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POLLUTANTS IN TANNERY EFFLUENTS

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DEFINITIONS AND ENVIRONMENTAL IMPACT

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LIMITS FOR DISCHARGE INTO WATER BODIES AND SEWERS

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This is a revised version of an earlier printed document.

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Chapter I[+]

DEFINITIONS AND ENVIRONMENTAL IMPACT

Introduction

Comparative presentation of different standards in one table is not an easy task. 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 existing and/or traditional small- scale tanneries, and, in some countries only a few parameters are subject to control while in others countless parameters, in some cases more than two hundred, are prescribed.

Standards within one and the same country can vary from one region to another. Typically, the central authority stipulates minima and local authorities can insist on even higher levels of purification. Furthermore, in many countries tannery effluents are not subject to specific limits; they are subsumed under overall legislation pertaining to the discharge of industrial waste. Finally, in compiling this information, it was not always possible to obtain the official version of the limits from the issuing authority direct: this certainly increases the risk of error and omission of the latest revisions. The figures in the tables should be treated with due caution; direct comparisons are seldom possible.

Background

The environment is under increasing pressure from solid and liquid wastes emanating from the leather industry. These are inevitable by-products of the leather manufacturing process and cause significant pollution unless treated in some way prior to discharge.

In some instances, liquid waste is discharged into sewage systems (indirect discharge) where it undergoes full-scale treatment before being returned to the environment via surface waters. In those cases, effluent treatment standards set by the authorities are governed by the scale of dilution with other effluents and domestic sewage, treatment plant capabilities, and problems related to plant and equipment management or maintenance. Under these conditions discharge limits are lower than those on discharge direct into surface waters. That notwithstanding, factors such as final sludge disposal and discharge limits for treated effluents that might be imposed on the sewage treatment authority also have to be taken into account.

Where effluent is discharged direct into streams and rivers, it needs to be of higher quality as the environment is sensitive and highly susceptible to damage. The greater the volume of the effluent compared to the volume of surface water, the higher the quality of the effluent demanded by the environment.

[+] This chapter was written by R. P. Daniels

Discharge limits are set with the objective of protecting the environment. The levels of the different pollutants in effluent are determined in two ways. The limits are:

(a) based on standards which have been widely applied and found generally acceptable. This method, however, tends to ignore specific individual situations.

(b) set along the lines of mass-balance, whereby the quality of the water upstream and the quality requirements of the water downstream [for industrial or drinking purposes] are determined. The difference between the two figures determines the tolerance levels at the point of discharge.

The second method takes account of individual site factors. Clearly, a small tannery with a high dilution factor should be seen in more favourable light than a large effluent volume with a relatively lower dilution factor. If the authorities set limits using the broader approach, specific individual situations tend to be ignored. It can result in the effluent load of a large tannery or group causing considerable damage or a small tannery being unduly penalised for discharging effluent into surface waters despite its good treatment facilities and high dilution factor.

The limits imposed should always relate to the volume of effluent and the total weight of pollutants. If better housekeeping reduces the volume of water used, thus increasing the concentration, the limits can be reasonably relaxed.

The effect of excessive pollutant levels commonly found in tannery effluents can be severe; their impact is described below for guidance. The main problems presented by those components are summarised together with an outline of the methods used by authorities to determine the levels of those components in effluent.

The list of values cited below are often those set by environmental protection agencies. They are expressed in two equivalent units: usually in milligrams/litre (mg/l), sometimes as parts per million (ppm).

For greater accuracy and conformity of analysis, attention is drawn to 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 relating to the range of parameters to be monitored, the frequency of analysis and the laboratory facilities required are to be found in the UNIDO paper entitled **Selection of Equipment for Laboratories Monitoring Pollution in the Tanning Industry, Manual on Laboratory Equipment and Reagents** (UNIDO document number V.94-24950 6955E, 12 July 1994, English, French, Spanish and Chinese)

1. Solids

The solids to be found in tannery effluent fall into several distinct categories.

1.1. Suspended solids

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

a. *Solids with a rapid settling rate (settleable solids)*

Settleable solids comprise material that can be seen in suspension when an effluent sample is shaken, but settles when the sample is left to stand. The majority of these solids settle within 5 to 10 minutes, although some fine solids require more than an hour to settle.

