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## 1. Emission factors

The implementation of the Pollutants Releases and Toxic Registers (PRTR) reporting system in the Mediterranean region is based on information of releases of a list of pollutants to water, air and land. Hence, many Mediterranean countries have not detailed information on the releases of the pollutants from point sources. Furthermore, many of the pollutants included in the list are not routinely analyzed in the effluents and emissions and therefore no extensive data sets are available.

To bypass the lack of specific analytical data, the pollutants releases can be estimated by using different techniques among them the Emission Factors (EF). This method relies on the existence of known relationship between the amounts of pollutant released in effluents or emissions and the quantity of raw materials or products for industrial process (or population). Therefore, the knowledge of the yearly production capacity could be translated into the yearly release rate of a specific pollutant. It has to be underlined that this approach lacks accuracy, especially when applying the same emission factor to estimate releases from similar industrial plants which are using different technological processes. Nevertheless, knowing its limitations, the method can be used to estimate pollutants releases until accurate data are made available.

This document presents emission factors for a number of contaminants released from different industrial process which have been calculated in different industrial sectors by national and international bodies. However, the countries are encouraged to use their own emission factors to quantify the releases and complete the PRTR reporting format.

### General methodology

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:

$$\text{TOTAL}_{ij} = A_j \times \text{EF}_{ij}$$

Where:

TOTAL <sub>ij</sub>	=	process emission (Kg/year) of pollutant i from industrial sector j
A <sub>j</sub>	=	amount of activity or production unit of process material in industrial sector j (tons /year)
EF <sub>ij</sub>	=	emission factor associated with pollutant i per unit of production in industrial sector j (Kg/ton)

The method constitutes the fundamental relationship for the evaluation of industrial process emissions. Emission factors can be calculated by analyzing the production process of a specific industrial plant and using complex mathematic formulae. However, EFs calculated for one plant can be used as a starting point for the estimation of the pollutant's emissions of other plants with similar industrial processes. This is the approach followed in the present document.

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## **Annex I**

### **Emission Factors for Pollutants Released by Industry and Urban Centers**

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## PREFACE

The major industrial sectors in the Mediterranean are (RAC/CP, 2001) according to their importance in the Mediterranean region are:

- Petroleum refineries
- Food industries and Food processing
- Fertilizers and Inorganic Chemicals
- Metallurgy
- Leather processing
- Cement
- Textile dyeing
- Paper and pulp
- Organic Chemicals
- Energy production
- Gas production
- Pharmaceuticals

Also in the Mediterranean region the land based pollution sources include:

- Urban effluents (cities and tourism)

The estimation of the emission factors will be based on these sectors.

Most emission factors are expressed as Kg of pollutant per  $10^3$  Kg of product or raw material. For Dioxins and Furans (PCDD/PCDF) emission factors are calculated as  $\mu\text{g I-TEQ} / 10^3$  product.

I-TEQ: International Toxic Equivalent. Of all 75 dioxins and 135 furans, the 17 congeners with chlorine atoms in the 2,3,7, and 8 positions are of particular environmental concern. The most toxic congener is 2,3,7,8- tetrachlorodibenzodioxin (TCDD). By convention it is assigned a toxicity rating (called Toxic Equivalent Factor, or TEF) of 1. The remaining 2,3,7,8-positional congeners are then assigned lower TEFs, relative to 2,3,7,8-TCDD. The toxicity of a mixture of PCDD/Fs, relative to 2,3,7,8-TCDD, can be expressed by multiplying the concentrations of those 2,3,7,8-congeners present in the mixture by their respective TEFs. The resulting products are called Toxic Equivalents (TEQs), with units identical to that in which the concentrations of the individual congeners are expressed. The TEQ of the mixture is obtained by summing the individual TEQs. The scheme of toxic equivalence factors (TEFs), which has been adapted internationally, is given bellow. The TEFs are termed as International TEFs or I-TEFs. For all other congeners that may be present in the sample, a TEF value of 0 is assigned. The summation of individual TEQs for a mixture of PCDD/PCDFs is termed the "International Toxic Equivalent" or "I-TEQ" of the mixture

Toxic equivalence factors (TEF) used in the NATO/CCMS (1988) system

Congeners (position of chlorine atoms)	I-TEFs	Congeners (position of chlorine atoms)	I-TEFs
<u>Dioxins</u>		<u>Furans</u>	
2,3,7,8	1	2,3,7,8	0.1
1,2,3,7,8	0.5	1,2,3,7,8	0.05
1,2,3,4,7,8	0.1	2,3,4,7,8	0.5
1,2,3,6,7,8	0.1	1,2,3,4,7,8	0.1

Congeners (position of chlorine atoms)	I-TEFs	Congeners (position of chlorine atoms)	I-TEFs
1,2,3,7,8,9	0.1	1,2,3,6,7,8	0.1
1,2,3,4,6,7,8	0.01	1,2,3,7,8,9	0.1
1,2,3,4,6,7,8,9	0.001	2,3,4,6,7,8	0.1
		1,2,3,4,6,7,8	0.01
		1,2,3,4,7,8,9	0.001
		1,2,3,4,6,7,8,9	0.001

## 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, coking, 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 <sup>3</sup> L fresh feed	0.630	NA			13,14
Moving-bed catalytic cracking units Kg/10 <sup>3</sup> L fresh feed	0.250	NA			
Compressor engines Reciprocating engines Kg/10 <sup>3</sup> m <sup>3</sup> gas burned	21.8	NA			
Compressor engines Gas turbines Kg/10 <sup>3</sup> m <sup>3</sup> gas burned	0.28	NA			
Blowdown systems (Uncontrolled) Kg/10 <sup>3</sup> L fresh feed	1,662	NA			
Blowdown systems (vapor recovery system and flaring) Kg/10 <sup>3</sup> L fresh feed	0.002	NA			
Vacuum distillation column condensers (Uncontrolled) Kg/10 <sup>3</sup> L fresh feed	0.14	NA			
Fugitive emission (total) Kg/m <sup>3</sup> .day capacity	0.39	NA			

\* NA : Not available

Liquid emissions (Kg/10<sup>3</sup>m<sup>3</sup> crude oil)

Process	Petroleum hydrocarbons	Phenol	Cr	PAH	BOD <sub>5</sub>	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	
<b>Typical overall situation</b>	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 <sub>3</sub>	VOC	H <sub>2</sub> S		Source
	NA	NA	NA		

Liquid emissions

Process	BOD <sub>5</sub>	N	Total P		Source
<b>Livestock production</b> (Kg of pollutant/ 10 <sup>3</sup> 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		
<b>Slaughterhouse</b> (Kg of pollutant/ 10 <sup>3</sup> 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<sub>2</sub>S and trimethylamine [(CH<sub>3</sub>)<sub>3</sub>N] and VOC (from cooker).

Air emissions (Kg of pollutant/ 10<sup>3</sup> Kg of raw fish processed)

Process	H <sub>2</sub> S	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<sup>3</sup> Kg of fish produced)

Process	BOD <sub>5</sub>	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 months 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 <sub>5</sub>	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 (NO<sub>x</sub>, SO<sub>2</sub>, CO and CO<sub>2</sub>) are the primary pollutants emitted from sugarbeet processing industry.

Air emissions (Kg of pollutant /10<sup>3</sup> 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				
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<sup>3</sup> Kg of beet feed)

Process	BOD <sub>5</sub>			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 BOD<sub>5</sub> 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<sup>3</sup> Kg oil produced)

Process	BOD <sub>5</sub>	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<sup>3</sup> Kg raw oilseed)

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

#### Liquid emissions oil (Kg of pollutant /10<sup>3</sup> Kg oil produced)

Process	BOD <sub>5</sub>	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*			
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\* (Kg of pollutant /10<sup>3</sup> 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-propyl alcohol, isobutyl alcohol, isoamyl alcohol) and acetaldehyde, and hydrogen sulfide. Liquid effluents are

### Air emissions

Process					Source

### Liquid emissions (Kg of pollutant/ 10<sup>3</sup> L product)

Process	BOD <sub>5</sub>		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<sup>3</sup> 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<sup>3</sup> of barley)

Process	VOC			Source
Brewing	0.25			16

### Liquid emissions (Kg of pollutant/ 10<sup>3</sup> L of beer produced)

Process	BOD <sub>5</sub>		Source
Total brewery	6.25		15

## 2.9. Soft drinks

For the production of soft drink are used already pre-concentrated juices. The water that will be used for the preparation of soft drinks is treated for alkalinity (addition of iron sulfate, sodium hypochlorite 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<sup>3</sup> L product)

Process	BOD <sub>5</sub>		Source
With syrup production	4.33		15
Without syrup production	2.15		

