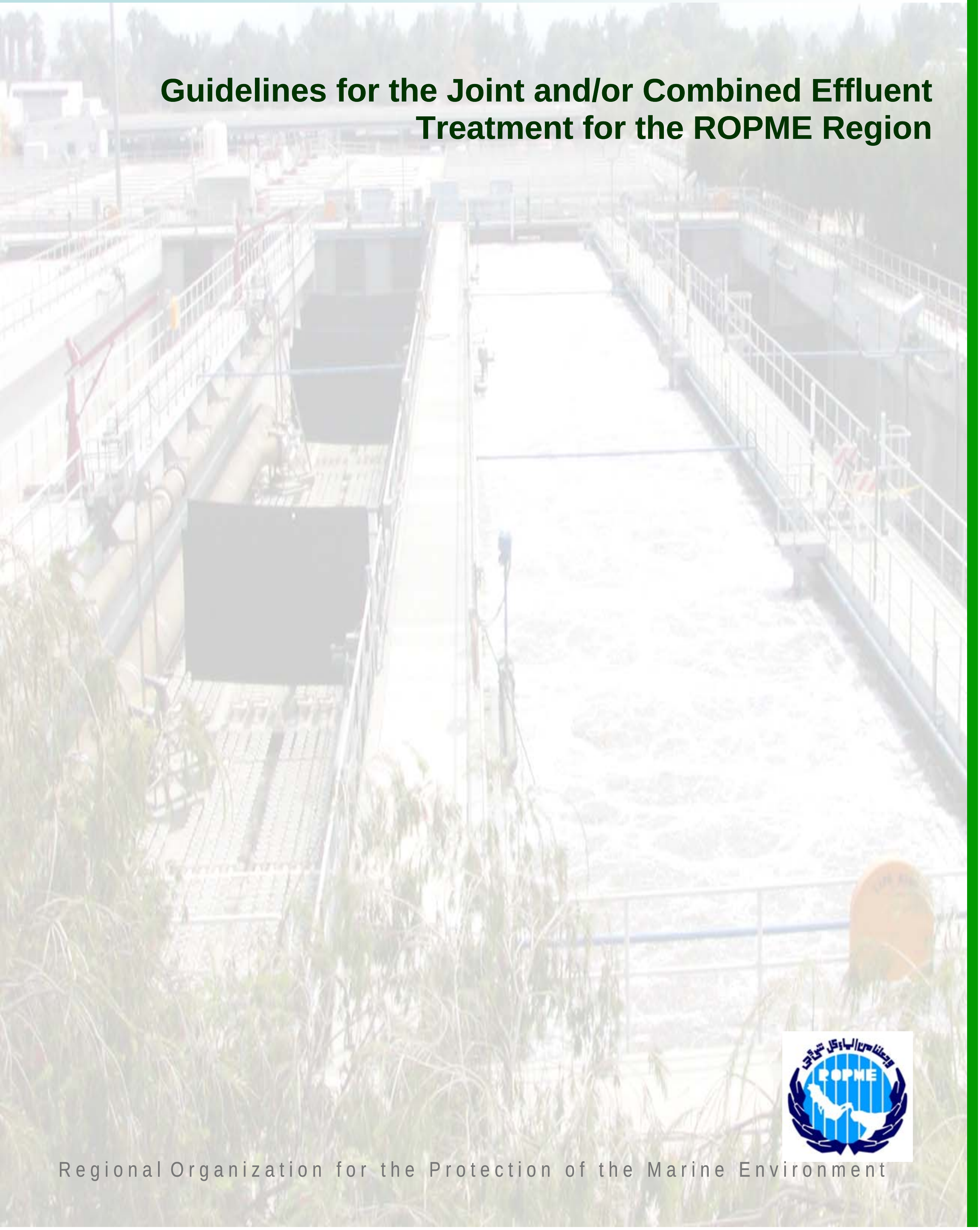
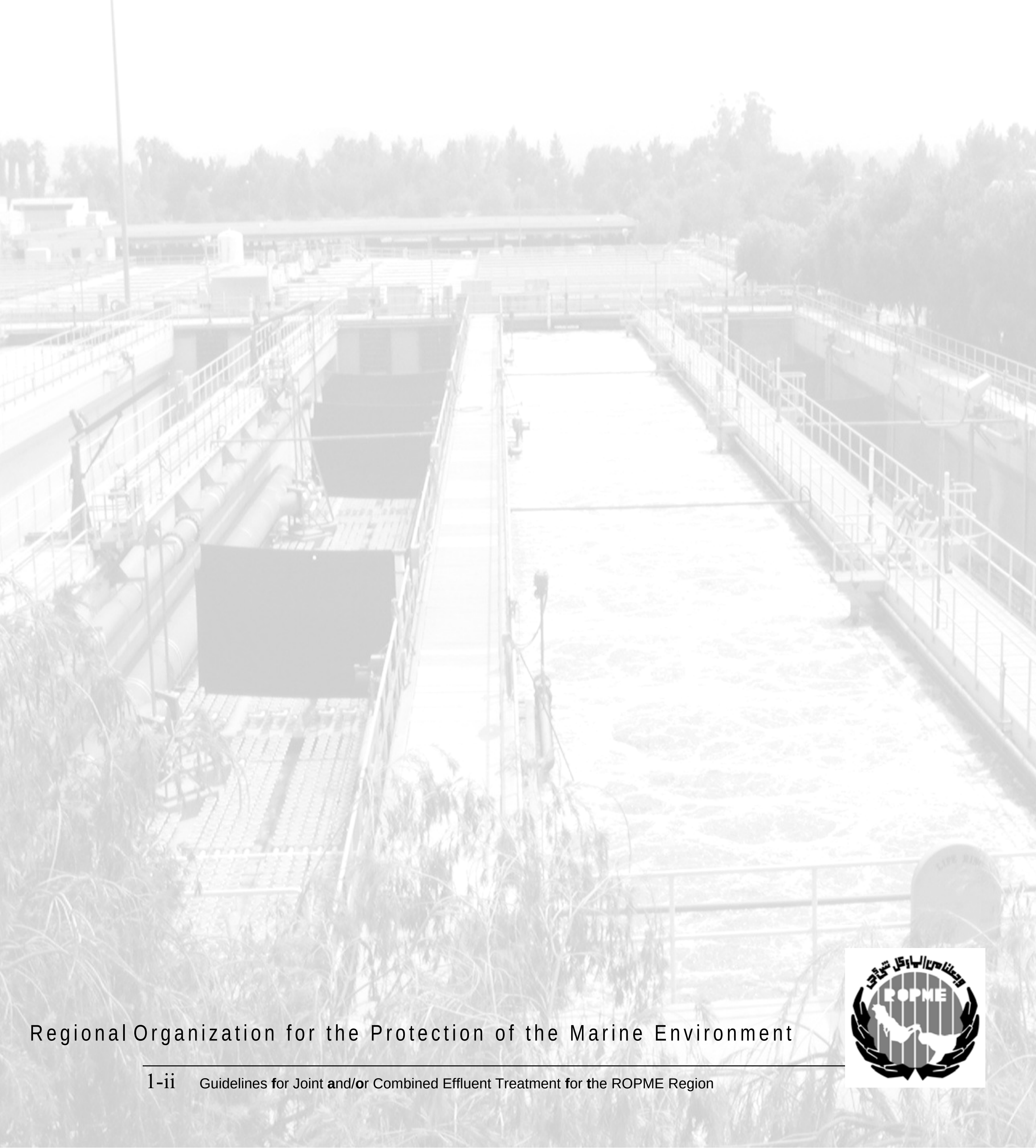
Guidelines for the Joint and/or Combined Effluent Treatment for the ROPME Region



Regional Organization for the Protection of the Marine Environment

First Draft. 2005

Guidelines for the Joint and/or Combined Effluent Treatment for the ROPME Region



Regional Organization for the Protection of the Marine Environment

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Foreword

Of the many critical approaches to protecting the marine environment, judicious management of effluents from land-based activities is an important aspect of high priority. In the ROPME Sea Area (RSA), the closed nature of the marine environment poses natural restriction to circulation, which in turn simulates an amplified effect of pollutants on the biota by longer time of residence. Thus, it is imperative that we evolve context specific guidelines for the discharge of land-based effluents into the coastal waters and develop appropriate methods of waste treatment that would minimize pollution and environmental degradation. ROPME is constantly reminded of the grim scenarios that may emerge if the discharges from land-based activities into the RSA are not properly regulated. This has been the background to the efforts made by ROPME in the recent times to collect and collate the essential information on LBA for the management of discharges into the coastal waters as a first step towards mitigation of emerging problems. This document on guidelines epitomizes our collective efforts.

ROPME received generous support from UNEP/GPA in this important endeavour and a Memorandum of Understanding between our institutions guided the activities leading to the document. Under the provisions of the Memorandum, ROPME enlisted the services of a project consultant, Mr. Dimitrios Tsotsos, who completed the difficult task of compiling the text of the draft 'Guidelines' within a short time. A meeting was held in Doha, Qatar during late June 2005 to discuss in detail the draft guidelines and I acknowledge the guidance provided by the representatives of Member States and the inclusions they suggested. With all these, I sincerely hope that the serious and genuine attempt on behalf of ROPME and UNEP/GPA would be considered a landmark and a new beginning on the path of environmental protection in the Region.

ROPME hopes to receive constructive feedback from Member States and other concerned entities on the document, enabling timely revision and further development of the guidelines in the efforts towards mitigating the avoidable negative effects of land-based activities.

Dr. Abdul Rahman Al-Awadi
Executive Secretary, ROPME

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1. INTRODUCTION

1.1 Scope of the document

The scope of this document is to present collected and evaluated information about issues concerning the joint and/or combined treatment of municipal and industrial effluents in a way, which will help its users to assess the various options needed for taking practical and realistic measures for the effective control of these wastewaters.

As a matter of fact, industrial wastewaters have to be adequately treated for two reasons namely a) to maintain the quality of the water recipient when they are directly discharged into water bodies and b) to protect the municipal wastewater collection and treatment facilities in cases of industrial effluent discharges into the municipal sewer. Although the first reason seems understandable and asks for full treatment efficiencies, the second is frequently underestimated assuming that the municipal wastewater treatment plants can cope with the additional quantities to be treated without severe implications.

According to the Protocol for the Protection of the Marine Environment against Pollution from Land Based Sources of the Kuwait Convention (Appendix I), the terms combined and joint treatment are defined as follows (Article I):

- **"combined treatment"** means common treatment of industrial effluents along with domestic sewage
- **"joint pretreatment/treatment"** means common pretreatment/treatment of the effluent from more than one industrial source.

In the same Protocol (Article V) it is pointed out that the whole issue of combined/joint treatment is of vital importance for the industrial development in the ROPME Region especially for the promotion of the activities of Small/Medium sized industrial Enterprises (SMEs), which should not be faced with insuperable obstacles for meeting the relevant environmental standards. Within this context and having in mind the limited available resources of SMEs, agglomeration of industries in a way that enhances the possibility of joint effluent pretreatment and/or treatment and the location within the limits of city's sewer systems of certain types of industry so as to enhance combined treatment of industrial and domestic wastes are the main options to be considered during the decision making process.

In order to come to practical suggestions about how combined and joint treatment can be implemented, an insight into some important aspects of the management of industrial effluents is needed so that the most appropriate types of industrial activities can be grouped according to common characteristics needed for the relevant treatment systems. These aspects are twofold namely the nature of the effluents themselves (i.e. parameters) and the suitable wastewater treatment methods for each case.

This document will not deal with any issues relevant to the final discharge of treated effluents into water recipients, which is beyond its scope. It will only describe aspects of pretreatment of industrial wastewaters from SMEs needed for combined treatment as well as how several industrial facilities can cope with a common treatment system for their effluents.

1.2 Target groups

The target groups of this document are:

decision makers/planners at central/national level, who are responsible to develop the policy and the prescriptions needed for industrial pollution control
regional authorities responsible for the implementation of the environmental policy at local level
inspectors responsible for effluent monitoring
operators of treatment plants, who will become acquainted with the requirements needed for the smooth operation of their plants
industrial managers of SMEs, who have to comply with the set effluent standards.

1.3 Structure of the document

In order to evaluate all aspects relevant to the selection of the two main treatment options (i.e. combined municipal/industrial wastewater treatment, joint treatment of industrial effluents), it is important to assess the whole set of information regarding industrial wastewater treatment, namely, which kind of industries (e.g. SMEs) can be connected with municipal wastewater treatment facilities, how and to which extent industrial effluents have to be treated before being connected with municipal sewers, which problems can be caused by certain parameters etc. The possibility of joint effluent pretreatment and/or treatment from SMEs is also elaborated.

This document attempts to highlight these issues by providing information about types of **industrial effluents** to be treated and of the relevant **pollutants (Chapter 2).** In **Chapter 3**, the various treatment processes for the main pollutants are presented. **Chapter 4** deals with important aspects associated with **combined treatment** namely **pretreatment standards, setting up the relevant programs** etc. The alternative of **joint treatment** of effluents originating from several industrial activities is described in **Chapter 5.**

There are also four Appendices to the document, with Appendix IV on pre-treatment standards for the discharge of industrial effluents into municipal sewers of some ROPME Member States.

2. INDUSTRIAL WASTEWATERS

2.1 Major industrial activities – effluents

There are several industrial activities, which are of particular concern when we consider the impacts of their effluents on the marine environment or on the proper functioning of biological treatment plants. The relevant parameters contained in industrial effluents can be classified as follows (Table 2.1):

Table 2.1 Contaminants of industrial wastewaters

Nature of contaminant	Contaminant	Potential effect(s)
Physical	Suspended solids	Lead to development of sludge deposits & anaerobic conditions, mechanical problems (clogging)
	Settleable solids	
Chemical	Biodegradable organics	Lead to depletion of oxygen and the development of septic conditions
	Nutrients (compounds of nitrogen & phosphorous)	Eutrophication
	Surfactants, POPs (e.g. phenols, pesticides etc.)	Adverse effect on aquatic life & on biological treatment methods, contamination of sewage sludge for final disposal
	Heavy metals	Adverse effect on aquatic life & on biological treatment methods, contamination of sewage sludge for final disposal
	Dissolved inorganic solids	To be removed if wastewater has to be reused
	Acids, dyes	Corrosion of pipelines & inhibition of biological treatment processes

Source:

- The wastewater treatment handbook, Commission of the European Communities, DG for Regional Policies – DG for the Environment (produced by AMBER)
- ROPME expert meeting on technical guidelines for the management of land-based activities (Qatar, 25-27.6.05)

Concerning the main issue to be tackled here, namely the protection of the biological processes of the treatment plants and of the sewage collection pipelines, the contaminants of concern are:

- suspended/settleable solids
- surfactants, phenols, pesticides
- heavy metals
- acids, dyes

In more details, Table 2.2 gives an overview of the main industrial activities and the relevant key polluting parameters contained in their effluents.

Table 2.2 Characteristics of industrial effluents

Industrial activity	Waste characteristics	Parameters of concern
Canned/preserved seafood	Protein, fats, organics, odor	BOD, COD, TSS, oil & grease
Canned/preserved fruits & vegetables	SS, colloidal/dissolved organics	BOD
Diary products	Dissolved organics, fats, lactose	BOD, COD, TSS, TDS, pH
Brewery	Dissolved organic solids, fermented starches	BOD
Meat and poultry products	Dissolved and suspended organics, proteins, fats	BOD, COD, TDS, oil & grease
Animal feedlots	Organic suspended solids	BOD, COD, color, oil & grease
Sugar beet	Dissolved/suspended organics	BOD, COD, TSS, TDS
Pharmaceutical products	Suspended & dissolved organics incl. vitamins	BOD, TSS, TDS
Coffee production	Organics	BOD, TSS
Grain mills	Organics, solids	BOD, COD, TSS, pH, P
Soft drinks	Suspended solids, organics	BOD, COD, TSS, pH
Textiles	Highly alkaline, colored, high temperature	BOD, COD, TSS, pH, Cr, Zn, toxic organics
Tanneries	High total solids, salt, lime, chromium, sulfides	BOD, COD, TSS, Cr, sulfides
Pulp & paper	Organics, high colloidal suspended and dissolved solids, color	BOD, TSS, pH, color
Photographic products	Alkaline, organic/inorganic reducing agents	Metals, CN^-
Steel	Acids, phenols, oils, fine suspended matter	BOD, CN^-, Pb, Zn, sulfides
Non-ferrous metals	Metals, acids, slag, lime sludge	TDS, TSS, pH, F, Cu, Pb, Zn, Cd, As, Se
Metal plated products	Acids, metals, toxic materials	TSS, pH, CN^-, P, F, Cr, Cu, Pb, Zn, Cd, Fe, Ni

Industrial activity	Waste characteristics	Parameters of concern
Oil refineries	Dissolved salts, high organics, odor, sulfur compounds, hydrocarbons	BOD, COD, NH_3, Zn, Pb, phenols, oil & grease, PAH, sulfides
Petrochemicals	Organic compounds, acids	BOD, COD, oil & grease, PAH, pH, phenols, urea
Rubber production	High suspended, chlorides	BOD, COD, TSS, Pb, Zn
Glass	Color, suspended solids	BOD, COD, TSS, pH, phenols
Glue manufacture	Mineral acids, organics	BOD, COD, pH, Cr, phenols
Candle manufacture	Fatty acids	BOD, COD, TDS
Paints & inks	Dissolved organics, metals, oils	BOD, COD, TSS, TDS, pH, Cr, Cu, Pb, Zn, Cd, Fe
Fertilizers	Clays, slimes, acid wastes	TSS, pH, P, NH_3, F, K
Explosives	TNT, acids, metals, oils	COD, NH_3
Pesticides	High organic matter, toxics, acids	BOD, COD, toxic organics
Plastics & resins	Acids, caustic, nitrogenous compounds, phenols, formaldehyde	BOD, COD, TSS, TDS, pH, F, Cr, phenols
Steam power	High volumes, high temperature, inorganic & dissolved solids	TSS, pH, Cr, Cu, Zn, Fe, phenols
Coal processing	Suspended solids, acid, sulfuric acid	COD, TSS, pH, SO_4^{--}
Soap & detergents	Organic& saponified soaps	BOD, COD, TSS, TDS, oil & grease

Source:

- Code of practice for environmentally sound management of liquid waste discharge in the Mediterranean Sea, UNEP/MAP – PAP/RAC, 1990
- ROPME expert meeting on technical guidelines for the management of land-based activities (Qatar, 25-27.6.05)

2.2 Assessment of pollution loads

The collection of data of initial pollution loads for any industrial production process is usually based on the **calculation** of waste quantities by applying **emission factors** specific for each industrial branch and on the **monitoring results** of each waste stream within the factory. Both methods have their own benefits and problems and have to be carefully applied, in order to come to reliable results.

2.2.1 Emission factors

Emission factors are the waste quantities generated per specific production process expressed in tons of waste parameters per ton of raw material used for the manufacture of a specific product (e.g. tons BOD_5/ton of raw hides in a tanning process).

The general methodology employed to estimate releases/emissions associated with each industrial process involves the knowledge of production data at the activity level, i.e. amount of material produced or consumed and an associated emission factor per unit of consumption/production according to the following method:

$TOTAL_{ij} = A_j \times EF_{ij}$
Where:

$TOTAL_{ij}$ = process emission (Kg/year) of pollutant i from industrial sector j

A_j = amount of activity or production unit of process material in industrial sector j (tons/year)

EF_{ij} = emission factor associated with pollutant i per unit of production in industrial sector j (Kg/ton)

Emission factors can be calculated by analyzing the production process of a specific industrial plan. The in-depth analysis of the production process determines the level of accuracy of the derived emission factors and consequently the reliability of the figures of the calculated waste quantities. This analysis should be based on the estimation and measurement of inputs and outputs of raw materials, products, water, energy and waste emissions for each industrial production unit, so that a reliable correlation of waste quantities with production data can be made.

Having applied the emission factors for one industrial activity, the waste quantities generated can be estimated. This is the starting point – baseline for taking any decision about pollution reduction and treatment options. In Appendix II the relevant waste factors for various industrial activities are presented.

A common mistake made by applying this method is the adoption of emission factors produced elsewhere without verification with the prevailing actual conditions of a specific case. For example, process water consumption differs substantially in the same industrial process in various countries according to the abundance or scarcity of water resources, therefore wastewater quantities per production unit expressed as m^3/ton of raw material and published in the literature should not be adopted without in-plant tests for the actual cases. Therefore it must be underlined that the default emission factors should be considered as a starting point from which countries can develop their own national assumptions and data. Indeed, national assumptions and data are always preferred because the default assumptions and data may not always be appropriate for specific national contexts.

Example of application of waste factors

Two textile plants

The plant **TEX1** is a manufacturing plant only (cotton) with a production of 10,000 Kg of cotton/day. The plant **TEX2** is a finishing/dyeing plant (acrylic/wool) with a production of 7,000 Kg wool and 18,000 Kg acrylic per day. Both textile plants operate for 280 days per year.

