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REGIONAL PROGRAMME OF POLLUTION CONTROL
IN THE TANNING INDUSTRY IN SOUTH-EAST ASIA
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POLLUTANTS IN TANNERY EFFLUENTS

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DEFINITIONS AND ENVIRONMENTAL IMPACT

*

*LIMITS FOR DISCHARGE
INTO WATER BODIES AND SEWERS*

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This document has not been edited.

The views expressed are those of the authors and not necessarily shared by UNIDO.

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FOREWORD

In 1994, UNIDO prepared, as a response to frequent inquiries from tanners and environmental protection agencies in developing countries, a working paper with an overview of pollutant discharge standards in some thirty countries.

Due to great interest the paper was widely distributed and it was also partially published in the November 1994 issue of the magazine World Leather.

Comparative presentation of different standards in one table is not at all easy as different countries often have different methods of defining discharge limits. Some legislative authorities define the quality of (treated) effluents, some the quality of the recipient water after receiving and mixing with the effluent, some specify the permitted quantity of impurities to be discharged into the recipient per day, whereas in some cases limits are linked to the total amount of waste water discharged. Quite often the legislators are more lenient towards the existing and/or traditional small-scale tanneries, and, in some countries only a few parameters are subject to control while in others there are many, in some cases more than two hundred of them.

Standards within the same country can vary from one region to another. Typically, the central authority stipulates the minimum and local authorities can insist on even higher levels of purification. Furthermore, in many countries there are no specific limits for tannery effluents; they are part of overall legislation pertaining to discharge of industrial waste. Finally, in compiling this information, it was not always possible to obtain the official version of the limits directly from the issuing authority which certainly increases the risk of error and of missing the latest revisions.

Aware of these constraints as well as of inadequate reliability of data compiled from various sources, the foreword of the first issue invited readers to send UNIDO their comments and more accurate information. All corrections received together with data for seven additional countries are included in this new edition.

The need for cautious interpretation of the figures in the tables cannot be overemphasized; direct comparisons are seldom possible.

A new section has been added providing a tanner not too familiar with environmental standards with some very basic information about the main polluting components, the key parameters and their negative impact on environment and principles of laboratory analysis. We trust that the readers will find it useful.

We consider that this is a kind of never-ending job and we would again welcome comments, suggestions and, certainly, corrections of figures presented in this paper enabling us to introduce them into the next edition.

Jakov Buljan
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Chapter I

POLLUTANTS IN TANNERY EFFLUENT

*

DEFINITIONS AND IMPACT

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Introduction

The environment is under increasing pressures from solid and liquid wastes as by-products from manufacture and tannery effluent create significant pollution unless there has been a form of treatment before discharge.

Sometimes discharges are to sewerage systems where there may be comprehensive treatment before return to the environment via surface waters. In these cases, standards set by the authorities treating the effluent are dependent on the dilution with other effluents and domestic sewage, the capabilities of the treatment plant, and problems that might be experienced in the management or maintenance of the plant and equipment. The limits to discharge for the tanner are thus lower than when discharge is to surface waters. However, factors such as the disposal of final sludge, and discharge limits for the treated effluent that might be imposed on the sewage treatment authority also have to be taken into account.

Where effluent discharge is directly into streams and rivers, the effluent needs to be of higher quality as the environment is sensitive and readily damaged. The greater the volume of the effluent compared to the volume of surface water, then the higher the quality of the effluent demanded by the environment.

Discharge limits are set with the objective of protecting the environment, and there are two basic ways that determine the levels of the different effluent components.

1. Based on data which has been applied and found generally acceptable in a wide range of global situations. This method does not tend to take into account individual situations.
2. Situations when a mass-balance is applied. In this method the quality of the water upstream is determined, and the quality requirements of the water downstream i.e., for industry or potable use. The difference between the two figures is determined, and this sets the tolerance levels at the point of discharge.

The second technique takes into account individual site factors. Clearly, a small tannery with a high dilution factor should be seen more favorably than a large effluent volume with a relatively small dilution. If the limits have been set by authorities using the broader approach, individual situations tend not to be taken into account. This can mean that either the load from a large tannery or group can cause considerable damage, or that the small tannery with good treatment facilities and high dilution factor into surface waters can be unduly penalized.

The limits imposed should always relate to the volume of effluent to account for the total weight of pollutants. If better housekeeping reduces the volume of water used, thus increasing the concentration, then there is good reason for some relaxation of the limits.

Often limits and guidelines do not reflect the individual situation, but there is a need to protect the environment from overload. The effect of excessive constituent levels commonly found in tannery effluents can be severe and is presented for guidance.

The following list of values are often required by the environmental protection agencies. They are usually expressed in milligrams/liter (mg/l) sometimes as parts per million (ppm).

The main problems presented by these components is given, and outline of the methods used by authorities to determine the levels of these components in effluent.

For higher accuracy and conformity of analysis it is recommended to use the latest edition of the **Standard Methods for the Examination of Water and Wastewater**, prepared and published jointly by: **American Public Health Association, American Water Works Association and Water Environment Federation.**

Practical suggestions to a tanner regarding the range of parameters to be monitored, frequency of analysis and on laboratory facilities required can be found in the paper **Selection of Equipment for Laboratories Monitoring Pollution in the Tanning Industry, Manual on Laboratory Equipment and Reagents**, published by UNIDO, 12 July 1994 and available in English, French, Spanish and Chinese.

1. Solids

There are several different classes of solids found in tannery effluent.

1.1. *Suspended solids (SS)*

The suspended solids component of an effluent is the quantity of insoluble matter contained in the waste water. These insoluble materials cause a variety of problems when they are discharged from a site, and essentially are made up of solids with two different characteristics.

a. *Settleable Solids*

This is material which can be seen in suspension when an effluent sample is shaken, but settles out when the sample is allowed to stand. The majority of these solids settle out within 5 to 10 minutes, although some settling of fine solids can still be taking place after 1 hour.

