75 occurring at river discharge above 4.6 m^3/s, the emission standard for surface tension is set to 60 mN/m. Below a dilution of 75, the limit value is determined with 65 mN/m to achieve an accepted degree of foam formation in the river. Lab-scale experiments proved that the newly defined emission standards for surface tension can be accomplished by ozonation of the treated wastewater. The tanneries preferred a different style of quaternary treatment designed as a combination of dissolved air flotation, neutralisation, sedimentation and filtration. The results of a pilot plant installation at one of the tanneries demonstrated that the limit values can be achieved by this type of treatment. In 2010, one tannery has already implemented the quaternary treatment resulting in a decreased instream foam formation (Schilling et al., submitted)

Conclusions

1 Recapitulation

For years, rivers served as receiving waters for municipal and industrial wastewaters as well as for diffuse runoff from agricultural land, which makes them highly vulnerable to pollution. The resulting continuous degradation of the aquatic ecosystem became a great issue for the scientific community in the last decades. Moreover, the importance of protecting the sensitive freshwater resources was acknowledged by politicians as well. Thus legislation (e.g. European Water Framework Directive – EU-WFD and US Clean Water Act) has been adopted to stop further deterioration and restore the aquatic ecosystem to a healthy state. Surprisingly, the water quality parameter “foam” has been neglected in the new legislations, even if several substances causing foam formation (e.g. tensides) are regulated in the EU-WFD. But neither emission nor instream criteria for foam, let alone limit values, exist in the European Union or the United States to date (Ruzicka et al., 2009b). This is even more remarkable, as foams are ubiquitous in the environment, commonly seen as discoloured patches on streams, rivers, lakes and sea water. They often are assumed to be anthropogenic in origin as they are aesthetically unpleasant, yet they frequently appear in pristine environments indicating a natural origin. In contrast to “hidden” chemical pollution, e.g. heavy metals, pesticides etc. the visibility of foam alarms the public (Schilling and Zessner, 2011). In consequence, the formation of foam becomes, yet again, a relevant topic for freshwater ecosystems. Its “revival” may be a result of the more sensitive attitude of people towards their environment. Thus, identification of foam causing substances, their origin and elimination as well as the handling of the legal aspects and the public concern are new challenges to be met, in order to solve foam formation problems (Ruzicka et al., 2009b).

The presence of foam on a transboundary river shortly after the Austrian-Hungarian border ignited a discussion on the sources of the foam as well as possible abatement measures. The foam formation was not only heavily disputed in the media and the public, but strained the Austrian-Hungarian political relationship.

Consequently, several questions had to be addressed to find potential measures to reduce the foam formation. This study tried to:

- provide information on foam information in the aquatic environment
- design parameters to quantify foam emission as well as instream foam
- determine the origin of the foam as well as parameters influencing the foam formation
- develop a model approach to forecast the foam formation depending on the influencing variables
- formulate measures to reduce the foam formation to an acceptable level
- define an acceptable level of instream foam formation
- adapt the legislation to allow implementation of measures and to keep the acceptable level of foam formation

2 Main findings

The main findings are structured according to the chapters of the thesis:

Foam in the aquatic environment (Schilling and Zessner, 2011):

- Foam formation is observed in nearly every aquatic environment, such as rivers, lakes and oceans. Although the majority of studies show that foam is the product of natural processes and factors, the public tends to associate foam formation with manmade pollution. Public concern is likely to be enhanced due to the visibility of foam, which lead to it being more obvious than “hidden” chemical pollution.
- Apart from the aesthetic aspects of foam, foam formation involves several other ecological aspects. Due to its enrichment capacity, carbon, nutrients, metals, hydrocarbons and even pesticides accumulate in foam.
- Foam is also believed to be an important food resource and a site of nutrient recycling which transfers energy to the consumer level. Some literature deals with the importance of foam as a habitat, especially for benthic and periphytic organisms.

Measurement of instream foam formation and quantification of foam in effluents (submitted to Water Research):

- Currently no parameters for emitted foam or other qualitative criteria for immission based foam formation exist. In this regard, the innovative aspect of the thesis was to develop completely new variables to determine the foam potential of emissions as well as the foam formation within a river.

- The foaming factor and consequently the foam potential are introduced as parameters to quantify foam from effluents. The foaming factor and the surface tension of an effluent show good correlation indicating that the foaming factor is an appropriate sum parameter for surface-active substances.
- The foam index represents a 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 varying foaming conditions on spatial as well as temporal scale. Although the introduced foam index is only valid for the investigated river, it can be effortlessly adapted to other surface waters.

