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INDUSTRIAL WASTEWATER-TYPES, AMOUNTS AND EFFECTS

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Keywords: Wastewater, industry, environment, pollution, effect, amount, types

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Summary

Industrial wastewater is one of the important pollution sources in the pollution of the water environment. During the last century a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas. This resulted in serious pollution problems in the water environment and caused negative effects to the eco-system and human's life.

There are many types of industrial wastewater based on different industries and contaminants; each sector produces its own particular combination of pollutants. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produced.

The amount of wastewater depends on the technical level of process in each industry sector and will be gradually reduced with the improvement of industrial technologies. The increasing rates of industrial wastewater in developing countries are thought to be much higher than those in developed countries. This fact predicts that industrial wastewater pollution, as a mean environment pollution problem, will move from developed countries to developing countries in the early 21st century.

1. Introduction

Until the mid 18th century, water pollution was essentially limited to small, localized areas. Then came the Industrial Revolution, the development of the internal combustion engine, and the petroleum-fuelled explosion of the chemical industry. With the rapid development of various industries, a huge amount of fresh water is used as a raw material, as a means of production (process water), and for cooling purposes. Many kinds of raw material, intermediate products and wastes are brought into the water when water passes through the industrial process. So in fact the wastewater is an "essential by-product" of modern industry, and it plays a major role as a pollution sources in the pollution of water

environment.

2. The types of industrial waste water

There are many types of industrial wastewater based on the different industries and the contaminants; each sector produces its own particular combination of pollutants (see Table 1).

Sector	Pollutant
Iron and steel	BOD, COD, oil, metals, acids, phenols, and cyanide
Textiles and leather	BOD, solids, sulfates and chromium
Pulp and paper	BOD, COD, solids, Chlorinated organic compounds
Petrochemicals and refineries	BOD, COD, mineral oils, phenols, and chromium
Chemicals	COD, organic chemicals, heavy metals, SS, and cyanide
Non-ferrous metals	Fluorine and SS
Microelectronics	COD and organic chemicals
Mining	SS, metals, acids and salts

Table 1: Water Pollutants by the Industrial Sector

The metal-working industries discharge chromium, nickel, zinc, cadmium, lead, iron and titanium compounds, among them the electroplating industry is an important pollution distributor. Photo processing shops produce silver, dry cleaning and car repair shops generate solvent waste, and printing plants release inks and dyes. The pulp and paper industry relies heavily on chlorine-based substances, and as a result, pulp and paper mill effluents contain chloride organics and dioxins, as well as suspended solids and organic wastes. The petrochemical industry discharges a lot of phenols and mineral oils. Also wastewater from food processing plants is high in suspended solids and organic material. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produced.

Generally, industrial wastewater can be divided into two types: inorganic industrial wastewater and organic industrial wastewater.

2.1 Inorganic industrial wastewater

Inorganic industrial wastewater is produced mainly in the coal and steel industry, in the nonmetallic minerals industry, and in commercial enterprises and industries for the surface processing of metals (iron picking works and electroplating plants). These wastewaters contain a large proportion of suspended matter, which can be eliminated by sedimentation, often together with chemical flocculation through the addition of iron or aluminum salts, flocculation agents and some kinds of organic polymers.

The purification of warm and dust-laden waste gases from blast furnaces, converters,

cupola furnaces, refuse and sludge incineration plants, and aluminum works results in wastewater containing mineral and inorganic substances in dissolved and undissolved form.

The pre-cooling and subsequent purification of blast-furnace gases requires up to 20 m³ water per t of pig iron. On its way into the gas cooler the water absorbs fine particles of ore, iron and coke, which do not easily settle. Gases dissolve in it, especially carbon dioxide and compounds of the alkali and alkaline earth metals, if they are water-soluble or if they are dissolved out of the solid substances by gases washed out along with them.

In the separation of coal from dead rock, the normal means of transport and separation is water, which then contains large amounts of coal and rock particles and is called coal-washing water. Coal-washing water is recycled after removal of the coal and rock particles through flotation and sedimentation processes.

Other wastewater from rolling mills contain mineral oil and require additional installations, such as scum boards and skim-off apparatus, for the retention and removal of mineral oils. Residues of emulsified oil remaining in the water also need chemical flocculation.