These solids are produced from all parts of leather making and are comprised of fine leather particles, residues from various chemical discharges and products from different waste liquors reacting together. A very large quantity is generated from beamhouse processes.

If the waste waters are for treatment as provided by sewage works or common effluent treatment, the main problems are due to the considerable volume of the sludge formed as the solids settle out. Sludge often contain up to 97% water creating huge quantities of 'light' sludge. Even viscous sludge contain water at around 93%, and can easily cause blockages in sumps, sludge pumps and pipe work. All of this sludge has to be removed, transported, dewatered, dried and deposited causing high demands on plant, equipment and resources.

If the discharge is into surface water, then the flow rate will strongly influence how far the material carries before it settles out on the bed of the stream or river.

Even a thin layer of settled sludge can form a blanket that cuts off oxygen from that area of the river or lake bed. The plant and aquatic life die creating foul conditions.

b. *Semi-colloidal solids*

These are very fine solids that for practical purposes will not settle out from an effluent sample, even after standing for a considerable time. They can, however, be filtered from solution and therefore, together with the more readily settleable solids, form the suspended solids of an effluent as measured analytically.

The majority of these solids are protein residues from the beamhouse operations - mainly liming processes - but high quantities are also produced from poor uptake in vegetable tanning processes. Other sources are from poor uptake in retanning areas.

These solids will not directly cause sludge problem, but they can break down in the long term. This is by bacterial digestion producing solids which will eventually settle, and also a high oxygen requirement. This oxygen demand is considered in Section 2.

The suspended solids analysis measures both of these components and the technique is simple. A known volume of the effluent is taken and filtered through a filter paper which is then dried and reweighed. The difference between this weight and that of the original paper is the weight of the dry solid material contained in the sample.

1.2. *Settleable solids*

Although the suspended solids analysis is the most common method used to assess insoluble matter, sometimes the settleable solids content is required. This measures the solids component with the fast settling rate (*refer 1.1. Suspended Solids (SS) - a. Settleable Solids*). This can be determined by allowing the shaken sample to settle and filtering a known volume of the semi-colloidal matter remaining in suspension. After drying and weighing, the quantity of semi-colloidal matter can be calculated. The difference between the suspended solids and this figure is the level of settleable solids.

1.3. *Gross solids*

These solids are larger than a sampling machine can handle and are therefore not measured. Their presence is, however, obvious and fully recognized due to the dangers that they present.

The waste components that generate this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and frequently broken down paper from bags. They can be removed easily by coarse bar screens set in the waste water flow, but if they pass from the factory they settle out very rapidly.

Major problems can develop with these materials if they settle in pipe work as they provide a source of blockage. The problem can become very serious when effluents have to be pumped as often the blockages occur in inaccessible pipe work. The costs of replacing a burned out motor or broken rotors is high.

If discharged into gullies, ditches or water courses the debris rapidly accumulates causing blockage and stagnation.

2. *Oxygen demand*

Many components in effluents are broken down by bacterial action into more simple components. Oxygen is required both for the survival of these bacteria (aerobic bacteria) and for the breakdown of the components. This breakdown can occur quite rapidly or may take a very long time according to composition.

If the effluent creates a high oxygen demand and is discharged directly into surface water then the sensitive balance maintained in the water is overloaded. Oxygen is stripped from the water causing oxygen dependent plants, bacteria, fish and the river to die. An environment where bacteria which are non-oxygen dependent (anaerobic) then becomes established creating toxic conditions in the waterway.

A healthy river can tolerate low levels of oxygen demanding substances, but the load created by tanneries is often very high, and the effluent requires treatment before discharge. This is

often provided by using bacteria in a properly operated effluent treatment plant, and high levels of oxygen are demanded by the process. This oxygen can be induced into the effluent by blowing in large volumes of air, but this requires a high level of energy. The plant has high capital and operational costs.

If the process works ideally, then water and carbon dioxide are produced in large volumes, but the process depends upon the growth of bacteria. As these die they form a sludge that has to be treated and ultimately disposed. This sludge has a high water content and is often quite difficult to dewater adding considerably to the treatment costs.

To assess the impact of an effluent on either discharge to surface waters or to set a value on the costs of treatment, the oxygen demand needs determining and this can be achieved in two different ways.

2.1. Biochemical Oxygen Demand (BOD₅)

The technique for measuring the Biochemical Oxygen Demand (BOD) is complex. Essentially, the shaken effluent sample is allowed to stand for one hour so that all settleable solids are excluded from the analysis. The liquor (supernatant) above the precipitate is drawn off and used in the analysis. A suitable volume of this sample is diluted in water, pH adjusted, and seeded with bacteria (often settled sewage effluent). The samples are then incubated for 5 days in the dark at $20 \pm 1^\circ\text{C}$. Oxygen dissolved in the water is used by the bacteria as the organic matter in the sample is broken down. The remaining oxygen is determined either by an oxygen meter or by analysis. By comparison to effluent free blank samples, the level of oxygen demanded by the effluent can be calculated.

The BOD₅ analysis, generally termed BOD, is widely used to assess the environmental demands of a waste water. There are various weaknesses with this method of detection: the bacterial cultures can vary and the analysis is sensitive. If the most stringent care is not taken in preparation and analysis the results can be misleading.

It should also be remembered that although this is a measure of the oxygen requirements of bacteria under controlled conditions, many effluents components take longer than this time to break down. Some chemicals will only be partially broken down, while others may not be significantly affected. Typically, vegetable tanning wastes have a long breakdown period often quoted up to 20 days. These longer digestion periods can apply to a variety of the chemicals used in manufacturing leathers including certain retanning agents, some synthetic fatliquors, dyes and some residual proteins from hair solubilization.

This longer breakdown period spreads the environmental impact to a greater area as the waste water components are carried greater distances before breakdown.

2.2. Chemical Oxygen Demand (COD)

This method measures the oxygen required to totally oxidize the effluent sample. It sets a value on the materials that would normally be digested in the BOD₅ analysis, the longer term biodegradable products, and also chemicals that are not affected by bacterial activity.