## 3. Fertilizers and Inorganic Chemicals

### 3.1. Synthetic ammonia

Synthetic ammonia (NH<sub>3</sub>) 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<sup>3</sup> Kg product)

Process	Total organic compounds	NH <sub>3</sub>		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<sup>3</sup> Kg product)

Process	Oil	BOD <sub>5</sub>		source
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Total plant	11	0.4		15

### 3.2. Urea

Urea [CO(NH<sub>2</sub>)<sub>2</sub>] 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<sup>3</sup> Kg product)

Process	NH <sub>3</sub> (uncontrolled)	NH <sub>3</sub> (controlled)		source
Solution formation and concentration	9.23	NE		13,14
Non fluidized bed prilling - Agricultural grade - Feed grade	0.43 NE	NE NE		
Fluidized bed prilling - Agricultural grade - Feed grade	1.46 2.07	NE 1.07		
Drum granulation	1.07	NE		
Rotary drum cooler	0.0256	NE		

Liquid emissions (Untreated) (Kg/10<sup>3</sup> Kg product)

Process	BOD <sub>5</sub>	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<sup>3</sup> Kg product)

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

Liquid emissions (Untreated) (Kg/10<sup>3</sup> Kg product)

Process				Source

**3.4. Phosphate fertilizers and phosphoric acid**

Normal superphosphates fertilizers (15 – 21% phosphorus as P<sub>2</sub>O<sub>5</sub>) 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<sup>3</sup> Kg P<sub>2</sub>O<sub>5</sub> produced)

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

Liquid emissions (Kg/10<sup>3</sup> Kg P<sub>2</sub>O<sub>5</sub> produced)

Process	F-	Pb, As, Cr, Hg	P <sub>2</sub> O <sub>5</sub>	NH <sub>3</sub>	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 or scrubbers). The scrubbing devices produce liquid effluents, which contain heavy metals (zinc, lead, cadmium), cyanide, ammonium and organic matter (COD).

Air emissions (Kg/ 10<sup>3</sup> 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<sup>3</sup> Kg product)  
- (\*µg I-TEQ/t of product)

Process	Total N	Pheno I	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 <sup>3</sup> 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<sup>3</sup> 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<sub>2</sub>O<sub>3</sub>) 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, CO<sub>2</sub>, volatile organics, PAHs, dioxins, sulfur dioxide, and perfluorinated carbons (PFCs). The source of fluoride emissions from reduction cells is the fluoride electrolyte, which contains cryolite (Na<sub>3</sub>AlF<sub>6</sub>), aluminum fluoride (AlF<sub>3</sub>) and fluorspar (CaF<sub>2</sub>). The dissociation of molten cryolite is the source of the PFCs – tetrafluoromethane (CF<sub>4</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) – 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<sup>3</sup> 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
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Liquid emissions (Kg of pollutant/ 10<sup>3</sup> Kg of Al produced)

Process	Fluor	Oil				Source
Alumina from bauxite	4.2	NA				15
<u>Aluminum production</u>						
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 <sup>3</sup> Kg product)	NA	NA	NA	2.5	13,14,15
Ore crushing (Kg/10 <sup>3</sup> Kg ore crushed)					
Uncontrolled	NE	NE	NA	0.15	13,14,15
Controlled				0.001	
Ore screening (Kg/10 <sup>3</sup> Kg ore crushed)	NE	NE	NA	0.001	13,14
Controlled					
Sintering (Kg/10 <sup>3</sup> Kg sinter produced)	NA	NA	NA	0.009	
Sinter building fugitives (Kg/10 <sup>3</sup> Kg sinter produced)	NA	NA	NA	0.016	
Blast Furnace (Kg/10 <sup>3</sup> Kg bullion produced) or Uncontrolled or Centrifugal collector	NA	NA	NA	0.034 29 4.35 2.61	13,14

Process	PCDD/ PCDF	VOC	Hg	Pb	Source
or Fabric filter					
Dross Reverberatory Furnace (Kg/10 <sup>3</sup> 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<sup>3</sup> 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<sup>3</sup> 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<sup>3</sup> 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. Reveratory and blast furnaces account for the vast majority of the total lead emissions.

Air emissions (Kg pollutant/10<sup>3</sup> Kg product)  
(\*µg I-TEQ/t of product)

Process	PCDD/PCDF	VOC	PAH	Pb	Source
Sweating (Kg pollutant/10 <sup>3</sup> Kg charge) Uncontrolled Controlled	NA	NA	NA	4-8 ND	13,14
Reveratory 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

Process	PCDD/ PCDF	VOC	PAH	Pb	Source
From PVC battery separators	80	NA	NA	NA	17
From PVC/Cl <sub>2</sub> 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<sup>3</sup> Kg product)  
(\*µg I-TEQ/t of product)

Process	PCDD/ PCDF	VOC	PAH	Pb	Source
Reveratory 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<sup>3</sup> 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			
<b>Total production</b>	<b>6.94-8.0</b>			

Liquid emissions (Kg of pollutant/10<sup>3</sup> 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<sub>3</sub>O<sub>4</sub>); 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<sup>3</sup> product)

Process	Pb			Source
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<b>Lead oxide Production</b>				13,14
Barton pot	0.22			
Calcining				
Baghouse inlet	7.0			
Baghouse outlet	0.024			
<b>Pigment production</b>				
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<sup>3</sup> product)

Process	VOCs	Metals		Source
	NA	NA		

Liquid emissions (Kg pollutant/10<sup>3</sup> 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 <sup>6+</sup> )	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), formaldehyde, 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 unhairing. 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 delimiting 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 than 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 <sub>5</sub> Kg/tn of hides	Total N Kg/tn of hides	Cr <sub>2</sub> O <sub>3</sub> 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 <sub>5</sub> Kg/tn of hides	Total N Kg/tn of hides	Cr <sub>2</sub> O <sub>3</sub> 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 <sub>5</sub> 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<sub>2</sub> (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<sup>3</sup> 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<sup>3</sup> Kg fabric)

Process	BOD <sub>5</sub>	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<sup>3</sup> Kg fabric)

Process	BOD <sub>5</sub>	COD			Source
Cotton	5-15	3,500 – 13,500			2,16
Wool	1.5	NA			
Acetate	2	NA			

iii) Dyeing (Kg of pollutant/ 10<sup>3</sup> Kg fabric)

Process	BOD <sub>5</sub>				Source

Process	BOD <sub>5</sub>				Source
Cotton	2 - 80 (30)				2,3,16
Wool	9 - 34				
Rayon	2 - 50				
Acetate	5 - 100				
Nylon	NA				
Acrylic	2 - 50				
Polyester	30 - 600				

iv) Finishing (Kg of pollutant/ 10<sup>3</sup> Kg fabric)

Process	BOD <sub>5</sub>				Source
Rayon	20				3,16
Acetate	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, etc) and the paper mass is pressed, dried and cut.

Air emissions (in the kraft process) are mostly produced from the recovery furnace, the lime kiln 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<sup>3</sup> Kg of air dried unbleached pulp, untreated emissions) for kraft pulping (RSH: Methyl mercaptane, RSR: Dimethyl sulfide, RSSR: Dimethyl disulfide). (\*µg I- TEQ/ 10<sup>3</sup> product)

Process	SO <sub>2</sub>	PCDD/ PCDF*	H <sub>2</sub> S (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	

Process	SO <sub>2</sub>	PCDD/ PCDF*	H <sub>2</sub> S (as S)	Pb	Hg	RSH, RSR, RSSR (as S)	Source
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<sup>3</sup> air dried pulp)

Process	BOD <sub>5</sub>	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<sup>3</sup> paper produced)  
(\*µg l- TEQ/ 10<sup>3</sup> product)

Process	BOD <sub>5</sub>	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 noncrystalline 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<sup>3</sup> 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 terephthalate (PET)

Polyethylene terephthalate (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 fibers), in food and household products packaging, photographic film, magnetic tape, electrical insulation etc. PET is produced from ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). The air emissions from the process include VOCs and particulate matter.