Cause and effect relationship between foam formation and treated wastewater effluents in a transboundary river (Ruzicka et al., 2009a):

- The river monitoring highlighted that foam did not occur directly after the discharge of a wastewater treatment plant emitting foaming effluent, but occurred after certain river weirs.
- Further investigations showed several preconditions for foam formation: (1) the summation of several wastewater treatment plants with foaming effluent; (2) adequate allocation of energy is needed to cause foam on the river surface; (3) the river discharge plays a major role, as dilution of emitted foam causing substances resulted in less or no foam formation due to point sources, but increased foam occurrence by diffuse pollution.
- The investigations highlighted a strong correlation between foam formation on the river and the discharge conditions of three tanneries emitting effluents with a high foam potential.
- No single substances were found to be responsible for the foam in the effluents of the tanneries. Most probably the foam is a result of the mixture of several high-molecular surface-active substances with low biodegradability that are not degraded during the wastewater treatment.
- The resulting model approach provides the calculation of foam indices under varying foam potential emissions and river discharge conditions. Although the model is developed for the specific local situation, via the adaption of foam the index and knowledge about the main influencing factors for foam formation, a

similar model approach as the one presented in this paper could be designed for other rivers. Thus, it is a useful tool to evaluate the development and implementation of measures reducing foam.

- As no legal framework exists for instream foam formation, a limit value for a maximum foam occurrence had to be defined. A foam index <3.5 was empirically derived as the “not accepted degree of foam formation”, which was approximately the foam index corresponding with protests from Hungarian locals about foam formation.
- According to the model’s results, a foam index <3.5 (which is the “not accepted” degree of foam formation) would be assured by the elimination of 70% of the foam potential with 95% probability. Investigations concerning foam-abatement measures identified ozonation as an appropriate way to reduce foam potential emissions.

Adapting the Austrian emission directive for tanning industries as consequence of foam formation on surface waters (submitted to Water, Science and Policy):

- The implementation of measures at the tanneries to reduce the emission of foaming effluent required the adaptation of the Austrian emission directive for tanning industries, as all tanneries treated their wastewater according to the hitherto best available technique (BAT). The Directive had to be amended by a parameter representing the foam causing substances, appropriate emission standards and a new BAT to reach those standards.
- Surface tension was introduced as a sum parameter for surface-active substances.
- As instream foam formation is highly influenced by the river discharge, two limit values depending on the dilution of the designed discharge of all tanneries with river water were defined to provide the cost-efficiency of the foam-abatement measures. In case of a dilution ≥ 75 occurring at river discharge above 4.6 m^3/s, the emission standard for surface tension is set to 60 mN/m. Below a dilution of 75, the limit value is determined with 65 mN/m to achieve an accepted degree of foam formation in the river.
- Lab-scale experiments proved that the newly defined emission standards for surface tension can be accomplished by ozonation of the treated wastewater. The tanneries preferred a different style of quaternary treatment designed as a

combination of dissolved air flotation, neutralisation, sedimentation and filtration.

- The results of a pilot plant installation at one of the tanneries demonstrated that the limit values can be achieved by this type of treatment.

3 Outlook

Due to the strong regulation in Europe (EU WFD) the chemical and ecological status of the surface waters will increase over the next years. It is likely that the more the water quality improves due to the removal of “hidden” chemical pollution, the more visible peculiarities such as formation of foam will be recognized by researchers as well as by the public.

In consequence, a standardized parameter for the quantification of instream foam will be necessary. Although the foam index proved to be a useful tool to differentiate between varying foaming conditions, the quantification of foam is not possible by its application. Currently, a method to determine the instream foaming factor is under development, which will allow the calculation of the foam potential of the river. By the means of the foaming factor, the foam potential of a river can be assessed at sampling sites where no foam occurs, e.g. because of the lack of energy input.

The foam index is only applicable at sites, where foam is visible, e.g. after dams and weirs. At present, an image-interpretation software is under way to provide an objective assessment of the FI. The resulting automated evaluation of the foam index allows several areas of applications such as surveillance. In the case of the investigated river it will be implemented into an online monitoring tool displaying not only the physical and chemical parameters and the discharge, but also the foam index situation of the river.

Furthermore, the implementation of legal standards is necessary to prevent excessive foam formation on surface waters. In Austria, the term “not accepted degree of foam formation” has been defined at foam index > 3.5. This threshold was introduced to implement foam abatement measures, but is not legally binding. In the future, a limit value for instream foam formation could be implemented into the EU Water Framework Directive.

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