Environmental Impact of the Chemical Industry

9

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9.1 The environment and human interactions

The earth is a complex and dynamic system, involving the transfer of material on both micro and macro scales. The processes operating on and within the earth can be simply viewed as a series of interlinked compartments with the links allowing material and energy flow in different directions. The general situation, shown in Figure 9.1, summarizes our understanding of the earth's system from a geological viewpoint, in which the fluid flows of rocks or magma within the earth are responsible for the reworking of the earth's crustal materials.

In the context of human behaviour, it is the understanding of surface processes that are of most importance to us. Geological timescales and

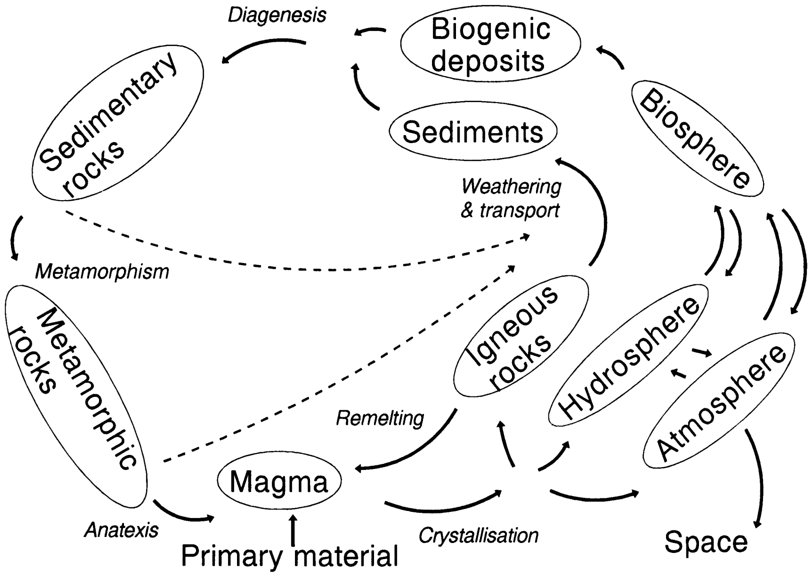

Figure 9.1 A simplified view of earth processes—the Geochemical Cycle. Based on Reference 1.

A. Heaton (ed.), *An Introduction to Industrial Chemistry*

Table 9.1 Sizes and vertical mixing of various earth reservoirs. Based on References 2 and 3

Sphere	*Mass (kg)*	*Mixing time (years)*
Biosphere	$4{\cdot}2 \times 10^{15}$	60
Atmosphere	$5{\cdot}2 \times 10^{18}$	$<0{\cdot}2$*
Hydrosphere	$2{\cdot}4 \times 10^{21}$	1600†
Crust	$2{\cdot}4 \times 10^{22}$	$>3 \times 10^{7}$
Mantle	$4{\cdot}0 \times 10^{24}$	$>10^{8}$

* Surface boundary layer = 1 hour, to tropopause = 1 month, to lower stratosphere 50 years.

† Surface mixed layer = 10 hours, base of thermocline = 2·5 years, Pacific/Atlantic deep ocean 100–1000 years.

major earth movements take place over many millions of years and are only significant when catastrophic events, such as earthquakes and volcanoes occur. Of more immediate concern are those processes operating on the earth's surface that serve to modify or affect systems within our own lifetime (i.e. tens of years). The rates of the processes in operation in the various compartments of the environment are dependent on the nature of the processes themselves. This is highlighted in Table 9.1 which summarizes the sizes, in terms of mass and vertical mixing times, of each of the major earth compartments. From our own everyday observations of climate and other surface processes such as river flow and tidal movement, these time scales can be readily appreciated. Yet within these general compartments, the mixing and movement of materials is not uniform. For example, mixing times of a non-reactive pollutant gas[2] may be of the order of hours within the boundary layer (the atmosphere in contact with the earth's surface to 1 km height), in which flow is affected by surface features; the order of days within the free troposphere (1–10 km from the surface of the earth), within which climatic turbulence occurs to give us weather systems; and the order of years for mixing within the stratosphere (between 10 and 50 km from the surface of the earth).