The method is very aggressive. A suitable volume of effluent is boiled with a powerful oxidizing agent (potassium dichromate) and sulphuric acid. As the effluent components oxidize they

remove oxygen from the potassium dichromate and this removal is determined by titration.

This method is often favored as it provides rapid results (hours as opposed to days). It is more reliable and cost effective as it is easier to manage larger numbers of samples.

These results are always higher than the BOD₅ results. As a rule of thumb the ratio between COD:BOD is 2.5:1, although variation can be found in untreated effluent samples as great as 2:1 and 3:1. This is dependent upon the chemicals used in the different leather making process and their rate of biodegradability.

It should be noted that both of these techniques are based on settled effluent, not filtered. The semi-colloidal material that forms part of the suspended solids is also included in the BOD and COD determinations. Normally 1 mg/l suspended solids will generate a COD increase of approximately 1.5 mg/l.

2.3. Permanganate value (PV 4 hours)

This technique is occasionally used and depends upon chemical oxidation provided by potassium permanganate. Determination by COD has almost completely replaced this method.

3. Nitrogen

Nitrogen is contained in several different components in tannery effluent and sometimes there is a need to differentiate between these sources.

3.1. Total Kjeldahl Nitrogen (TKN)

Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia from delimiting materials, and the nitrogen content of proteinaceous materials resulting from liming/unhairing operations.

There are two direct problems resulting from these sources of nitrogen.

1. Nitrogen is required for plant growth, but high levels made available from nitrogen containing substances overstimulate this development. Water based plants and algae grow too rapidly, so waterways become clogged and the flow can become restricted. As these plants die, there is a disproportionately high amount of organic matter for breakdown. If the natural supply of oxygen from the river is exceeded by this load, then plants, fish and aerobic bacteria die and ultimately anaerobic conditions develop.
2. Nitrogen released from the breakdown of proteins and from the delimiting process exists in the ammoniacal form. This can be converted by bacteria through several stages to form water and nitrogen gas which is released to the atmosphere. Both of these breakdown products are non toxic, but large quantities of oxygen are needed in the process. If this oxygen demand is greater than the natural level of supply in a water course, then toxic anaerobic conditions rapidly develop.

These nitrogen containing compounds can be broken down by biological effluent treatment in a similar way to treating effluents to reduce the BOD. The oxygen demand is very high - hence plant size and energy costs - and calculations show that with a typical tannery effluent, around

40% of the oxygen requirements are taken up by removing the nitrogen component.

The nitrogen containing compounds can be determined by the Kjeldahl method of analysis. In this technique, all the nitrogen containing matter is digested by boiling with sulphuric acid to form ammonium compounds. In a second stage this ammonia is released by boiling with sodium hydroxide, then trapped in boric acid solution. The level of ammonia released is determined by titration, and the value as nitrogen calculated.

3.2. Ammonium content as Nitrogen (N)

This is sometimes required in discharge limits and often confused with TKN. As ammonium compounds are part of the TKN the problems associated with rapid plant growth and oxygen demand are the same. These compounds mostly result from the deliming process, with a comparatively small quantity produced from liming and unhairing. The analysis is similar to TKN but omits the initial digestion stage. This excludes the nitrogen component resulting from protein wastes.

4. Sulphide (S^{2-})

The sulphide content of a tannery effluent results from the use of sodium sulphide and sodium hydrosulphide, and the breakdown of hair in the unhairing process.

There are many problems associated with this material:

Under alkali conditions sulphides largely remain in solution. When the pH of the effluent falls below 9.5, hydrogen sulphide is evolved from the effluent - the lower the pH, the greater the rate of evolution. Characterized by its smell of rotten eggs a severe odour problem is created.

This gas is as toxic as hydrogen cyanide and even low level exposure will cause headaches and nausea, and there is a danger of attack to the surface of the eye. At higher levels death can rapidly result and there are many deaths recorded from sulphide build up in sewage systems.

Hydrogen sulphide gas is also fairly soluble, and when dissolved by condensation weak acids can be formed with resultant corrosion. This typically weakens metal roofing, girders and metal building supports. In sewers major problems can result by corrosion of metal fitting, reinforcement and pipework.

If discharged to surface water, there are toxicological dangers even at low concentrations. Sulphides can also be oxidized into non-toxic compounds by certain bacteria in rivers, but this creates an oxygen demand and if excessive there is damage to aquatic life.

There are several methods of determining sulphides in effluent. One of the most accurate relies on the acidification of suitable quantities of effluent to generate hydrogen sulphide. This is flushed through the apparatus using nitrogen gas, trapped and converted into zinc sulphide. The level of sulphide is determined by titration.

5. Neutral salts

There are two common types of salts found in tannery effluent.

5.1. Sulphates (SO_4^{2-})

Sulphates are a component of tannery effluent, having been introduced either by the use of sulphuric acid, or through using products with a high sodium sulphate content. Many auxiliary chemicals contain sodium sulphate as a by-product of their manufacture. For example, chrome tanning powders contain high levels of sodium sulphate and also many synthetic retanning agents.

An additional source is created by removing the sulphide component from effluent by aeration as the oxidation process creates a whole range of products including sodium sulphate. These sulphates can be precipitated by calcium containing compounds, forming calcium sulphate which has a low level of solubility. Problems are associated with soluble sulphates, however, for two main reasons:

1. Complete chemical removal of sulphates from solution is not viable. Under certain biological conditions, it is possible to remove the sulphate from solution and bind the sulphur into microorganisms. Generally, however, the sulphate either remains as sulphate, or is broken down by anaerobic bacteria to produce hydrogen sulphide and odour. This process occurs very rapidly in effluent treatment plants, sewage systems and water courses if effluents remain static.

This bacterial conversion to hydrogen sulphide in sewage systems results in corrosion of metal parts, and gradual erosion of concrete will take place unless the concrete is sulphate resistant.