Air emissions (Kg pollutant/10<sup>3</sup> Kg of product)

Process	VOC (non methane)	Source
Total plant (spray condensers)		13,14

Total plant (no spray condensers)	0.36			
	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<sup>3</sup> 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 main 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<sup>3</sup> of product)

Process	VOC (non-methane)			Source
Paint	15			13,14
<b>Varnish</b>				
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 (CaCO<sub>3</sub>) 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<sub>2</sub>, 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<sup>3</sup> of product)  
(\* µg I-TEQ/ 10<sup>3</sup> of product)

Pollutant	Emission factor	Pollutant	Emission factor	Source
Arsenic (FF)	6.5 X 10 <sup>-6</sup>	Benzo(a)anthracene (FF)	2.1 X 10 <sup>-8</sup>	13,14

Pollutant	Emission factor	Pollutant	Emission factor	Source	
Cadmium (ESP) (FF)	4.2 X 10 <sup>-6</sup> 1.1 X 10 <sup>-6</sup>	Benzo(b)fluoranthene (FF)	2.8 X 10 <sup>-8</sup>		
Chromium (ESP) (FF)	3.9 X 10 <sup>-6</sup> 7.0 X 10 <sup>-5</sup>	Benzo(g,h,i)perylene (FF)	3.9 X 10 <sup>-8</sup>		
Copper (FF)	0.0026	Biphenyl (ESP)	3.1 X 10 <sup>-6</sup>		
Fluoride (ESP)	0.00045	Chlorobenzene (ESP)	8.0 X 10 <sup>-6</sup>		
HCl (ESP) (FF)	0.025 0.073	Formaldehyde (FF)	0.00023		
Mercury (ESP) (FF)	0.00011 1.2 X 10 <sup>-5</sup>	Indeno(1,2,3,- cd)pyrene (FF)	2.5 X 10 <sup>-5</sup>		
Ammonia (FF)	0.0051	Phenol (ESP)	5.5 X 10 <sup>-5</sup>		
Lead (ESP) (FF)	0.00036 3.8 X 10 <sup>-5</sup>	Toluene (ESP)	0.00010		
Benzene (ESP) (FF)	0.0016 0.0080	Total PCDD (FF)	1.4 X 10 <sup>-9</sup>		
Benzo(a)pyrene (FF)	6.5 X 10 <sup>-8</sup>	Total PCDF (FF)	1.4 X 10 <sup>-10</sup>		
		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, NO<sub>x</sub>, SO<sub>2</sub>). Materials and fuels containing chlorine may produce PCDDs/PCDFs.

#### Air emissions

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<sup>3</sup> of product)  
(\* µg I-TEQ/ 10<sup>3</sup> of product)

Process	VOC	Pb	Hg	PCDD/PCDF	Source
<b>Melting furnace</b>					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*	
Total plant (dust abatement)				0.015	17

Liquid emissions



Process	BOD <sub>5</sub>	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<sup>3</sup> of coal fed, as fired)  
(\* µg I-TEQ/ 10<sup>3</sup> of product)

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

### 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<sup>3</sup> Liter of fuel oil)  
(\* ng I-TEQ/ 10<sup>3</sup> of diesel)

Pollutant	Emission Factor	Pollutant	Emission Factor	Source
Benzene	0.25 X 10 <sup>-4</sup>	Toluene	0.74 X 10 <sup>-3</sup>	13,14
Benz(a)anthracene	0.48 X 10 <sup>-6</sup>	Benzo(b,k)fluoranthene	0.18 X 10 <sup>-6</sup>	
Fluoranthene	0.54 X 10 <sup>-6</sup>	Benzo(g,h,i)perylene	0.26 X 10 <sup>-6</sup>	
Phenanthrene	0.13 X 10 <sup>-5</sup>	Indeno(1,2,3-cd)pyrene	0.26 X 10 <sup>-6</sup>	
As	0.14 X 10 <sup>-3</sup>	Cd	0.47 X 10 <sup>-4</sup>	
Cr	1.0 X 10 <sup>-4</sup>	Cr (VI)	0.30 X 10 <sup>-4</sup>	
Cu	0.21 X 10 <sup>-3</sup>	F	0.45 X 10 <sup>-2</sup>	
Hg	0.14 X 10 <sup>-4</sup>	Ni	1.0 X 10 <sup>-2</sup>	
PCDD/PCDF	14*	PAH (10 PAHs) (heavy oil)	0.44 X 10 <sup>-3</sup>	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 than 5.7 mg/ Nm<sup>3</sup>. The H<sub>2</sub>S 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

Thousands 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	-	-	-	-	

## 13. Urban centers

Urban centers produce a great variety of air and liquid effluents, because of the multitude of human activities. Residential fuel burning (mainly distilled fuel oil – diesel) is a major source of air pollutants. Air emissions are similar to those reported for industrial uses of the same fuel.

Air emissions (Kg pollutant/10<sup>3</sup> Liter of fuel oil)  
(\* ng I-TEQ/ 10<sup>3</sup> Kg of diesel or gasoline)  
(\*\* g / 10<sup>3</sup> Kg of diesel oil)

Pollutant	Emission Factor	Pollutant	Emission Factor	Source
Benzene	0.25 X 10 <sup>-4</sup>	Toluene	0.74 X 10 <sup>-3</sup>	13,14
Benz(a)anthracene	0.48 X 10 <sup>-6</sup>	Benzo(b,k)fluoranthene	0.18 X 10 <sup>-6</sup>	
Fluoranthene	0.54 X 10 <sup>-6</sup>	Benzo(g,h,i)perylene	0.26 X 10 <sup>-6</sup>	

Pollutant	Emission Factor	Pollutant	Emission Factor	Source
Phenanthrene	0.13 X 10 <sup>-5</sup>	Indeno(1,2,3-cd)pyrene	0.26 X 10 <sup>-6</sup>	6
As	0.14 X 10 <sup>-3</sup>	Cd	0.47 X 10 <sup>-4</sup>	
Cr	1.0 X 10 <sup>-4</sup>	Cr (VI)	0.30 X 10 <sup>-4</sup>	
Cu	0.21 X 10 <sup>-3</sup>	F	0.45 X 10 <sup>-2</sup>	
Hg	0.14 X 10 <sup>-4</sup>	Ni	1.0 X 10 <sup>-2</sup>	
PCDD/PCDF Diesel oil for central heating	14*	PAH (15 PAHs)	1**	

However, more pollutants are emitted to the air traffic (car's internal combustion engine's exhausts) and dust (containing metals and organic pollutants).

Air emissions g of pollutant / 10<sup>3</sup> Kg of fuel (diesel or gasoline)  
\* ng I-TEQ/ 10<sup>3</sup> Kg of diesel or gasoline

Process	PCDD/PCDF	PAH [B9a0P, B(b)F, B(k)F, I(1,2,3-cd)P]	Source
Diesel oil (cars)	14*	0.43 (passenger's) 0.40 (heavy vehicles)	6
Leaded gasoline (cars)	2200*	0.15 (passenger's) 0.20 (heavy vehicles)	
Unleaded gasoline (cars)	104*		
Leaded fuel	2.2		17
Unleaded catalyst	0.0		
Diesel	0.1		
Heavy oil	4.0		

Liquid effluents originate from sewers and rainwater runoff. Both wastewater streams are polluted with degradable organic matter, nutrients, petroleum hydrocarbons (including PAHs), heavy metals and synthetic organics. Pollutants sources include specific semi-industrial activities in the city, households, facilities (such as automotive fuel stations), as well as, diffuse sources from the road surfaces and the building surfaces. It very difficult to produce emissions factors for pollutants from all these processes in a city, because of the great variability of activities between urban centers. Therefore only general data can be provided in the present document and details have to be produce separately for each region.

Liquid emissions (Kg of pollutant / person / year)  
\*\* 10<sup>-3</sup> Kg PAH / Km per year {6 PAH: [Fluoranthene, Benzo(a)pyrene, Benzo(ghi)perylene, Indeno(123cd)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene]}

Process	BOD <sub>5</sub>	N	P	Metals	PAH	Source
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<b>Process</b>	<b>BOD<sub>5</sub></b>	<b>N</b>	<b>P</b>	<b>Metals</b>	<b>PAH</b>	<b>Source</b>
Household	22	3.6	0.4	Pb: 0.19-0.90 X 10 <sup>-3</sup> Cd: 0.5 X 10 <sup>-4</sup>	55 X 10 <sup>-6</sup> (9 PAHs) 4.1 X 10 <sup>-6</sup> [B(a)P]	6
Runoff from roads	NA	NA	NA	NA	NA	
Inside built-up area	NA	NA	NA	NA	9.7**	
Outside built-up area	NA	NA	NA	NA	48**	

## **ADDENDUM 1**

### **PCBs, BATTERIES AND LUB OIL IN THE ENVIRONMENT Production, use and disposal**

#### **INTRODUCTION**

During the previous Technical Report (March 2002) a number of pollutants were not included, due to lack of information. These pollutants include the polychlorinated biphenyls (PCBs), the Ni-Cd batteries and the used lubrication oil (luboil).

These pollutants are not released through some specific industrial process.

- PCBs are not legally used any more in most Mediterranean countries and should not be manufactured. However, the already existing stocks (in use or in storage) constitute a possible source to the environment, along with the release of the compounds from contaminated aquatic sediments and illegal dumpsites.
- Ni-Cd batteries (for industrial or domestic uses) are partly recycled and partly disposed off in municipal landfills or in the environment.
- Luboil is mostly collected in vehicle service stations, but can be accidentally or illegally released to the urban wastewater stream.