Human activity on the surface of the earth has had an environmental impact since the first tools and manipulation of resources occurred. But only since the industrial revolution of the 18th and 19th centuries have human activities had a measurable effect on a global scale[4]. To support the maintenance and development of society, humans have developed and refined means to utilize the resources available from within and upon the surface of the earth. This utilization has developed from, in the most part, agricultural practices towards an industrially and technologically dominated society.

The resources available can be classified in a number of ways and are summarized in Figure 9.2, namely:

(i) *Stock resources:* those which are non-renewable and are not re-

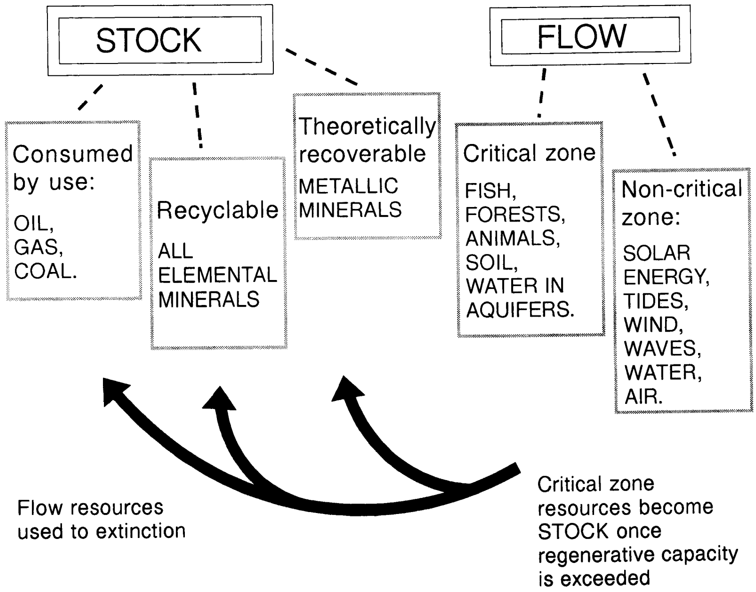

Figure 9.2 The definition and classification of types of resources and their relationship to the sustainability of society. Based on Reference 5.

generated on the human timescale, being consumed by use. However, there exists the possibility for some stock resources to be recycled.

(ii) *Flow resources:* those which are naturally removed in the human timescale. These can be further subdivided into those in the *critical zone* which can be exploited but can also be affected by human activity and those which are *non-critical zone* which can be exploited and are renewable. For some of this latter group one must also add a cautionary note of care that the rates of exploitation and renewal are balanced.

So within any developing society there is an underlying need to capture resources from the earth, process raw materials and utilize the products. The environmental effects of these activities can be severe and can arise at a number of stages[6]:

(i) the removal from a natural location
(ii) handling at the point of removal
(iii) transport and storage
(iv) process handling
(v) the generation and disposal of wastes

An increasing world population and technologically advancing society, increase the net pressure of human activity on the environment. Figure 9.3

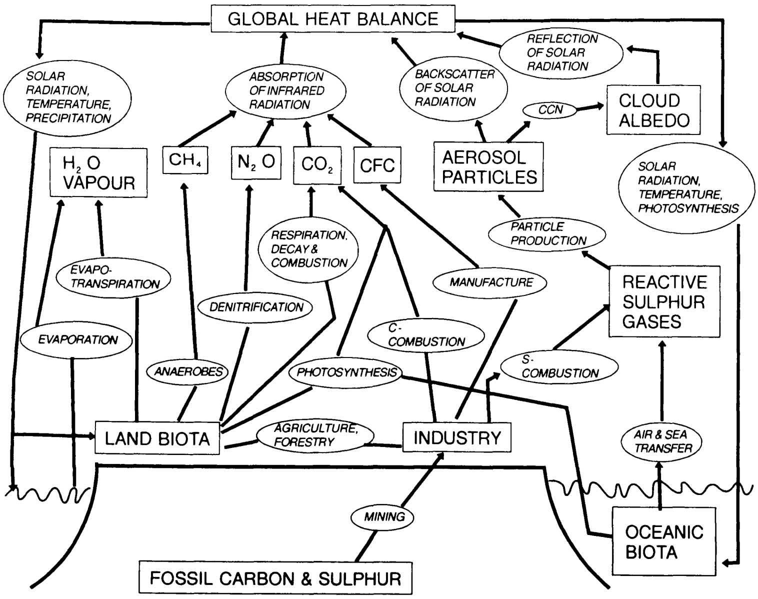

Figure 9.3 The major components of earth surface processes, illustrating human interaction. Based on Reference 6.

shows the types of processes involved in the surface cycling of materials and climate and their effect on observable components of the earth. From this it is easy to see the potential significance of human interactions, through industrial activity and the areas that will be sensitive to increasing activity. This is perhaps more easily appreciated by the more complex schematic in Figure 9.4, which concentrates on the objectives of industrial activity, that is, to produce materials that have a use in society. In so doing, significant amounts of waste of all types are released into the environment.