2. If breakdown does not occur, then there is the risk of increasing the total salts concentration in surface waters and ground water.

Sulphate analysis is performed by adding barium chloride solution to a filtered sample of effluent. The sulphates are precipitated as barium sulphate and filtration, drying and calculation can determine the sulphate level.

5.2 Chlorides (Cl^-)

Chloride as sodium chloride is introduced into tannery effluents usually from the large quantities of common salt used in hide and skin preservation and from the pickling process. As they are very soluble and stable, they remain unchanged by effluent treatment and nature and remain in the environment. Considerable quantities of salt are produced by industry, and levels can rapidly rise to the maximum acceptable for potable water. Increasing salinity in ground water, especially in areas of high industrial population is now becoming a serious environmental problem.

Inhibition of growth is experienced with plants, bacteria and fish in surface waters, and at high levels can lead to breakdown of cell structure. If the water is used for irrigation, the salt content increases at surface level due to evaporation and crop yields fall. When flushed from the soil by rainfall, chlorides re-enter the eco-system and may enter the ground water. Only if discharges

are into tidal/marine environments are high salt contents acceptable.

The level of salt as chloride under acid conditions can be determined by titrating a known volume of effluent with silver nitrate solution using potassium chromate as an indicator.

Under neutral or alkali conditions, an excessive addition of silver nitrate is made. This excess is then determined by back titration with potassium thiocyanate using ferric alum as the indicator.

6. Oils and grease

Natural oils and greases are released from within the skin structure during leather manufacture. There may also be some fatty substances produced from inter-reactions when waste waters mix if fatliquor exhaustion is poor.

As greases and fatty precipitates float, they can form mats which collect and bind other materials causing a potential blockage problem especially with effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, the transfer of oxygen from the atmosphere will be reduced.

If these fatty substances are in the form of an emulsion, being biodegradable they create a very high oxygen demand.

These components are determined by shaking the effluent sample with a suitable solvent and allowing the solvent to separate into a layer on top of the effluent. This solvent dissolves fatty matter, and a quantity can be drawn off and evaporated to dryness. This leaves residual grease for weighing and calculation.

7. pH value

Acceptable limits for the discharge of waste waters to both surface waters and sewers are found from ranging between pH 5.5 to 10.0. Although tighter limits are often set, there is always greater tolerance to the alkali side. This is because carbon dioxide from the atmosphere and from biological processes in healthy surface water systems tend to lower pHs very effectively to neutral conditions. If the pH of surface waters is moved too far either way from the pH range 6.5 - 7.5, then there is loss of more sensitive fish and plant life.

Municipal and common treatment plants prefer discharges to be more on the alkali side as the corrosive effect on concrete is reduced. Metals tend to remain insoluble and more inert, and any evolution of hydrogen sulphide is minimized. When biological conditions are carried out as part of treatment the pH is lowered to more neutral conditions by evolved carbon dioxide.

8. Chromium compounds

As metal compounds are not biodegradable and can be viewed as remaining long term in the environment, or being accumulative, these receive close attention. There are two forms of chrome associated with the tanning industry, and their properties are often confused.

8.1 Chrome 3⁺ (trivalent chrome, chrome III)

Chromium is mainly produced as waste from the chrome tanning process, as part of retanning systems and by displacement from leathers by retanning and dyeing processes.

This chrome is discharged from processes in the soluble form but when it is mixed with other tannery waste waters from other processes, especially if proteins are present, there is a very rapid reaction. Precipitates are formed, mainly protein-chrome, which add to the sludge generation.

However, very fine colloids are also formed as discussed in Section 1.1.b and these have been made very stable by the chrome - in effect the protein has been partially tanned. This makes this component more resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited.

When these fine solids are successfully broken down, there will be a precipitate as chromium hydroxide formed which will remain long term in the eco-system.

If chrome discharges are excessive there is the possibility of chromium remaining in solution. In this state it is toxic at low concentrations to daphnia thus affecting the fish food chain, and it can also inhibit photosynthesis.

There are several methods of determination, but the first stage usually comprises boiling a known volume of sample with concentrated nitric acid to ensure complete solution of the chrome. After suitable dilution, the chromium level is determined by atomic absorption. Iodine/thiosulphate titrations are sometimes used where high levels of chrome are expected, but this technique is not accurate at low concentrations.

8.2 Chrome 6⁺ (hexavalent chrome, chrome VI)

The presence of chromium in this form is unlikely in tannery effluents unless dichromates are being used as part of chrome manufacture. Dichromates are toxic to fish life as there is easy penetration of cell walls. Absorption is mainly through the gills and it is accumulative.

Analysis is specialized as concentrations normally anticipated are very low and are based on colorimetric measurement at 670 nm.

9. Other metals

Other metals which might be discharged from tanneries and where limits to discharge may be set include aluminium and zirconium .

These metals have different toxicities according to the chemical species, also by the presence of other organic matter, complexing agents and the pH of the water. In particular, aluminium appears to inhibit the growth of green alga and crustaceans are sensitive to low concentrations.

Cadmium, sometimes used in yellow pigments and is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. If it becomes a component of potable water it can cause bone embrittlement (*Ref item 12 - Toxicity of effluent components*).

10. Solvents

The sources of solvents are degreasing and finishing operations. Solvents in effluents discharged to surface waters can form a micro-film on the surface of the waters inhibiting uptake of oxygen. The breakdown of solvents is variable. Some inhibit bacterial activity and remain in the ecosystem for long periods of time. Analysis is highly specialized.

11. Sampling techniques

The composition of an effluent sample is also dependent upon the sampling technique. This can affect the apparent performance of a tannery against set limits.

There are two main methods that are acceptable.

1. Composite: samples taken over a 24 hour period and mixed together.
2. Spot samples: a single sample is taken for analysis.

Ideally, composite samples should be taken by automatic sampler, with 24 samples taken at 1 hour intervals and mixed before analysis. If charges are made, then these are normally based on these values.