These solids originate from all stages of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. Large volumes are generated during beamhouse processes.

If the waste waters are to be treated in sewage works or undergo traditional effluent treatment, the main problems that arise are due to the large volume of sludge that forms as the solids settle. Sludge often contains up to 97% water, giving rise to huge quantities of 'light' sludge. Even viscous sludge has a water content of around 93%, and can easily block sumps, sludge pumps and pipes. All this sludge has to be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources.

If the waste water is to be discharged into surface water, the rate of flow will determine the distance the material is carried before settling on the stream or river bed.

Even a thin layer of settled sludge can form a blanket that deprives sections of the river or lake bed of oxygen. Plant and aquatic life dies and decomposition sets in.

b. *Semi-colloidal solids*

Semi-colloidal solids are very fine solids that, for all practical purposes, will not settle out from an effluent sample, even after being left to stand for a considerable period of time. They can, however, be filtered from solutions. Together with the more readily settleable solids, they thus comprise the suspended solids of an effluent that can be measured analytically.

Most of these solids are protein residues from the beamhouse operations - mainly liming processes; however, large quantities are also produced owing to poor uptake in vegetable tanning processes, another source being poor uptake during retanning.

Semi-colloidal solids will not directly cause a sludge problem. They can be broken down over an extended period by bacterial digestion and they produce solids, which will eventually settle (see section 2 below).

Suspended solids analysis measures both components and the technique is simple. A known volume of effluent is taken and filtered through a filter paper which is then dried and re-weighed. 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 suspended solids analysis is the method most commonly used to assess insoluble matter, analysis of the settleable solids content is sometimes required. The settleable solids content is determined by leaving the shaken sample to settle and then 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 settleable solids content.

1.3. Gross solids

Gross solids are larger than a sampling machine can handle, hence they are not measured. Their presence, however, is clear to see and the dangers they pose are fully recognised.

The waste components that give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by means of coarse bar screens set in the waste water flow. If, however, they emerge from the factory, they settle out very rapidly.

Major problems can develop, if these materials settle in the pipe work as they lead to blockages. The problems can be very serious when blockages occur in inaccessible pipework. The cost of replacing a burned out motor or broken rotors is high.

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

2. Oxygen demand

Many components in effluents are broken down by bacterial action into more simple components. Oxygen is required for both the survival of these bacteria (aerobic bacteria) and the breakdown of the components. Depending on their composition, this breakdown can be quite rapid or may take a very long time.

If effluent with a high oxygen demand is discharged directly into surface water, the sensitive balance maintained in the water becomes overloaded. Oxygen is stripped from the water causing oxygen dependent plants, bacteria, fish as well as the river or stream itself to die. The outcome is an environment populated by non-oxygen dependent (anaerobic) bacteria leading to toxic water conditions.

A healthy river can tolerate substances with low levels of oxygen demand. The load created by tanneries, however, is often excessive, and the effluent requires treatment prior to discharge. This is often achieved by using bacteria in a properly operated effluent treatment plant: a process demanding high levels of oxygen. Oxygen induction can be achieved by blowing large volumes of air into the effluent: a process entailing a high-energy demand and, as a corollary, high capital and operational costs.

Under normal working conditions, both water and carbon dioxide are produced in large volumes; the process, however, depends upon bacterial growth. As the bacteria die, they form sludge that has to be treated and ultimately disposed of. This sludge has high water content and is often quite difficult to dewater, thus adding considerably to the treatment costs.

In order to assess an effluent's impact on discharge to surface waters or determine the costs of treatment, the oxygen demand needs to be determined. This can be achieved in two different ways:

2.1. Biochemical oxygen demand (BOD_5)

The technique for measuring biochemical oxygen demand (BOD) is complex. Essentially, the effluent sample once shaken is left to stand for one hour so that all settleable solids are excluded from the analysis. The liquor above the precipitate (supernatant) 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 in the dark for five days at 20 ± 1°C. The oxygen dissolved in the water is used by the bacteria while over time the organic matter in the sample is broken down. The oxygen remaining is determined either by means of an oxygen meter or by analysis. The level of oxygen demanded by the effluent can be calculated by comparison to the blank effluent-free samples.