In many cases, wastewater is produced in addition to solid substances and oils, and also contains extremely harmful solutes. These include blast-furnace gas-washing wastewater containing cyanide, wastes from the metal processing industry containing acids or alkaline solutions (mostly containing non-ferrous metals and often cyanide or chromate), wastewater from eloxal works and from the waste gas purification of aluminum works, which in both cases contain fluoride. Small and medium sized non-metallic-minerals plants and metal processing plants are so situated that they discharge their wastewater into municipal wastewater systems and have to treat or purify their effluents before discharge, in compliance with local regulations.

2.2 Organic industrial wastewater

Organic industrial wastewater contains organic industrial waste flow from those chemical industries and large-scale chemical works, which mainly use organic substances for chemical reactions.

The effluents contain organic substances having various origins and properties. These can only be removed by special pretreatment of the wastewater, followed by biological treatment. Most organic industrial wastewaters are produced by the following industries and plants:

- The factories manufacturing pharmaceuticals, cosmetics, organic dye-stuffs, glue and adhesives, soaps, synthetic detergents, pesticides and herbicides;
- Tanneries and leather factories;
- Textile factories;
- Cellulose and paper manufacturing plants;
- Factories of the oil refining industry;
- Brewery and fermentation factories;

- Metal processing industry.

As examples, some special types of wastewater produced by the industries mentioned above are briefly introduced as follows.

Wastewater produced from the pharmaceutical industries

The quality of the wastes from the production of pharmaceuticals varies a great deal, owing to the variety of basic raw materials, working processes and waste products. It is a characteristic of the pharmaceutical industry that very many products as well as intermediate products are manufactured in the same plant. Thus different kinds of effluent with widely varying qualities flow from the different production areas.

For large chemical industries it is also usual to manufacture pharmaceutical products together with other chemical products. Some times waste substances include the extraction residues of natural and synthetic solvents, used nutrient solutions, specific poisonous substances, and many other organics.

The wastewater produced by the pharmaceutical industry has a very bad quality for wastewater treatment. Usually the concentration of COD is around 5000 – 15000 mg/L, the concentration of BOD₅ is relative low, and the ratio of BOD₅/COD is lower than 30% which means the wastewater has a poor biodegradability. Such wastewater has bad color and high (or low) pH value, and it needs a strong pretreatment method, followed by a biological treatment process with a long reaction time.

Wastewater produced by tannery plants

A tannery is one of the most water intensive plants, and its production process consists of several steps. The quality of water depends only to a slight degree on the type of hides and the mechanical and chemical methods used in tanning. In a tannery with chrome and bark tanning, the wastewater resulting from the different processes are as follows:

▪ Soaking and washing	22.5%
▪ Liming	17.5%
▪ Rinsing	5.5%
▪ Plumping and bating	19.0%
▪ Chrome tanning	2.0%
▪ Bark tanning	2.0%
▪ Washing and drumming	31.5%

In fact the wastewater flow is very uneven. The peak flow can be 250% of the hourly average flow rate.

The wastewater produced by a tannery (including preparation of the hides) has a fairly acid pH and high chloride content (up to 5 g Cl/L). It contains a high concentration of COD (about 1500 – 2500 mg/L), a high amount of settable substances (10 – 20 g/L) and emulsified fat, and tends to form foam. The dichromate content can reach a peak value of 2000 mg/L. So the tannery wastewater is a killer to the water environment if it is

discharged without good treatment.

Wastewater produced by brewery industry:

Barley is the most important grain used for brewing beer, with the addition of rice, oats, rye, wheat and millet. The manufacture of beer consists of three processes, which are preparation of malt from barley, preparation of beer wort and fermentation.