Where spot samples are taken, there are usually allowances for variation in effluent strength, often allowing a 50 per cent increase in strength although this may not apply to all components.

The position of the sampling head is important. If it is too low, then there is the possibility of sludge being drawn into the sampler. This is also an important point when spot samples are taken as these are often manual. The sampling point should always be the same to reduce variables.

Duplicate samples

When samples are taken by an authority a duplicate sample should be held by the tannery. The sample should be shaken before the duplicate is poured, and the sample bottle should be clean, fully filled, airtight and kept under cold conditions. It is not unknown for samples to be incorrectly identified, or mistakes in analysis. Duplication always gives a visual check against the original, and the chance for a second analysis if there are reasons for doubt.

12. Toxicity of effluent components

The toxicity of effluent components following dilution in surface waters is a complex subject and there is a shortage of specific data. This is due to the wide variety of aquatic life, the nature of individual components, and their degradation rate both in suspension or as part of a sediment. It is not possible to be specific for complex and multiple components of effluent and the effects on fish, invertebrates, algae and daphnia can be quite different.

A measure of toxicity can be expressed as LD50, representing the dose which will kill 50 per cent of a sample of a species. Not every species react to the same degree to a given exposure,

and the type of response to an equal dose of a chemical may be very different. When values are given the species under test should be stated, and the time period taken for evaluation, normally 24 or 96 hours or 14 days.

Environmental Quality Standards are also used as a method of control for the protection of aquatic life, based on fate, behaviour and aquatic toxicity. Much of this information is drawn from research data covering a variety of sources and species to find the most sensitive. Considerable data is often available to form conclusions, but when data is scarce conclusions may include expert judgement. The EQS may be defined as the concentration of a substance which must not be exceeded if a specific use of the aquatic environment is to be maintained.

Regarding metals that might be present in the tannery effluents - chromium, aluminium and perhaps zirconium, these are all classed as "high/moderate-acute" and "chronic toxicity" to organisms and may accumulate. An acute effect may be defined as having a specific effect up to 96 hours on fish, and chronic effects may need a 21 day test period or even involve full life cycles including counting of eggs and their fertility.

The toxicity of many metals also varies according to pH, temperature and water hardness. With reference to Cr 3+, investigation have been performed on fish (unspecified) under condition of exposure insufficient to cause severe toxicity, but sufficient to cause visual changes in behaviour. These dosages were at the level of 0.2 mg/l. It is understood however, that daphnia has an even grater sensitivity, thus presenting a potential hazard to the fish food chain.

It should be noted that zinc and copper, although not used in processing leather, are described as high/acute and chronic toxicity of aquatic life. These have maximum levels of 0.3 mg/l total and 0.04 mg/l (dissolved) respectively as given in Standards required by E.C. Fish Directive for salmon. Similar toxicity definitions apply to Cr 3+, and it is stated that dosages of 0.2 mg/l caused behaviour change in fish (unspecified). In the absence of more specific data, loadings in these orders might be considered as maximum permissible values for surface waters.

No limits are set for COD, as substances (and toxicity) cannot be specified. Other limits found in the Standards required for EC Fish Directives are presented in the table:

Suspended solids	< 25 mg/l
BOD/5 days	< 5 mg/l
Ammonia (as NH ₃)	< 0.025 mg/l
Kjeldahl Nitrogen	< 0.78 mg/l

It should be noted that there are no values for sulphides, but the presence of sulphides will be included in the BOD analysis.

13. Direct Toxicity Assessment

The use of chemical/biological methods of analysis with regard to toxicity limits of specific effluent components has been the basis for determining the limits for discharge into receiving waters. These techniques, however, cannot always account for:

1. unexpected toxic effects from the reaction of seemingly innocuous substances when mixed together.

2. some substances being toxic to aquatic life at levels too low for detection techniques to measure.

New techniques are under investigation in the USA and Europe that break away from the traditional approach. This involves taking samples of the effluent and testing the effect at various dilutions on organisms of increasing complexity, such as algae, daphnia, water fleas and fish that might be found in surface waters. Known as Direct Toxicity Assessment, this technique should provide a means of testing the effects of complex discharges under near to real life.

It is noted that where tannery discharges are directly into sewers, the responsibility for final discharge will be held by municipality. Where industrial waste waters are directly received surface waters, however, the industry may be directly affected, and investigations might lead to redefinition of limits at local and national levels.

Chapter II

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

M. Bosnic and J. Buljan

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

ARGENTINA - CHINA

PARAMETER	ARGENTINA Surface	ARGENTINA Sewer	AUSTRALIA Surface	AUSTRALIA Sewer	AUSTRIA Surface	AUSTRIA Sewer	BRAZIL Surface	BRAZIL Sewer	CHINA Surface	CHINA Sewer (Beijing)
1. pH	5.5 - 10	5.5 - 10	6.0 - 9.0	6.0 - 10.0	6.5 - 8.5	6.0 - 9.5	5.0 - 9.0		6.0 - 9.0	6.0 - 9.0
2. Temperature °C	45	45	45	38	30	30	<40	40		35
3. Conductivity µS/cm										
4. Suspended solids mg/l			60	*	70	150			200	500
5. Settleable solids ml/l	0.5	0.5					1.0			10
6. BOD, mg O ₂ /l	50	200	40	*	25		60		150	500
7. COD mg/l	250	700			200				300	500
8. TDS mg/l										
9. Sulphide mg S ²⁻ /l		1		1 - 5	0.1	2.0	0.2	5	1	10
10. Chrome (III) mg/l								5	1.5	2.0
11. Chrome (VI) mg/l					0.1	0.1				0.5
12. Chrome total mg/l	0.5	2	0.3	1 - 20	1.0	3.0	0.5		1.5	
13. Chlorides mg/l	*	*	*	*						
14. Sulphates mg/l	*	1000		2000		*				
15. Ammonia mg N/l	3	10		100 - 200	15	*	5			
16. TNK mg N/l	10	30			*		10			
17. Phosphorus mg P/l					2.0		1			
18. Oil/grease mg/l	100	100		100 -1000	20	100	20 - 30	100		100
19. Phenols mg/l	0.5	0.5	0.05 0.5	100			0.1 - 0.5			5
20. Detergents mg/l										
21. Solvents mg/l:										
21.1. Hydrocarbons mg/l			none	30	10	20				
21.2. Nitrogenous mg/l			none	none						
21.3. Chlorinated mg/l	1	2	none	5	0.5	0.5				