BOD_5 –load calculation

According to Appendix II, the BOD_5 emission factor (cotton, no dyeing) is 23 kg $BOD_5/10^3$ kg fabric, for the bleaching operation 10 kg $BOD_5/10^3$ kg fabric, for wool dyeing 21 kg BOD_5/kg fabric, for acrylic finishing 60 kg BOD_5/kg fabric and for acrylic dyeing 26 kg BOD_5/kg fabric. Therefore the total BOD_5 load is as follows:

TEX1 (cotton, no dyeing):

Washing and wetting 10,000 Kg/day fabric X 23 Kg $BOD_5/10^3$ Kg fabric = **230 Kg BOD_5**
Bleaching 10,000 Kg/day fabric X 10 Kg $BOD_5/10^3$ Kg fabric = **100 Kg BOD_5**

TOTAL BOD_5 of TEX1 = 230 + 100 = 330 Kg BOD_5/day and if the water consumption for the 2 unit operations of this plant is 100 m^3/day, then the assumed final BOD_5 concentration (before any treatment) for the 2 operations is 330,000,000 mg BOD_5/100,000 liters = 3300 mg/l

330 Kg BOD_5 X 280 days/year = 92,400 Kg / year

TEX2 (wool / acrylic, finishing, dyeing):

Wool

Dyeing 7,000 Kg fabric/day X 21 Kg $BOD_5/10^3$ Kg fabric = 147 Kg BOD_5

Acrylic

Finishing 18,000 Kg/day fabric X 60 Kg $BOD_5/10^3$ Kg fabric = 1,800 Kg BOD_5

Dyeing 18,000 Kg/day fabric X 26 Kg $BOD_5/10^3$ Kg fabric = 468 Kg BOD_5

TOTAL BOD_5 of TEX2 = 147 + 1,800 + 468 = 2,415 Kg BOD_5

If the water consumption of these unit operations is 250 m^3/day, then the assumed final BOD_5 concentration is 2,415,000,000 mg BOD_5/250,000 liters = 9660 mg/l

2,415 Kg BOD_5 X 280 days/year = 676,200 Kg / year

2.2.2 Monitoring

Monitoring of industrial effluents usually occurs in 2 ways:
- in-plant/self monitoring by the industry
- monitoring by the authorities

Authorities take effluent samples from the final sewer well where the effluents are discharged either to municipal sewer or to water recipients, as part of their controlling function. Therefore the authorities' controlling function does not help very much in the self-evaluation of the industry concerning its pollution loads, since, in order to comply with the effluent regulations, it has to have met the relevant requirements before the visit of the controlling inspectors.

Concerning in-plant/self monitoring and in order to come to reliable results (i.e. assessment of the initial pollution loads), all waste streams in a production unit must be segregated and separately measured. This is rather complicated and time/resource consuming and has to be done just for the estimation of the emission factors (see § 2.2.1). Usually all separate wastewater streams are combined and discharged either to the facility's own treatment plant or to the municipal sewer according to set pre-treatment standards.

3. TREATMENT METHODS FOR INDUSTRIAL WASTEWATERS

3.1 Introduction

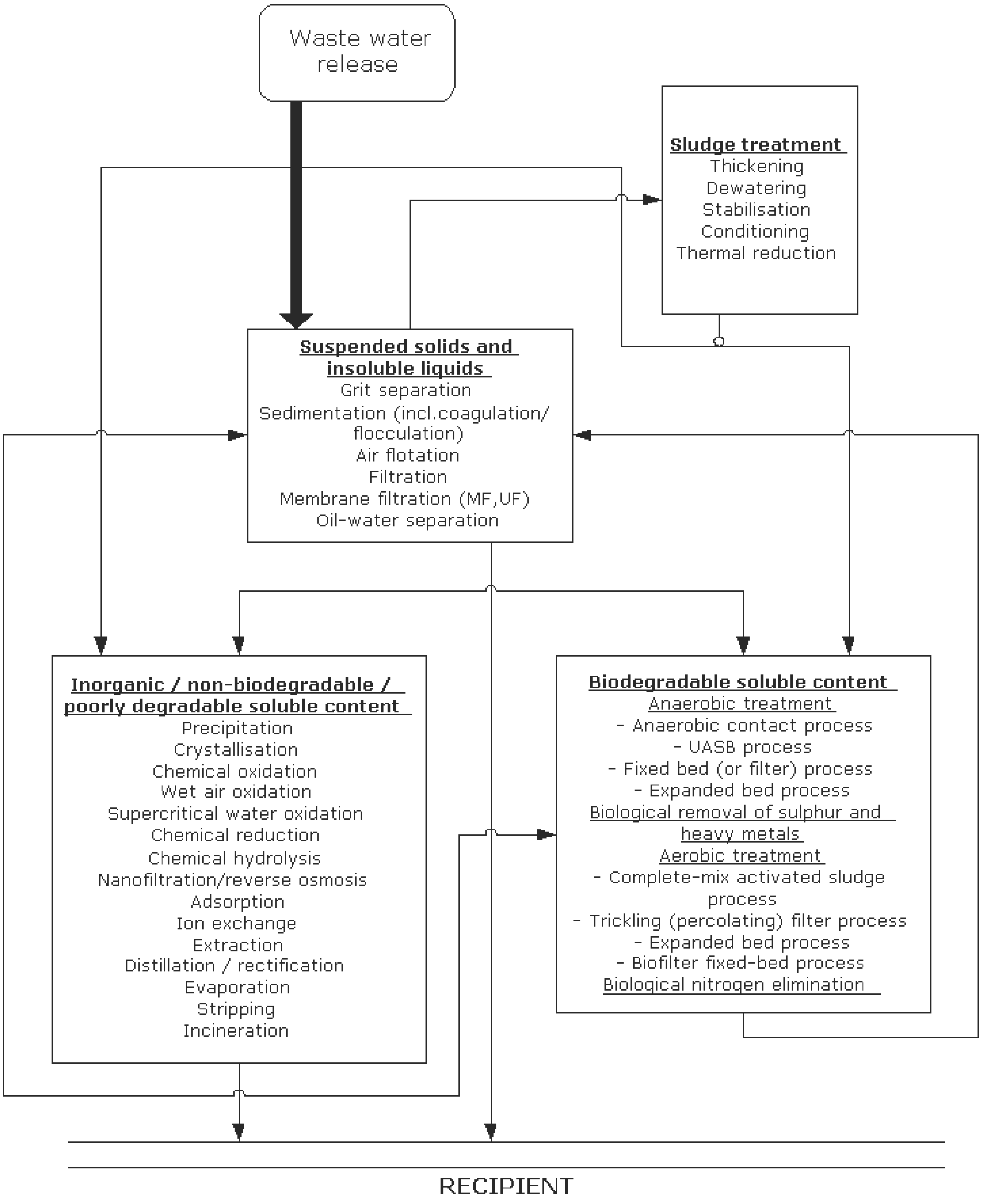
There are 2 major types of industrial effluents, which are to be treated, namely, those of organic composition, which can be accepted by Municipal Wastewater Treatment Plants (MWTP) and those having non-organic toxic compounds. The latter can seriously affect the treatment plant's operation and the life-time of the sewage collection pipelines (see § 4.2.1).

There are various techniques for the removal of chemical substances from industrial waste streams, which will be briefly analyzed in this chapter. These techniques are to provide essential pretreatment in each industrial plant having the same kind of pollutants before the relevant effluents can be discharged into the municipal sewer system. These pretreatment requirements are usually met by physical-chemical and biological processes.

Physical treatment methods consist of processes such as membrane technologies, carbon adsorption, distillation, filtration, ion exchange, oil and grease skimming, oil/water separation, sedimentation, steam stripping and solvent extraction. Chemical treatment methods include chemical oxidation, chemical precipitation, chromium reduction, coagulation, cyanide destruction, dissolved air flotation, electrochemical oxidation, flocculation, hydrolysis, and neutralization (pH control). Biological treatment methods include biological nitrogen removal, activated sludge, extended aeration, anaerobic processes, rotating biological contactors and trickling filters.

This chapter deals explicitly with those methods, which are suitable for the removal of industrial pollutants applied either as pretreatment methods (i.e. before their discharge into a MWTP) on-site or as end-of-pipe systems in centralized wastewater treatment plants (CWTP) where joint treatment of effluents from more than 1 industrial source is the selected option. Biological treatment methods, which are applicable for organic pollutants are not dealt here since they are similar to those ones applied for municipal wastewaters. In Figure 3.1 wastewater techniques in relation to type of contaminants are schematically presented.

Figure 3.1 Wastewater treatment techniques in relation to types of contaminants



Source: European Commission, Reference Document on Best Available Techniques in common wastewater and waste gas treatment/management systems in the chemical sector, 2003

3.2 Treatment processes for industrial effluents

3.2.1 Industrial pollutants

Each industrial activity has its own production characteristics, which, besides the generation of various effluents/pollutants, are associated with the actual conditions of the production processes. These conditions are either the use of large water quantities or the intermittent (batch) operation of some unit operations, which generate sudden loads of wastewaters to be discharged to a treatment plant. In Table 3.1 these characteristics and the suggested treatment practices are summarized.

Table 3.1 Treatment methods for selected industries

Industrial activity	Flow characteristics	Main contaminants	Typical treatment
Meat products	intermittent	BOD, COD, TSS, TDS, chlorine demand, color, coliforms, oil and grease organic nitrogen	Screening, oil and grease removal, equalization
Dairy products (milk handling and milk products)	intermittent/continuous	BOD, COD, TDS, grit, chlorine demand, color, alkalinity, turbidity, detergents, coliforms	Oil and grease removal, equalization and neutralization
Cotton and synthetics .	Intermittent/continuous	BOD, COD, TSS, TDS, chlorine demand, color, alkalinity, detergents, heavy metals, phosphorus	Coarse solid separation, chemical precipitation, equalization, neutralization
Chrome tanning and finishing	intermittent	BOD, COD, TSS, TDS, grit acidity/alkalinity, heavy metals, oil and grease	Grit removal, equalization, chemical precipitation, neutralization

Industrial activity	Flow characteristics	Main contaminants	Typical treatment
Vegetable tanning	intermittent	BOD, COD, TSS, TDS, grit, oil and grease, acidity/alkalinity	Coarse solid separation, grit removal, equalization, neutralization
Petroleum refining	continuous	BOD, COD, TSS, grit, heavy metals, oil and grease, phenols, cyanides, sulphides	Oil separation, equalization, chemical coagulation, dissolved air flotation
Metal finishing	intermittent/continuous	TDS, cyanide, ammonia, hexavalent chromium, heavy metals, acidity/alkalinity	equalization, neutralization, cyanide removal, chromium reduction, chemical precipitation, solids separation
Pulp and paper	continuous	BOD, COD, TSS, TDS, chlorine demand, heavy metals, acidity	Grit removal, coarse solids separation, neutralization

Source: UNEP/MAP, Guidelines for authorizations for the discharge of liquid wastes into the Mediterranean Sea, Technical Reports Series No. 107, 1996

3.2.2 Industrial wastewater treatment processes

Physical processes
Screening: removal of coarse solids by use of a straining device
Sedimentation: gravity settling of pollutants out of the wastewater
Flotation: use of small gas bubbles injected into the wastewater which causes pollutant particles in the wastewater to rise to the surface for subsequent removal
Air stripping: removal of volatile and semi-volatile organic compounds from wastewater by use of air flow
Equalization: collection of waste streams from various intermittent discharging points and maintenance of constant hydraulic velocity

Chemical processes
Neutralization: adjustment of alkalinity and acidity to the same concentration (pH 7)

Coagulation/Precipitation: addition of chemicals to wastewater to change the chemical composition of pollutants so that the newly formed compounds settle out during sedimentation
Adsorption: use of a chemical which causes certain pollutants to adhere to its surface
Disinfection: use of a chemical (or other method such as ultraviolet radiation) to selectively destroy disease-causing organisms
Breakpoint chlorination: addition of chlorine to the level that chloramines will be oxidized to nitrous oxide and nitrogen, and chlorine will be reduced to chloride ions.

3.2.3 Specific pollutants and relevant treatment processes

Each pollutant can be removed by applying one or a combination of treatment methods according to the various requirements set by the regulating authorities. They can be applied at pretreatment stage, either in case of subsequent discharge into a municipal sewer or if there is a necessity of their removal before their discharge into a centralized industrial wastewater treatment plant (joint treatment).

Arsenic
Sulphide precipitation, co-precipitation with iron or aluminum hydroxide, activated carbon adsorption, ion exchange.

Barium
Chemical precipitation as sulphate or as barium carbonate

Cadmium
Sulfide or hydroxide precipitation, ion exchange, electrolysis, ion flotation, electrodialysis, reverse osmosis, liquid-liquid extraction, activated carbon adsorption. These removal methods are essentially those employed for most heavy metals wastes encountered in the plating and metal processing industries.

Chromium
Chemical precipitation and ion exchange. If chromium is at hexavalent state it is reduced to trivalent state by the use of a reducing agent (sulphur dioxide) at pH=3. Activated carbon is used for the removal of hexavalent chromium .

Copper
Chemical precipitation as hydroxide, ion exchange, evaporation, electrolysis, recovery by evaporation (to obtain water suitable for re-use in plating baths in the metal processing industry). Other processes are reverse osmosis and activated carbon.

Lead
Chemical precipitation (carbonate or hydroxide), ion exchange

Mercury
Precipitation, ion exchange, activated carbon adsorption, coagulation, reduction of ionic mercury to elemental form and removal by filtration. The selection depends upon the chemical nature and initial concentration of mercury, the presence of other constituents in the wastewater that may interfere with that specific treatment, and the degree of mercury removal that must be achieved. Ion exchange seems to be effective for the removal of inorganic mercury down to levels of 1 to 5 µg/l. Organic and

inorganic mercury can be removed from wide variety wastewaters with the use of flocculants such as alum, iron salts and lime.

Nickel
Precipitation, ion exchange, evaporative recovery, reverse osmosis.

Zinc
Precipitation, ion exchange, evaporative recovery, reverse osmosis.

Crude oils and hydrocarbons of petroleum origin
API separator, cyclone oil/water separation, air flotation, chemical coagulation, granular media filtration

Cyanides
Chlorination, electrolytic decomposition, ozone oxidation, evaporative recovery, reverse osmosis, ion exchange, catalytic and thermal oxidation.

Phosphate compounds
Chemical precipitation with iron and aluminum salts as well as hydrated lime

Phenols
Biological treatment (when the concentrations are not so great as to cause toxic phenomena in bacterial flora), activated carbon adsorption.

In Table 3.2 a summary of the treatment processes is presented. In chapter 5 (§ 5.3.) some operational details for the most important treatment methods are presented.

Table 3.2 Industrial treatment processes

Pollutant	Processes	Removal (%)
As	sulphide precipitation chemical precipitation activated carbon adsorption ion exchange	
Ba	chemical precipitation	90-99
Cd	chemical precipitation ion exchange electrolysis air flotation electrodialysis reverse osmosis liquid-liquid extraction activated carbon adsorption	90-99
Cr	chemical precipitation ion exchange	55-99

Pollutant	Processes	Removal (%)
Cu	chemical precipitation ion exchange evaporation electrolysis recovery by evaporation reverse osmosis activated carbon	95-99
Pb	chemical precipitation ion exchange	90-99
Hg	Precipitation ion exchange activated carbon adsorption coagulation reduction of ionic mercury to elemental form and filtration	70
Ni	Precipitation ion exchange evaporative recovery reverse osmosis.	N/A*
Zn	Precipitation ion exchange evaporative recovery reverse osmosis	95-97
Crude oils/hydrocarbons	API separator air flotation chemical coagulation	60-99 70-95
CN	chlorination electrolytic decomposition ozone oxidation evaporative recovery reverse osmosis ion exchange catalytic/thermal oxidation	93-99 (chlorination)
Phosphates	chemical precipitation	95
Phenols	activated carbon adsorption biological treatment	N/A*

* N/A = not available

Source:

- UNEP/MAP, Guidelines for treatment of effluents prior to discharge into the Mediterranean Sea, Technical Reports Series No. 111, 1996
- European Commission, Reference Document on Best Available Techniques in common wastewater and waste gas treatment/management systems in the chemical sector, 2003

4. COMBINED TREATMENT

4.1 Introduction

Household wastes show little variation from one day to the next, at least in comparison to industrial wastewater, so that municipal wastewater treatment plants (MWTP) can be designed on the basis of a rather constant daily flow. Some industrial waste is similar to domestic waste: for example, the food and paper industries have waste streams that consist primarily of organic compounds. Thus many industrial wastes can potentially be discharged into and treated in these plants. However, some parameters contained in industrial effluents can also cause serious problems for MWTPs. In Table 4.1 the risks associated with combined treatment of industrial and municipal wastewaters are presented.

Table 4.1 Risks of combined treatment

Disturbance	Risk	Effect
Mixed drainage (rain/ effluents)	Hydraulic overload	Increased pollutant discharge, loss of activated sludge bacteria
Discharge of chemicals in increased quantities	Collapse of nitrification stage	Several weeks needed for restoration
Discharge of persistent contaminants	To be diluted in the MWTP	Discharged into receiving waters without degradation, adsorbed in sludge, stripped into atmosphere during aeration
Discharge of cooling waters	Dilution of waste streams	Increased costs of treatment

Therefore, the combined treatment of municipal and industrial effluents can be achieved only if their composition is similar to each other. That means that only those industries generating organic pollutants can be connected to municipal sewers. However, even in that case, very concentrated effluents (i.e. high BOD levels) in large quantities (e.g. from large food processing industries) are not always acceptable by MWTP operators, since they can change the overall balance of the incoming BOD-quantities. The latter applies also for very large wastewater quantities (e.g. cooling water) as it is said above.

In this chapter, a general overview of pretreatment requirements is presented, in order to allow industrial managers and inspecting authorities to understand the nature of the issue and to be informed about the various pretreatment standards.

4.2 Pretreatment programs

4.2.1 Scope

Pretreatment of industrial wastewaters is a means to manage toxic contaminants in treated wastewater effluents and sludge residuals before their discharge into a municipal sewer. It is defined as **the removal of toxic materials at the industrial plant before the wastewater is released to the municipal sewer.** Because industrial activity is a substantial source of toxic chemicals in sludge and reclaimed wastewater in populated areas, pretreatment programs have been effective in reducing the concentrations of most heavy metals in wastewater, which is discharged into municipal sewers and consequently in the final effluents and the sludge.

As a general framework, the scope of pretreatment of industrial effluents is:

A. To prevent the introduction of pollutants into the treatment works which will interfere with the operation of the treatment works or contaminate the resulting sludge
B. To prevent the introduction of pollutants into the treatment works, which will pass through the treatment works or otherwise be incompatible with the treatment works and finally will reach the water recipient causing adverse effects
C. To avoid adverse impacts on the material of the wastewater collection pipelines such as corrosion and deposition of settleable heavy metals
D. To improve the opportunity to recycle and reclaim municipal and industrial wastewaters and sludge from the treatment works
E. To ensure that the quality of the treatment plant sludge is maintained at a level, which allows its use and disposal in compliance with applicable statutes and regulations, including composting for land application
F. To protect the treatment work's personnel who may be affected by toxic wastewater and sludge components in the course of their employment, as well as to protect the general public
G. To provide for fees for the equitable distribution of the cost of operation and maintenance of the treatment works.

Besides the obligation of industrial facilities to meet pretreatment standards for the MWTP's protection, there are some explicit advantages for applying pretreatment schemes before the final discharge of the effluents into the MWTP, namely:

- the operators of the various industrial installations show a more responsible attitude for individual waste stream management and treatment, since they are directly responsible for the quality of their own waste streams
- more flexibility for works enlargement or for reacting to changing conditions

- pretreatment facilities at source are tailor-made and thus show better performance to the actual prevailing conditions
- avoidance of dilution by mixing different waste streams thus resulting in a higher and cost effective treatment efficiency.

Therefore the effectiveness of the pretreatment schemes is interesting both for the individual industrial installations as well as for the MWTP managers.

4.2.2 Pollutants subject to pretreatment

4.2.2.1 Types of pollutants

Conventional and toxic pollutants describe two broad categories of contaminants in wastewaters. Conventional pollutants are contained in the sanitary wastes of households, commercial establishments and industry and include sand, leaves, bits of trash, ground up food from sink disposals, laundry and bath waters and human wastes. Most MWTPs have, therefore, been designed to remove conventional pollutants. There are the following broad categories of **conventional pollutants:**

1. *Biochemical Oxygen Demand (BOD)* - This pollutant category measures the tendency of wastewaters to use oxygen in the receiving waters (i.e., the surface water bodies into which the wastewaters are discharged). Oxygen is consumed when organisms in the receiving waters metabolize the organic material in the wastewater. If too much oxygen is consumed, fish or other aquatic life in the receiving waters might be endangered. Thus, MWTPs are designed to reduce the BOD of the wastewater.
2. *Suspended Solids*- This parameter is a measure of the concentration of solid particles that are suspended in the wastewater.
3. *Faecal Coliform* - Faecal coliform bacteria are found in the digestive tract of humans and animals. Their presence in water indicates the potential presence of harmful organisms that can thrive in the human digestive system, such as dysentery, protozoa, typhoid bacteria, and other pathogenic (i.e., disease-causing) microorganisms. Fecal coliform bacteria are used as a measure of health risk since they are more easily detected than the pathogens.
4. pH - pH is a measure of the acidity or alkalinity of wastewater. Most surface waters have a nearly neutral pH. Many aquatic species will not thrive or may die if the pH of their habitat changes even slightly.
5. *Oil and Grease* - These pollutants interfere with MWTP treatment processes, impair the use of sludge as a soil conditioner and degrade receiving water quality when present in excessive amounts.

Toxic pollutants are those pollutants, which are harmful to one or more forms of animal or plant life. They are primarily grouped into organics and metals.