Waste can be defined as[7]:

(i) any substance which constitutes a scrap material or an effluent or other unwanted surplus substance arising from the application of any process; and
(ii) any substance or article which requires to be disposed of as being broken, worn out, contaminated or otherwise spoiled.

Ultimately, the fate of anything used by humans is that it becomes waste material. If the primary activity of industry is to produce a product, which has a use in society, this activity has the potential to generate waste at many stages in the process. The waste material may be released to the environment at the point of generation or at a later stage. It is important to understand the interaction of any release with the environment and particularly in relation to the biogeochemical cycles, so that any likely environmental

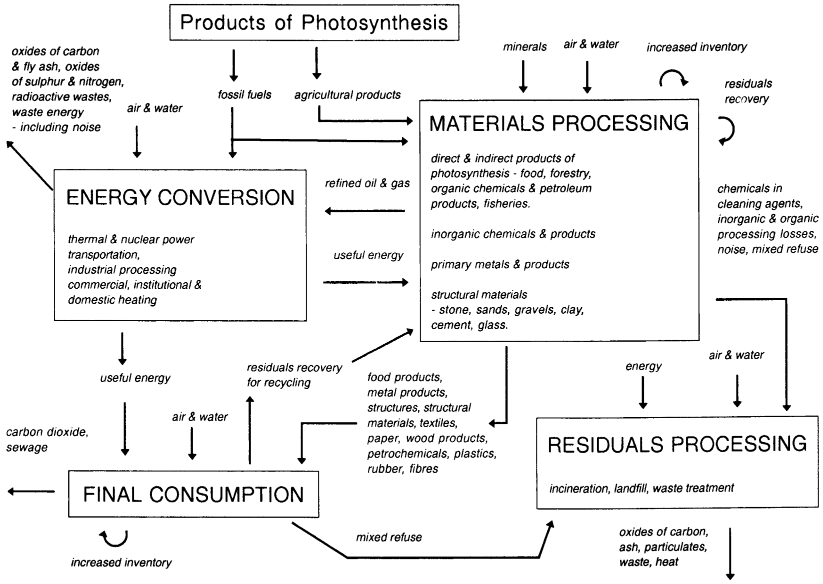

Figure 9.4 The flow of materials in technological society. Based on Reference 1.

impact can be assessed. If that impact is negative, then the release is generally viewed as being a pollution incident.

As a consequence of the complexity of environmental processes, the diversity of industrial activity and inter-relationships between humans and the environment, the term pollution has wide-ranging implications. In a formal sense, a pollutant may be defined as[8]:

> A substance or effect which adversely alters the environment by changing the growth rate of species, interferes with the food chain, is toxic or interferes with the health, comfort, amenities or property values of people.

When this definition is considered with the description of waste, it is apparent that any human activity generates both waste and pollution. Differentiation between the two is difficult. It is generally accepted now, that humans must be more efficient in managing their activities on the surface of the planet if there is to be a sustainable development of society and preservation of the quality of life. As a result of past practices, scientific research and an improving understanding of our own impact on the environment, recent legislative changes have meant that industry, often viewed as the primary polluter, is pressurized to clean up and minimize its environmental impact.

This chapter gives a short, introductory overview of the industrial sources of pollution, present practices, and the constraints of minimizing the environmental impact with particular reference to the chemical industry.

The subject is naturally diverse and rapidly changing, so only a superficial treatment can be given at this stage; in particular the fundamental principles will be emphasized.