Note: * specific requirements have to be fulfilled

The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

COLOMBIA - DENMARK

PARAMETER	COLOMBIA Surface	COLOMBIA Sewer	COSTA RICA Surface	COSTA RICA Sewer	CROATIA Surface	CROATIA Sewer	CZECH REP. Surface	CZECH REP. Surface	DENMARK Surface	DENMARK Sewer
1. pH		5 - 9	5 - 9	6 - 9	*	6.5 - 9.0			6.5 - 8.5	6.5 - 9.0
2. Temperature °C	40		15 - 40	<40	*	40			30	35
3. Conductivity µS/cm										
4. Suspended solids mg/l		1000	200	500	*	400			30	
5. Settleable solids ml/l			1	1	*	15				
6. BOD, mg O ₂ /l			400	300	*	450	50			
7. COD mg/l		1000	600	1000	*	700	300			
8. TDS mg/l				1500						
9. Sulphide mg S ²⁻ /l			25		*	1	2		2	
10. Chrome (III) mg/l					*					
11. Chrome (VI) mg/l					*					
12. Chrome total mg/l	5		1.5	2.5	*		2		0.2	2
13. Chlorides mg/l				500	*					
14. Sulphates mg/l				500	*	300			300	
15. Ammonia mg N/l					*	15			2.0	
16. TNK mg N/l					*	80			5	
17. Phosphorus mg P/l										
18. Oil/grease mg/l		250	30	100	*	100			5	
19. Phenols mg/l			1	5	*	1.5				
20. Detergents mg/l										
21. Solvents mg/l:					*	trace				
21.1. Hydrocarbons mg/l				20						
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l				0.5						

Note: * specific requirements have to be fulfilled

The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

EGYPT - GREECE

PARAMETER	EGYPT Surface	EGYPT Sewer	FINLAND Surface	FINLAND Sewer	FRANCE Surface	FRANCE Sewer	GERMANY Surface	GERMANY Sewer	GREECE Surface	GREECE Sewer
1. pH	6.0 - 9.0	6.0 - 9.0	6.0 - 10.0	6.0 - 10.0	5.5 - 8.5	6.5 - 8.5		6.5 - 10.0	6.5 - 9.0	6.5 - 9.0
2. Temperature °C			35	35	30	30		35	28 - 35	35
3. Conductivity µS/cm										
4. Suspended solids mg/l	200	200	*	*	35	600			25 - 50	500
5. Settleable solids ml/l									0 - 0.5	10
6. BOD, mg O ₂ /l	500	500	*	*	30	800	25		15 - 40	500
7. COD mg/l	100	100	*	*	125	2000	250		45 - 150	1000
8. TDS mg/l										
9. Sulphide mg S ²⁻ /l	10	10	5	5		2	2	2	1 - 2	1
10. Chrome (III) mg/l			0 - 0.5	0 - 0.5	1.5	1.5			0.1 - 2	2
11. Chrome (VI) mg/l			none	none	0.1	0.1			0.02 - 0.5	0.5
12. Chrome total mg/l	1	1	10	20			1	1	2.5	2.5
13. Chlorides mg/l				2500						
14. Sulphates mg/l				400				*	1000	1500
15. Ammonia mg N/l	100	100		50			10	*	10 - 20	25
16. TNK mg N/l					30	150				
17. Phosphorus mg P/l							2			
18. Oil/grease mg/l	100	100						*	5 - 20	40
19. Phenols mg/l				50	0.1	0.1		*	0.25 - 0.5	5
20. Detergents mg/l										
21. Solvents mg/l:			3	3				*		
21.1. Hydrocarbons mg/l					10	10			0.2	
21.2. Nitrogenous mg/l									0.1 - 0.2	
21.3. Chlorinated mg/l					AOX 5	AOX 5	AOX 0.5		1	

Note: * specific requirements have to be fulfilled
 The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

HUNGARY - IRELAND

PARAMETER	HUNGARY Surface	HUNGARY SEWER	INDIA Surface	INDIA Sewer	INDONESIA Surface	INDONESIA Sewer	IRAN Surface	IRAN Sewer	IRELAND Surface	IRELAND Sewer
1. pH	5.0 - 10.0	6.5 - 10.0	5.5 - 9.0	5.5 - 9.0	6.0 - 9.0		6.5 - 8.5		7.5 - 10.0	7.5 - 10.0
2. Temperature °C			40 - 45	40 - 45						
3. Conductivity µS/l										
4. Suspended solids mg/l			100	100	150	150	40		800 - 1000	800 - 1000
5. Settleable solids ml/l										
6. BOD, mg O ₂ /l			30	500	150	150	30		500 - 1700	500 - 1700
7. COD mg/l	50 - 150		250	250	300	300	40		1500 - 2600	1500 - 2600
8. TDS mg/l										
9. Sulphide mg S ²⁻ /l	0.01 - 5	1	2	2			2		5 - 35	5 - 35
10. Chrome (III) mg/l	2.0 - 5.0	5	2	2			3		15	15
11. Chrome (VI) mg/l	0.5 - 1	1					0.5		0.1	0.1
12. Chrome total mg/l		5	2	2	2	2				
13. Chlorides mg/l										
14. Sulphates mg/l		400	1000	1000			400			
15. Ammonia mg N/l	2 - 3	200	50	50	10	10	3.5		15 - 200	15 - 200
16. TNK mg N/l										
17. Phosphorus mg P/l							4			
18. Oil/grease mg/l	8 - 50	60	30 - 100	30 - 100	5	5			30	30
19. Phenols mg/l			5 - 50	5 - 50			1		0.05	0.05
20. Detergents mg/l							1.5			
21. Solvents mg/l:										
21.1. Hydrocarbons mg/l										
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l									0.05	0.05