1. *Organic Pollutants* - These pollutants include pesticides, solvents, PCBs, and dioxins. Some of these compounds are lethal to animal life in the range of 1 ppm.
2. *Metals* - The metals of concern are known as the “heavy” metals and include lead, silver, mercury, copper, chromium, zinc, and cadmium. Most heavy metals are not

immediately lethal, however they can accumulate in vital organs of animals, including humans, causing health problems.

3. *Asbestos* and *cyanide* are two other non-organic toxic pollutants frequently found in industrial wastewater.

Removal of toxic pollutants by industrial pretreatment is critical, since most MWTPs are not designed to eliminate these pollutants.

There is a general classification of pollutants, which should not be introduced into a MWTP:

- Pollutants which can create a fire or explosion hazard in the MWTP with a closed cup flashpoint of < 60 ^{0}C
- Pollutants, which will cause corrosive structural damage to the MWTP and collection system, but in no case discharges with pH < 5.0
- Solid or viscous pollutants in amounts, which will cause obstruction to the flow in the MWTP or collection system resulting in interference
- Any pollutant, including oxygen demanding pollutants (BOD, etc.) released at a flow rate and/or pollutant concentration which will cause interference with the MWTP
- Heat in amounts, which will inhibit biological activity in the MWTP resulting in interference, but in no case heat in such quantities that the temperature at the MWTP exceeds 40 ^{0}C
- Petroleum oil, non-biodegradable cutting oil or products of mineral oil origin in amounts that will cause interference or pass through pollutants, which result in the presence of toxic gases, vapors, or fumes within the MWTP in a quantity that may cause acute worker health and safety problems
- Any trucked or hauled pollutants, except at discharge points designated by the MWTP

Generally, the following priority pollutants should be considered for setting pretreatment standards in cases of combined treatment (Source: USEPA, local limits development guidance, 2004):

- Arsenic
- Cadmium
- Chromium
- Copper
- Cyanide
- Lead
- Mercury
- Molybdenum
- Nickel
- Selenium
- Silver
- Zinc
- 5-day Biochemical Oxygen Demand
- Total Suspended Solids
- Ammonia

An extensive list of priority pollutants as categorized by the US Environment Protection Agency (USEPA) is presented in Appendix III.

4.2.2.2 Sampling points

At MWTP influent point

Samples should be taken at the plant's headworks to determine the average and maximum levels at which relevant pollutants enter the treatment plant. Influent sampling provides data to be used in calculating specific removal efficiencies. The sample should be drawn from a location that permits the collection of raw wastewater before it is mixed with any waste streams returned to the headworks from operations within the MWTP.

At MWTP effluent point

Sampling the treatment works' effluent is essential to determine the plant's overall removal efficiency.

MWTP sludge

Sludge should be sampled at the time of its disposal and after addition of conditioners to determine the percentage of solids it contains. The frequency of sampling depends on the amount of sludge generated annually.

Other MWTP sites

Site-specific data on pollutant concentrations in various unit processes is valuable for developing site-specific inhibition values. For example, a MWTP that digests its sludge should sample the digester contents to determine the levels of pollutants, primarily metals, which can cause digester upset.

At the collection system

It is important in determining the amount of loading generated by industrial installations and discharged into the collection system. As a matter of fact, samples should be taken from all points of the municipal collection system where industrial effluents are discharged, in order to check the industries' compliance with set pretreatment standards. The MWTP manager should know the mass of each priority pollutant discharged by each industrial installation, in order to rank them by size and environmental importance. By knowing each facility's level of discharge, the MWTP manager can assess which facilities will have difficulty meeting any effluent limits.

4.2.2.3 Pretreatment standards

Following the criteria and characteristics mentioned in the previous paragraphs, specific prescriptions are set for various parameters to be discharged into MWTPs, which define the parameters and allowable concentrations. These prescriptions vary from country to country, region, city etc. and cannot be uniformly described. A general permitting rule applicable in many countries is that **all industrial wastewaters need to be pretreated up to the level of raw municipal wastewater before their discharge into the municipal sewer collection system.** The relevant pretreatment installations have to be operated within the industrial facility to the extent needed.

USEPA has developed detailed effluent limitations for each industrial category connected with an MWTP (USEPA, Code of Federal Regulations 40, Section 403 and Subchapter N). Examples of regulations concerning effluent discharges into municipal sewers are presented in Table 4.2. These regulations are developed according to the prevailing local conditions, therefore they cannot be taken as a "universal" guide for all cases: each MWTP manager has to set his own pretreatment standards according to the local situation. In Appendix IV some pre-treatment standards applicable in the ROPME Region are presented.

Table 4.2 Effluent limitations (values in mg/l except pH & temperature)

PARAMETER	Athens (Greece)	Manchester (GB)	Industry producing hydrocarbons (Austria)	Venice area (Italy)	NWT Canada
pH	6-9		6.5 - 10	5.5 -9	6.5 – 10.5
Temperature	35 °C		40°C		
BOD_5	500	350		250	500
COD	1000			500	
SS	500	350	150	200	600
Oil& grease (mineral)	15	100			150
Nitrates	20				
Phosphates	10				
Sulfates	1				1500
Al	10			2	50
As	0.5			0.5	1
Cd	0.5			0.02	2
Cr^{3+}	2				5
Cr^{6+}	0.5			0.2	
Cu	1	4.5	0.5	0.4	5
CN	3	2.8	0.5	1	2
Fe	15			4	50
Pb	5	0.95	0.5	0.3	5
Mn	10				
Ni	10		0.5	4	5
Phenols	5			1	1
Hg	0.01	0.02	0.01	0.005	0.1
Zn	20	10.4	1	1	5

Source:

- European Commission, Reference Document on Best Available Techniques in common wastewater and waste gas treatment/management systems in the chemical sector, 2003
- Guideline for industrial discharges in the North Western Territories, The Environmental Protection Service of the NWT Department of Resources, Wildlife and Economic Development, 1998
- Effluent regulations for industrial discharges into the sewer system of the Greater Athens Area
- City of Manchester's industrial permits

4.2.3 Organization of a pretreatment program

In setting up a pretreatment program, both national and local authorities as well as MWTP operators must closely cooperate together, in order to facilitate its successful design and implementation. As a matter of fact, the full responsibility of its success relies more on local level (inspectorates, plants' operators), since they know better the prevailing local circumstances, whereas national/central authorities have to develop the overall concept (i.e. updating of priority pollutants, elaboration of scientific background for setting permitting standards, development of monitoring procedures, classification of industrial activities etc.).

4.2.3.1 National authorities

As mentioned above, national/central authorities are responsible to develop the overall concept needed for the implementation of local pretreatment programs. This is particularly the case, since they have the capacity and the means to conduct, in cooperation with scientific institutions, the necessary scientific studies for the definition of the priority pollutants for pretreatment. These studies will deal with:

- the investigation of the ability of treatment processes to cope with various pollutants and the assessment of all relevant adverse impacts to plants' operation
- new treatment methods capable to eliminate priority pollutants
- recycling techniques for in-plant reduction of waste streams
- the ability of water recipients to accept the final effluents from MWTPs (after treatment) containing toxic substances.

More specifically, the national/central authorities are responsible to:

1. Plan, develop and propose general effluent standards, on which pretreatment methods and plans should be based
2. Prepare the legislation required for the implementation of the national pretreatment program

3. Prescribe environmental management procedures to be implemented by industrial managers, in order to cope with set pretreatment effluent standards and to minimize effluent discharges into MWTPs
4. Classify the relevant industrial activities, which generate the relevant effluents
5. Develop monitoring techniques for effluent control and distribute them to the relevant local authorities
6. Prepare relevant guidance documents to be used by local authorities and MWTP operators

4.2.3.2 Local authorities

Local authorities (regions, districts, municipalities) are responsible for various tasks on local level aiming at the smooth implementation of the pretreatment program at local level. Their role is important, since they have to adapt the general pretreatment rules and standards on the existing circumstances, which cannot be described in all details in the general plan. There are **planning** and **controlling** tasks to be implemented as well as duties of **coordination** and **cooperation**.

4.2.3.2.1 Planning

Local authorities are responsible to establish local regulations to legally implement and enforce pretreatment requirements. The general concept for the establishment of these regulations should contain the following elements:

- Review and adaptation of the national pretreatment program to local needs. This means that a supervising authority will find out those institutions, which are capable to conduct the program and develop the locally applicable pretreatment standards
- Elaboration of a survey of all existing MWTPs in the regions concerned and of the relevant industrial activities
- Notification of all MWTP operators about their responsibilities and how they shall implement the program’s requirements
- Inventory of all industrial facilities in the region, which potentially will discharge their effluents into the MWTPs
- Initiate enforcement actions against noncompliant MWTPs and/ or industries
- Development of permitting regulations for industrial effluent discharges into the MWTP
- Modification of the pretreatment program on the basis of feedback from the permitting process and the monitoring results
- Preparation of regional reports and submission to the national authorities.

This framework, when completed and implemented, will enable the controlling authorities, industrial users and MWTP operators to conduct their own tasks and fulfill their responsibilities.

4.2.3.2.2 Control

The local inspectorates have to fulfill several tasks, which are associated with the day-to-day work of the practical implementation of the pretreatment program. The tasks are as follows:

- Issuing of permits for effluent discharge into the MWTPs on the basis of the nationally defined priority pollutants, the existing pollution control methods/ techniques and the set effluent standards
- Monitoring of industrial effluents and of the final effluents from MWTPs
- Evaluation of compliance of industrial users with the approved permits
- Preparation of compliance reports and submission to the local planning authorities
- Implementation of the enforcement/ inspection plan

In particular the whole **inspection plan** for industrial users looks as follows:

- Provide current data on industrial facilities
- Confirm or determine facilities' compliance status
- Determine completeness and accuracy of the facilities' performance/compliance records
- Assess the adequacy of each industry's self-monitoring and reporting requirements
- Assess the adequacy of imposed limitations and pollutants of concern
- Evaluate operation and maintenance and overall performance of an industrial pretreatment system
- Reveal issues requiring action
- Identify non-compliance which needs resolution
- Suggest pollution prevention opportunities
- Collect samples
- Obtain data to support enforcement actions

4.2.3.2.3 MWTP managers/operators

MWTP managers and operators have, beyond their task to run the installation, the responsibility to develop and implement procedures to ensure compliance of industrial installations with the approved pretreatment program. This means that MWTP managers should be able to:

- Identify and locate all industrial installations (users) subject to the pretreatment program. The list of these users must be frequently updated and submitted to the local authorities
- Identify the character and volume of pollutants contributed by such users
- Notify users of applicable pretreatment standards and requirements
- Receive and analyze reports submitted by the users
- Sample and analyze industrial discharges and evaluate the need for control plans
- Investigate instances of noncompliance
- Comply with public participation requirements.

MWTP managers shall also control all industrial users connected with the MWTP in cooperation with the local inspectorates. Accordingly they shall:

- Deny or condition discharges to the MWTPs
- Require compliance with pretreatment standards and requirements

- Control industrial discharges through permits and orders
- Require users' compliance schedules when necessary to meet applicable pretreatment standards and/or requirements and the submission of reports to demonstrate compliance
- Inspect and monitor industrial discharges
- Obtain remedies for industrial users' noncompliance
- Comply with confidentiality requirements.

Before embarking into any control function, the MWTP managers should define the **local limits** for pollutant discharge by industries or an estimate, pollutant by pollutant, of the total waste loading that the plant can safely accept from non-household sectors. Then the allowable discharges for each pollutant have to be allocated to the industrial users. Evidently, the most common allocation method is to set uniform-concentration local discharge limitations for each industrial user concerning the same priority pollutant.

Development of local limits is a continuing, dynamic process. A re-evaluation of specific local limits must be conducted whenever there are significant changes in industrial effluents discharge conditions or installed treatment technologies at the MWTP. For example, in case some priority pollutants are no longer present or are present only in very low (undetectable) concentrations that will not cause pass through, interference, or degradation of sludge quality of the MWTP. However, MWTP managers should understand that dropping a particular local limit completely may motivate industrial users to discontinue a pretreatment process designed to remove or recycle that particular pollutant.

Local limits can and should be modified after the following items/questions are answered:

- Has the treatment plant been modified, or has a new treatment plant been brought on line?
- Have the treatment plant processes or operation changed in a way that affects the removal efficiencies?
- Has the flow to the treatment plant changed significantly?
- Is the MWTP subject to new or revised national effluent limits?
- Have the national water quality standards changed for the receiving water?
- Has the MWTP changed, or intend to change, its sludge disposal method? If yes, will this change affect the sludge quality standards that the MWTP must meet?
- Have loadings been affected by new industrial users discharging to the MWTP?
- Have loadings been affected by industrial users that have stopped discharging to the MWTP?
- Have loadings been affected by changes in discharges from current industrial users?
- Are new data available about the MWTP or the industrial users that invalidate assumptions made during the last local limits development?

4.2.3.3 Industrial users

Industrial users are required to comply with all applicable pretreatment standards and requirements. Demonstration of compliance requires that they should self-monitor their own effluents, submit and maintain relevant records.. This task is essential and has to be conducted regularly. The frequency of sampling and reporting has to be agreed with the permitting authorities in the region.

Self-monitoring and reporting requirements vary according to the complexity of the effluents to be discharged and the contained pollutants. Generally an industrial user connected to MWTP must conduct self-monitoring as part of several different reporting requirements. This includes the report about the initial situation (baseline monitoring) and periodic compliance reports.

Based on the specific pollutants regulated by relevant pretreatment standards, different types of samples may have to be collected. Grab samples (i.e. an individual sample collected from a waste stream in less than 15 minutes without regard for flow or time) must be collected for pH, cyanide, total phenols, oil and grease, sulfide, and volatile organics. 24-hour flow proportional (i.e. a sample consisting of a minimum of eight discrete sample aliquots collected proportional to the flow rate of the liquid being sampled over the compositioning period and combined to form a representative sample) or time proportional (i.e. a sample consisting of a minimum of eight equal volume, discrete sample aliquots collected at equal time intervals over the compositing period and combined to form a representative sample) composite samples must be collected for all other pollutants.

The control authorities must ensure that the permits specify sampling location(s), required sampling frequencies, sample types to be collected, sampling and analytical procedures and associated reporting requirements. For certain industries (i.e., electroplating, metal finishing, electrical and electronic components) control authorities have the option of allowing the industrial users to prepare and implement a plan for toxic pollutants. This plan should identify all potential sources from which toxic materials could enter the waste stream and propose control measures to eliminate this possibility.

A summary of all reporting requirements is presented in Table 4.3.

Table 4.3 Reporting requirements for industrial users

REPORT	PURPOSE
Baseline monitoring report	o to provide baseline information on industrial facility to control authority o to determine wastewater discharge sampling points o to determine compliance status with pretreatment standards
Compliance schedule progress reports	o to track progress of the industrial facility through the duration of a compliance schedule o to notify control authority as to whether compliance with the applicable pretreatment standards has been achieved o if facility is noncompliant, to specify how compliance will be achieved o to provide the control authority with current information on the discharge of pollutants to the MWTP
Notice of potential problems	o to alert the MWTP to the potential hazards of the discharge
Noncompliance notification	o to alert the MWTP of a known violation and potential problems which may occur
Notification of changed discharge	o to notify MWTP of anticipated changes in wastewater characteristics and flow which may affect the MWTP
Notification of hazardous wastes discharge	o to notify MWTP about discharges of hazardous wastes
Upset/ bypass	o to notify MWTP of unintentional and temporary noncompliance with standards o to notify MWTP of noncompliance and potential problems which may occur

4.2.3.4 Coordination/cooperation

Planning authorities should also fulfill some additional tasks regarding the smooth implementation of the pretreatment program. These tasks go beyond the regulatory requirements of the program and simply try to improve the cooperation between themselves, the MWTP operators, the industries concerned and finally the general public.

Examples of such tasks are:

1. Agreements between the authorities and the industry to develop/introduce waste prevention techniques. They can, for example, participate in commonly funded programs together with scientific institutions.

2. Education/training of MWTP operators and industrial managers on waste management, risks of waste handling, safety at work etc.
3. Information/awareness campaigns for the general public about the operation of plants, environmental impacts caused by effluent discharge, water quality issues etc.

These additional duties will allow all interested partners (i.e. authorities, MWTP managers/operators and industrial users) to better understand the existing problems and to act preventive, namely to tackle any problems at the earliest possible level thus finding the most cost effective solutions.

5. JOINT TREATMENT OF EFFLUENTS

5.1 Introduction

The **joint treatment** of industrial effluents is considered as the centralized treatment of wastewaters originating from more than one industrial source. As already mentioned (chapter 4), wastewaters containing organic pollutants can in principle be treated together with municipal wastewater in MWTPs, whereas effluents with inorganic/chemical constituents have to be pretreated up to a level of raw municipal wastewaters before being discharged into MWTPs. In this chapter, the case of centralized wastewater treatment plants (CWTPs) dealing with effluents of chemical composition is analyzed. These plants are located in industrial areas/parks where many SMEs are located, which do not have the capacity of separate full treatment of their effluents before discharging them into a receiving water body. However, prior to the final discharge of the effluents from each industrial unit into CWTPs, some preparatory steps have to be undertaken, in order to minimize the final quantity of wastewaters to be treated by the CWTP, namely in-process reduction of wastewaters, separate collection of waste streams, etc. These steps/ practices are described in this chapter, in order to assist industrial managers in their efforts to minimize the waste streams reaching the CWTPs and maximize in-plant material recovery/recycling. Additionally these practices, if applied, help reducing the final wastewater loads/quantities to be discharged into CWTPs and thus decreasing the actual investment and operational costs for treatment.

The relevant CWTPs are equipped with all necessary end-of-pipe techniques/units (chapter 3) to deal with the complex nature of the various components. These techniques are classified according to their ability to treat the various wastewater compounds (§ 5.3.).

It is envisaged that CWTPs show clear advantages in comparison with individual (decentralized) treatment plants since it is possible to:

- make use of synergetic effects of combined waste streams e.g. for pH adjustment
- benefit from mixing procedures resulting in, e.g. temperature balance
- better use of the dosage of chemicals and the equipment, thus decreasing operating costs
- equalize the feed load, as long as the various daily process lines of the waste streams can be correspondingly structured or can be matched to each other (e.g. neutralization)

5.2 In-plant practices

The objectives for in-plant practices are to:

- maximize the amount of waste materials and residuals that are recycled rather than disposed as residuals, as wastewater, or as waste material
- maximize recycling and reuse of wastewaters generated on site

- minimize the introduction of uncontaminated wastewaters into the treatment waste stream
- identify, register and segregate wastes for treatment particularly where waste segregation would improve treatment performance and maximize opportunities for recycling

Details about wastewater recycling methods for various industrial processes can be found in the literature.

After having applied any in-plant wastewater reduction measures, the final effluent quantities from each industrial unit to be discharged into the CWTP is to be accepted by the CWTP managers according to the set discharge standards.

5.2.1 Methods for the reduction of wastewater generation and pollution loads in industrial processes

There are many possibilities for the reduction of water usage in industrial processes, which consequently will lead to relevant reduction of wastewater quantities to be treated. As a matter of fact, the extent of water reuse and recycling depends on the creativity and willingness of the industrial managers involved and less on any technical barriers. A general strategy for the minimization of fresh water consumption in the industry can have the following elements:

- process alteration/introduction of clean technologies
- change of water cooling to air cooling
- reuse/recycling of un- or slightly contaminated wastewater in other processes not influenced by the contaminants
- checking of fresh water quantities required for waste gas abatement techniques (e.g. wet scrubbers, wet cyclones, etc.)

In the following paragraphs examples of these methods applicable in typical SMEs are presented. They can be classified as **clean technologies** (i.e. methods, which use less raw materials and water for the production process), simple **good housekeeping measures** and **waste stream segregation.** By applying these methods, not only wastewater quantities but also the loss of raw materials are reduced. It must be pointed out however, that these in-plant measures are sometimes feasible only in **new** plants whereas **existing** industries, especially SMEs, can only apply simple good housekeeping methods.

5.2.1.1 Metal finishing

Substitution of chemicals

- zinc and copper baths can replace the most environmentally dangerous cyanide baths in the zinc and copper coating processes respectively without any significant impact on the final product’s quality

- the development of highly corrosion-resistant zinc plating has eliminated the necessity to use, for the same purpose (corrosion protection), the highly toxic cadmium
- chromium (III) can replace the toxic chromium (VI) in making up baths for chrome plating

5.2.1.1.1 Change/modification of processes

- the development from deep pickling tanks to turbulent pickling (spraying of acid directly onto the strip) leads to increased process efficiency and reduction of pickling loss by 20-30%
- replacement of the traditional hot-dip galvanization by a closed circuit system can lead to a substantial reuse of process water and to a reduction of hazardous waste flows by approximately 70 - 80%

5.2.1.1.2 Regeneration of baths

- filtration/centrifugation of various baths (alkaline cleaning, degreasing, chromating, phosphating etc.) removes bath impurities and separates highly concentrated wastes, which, otherwise, would have reached the effluents
- grease and oil removal from degreasing baths with “in situ” cleaning by bacteria (“biological degreasing”) can keep unlimited bath’s life time
- freezing of copper cyanide may be used to concentrate and separate dissolved impurities

5.2.1.1.3 Minimization of the consumption of water

- the installation of counter – current rinse cascade can dramatically reduce the water consumption (up to 90%) without changing the rinsing effect
- spray or jet rinse in zinc, copper or nickel plating helps decreasing the water consumption

Recovery/reuse of chemicals

- in galvanizing processes spent hydrochloric acid from combined pickling and stripping with high concentrations of iron and zinc can be processed and recovered like a flux bath
- spent flux baths can be recycled, the salts in the spent flux solution can be reused for flux agent production

Simple good housekeeping measures

- progressive reuse of cleaning solutions from the rear of a series of baths to the front of the sequence
- optimization of the rinsing quality of the baths, e.g. by agitation of the rinse water, results in reduction of water consumption
- allowing sufficient dripping time for treated work pieces over the plating bath or using an additional drag-out tank is one of the simplest and cost-efficient method for the reduction of spent chemicals
- the control of the rinsing time and the quantity of water used can reduce water consumption by at least 50%
- the use of static rinse tanks instead of flow rinsing arrangements the drag-out accumulates in the tanks and can therefore be recovered.