9.2
Sources of pollution

From Figure 9.4, it is apparent that through the activity of any industry, a range of pollutants may be released into the environment. The precise composition will vary depending on the nature of industrial activity at a particular site. Most industry, in addition to the extraction of primary raw materials and energy production, requires a considerable amount of water to aid process control. As a consequence, the major environmental impact from industrial activities is the release of material to the atmosphere and to the hydrosphere, through direct discharge to water courses, leaching into the water table and stack emissions. This allows transport of the pollutants away from the site. In addition, the direct contamination of industrial sites has relatively recently become the focus of considerable attention. Changing economic constraints on industrial activity and the rationalization of the industrial base in many developed countries has resulted in the closure of sites, and the redevelopment of land for other domestic or leisure uses has highlighted a significant environmental legacy[9–11].

It is important to remember that the release of pollutants from industrial activity has a geographical control. Overall, the global amounts of naturally occurring materials may be far greater than the industrial releases of certain substances. It is the relative concentration and proximity to sensitive ecosystems and population centres that exaggerates the resulting environmental impact.

9.2.1 *Atmospheric pollution*

The natural composition of air includes the major gases ($N_2 \sim 78\%$; $O_2 = 20.9\%$; $Ar = 0.9\%$; $CO_2 = 0.035\%$; $H_2O = 0.53\%$) and many hundreds of trace components. Some of these can be explained by natural releases or direct industrial activities (*primary pollutants*) and others, that are formed indirectly by chemical processes in the atmosphere (*secondary pollutants*)[12]. It therefore follows that, in minimizing the environmental impact of industrial activity, not only must direct pollutant releases be considered, but also the release of compounds which may have a role in secondary pollutant production.

Natural emissions from biological, geological and meteorological processes include: oxides of sulphur and nitrogen, hydrogen sulphide and ammonia. These compounds, though oxidation in the atmosphere can form acidic and readily soluble compounds, that when dissolved in water, contribute to natural acidity of rainwater, greatly increasing the weathering ability of surface waters. Table 9.2 summarizes the major species of these

Table 9.2 Compounds of sulphur and nitrogen observed in the atmosphere. Based on Reference 13

Species	*Concentration*	*Sources*	*Sinks*
SO_2	0–0·5 ppm v (urban)	Oxidation of fossil fuel S	Direct reaction with Earth surface, oxidation to sulphate
	20–200 ppt v (remote)	Oxidation of S gases	
H_2S	0–40 ppt v	Biological decay of protein in anaerobic water	Oxidation to SO_2
CH_3SH	sub-ppb v	Paper pulping	Oxidation to SO_2
CH_3CH_2SH	sub-ppb v		Oxidation to SO_2
OCS	500 ppt v		Destruction in the stratosphere
CH_3SCH_3	20–200 ppt v	Oceanic phytoplankton and algae	Oxidation to SO_2
CH_3SSCH_3	small		Oxidation to SO_2
CS_2	10–20 ppt v		Destruction in the stratospheric and tropospheric OH
NH_3	0–20 ppb v	Biological	Precipitation
$RNH_2 \ldots R_3N$		Biological	Precipitation
N_2	78·084%	Primitive volatile, denitrification	Biological nitrification
N_2O	0·1–0·4 ppm v	Biological	Photolysis in the stratosphere
(N_2O_3)		Reaction intermediate	
NO	0–0.5 ppm v	Oxidation of N_2 in combustion	HNO_3
NO_2		NO oxidation	HNO_3
HNO_2		OH + NO	Precipitation
HNO_3		$OH + NO_2$	Precipitation

Units: ppm v = 1 in 16^6 by volume
ppb v = 1 in 10^9 by volume
ppt v = 1 in 10^{12} by volume.

elements present in the atmosphere and highlights the main sources. The natural production paths are very numerous and global levels generally exceed anthropogenic releases[12,13]. The main anthropogenic sources being primarily from combustion-related processes. In addition to nitrogen and sulphur-containing species, hydrocarbons (primarily methane) are released naturally from anaerobic digestion in rice paddies, wetlands, tundra and from ruminant animals, and the amounts from these sources appear to be affected by human activities. Other heavier hydrocarbons, such as terpenes, are released through natural degradation processes and greatly exceed anthropogenic emissions.