The information provided in the following pages attempts to identify the magnitude of the environmental problem related to the above-mentioned compounds.

#### **A. POLYCHLORINATED BIPHENYLS (PCBs)**

The following report is mainly based on the OSPAR Priority Substances Series (OSPAR Commission 2001) and the Guidelines for Identification of PCBs and Materials Containing PCBs (UNEP Chemicals, 1999).

##### **1. Sources of PCBs**

###### **1.1. Introduction**

PCBs have been produced commercially since 1929, both for “closed” uses, such as use as insulation and cooling fluids in transformers, dielectric fluid in capacitors and as hydraulic fluids, and for “open” uses, such as grouting and sealants and as plasticisers in paints. Production in Europe was stopped in the mid-1980s. Since then, the main sources have been losses from PCB-containing units, waste disposal, remobilisation of PCB-containing sediments and, to an unknown extent, formation as by-products in various thermal and chemical processes. In contaminated estuaries, concentrations in sediments can reach several hundred µg/kg (dry weight). In remote areas, the range found is 0,1 – 20 µg/kg (dry weight). Concentrations in biota can be as high as 1 900 µg/kg (wet weight). Emissions and concentrations have dropped since the 1970s, but concentrations may now be levelling off as remobilised sediments become the major source.

EC Directives ban their use in open applications, as raw material and intermediates, and require PCBs to be inventoried and destroyed. The UN Economic Commission for Europe

Protocol on Persistent Organic Pollutants (POPs) has a similar requirement for destruction, while the newly signed UNEP POPs Convention will ban PCB production and require destruction of stockpiles and careful handling of wastes.

In principal, emissions will occur from production, from use, from waste and from waste disposal. In Europe, the production of PCBs ceased in 1985 at the latest. However, there are strong indications that some countries (e.g. the People's Republic of China) may still be producing PCBs. This explains why PCB containing capacitors can still occasionally be found in new appliances.

### 1.2. Uses of PCBs

The main uses of PCBs are presented in Table 1.1.

**Table 1.1: Applications of PCBs**

Category	Application	Chlorine content [wt. %]
Closed system	Transformers	40-60
	Capacitors	20-55
Circulatory systems	Hydraulic oils	30-60
	Thermal oils	ca. 40
	Lubricating oils	20-55
Open systems	Plasticiser for rubber	20-70
	Plasticiser for synthetic resins	50-70
	Carbonless copy paper	ca. 40
	Adhesives	20-55
	Paints, printing inks, sealants	ca. 55

The main uses in closed systems were in the electricity and mining industries and involved:

- transformers (insulation and cooling fluids);
- capacitors (dielectric); and
- hydraulic fluids (incl. fireproofing).

PCBs are used pure or in mixtures with other substances. Such mixtures, for example, are the askarels, which are used in power transformers. They consist of approximately 65 % PCB and approximately 35 % tri- or tetrachlorobenzene.

Closed application means that - in principle - PCBs cannot be released to the environment during use (e.g. PCBs as dielectric fluid in transformers). However, according to an estimate (Callahan, 1983 cited in Ifeu, 1998), 2 % of transformers and 3 % of large capacitors in the USA had leaks so that significant releases also from such closed applications can be assumed.

### 1.3. Disposal

In order to examine the emissions of PCBs, which can arise at the end of a product's life cycle, it is necessary to consider the legal provisions for its disposal. Council Directive 96/59/EC contains stipulations regarding the elimination of PCBs. The Directive applies to wastes with PCB concentrations  $\geq 50$  ppm and volumes  $\geq 5$  litres of PCBs.

Key features of the Directive are:

- within 3 years of its adoption in 1996, EU Member States must submit an inventory and detailed plans for the disposal of the relevant PCB wastes and the decontamination/disposal of the relevant equipment. These will have to cover all equipment containing more than 5 litres of PCB;
- the year 2010 has been set as a deadline for complete disposal or decontamination of equipment containing PCBs. The only exception is for transformers containing between 500 and 50 ppm of PCB, which are allowed to remain in service until their end of life.

It can be assumed that uncontrolled disposal via household wastes is mainly restricted to smaller electrical appliances. Studies currently available indicate a proportion of these small appliances in household waste of approximately 1 % by weight of the overall quantity of household waste.

When small capacitors containing PCBs are dumped in landfill sites, PCBs are released due to rotting casings. PCB containing capacitors may also be damaged as a result of compacting. At the beginning of the 1980s the PCB content of the residual waste disposal of a household waste incinerating plant was between 0,26 - 0,35 g/t dry material or 0,175 - 0,25 g/t moist waste. These values are probably also valid for solid waste landfills.

Another important source is the deposition of PCBs from the air subsequent to volatilisation from contaminated water and soil. The diffuse re-circulation of PCBs from soils, sewage sludge etc. has been estimated to become the relatively most important source of PCBs in a long-term perspective (Annema, 1995).

Contamination of sewage sludge with PCBs possibly occurs via contamination through recycled hygiene paper. A summary of the data provided by various authors showed that at the end of the 1980s 100 % of the sewage sludge in the Federal Republic of Germany was contaminated with PCBs. The PCB contamination varied between 0,05 - 15 mg/kg dry material.

## **2. Quantification of sources – assessment**

In order to present an indication of the importance of the different sources of PCBs, cumulative data for former West Germany for closed and open applications up to 1984 are shown in the following table (Table 2.1) with a total use of > 72 500 tonnes:



Table 2.1: Cumulative data on the PCB quantity used in former West Germany up to 1984

PCB applications (former West Germany)	Production [t]	Applied [t]
Closed systems (71%)		
Electrical Industry		
Askarel transformers	27 900	22 826
Capacitors	18 600	13 127
Mining	12 500	12 500
Oil radiators	< 0,05	
Coils	< 0,46	
Open systems (29%)		
Sealing materials, paints, plastics, etc.	24 000	> 24 000
<b>Total</b>	<b>83 000</b>	<b>approx. 72 500</b>

Because disposal of waste containing PCBs is subject to a mandatory registration, information on quantities of PCB already disposed of is available, and the quantity at present in use can be estimated. For example, Askarel transformers can be assumed to have a minimum service life of 25 years. As the oldest transformers were made in 1960, their replacement must have begun in 1985. At the end of 1988, 10 361 drained and cleaned askarel transformers were stored in West Germany in underground waste disposal facilities. Assuming an average quantity of 870 kg PCB per transformer, a quantity of 9 014 tonnes PCB can be estimated to have been disposed of. This means that based on the cumulative applied quantity of 22 826 tonnes in 1984, in 1988, approximately 13 812 tonnes PCBs may be still in use in askarel transformers in the former West Germany.

### 2.1. Uncontrolled applications

Because of the definitions applied, a number of PCB-containing products and wastes there is no requirement to carry out an inventory under Council Directive 96/59/EC. These include large volume wastes with a low PCB concentration (e.g. mineral oil contaminated with PCB) and products with a small volume of pure PCBs (e.g. capacitors in strip light fittings). Such uses are called 'uncontrolled' applications.

### 2.2. Open applications

The PCB quantities used in open applications are especially difficult to retrieve and estimate. All open applications can be considered uncontrolled. Until the use in open applications was banned in the early 1970s, approximately 25 000 tonnes PCBs went into open applications in Germany and 4 000 tonnes in Belgium (see table 2.3). With a service life of the relevant products of 15-25 years, most of these open applications would already have been forwarded to waste treatment by the year 1994.

On the other hand, it can be assumed that certain applications, for example in construction materials, were designed for longer periods of use (40 years for some paints and sealing materials). Consequently, sealing materials probably represent the most important still relevant source of emissions from open applications during the 1990s. Recent findings in Switzerland confirm that sealing materials could still represent an important source. Until now only a few samples have been analysed and the PCB concentrations found varied

considerably. A monitoring campaign will be started in order to get an idea about the extent of the problem.

According to the German Federal Health Office, the total quantity of sealing material containing PCBs used in the construction sector was approximately 20 000 tonnes. In this context, sealants produced on the basis of polysulphide polymer (trade name Thiokol) are particularly relevant. In measurements conducted by the German Federal Environmental Agency at the beginning of the 90's PCB concentrations of 5 - 210 g/kg were found in 12 of 34 sealing materials examined. The 12 samples showed an average PCB content of 110 g/kg. A general estimate using this value for sealants containing PCBs results in 2 200 tonnes PCBs in this sector.

Another source of relevant emissions to the hydrosphere was the use of PCBs in the production of carbonless copy paper. This use is responsible for the fact that elevated PCB values were still measured in recycled paper for a long time after discontinuation of the production in 1972. In the first half of the 1980s values of > 10 ppm and at the start of the 1990s up to 4 ppm were found in Germany. The use of such recycled paper in toilet paper presumably led to a considerable contribution into the hydrosphere. However no exact quantitative data can be supplied.