Note: * specific requirements have to be fulfilled
 The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

ITALY - NETHERLANDS

PARAMETER	ITALY Surface	ITALY Sewer	JAPAN Surface	JAPAN Sewer	KENYA Surface	KENYA Sewer	MEXICO Surface	MEXICO Sewer	NETHERLANDS Surface	NETHERLANDS Sewer
1. pH	5.5 - 9.5	5.5 - 9.5	5.0 - 9.0	5.0 - 9.0	6 - 9	6.0 - 9.0	6 - 9		6.5 - 8.5	6.5 - 10.0
2. Temperature °C	30 - 35	30 - 35			25				30	30
3. Conductivity µS/cm										
4. Suspended solids mg/l	40 - 80	200	200	200-300	30	300	200		80	*
5. Settleable solids ml/l							5.0			
6. BOD ₅ mg O ₂ /l	40	250	160	160	20	450	200		5	*
7. COD mg/l	160	500	160	160					*	*
8. TDS mg/l										
9. Sulphide mg S ²⁻ /l	1	2	2	2			0.1		*	*
10. Chrome (III) mg/l		4								1
11. Chrome (VI) mg/l	0.2	0.2					0.1		none	none
12. Chrome total mg/l	2	4	2	2	1		1.0		0.05	2
13. Chlorides mg/l	1200	1200				3000			200	*
14. Sulphates mg/l	1000	1000				100			150	300
15. Ammonia mg N/l	10 - 15	30				100			*	*
16. TNK mg N/l									3	
17. Phosphorus mg P/l			1							
18. Oil/grease mg/l	20	40	30	30 - 50	trace	100	30		*	*
19. Phenols mg/l	0.5	1	5	5	2					
20. Detergents mg/l										
21. Solvents mg/l:									none	none
21.1. Hydrocarbons mg/l	0.2	0.4								
21.2. Nitrogenous mg/l	0.1	0.2								
21.3. Chlorinated mg/l	1	2								

Note: * specific requirements have to be fulfilled

** N/S: No Standard or Not specified

The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

NEW ZEALAND - POLAND

PARAMETER	NEW ZEALAND Surface	NEW ZEALAND Sewer	NICARAGUA Surface	NICARAGUA Sewer	PAKISTAN Surface	PAKISTAN Sewer	PHILIPPINES Surface	PHILIPPINES Marine coastal waters	POLAND Surface	POLAND Sewer
1. pH		6.0 - 9.0	6 - 9	6 - 10	6 - 9	6 - 9	6.5 - 9.0	6-9	6.5 - 9.0	
2. Temperature °C		55		50	40				35	
3. Conductivity µS/cm										
4. Suspended solids mg/l			150	400	200		90	200	35	
5. Settleable solids ml/l			5							
6. BOD, mg O ₂ /l			120	400	80		80	120	30	
7. COD mg/l			250	900	150		150	250	150	
8. TDS mg/l				1500					2000	
9. Sulphide mg S ²⁻ /l		1 - 5	0.2	5	1				0.2	
10. Chrome (III) mg/l									0.5	
11. Chrome (VI) mg/l				0.5			0.2	0.5	0.2	
12. Chrome total mg/l		5 - 50	10	3.5	1					
13. Chlorides mg/l				1500	1000				1000	
14. Sulphates mg/l				1500	1000				500	
15. Ammonia mg N/l					40				6	
16. TNK mg N/l									30	
17. Phosphorus mg P/l									5	
18. Oil/grease mg/l			30	150	10		10	15	50	
19. Phenols mg/l			0.1	1	0.3				0.5	
20. Detergents mg/l				10					10n.1+5i***	
21. Solvents mg/l:										
21.1. Hydrocarbons mg/l										
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l										

Note: * specific requirements have to be fulfilled

The figures in the table were compiled from various sources and cannot be considered as official.

*** Present the values after year 2000

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

SOUTH AFRICA - TANZANIA

PARAMETER	SOUTH AFRICA Surface	SOUTH AFRICA Sewer	SPAIN Surface	SPAIN Sewer	SRI LANKA Surface	SRI LANKA Sewer	SWITZERLAND Surface	SWITZERLAND Sewer	TANZANIA Surface	TANZANIA Sewer
1. pH	5.5 - 9.5	5.5 - 12.0	5.5 - 9.5	8 - 10	5.5 - 9.0		6.5 - 8.5	6.0 - 9.5	5.5 - 9.0	
2. Temperature °C	35	43	30				30	40		
3. Conductivity µS/cm										
4. Suspended solids mg/l	25	400 - 2000	80 - 300	500 - 750	100		20		100	
5. Settleable solids ml/l	N/S	N/S	0.5 - 2							
6. BOD ₅ mg O ₂ /l	N/S (10)	N/S (200-1400)	40 - 300	750 - 1000	60		20		30	
7. COD mg/l	30	2000-5000	160 - 500	1500 - 2500	250					
8. TDS mg/l										
9. Sulphide mg S ²⁻ /l	1	5-50	1 - 2	1 - 20	2.0		0.1	1		
10. Chrome (III) mg/l	0.5	N/S	2 - 4				2	2		
11. Chrome (VI) mg/l	0.05	N/S	0.2 - 0.5	0.5	0.5		0.1	0.5	0.1	
12. Chrome total mg/l	0.5	5 - 50		3 - 5	2.0		2	2		
13. Chlorides mg/l	N/S	1000	2000	2000	1000		200		1000	
14. Sulphates mg/l	N/S	500 - 1000	2000	2000				300		
15. Ammonia mg N/l	10	20 - 30	15 - 50	85						
16. TNK mg N/l	N/S	50								
17. Phosphorus mg P/l										
18. Oil/grease mg/l	2.5	50 - 100	20 - 40	150	10.0		20			
19. Phenols mg/l	0.1		0.5 - 1	2	1.0		5	5		
20. Detergents mg/l										
21. Solvents mg/l:	N/S	N/S								
21.1. Hydrocarbons mg/l	N/S	N/S	none	none			20	20		
21.2. Nitrogenous mg/l	N/S	N/S								
21.3. Chlorinated mg/l	N/S	N/S					0.1	0.1		