A part of the wastewater produced by the brewery industry comes from the processes mentioned above, which includes the washing and rinsing water to clean the barley, all machines and filters, and especially bottles and barrels. This type of wastewater contains the high concentration of suspended solids and detergents. The other part of wastewater is produced by the fermentation process, and it has a very high concentration of COD and BOD₅ caused by soluble and insoluble organics. The composition and amount of wastewater produced by different processes are shown in Table 2. The characteristic of mixed brewery wastewater shows the following composition: COD: 1500 – 5000 mgO₂/L; BOD₅: 1000 –3000 mg/L; P_{total}: 5 – 30 mg/L; P_{PO₄}: 2 – 5 mg/L and settable solids: 3 – 30 mg/L. The brewery wastewater is approximately three to four times more concentrated than sewage. There are no toxic contaminants in brewery wastewater, and most organic substances of the wastewater are biodegradable. So after the removal of suspended solids, usually an anaerobic biological treatment process is used to reduce the organic concentration of the wastewater, and then followed by an aerobic biological treatment process to make the quality of effluent meet the discharge standards.

Type of wastewater	pH	Dry residue (mg/L)	Suspended Solids (mg/L)	BOD ₅ (mg/L)
Barrel Cleaning	7.1	980	250	21
Bottle cleaning				
a) washing solution	11.5	71700	310	870
b) rinsing water	7.2	940	95	16
Filter cloth washing				
a) mash filter	6.7	1070	1846	325
b) cooler sludge filter	6.7	1290	456	694
Fermentation				
a) fermenting without yeast	5.3	2060	3944	3550
b) fermenting with yeast	5.0	-----	-----	70250
c) storage without yeast	6.8	1010	164	502
d) storage with yeast	5.2	-----	10900	84500
e) beer filter	5.9	1940	37835	2000

Table 2: Composition of wastewater produced by different processes

3. The amounts of industrial waste water

As industrial wastewater is discharged by different industry sectors in different areas and countries, it is difficult to present an accurate amount of the total discharge of industrial wastewater in the world. Among the industry sectors mentioned above, the largest water consumer and wastewater producer is the iron and steel industry, followed by the

petroleum refining industry, textile industry, pulp and paper industry, and fertilizer industry.

Industry	World total		Developed countries		Developing countries	
	1980	2000	1980	2000	1980	2000
Iron and steel	112,147	224,294	104,296	168,220	7,850	56,073
Non-ferrous metals	17,705	35,410	16,466	26,557	1,239	8,853
Fertilizer	9,541	19,082	8,873	14,311	668	4,770
Food and agriculture	5,139	10,278	4,779	7,703	360	2,570
Pulp and paper	22,194	44,388	20,640	33,291	1,554	11,097
Textile	22,908	45,816	21,308	34,362	1,603	11,454
Rubber	4,538	9,076	4,220	6,807	318	2,269
Petroleum refining	36,475	72,950	33,922	54,713	2,553	18,237
Miscellaneous	6,350	12,700	5,905	9,525	495	3,175
Total	236,997	467,994	220,407	355,496	16,590	118,498

Table 3: Estimated industrial effluent loads, 1980 and for year 2000 (106t)

Based on the report of WHO and UNEP, the amount of industrial wastewater generated is dramatic. Table 3 gives estimates for a variety of industrial wastewater in developed and developing countries for 1980. Most wastewater is estimated to double from the current value by the year 2000.

There are big differences of the wastewater amounts discharged from different industry sectors. The percentages of the wastewater discharged by each major industry sector in the wastewater amounts of the whole of industry are shown in Fig.1, which is based on the estimated amounts in year 2000.

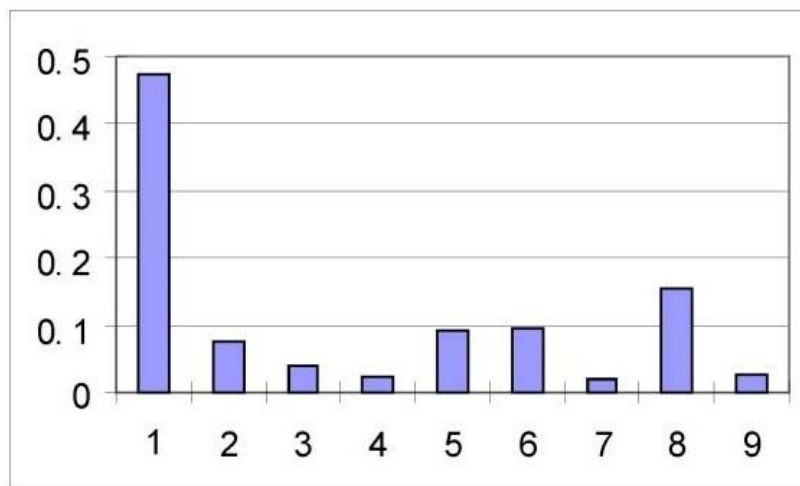


Figure1: The percentage of wastewater discharged by each industry sector in the wastewater of all industry