Refurbishment of metallic constructions such as pylons and bridges coated with paints against corrosion can also be an important source for PCB emissions and emissions of other hazardous substances such as PAH or lead, if the work is not done properly. In Switzerland a guideline is in preparation defining strict rules to be followed when carrying out such work.

As an example, in Belgium, a more detailed inventory of PCB volumes in open applications has been established and the information is presented in tables 2.3-2.7.

In the following tables an estimate of the emissions of PCBs from small, uncontrolled applications is shown. In the different columns the estimated PCBs quantities are shown with the titles "Estimate of PCB quantity marketed", "Extrapolation of PCB quantity still present in 2000" and "End of life in Environment in 2000 since 1980". Some explanation of the method used to make the estimates is necessary:

- a. the distribution of quantities between the two last mentioned columns in the tables is calculated with regard to the period of use;
- b. in the general approach, emissions during the "use" (and thus before the "end of life") have been intentionally omitted. If they had been taken into account, the "Quantity still present (in use) in 2000" figures would be slightly inferior whereas the "End of life in Environment" quantities would have been slightly superior. It has been assumed that the appliances/material at the end of the life are finally disposed of on landfills.

#### "Paints" (uncontrolled and open applications)

These PCB-containing paints can be found in some sectors (e.g. transport and infrastructure, households, office, SME, waste disposal....) and constitute an important source of emissions of PCBs during life cycle and at the end of life stage.

Table 2.2 Inventory of PCB-containing paints in Belgium

The "paint" terminology includes :	Period of Application	Estimate of PCB quantity Marketed	Life Cycle (in years)	Extrapolation of PCB quantity still present in 2000	Emission T/y in 2000	End-of-life in Environment in 2000 since 1980
Chlorinated rubber paint	Up to 1973	2 625 t	25	13 t	0 – 0,86	2 612 t
Vinyl chloride paint	Up to 1973	800 t	25	4 t	0 - 0,28	796 t
Latex paint	Up to 1963	45 t	40	6,4 t	0 – 0,65	38,6 t
Other paint	1960-1982					
Not specified						
Total:		3 470 t		23,4 t ->	1,79 t/y	3 446 t
The yearly emissions are 0-7 % (RIVM 1995)						

The extrapolation of PCBs still present in Belgium in 1999 is calculated without considering emissions during life cycle.

It is important to note that the confinement of PCBs within paints (matrix) leads to emissions that are more important than for condensators (where PCBs are confined into a metallic capsule). This is due to the physical and photochemical alterations of these paints (emissions up to 7%). At the end of their technical life, the paints are taken away (chemical, thermic or physical treatment of the painted surfaces); in some cases, the treated material itself is destroyed. In all of these cases, the destruction of the old paint is the general rule. The destruction of the matrix gives rise to even higher emissions of PCBs. But these have not, so far, been documented.

#### Concrete (uncontrolled and open applications)

Concrete is a source of emissions in the air during use and during waste disposal. The concrete terminology includes:

- concrete additives
- grouting
- polymer composite cement (PCC)
- other
- not specified

Table 2.3: Emission inventory of PCB-containing concrete in Belgium

Countries	Concrete	Period of application	Estimate of PCB quantity Marketed	life cycle (in years)	Extrapolation of PCB quantity still present in 1999	Emission t/year	End-of-life in Environment In 1999 since 1969
Belgium	PCC	1960 –1969	40 t	40	2,9 t	0,198 t/y	37,16 t
The yearly emissions are 0-7 % (RIVM 1995)							*

Note that the "end of life" consideration for paints are also valid in this case.

#### Emission inventory of PCB-containing Mastic

Mastic is a source of emissions in air and in the waste disposal.

Table 2.4: Belgium

Countries	Mastic	Period of application	Estimate of PCB quantity marketed in Belgium	life cycle (in years)	Extrapolation of PCB quantity still present in Belgium in 1999	Emission t/year in 1999	End-of-life in environment in 1999 since 1973
Belgium	Thiokol	Up to 1973	63 t	40	5,46 t	0,38 t/y	57,54 t
The yearly emissions are 0- 7 % (RIVM 1995)							

The extrapolation of PCBs still present in Belgium in 1999 is calculated without dispersion and emissions during the life cycle. Note that the “end of life” considerations for paint and concrete are also valid here.

#### Glue (uncontrolled and open applications)

Glue is a source of emissions in air during use and during waste disposal. The glue terminology includes:

- glue;
- not specified.

Table 2.5: Emission inventory of PCB containing glue in Norway

Countries	glue	Period of application	Estimate of PCB quantity marketed	life cycle (in years)	Extrapolation of PCB quantity still present in 1999	Emission t/year in 1999	End-of-life in Environment In 1999 since 1975
Norway	1	1965-1975	250	40	35	2,45 t/y*	215 t

\* the same emission coefficient as the one for thiokol (0 – 7%) has been used.

Note that the “end of life” considerations for paint, concrete and mastic are also valid here.

#### Other products

In 1983, the US-EPA made a list of potentially PCB-containing products, based on a theoretical study of 200 chemical processes that can generate PCB as a by-product. The processes were ordered according to their potential for PCB creation; the substances produced this way and with a high potential were put on the EPA list. It is expected that these substances contain 25 – 50 ppm PCBs.

No analysis data on the PCB content is available for any of these products, because the European industry is not bound to analyse PCBs in products.

In Belgium, PVC dust has been analysed and PCB concentrations were about 40 ppb. This dust is used by companies who manufacture their PVC products by modifying the formulation with adjuvants and pigments. As the dust is reworked, contamination of PCBs might increase. No further data on these products are available.

#### 2.3. Closed applications

With regard to closed applications, PCBs are released through leaks and partly also as a result of fires when electrical plants and appliances containing PCBs burn. As most of the Askarel transformers and large power capacitors ought to be disposed of by the end of 1999, mainly small PCB containing capacitors are still in use.

To date, about a third of the small PCB-containing capacitors is still in use (see table 2.6). These mainly involve capacitors in strip light fittings. However, the number of capacitors that were installed in lights along motorways and municipal roads cannot be neglected. This use entails a possible danger to the public health because capacitors sometimes leak or even explode. Another likely area in which many PCB containing capacitors are found is in washing machines and domestic fuel oil burners and central heating circulation pumps. When waste is shredded, the small capacitors contribute largely to the contamination with PCBs.

The situation with regard to closed applications in Belgium is given in table 2.6.

### Small capacitors

These are found in some important sectors/locations (e.g. agricultural activities, transport and infrastructure, households, office, waste disposal,) and constitute an important source of emission (end of life) and discharge (during life cycle).

Table 2.6: Belgium

The capacitor terminology Includes :	Period of application	Estimate of PCB quantity marketed in Belgium	life cycle (in years)	Extrapolation of PCB quantity still present in Belgium in 2000	Emission t/y in 2000	End-of-life in Environment in 2000 since 1980
1. Capacitors in strip light fittings (indoors),	1960-1982	690 t	20	127 t	2,03	563 t
2. public lights on motorways and national roads, municipal roads	1960-1982	103 t	25	33 t	0,53	70 t
3. capacitors in burners of CH installations	1960-1982	28 t	20	5 t	0,08	23
4. capacitors in pump of CH installations	1960-1982	73 t	15	7 t	0,1	66
5. capacitors in washing machines	1960-1982	29-100 t	15	14 t	0,224	86
6. capacitors in UPS installations	Up to 1982	> 0	3-5 small 15 large	> 0		0
7. electrical bushings						
8. other small capacitors (oil radiators)	1960-1986	23 t	25	12 t	0,192	11
9. not specified						
	Total:	1 017		198 t	3,16 t/y	819 t

CH: central heating

UPS: Uninterrupted Power Supply

It should be noted that the extrapolation of PCBs still present in Belgium in 2000 is calculated without considering dispersion and emissions during the period of use.

The last column gives an estimate of the amount of PCBs in the environment after the "end of the application's life" ». This particular period is complex as it is composed of a period of "retirement" followed, in the absence of identification criteria for the dangerous potential of these products, by a redirection to landfills, "household waste" incineration facilities or to metal recovery facilities. In all these cases, the period during which the condenser's "physical integrity" has been intact is difficult to estimate. Therefore, calculation hypotheses are, thus far, difficult exercises.

Furthermore, the list in table 2.7 gives an indication of the potentially relevant equipment sectors and illustrates the risk potential still existing in this sector.