5.2.1.2 Textiles

Substitution of chemicals

- mineral oil-based lubricants in the spinning process, which cannot be fully degraded in biological treatment plants and can also contain hazardous substances (poly - aromatic hydrocarbons) can be replaced with formulations based on glycols
- use of biodegradable washing agents in the various washing processes can reduce BOD load by 25 – 35%

Modification of processes

- bleaching after dyeing the cotton fabric with reactive dyes lead to water savings by more than 15%
- use of a new jet technology (AFS airflow system) allows optimum penetration of dyestuffs and chemicals in the fabric, so that water consumption can be decreased by 50%

Water recycling

- water reuse (e.g. reuse of final rinsing baths, dye bath reuse, use water for pre-washing carpets in after-washing, counter-current flows in continuous washing)
- reuse of cooling water as process water (also heat recovery)
- reuse of wastewater during the mercerising process results in reduction of wastewater quantities by up to 85% and of the polluting load of NaOH and COD by 72% and 55% respectively
- a separated collection and treatment of effluents from dyeing/rinsing process and reuse of hot water for rinsing allows considerable reductions of wastewater volume and the contained quantities of NaOH and COD by 62%, 53% and 88% respectively

Reuse of chemicals

- collection of dye baths and reuse on other products can save fresh water by 25% and reduce wastewater quantities by 30%

Simple good housekeeping measures

- process optimization by improved control of process parameters such as temperature, chemical feed, dwell times, moisture (for dryers), etc.
- use of high-quality water (where needed) in wet processes in order to avoid/reduce the use of chemicals to prevent side effects caused by the presence of impurities
- avoiding/ minimizing any kind of surplus of applied chemicals and auxiliaries (e.g. by automated dosing and dispensing of chemicals)
- optimizing scheduling in production (e.g. in dyeing: dyeing dark shades after pale shades reduces water and chemicals consumption for machine cleaning)
- giving preference to low add-on devices for chemicals
- combination of different wet treatments in one single step (e.g. combined scouring and desizing, combined scouring/desizing and bleaching)

5.2.1.3 Leather tanning

Substitution of chemicals

- use of less persistent/toxic biocides instead of halogenated organic compounds
- processing of fresh (unsalted) hides will reduce the chloride load reaching the effluents by approx. 90%
- use of high-exhausting dyestuffs and fatliquoring systems
- use of enzymes in the unhairing process can reduce the consumption of sulphides

Increased efficiency of used chemicals

- by careful control of process parameters the conventional chrome tanning efficiency can be increased up to 80% and the chromium content of the effluents accordingly reduced
- modification of tanning agents to enhance chromium (III)-salt uptake can considerably reduce the chromium content of the effluents (approx. by 95%)

Recovery of chemicals

- chrome tanning effluents are collected, chromium is recovered through precipitation and separation, re-dissolved and re-introduced in the tanning process by replacing 20-35% of the “fresh” added chrome tanning salt (this process leads to a substantial reduction of the chromium content of the effluents to be finally treated)

Simple good housekeeping measures

- “batch” instead of “running water” wash can reduce the water consumption and consequently the effluent quantity by 50%
- use of short floats
- screening to remove coarse material from effluents can reduce by up to 40% the content of suspended solids in the final wastewater stream.

5.2.2 Waste stream identification and segregation

Waste segregation is one of the most important tools available for maximizing waste recycling and improving treatment performance: for example, separate treatment of wastes containing different types of metals allows the recovery of the individual metals from the resultant sludge.

Before deciding which waste streams and how they should be segregated, a source inventory throughout each industrial plant should be elaborated, in order to identify the sources of wastewater generation and assess the segregation possibilities and the potential for the application of waste reduction practices. In doing so, a site inventory of each production unit has to be accomplished. The information to be collected from an industrial plant to allocate the wastewater sources looks as follows:

- location
- climate, geography, soil and groundwater conditions, receiving waters
- size of the site
- production units

- production plants
- typical production plant data
- information on the production processes giving a brief description
- simplified process schemes with sources of waste streams
- details of the chemical reactions and supporting operations
- information on operating material, intermediate and final products
- operating mode (continuous or batch)
- potential emergency situations (spills, leakages)
- sewerage system (sewer, treatment units, rainwater drainage)

5.2.2.1 Stream inventory/register

The compilation of relevant basic data on the composition and quantity of wastewater is usually done in a stream inventory where the emitted streams are listed respective to their source, i.e. the production process from which they originate. The purpose of this inventory is to identify the most important emission sources and to allow a prioritization of the relevant reduction measures to be taken:

- listing of the sources
- evaluation of the causes of emissions from each source
- quantification of the amount of emissions from each source
- validation of results through a material balance (i.e. ranking of importance of waste streams)

A stream register consists of:

- information about the production process
- chemical reaction formula including raw materials, products, by-products
- process flow sheet of each production unit showing the exact origin of the various emissions/discharges
- information about the emitted waste streams
- components (load, concentration)
- stream flow rate (e.g. continuous, batch)
- contaminants/parameters

5.2.2.2 Sources of wastewaters

Wastewaters from industrial production processes originate from various sources, namely from:

- actual chemical synthesis
- mother liquors
- washing waters from purification of products
- vapor condensates
- wastewater from flue gas clean-up
- wastewater from equipment cleaning
- wastewater from vacuum generation

- other on-site sources
- conditioning of utility water
- bleed from boiler feed water systems
- blow-down from cooling cycles
- back-washing of filters
- laboratory and pilot-scale plants
- sanitation wastewaters
- collected rainwater from contaminated areas

Generally wastewaters from industrial plants contain:

- non-reacted raw material
- production residues
- intermediate compounds
- by-products

Concerning **wastewater quantities**, the majority (70-90%) consists of streams with low pollution level e.g.:

- cleaning water
- wastewaters from vacuum generation
- washing waters from exhaust air clean-up
- wastewaters from product pumps

Concerning **pollution loads**, the more highly concentrated waste streams originate from the actual chemical synthesis (approx. 80-90% of the total pollution load)

5.2.2.3 Segregation of waste streams

Taking into account the results of the wastewater register, the separate collection, recycling and on-site treatment of the various waste streams ensures the optimum possible discharge of wastewater to the CWTP with the least possible impacts on its operational performance and on the water recipient. A classification of the various separate collection systems is presented below:

- rainwater
- cooling water according to the grade of pollution
- wastewaters suitable for direct discharge into water recipients without any treatment
- sanitary wastewater
- drains for various process waters according to their origins
- drains for decentralized (on-site) treatment
- drains for centralized (off-site/joint) treatment
- separate drains for organic and inorganic wastewaters thus avoiding dilution of both parts

5.3 Centralized treatment of industrial effluents

After having applied all the necessary in-plant measures to reduce all wastewater quantities generated by industrial activities, the remaining (unavoidable) effluents from all industrial plants are collected and transferred to a CWTP. The CWTP has to be able to deal with the specific characteristics of the relevant waste streams thus being connected with the relevant collection systems from each industrial plant. In general, there are some broad wastewater categories for which the relevant treatment methods can be applied (Table 5.1). A CWTP should be, therefore, equipped with the relevant treatment units, in order to deal with the various wastewater categories.

Table 5.1 Wastewater categories

CATEGORY	TYPES OF WASTEWATER
Metals	• spent electroplating baths • metal finishing rinse water • chromate wastes • cyanide-containing wastes • waste acids and bases with or without metals • cleaning, rinsing, surface preparation solutions from electroplating or phosphating operations • alkaline and acid solutions used to clean metal parts or equipment
Oils	• used oils • oil-water emulsions or mixtures • lubricants • coolants • contaminated groundwater clean-up from petroleum sources • used petroleum products • oil spill clean-up • rinse/wash waters from petroleum sources • tank clean-out from petroleum or oily sources • aqueous and oil mixtures from parts cleaning operations • wastewater from oil bearing paint washes
Organics	• solvent-bearing wastes • wastewater from paint washes • wastewater from adhesives and/or epoxies formulation • wastewater from organic chemical product operations • tank clean-out from organic, non-petroleum sources
Inorganic salts	• chlorides • sulfides • acids
Suspended solids	

Source:

- USEPA, Effluent guidelines – centralized treatment, development document, 2000
- European Commission, Reference Document on Best Available Techniques in common wastewater and waste gas treatment/management systems in the chemical sector, 2003

A CWTP has to be equipped with all necessary treatment units to deal with the various wastewater types. In the following paragraphs the various treatment methods suitable for the relevant wastewater types will be presented. These methods are considered as the most suitable (BAT) for each wastewater category and they can be applied either on-site or as final treatment step (as such or in combination) in a CWTP (Source: European Commission, Reference Document on Best Available Techniques in common wastewater and waste gas treatment/management systems in the chemical sector, 2003)

5.3.1 Treatment methods for metals

In Table 5.2 the various BAT methods for the removal of heavy metals are presented.

Table 5.2 BAT methods for the removal of heavy metals

	Precipitation or air flotation/ filtration	Crystallization	Ion exchange	Nanofiltration/ reverse osmosis
Purpose	Transfer of dissolved heavy metal compounds to insoluble compounds	Growth of heavy metal compounds on granular seed material in a fluidized bed	Replacement of heavy metal ions in the aqueous phase by other ions from ion exchange resin	Separation of heavy metal ions by membrane permeation
Application	Removal of heavy metals from waste streams preferably for higher concentrations. Recovery possible in principle	Removal of heavy metals by producing conditions that enable precipitation	Solutions containing heavy metal ions with low feed concentrations. Recovery is possible	Achieving high grade of purity to recycle and reuse water. Recovery is possible
Application limits	Adjustment of pH, not applicable at low concentrations		High ionic strength, corrosive agents to be avoided, temperature limit about 60^0C	Low thermal and chemical resistance

	Precipitation or air flotation/ filtration	Crystallization	Ion exchange	Nanofiltration/ reverse osmosis
Consumables	Precipitation agent-flocculant/coagulant	Crystallization chemicals	Regeneration liquid, fouling surpressors	Chemicals for cleaning Energy: 1-3 kWh/m^3
Cross media effects	Disposal of sludge, odor emissions	High salt loads in case of over dosage of crystallization chemicals	Regeneration returns high concentrations of heavy metal solutions	Concentrate needs further treatment e.g. ion exchange
Space requirements		Comparable to ion exchange and nanofiltration/ reverse osmosis	Comparable to crystallization and nanofiltration/ reverse osmosis	Comparable to crystallization and ion exchange
Performance (% of removal)			80-99	>90
Achievable emission levels (mg/l)	Highly dependent on production process from which they originate	Zn 1 Ni 1	0.1-10	Near to zero

5.3.2 Treatment methods for oils

BAT for free oils/hydrocarbons is to remove them when they appear as large slugs with the aim of recovery maximization by applying an appropriate combination of:

- oil/water separation by cyclone, microfiltration or API separator when large slugs of free oil/hydrocarbons can be expected, otherwise parallel plate interceptor (PPI) and corrugated plate interceptor can be considered as alternatives
- microfiltration, granular media filtration, gas flotation

Emission values are expected to a range of 0.05 – 1.5 mg/l

5.3.3 Treatment methods for organics-inorganics

There are some waste streams containing organic (and some inorganic) compounds unsuitable for biological treatment, which cannot be discharged into MWTP and therefore they have to be treated in a CWTP namely:

- compounds poorly or not biodegradable
- toxic substances which inhibit the biological process

In Table 5.3 the various BAT methods for the removal of organics are presented.

Table 5.3 BAT methods for the removal of organic-inorganic materials

	Oxidation	**Reduction**	**Hydrolysis**	**Wet air oxidation**	**Super-critical water oxidation**
Purpose	Conversion of pollutants by peroxide with UV or ferrous salts	Conversion of pollutants by SO_2, $FeSO_4$, NaHS	Reaction of pollutants with water, breaking into smaller compounds	Reaction with oxygen (high temperature + pressure) in aqueous phase	Wet air oxidation in the super-critical region of water (pressure > 22 Mpa, >374^0C)
Application	Oxidize organic/inorganic material. Can replace biological treatment	Reduction of inorganic material	Destruction of non-biodegradable substances into smaller biodegradable compounds	Oxidize organic compounds. Can replace biological treatment	Destroy contaminants with low biodegradability and/or high toxicity. Can replace biological treatment
Application limits	UV application requires solid-free solutions	Strict control of pH	Not suitable for pollutants with low water solubility	Not recommended for low COD concentrations, fluoride < 10 mg/l, low salt loads	
Consumables	Oxidation agent, agent to destroy surplus oxidant	Reduction agent, agent to destroy surplus reduction agent	Steam/hot water for heating, chemicals to adjust pH and redox potential	Air or oxygen	Air or oxygen
Cross media effects					
Space requirements					
Performance (% of removal)	TOC > 90			COD: 60-99	Organic compounds: > 99
Achievable emission levels (mg/l)					

Table 5.3 continued

	Nanofiltration/ reverse osmosis	Adsorption	Extraction
Purpose	Separation of most contaminants	Transfer of soluble pollutants to a solid adsorbent	Transfer of soluble pollutants into a solvent
Application	Achieving high grade of purity to recycle/ reuse water. Recovery is possible	Remove organic, colored, odorous and/or toxic pollutants. Recovery is possible	Remove organic non-biodegradable and/or toxic pollutants at high concentration. Recovery is possible
Application limits	Low thermal and chemical resistance	Low pollutant load, limited TSS load because of clogging	Wastewater preferably free of TSS and emulsions
Consumables	Chemicals for cleaning	Adsorbent, chemicals for regeneration	Replacement of solvent losses
Cross media effects	Concentrate needs further treatment	Off-gases during regeneration require treatment	Treatment of wastewater to remove dissolved solvent
Space requirements		At least 2 columns per application	
Performance (% of removal)	High efficiency	High efficiency depending on pollutant	Good efficiency for special pollutants with high feed concentration
Achievable emission levels (mg/l)			

Table 5.3 continued

	Distillation/ rectification	Evaporation	Stripping
Purpose	Transferring volatile contaminants from the water phase into the vapor phase	Distillation of water leaving a concentrate as bottom residue	Transference of volatile pollutants into the gaseous phase by blowing air or steam through the wastewater
Application	Recovery of bulk contaminants	Concentration of wastewater to recycle valuable substances	Removal of volatile organic/inorganic compounds. Recovery is possible
Application limits	Large feed concentration required	Avoid foam generating substances, not applicable to volatile pollutants	Restricted to volatile pollutants

	Distillation/ rectification	**Evaporation**	**Stripping**
Consumables	Steam for heating	Steam, chemicals (when pretreatment is necessary)	Anti-fouling agents When steam is used: 0.1-0.3 tons/m^3
Cross media effects	Off-gas requires further treatment	Condensate might need further treatment	Gas streams need treatment (scrubbing, adsorption, incineration)
Space requirements		Comparatively low	
Performance (% of removal)	Good performance under special conditions	Nearly complete pollutant removal	Good efficiency
Achievable emission levels (mg/l)			

5.3.4 Treatment methods for inorganic salts

The inorganic salts and acid content of wastewaters can influence the quality of the receiving waters as well as the operation of sewerage systems (e.g. corrosion of pipes, valves and pumps, malfunctioning of downstream biological treatment). Central treatment of inorganic salts can be applied although it is more cost-effective if removal is done on-site. Table 5.4 presents the most common BATs for the removal of inorganic salts.

Table 5.4 BAT methods for the removal of inorganic salts

	Evaporation	**Ion exchange**	**Reverse osmosis**	**Biological sulphate control**
Purpose	Distillation of water leaving a concentrate as bottom residue	Replacement of cations by H^+ and anions by OH^- ions thus replacing salts by water	Separation of all water contaminants by membrane permeation	Anaerobic reaction of sulphate to sulphur
Application	Crystallization of inorganic salts and separation from wastewater, concentration of non-volatile substances. Substance recovery possible	Solutions containing salts. Recovery is possible	Achieving high grade of purity to recycle water, concentration increase of contaminants for further treatment or recovery. Recovery is possible	Removal of sulphate. Recovery of sulphur

	Evaporation	Ion exchange	Reverse osmosis	Biological sulphate control
Application limits	Avoid foam generating substances	Avoid high ionic strength, temperature limit 60^{0}C, corrosive agents can damage resin	High concentrations can cause high osmotic pressure (difficult to operate). Low thermal and chemical resistance	Very slow reaction, COD/sulphate needs to be at least 1:1
Consumables	Steam	Regeneration liquid, fouling surpressors	Chemicals for cleaning	Chemicals (neutralizing agent, flocculant)
Cross media effects	Condensate might need further treatment, noise emission	Recovery returns high concentrations of salt removed	Concentrate needs further treatment e.g. ion exchange to enable recovery	Sulphur can be used for sulphuric acid production
Space requirements	Comparatively low	Comparatively low	Comparatively low	
Performance (% of removal)	Complete salt removal	80-89	Close to 100	94
Achievable emission levels (mg/l)		0.1 - 10	Near to zero	75

5.3.5 Treatment methods for suspended solids

Total suspended solids (TSS) have to be removed from wastewater streams, since they can cause damage to downstream facilities (e.g. clogging of pumps/pipes and of treatment facilities). In doing so, some steps have to be undertaken:

- Sedimentation/air flotation to catch the main TSS load and/or flocculation/coagulation for finely dispersed solids (to produce settleable flocs)
- Mechanical filtration if the solid content has not been reduced enough to prevent clogging in subsequent treatment facilities, such as membrane filtration, adsorption, chemical oxidation
- Microfiltration or ultrafiltration, if the waste stream needs to be solid-free to prevent clogging in nanofiltration or reverse osmosis facilities

BAT methods for TSS removal are summarized in Table 5.5.

Table 5.5 BAT methods for the removal of TSS

	Sedimentation	Air flotation	Filtration	Microfiltration/ Ultrafiltration
Purpose	Clarification from SS and/or floc	Clarification of process water when sedimentation is not appropriate	Final separation stage after sedimentation or air flotation to achieve low particulate emissions	Clarification to solid-free wastewater for downstream treatment (e.g. reverse osmosis)
Application	Separation of solids from wastewater. In principle TSS recoverable	Separation of unsettleable solids. Separated material can be recovered	Separation of solids from wastewater. Material recovery depends on filter type	Separation of all solid material, colloidal particles, bacteria/viruses. Suitable for material recovery
Application limits	Particles to be settleable, otherwise use of flocculants/ coagulants. No limits to TSS content	No foaming detergents	To avoid finely dispersed solids	Chemicals can damage membrane material, low TSS feed load to avoid clogging
Consumables	Flocculants/ coagulants	Flocculant (2.5-4.5 kg/ton TSS)		Antiscaling, antifouling and backwashing chemicals
Cross media effects	Sludge disposal, noise/odor emissions	Sludge disposal, noise/odor emissions	Sludge disposal after backwashing	Residue disposal, noise emissions
Space requirements				Module arrangement, space requirement low compared to other techniques
Performance (% of removal)	TSS 60-90 Settleable solids 90-95	85 - 98	50 - 99	Close to 100
Achievable emission levels (mg/l)	< 10	10 - 20	< 10	

6. CONCLUSIONS - RECOMMENDATIONS

Summarizing the logical approach described in this document, a short outline of the necessary steps to be taken before embarking on combined or joint treatment is presented below:

1. Assess the pollution load coming out from each installation by elaborating a thorough source inventory by using either the calculative method (i.e. application of emission factors linking production capacity with effluent quantities) or by monitoring effluent quality.

2. Segregate waste streams in a facility whenever possible. Group them according to their characteristics (i.e. effluents containing heavy metals, oils/hydrocarbons, inorganic/organic persistent pollutants etc.).

3. Apply BAT, good housekeeping practices for those effluents where by-products can be recovered, recycling can be applied, clean technologies can be introduced. By doing so, final effluent quantities to be treated, will be reduced.

4. As a general rule, treat effluents to a level of raw municipal wastewaters before discharging them into municipal wastewater treatment plants unless locally determined pretreatment standards prescribe otherwise. Apply end-of-pipe techniques to remove contaminants, which can harm the subsequent biological treatment process.