The BOD_5 analysis, generally termed BOD, is widely used to assess the environmental demands of waste water. This method of detection has various weaknesses: the bacterial cultures can vary and the analysis is a highly sensitive process. If the most stringent care is not taken during the preparation and the analysis itself, the results can be misleading.

It should also be remembered that although BOD is a measure of the oxygen requirements of bacteria under controlled conditions, many effluent components take longer than the period of analysis 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 as being 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 residual proteins from hair solubilisation.

This longer breakdown period means that the environmental impact is spread over a larger area as the waste water components are carried greater distances before breaking down.

2.2. Chemical oxygen demand (COD)

This method measures the oxygen required to oxidise the effluent sample wholly. It sets a value for the materials that would normally be digested in the BOD_5 analysis, the longer term biodegradable products, as well as the chemicals that remain unaffected by bacterial activity.

The method is very aggressive. A suitable volume of effluent is boiled with a powerful oxidising agent (potassium dichromate) and sulphuric acid. As the effluent components oxidise, they use oxygen from the potassium dichromate, the amount used being determined by titration.

This method is often favoured 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.

The results are always higher than those obtained using the BOD_5 analysis. As a rule of thumb, the ratio between COD: BOD is 2.5:1, although in untreated effluent samples variations can be found as great as 2:1 and 3:1. This depends on the chemicals used in the different leather making processes and their rate of biodegradability.

It should be noted that both 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. COD determination has almost completely replaced this method.

3. Nitrogen

Nitrogen is contained in several different components in tannery effluent. Sometimes these sources have to be differentiated.

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 deliming materials) and the nitrogen contained in proteinaceous materials (from liming/unhairing operations).

These sources of nitrogen pose two direct problems.

1. Plants require nitrogen in order to grow, but the high levels released by substances containing nitrogen over-stimulate growth. Water-based plants and algae grow too rapidly, whereupon waterways become clogged and flows are impaired. As the plants die, a disproportionately high amount of organic matter has to be broken down. If the load outstrips the natural supply of oxygen from the river, plants, fish and aerobic bacteria die and ultimately anaerobic conditions develop.

2. The nitrogen released through protein breakdown and the deliming process is in the form of ammonia. The latter can be converted by bacteria over several stages into water and nitrogen gas which is ultimately released into the atmosphere. Both of these breakdown products are non-toxic, yet large volumes of oxygen are needed in the process. If oxygen demand is greater than the level supplied naturally by the water course, toxic anaerobic conditions can rapidly develop.

The nitrogenous compounds can be broken down by combining intensive aerobic and anoxic biological treatment. The oxygen demand is very high, thus leading to correspondingly high operational and energy costs. Calculations show that with typical tannery effluent, some 40% of the oxygen requirements are spent on removing the nitrogen component.

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

3.2. Ammonium content as nitrogen (N)

Often confused with TKN, this value is sometimes required in discharge limits and. As ammonium compounds are part of TKN, the problems associated with rapid plant growth and oxygen demand are the same. These compounds are mostly the outcome of the deliming process, with comparatively small volumes being 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 in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide, and the breakdown of hair in the unhairing process.

The sulphides pose many problems:

Under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Characterised by a smell of rotten eggs, a severe odour problem occurs.

Comparable in toxicity to hydrogen cyanide, even a low level of exposure to the gas induces headaches and nausea, as well as possible damage to the eye. At higher levels, death can rapidly set in and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded.

Hydrogen sulphide gas is also fairly soluble. When absorbed, weak acids can form and cause corrosion. This weakens metal roofing, girders and building supports. In sewers, major problems can arise as metal fittings, structural reinforcements and pipework corrode.

If discharged to surface water, even low concentrations pose toxicological hazards. Sulphides can be oxidised into non-toxic compounds by certain bacteria in rivers; however, this creates oxygen demand which, if excessive, can harm aquatic life.

Sulphides in effluent can be determined in several ways. One of the most accurate methods relies on the acidification of suitable quantities of effluent to generate hydrogen sulphide. This is flushed through the apparatus using nitrogen gas, whereafter it is trapped and converted into zinc sulphide. The amount of sulphide is determined by titration.

5. Neutral salts

Two common types of salts are to be found in tannery effluent.