Table 2.7: Occurrence of PCB capacitors in electrical equipment (Schiemann, 1996, cited in Ifeu, 1998)

<i>Type of equipment</i>	<i>Number of units examined</i>	<i>Equipment with PCB Capacitors</i>	<i>Proportion</i>
Office machinery	20	5	25,0
Extractor hood	12	4	33,3
Electric motor	11	2	18,2
Television	670	10	1,5
Dishwasher	143	6	4,2
Other domestic appliances	16	2	12,5
Cooling equipment	211	1	0,5
Copier	19	2	10,5
Strip light fittings	517	354	68,5
Oil burner	19	10	52,6
Radio/phono/others	89	3	3,4
Lawn-mower	13	0	0
Vacuum cleaner	55	1	1,8
Hood-type hair dryer	16	9	56,3
Washing machine	500	49	9,8
Laundry dryer	16	0	0
Commercial equipment	32	4	12,5
Other appliances	6	0	0
<b>Total/Average</b>	<b>2 365</b>	<b>462</b>	<b>19,5</b>

As in Belgium, it appears that small PCB containing capacitors are mainly still in use in strip light fittings in Germany.

For Germany, table 2.8 shows a PCB emission inventory estimated for the period 1994/95 by Ifeu (1998).

The emissions of PCBs to air will ultimately end up in the soil or surface water through deposition. The PCBs in water will cling to the sediment because of the strong adsorption of these substances, which is why they can be found bound to soil particles. It can therefore be concluded that the emissions of PCBs will ultimately end up as a large-scale diffuse contamination of soil and sediments.

Table 2.8: CB emission inventory Germany (period 1994/95)

Source	PCB [kg]
open applications*	max. 16 000
Closed applications	max. 10 989
Diffuse land fill gas release	max. 5,9
Landfill gas incineration	0,02
Domestic waste incineration	0,32
Transport -diesel powered vehicles	0,26
sinter plants	92
Secondary steel production	206
fire places	789
Total:	30 894 kg
Source: Ifeu estimates (Ifeu, 1998)	
* only for PCB containing sealants	

A summary of the assessment of PCB fluxes and inventories relevant to the OSPAR area is furthermore presented in Eurochlor, 1999, combining the information given in Axelman, 1997 and Ritter *et al.*, 1996. It was estimated that the total amount of PCBs released to the environment in the Northern Hemisphere is about 100 000 tonnes, 75% having been released between 1955 and 1970. Current emissions are assumed to be between 10 and 100 tonnes per year both in the OSPAR area and in North America, the larger part of it coming from electrical equipment. A study carried out in Sweden indicated that in the OSPAR area, about 5 000 tonnes PCB could still be present in old buildings in the form of various surface coatings and sealant.

It was stated also in the Eurochlor report, 1999 that due to the persistent and semi-volatile character of PCBs "old emissions" are still present in the environment and are further spread via a distribution mechanism of deposition and volatilisation. The "new emissions" should then be considered in a global approach

In the following table 2.9 the results of Axelman (1997) are shown.

These results indicate that most of the existing PCBs are adsorbed to soil, litter and sediment. They are progressively volatilised to the atmosphere where the main but slow degradation takes place. The overall degradation process is however very slow, in particular for the highly chlorinated congeners. In this context the present emissions may act as a continuous supply to maintain constant atmospheric concentrations.

Table 2.9: PCB inventories and fluxes according to Axelman (1997; cited in Eurochlor, 1999)

	PCB #28	PCB#153
<b>Emissions</b>		
Total "old" emissions [t]	14 000	4 850
"New" emission [t/a]	6	0,6
<b>Inventories</b>		
in atmosphere [t]	62	17
in surface water [t]	6	7
in deep water [t]	45	54
in shelf sediment [t]	10	53
in soil [t]	917	760
in biomass and litter [t]	122	74
<b>Total</b>	<b>1 117</b>	<b>950</b>
<b>Losses/degradation</b>		
in atmosphere [t/a]	92	3,5
in sea water [t/a]	1	1,3
in sediment [t/a]	1	5
in soil and biomass [t/a]	0,3	0,2
<b>Total [t/a]</b>	<b>94,3</b>	<b>10</b>
Total [% inventory/a]	8	1

In the framework of an EU project on POP emissions in the Baltic region (Pacyna *et al.*, 1999) the following estimates of emissions of PCBs are given.

The historic development of emissions of PCBs have been estimated with respect to national reduction measures and assumptions. Because there was only scarce information on measured emissions of PCBs, the emissions of PCBs in table 2.10 have therefore been calculated from statistical data on activity and population using default emission factors. For Germany for example, the estimates are higher than those presented by Ifeu. However, it is not possible to judge the reason for the difference between both emissions.

Table 2.10: Estimated PCB emissions [t/a] (Pacyna *et al.*, 1999)

Year	BE	DK	FIN	FR	GER	LUX	NL	NOR	PT	SP	SWE	SWI	UK	Emission for Europe (including Eastern Europe)
1970	49,5	24,9	23,5	258,1	402,1	2,1	65,8	19,6	18,2	170,5	41,1	31,7	282,4	1 729
1975	40,3	20,5	19,3	214,8	323,8	1,8	55,1	16,2	17,9	143,6	33,7	25,9	228,0	1 428
1980	20,4	10,5	9,9	110,2	164,2	0,9	28,6	8,3	19,7	75,9	17,1	12,9	114,8	757
1985	20,2	10,4	9,9	111,7	160,1	0,9	29,2	8,4	20,1	77,7	16,9	13,2	114,7	758
1990	1,8	1,01	2,7	19,96	43,2	0,13	0,25	0,4	0,6	8,7	1,9	1,7	3,8	116
1995	1,8	1,02	2,7	20,4	42,4	0,13	0,25	0,4	0,6	8,7	2,0	1,7	3,7	113

#### 2.4. Conclusions

Based on the above monitoring data and various data sources on remaining PCB sources and PCB emission estimates and also taking into account the uncertainty of these release



estimates it can be concluded that the input into the environment has decreased significantly. A clear downward trend can be observed.

However, relevant emissions are estimated still to take place with regard to open and closed uncontrolled applications. For Belgium, the estimates show that these are of the same order as the ones from "controlled" applications (see table 2.11).

Table 2.11: Sum of all estimated emissions in Belgium

<b>Applications</b>		<b>Emissions in 2000 t/year</b>	
Small applications and products	Large applications	Small applications and products	Large applications (EMEP data )
Thiokol	-	0,38	-
PCC	-	0,2	-
Chlorinated rubber paint	-	0,86	-
vinyl chloride paint	-	0,28	-
latex paint	-	0,65	-
Capacitors in strip light fittings (indoors),	-	2,03	-
public lights on motorways and national roads, municipal roads	-	0,53	-
Capacitors in burners of CH installations	-	0,08	-
Capacitors in pump of CH installations	-	0,1	-
Capacitors in washing machines	-	0,224	-
<b>Oil radiators</b>	-	0,192	-
	Transformers & capacitors		5,2
<b>Total</b>		<b>5,52</b>	<b>5,2</b>

At this stage, we can observe that the emissions of PCBs from small, uncontrolled applications are still very important for 2000. They represent about a half of the total emissions from products in use.

It should be noted that, even for small uncontrolled applications, most emissions originate from the "end of life" applications (wastes).

With time, the "emissions from wastes" will predominate.

Although the above inventories give valuable information for the assessment of the emissions of PCBs and the size of the problem, one should be aware that estimates, thus far, remain very uncertain and often represent maximum levels based on a conservative approach.

As a conclusion it can be stressed that emissions of PCBs, on which law-makers and environmental authorities have focused for many years, still cannot be controlled comprehensively despite all abatement results. Since there is still a significant potential for emissions, further legal regulations containing binding specifications, in particular for waste disposal, may be required.

### 3. Legislative measures

#### 3.1. International Agreements

OSPAR Decision 92/3 on the Phasing out of PCBs and Hazardous PCB Substitutes does not differentiate between “large” and “small” PCBs. Therefore, this Decision is understood to cover all applications of PCBs. The current round of implementation reporting provided an indication of the extent to which the Decision has been complied with and the problems which might have occurred. Because of the limited number of implementation reports submitted, only a short description of the information provided was possible. Nevertheless, from the information provided it may be concluded that in some Contracting Parties, intensified administrative action concerning safe disposal of e.g. small capacitors has taken place since the previous assessment carried out in 1997.

The HELCOM Recommendation 6.1 regarding the elimination of the use of PCBs and PCTs (1985) addresses the ban on the production and marketing of articles and equipment containing PCBs/PCTs from 1987 onwards. This Recommendation is complemented by a provision in the 1992 Helsinki Convention (Annex 1, part 2.2) banning all uses except in existing closed systems until the end of service life.