Natural releases to the atmosphere are geographically variable and superimposed on these are emission to the atmosphere from both stationary and mobile point-sources, of domestic and industrial origin. The routine combustion of fossil fuels for energy production releases significant quantities of CO_2 and H_2O. In addition, CO_2 is released through natural metabolic processes. The increased use of fossil fuels for energy production has increased the total release to the atmosphere of CO_2 and there is some evidence that the natural sinks for atmospheric CO_2, such as photosynthesis, are able to absorb only part of this increase[12,14]. At present there appears to be a net increase of ~0.3% of the atmospheric CO_2 concentration per year[12,15]. The significance of CO_2 in the regulation of global energy balances, means that considerable attention has been given to the control of releases from direct and indirect human activity[16].

Carbon monoxide (CO) can be a significant component of combustion gases from power production, but releases are more significant through the use of internal combustion engines[15]. Through incomplete combustion, flue gases can contain several percent CO. In the production of iron and other metals, oxygen supply is minimized and CO emissions are high[17]. The internal combustion engine, used widely for transportation and mobile energy sources, releases a diverse range of pollutants, including CO. Levels of CO (and hydrocarbons) are higher from petrol engines than from diesel and depend greatly on engine capacity and speed[17,18].

Soot formation generally accompanies incomplete fuel consumption through the polymerization of carbon nuclei[12,17]. Particles of soot have dimensions commonly $< 1\,\mu m$ and through effective light scattering properties are easy to see. They also act as nucleating centres for vapour and salt deposition, as gas streams cool. In industrial processes, temperature control is normally adequate to remove the problem of soot production. Domestic combustion, however, is less controlled and with internal combustion engines, the diesel engine is particularly prone to soot and particle release. Size is the most important physical property of soot or particulates[19], as the exposure to humans is dominated by the inhalation pathway. Ash deposits of inert residues from solid fuels are also of concern and particularly problematic with low quality, bituminous fuels. The chemical composition of each can contain high levels of heavy metals, high molecular weight hydrocarbons and halocarbons[12].

High molecular weight hydrocarbons are often produced during incomplete combustion and these are often carcinogenic. Polycyclic aromatic hydrocarbons (PAHs) are a good example of one class that has been relatively well studied[12,15]. These are released from all types of combustion processes and can be particularly hazardous in residues from old coal gas plants[9].

The presence of sulphur in most fossil fuels results in the release of SO_2 and minor amounts of SO_3. The oxides of sulphur react in the atmosphere to form sulphuric acid. Further industrial sources are in the roasting of metallic ores (often found as sulphides). The modification of combustion conditions cannot reduce sulphur released and control is usually by pretreatment of the fuel or desulphurization of post-combustion gases[12,17].

Oxides of nitrogen (primarily NO and NO_2), also have a role in the generation of acid rain at low altitudes and play a crucial role in the ozone balance at higher altitudes[12,20]. Production during combustion involves the high temperature reaction of N_2 and O_2 from air in the combustion chamber and from nitrogenous constituents of the fuel. NO is the main product and variations in burner design are being used to reduce emissions from power stations[17].

Halogen-containing compounds are a major contributor to the acidic component of fuel combustion gases. Hydrogen chloride from chlorides in the fuel or the incineration of chlorinated plastics is corrosive to plant construction materials[17,20]

The most widely known halogen-containing pollutants are the chlorofluorocarbons (CFCs) used as aerosol propellants, refrigerants, solvents and for foam blowing[20]. Free chlorine in the upper atmosphere, from the photodissociation of CFCs, has been postulated as the cause of ozone depletion observed, at an increasing frequency, above the North and South Poles[6,21]. The Montreal Protocol was an international agreement, signed by a number of nations in 1987[20], in an attempt to reduce this effect by banning substances which are thought to contribute. It has met with limited success in reducing emissions, but has helped to stimulate the search for alternative materials[22]. Other fluorine releases at ground level include emissions of hydrogen fluoride from brick kilns, primary aluminium smelting and fluoroapatite fertilizer works[19,20].

All industrial processes release dusts other than soot. There are many sources and forms including fuel ash, metal oxide fumes and silica and releases tend to be localized. Fugitive emissions from outdoor industrial activity or processes associated with the mining and preparation of raw materials can generally be controlled through careful industrial practice. Water is often used to minimize dust raised, resulting in the transfer of an atmospheric pollution problem to one of either aquatic or solid waste.

The final source pollutants, released by industry are volatile organic compounds or VOCs. These encompass solvents and volatile, petroleum based spirits released from paints, petroleum manufacture, distribution and storage[12]. They are often an important fugitive emission and numerous examples exist of methods of control. Simple process control methods, monitoring and tightening of leaking seals[23], removal of volatile components in liquid waste streams[24] are often adequate enough to reduce releases significantly.