It should be indicated that the amount of wastewater depends on the technical level of process in each industry sector. To produce unit products the water consumption and wastewater discharge are much higher in a process with a backward technology than that with an advanced technology. So the amount of industrial wastewater will be gradually

reduced with the improvement of industrial technologies. On the other hand, the increasing rates of industrial wastewater are uneven in different areas and countries, which in developing countries are thought to be much higher than that of developed countries. The increasing rates will be eight times for fertilizer effluents, eight times for effluents from the food and agriculture industry, six times for textile industry wastes, eight times for pulp and paper effluents, six times for iron and steel industry wastes. This fact predicts the industrial wastewater pollution, as a mean environment pollution problem, will move from developed countries to developing countries in early next century.

4. The effects of industrial waste water

During the industrial era of the nineteenth and twentieth centuries a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas. This resulted in serious pollution problems in the water environment and caused negative effects to the eco-system and human life.

Most pollution situations have evolved gradually over time until they have become apparent and a measurable recognition of a pollution problem, therefore, usually took considerable time, and application of the necessary control measures took even longer. Since the middle of the twentieth century, and concurrent with the accelerated onset of industrial growth, several water pollution local overloads of the aquatic ecosystem suddenly became widespread and similarly alarming reports came in from various parts of the world. The following types of problem, as they became apparent in European freshwaters occurred in chronological order.

During the 1950s severe seasonal depletion of the oxygen levels in major rivers caused a general degradation of their quality and increased difficulties in drinking water treatment. Overloading with biodegradable organic wastes from riparian municipalities and industries was mainly to blame. Costly programs for mechanical – biological treatment of all major effluent discharges gradually reversed the situation. As a result the majority of river stretches in developed countries today enjoy sufficient oxygen levels to support a variety of fish and provide an acceptable basic water quality for drinking water production.

During the 1960s it became apparent that removal of organic matter from domestic and industrial wastewater removed the primary oxygen demand for biodegradation, but did not prevent the secondary effect of algal blooms in lakes and reservoirs stimulated by the nutrients phosphorus and nitrogen in the wastewater effluent. Reduction of one of the essential nutrients, phosphate, was generally adopted as the most effective strategy in the control of the eutrophication, which was resulting from the excess nutrient inputs. Improvements in lakes and reservoirs have, however, been slow and have taken a long time to become apparent.

During the 1970s the gradual increase of heavy metal concentrations in sediments and in the water of rivers and lakes reached alarming proportions. Bio-accumulation in fish, gave rise to many cases of intoxication particularly through consumption of coastal fish and resulted in sufficient public concern to bring about the implementation of the control

of heavy metal releases at source. As a consequence, for the last few years down wards trends are apparent for the most harmful metals, particularly mercury and lead.

Since the 1980s scientific and public concern over environmental pollution has entered a second phase. With the development of the modern chemical industry, the current production and use of tens of thousands of synthetic chemicals, with a thousand new ones added every year, inadvertently resulted in the release of these substances into the general environment. Thus they are today ubiquitous, notably in ground and surface waters of vital importance for public supply. The human health and eco-toxicological consequences of exposure to organic micro-pollutants in the aquatic environment are being studied intensively. The search for appropriate strategies for their control, elimination or containment is a major challenge for the early 21st century.

4.1 The effects of inorganic pollutants from industrial wastewater

Based on present global statistics of water pollution, the major pollutants from industrial wastewater can be divided into two types – inorganic pollutants and organic pollutants. As they have different characteristics, inorganic and organic pollutants have different effects to the water pollution.