The UN-ECE Protocol on Persistent Organic Pollutants (POPs) requires ratifying countries (whose economies are not in transition) to destroy or decontaminate equipment containing more than 50 ppm PCBs (and liquid PCBs containing more than 50 ppm) by 2015. In the case of dioxins this Protocol also requires ratifying countries to reduce continually annual emissions (in relation to a specified base year), by the use of a number of measures outlined in the Protocol. These measures include the use of defined limit values (emission standards) and best available techniques. However, the Protocol acknowledges that the time may come when all such measures have been implemented and no further reductions can be achieved. It should also be mentioned that the UNEP Convention on Persistent Organic Pollutants includes, among others, a ban on PCB production and use as well as a requirement concerning the destruction of stockpiles and the handling of wastes.

Furthermore, it is worth mentioning some previous agreements:

- 1973 recommendation from OECD (control and restrict the flow of PCBs into the environment);
- 1976 WHO (discussing and evaluating the data available then on exposure level and effects of PCBs and PCTs on human health, and, to a lesser extent, on the environment);
- 1978 IARC (international agency for research on cancer);
- 1982 OECD (the 24 OECD member states have restricted the manufacture, sale, import, export, and use of PCBs, and established systems for these compounds).

### 3.1.1 EU Legislation

The use of PCBs in open applications such as printing inks and adhesives was banned in the European Community in 1976 under Council Directive 76/403/EEC.

The use of PCBs as a raw material or chemical intermediate has been banned in the EU since 1985 (Council Directive 85/467/EEC, 6<sup>th</sup> amendment to Directive 76/769/EEC)

The disposal of PCBs and polychlorinated terphenyls (PCTs) has been regulated by Council Directive 96/59/EC. Key features of this Directive are:

- within 3 years of its adoption in 1996, EU Member States must submit an inventory and detailed plans for the disposal of the relevant PCB wastes and the decontamination/disposal of the relevant equipment. These will have to cover all equipment containing more than 5 litres of PCBs (see also paragraph 1.7).
- the year 2010 has been set as a deadline for complete disposal or decontamination of equipment containing PCBs (although OSPAR Contracting Parties should still be bound by the 1999 deadline set out in PARCOM Decision 92/3). The only exception is for transformers containing between 500 and 50 ppm of PCB, which are allowed to remain in service until their end of life.

With regard to national inventories within the framework of third Council Directive, it can be noted that many EU Member States appear to have difficulties in tackling and monitoring the remaining PCB containing equipment (see also paragraph 1.11).

## 4. Identification of possible measures

### 4.1 Tackling the stock of PCB containing sediments

In Annema *et al.*, (1995) the consequences for the PCB flux in the Netherlands were evaluated for the case that additional policy measures would be taken in the Netherlands with regard to:

- enhanced replacement of PCB containing equipment;
- elimination of upstream hot spots of contaminated river sediments through dredging; and
- dredging of the major downstream sedimentation areas.

Concerning the dredging of upstream hot spots it was recognised that the diffuse sources of PCB pollution are unknown (i.e. these hot spots are the result of past emissions and because of erosion in this area PCBs can be transported downstream to the Netherlands). It is therefore too difficult to reduce these PCB emissions by the development of additional measures in the Netherlands.

With regard to dredging the major downstream sedimentation areas with high PCB concentrations, it was stated that when disturbing the sediment layers from the 1960s and 70s, exposure may pose an acute risk, whilst otherwise the PCBs trapped in these layers appear to have only a limited impact. At locations with high levels in the top layers the risks of the presence of PCBs in the sediment would be significantly reduced by dredging and it was assumed that dredging the major sedimentation areas would result in a 20 % lower input into the North Sea.

With regard to the replacement of PCB-containing equipment it was estimated that in the Netherlands only slight changes in the fluxes of PCBs could be expected. It was therefore concluded in the Dutch report that a decrease in PCB fluxes could only be tackled with additional measures agreed at an international level, and by dredging the major sedimentation areas. Nevertheless, a 1998 report from the Netherlands to OSPAR on dumped dredged materials showed that the PCB content in the sediments that are annually dumped into the North Sea is rather low. The total input is less than 200 kg. Sediments are contaminated with PCBs and a lot of other hazardous substances. In theory it seems a good solution to remove and store contaminated sediments in landfills in order to stop the re-suspension of PCBs from sediments. However, it is not practicable in the Netherlands as the amount of sediment is so huge that it is physically (and also financially) impossible to store it all on land.

#### 4.2. PCB re-introduction through recycling

Measures could also be taken in order to prevent the re-introduction of PCBs in applications via recycling. This appears to be of particular importance with regard to flame retardant cable sheathings that may contain significant amounts of PCBs. It could be envisaged that in this context the introduction of PCBs through recycling is controlled under the proposed Directive of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE).

In general terms, all equipment which needs electricity to work properly is either electrical or electronic. Each electrical or electronic product consists of a combination of several basic building blocks. The basic building blocks common to electrical and electronic equipment are among other things cables, plastics containing flame retardants and capacitors. The most environmentally problematic substances contained in these components are heavy metals, such as mercury, lead, cadmium and chromium, halogenated substances, such as chlorofluorocarbons (CFCs), polychlorinated biphenyls (PCBs), polyvinyl chloride (PVC) and brominated flame retardants as well as asbestos and arsenic.

Proposals for two Directives of the European Parliament and of the Council on waste electrical and electronic equipment and on the restriction of the use of certain hazardous substances in electrical and electronic equipment are being developed by the European Commission and the EU Member States.

The first draft Directive includes provisions for the producer to bear the disposal costs. This is considered to contribute to an environmentally safe disposal, which will also stimulate the producer to use less hazardous substances and those which are recyclable, and to construct long lasting electronic equipment. The aim of the second draft Directive is to restrict the use of hazardous substances in electrical and electronic equipment and to contribute to the environmentally sound recovery and disposal of waste electrical and electronic equipment.

#### 4.3. Stop feeding the waste stream – closed applications

A safe disposal of all PCB appliances is also advocated by Ifeu (1998). It was proposed that the crucial reduction measure consists of the elimination of capacitors containing PCBs via a separate controlled disposal route when disposing of equipment with such capacitors.

In the case of small electric appliances commonly found in domestic waste it should be ensured that these are not disposed of with domestic waste. A collection scheme for small electrical appliances is a prerequisite. Possible methods of achieving this include:

- possibility of delivering appliances to recycling centres/landfills sites;

- possibility of returning such appliances when bulky refuse is collected;
- possibility of returning such appliances in separate containers when bulky refuse is collected;
- collection on request;
- return to the retail trade.

It is assumed that in more than 200 of the altogether 500 waste collection areas in Germany small electric appliances are provided for by the local waste collection/delivery systems. Despite this, the main disposal path is still presumed to occur via household wastes. For the future it is considered to be necessary to adjust the collection schemes, where possible, and to increase public awareness and acceptance of the relevant collection schemes. With regard to closed applications it is suggested to have PCB-containing appliances separated, where possible, by the municipal scrap collection centres or by scrap merchants and the PCB-containing components removed.

The main problem with small electrical applications lies in the fact that it is very often too difficult to distinguish between small PCB-containing components and PCB-free ones. Therefore, it might be considered whether all small electrical equipment wastes collected should be destroyed by high temperature incineration (at the moment, they are directed towards normal household-waste incinerators).

#### 4.4. Stop feeding the waste stream - open applications

For open applications it was stated in Ifeu, 1998 that PCBs are released via construction rubble or general scrap. The cost for separation is much higher than for closed applications and for practical reasons a safe disposal should be limited to suspected cases of PCBs. In such cases efforts should be made to separate the relevant components such as PCB-containing sealants prior to the demolition of the relevant building. It might also be examined whether, before the demolition of buildings dating from the years 1950-1975, their different components should be analysed and decontaminated (concrete, "mastic", paint).

In general it is concluded that in order to minimise emissions of PCBs, further logistic and educational measures among waste generators and recyclers, or further legal regulations containing binding specifications for dismantling should be developed. In the construction sector, financial mechanisms could also be used by the governments to promote that employers communicate to the authorities on the existence of the applications of PCBs or waste which contains PCBs when they are confronted with this kind of material.

A program is running in Sweden for the identification of PCBs in buildings. A voluntary agreement for the replacement of material that poses a risk has been set up by the estate owners and the building industry.

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## **B. BATTERIES**

### **1. Ni, Cd Batteries**

Nickel – Cadmium (Ni-Cd) batteries are used in advanced applications in the fields of aeronautics, space and defence, stand-by power, railways, power tools, telecommunications and other special applications. Ni-Cd batteries are sold as large industrial units (industrial batteries) and as power packs integrated in portable electrical equipment (portable batteries).

According to the data of CollectNiCad (Wiaux, 2002), an Association of Ni-Cd battery manufacturers and equipment manufacturers incorporating those batteries in their equipment, the Cd content of the batteries produced is approximately 14% by weight.