5. Discharge grouped effluents from various industrial sources in an area into centralized treatment plants.

7. REFERENCES

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14. Effluent regulations for industrial discharges into the sewers of the Greater Athens Area
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8. APPENDICES

8.1 APPENDIX I

PROTOCOL FOR THE PROTECTION OF THE MARINE ENVIRONMENT AGAINST POLLUTION FROM LAND BASED SOURCES

THE CONTRACTING STATES

BEING PARTIES to the Kuwait Regional Convention for Co-operation on the Protection of the Marine Environment from Pollution;

RECOGNIZING the danger posed to the marine environment and to human health by pollution from land-based sources and the serious problems resulting therefrom in coastal waters of many Contracting States, principally due to the release of untreated, insufficiently treated and/or inadequately disposed of domestic or industrial discharges;

NOTING that existing measures to prevent, abate and combat pollution caused by discharges from land-based sources need to be strengthened on a national and a regional basis;

BEING AWARE of Articles 194, 207, 212 and 213 of the United Nations Convention on the Law of the Sea (1982); and the Montreal Guidelines for the Protection of the Marine Environment against Pollution from Land-Based Sources (1985); and

DESIROUS to strengthen the implementation of Article III, paragraph (b) and Article VI of the Convention;

HAVE AGREED AS FOLLOWS:[*]

ARTICLE I

DEFINITIONS

For the purpose of this Protocol:

1. "Combined Treatment" means common treatment of industrial effluents along with domestic sewage;

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[*] A Meeting of the Plenipotentiaries was held in Kuwait on 21 February 1990 for signing the Protocol concerning the Protection of the Marine Environment against pollution from Land-Based Sources.

2. "Competent State Authority" means the Authority designated by the Contracting State for the purpose of this Protocol;

3. "Contracting State" means any State which has become a party to this Protocol;

4. "Convention" means the Kuwait Regional Convention for Co-operation on the Protection of the Marine Environment from Pollution;

5. "Council" means the organ of the Organization as referred to in subparagraph (i) of paragraph (b) of Article XVI of the convention;

6. "Freshwater Limit" means the place in watercourses where, at low tide and in a period of low freshwater flow, there is an appreciable increase in salinity due to the presence of sea-water;

7. "Joint Pretreatment/Treatment" means common pretreatment/treatment of the effluent from more than one industrial source;

8. "Land-based Sources" means municipal, industrial or agricultural sources, both fixed and mobile on land, discharges from which reach the Marine Environment, as outlined in Article III of this Protocol;

9. "Marine Environment" means the Protocol Area as defined in Article II of this Protocol;

10. "Organization" means the Regional Organization for the Protection of the Marine Environment established in accordance with Article XVI of the convention;

11. "Pollution" means "Marine Pollution" as defined in paragraph (a) of Article 1 of the Convention;

ARTICLE II
AREA OF APPLICATION

The area to which this Protocol applies (hereinafter referred to as the "Protocol Area") shall be the Sea Area as defined in Article II, paragraph (a) of the Convention, together with the waters on the landward side of the baselines from which the breadth of the territorial sea of the Contracting States is measured and extending, in the case of watercourses, up to the freshwater limit and including intertidal zones and salt-water marshes communicating with the sea.

ARTICLE III
SOURCES OF POLLUTION

This Protocol shall apply to discharges reaching the Protocol Area from land-based sources within the territories of the Contracting States, in particular:

a) from outfalls and pipelines discharging into the sea;

b) through rivers, canals or other watercourses, including underground watercourses;

c) from fixed or mobile offshore facilities serving purposes other than exploration and exploitation of the sea bed, its subsoil and the continental shelf; and

d) from any other land-based sources situated within the territories of the Contracting States, whether through water, through the atmosphere or directly from the coast.

ARTICLE IV
SOURCE CONTROL

1. The Contracting States undertake to implement the action programs based on source control as outlined in Annex I to this Protocol. To this end, they shall develop and implement, jointly or individually, as appropriate, the necessary programs and measures.

2. The programs and measures and the timetables for their implementation aimed at reducing pollution from land-based sources, shall be fixed by the Contracting States and periodically reviewed and revised, if necessary every two years, in accordance with the provisions of Article XIV of this Protocol.

ARTICLE V
JOINT AND/OR COMBINED EFFLUENT TREATMENT

1. The Contracting States in their endeavor not to inhibit the development of new industries, and especially that of small industrial operations, and recognizing the economic and technical difficulties often encountered by such operations in properly treating their effluent individually undertake to implement, to the extent possible, industrial location planning programs as outlined in Annex II to this Protocol. To this end, they shall develop and implement, jointly and/or individually , as appropriate, the necessary programs and measures.

2. The Regional guidelines and criteria along with programs and measures and the time-tables for their implementation, aimed at reducing pollution from land-based sources through joint and/or combined effluent treatment, shall be

fixed by the Contracting States and periodically reviewed and revised, if necessary every two years, in accordance with the provisions of Article XIV of this Protocol.

ARTICLE VI

REGIONAL AND LOCAL REGULATIONS/PERMITS FOR RELEASE OF WASTES

1. As outlined in Annex III to this Protocol, the Contracting States shall progressively develop and adopt, in cooperation with competent Regional and International Organizations as appropriate:

   a) Regional guidelines, standards or criteria, as appropriate, for the quality of sea-water used for specific purposes that is necessary for the protection of human health, living resources and ecosystems;

   b) Regional regulations for the waste discharge and/or degree of treatment for all significant types of land-based sources;

   c) Stricter local regulations for waste discharge and/or degree of treatment for specific sources based on local pollution problems and desirable water usage considerations.

   Stricter regulations for specific sources serve the purpose of preserving the quality of seawater required for the intended use. In developing such regulations the local ecological, geographical and physical characteristic, as well as, the level of existing pollution in the Marine Environment shall be taken into consideration.

2. The programs for the implementation of the above measures shall be adopted and shall take into account, for their progressive application, the cost of measures involved, the capacity to modify existing installations, the economic capacity of the Contracting States and their need for sustainable development.

3. Polluters shall be required to obtain a permit to discharge from the Competent State Authorities. Such permits shall allow for review and modification of discharge conditions reflecting the periodic update of regulations.

4. Guidelines, standards or criteria, as well as, regulations, programs and measures shall be developed and adopted in accordance with the provisions of Article XIV of this Protocol and periodically updated, if necessary every two years, to reflect the increasing information through the monitoring program described in Article VII of this Protocol, the changes in the industrial and other human activities and possible advances in Science and the pollution control technologies.

ARTICLE VII
MONITORING AND DATA MANAGEMENT

1. The Contracting States, within the framework of the provisions of Article X of the Convention, shall carry out monitoring activities, if necessary in co-operation with the competent Regional and International Organizations, in order to:

    a) collect data on natural conditions of the Protocol Area as regards its physical, biological and chemical characteristics;

    b) collect data on inputs of substances or energy that cause or potentially cause pollution from land-based sources, including information on the distribution of sources and the quantities of pollutants introduced to the Protocol area;

    c) assess systematically the levels of pollution within their internal and territorial waters, in particular with regard to the substances that may have a potential significant impact on the Marine Environment. For the selection of the sampling locations and substances to be measured, information available, inter alia, from source inventories, discharge outfalls and marine environment characteristics shall be considered; and

    d) evaluate the effectiveness of measures taken under this Protocol in meeting the environmental objectives.

2. Contracting States shall collaborate jointly or collectively to establish comparable monitoring programs, as well as analytical quality control programs and to promote data storage, retrieval and exchange.

ARTICLE VIII
ENVIRONMENTAL IMPACT ASSESSMENT

1. The Contracting States shall require on priority basis an assessment of the potential environmental impacts during the planning and implementation stages of selected development projects within their territories, particularly in the coastal areas, which may cause significant risks of pollution from land-based sources to the Protocol Area, in order to ensure that appropriate measures are taken to prevent or mitigate such risks.

2. The Contracting States shall develop, with the assistance of the Organization, technical and other guidelines concerning the assessment of the potential environmental impacts of development projects referred to in paragraph 1,

including possible trans-boundary effects. The assessment should, where appropriate, contain inter alia the following:

a) A description of the geographical location of the activities to be carried out;

b) A description of the initial ecological state of the marine environment and the coastal area, which may be effected by the activities;

c) An indication of the nature, aims and scope of the proposed activities;

d) A description of the methods, installations and other means to be used;

e) A description of the foreseeable direct and indirect long-term and short-term effects of the activities on the Marine Environment, including fauna, flora and the ecological balance;

f) A statement setting out the measures proposed to reduce to the minimum the risk of pollution by carrying out the activities and, in addition, possible process and pollution abatement alternatives to such measures;

g) An indication of the measures to be taken for the protection of the Marine Environment from pollution during and, as appropriate, at the end of the proposed activities;

h) Definition of commitments to ongoing environmental management and monitoring;

i) Cost-benefit analysis as appropriate;

j) A brief summary of the assessment;

3. The implementation of the selected projects referred to in paragraph 1 should be made subject to a prior written authorization from the Competent State Authorities which takes fully into account the findings of the environmental impact assessment.

4. The Contracting States shall co-operate with the Organization to develop procedures for the dissemination to all Contracting States of the reports on the results of such assessment with a view to enable the Contracting States which may be affected by the environmental impacts of the development projects to consult with the Contracting State concerned.

ARTICLE IX
SCIENTIFIC AND TECHNOLOGICAL CO-OPERATION

The Contracting States, in conformity with Article X of the Convention, shall co-operate in scientific and technological fields related to pollution from land-based sources, particularly research on inputs, pathways and effects of pollutants and on the development of new methods for their treatment, reduction or elimination. To this end, the Contracting States shall, in particular, endeavor to:

a) exchange scientific and technical information;
b) co-ordinate their research programs of common nature.

ARTICLE X
SCIENTIFIC, TECHNICAL AND OTHER ASSISTANCE

1. The Contracting States shall, directly or with the assistance of the Organization or competent Regional and International organizations, co-operate with a view to formulate and implement programs of assistance, particularly in the fields of science, education and technology, for the prevention, reduction and control of pollution from land-based sources.

2. Such technical assistance shall include, in particular, the training of scientific and technical personnel, as well as the acquisition, utilization, maintenance and production of appropriate equipment.

ARTICLE XI
WATERCOURSES SHARED BY STATES

1. If discharges from a watercourse which flows through the territories of Contracting States are likely to cause pollution of the Protocol Area, the Contracting States in question, in accordance with the provisions of this Protocol in so far as each of them is concerned, are called upon to co-operate with a view to ensuring its full application.

2. A Contracting State shall not be responsible for any pollution originating on the territory of a non-Contracting State. However, the Contracting State shall endeavor to co-operate with such State so as to make possible full application of the Protocol.

ARTICLE XII
EXCHANGE OF INFORMATION

1. The Contracting States shall inform one another directly or through the Organization of measures taken, of results achieved and, if the case arises, of difficulties encountered in the application of this Protocol. Procedures for the

collection and submission of such information shall be determined by the Council.

2. Such information shall include *inter alia*:

   a) Relevant statistical data in accordance with Articles VI and VII of this Protocol;

   b) Data resulting from monitoring as provided for in Article VII of this Protocol;

   c) Quantities of pollutants discharged or emitted from their territories;

   d) Measures taken in accordance with Articles IV, V and VI of this Protocol.

ARTICLE XIII
RESPONSIBILITY AND LIABILITY FOR DAMAGE

1. Contracting States shall ensure that recourse is available in accordance with their legal systems for prompt and adequate compensation or other relief in respect of damage caused by pollution of the Marine Environment by natural or juridical persons under their jurisdiction.

2. Contracting States shall formulate and adopt appropriate procedures for the determination of liability for damage resulting from pollution from land-based sources.

ARTICLE XIV
INSTITUTIONAL ARRANGEMENTS

The Council, in accordance with Article XVII of the Convention, shall be responsible for keeping under review the implementation of this Protocol. To this end, the Council shall, *inter alia:*

a) consider the efficacy of the measures adopted and the advisability of adopting any other measures, in particular in the form of annexes;

b) revise and amend any annex to this Protocol, as appropriate;

c) formulate , adopt and review programs and measures in accordance with Articles IV, V, VI, VII, IX and X of this Protocol;

d) adopt Regional guidelines, standards or criteria in accordance with Articles IV, V and VI of this Protocol;

e) formulate procedures for exchange of information in accordance with Articles VIII and XII of this Protocol;

f) consider information submitted by the Contracting States under Articles VIII and XII of this Protocol;

g) discharge such other functions as appropriate for the application of this Protocol; and

h) establish any such institutional mechanism as deemed necessary for the achievement of the objectives of this Protocol.

ARTICLE XV
GENERAL PROVISIONS

1. The provisions of the Convention relating to any Protocol shall apply to this Protocol.

2. Procedures for amendments to Protocols and their Annexes adopted in accordance with Articles XX and XXI of the Convention shall apply to this Protocol.

3. The Rules of Procedures and Financial rules adopted pursuant to Article XXII of the Convention, and amendments thereto, shall apply to this Protocol.

4. The Annexes form an integral part of this Protocol unless expressly provided otherwise thereto.

ARTICLE XVI
FINAL PROVISIONS

1. This Protocol shall be open for signature in the State of Kuwait from 21 February to 21 May 1990 by any State which is party to the Kuwait Regional Convention for Co-operation on the Protection of the Marine Environment from pollution.

2. This Protocol shall be subject to ratification, acceptance, approval or accession by the States parties to the Convention. Instruments of ratification, acceptance, approval or accession shall be deposited with the Government of Kuwait which shall assume the functions of the Depository.

3. This Protocol shall enter into force on the ninetieth day following the date of deposit of at least five instruments of ratification, acceptance or approval of, or accession to this Protocol by the States as referred to in paragraph 1 of this Article.

In WITNESS WHEREOF the undersigned Plenipotentiaries, being duly authorized by their respective Governments, have signed this Protocol.

DONE AT KUWAIT this twenty-first day of February, in the year one thousand nine hundred ninety in the Arabic, English and Persian languages, the texts being equally authentic.

Annex 1 to the protocol

POLLUTION ABATEMENT THROUGH SOURCE CONTROL

With regard to the issue of pollution abatement through source control referred to in Article IV of this Protocol, consideration should be given to the control and progressive replacement of products, installations and industrial or other processes causing significant pollution to the Marine Environment. In this regard, particular attention will be given, but not limited, to the following factors:

a) Curtailment and/or regulation of import, transportation, manufacturing or processing of certain harmful substances.
b) Change of raw materials.
c) Change of manufacturing processes.
d) Good operating and housekeeping practices.
e) Segregation of waste streams and minimization of pollutant dilution prior to treatment.
f) Recovery, re-use and recycling.

The programs, measures and the timetables required for the implementation of source control will be developed and priorities allocated on the basis of the results of on-going assessment studies.

Problem areas of Regional interest, where cost effective measures can be implemented, will receive attention for the purpose of establishing general management schemes. Such areas are, for example, the collection, treatment, and proper disposal of spent lubricating oils, blood and paunch from slaughterhouses, the control of fuel combustion processes and the implementation of source control in selected processes within large industries.

Annex 2 to the protocol

PROMOTION OF JOINT AND/OR COMBINED EFFLUENT TREATMENT

Without undue prejudice to the multifaceted constraints that often govern the selection of the location of new industries, a program will be undertaken, as referred to in Article VI of this Protocol, to promote:

a) agglomeration of industries in a way that enhances the possibility of joint effluent pretreatment and/or treatment, as the need may be;

b) location within the limits of city sewer systems of certain types of industry so as to enhance combined treatment of industrial and domestic wastes.

Promotion of joint and/or combined effluent treatment, if properly planned, could result in greatly reduced treatment, monitoring and enforcement costs as well as in increased treatment reliabilities. To this end, Regional guidelines and criteria will be developed dealing with topics of common interest, such as:

- the compatibility of effluent from different sources;
- pretreatment requirements prior to discharge into domestic and/or industrial sewer systems;
- cost sharing for the construction and operation of treatment plants.

Such guidelines and criteria will assist Contracting States in developing their own specific programs and measures. While initial plans may deal with the location problem of new industries, the end objective will be the progressive attraction of existing selected small industries as the infrastructure and facilities are developed in the designated areas.

Annex 3 to the protocol

GUIDELINES, REGULATIONS AND PERMITS FOR THE RELEASE OF WASTES

1. With a view to guidelines, standards or criteria, as well as to regulations, programs, measures, and discharge permits for release of wastes referred to in Article VI of this Protocol, particular attention will be given, inter alia, to the following factors:

    a) Regional regulations for the waste discharge and/or degree of treatment should be specific for each kind of source and, if necessary, may be different between existing and new sources. Their development should be based on treatment technology, cost and nature of pollutants considerations, as well as on an overview of the state of environment in the Protocol Area.

    b) Regional guidelines and, as appropriate, standards or criteria should be developed for the quality of sea water used for specific purposes.

    c) For areas where the water quality standards for the intended use cannot be achieved through the implementation of the above regional regulations, stricter local regulations for the waste discharge and/or degree of treatment should be developed. Such local regulations will apply to the specific sources in the areas under consideration.

    d) Regional regulations along with the programs, measures and the timetables required for the implementation should be developed on a priority basis, *inter alia*, for the following types of wastes:

        i) Ballast water, slops, bilges and other oily water discharges generated by land-based reception facilities and ports through loading and repair operations.

        ii) Brine water and mud discharges from oil and gas drilling and extraction activities from land-based sources.

        iii) Oily and toxic sludges from crude oil and refined products storage facilities.

        iv) Effluents and emissions from petroleum refineries.

        v) Effluents and emissions from petrochemical and fertilizer plants.

        vi) Toxic effluents and emissions from industries such as chlor-alkali, primary aluminum production, pesticides, insecticides, and lead recovery plants.

        - vii) Emissions from natural gas flaring and desulfurization plants.
        - viii) Dust emissions from major industrial sources, such as cement, lime, asphalt and concrete plants.
        - ix) Effluent and emissions from power and desalination plants.
        - x) Wastes generated from coastal development activities which may have a significant impact on the Marine Environment.
        - xi) Sewage and solid waste.

    - e) As the Diagram 1 attached to this Annex illustrates, pollution abatement is an iterative process. Pollution abatement action will start from high priority measures, which will be selected to be pragmatic cost-effective, while addressing the most critical environmental problems as perceived today. The monitoring program as specified in Article VII of this Protocol, will be providing the necessary feedback for the required corrective action by yielding the database for accessing the effectiveness of implemented programs, the current state of the environment and its trends. Corrective action, whenever required, will be taken through periodic updates of the regulations, programs and measures and review of the conditions in discharge permits, in accordance with the provisions of Articles IV and VI of this Protocol.

2. Provisions for establishing criteria governing the issue of permits for the discharging of waste matter in the Marine Environment, should also take into consideration inter alia the following:

    - a) Characteristics and Composition of Waste
        - i) Type and size of waste source, e.g. industrial process.
        - ii) Type of waste (origin, average composition).
        - iii) Form of waste (solid, liquid, sludge, slurry).
        - iv) Total amount (volume discharged, e.g. per year).
        - v) Discharge pattern (continuous, intermittent, seasonally variable, etc.).
        - vi) Concentrations with respect to major constituents.

vii) Properties: physical, e.g. solubility and density chemical and biochemical, e.g. oxygen demand, nutrients, and biological, e.g. presence of viruses, bacteria, yeast, parasites.

viii) Toxicity

ix) Persistence: physical, chemical and biological.

x) Accumulation and bio-transformation in biochemical materials or sediments.

xi) Susceptibility to physical, chemical and biochemical changes and interaction in the aquatic environment with other dissolved organic and inorganic materials.

xii) Probability of producing taints or other changes reducing marketability of resources, e.g. fish, shellfish, etc.

b) Characteristics of Discharge Site and Receiving Marine Environment.

i) Hydrographic, meteorological, geological, biological and topographical characteristics of the discharge site.

ii) Location and type of the discharge (outfall, canal, outlet, etc.) and its relation of other areas, e.g. amenity areas, spawning, nursery and fishing areas, shellfish grounds and exploitable resources.

iii) Rate of disposal per specific period, e.g. quantity per day, per week and per month.

iv) Initial dilution achieved at the point of discharge into the receiving marine environment.

v) Methods of packaging and containment, if any.

vi) Dispersion characteristics such as effects of current, tides and wind on horizontal transport and vertical mixing.

vii) Water characteristics, e.g. temperature, pH, salinity, stratification, oxygen indices of pollution - dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD) - nitrogen present in organic and mineral form including ammonia, suspended matter, other nutrients and productivity.

viii) Existence and effects of other discharges which have been made in the discharge site, e.g. heavy metal background levels and organic carbon content.

c) Availability of Waste Technologies

The methods of waste reduction and discharge for industrial effluent as well as domestic sewage should be selected taking into account the availability and feasibility of:

i) Alternative treatment processes;

ii) Re-use or elimination methods;

iii) On-land disposal alternative; and

iv) Appropriate low-waste technologies.

d) General Considerations and Conditions

i) Possible effects on amenities, e.g. presence of floating or stranded materials, turbidity, objectionable odour, discoloration and foaming.

ii) Effects on human health through pollution impact on : Edible marine organisms, bathing waters, aesthetics;, etc.

iii) Effects on marine ecosystems, in particular living resources, endangered species and critical habitats.

iv) Possible effects on other uses of the sea, e.g. impairment of water quality for industrial use, underwater corrosion of structure, interference with ship operations from floating materials, interference with fishing or navigation through deposit of waste or solid objects on the sea floor and protection of areas of special importance for scientific or conservations purposes.