The industrial era of the nineteenth century resulted in an acceleration of the use of natural substances such as As, Cd, Hg, Pb, Zn, S, etc., that could eventually be released into the aquatic environment. Characterizing the behavior of an inorganic compound with respect to its biodegradability and toxicity, i.e., the processes at the molecular organelle and cellular level, requires further insight into the interactions of different metals with complexing ligands at physiological levels. With respect to the entry of metals into cells it seems clear that, with the exception of uncharged chemical species of certain metals which appear capable of traversing the lipid component of membranes, most membrane transport must occur via metal interactions with membrane proteins. As with many toxic organic chemicals heavy metal toxicity is related mainly to the inhibition of enzyme activity.

Some pollutants are found to be concentrated in the food chain, from water to phytoplankton then up to the carnivorous mammals of fish-eating birds (the biomagnification process). For aqueous metal species it has been suggested that the “free” or aquometal ion form is the most available for organisms compared to the particulate, complex, or chelate forms. Water hardness plays a significant role in the intoxication of biota by heavy metals. In aquatic food chains those metals that are soluble (Ni, Cu, Zn, Tl, Cd) are generally more toxic to fish than to humans, i.e., the fish will die or cease reproducing before tissue levels become high enough to be toxic to humans consuming the fish. Cadmium in mollusks, and mercury in mollusks and fish, are however exceptions. When methyl mercury is absorbed from water it is deposited in muscle tissue by fish so effectively that bio-accumulation occurs despite the extremely low levels found in natural waters.

Inorganic pollution may be very high in regions of limited development particularly when it results from mining activities, as in some South American, Japanese, African, Chinese or Canadian regions. For example, in 1970 the Canadian scientists found mercury in the

sediments of Wagbi – Englan river basin. The mercury came from the wastewater discharged by a pulp – paper plant on the upstream of the river. During several years the plant discharged about 10 tones of mercury into the river, and scientists found the concentration of mercury in the bodies of fish was 30 times higher than that of standard. There were two villages by the river downstream. The pollution was catastrophic to the residents so that some people manifested the symptoms of mercury poisoning and the major economic activity – fishing had to be stopped. The effect had lasted for 20 years, and up till now the fish from this river can not be eaten.

4.2 The effects of organic pollutants from industrial wastewater

The direct effects caused by the discharge of industrial wastewater contained organic pollutants are the series pollution in the aquatic environment. The organic pollutants consume the oxygen in water and result in the oxygen lower than the limiting level to keep aquatic animals alive. As the organic pollution increasing sometimes the water becomes anaerobic condition and produces bad color and odor which results in the water losing its application functions. Because of the water pollution some areas are short of clean water which affects the living conditions of residents of cities and the development of the economy. Most river flow through industrial areas and cities are polluted at different levels. For example, 36.53 billion m³ is annually discharged into the water system of China, which includes 60% of industrial wastewater and 40% municipal wastewater. An investigation was conducted, and the results showed that only 5% river water in northern region and 15% river water in southern region of China could meet the standards of drinking water sources. In 135 monitored urban river sections, there are 52 sections which could not meet the water quality standards for irrigation. So industrial water pollution makes clean water resources decrease and plays a negative role in the problem of the water crisis.

The first synthetic substances were developed and used a hundred years ago. Unfortunately the treatment technology and the regulations to prevent the pollution of synthetic substances were not developed at the same time. Many industries directly or indirectly release synthetic organic substance from their production activities. Some synthetic organic substances are difficult to be decomposed by micro-organisms under natural condition and result in the accumulation and poisoning of the aquatic environment. As these substances do not occur naturally, it is not possible to set levels acceptable to the environment in advance, particularly for aquatic situations.

Various geo-chemical processes determine the ways in which organic pollutants are transported and transformed in the aquatic environment. In addition to the dispersion of pollutants by the process of dilution there are exchanges at the water/atmosphere interface, adsorption on particulate matter and transport in sediments. It is also necessary to assess the stability of these substances, measured in terms of biological breakdown and physicochemical breakdown through hydrolysis or photolysis. The relative importance of these various, and sometimes competing, bio-chemical characteristics depends on the chemical structure of the organic substances and their physico-chemical properties.