5.1. Sulphates (SO_4^{2-})

Sulphates are a component of tannery effluent, emanating from the use of sulphuric acid or 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, as do many synthetic retanning agents.

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

1. Sulphates cannot be removed completely from a solution by chemical means. Under certain biological conditions, it is possible to remove the sulphate from a solution and bind the sulphur into microorganisms. Generally, however, the sulphate either remains as sulphate or is broken down by anaerobic bacteria to produce malodorous hydrogen sulphide. 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 the corrosion of metal parts, and unless sulphate-resistant concrete will gradually erode.

2. If no breakdown occurs, the risk of increasing the total concentration of salts in the surface water and groundwater runs is incurred.

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

5.2 Chlorides (Cl^-)

Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Considerable quantities of salt are produced by industry and levels can rapidly rise to the maximum level acceptable for drinking water. Increased salt content in groundwater, especially in areas of high industrial density, is now becoming a serious environmental hazard.

Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the eco-system and may ultimately end up in the ground water. High salt contents are only acceptable if the effluents are discharged into tidal/marine environments.

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

Under neutral or alkaline conditions, excess silver nitrate is added. This excess is then determined by retro-titration with potassium thiocyanate, using ferric alum as the indicator.

6. Oils and grease

During leather manufacture, natural oils and grease are released from within the skin structure. If fat liquor exhaustion is poor, some fatty substances may be produced through inter-reaction when waste waters mingle.

Floating grease and fatty particles agglomerate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulgate, they create a very high oxygen demand on account of their bio-degradability.

The presence of oils and grease is 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 until dry. The residual grease can be weighed and calculated.

7. pH value

Acceptable limits for the discharge of waste waters to both surface waters and sewers vary, ranging between from pH 5.5 to 10.0. Although stricter limits are often set, greater tolerance is shown towards higher pH since carbon dioxide from the atmosphere or from biological processes in healthy surface water systems tends to lower pH levels very effectively to neutral conditions. If the surface water pH shifts too far either way from the pH range of 6.5 - 7.5, sensitive fish and plant life are susceptible to loss.

Municipal and common treatment plants prefer discharges to be more alkaline as it reduces the corrosive effect on concrete. Metals tend to remain insoluble and more inert, and hydrogen sulphide evolution is minimised. When biological processes are included as part of the treatment, the pH is lowered to more neutral conditions by carbon dioxide so evolved.

8. Chromium compounds

Metal compounds are not biodegradable. They can thus be regarded as long term environmental features. Since they can also have accumulative properties, they are the subjects of close attention. Two forms of chrome are associated with the tanning industry, whose properties are often confused.

8.1 Chrome 3^+ (trivalent chrome, chrome III)

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the retanning system and is displaced from leathers during retanning and dyeing processes.

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

However, as discussed in section 1.1.b, very fine colloids are also formed which are then stabilised by the chrome - in effect, the protein has been partially tanned. The components are thus highly resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited.

Once successfully broken down, chromium hydroxide precipitates and persists in the eco-system for an extended period of time.

If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, it has a toxic effect upon daphnia, thus disrupting the food chain for fish life and possibly inhibiting photosynthesis.

Chrome levels can be determined in a number of ways. The first stage, however, 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. Where high levels of chrome are expected, iodine/thiosulphate titrations are sometimes used. That technique, however, is inaccurate at low concentrations.

8.2 Chrome 6^+ (hexavalent chrome, chrome VI)

Tannery effluents are unlikely to contain chromium in this form. Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative.

Analysis is highly specialised. The concentrations normally anticipated are very low and analysis is based on colorimetric measurement at 670 nm.

9. Other metals

Other metals which might be discharged from tanneries and whose discharge may be subject to statutory limits include aluminium and zirconium.

Depending on the chemical species, these metals have differing toxicities that are also affected by the presence of other organic matter, complexing agents and the pH of the water. Aluminium, in particular, appears to inhibit the growth of green algae and crustaceans are sensitive to low concentrations. Cadmium, sometimes used in yellow pigments, is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. If present in drinking water, it can induce brittleness in bones (see section 12 below).

10. Solvents

Solvents originate from degreasing and finishing operations. Solvents in effluents discharged to surface waters can form a microfilm on the water surface, thus inhibiting the uptake of oxygen. Solvents break down in a variety of ways; some inhibit bacterial activity and remain in the eco-system for extended periods of time. Analysis is highly specialised.