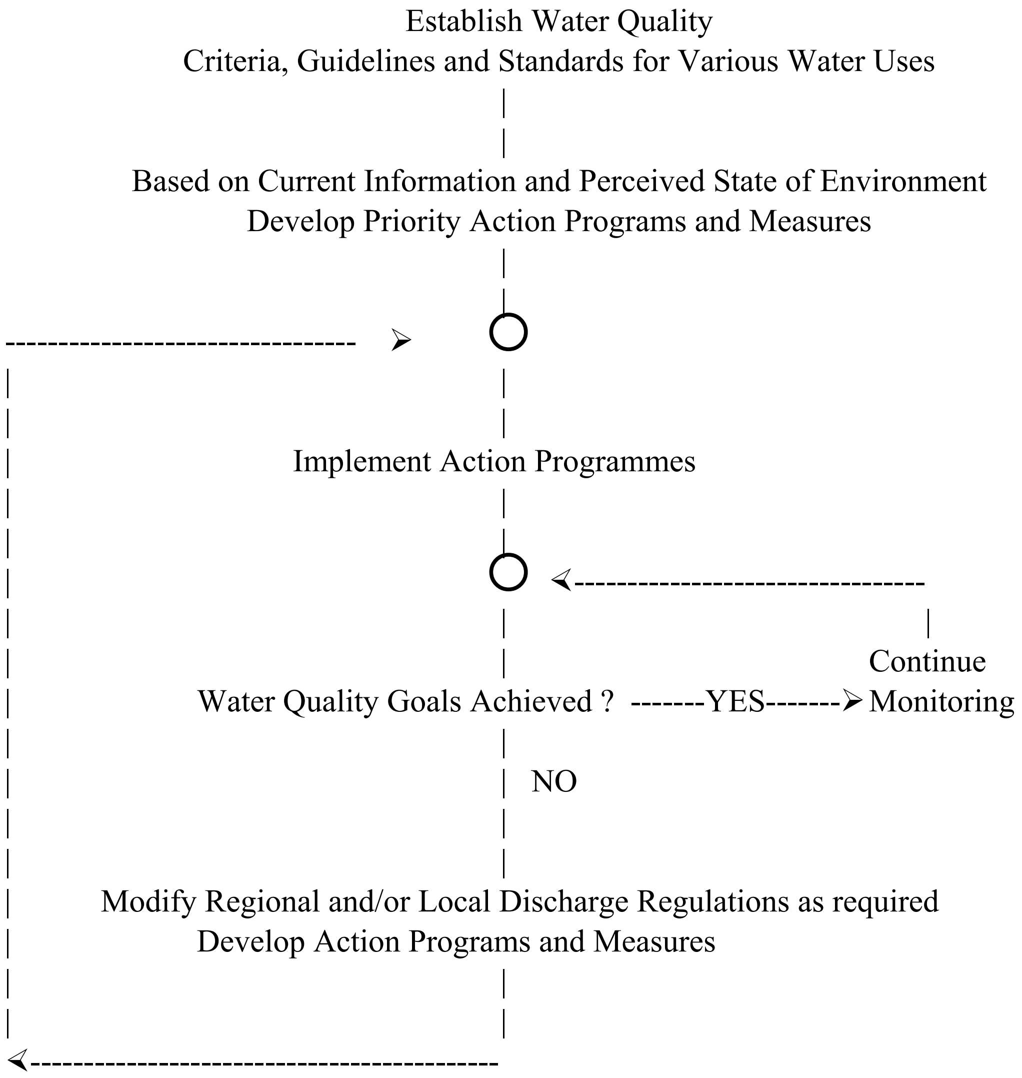

Diagram 1: Environmental Management Scheme

8.2 APPENDIX II

WASTE (EMISSION) FACTORS FOR THE CALCULATION OF POLLUTANTS GENERATION FROM INDUSTRIAL FACILITIES

1. PETROLEUM

1.1 PETROLEUM REFINING

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils and feedstocks for the petrochemical industry. Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations and they terminate with storage preparatory to shipping the refined products from the refinery. The petroleum refining industry employs a wide variety of processes, such as. Separation processes (atmospheric or vacuum distillation and light ends recovery), petroleum conversions processes (cracking – thermal or catalytic-, reforming, alkylation, polymerisation, isomerisation, cocking, visbreaking), petroleum treating processes (storage, blending, loading, unloading) and auxiliary facilities (boilers, wastewater treatment, hydrogen production, sulfur recovery plant, cooling towers, blowdown system, compressor engines).

Air emissions

Process	VOC	PAH			Source
Fluid Catalytic Cracking units (uncontrolled) Kg/10^3 L fresh feed	0.630	NA			13,14
Moving-bed catalytic cracking units Kg/10^3 L fresh feed	0.250	NA			
Compressor engines Reciprocating engines Kg/$10^3 m^3$ gas burned	21.8	NA			
Compressor engines Gas turbines Kg/$10^3 m^3$ gas burned	0.28	NA			
Blowdown systems (Uncontrolled) Kg/10^3 L fresh feed	1,662	NA			
Blowdown systems (vapor recovery system and flaring) Kg/10^3 L fresh feed	0.002	NA			

Process	VOC	PAH			Source
Vacuum distillation column condensers (Uncontrolled) Kg/10^3 L fresh feed	0.14	NA			
Fugitive emission (total) Kg/m3.day capacity	0.39	NA			

* NA : Not available

Liquid emissions (Kg/10^3m^3 crude oil)

Process	Petroleum hydrocarbons	Phenol	Cr	PAH	BOD_5	Source
Topping refineries	8.3	0.034	0.007	NA	3.4	15
Cracking refineries	31.2	4	0.25	NA		
Petrochemical Refinery (no lub oil)	52.9	7.7	0.234	NA	172	
Lub oil Refinery	120	8.3	0.046	NA	217	
Integrated Refinery (cracking, Lub Oil, Petrochemicals	74.9	3.8	0.49	NA	197	

1.2 TRANSPORTATION AND MARKETING OF PETROLEUM PRODUCTS

The transportation and marketing of petroleum liquids involve many distinct operations, each of which represents a potential source of evaporation loss. Crude oil is transported from production operations to a refinery by tankers, barges, rail tank cars and pipelines. Refined petroleum products are conveyed to fuel marketing terminals and petrochemical industries by these same modes. From the fuel marketing terminals, tank trucks to service stations, commercial accounts and local bulk storage plants deliver the fuels. Evaporative emissions occur during the transportation and marketing of petroleum liquids, and represent the main air emissions from the process. The liquid emissions are related to accidental spills and cannot be estimated in the present document.

Ships and barges are important means of petroleum transportation in the Mediterranean coastal zone, therefore the air emission related to this process are presented bellow.

Air emissions (Ships/barges mg/ L transferred product)

Process	Vessel tank condition	Previous cargo	VOC	PAH	source
Gasoline loading operation at marine terminals	Unclean	Volatile	315	NNA	13,14
	Ballasted	Volatile	205	NA	
	Clean	Volatile	180	NA	
	Gas-free	Volatile	85	NA	
	Any condition	Non volatile	85	NA	
	Gas-free	Any cargo	NA	NA	
Typical overall situation	Any cargo	215		NA	

Liquid emissions

				PAH	Source
				NA	

2. FOOD INDUSTRIES AND PROCESSING

In the industrial sector of food production and processing, the main concern is organic load and nutrients, which are found in liquid effluents from the plants. Usually there are no toxic or dangerous substances used in the processes.

2.1 LIVESTOCK PRODUCTION

Air emissions

Process	NH_3	VOC	H_2S		Source
	NA	NA	NA		

Liquid emissions

Process	BOD$_5$	N	Total P		Source
Livestock production (Kg of pollutant/ 10^3 Kg animal weight. year)					15,16
Beef cattle	460	NA	NNA		
Dairy cattle	380	NA	NA		
Swine feedlot	730	170	60		
Sheep	670	NA	NA		
Chicken	1,600	290	160		
Slaughterhouse (Kg of pollutant/ 10^3 Kg animal weight)					
Beef/pork	6	NA	NA		
Chicken	15	NA	NA		

2.2 FISH PROCESSING

Fish canning and byproduct manufacturing includes washing or thawing (for deep sea fishing products), eviscerating, washing and cooking. Then the fish is allowed to cool, head, fins and bones are removed and the remainder is cuted and canned. Oil, brine and/or water are added and the cans are sealed and pressure-cooked. Air emissions include odours (H_2S and trimethylamine [$(CH_3)_3N$] and VOC (from cooker).

Air emissions (Kg of pollutant/ 10^3 Kg of raw fish processed)

Process	H_2S	trimethylamine	VOC	Source
Cookers, canning	NA	NA	NA	12,14
Cookers, scrap				
- fresh fish	0.005	0.15	NA	
- Stale fish	0.10	1.75	NA	
Steam tube dryer	NE	NE	NE	
Direct-fired dryer	NE	NE	NE	

Liquid emissions (Kg of pollutant/ 10^3 Kg of fish produced)

Process	BOD$_5$	N	Oils and fat		Source
Tuna	16.2	1.2	6.48		15
Shrimp	51.7	10	12.2		
Crabs	5.25	1.0	0.26		
Sardine	9.2	NA	1.7		

* NE : No Emission

2.3 CANNED FRUIT AND VEGETABLES

The canning of fruit, vegetables and vegetable juices aim at the preservation of perishable food in a stable form that can be stored and shipped to distant markets during all moths of the year. The goal of the canning process is to destroy any microorganisms in the food and prevent recontamination by microorganisms. Heat is the most common agent used to destroy microorganisms. Removal of oxygen can be used in conjunction with other methods to prevent the growth of oxygen-requiring microorganisms. A typical canning operation may employ the following general processes: washing, sorting/grading, preparation, container filling, exhausting, container sealing, heat sterilization, cooling, labeling/casing and storage. Air emissions may arise from a variety of sources and include particulate matter and VOC (associated with thermal processing steps – cooking). No data are available for use in the development of emission factors. Liquid effluents are mainly rich in BOD, COD and suspended solids (SS).

Air emissions

Process	VOC				Source
	NA				

Liquid emissions

Process	BOD_5	COD			Source
	NA	NA			

2.4 SUGARBEET PROCESSING

Sugarbeet processing is the production of sugar from sugarbeets. Harvested sugarbeets are screened to remove loose dirt and pinch the beet tops and leaves from the beetroots. The beets are cleaned and then transported to the processing plant, where they are subject to operation including diffusion, juice purification, evaporation, crystallisation, dried pulp manufacture and sugar recovery from molasses. Particulate matter, VOC and combustion products (NOx, SO_2, CO and CO_2) are the primary pollutants emitted from sugarbeet processing industry.

Air emissions (Kg of pollutant /10^3 Kg of pressed wet pulp to the dryer)

Process	VOC				Source
Coal-fired pulp dryer	0.6				13,14
Natural gas-fired pulp dryer	NA				

Process	VOC				Source
Fuel oil- fired pulp dryer	0.06				
First Evaporator	NE				
Sulfur stove	NE				
First carbonation tank	NE				
Second carbonation tank	NE				

Liquid emissions (Kg of pollutant /10^3 Kg of beet feed)

Process	BOD_5			Source
High pollution effluents from the manufacturing process	4			15

2.5 OLIVE OIL PRODUCTION

Olive oil is produced with cold pressure of the olives in centrifuge or conventional mills. The oil produced is called “virgin olive oil” and is bottled and stored. If the produced olive oil is of inferior quality (higher acidity) it is refined following processes such as neutralization, deodorisation, decoloration and demargarination. The olive oil mills are often relatively small plants, serving the olive oil production of a specific area. Their production process is simple and no air pollutants are produced. However, the liquid effluents of the mills are very highly polluted, with BOD5 up to 50,000 mg/L, containing toxic compounds such as phenols. Olive oil production is a typical activity in the Mediterranean region and the management of its liquid effluents is a well-known environmental problem in the area.

Air emissions

Process	Hexane			Source
	NA			

Liquid emissions (Kg of pollutant /10^3 Kg oil produced)

Process	BOD_5	COD	Oil and fat		Source
Oil mill (total plant)	95	NA	NA		16

2.6 VEGETAL OIL PROCESSING (OTHER THAN COLD PRESSED OLIVE OIL)

The process is similar to all oilseeds and includes cracking, dehulling/hull removal, conditioning, flaking, and solvent extraction with hexane, oil desolvetizing and oil refining. Similar process is used for the production of kernel olive oil, from the pulp remaining after the cold pressure of olives for the production of olive oil. Air emissions include particulate matter, VOCs (mainly from the oil extraction solvent) and odour. Liquid emissions include vegetable oil from the plant and condensates.

Air emissions (L of pollutant /10^3 Kg raw oilseed)

Process	Hexane			Source
Total plant (soybean)	3.3			13,14

Liquid emissions oil (Kg of pollutant /10^3 Kg oil produced)

Process	BOD_5	COD	Oil and fat		Source
Oil processing (total plant)	12.9	21	6.5		15
Oil Refinery			NA		16
- Washing of neutral oil	1.0*	1.5*			
- Neutralization effluents	9.0*	15.1*			
- Condensers	0.34*	1.1*			
- Floor washing	0.15*	0.2*			

* (Kg of pollutant /10^3 Kg unprocessed oil)

2.7 WINE AND SPIRITS

Wine is an alcoholic beverage produced by the fermentation of sugars in fruit juices, primarily grape juice. Distilled spirits are produced with fermentation of grain, grape residues, or other fruits and the alcohol/water solution produced is distilled to concentrate the alcohol. The produced spirit can be bottled and shipped to the market or left for aging before marketing. From the distillation and aging processes are emitted small quantities of VOCs such as alcohols (ethyl alcohol, methyl alcohol, n-propul alcohol, isobutil alcohol, isoamyl alcohol) and acetaldehyde, and hydrogen sulfide. Liquid effluents are

Air emissions

Process					Source

Liquid emissions (Kg of pollutant/ 10^3 L product)

Process	BOD_5		Source
Wine transfer (retention of sludge) White or red wine	0.18 – 0.42		16
Wine transfer (no sludge retention) White wine	0.90 – 1.70		
Wine transfer (no sludge retention) Red wine	0.98 – 1.22		
Washing of tanks	0.87		
Cleaning of machinery*	0.18		

* (Kg of pollutant/ 10^3 Kg of processed grapes)

2.8 BEER PRODUCTION

Air emissions from the production of beer include mostly VOCs from the brewing tanks, and odours. Liquid effluents originate mainly from the washing of bottles to be filled and brewing tanks.

Air emissions (Kg of pollutant/ 10^3 of barley)

Process	VOC			Source
Brewing	0.25			16

Liquid emissions (Kg of pollutant/ 10^3 L of beer produced)

Process	BOD_5		Source
Total brewery	6.25		15

2.9 SOFT DRINKS

For the production of soft drink are used already preconcentrated juices. The water that will be used for the preparation of soft drinks is treated for alkalinity (addition of iron sulfate, sodium hypochloride and CaO), chlorine and trace organics removal (sand filtration) before the process. The concentrate juice is added to the water together with sugar and odor agents. No significant air emissions are generated from the soft drinks plants (additional to fuel burning). Liquid effluents originate from bottle washing (NaOH, phosphate salts from detergent, organic load), disposal of returned juices (expiration of the consumption date) and general washing of the machinery and floors.

Air emissions

Process					Source

Liquid emissions (Kg of pollutant/ 10^3 L product)

Process	BOD_5		Source
With syrup production	4.33		15
Without syrup production	2.15		

3. FERTILIZERS AND INORGANIC CHEMICALS

3.1 SYNTHETIC AMMONIA

Synthetic ammonia (NH_3) refers to ammonia that has been synthesized from natural gas. Nitrogen is obtained from the air, while hydrogen is obtained from either natural gas or naphtha, or the electrolysis of brine at chlorine plants. Air pollutants from the manufacture of synthetic anhydrous ammonia are emitted from 4 process steps: regeneration of the desulfurisation bed, heating of the catalytic stream, regeneration of carbon dioxide scrubbing solution and steam stripping of process condensates.

Air emissions (Uncontrolled) (Kg/10^3 Kg product)

Process	Total organic compounds	NH_3		Source
Desulfurization unit regeneration	3.6	NE		13,14
Carbon dioxide regenerator	0.52 (0.05 Kg/t is monoethanolamine)	1.0		
Condensate stream stripper	0.6 (mostly methanol)	1.1		

Liquid emissions (Kg/10^3 Kg product)

Process	Oil	BOD_5		source
Total plant	11	0.4		15

3.2 UREA

Urea [$CO(NH_2)_2$] also known as carbamide or carbonyl diamide, is mostly used in fertilizers mixtures, but also in plastics manufacturing and animal feeding. Emissions (air or liquid) from urea manufacturing is mostly ammonia (in particulate, gaseous or dissolved form). Air emissions may also include formaldehyde and methanol.

Air emissions (Kg/10^3 Kg product)

Process	NH_3 (uncontrolled)	NH_3 (controlled)		source
Solution formation and concentration	9.23	NE		13,14
Non fluidized bed prilling				
- Agricultural grade	0.43	NE		
- Feed grade	NE	NE		
Fluidized bed prilling				
- Agricultural grade	1.46	NE		
- Feed grade	2.07	1.07		
Drum granulation	1.07	NE		
Rotary drum cooler	0.0256	NE		

Liquid emissions (Untreated) (Kg/10^3 Kg product)

Process	BOD_5	N		source
Total plant	0.24	10		15

3.3 AMMONIUM SULFATE

Ammonium sulfate is commonly used as fertilizer and is the principal emitted compound from the manufacturing plants. In plants that produce ammonium sulfate from caprolactam, small amounts of VOCs are also emitted.

Air emissions (Kg/10^3 Kg product)

Process	VOC (in caprolactam plants			Source
Rotary dryers				13,14
- Uncontrolled	0.74			
- Controlled	0.11			
Fluid bed dryers				
- Uncontrolled	0.74			
- Controlled	0.11			

Liquid emissions (Untreated) (Kg/10^3 Kg product)

Process				Source

3.4 PHOSPHATE FERTILIZERS AND PHOSPHORIC ACID

Normal superphosphates fertilizers (15 – 21% phosphorus as P_2O_5) and phosphoric acid are prepared by reacting ground phosphate rock with concentrated sulfuric acid. Air emissions are produced from rock unloading and feeding, mixing operations in the reactor, storage and fertilizer handling operations, and include fluoride and particulate matter. Liquid emissions include fluoride, phosphorus and nitrogen.

Air emissions (Kg/10^3 Kg P_2O_5 produced)

Process	F	Hg		Source
Phosphate fertilizers				13,14
Scrubber	0.001	NA		
Exhaust stack	0.0025	NA		
Phosphoric acid				
Reactor Uncontrolled Controlled	 0.19 $1.9 X 10^{-3}$	 NA NA		
Evaporator Uncontrolled Controlled	 0.0022 $0.022 X 10^{-3}$	 NA NA		
Belt filter Uncontrolled Controlled	 0.032 $0.32 X 10^{-3}$	 NA NA		
Belt filter vacuum pump Uncontrolled Controlled	 0.0073 $0.073 X 10^{-3}$	 NA NA		
Gypsum settling & cooling ponds Uncontrolled Controlled	 NA NA	 NA NA		

Liquid emissions (Kg/10^3 Kg P_2O_5 produced)

Process	F-	Pb, As, Cr, Hg	P_2O_5	NH_3	Source
Phosphoric acid production	11.2	1.1	25.2	0.14	16

4. METALLURGY

4.1 GRAY IRON FOUNDRIES

Iron foundries produce high-strength castings used in industrial machinery and heavy transportation equipment manufacturing. Castings include crusher jaws, railroad car wheels and automotive and truck assemblies. Cast iron is an iron-carbon-silicon alloy containing 2 to 4 percent carbon and 0.25 to 3 percent silicon, along with varying percentages of manganese, sulfur and phosphorus. Alloying elements such as nickel, chromium, molybdenum, copper, vanadium and titanium are sometimes added. The major production operations in iron foundries are raw material handling and preparation, metal melting, mold and core production and casting and finishing.

Dust is the major pollutant emitted from the foundries. It is retained with various particulate matter collection equipment (bag filters, electrostatic filters of scrubbers). The scrubbing devices produce liquid effluents, which contain heavy metals (zinc, lead, cadmium), cyanide, ammonium and organic matter (COD).

Air emissions (Kg/ 10^3 Kg product)
(*µg I-TEQ/t of product)

Process	PCDD/ PCDF	VOC	Hg	Cd	Pb	Pb	Source
Coupola Uncontrolled	10	NA	NA	NA	0.05-0.6	NA	13,14,17
Electric arc	NA	0.03-0.15	NA	NA	NE	NA	
Electric induction	NA	NA	NA	NA	0.005-0.05	NA	
Reverberatory	NA	NA	NA	NA	0.007-0.06	NA	
Sinter plant	10*	NA	NA	NA	NA	NA	6

Liquid emissions (Kg/ 10^3 Kg product)
(*µg I-TEQ/t of product)

Process	Total N	Phenol	F	CN	Oil	PCDD/ PCDF	Source
Blast furnace (scrubber) Untreated	0.27	0.01	0.023	0.039	NA	NA	5
Hot rolling (Untreated)	NA	NA	NA	NA	1.87	NA	
Cold rolling (Untreated)	NA	NA	NA	NA	2.05	NA	
Sinter plants	NA	NA	NA	NA	NA	0.3*	6

4.2 IRON AND STEEL PRODUCTION

The production of steel at an integrated iron and steel plant is accomplished using several interrelated processes, such as: coke production, sinter production, iron production, iron preparation, steel production, semifinished product preparation, finished product preparation, heat and electricity supply and handling and transport of raw, intermediate and waste materials.

Air emissions include particulate matter, PAHs, cadmium and dioxins.