With most industrial activities, the high concentration of chemicals, by products or wastes, can result in high levels of associated odour. This is particularly of concern with food processing, tannery processes and the use or production of sulphur-containing compounds such as hydrogen sulphide. It is a particularly difficult class of pollution to deal with as individual senses vary. In addition, the levels at which odorous agents are sensed, whilst a nuisance, may not be toxic[25].

9.2.2 *Aquatic pollution*

The use of water for drinking, cleaning, power production and as a raw material in many processes coupled with the sensitivity of aquatic ecosystems to environmental disturbances, has resulted in the need for careful water management practices. There exist a number of well documented examples, where uncontrolled discharges have resulted in the destruction of local aquatic ecosystems[26–28]. The two main factors to consider are the transport times and the relative dilution afforded by the receiving water body[28].

The major sources of water pollution are from sewer outfalls or industrial discharges (*point sources*), or directly from air pollution or agricultural and urban runoff (*diffuse sources*). Pollutants are varied in type and effect, and include: inorganic and organic compounds with direct toxicity; nutrients that stimulate aquatic microbial activity and hence oxygen depletion; inert solids that obscure the transmission of light through the water and silt up channels changing water flows; waste heat that creates artificially high temperatures within water courses; radionuclides; and infections agents[29,30].

The identification of point sources of pollution is relatively straightforward, as is the imposition of remedial action through monitoring, legislation and treatment. Diffuse sources are much more difficult to assess and control, with great difficulty in pinpointing the source and hence apportioning blame. The majority of pollution incidents in water courses come from organic pollution namely organic rich slurries from farms, industrial processes and sewage from sewage treatment plants receiving both industrial and non-industrial liquid wastes[29].

The polluting power of these organic discharges derives from their residual biodegradable components which, if released into water courses would stimulate microbial activity, depleting oxygen levels in the water and killing higher organisms indirectly. As such, this form of pollution is relatively well understood and straightforward to control through engineered systems. The quality of discharges or receiving waters is routinely measured by the chemical (COD) and biochemical (BOD) oxygen demand tests[31]. The COD is the amount of oxygen consumed in the complete oxidation of carbonaceous matter in effluent samples using potassium dichromate. The BOD test involves the determination of dissolved oxygen in a sample before and after generally a 5-day period of incubation in darkness at 20°C with a microbial seed (BOD_5). This gives a measure of the amount of microbial nutrient in the sample and a reflection of the waste impact on discharge to a water course.

Additionally, however, both the solid and liquid component of waste discharges may contain chemical substances at sufficient concentrations to cause direct harm[32]. These are commonly: chlorides; sulphates, naturally and from human wastes; nitrogen and phosphorus, in various forms from human wastes; fertilizers and specific chemicals such as phosphorus from detergents; carbonates, bicarbonates, calcium and magnesium salts; toxins, heavy metals such as Cd, Cr, Cu, Hg, Pb, Zn; trace organics, pesticides, polycyclic aromatic hydrocarbons (PAHs), chlorinated hydrocarbons and phenols.

In the U.K., driven by legislative controls, a number of substances have been identified as priority pollutants and are subject to controls on their discharge by either the principle of discharge being allowed to levels that the receiving water can support (environmental quality standards/environmental quality objectives, EQS/EQOs), or a uniform discharge level (uniform emission standards, UES) no matter what the characteristics of the receiving water. A series of priorities has been assigned, which relates to the toxicity of the substances. These have become known as *black, grey* and *red* list substances[29]. The pollutant characteristics and substances involved are summarized in Table 9.3.

Major diffuse sources of pollution are difficult to locate and hence control. However, there are three main types of pollution with major impact on aquatic systems; these are acid rain, nitrate and pesticides.