11. Sampling techniques

The composition of an effluent sample is also dependent upon the sampling technique which, in turn, can have a bearing upon the apparent performance of a tannery against set limits.

Two main sampling methods 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 being taken at hourly intervals and mixed before analysis. If charges are levied for excessive loads, they are normally based on these values.

Where spot samples are taken, allowance is usually made for variation in effluent strength. A 50 per cent increase in strength is often allowed, although this may not apply to all components.

The position of the sampling head is decisive. If it is too low, sludge might be drawn into the sampler. This is also an important factor when spot samples are taken, since they are often taken manually. The sampling point should always be the same so as to reduce variables.

Duplicate samples

When samples are taken by an authority, a duplicate sample should be retained by the tannery. The sample should be shaken before the duplicate is poured; the sample bottle should be clean, filled to the brim, airtight and kept under cold conditions. It is not unknown for samples to be incorrectly identified or mistakes to be made during analysis. Duplication always permits a visual check against the original and provides a chance for a second round of 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. Specific data are in short supply. The lack of specific data is due to the wide variety of aquatic life, the nature of individual components and their degradation rate, either in suspension or as part of a sediment. It is not possible to attain a high degree of specificity for complex and multiple effluent components, whose 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 species. Not every species reacts to the same degree to a given exposure, and the type of response to an equal dose of a chemical may differ widely. When values are given, the species under test should be stated and the time period taken for evaluation should normally be 24 or 96 hours or 14 days.

Environmental quality standards are also used to monitor the protection of aquatic life, based on fate, behaviour and aquatic toxicity. Much of this highly sensitive information is drawn from research data covering a variety of sources and species. Considerable data are often available to facilitate the decision-making process, in their absence, however, conclusions may include expert judgement. Environmental quality standards 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.

The metals that might be present in tannery effluents (viz. chromium, aluminium and perhaps zirconium) are all classified as having a 'high'/'moderately acute' or 'chronic' toxic effect upon organic life and being 'accumulative'. An 'acute' effect may be defined as one that has a specific effect on fish within 96 hours, whereas a 'chronic' effect may need a 21 day test period or even involve complete life cycles, the determination of egg-counts and fertility factors.

The toxicity of many metals also varies according to the pH level, temperature and water hardness. Where Cr^{3+} is concerned, investigations have been performed on fish (unspecified) under conditions of exposure insufficient to cause severe toxicity, yet sufficient to cause visible changes in behaviour. These dosages were 0.2 mg/l. It is understood however, that daphnia are even more susceptible, thus posing a potential hazard to the food chain for fish.

Although not used in leather processing, zinc and copper are described as having a 'high/acute' and 'chronic' toxic effect on aquatic life. The maximum levels are 0.3 mg/l total and 0.04 mg/l (dissolved) respectively as given in the standards set by the E.U in its Fish Directives for salmon. Similar toxicity definitions apply to Cr^{3+}, and it is stated that dosages of 0.2 mg/l induce behavioural change in fish (unspecified). In the absence of more specific data, loadings of this order might be considered 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 set by the E.U in its Fish Directives are presented below:

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

There are no values for sulphides, but their presence is included in the BOD analysis.

13. Direct toxicity assessment

Chemical/biological analyses of the toxicity limits for specific effluent components have served as a basis for determining discharge limits into recipient waters. These techniques, however, cannot always account for:

1. Unexpected toxic effects from the reaction of seemingly innocuous substances upon admixture; and
2. Some substances being toxic to aquatic life at levels too low to be detected by normal methods.

A new technique that departs from the traditional approach is under investigation in the United States and Europe. It 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 conditions near to real life.