Industrial batteries are easier to be collected since they are relatively bulk and are concentrated in specific areas. Portable batteries are usually more difficult to be recycled, however it seems that recycling is feasible in large scale. The mass balance of portable Ni-Cd batteries in the EU plus Norway and Switzerland is approximately 13,100 t/year (2000). It is estimated that 8,700 t/y (66%) are in use by the end user while 4,400 t/y (33%) are available for collection. From these 4,400 t/year, 400 t/y (9%) are collected with industrial wastes, 2,200 t/y (50%) are collected separately and processed for recycling and 1,800 t/y (41%) are present in Municipal Solid Wastes. As an estimation for the occurrence of portable Ni-Cd batteries in home appliances, it can be assumed that there are 2.7 Kg of electrical equipment per capita and 0.1 Kg of power tool per capita, in industrialised societies.

Recycling is applied in several European countries with different degrees of success. It was calculated for the year 2000 that the collection efficiency in 6 European countries where such recycling programs are in operation, ranged from 63.7 to 96.1% (average 71.6%) for portable batteries, which are the most difficult to be collected. In specific detailed field studies in European countries where recycling was in operation, it was found that Municipal solid wastes may contain from 4 up to 23 g of Ni-Cd batteries per tonne of waste. However, in other Mediterranean areas where no batteries collection programme is in operation, the amount of Ni-Cd batteries ending up in the dumping sites is expected to be much higher.

### **2. Acid-lead batteries**

According to European data, the amount of acid-lead batteries consumed for the year 2000 is ranged between 0.19 to 0.34 tons/year/inh. The average weight collected varies between 1.85 to 3.37 kg/y/inh. The values are indicated in the following table.

Table 2.1

<b>Country</b>	<b>Amount declared tons/y/inh.</b>	<b>Average weight collected kg/y/inh.</b>	<b>No. Motor vehicles per 1000 people</b>
Austria	0.19	2.03	521
Denmark	0.28	2.91	413
Italy	0.29	2.89	591
Sweden	0.34	3.37	468
The Netherlands	0.19	1.85	421
Norway	0.32	1.95	498

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## **C. LUB OIL**

Used lubrication oil is collected in all areas where motors are in operation. That includes gasoline stations (motor vehicles), in harbours and ship repair stations, industries, and also in urban areas. In most countries, oil collection and regeneration in specialised industrial plants is taking place and only a small part is either stored or disposed off. Also a part of the used lub oil is used as fuel.

Few available data were found for the actual life cycle of the used lub oil in the Mediterranean countries. Depending on the collection efficiency, and the availability of lub oil regeneration units in the area, the amount of uncontrolled disposal of the lub oil may vary considerably. As an example, data from Greece (2001) indicate that 62% of the produced oil is regenerated, 23% is been used a fuel with energy recovery, 7.5%is used for several other purposes and 7.5% is disposed off without any control. However, the situation in other Mediterranean countries may be quite different.

## References

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## ADDENDUM 2

### CALCULATION OF THE STORMWATER RUNOFF AND POLLUTANT LOAD FROM LAND AREAS

#### Introduction

Stormwater runoff is an important factor, which influences the receiving water quality when it drains an area where priority pollutants are been used or stocked. Intensively cultivated areas, as well as, industrial and urban developments are land surfaces with stormwater runoff enriched in toxic substances. This is particularly important where stockpiles of obsolete chemicals are present in badly managed industrial areas.

In order to estimate the pollutant's load from surface runoff, three steps are required:

- Calculate the quantity of the stormwater runoff, based on rainfall data and surface characteristics
- Measure the pollutant's concentrations in the stormwater runoff
- Calculate the pollutant's load in the stormwater runoff

It must be underlined, that for the completion of this calculation, monitoring data on the runoff quality are required.

#### Estimation of the stormwater runoff flow from the land areas

The flow of the runoff can be estimated by multiplying the annual amount of rainfall by the land area of the facility (urban, industrial or agricultural). Rainfall data (in mm of rain per year) are usually available from the nearest meteorological station. Snowfall data can be converted to equivalent mm of rain (100 mm of snow is equivalent to 8.5 mm of rain). The rainwater volume will be then multiplied by a **runoff coefficient**, which represents the fraction of the rainfall that does not seep into the ground but runs off as stormwater. Of course, the runoff coefficients are directly related to how the land in the drainage area is been used. Covered areas (concrete, pavement, asphalt) have a higher runoff coefficient that uncovered areas. Proposed runoff coefficients are presented in Table 1 (USEPA, 2000).

Table 1. Runoff coefficients related to different land characteristics or uses

Description of the land area	Runoff Coefficient
Business	
Downtown areas	0.70 – 0.95
Neighborhood areas	0.50 – 0.70
Industrial	
Light areas	0.50 – 0.80
Heavy areas	0.60 – 0.90
Industrial	
Railroad yard areas	0.20 – 0.40
Unimproved areas	0.10 – 0.30
Streets	
Asphaltic	0.70 – 0.95
Concrete	0.80 – 0.95
Brick	0.70 – 0.85
Drives and walks	0.70 – 0.85

Description of the land area	Runoff Coefficient
Roofs	0.75 – 0.95
Lawns: sandy soil	
Flat, 2%	0.05 – 0.10
Average, 2 – 7%	0.10 – 0.15
Steep, 7%	0.15 – 0.20
Lawns: heavy soil	
Flat, 2%	0.13 – 0.17
Average, 2 – 7%	0.18 – 0.22
Steep, 7%	0.25 – 0.35

For the calculation of the amount of rainwater that ends up in the stormwater runoff, the most appropriate runoff coefficient has to be used for the site under investigation. However, in most cases the area under consideration includes different kind of surfaces. Therefore, in order to take into consideration these differences, a **weighted-average runoff coefficient** has to be used for the total land area.

The weighted-average runoff coefficient will be calculated by multiplying the area of each different type of surface (in percent of the total area) by its appropriate runoff coefficient.

Therefore:

**Weighted-average runoff coefficient =**

**= (Area a% of total) (C1) + (Area b% of total) (C2) +...+ (Area z% of total) (Ci)**

Where:           a + b + ... + z = 100  
                     Ci = the runoff coefficient for a specific land use of Area i.

The total stormwater runoff will be the calculated as follows:

**Total stormwater runoff = Rainfall x Total land area x Runoff coefficient**

Were:           Total stormwater in **m<sup>3</sup>**  
                     Rainfall in **m/year**  
                     Total land area in **m<sup>2</sup>**

Once the total yearly flow of the stormwater is calculated, the total pollutant load transported to the receiving water body through the runoff can also be calculated:

**Total pollutant's load = Total stormwater runoff x Pollutant concentration in runoff water**

Where:           Total pollutant's load in **Kg**  
                     Total stormwater runoff in **m<sup>3</sup>**  
                     Pollutant concentration in the runoff water in **Kg/m<sup>3</sup>**

### Example

An industrial facility is located in a Mediterranean region, which has an annual precipitation of 400 mm of rain. The total area covered by this facility is 150000 m<sup>2</sup>. The area in the facility is 50% unimproved area, 10% asphaltic streets and 40% concrete pavement. Furthermore, monitoring data indicate that the average concentration of Cu in the stormwater runoff from the industrial facility is 1.2 mg/l.

In order to calculate the total amount of copper discharged to surface water through the stormwater runoff the following calculations have to be made:

First the total stormwater runoff has to be calculated.

Land use	% Total Area	Runoff coefficient
Unimproved area	50	0.20
Asphaltic street	10	0.85
Concrete pavement	40	0.90

$$\begin{aligned} \text{Weighted average runoff coefficient} &= (50\%) \times 0.20 + (10\%) \times 0.85 + (40\%) \times 0.90 = \\ &= \underline{0.545} \end{aligned}$$

Therefore,

$$\begin{aligned} \text{Total Stormwater Runoff} &= (\text{Rainfall}) \times (\text{land area}) \times (\text{runoff coefficient}) = \\ &= 0.4 \text{ m/year} \times 150,000 \text{ m}^2 \times 0.545 = \underline{32,700 \text{ m}^3/\text{year}} \end{aligned}$$

Since the copper concentration in the stormwater runoff is 1.2 mg/l (1.2 g/m<sup>3</sup>)

The total amount of Cu from the stormwater runoff will be:

$$\begin{aligned} \text{(Total Cu load in the stormwater runoff)} &= (\text{Total stormwater runoff}) \times (\text{Cu} \\ \text{concentration}) &= 32,700 \text{ m}^3/\text{year} \times 1.2 \text{ g/m}^3 = 39,240 \text{ g of Cu} = \underline{39.24 \text{ Kg of Cu}} \end{aligned}$$

### Conclusion:

**The total Cu load entering the receiving water body from stormwater runoff in the industrial area is 39.24 Kg per year.**

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