The resulting categories of chemical substances have opposing properties as follows:

- Volatile substances/non-volatile substances

- Hydrocarbons/halogenated hydrocarbons
- Saturated hydrocarbons/aromatic hydrocarbons

The estimated annual loads of organic pollutants in selected world rivers are shown in Table 4.

According to the investigation, many rivers and lakes have been polluted with synthetic substances. For example, the River Trent in the UK for PCBs, from the Chinese rivers for HCH isomers and from Japan several monitoring stations (Lake Biwa, and the Yodo and Ohta rivers in Japan) for PCBs. Levels above $1,000 \text{ ng l}^{-1}$, indicating either potentially severe damage or inadequate analysis technique, were found in the Rivers Rufigi in Tanzania ($30 \mu\text{g l}^{-1}$ dieldrin), Canca juanchito in Colombia ($1.2 \mu\text{g l}^{-1}$ DDT; $3.0 \mu\text{g l}^{-1}$ dieldrin), Gombak in Malaysia ($30.6 \mu\text{g l}^{-1}$ dieldrin) and all the monitoring stations in Indonesia (PCBs levels from 0.4 to $6.9 \mu\text{g l}^{-1}$). As new synthetic organics are produced every day and it is difficult to determine their long-term effects for the eco-system before application, the pollution of synthetic organics will be a major challenge in the environmental pollution prevention field in the future.

Country	Sites	Flow rate			
		($\text{km}^3 \text{ y}^{-1}$)	PCB	Lindane	DDT
Argentina	Parana	420			
France	Loire	30	60—110	400—600	
	Seine	12	230—430		
	Var	2.8	10		
Netherlands	Elbe	24	564		
	Ems	4	16		
	LJssel	6	380		
	Scheldt	10	105		
	Weser	12	198		
UK	England	*	73—434	723—819	119—471
	Northern				
	Ireland	*	0.7—38	40—43	1.8—38
	Scotland	*	9—190	220--239	12--201
USA	Niagara	202	1700--1900		

* Sum of river contribution and urban discharge

Table 4: Estimated annual load of organic pollutants in selected world rivers (kg y^{-1})

5. Other factors related to the effect of industrial wastewater

Major industrial accidents may have important ecological significance, although their effects on inland waters are not always clear. The most commonly reported catastrophic

events include tank and pipe explosions or bursts, rail accidents and fires. Past industrial accidents at Seveso and Bhopal have not been thoroughly studied for their effects on water quality, whereas the most recent Chernobyl explosion and the Sandoz Basel fire have been more extensively studied. The principal characteristics of these events were their transboundary effects and the absence of remedial measures at the regional level. Only time and dilution will progressively improve the quality of the affected aquatic environment. Although catastrophic events of industrial, geologic (landslides, earthquakes, volcanoes, etc.) or climatic (typhoons etc.) origin have the same order of magnitude of injured people and economic damage, their effects on water quality are probably not on the same scale. Industrial accidents causing spillage of long-lasting pollutants (radioactive elements, metals and persistent organic substances) are likely to cause the most damage to the aquatic environment.