Acid rain has been shown to be derived from the release of oxides of sulphur and nitrogen from the combustion of fossil fuels (oil, coal and gas), the principal cause being power production. It is a major problem in Europe and eastern and northern America[6,29,33] where the acidity of rainfall is enhanced by the water solubility of these gases. Certain upland regions have soils with a low capacity for the neutralization of an enhanced acidity and

Table 9.3 The classification categories for *black, grey* and *red* list substances which are subject to varying degrees of control in the aquatic environment. Based on Reference 29

(A) List I (*black*)—based on toxicity, persistence, bioaccumulation
1. Organohalogens, or substances which may form organohalogens
2. Organophosphorus compounds
3. Organotin compounds
4. Compounds exhibiting carcinogenicity in or via the aquatic environment
5. Mercury and its compounds
6. Cadmium and its compounds
7. Persistent mineral oils and petroleum hydrocarbons
8. Synthetic substances that float, remain in suspension, sink or interfere with the use of waters

(B) List II (*grey*)—based on possible effects, can be confined and depend on the characteristics and location of water body into which they are discharged
1. The following metalloids and metals and compounds:
   Zn, Cu, Ni, Cr, Pb, Se, As, Sb, Mo, Ti, Sn, Ba, Be, B, U, V, Co, Tl, Te, Ag
2. Biocides and derivatives, not part of List I
3. Substances affecting taste and/or smell of products for human consumption derived from the aquatic environment and compounds
4. Toxic or persistent organic compounds of Si or may give rise to such
5. Inorganic compounds of phosphorus and elemental phosphorus
6. Non-persistent mineral oils and petroleum hydrocarbons
7. Cyanides, fluorides
8. Substances which have an adverse effect on the oxygen balance, particularly NH_4^+, NO_2^-

(C) UK *red list*—26 initial priority substances identified from carcinogenicity and toxicity studies:
mercury and cadmium and compounds, gamma-hexachlorocyclohexane, DDT, pentachlorophenol, hexachlorobenzene, hexachlorobutadiene, aldrin, dieldrin, endrin, polychlorinated biphenyls (PCBs), dichlorvos, 1,2-dichloroethane, trichlorobenzene, atrazine, simazine, tributyl- and triphenyl-tin compounds, trifluralin, fenitrothion, azinphos-methyl, malathion, endosulfan.

an increase in lake and river acidity has been observed, with observable toxic effects on both local terrestrial and aquatic ecosystems. In some situations, increased acidity has been shown to mobilize aluminium from surface soils increasing the impact of acidification[33]. The effect can only be controlled by reducing emissions from energy production. In the short term, liming acidified lakes and soils, to restore natural pH, has been found to reverse the effects.

Nitrates released to aquatic systems, from the intensive use of fertilizers to improve crop and livestock yields, has resulted in high nitrate levels in drinking water. Recent evidence suggests that the previously high rates of increase in nitrate contamination of water supplies, is reducing. It is thought that this has been primarily through improvements in land management practices[29,34].

As with nitrates, the increased demands on crop and livestock yields by an ever increasing population has required the intensive use of pesticides. Widespread application in agriculture has resulted in a significant diffuse source to aquatic systems. Many pesticides feature in the lists of priority pollutants (Table 9.3). The nature of environmental residues, behaviour and fate are still uncertain for many compounds[29,35].

In assessing the impact of pollutants in aquatic systems, an overall understanding of the likely pathway and fate must be obtained. The possible reaction paths of a pollutant or any chemical released directly into a water course are summarized in Figure 9.5.

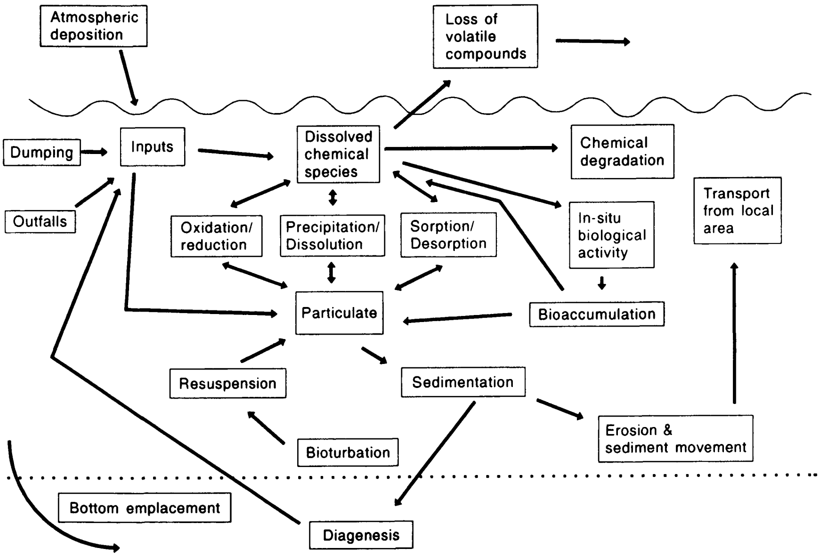

Figure 9.5 A schematic summary of the sources and possible fate of pollutants released into aquatic systems. The pathway followed depends on the physical and chemical properties of the pollutant and the physical, chemical and biological characteristics of the receiving water. Based on References 36 and 37.