Where tannery effluents are discharged directly into sewers, the responsibility for final discharge will be borne by the municipality. Where industrial wastes are directly received into surface waters, however, the industry might be directly affected and investigations might lead to a redefinition of limits at both the 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	BANGLADESH Sewer	BRAZIL Surface	BRAZIL Sewer	CHINA Surface (1997)	CHINA Surface (2000)	CHINA Sewer (Beijing) 1997	CHINA Sewer (Beijing) 2000
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	6.0 - 9.0	6.0-9.0
2. Temperature °C	45	45	45	38	30	30		<40	40			35	35
3. Conductivity μS/cm													
4. Suspended solids mg/l			60	*	70	150	500			200	70 - 150	500	400
5. Settleable solids ml/l	0.5	0.5						1.0				10	10
6. BOD_5 mg O_2/l	50	200	40	*	25		250	60		150	20 - 100	500	600
7. COD mg/l	250	700			200		400			300	100 - 300	500	1000
8. TDS mg/l													
9. Sulphide mg S^{2-}/l		1		1 - 5	0.1	2.0	2.0	0.2	5	1	1	10	10
10. Chrome (III) mg/l									5	1.5	1.5	2.0	2.0
11. Chrome (VI) mg/l					0.1	0.1					0.5	0.5	0.5
12. Chrome total mg/l	0.5	2	0.3	1 - 20	1.0	3.0	2.0	0.5		1.5	1.5		1.5
13. Chlorides mg/l	*	*	*	*									
14. Sulphates mg/l	*	1000		2000		*							
15. Ammonia mg N/l	3	10		100 - 200	15	*		5					
16. TKN 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	20 - 30	100		10 - 15	100	100
19. Phenols mg/l	0.5	0.5	0.05 0.5	100				0.1 - 0.5			0.5	5	2.0
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	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_5 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. TKN 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_5 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. TKN 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	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_5 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. TKN 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	NEPAL	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	6.0-9.0	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	100	80	*
5. Settleable solids ml/l							5.0			
6. BOD$_5$ mg O$_2$/l	40	250	160	160	20	450	200	100	5	*
7. COD mg/l	160	500	160	160				250	*	*
8. TDS mg/l								2100		
9. Sulphide mg S^{2-}/l	1	2	2	2			0.1	2.0	*	*
10. Chrome (III) mg/l		4								1
11. Chrome (VI) mg/l	0.2	0.2					0.1	0.1	none	none
12. Chrome total mg/l	2	4	2	2	1		1.0	2.0	0.05	2
13. Chlorides mg/l	1200	1200				3000		600	200	*
14. Sulphates mg/l	1000	1000				100			150	300
15. Ammonia mg N/l	10 - 15	30				100			*	*
16. TKN 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 Sewer	NICARAGUA Surface	NICARAGUA Sewer	PAKISTAN Surface	PHILIPPINES Marine coastal waters	PHILIPPINES Surface		POLAND SUrface
						Old plants	New plants	
1. pH	6.0 - 9.0	6 - 9	6 - 10	6 - 9	6-9	5.0-9.0	6.0-9.0	6.5 - 9.0
2. Temperature °C	55		50	40				35
3. Conductivity µS/cm								
4. Suspended solids mg/l		150	400	200	200	200	150	35
5. Settleable solids ml/l		5						
6. BOD$_5$ mg O$_2$/l		120	400	80	120	150	120	30
7. COD mg/l		250	900	150	250	250	200	150
8. TDS mg/l			1500			2000	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		0.5			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. TKN mg N/l								30
17. Phosphorus mg P/l								5
18. Oil/grease mg/l		30	150	10	15			50
19. Phenols mg/l		0.1	1	0.3				0.5
20. Detergents mg/l			10					10n.i+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 Serwer	SPAIN Surface	SPAIN Sewer	SRI LANKA Surface	SRI LANKA Sewer	SWITZERLAND Surface	SWITZERLAND Sewer	TANZANIA Surface
1. pH	5.5 - 9.5	5.5 - 12.0	5.5 - 9.5	8 - 10	5.5 - 9.0	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	150	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	100	20		30
7. COD mg/l	30	2000-5000	160 - 500	1500 - 2500	250	300			
8. TDS mg/l									
9. Sulphide mg S^{2-}/l	1	5-50	1 - 2	1 - 20	2.0	5.0	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	0.5	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	20.0	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. TKN 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	5.0	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	TUNISIA Surface	TUNISIA Sewer	TUTKEY Surface	TURKEY Sewer	UGANDA Surface	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$_5$ 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. TKN 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
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									4300
4. Suspended solids mg/l	150		60		60	400	100	200	100
5. Settleable solids mg/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. TKN 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. TKN 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.