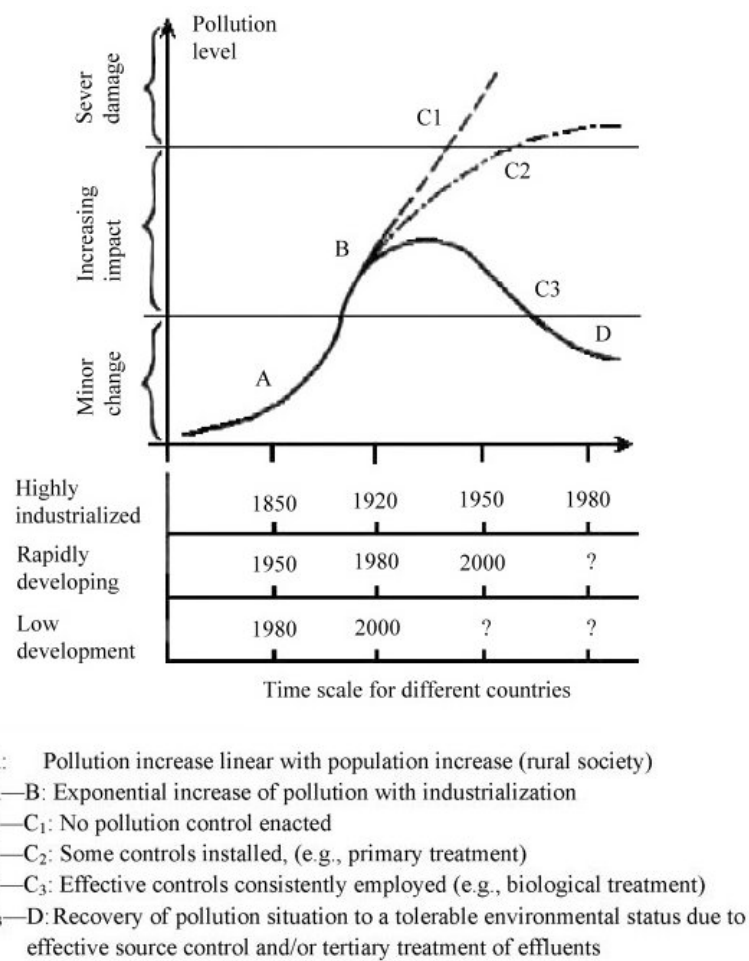


Figure 2: Conceptual model of water pollution occurrence and control

It should be indicated that the effects of industrial wastewater are not only related to the amount and concentration of pollutants, but also related to the control strategies and methods adopted. The increase in public awareness, political will and technological progress has allowed control strategies not only to be found, but also implemented. The effectiveness of problem reduction achieved as a direct function of the degree of control introduced, i.e., of economic commitment made, can best be demonstrated through the

example of domestic sewage pollution.

As shown schematically in figure 2, four phases of problem evolution can be identified in relation to the progress in socio-economic development:

- Phase I: a linear increase in low-level pollution in relation to population figures (typical pattern for agricultural society);
- Phase II: exponential pollution increase with industrial production, energy consumption and agricultural intensification (typical pattern for newly industrializing countries);
- Phase III: containment of pollution problems due to the implementation of control strategies (typical pattern for highly industrialized countries);
- Phase IV: reduction of pollution problems, principally at the source, to a level which is ecologically tolerable and does not interfere with water uses (desired ultimate situation).

This general sequence of phases is more or less applicable not only to different types of pollution problems, but also to countries at different present levels of socio-economic development. A simplified global scheme with three categories can be used for this purpose:

- highly industrialized countries;
- newly industrializing countries;
- low-development countries with predominantly traditional agricultural economies.

For each of these three categories the occurrence and control of the domestic sewage pollution problem have followed a different time schedule, as indicated in figure 2. The extent to which environmental management services have been installed and how far they are commensurate with the pollution problems largely determines the resulting state of the quality of a country's water resources.

Furthermore, the different types of pollution problems occur in developing countries in much more rapid succession than in Europe, due to the modern international trade of chemicals, ubiquitous dispersion of persistent contaminants and changing hydro-geological cycles, etc. Thus developing countries are, and will be faced more and more with situations where second and third generation pollution issues appear before much control over "traditional" pollution sources has been achieved.

Glossary

Biodegradability:	The degree of an organic substance, which can be degraded by microorganisms.
WHO:	World Health Organization
UNEP:	United Nations Environment Programme
BOD:	Biological Oxygen Demand
COD:	Chemical Oxygen Demand
SS:	Suspended Solid

PCBs:	Polychlorinated Biphenyls
HCH:	Hexachloro-Cyclo-Hexane
DDT:	Dichloro-Diphenyl-Trichloroethane

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Biographical Sketch

Han-chang SHI is a professor of the Department of Environmental Science and Engineering, Tsinghua University and the director of State Key Joint Laboratory of Environment Simulation and Pollution Control in P. R. China. He graduated from the Department of Environmental Science and Engineering, Tsinghua University in 1984 and studied in Water Research Center in the U.K. and University of Michigan in the U.S.A. as a senior visiting scholar during 1989 and 1994. The major research fields of him are biological wastewater treatment, refractory and toxic organics treatment using anaerobic acidification process, modeling and simulation of aerobic biological wastewater treatment process, and low toxic wastewater treatment using photo-oxidation process.