Air emissions

Process	PAH (Kg/ 10^3 Kg coal burned)	PCDD/PCDFs (µg I-TEQ/t of product)	Hg	Cd	Pb	Source
Iron and steel production	0.028	1	NA	NA	NA	6
Dirty scrap, limited control		10				17

Liquid emissions (Kg/10^3 Kg product)

Process	Phenol	Cr	Zn	CN	Oil	Source
Blast furnace (scrubber wastes) untreated	0.01	NA	NA	0.045	NA	15
Basic oxygen furnace	NA	NA	NA	NA	NA	
Open hearth furnace	NA	NA	1.01	NA	NA	
Electric arc furnace	NA	NA	1.58	NA	NA	
Hot rolling mills (untreated)	NA	NA	NA	NA	1.87	5
Cold rolling (untreated)	NA	NA	NA	NA	2.05	
Galvanizing (untreated)	NA	0.015	0.405	NA	NA	

4.3 PRIMARY ALUMINUM PRODUCTION

Primary aluminum production begins with the mining of bauxite ore, a hydrated oxide of aluminum consisting of 30% – 56% alumina (Al_2O_3) and lesser amounts of iron, silicon and titanium. The ore is refined into alumina, which is then transferred to a primary aluminum plant for electrolytic reduction to aluminum. The refining and reducing processes could be done in the same plant or in different facility. Air emissions include gaseous hydrogen fluoride and particulate fluorides, alumina, CO, CO2, volatile organics, PAHs, dioxins, sulfur dioxide, and perflorinated carbons (PFCs). The source of fluoride emissions from reduction cells is the fluoride electrolyte, which contains cryolite (Na_3AlF_6), aluminum fluoride (AlF_3) and fluorspar (CaF_2). The dissociation of molten cryolite is the source of the PFCs – tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) – which are formed during anode effects. Liquid effluents include the “red muds” produced during the bauxite processing (which are mainly solid wastes). The production of aluminum is a relatively “dry” process and liquid effluents are mainly produced from cooling water, runoff. The later effluents contain Al and dissolved fluoride compounds

Air emissions (Kg of pollutant/ 10^3 Kg of Al produced)

Process	Gaseous Fluoride	Particulate fluoride	VOC	PAH	PCDD/F	Source
Anode baking furnace						13,14
- Uncontrolled	0.45	0.05	NA	NA	NA	
- Spray tower	0.02	0.015				
- Electrostatic precipitators (ESP)	0.02	0.015				
Prebake cell						
- Uncontrolled	12	10	NA	NA	NA	
- Fugitive	0.6	0.5				
- Emissions to collector	11.4	9.5				
- Spray tower	0.7	1.9				
- Dry alumina scrubber	0.1	0.2				
Vertical Soderberg stud cell						
- Uncontrolled	16.5	5.5	NA	NA	NA	
- Fugitive	2.5	0.85				
- Emissions to collector	14.0	4.7				
- Spray tower	0.15	1.15				
- Ventouri scrubber	0.15	0.2				
- Dry alumina scrubber	0.15	0.1				

Process	Gaseous Fluoride	Particulate fluoride	VOC	PFC	PCDD/ PCDF	Source
Horizontal Soderberg stud cell						13,14
- Uncontrolled	11.0	6.0	NA	NA	NA	
- Fugitive	1.1	0.6				
- Emissions to collector	9.9	5.4				
- Spray tower	3.75	1.35				
- Scrubber plus wet ESP	0.1	0.1				
- Dry alumina scrubber	0.2	0.1				
Aluminum production (average)	NA	NA	NA	0.06	NA	13,14

Liquid emissions (Kg of pollutant/ 10^3 Kg of Al produced)

Process	Fluor	Oil				Source
Alumina from bauxite	4.2	NA				15
Aluminum production						
Anode prebaking	0.12	0.03				
Reduction cells	1.5	NA				

4.4 PRIMARY LEAD SMELTING

Lead is found naturally as a sulfide ore containing small amounts of copper, iron, zinc, precious metals and other trace elements. The lead in the ore, after being concentrated into metallurgical lead, is processed through 3 major steps: sintering, reduction and refining. Emission of lead and particulate occur in varying amounts from nearly every process within primary lead smelters/refineries (point emission sources and fugitive emissions).

Air emissions

Process	PCDD/ PCDF	VOC	Hg	Pb	Source
Fugitive emissions (Kg/ 10^3 Kg product)	NA	NA	NA	2.5	13,14,15
Ore crushing (Kg/10^3 Kg ore crushed) Uncontrolled Controlled	NE	NE	NA	0.15 0.001	13,14,15
Ore screening (Kg/10^3 Kg ore crushed) Controlled	NE	NE	NA	0.001	13,14
Sintering (Kg/10^3 Kg sinter produced)	NA	NA	NA	0.009	
Sinter building fugitives (Kg/10^3 Kg sinter produced)	NA	NA	NA	0.016	
Blast Furnace (Kg/10^3 Kg bullion produced) or Uncontrolled or Centrifugal collector or Fabric filter	NA	NA	NA	0.034 29 4.35 2.61	13,14
Dross Reverbatory Furnace (Kg/10^3 Kg lead produced) Uncontrolled or Centrifugal Collector or Fabric filter	NA	NA	NA	2.4 0.36 0.07	15

Liquid emissions

Process				Hg		Source
				NA		

4.5 PRIMARY COPPER SMELTING

Copper is separated from copper sulfide ore concentrates using pyrometallurgical smelting methods. Process steps include mining, concentration, roasting, smelting, converting and fire and electrolytic refining. Air emissions from primary copper smelters are principally particulate matter and sulfur oxides and are generated from roasters, smelting furnaces and converters. Fugitive emissions are generated during material handling operations. Liquid effluents are generated from the scrubbers (roasters, etc.).

Air emissions (Kg pollutant/10^3 Kg ore processed)

Process	PCDD/ PCDF	VOC	Hg	Pb	source
Roasting	NA	NA	NA	0.075	13,14
Smelting	NA	NA	NA	0.036	
Converting	NA	NA	NA	0.13	

Liquid emissions

Process						Source

4.6 SECONDARY ALUMINUM PRODUCTION

Secondary aluminum producers recycle aluminum from aluminum-containing scrap. The process involves two general categories of operations, scrap pretreatment and smelting/refining. Pretreatment operations include sorting, processing and cleaning scrap. Smelting/refining operations include cleaning, melting, refining, alloying and pouring of aluminum recovered from scrap. Air emissions include particulate matter and metals, as well as, VOCs and dioxins because of the thermal destruction of plastics and oils present in the scrap. There are not enough data to calculate emission factors for these industrial plants.

Air emissions (Kg pollutant/10^3 Kg product)
(*µg I-TEQ/t of product)

Process	VOCs	PCDD/PDCDF	Source
Total plant	NA	22*	6
Total plant dust removal	NA	150	17
Well controlled		35	17
Optimized process		1	17

Liquid emissions (Kg pollutant/10^3 Kg product)

Process	Oil					Source
Secondary aluminum smelting	0.65					15

4.7 SECONDARY LEAD SMELTING

Secondary lead smelters produce lead and lead alloys from lead bearing scrap material. An important part of all secondary lead is derived from scrap automobile batteries. Each battery contains approximately 8.2 Kg of lead, consisting of 40% of lead alloys and 60% lead oxide. Other raw materials used in secondary lead smelting include wheel balance weights, pipe, solder, drosses and lead sheathing. Secondary lead smelting includes three major operations: scrap pretreatment, smelting and refining. Reverbatory and blast furnaces account for the vast majority of the total lead emissions.

Air emissions (Kg pollutant/10^3 Kg product)
(*µg I-TEQ/t of product)

Process	PCDD/ PCDF	VOC	PAH	Pb	Source
Sweating (Kg pollutant/10^3 Kg charge) Uncontrolled Controlled	NA	NA	NA	4-8 ND	13,14
Reverbatory smelting Uncontrolled Controlled	NA	NA	NA	32 NE	
Blast smelting cupola Uncontrolled Controlled	NA	NA	NA	52 0.15	
Kettle refining Uncontrolled Controlled	NA	NA	NA	0.006 NE	
Casting Uncontrolled Controlled	NA	NA	NA	0.007 NE	
Total plant	1	NA	NA		6
From PVC battery separators	80	NA	NA	NA	17
From PVC/Cl_2 free scrap blast furnaces	8	NA	NA	NA	17

Liquid emissions

Process						Source

4.8 SECONDARY COPPER SMELTING

Secondary copper recovery is divided in 4 separate operations: scrap pretreatment, smelting, alloying and casting. Pretreatment includes the cleaning and consolidation of scrap in preparation for smelting. Smelting consists of heating and treating the scrap for separation and purification of specific metals. Alloying involves the addition of one ore more other metals to copper to obtain desirable qualities characteristic of the combination of metals.

The principal pollutant emitted secondary copper smelting activities is particulate matter. As a characteristic of secondary metallurgical industries, pyrometallurgical processes used to separate or refine the desired metal, such as the burning of the insulation from copper wire, result in emission of metal oxides and unburned insulation. Similarly, drying of chips and borings to remove excess oils and cutting fluids can cause discharges of VOCs, PAH and products of incomplete combustion (dioxins/furans).

Air emissions (Kg pollutant/10^3 Kg product)
(*µg I-TEQ/t of product)

Process	PCDD/ PCDF	VOC	PAH	Pb	Source
Reverbatory furnace high lead alloy – 58% Red/yellow brass Other alloy – 7%	NA	NA	NA	 25 6.6 2.5	13,14
Total plant	50	NA	NA	NA	6
Total plant basic technology	800	NA	NA	NA	17
Total plant well controlled	50				17
Total plant PCDD/F control	5				17

Liquid emissions

Process						Source

4.9 STORAGE BATTERY PRODUCTION

Lead acid storage batteries are produced from lead alloy ingots and lead oxide. Lead oxide may be prepared by the battery manufacturer or may be purchased from a supplier. Battery grids are manufactured by either casting or stamping operations and are filled with pastes. A mixture of lead oxide powder, water and sulfuric acid produces the positive paste and the same ingredients in slightly different proportions with the addition of an expander (generally a mixture of barium sulfate, carbon black and organics) make the negative paste. Pasting machines force the pastes into the interstices of the grids, which are then made into plates. The plates are then cured and processed before they are assembled in the battery case. Air emissions include lead, sulfuric acid mist and particulate matter. Liquid effluents are enriched in lead and may have very low pH (pH < 1).

Air emissions (uncontrolled) (Kg of pollutant/10^3 batteries)

Process	Pb			Source
Grid casting	0.35-0.40			13,14
Paste mixing	0.50-1.13			
Lead oxide mill	0.05			
3-process operation	4.79-6.60			
Lead reclaim furnace	0.35-0.63			
Small parts casting	0.05			
Total production	6.94-8.0			

Liquid emissions (Kg of pollutant/10^3 batteries)

Process	Pb					Source
	NA					

4.10 LEAD OXIDE AND PIGMENT PRODUCTION

Lead oxide is a general term and can be either lead monoxide or “litharge” (PbO); lead tetroxide or “red lead” (Pb_3O_4); or black or “gray” oxide, which is a mixture of 70% monoxide, and 30% metallic lead. Black lead is made for specific use in the manufacture of lead acid storage batteries. Litharge is used in the manufacture of various ceramic products, in capacitors, as a catalyst in organic chemical industry, in oil refining, in the production of lead chemicals, dry colors, etc. Red lead is the major lead pigment, which is principally used in ferrous metal protective paints, as well as in the manufacturing other lead pigments.

Air emissions (controlled) (Kg/10^3 product)

Process	Pb			Source
Lead oxide Production				13,14
Barton pot	0.22			
Calcining				
Baghouse inlet	7.0			
Baghouse outlet	0.024			
Pigment production				
Red lead	0.50			
White lead	0.28			
Chrome pigments	0.065			

Liquid emissions

Process						Source

4.11 ELECTROPLATING

Electroplating is the process of applying a metallic coating to an article by passing an electric current through an electrolyte in contact with the article, thereby forming a surface having properties or dimensions different from those of the article. A great variety of metals and alloy substrates are electroplated on a commercial scale for specific uses, or for decoration. Electroplating processes include a pretreatment step (polishing, grinding and degreasing), alkaline cleaning, acid dipping, and electroplating. Air emissions consist of particulate matter (enriched in heavy metals) and VOCs, while liquid effluents contain heavy metals and have a very low pH (acidic effluents).

Air emissions (Kg pollutant/10^3 product)

Process	VOCs	Metals		Source
	NA	NA		

Liquid emissions (Kg pollutant/10^3 anode – substrate for electroplating)

Process	Cd	Cr	Cu	CN	Ni	Zn	Source
Cadmium Electroplating	NA	NA	NA	12.7	NA	NA	15
Chromium Electroplating	NA	734 (total) 297 (Cr^{6+})	NA	NA	NA	NA	
Copper electroplating	NA	NA	9.77	20	NA	NA	
Nickel Electroplating	NA	NA	NA	NA	3.98	NA	
Zinc Electroplating	NA	NA	NA	32.5	NA	224	

5. LEATHER TANNING

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting and keep them supple and durable. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents are trivalent chromium and vegetable tannins. Alum, syntans (man-made chemicals), formaldeyde, glutaraldehyde and heavy oils are other tanning agents.

Leather tanning is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. The first steps of the process (also called "beamhouse processes") include trimming, soaking, fleshing and unhearing. The "tanyard processes" include bathing, pickling, tanning, wringing and the "finishing processes" include conditioning, staking, dry milling, buffing, spray finishing and plating.

Air emissions

There are several sources of air emissions in the leather tanning and finishing industry, including VOCs when organic solvents are used during finishing process. Also ammonia emissions may occur during some of the wet processing steps, such as deliming and unhairing, or during drying. Emissions of sulfides may occur during liming/unhairing or from the conversion of alkaline sulfides in tannery wastewater to hydrogen sulfide if the pH is less that 8. Chromium emissions may occur from chromate reduction (US EPA, AP-42, 2001).

Air emissions

Process		Metals	Source
		NA	

Liquid emissions

On a recent study of the Greek Ministry of the Environment, Urban Planning and Public Works (YPEHODE, 2001), average emission factors are presented, based on measurements of Greek tanneries. The factors were calculated from real data, involving tanneries processing different kind of hides

Process	BOD_5 Kg/tn of hides	Total N Kg/tn of hides	Cr_2O_3 Kg/tn of hides	Phenol Kg/tn of hides	Oil Kg/tn of hides	Source
Cow skins for shoes (upper leather)	90	14	6.5	NA	NA	4,16
Sheep skins for clothes and leather goods	90	24	16	NA	NA	

Process	BOD_5 Kg/tn of hides	Total N Kg/tn of hides	Cr_2O_3 Kg/tn of hides	Phenol Kg/tn of hides	Oil Kg/tn of hides	Source
Goat skins for shoemaking	85	24	23.2	NA	NA	
Pig skins for clothes	50	24	6.6	NA	NA	
Croupon (cow skins) for shoe soles	40	13.5	NA	NA	NA	

In the literature are also found emission factors from the tanneries relative to the processes used, which are presented in the following Table.

Process	BOD_5 Kg/tn of hides	Total N Kg/tn of hides	Cr Kg/tn of hides	Phenol Kg/tn of hides	Oil Kg/tn of hides	Source
Hair pulp, chrome tan, retan wet finish	95	17	4.3	0.11	19	15
Hair shave, chrome tan, retan, wet finish	69	13	4.9	0.24	43	
Hair save, vegetable tan, retan, wet finish	67	9.2	0.2	NA	33	
Hair pulp or shave, chrome tan, no finish	110	16	4.4	NA	6.6	
No beamhouse tanneries (tan, retan, wet finish)	37	3.7	2.6	NA	7	
Finish only	67	6	1.2	NA	24	

6. TEXTILE MANUFACTURING AND DYEING

The sector includes the manufacturing of textiles (cotton, wool, synthetic fibbers) as well as the finishing-dyeing processes. During the manufacturing process there are no important emissions of pollutants (air or liquid). On the other hand, the finishing and dyeing processes involve the use of chemicals, resulting in pollutant emissions. The main steps in the finishing – dyeing processes include bleaching, dyeing (or printing) and finishing. The dyeing substances are mostly synthetic organic compounds and hydrocarbides and additional substances are used for better results. Dyes are in solutions applied to impart color by becoming physically or chemically incorporated into individual fibers. Therefore solvents (organic or inorganic) are also used in textile dyeing plants. More than 100 different chemical compounds are found in the effluents of dyeing-finishing plants (US EPA, 1979 and Environment Canada, 1989), including phthalates (such as 2-ethylhexyl phthalate and di-n-butyl phthalate), naphthalene, phenols, toluene, trichloro- and tetrachloro- ethylene, chlorophorme, ethylbenzene, dichlorobenzene and heavy metals (such as chromium, copper, zinc, arsenic, cadmium, lead, nickel and mercury).

Air emissions

Air emissions from dyeing-finishing plants include: VOCs (use of plasticisers, solvents), acidic or basic gases (wool carbonization, cotton mercerization, bleaching), ClO_2 (bleaching), dust from paints and raw materials. However, there are no available data on air emission factors for all the textile industry. The US EPA produced some air emission factors for the plants of textile fabric printing that are presented in the following Table.

Textile fabric printing organic emission factors (Kg of pollutant/ 10^3 Kg fabric, average)

Process	VOCs			Source
Roller	142			13,14
Rotary screen	23			
Flat screen	79			

Liquid emissions

The liquid effluents derive mainly from the wet processing of the material and their quality depends on the process applied in each plant.

i) Washing and wetting (Kg of pollutant/ 10^3 Kg fabric)

Process	BOD_5	COD			Source
Cotton	23	94			1,2,16
Wool	47	113			
Rayon	14	86			
Accetate	NA	NA			
Nylon	NA	NA			
Acrylic	14	86			
Polyester	14	86			

ii) Bleaching (Kg of pollutant/ 10^3 Kg fabric)

Process	BOD_5	COD			Source
Cotton	5-15	3,500 – 13,500			2,16
Wool	1.5	NA			
Acetate	2	NA			

iii) Dyeing (Kg of pollutant/ 10^3 Kg fabric)

Process	BOD_5				Source
Cotton	2 - 80 (30)				2,3,16
Wool	9 - 34				
Rayon	2 - 50				
Accetate	5 – 100				
Nylon	NA				
Acrylic	2 – 50				
Polyester	30 – 600				

iv) Finishing (Kg of pollutant/ 10^3 Kg fabric)

Process	BOD_5				Source
Rayon	20				3,16
Accetate	40				
Nylon	10				
Acrylic	60				
Polyester	2 - 80				

7. PAPER AND PULP

There are two main stages in the fabrication of paper: the production of paper pulp from wood (or other cellulose bearing raw materials such as straw, cotton, cannabis, etc.) and the production of paper from the paper pulp. The production of paper pulp involves the extraction of cellulose from wood by dissolving the lignin that binds the cellulose fibers together. The processes usually applied in chemical pulping are: kraft, sulfide, neutral sulfite semichemical and soda. For paper production, the paper pulp is cleaned, filling compounds are added (such as kaolin, gypsum, aluminum sulfate, etch) and the paper mass is pressed, dried and cut.

Air emissions (in the kraft process) are mostly produced from the recovery furnace, the lime klin and the smelt-dissolving tank. These emissions are mainly sodium and calcium salts carried by particles. Hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide are also emitted and are responsible for the characteristic odor of the kraft mill. Sulfur dioxide is emitted mainly from oxidation of reduced compounds in the recovery furnace.

Air emissions (Kg of pollutant / 10^3 Kg of air dried unbleached pulp, untreated emissions) for kraft pulping (RSH: Methyl mercaptane, RSR: Dimethyl sulfide, RSSR: Dimethyl disulfide). (*µg I- TEQ/ 10^3 product)

Process	SO_2	PCDD/ PCDF*	H_2S (as S)	Pb	Hg	RSH, RSR, RSSR (as S)	Source
Digester relief and blow tank	NE	NA	0.02	NA	NA	0.6	13,14
Brown stock washer	NE	NA	0.01	NA	NA	0.2	
Multiple effect evaporator	NE	NA	0.55	NA	NA	0.05	
Recovery boiler & direct evaporator	3.5	NA	6	NA	NA	1.5	
Noncontact recovery boiler without direct contact evaporator	NE	NA	0.05	NA	NA	NE	
Smelt dissolving tank	0.1	NA	0.1	NA	NA	0.15	
Lime klin	0.15	NA	0.25	NA	NA	0.1	
Turpentine condenser	NE	NA	0.005	NA	NA	0.25	
Miscellaneous	NE	NA	NE	NA	NA	0.25	
Total plant	NA	0.17*		NA	NA	NA	6
Boilers	NA	0.07-0.04		NA	NA		17

It must be said that other processes in the production of paper pulp, produce different air emissions. However, there were no available detailed data for these different processes to be included in the present survey.

Liquid emissions

Paper pulp production and paper production plants produce different effluents.

Paper pulp production (Kg of pollutant/ 10^3 air dried pulp)

Process	BOD_5	Hg	Tributyltin		Source
Mechanical mill	8 – 13	NA	NA		15
Sulfate pulp (kraft method)	31	NA	NA		
Sulfite method	130	NA	NA		
Semichemical method	27	NA	NA		

Paper production from pulp (Kg of pollutant/ 10^3 paper produced)
(*µg I- TEQ/ 10^3 product)

Process	BOD_5	COD	PCDD/ PCDF*	Hg	Source
Packaging paper	NA	27 – 36	NA	NA	3,16
Sanitary paper	NA	26 – 35	NA	NA	
Writing & printing paper without inc. removal	18	35	NA	NA	
Writing & printing paper with inc. removal	10	20	NA	NA	
Total plant	NA	NA	10	NA	6

8. ORGANIC CHEMICALS

8.1 POLYVINYL CHLORIDE

The manufacture of most resins and plastics begins with the polymerization or linking of the basic compound (monomer), usually a gas or liquid, into high molecular noncrystallic solids. The manufacture of most plastics involves an enclosed reaction or polymerization step, a drying step and a final treating and forming step. The major sources of air contamination in plastics manufacturing are the raw materials or monomers, solvents, or other volatile liquids emitted during the reaction. In the production of polyvinyl Chloride, the major air pollutant is the vinyl chloride monomer, as well as VOC from the solvents used.