Note: * specific requirements have to be fulfilled

** N/S: No Standard or Not specified

The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

THAILAND - UNITED KINGDOM

PARAMETER	THAILAND Surface	THAILAND Sewer	TUNISIA Surface	TUNISIA Sewer	TURKEY Surface	TURKEY Sewer	UGANDA Surface	UGANDA Sewer	UK Surface	UK Sewer
1. pH	5.5 - 9.0		6.5 - 8.5	6.5 - 9.0	6 - 9	6 - 10	6.0 - 8.0		6.0 - 9.0	6.0 - 10.0
2. Temperature °C	40		25	35		40	20 - 35		25	40
3. Conductivity µS/cm										
4. Suspended solids mg/l	150		30	400	150	350	50		30 - 50	500 - 1000
5. Settleable solids ml/l			0.3							
6. BOD, mg O ₂ /l	20 - 60		30	400	100	250	30		20 - 30	
7. COD mg/l			90	1000	200	800	100			2000 - 6000
8. TDS mg/l	5000						1000			
9. Sulphide mg S ²⁻ /l	1		0.1	3	1	2	1.0		1	2 - 5
10. Chrome (III) mg/l	0.75		0.5	2					2 - 5	10 - 35
11. Chrome (VI) mg/l	0.25		0.05	0.5	0.3		0.05		0.1	0.1
12. Chrome total mg/l					2	5	1.0		1 - 2	1 - 20
13. Chlorides mg/l			600	700			30		4000	5000
14. Sulphates mg/l			400	600		1700	500			1000 - 1200
15. Ammonia mg N/l							10		100	10 - 100
16. TNK mg N/l			1	100		100	10			
17. Phosphorus mg P/l							10			
18. Oil/grease mg/l	15				20	100	10			50 - 500
19. Phenols mg/l	1					10	0.2			
20. Detergents mg/l							10			
21. Solvents mg/l:									none	none
21.1. Hydrocarbons mg/l							*		none	none
21.2. Nitrogenous mg/l							*		none	none
21.3. Chlorinated mg/l							*		none	none

Note: * specific requirements have to be fulfilled

The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

URUGUAY - ZAMBIA

PARAMETER	URUGUAY Surface	URUGUAY Sewer	USA Surface	USA Sewer	VENEZUELA Surface	VENEZUELA Sewer	VIETNAM Surface	VIETNAM Sewer	ZAMBIA Surface	ZAMBIA Sewer
1. pH	6.0 - 9.0	5.5 - 9.5	6.0 - 9.0	6.0 - 10.0	6.0 - 9.0	6.0 - 9.0	5.5 - 9.0	5.0 - 9.0	6.0 - 9.0	
2. Temperature °C	30	35					40	45	40	
3. Conductivity µS/cm									4 3 0 0	
4. Suspended solids mg/l	150		60		60	400	100	200	100	
5. Settleable solids ml/l		10							0.5	
6. BOD ₅ mg O ₂ /l	60	700	40		60	400	50	100	50	
7. COD mg/l					350	1000	100	400	90	
8. TDS mg/l									3000	
9. Sulphide mg S ²⁻ /l	1	5		24	0.5	2	0.5	1.0	0.1	
10. Chrome (III) mg/l				8 - 19			1.0	2.0		
11. Chrome (VI) mg/l					0.5	0.5			0.1	
12. Chrome total mg/l	1	3	1	8 - 19	2	3	2.0	2.0		
13. Chlorides mg/l						300			800	
14. Sulphates mg/l						400			1500	
15. Ammonia mg N/l	5								10	
16. TNK mg N/l					10	80	60	60	15	
17. Phosphorus mg P/l	5								1	
18. Oil/grease mg/l	50	200			20	150	10	30	20	
19. Phenols mg/l	0.5			10	0.5	0.5			0.2	
20. Detergents mg/l	4								2.0	
21. Solvents mg/l:										
21.1. Hydrocarbons mg/l									10	
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l									0.5	

Note: * specific requirements have to be fulfilled

The figures in the table were compiled from various sources and cannot be considered as official.

POLLUTION LIMITS FOR DISCHARGE OF EFFLUENTS INTO WATER BODIES AND SEWERS

ZIMBABWE

PARAMETER	ZIMBAWE Surface	ZIMBABWE Sewer								
1. pH	6.8 - 9.0	> 7.5								
2. Temperature °C	45 max.	45								
3. Conductivity µS/cm										
4. Suspended solids mg/l	600	6000								
5. Settleable solids ml/l	10									
6. BOD ₅ mg O ₂ /l	1000									
7. COD mg/l	3000	6000								
8. TDS mg/l										
9. Sulphide mg S ²⁻ /l		200								
10. Chrome (III) mg/l										
11. Chrome (VI) mg/l										
12. Chrome total mg/l	10	10								
13. Chlorides mg/l	1000	4000								
14. Sulphates mg/l	1000	300								
15. Ammonia mg N/l										
16. TNK mg N/l										
17. Phosphorus mg P/l	30									
18. Oil/grease mg/l	50	450								
19. Phenols mg/l										
20. Detergents mg/l	20									
21. Solvents mg/l:										
21.1. Hydrocarbons mg/l										
21.2. Nitrogenous mg/l										
21.3. Chlorinated mg/l										

Note: * specific requirements have to be fulfilled

The figures in the table were compiled from various sources and cannot be considered as official.