Air emissions (g/10^3 Kg of product)

Process	VOCs	Vinyl Chloride	PCDD/F	Source
Total production	NA	235		*
Total production			N.E.	*

Liquid emissions

Process		PCDD/F	Vinyl Chloride			Source
Total production		0.03	5 (suspension)			17, *
			10 (emulsion)			

* Eurochlor - OSPAR

8.2 POLYETHYLENE TETRAPHTHALATE (PET)

Polyethylene tetraphthalate (PET) is a thermoplastic polyester resin. Low-viscosity PET is used in textile applications as well as in the production of apparel fiber, bottles and photographic film. High-viscosity PET is used in tire cord, seat belts, etc. PET is used extensively in the manufacture of synthetic fibers (polyester fibbers), in food and household products packaging, photographic film, magnetic tape, electrical insulation etc. PET is produced from ethylene glycol and either dimethyl tetraphthalate (DMT) or tetraphthalic acid (TPA). The air emissions from the process include VOCs and particulate matter.

Air emissions (Kg pollutant/10^3 Kg of product)

Process	VOC (non methane)			Source
Total plant (spray condensers)	0.36			13,14
Total plant (no spray condensers)	3.6			

Liquid emissions

Process						Source

8.3 LEAD ALKYL

Tetraethyl lead (TEL) and tetramethyl lead (TML) are the two alkyl lead compounds that are used as antiknock gasoline additives. Lead alkyl is produced in autoclaves by the reaction of sodium/lead alloy with an excess of either ethyl (for TEL) or methyl (for TML) chloride in the presence of an acetone catalyst. The reaction mass is distilled to separate the product, which is then purified, filtered and mixed with chloride/bromide additives. Lead air emissions from the sodium/lead alloy process consist of particulate lead oxide from the recovery furnace (and to a lesser extent, from the melting furnace and alloy reactor), alkyl lead vapor from process vents and fugitive emissions from the sludge pit. Lead may also be present in the plant's wastewater.

Air emissions (Kg pollutant/10^3 Kg of product)

Process	Lead			Source
- Electrolytic	0.5			13,14
- Sodium lead alloy				
Recovery furnace	28			
Process vessels, TEL	2			
Process vessels, TML	75			
Sludge pits	0.6			

Liquid emissions

Process						Source

8.4 PAINT AND VARNISH

The manufacturing of paint involves the dispersion of colored oil or pigments in a vehicle, usually an oil or resin, followed by the addition of an organic solvent for viscosity adjustment. These processes take place in large mixing tanks. VOCs are the maim group of pollutants that emitted in the air from the paint production plant, since at least 1% – 2% of the solvent is lost even under well controlled conditions. Particles (paint pigments) are also emitted (0.5 – 1% of the pigment handled).

Varnish production involves the mixing and blending of various ingredients, while heating is used to initiate chemical reactions. VOCs are also the major group of air emitted pollutants. Emissions from varnish production ranges from 1% to 6% of the raw material.

Air emissions (Uncontrolled) (Kg pollutant/10^3 of product)

Process	VOC (non-methane)			Source
Paint	15			13,14
Varnish				
Bodying oil	20			
Oleoresinous	75			
Alkyd	80			
Acrylic	10			

Liquid emissions

Process						Source

9. CEMENT AND NON-METALLIC PRODUCTS

9.1 CEMENT

Portland cement is a fine powder that consists of a mixture of hydraulic cement materials comprising primarily calcium silicates, aluminates and aluminoferrites. More than 30 raw materials are known to be used in the manufacture of Portland cement and can be divided in four categories: calcareous, siliceous, argillaceous and ferrifeous. These materials are chemically combined through pyroprocessing and subsequent mechanical processing operations to form cement. There are 4 different methods for cement production (dry, semi-dry, wet and semi-wet) depending on the raw materials, which are used. The basic process includes calcination of calcium carbonate (CaCO3) to calcium oxide (CaO), reaction of CaO with silica, aluminum and iron bearing constituents (clinker formation) and blending and grinding of clinker with gypsum to produce cement. Air emissions from the cement manufacturing process includes particulate matter, SO_2, CO, VOCs, ammonia, metals and polychlorinated dibenzo dioxins/furans (PCDD/F). Liquid effluents may originate from the scrubbing equipment for the retention of air emissions.

Air emissions (Kg pollutant/10^3 of product)
(* µg I-TEQ/ 10^3 of product)

Pollutant	Emission factor	Pollutant	Emission factor	Source
Arsenic (FF)	6.5 X 10^{-6}	Benzo(a)anthracene (FF)	2.1 X 10^{-8}	13,14
Cadmium (ESP) (FF)	 4.2 X 10^{-6} 1.1 X 10^{-6}	Benzo(b)fluoranthene (FF)	2.8 X 10^{-8}	
Chromium (ESP) (FF)	 3.9 X 10^{-6} 7.0 X 10^{-5}	Benzo(g,h,i)perylene (FF)	3.9 X 10^{-8}	
Copper (FF)	0.0026	Biphenyl (ESP)	3.1 X 10^{-6}	
Fluoride (ESP)	0.00045	Chlorobenzene (ESP)	8.0 X 10^{-6}	
HCl (ESP) (FF)	0.025 0.073	Formaldehyde (FF)	0.00023	
Mercury (ESP) (FF)	0.00011 1.2 X 10^{-5}	Indeno(1,2,3,-cd)pyrene (FF)	2.5 X 10^{-5}	
Ammonia (FF)	0.0051	Phenol (ESP)	5.5 X 10^{-5}	
Lead (ESP) (FF)	0.00036 3.8 X 10^{-5}	Toluene (ESP)	0.00010	
Benzene (ESP) (FF)	0.0016 0.0080	Total PCDD (FF)	1.4 X 10^{-9}	
Benzo(a)pyrene (FF)	6.5 X 10^{-8}	Total PCDF (FF)	1.4 X 10^{-10}	
		PCDD/PCDF	0.15*	6,17

ESP: electrostatic precipitator; FF: fabric filter

Liquid emissions

Process						Source

9.2 LIME MANUFACTURING

Lime is the high-temperature product of the calcination of limestone. The resulting lime is reacted with water to form hydrated lime. The basic processes in the production of lime are: quarrying raw limestone, preparing limestone for the kilns by crushing and sizing, calcinating limestone, processing the lime by hydrating and miscellaneous transfer, storage and handling operations. The major air emissions are particulate matter and gaseous pollutants from the kilns (CO, NOx, SO_2). Materials and fuels containing chlore may produce PCDDs/PCDFs.

Air emissions (Kg pollutant/10^3 of product)
(* µg I-TEQ/ 10^3 of product)

Process	PCDD/Fs			Source
Total plant (cyclone)	10			17
Total plant (dust abatement)	0.07			17

Liquid emissions

Process						Source

9.3 GLASS MANUFACTURING

Commercially produced glass can be classified as soda'lime, lead, fused silica, borosilicate 96% silica. The products of the industry are flat glass, container glass and pressed and blown glass. The procedures for manufacturing glass are the same for all products except forming and finishing. The raw materials are crushed mixed and homogenized ant then fed to the melting furnace. The molten glass flows to the refiner and then is shaped by pressing, blowing, drawing, rolling or floating, to produce the desired product. The end product undergoes finishing (decorating or coating) and annealing (removing unwanted stress area in the glass) and then is inspected and prepared for shipment. The melting furnace contributes over 99% of the total air emissions (volatilization of materials and particles). Emissions from the forming and finishing phases depend upon the type of glass being manufactured. Grease and oil vaporization occurs from container, press and blow machines.

Air emissions (Kg pollutant/10^3 of product)
(* µg I-TEQ/ 10^3 of product)

Process	VOC	Pb	Hg	PCDD/PCDF	Source
Melting furnace					13,14
Container - Uncontrolled - Scrubber	 0.1 0.1	 NA	 NA	 NA	
Flat - Uncontrolled - Scrubber	 < 0.1 < 0.1	 NA	 NA	 NA	
Pressed and blown - Uncontrolled - Scrubber - Baghouse - ESP	 0.2 0.2 0.2 0.2	 NA	 NA	 NA	
Forming and finishing - Container - Flat - Pressed and Blown	 4.4 none 4.5	 NA	 NA	 NA	
Lead glass manufacturing All processes	NE	2.5	NA	NA	
Total plant	NA	NA	NA	0.21*	6,17
Total plant (dust abatement)				0.015	17

Liquid emissions

Process	BOD_5	Oil		Source
All processes	NA	0.001		15

10. ENERGY PRODUCTION

10.1 LIGNITE COMBUSTION

Lignite is a coal in the early stage of coalification, with properties intermediate to those of bituminous coal and peat. Lignite is pulverized, dried and then fed to a boiler. The emissions generated from firing lignite include particulate matter, sulfur oxides, nitrogen oxides, carbon monoxide, organic compounds (including PAHs, PCDD/PCDF), trace elements and acid gases.

Air emissions (Kg pollutant/10^3 of coal fed, as fired)
(* µg I-TEQ/ 10^3 of product)

Pollutant	Emission Factor	Pollutant	Emission Factor	Source
PAH (controlled)				13,14
Benzo(a)anthracene	4.0 X 10^{-8}	Benzo(a)pyrene	1.9 X 10^{-8}	
Benzo(b,j,k)fluoranthene	0.55 X10^{-7}	Benzo(g,h,i)perylene	1.4 X 10^{-8}	
Fluoranthene	3.6 X 10^{-7}	Indeno(1,2,3,-cd)pyrene	3.1 X 10^{-8}	
Napthalene	0.65 X 10^{-5}	Phenanthrene	1.4 X 10^{-6}	
Metals (controlled)				
As	2.0 X 10^{-4}	Cd	2.6 X 10^{-5}	
Cr	1.3 X 10^{-4}	Cr (VI)	4.0 X 10^{-5}	
Pb	2.1 X 10^{-4}	Hg	4.2 X 10^{-5}	
Ni	1.4 X 10^{-4}			
PCDD/PCDF Coal Lignite	 2.0* 0.6*	PAH (10 PAHs) (Coal)	2.8 X 10^{-5}	15

Liquid emissions

Process			Hg			Source
			NA			

10.2 FUEL OIL COMBUSTION

Two major categories of fuel may be burned for energy production: distillate oils and residual oils. Distillate oils are more volatile and less viscous than residual oils, which contain significant quantities of ash, nitrogen and sulfur. Emissions include particulate matter, sulfur oxides, NOx. CO, VOC, semivolatile and condensable organic compounds (referred as TOC – total organic compounds), trace elements, PAH and PCDD/PCDFs.

Air emissions (Kg pollutant/10^3 Liter of fuel oil)
(* ng I-TEQ/ 10^3 of diesel)

Pollutant	Emission Factor	Pollutant	Emission Factor	Source
Benzene	0.25 X 10^{-4}	Toluene	0.74 X 10^{-3}	13,14
Benz(a)anthracene	0.48 X 10^{-6}	Benzo(b,k)fluoranthene	0.18 X 10^{-6}	
Fluoranthene	0.54 X 10^{-6}	Benzo(g,h,i)perylene	0.26 X 10^{-6}	
Phenanthrene	0.13 X 10^{-5}	Indeno(1,2,3-cd)pyrene	0.26 X 10^{-6}	
As	0.14 X 10-3	Cd	0.47 X 10-4	
Cr	1.0 X 10-4	Cr (VI)	0.30 X 10-4	
Cu	0.21 X 10-3	F	0.45 X 10-2	
Hg	0.14 X 10-4	Ni	1.0 X 10-2	
PCDD/PCDF	14*	PAH (10 PAHs) (heavy oil)	0.44 X 10^{-3}	6

Liquid emissions

Process	Oil	PAH	PCB/PCT			Source
	NA	NA	NA			

11. GAS PRODUCTION

Natural gas from high-pressure wells is usually passed through field separators at the well to remove hydrocarbon condensates and water. Natural gas is considered “sour”, if hydrogen sulfide is present in amounts greater that 5.7 mg/ Nm^3. The H_2S must be removed before the gas can be utilized. The major air emission sources in natural gas processing are compressor engines, acid gas wastes, fugitive emissions from leaking process equipment and, if present, glycol dehydrator vent streams. Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethylbenzene and xylene, as well as a wide range of less toxic organics (US EPA, 2001).

No available data on emission factors for the gas production plants were found in the literature.

Air emissions

Process				Source

Liquid emissions

Process						Source

12. Pharmaceuticals

Thousand of individual products are categorized as pharmaceuticals. These products usually are produced in modest quantities in relatively small plants using batch processes. A typical pharmaceutical plant will produce different products at different times. Pharmaceutical industries use organic chemicals as raw materials or solvents, which are usually recovered for further use. Emissions consist almost entirely of organic solvents that escape from dryers, reactors, distillation systems, storage tanks and other operations. These emissions are exclusively nonmethane organic compounds. It is not practical to attempt to evaluate emissions from individual steps in the production process because of the great variety of batch operations that may be carried out at a single production plant. It is more reasonable to obtain data on total solvent purchases by a plant and to assume that these represent replacements for solvent lost by evaporation. Estimates can be refined by subtracting the materials that do not enter the air or the liquid effluents because of being incinerated or incorporated into the pharmaceutical product by chemical reaction.

Percentage of solvent deposition (%)

Solvent	Air emissions	Liquid wastes	Incineration	Solid wastes	Product	Source
Benzene	29	37	16	8	10	13,14
Carbon Tetrachloride	11	7	82	-	-	
Chloroform	57	5	-	38	-	
Freons	0.1	-	-	-	99.9	
Toluene	31	14	26	29	-	
Trichloroethane	100	-	-	-	-	

8.3 APPENDIX III

Priority Pollutants Subject to Pretreatment

001 Acenaphthene
002 Acrolein
003 Acrylonitrile
004 Benzene
005 Benzidine
006 Carbon tetrachloride
007 Chlorobenzene
008 1,2,4-trichlorobenzene
009 Hexachlorobenzene
010 1,2-dichloroethane
011 1,1,1-trichloreothane
012 Hexachloroethane
013 1,1-dichloroethane
014 1,1,2-trichloroethane
015 1,1,2,2-tetrachloroethane
016 Chloroethane
018 Bis(2-chloroethyl) ether
019 2-chloroethyl vinyl ethers
020 2-chloronaphthalene
021 2,4,6-trichlorophenol
022 Parachlorometa cresol
023 Chloroform
024 2-chlorophenol
025 1,2-dichlorobenzene
026 1,3-dichlorobenzene
027 1,4-dichlorobenzene
028 3,3-dichlorobenzidine
029 1,1-dichloroethylene
030 1,2-trans-dichloroethylene
031 2,4-dichlorophenol
032 1,2-dichloropropane
033 1,2-dichloropropylene
034 2,4-dimethylphenol
035 2,4-dinitrotoluene
036 2,6-dinitrotoluene
037 1,2-diphenylhydrazine
038 Ethylbenzene
039 Fluoranthene
040 4-chlorophenyl phenyl ether
041 4-bromophenyl phenyl ether
042 Bis(2-chloroisopropyl) ether
043 Bis(2-chloroethoxy) methane
044 Methylene chloride
045 Methyl chloride

046 Methyl bromide
047 Bromoform
048 Dichlorobromomethane
051 Chlorodibromomethane
052 Hexachlorobutadiene
053 Hexachlorocyclopentadiene
054 Isophorone
055 Naphthalene
056 Nitrobenzene
057 2-nitrophenol
058 4-nitrophenol
059 2,4-dinitrophenol
060 4,6-dinitro-o-cresol
061 N-nitrosodimethylamine
062 N-nitrosodiphenylamine
063 N-nitrosodi-n-propylamine
064 Pentachlorophenol
065 Phenol
066 Bis(2-ethylhexyl) phthalate
067 Butyl benzyl phthalate
068 Di-N-Butyl Phthalate
069 Di-n-octyl phthalate
070 Diethyl Phthalate
071 Dimethyl phthalate
072 benzo(a) anthracene
073 Benzo(a)pyrene
074 Benzo(b) fluoranthene
075 Benzo(b) fluoranthene
076 Chrysene
077 Acenaphthylene
078 Anthracene
079 Benzo(ghi) perylene
080 Fluorene
081 Phenanthrene
082 Dibenzo(,h) anthracene
083 Indeno (1,2,3-cd) pyrene
084 Pyrene
085 Tetrachloroethylene
086 Toluene
087 Trichloroethylene
088 Vinyl chloride
089 Aldrin
090 Dieldrin
091 Chlordane
092 4,4-DDT
093 4,4-DDE
094 4,4-DDD
095 Alpha-endosulfan
096 Beta-endosulfan
097 Endosulfan sulfate

098 Endrin
099 Endrin aldehyde
100 Heptachlor
101 Heptachlor epoxide
102 Alpha-BHC
103 Beta-BHC
104 Gamma-BHC
105 Delta-BHC
106 PCB–1242
107 PCB–1254
108 PCB–1221
109 PCB–1232
110 PCB–1248
111 PCB–1260
112 PCB–1016
113 Toxaphene
114 Antimony
115 Arsenic
116 Asbestos
117 Beryllium
118 Cadmium
119 Chromium
120 Copper
121 Cyanide, Total
122 Lead
123 Mercury
124 Nickel
125 Selenium
126 Silver
127 Thallium
128 Zinc
129 2,3,7,8-TCDD

8.4 APPENDIX IV

PRE-TREATMENT STANDARDS FOR THE DISCHARGE OF INDUSTRIAL EFFLUENTS INTO MUNICIPAL SEWERS

8.4.1 Kingdom of Bahrain

Parameter	Unit	Limit
Synthetic detergents	mg/l	100
CN^-	mg/l	10
Sulphides	mg/l	10
Sulphates	mg/l	1000
Tar & tar oils	mg/l	20
Oil & grease 1. floating 2. emulsified	mg/l	 50 150
SS	mg/l	500
COD	mg/l	500
Total toxic metals	mg/l	10
Cd	mg/l	1
Cr total	mg/l	5
Cu	mg/l	5
Pb	mg/l	5
Ni	mg/l	5
Ag	mg/l	5
Zn	mg/l	5
As	mg/l	5
Hg	mg/l	0.01
pH		6 – 9
• Calcium carbide • Chlorinated hydrocarbons • Volatile petroleum products • Radioactive substances	mg/l	0

8.4.2 State of Kuwait

Pollutant	Symbol	Unit	Maximum Unit
Biological Oxygen Demand	BOD5 (5 day, 20^0C)	mg/L	500
Chemical Oxygen Demand	COD	mg/L	750
Total Suspended Solids	TSS	mg/L	300
Phenol	Total Recoverable Phenol	mg/L	1
Fluorides	F	mg/L	1000
Sulfides	S	mg/L	10
Arsenic	As	mg/L	0.1
Cadmium	Cd	mg/L	0.1
Cyanides	Cn	mg/L	0.1
Chromium	Cr	mg/L	1.0
Nickel	Ni	mg/L	0.2
Mercury	Hg	mg/L	0.002
Copper	Cu	mg/L	0.5
Zinc	Zn	mg/L	2.0
Lead	Pb	mg/L	0.5
Silver	Ag	mg/L	4.0
Tar & Tar Oil		mg/L	Nil
Floating Oil & Grease		mg/L	5
Emulsified Oil & Grease		mg/L	5
Most Probable number of total Coliform		MPN/100ml	1000
Most Probable number of faecal Coliform		MPN/100ml	100
Egg parasites			Nil
Worm parasites			Nil

8.4.3 State of Qatar

Parameter	Unit	Limit
Synthetic detergents	mg/l	30
Detergents	mg/l	100
CN^-	mg/l	1
Sulphides	mg/l	10
Sulphates	mg/l	1000
Tar & tar oils	mg/l	20
Oil & grease	mg/l	15
SS	mg/l	500
COD	mg/l	3000
BOD_5	mg/l	1000
TDS	mg/l	4000
TOC	mg/l	1000
Total chlorinated hydrocarbons	mg/l	0.5
Calcium carbonates	mg/l	3000
Total toxic metals	mg/l	10
Cd	mg/l	10
Cr total	mg/l	2
Cu	mg/l	4
Pb	mg/l	5
Ni	mg/l	4
Ag	mg/l	4
Zn	mg/l	5
As	mg/l	5
Hg	mg/l	0.1
pH		5 – 10
Temperature	°C	60

8.4.4 Kingdom of Saudi Arabia

Parameter	Unit	Limit
Phenols	mg/l	150
CN^-	mg/l	1
SS	mg/l	2000
COD	mg/l	1500
TOC	mg/l	1000
Total chlorinated hydrocarbons	mg/l	0.5
Cd	mg/l	0.5
Cr total	mg/l	2
Cu	mg/l	1
Pb	mg/l	1
Ni	mg/l	2
Ag	mg/l	4
Zn	mg/l	10
As	mg/l	1
Hg	mg/l	0.01
pH		5 – 10
Temperature	^oC	60

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