The key characteristics of the water body must also be considered. Surface waters differ from ground waters, where in the latter, flow rates are slower and residence times for contaminants are much longer. The subsurface waters are ecologically less diverse and consequently more sensitive to pollution. Being remote from the earth's surface, any contamination is a major problem. A good example is the problem of high levels of nitrate in groundwaters in southern Britain[34]. A high proportion of drinking water is extracted from the ground and in areas where arable land overlies aquifers with no intervening impermeable clay deposits, levels are high enough to require dilution with less contaminated water before use.

9.2.3 *Land contamination*

The surface few metres of the continents consists of an extremely complex covering of disaggregated materials, comprising: minerals, decaying organic matter, water, air and flora and fauna. This is known as soil. It is a valuable resource and supports the growth of crops and provides land for building and transport. Importantly it also acts as a sink, a filter and a reaction matrix and medium for contaminants, and is a crucial component in the discussion of industrial pollution. Most of the world's soils are contaminated to some extent by man's activities. These can again be from local and global, diffuse and point sources. The chemical composition of soil needs to be defined for its compliance with certain 'trigger' concentrations determined by the proposed end use of the land. Major sources of contaminants from industrial sources, posing significant risks are summarized in Table 9.4.

Soil properties and characteristics profoundly influence the impact of pollutants[38]. Soil minerals comprise an intimate mixture which includes clay minerals, quartz, and hydroxides of iron, aluminium and manganese, as well as fragments of primary rocks. Soil organic matter represents the accumulation of organic residues of plants and animals at varying stages of decomposition and as such supports a diverse and significant microbial population. Other soil properties, such as permeability, through water and gas-filled voids or pores, either in solution or the gas phase, is influenced by grain size and compaction through previous use. The flow of material and degree of saturation influences the oxidizing and reducing (redox) status of the soil, which, along with the pH, is important in determining the mobility of pollutants and the degradation of organic contamination. From Table 9.4 it can be seen that the major groups of land contaminants are: heavy metals, organic compounds and sewage sludges.

The heavy metal contaminants are strongly adsorbed by soil constituents such as organic matter, clays and metal hydroxides. Mobility and bioavailability in turn being determined by soil pH, organic matter content and redox conditions. Most metals are more mobile under acid conditions.

Table 9.4 Sources and types of land contaminants. Based on References 9, 10 and 28

Atmospheric fallout
Fossil fuel combustion—S & N oxides and acid radicals
Pb, PAHs from automobile exhausts
Metal smelting—As, Cd, Cu, Cr, Ni, Pb, Sb, Tl, Zn
Chemical industries—organic micropollutants, Hg
Waste incineration—TCDDs, TCDFs
Radioisotopes from reactor accidents—Windscale, UK, 1957; Chernobyl, USSR, 1986
Large fires—soot, PAHs

Agricultural chemicals
Herbicides—2,4-D, 2,4,5-T containing TCDD, B and As compounds
Insecticides—chlorinated hydrocarbons, DDT
Fungicides—Cu, Zn, Hg, organic molecules
Acaricides—tar oil
Fertilizers—Cd, U in phosphates

Waste disposal (controlled and uncontrolled)
Farm manures, sewage sludges, domestic composts—heavy metals, viruses, pathogens, organic pollutants
Mine wastes—SO_4^{2-}, Fe, heavy metals
Seepage of landfill leachate
Ash from fossil fuels, incinerators, bonfires—heavy metals, PAHs
Burial of diseased livestock—viruses, pathogens

Incidental accumulation of contaminants
Corrosion of metal in contact with soil—Zn (galvanized), Cu, Pb (roofing)
Wood preservatives—PCP, creosote, As, Cu, Cr
Leakage from storage tanks—petrol, chlorinated solvents
Warfare—organic pollutants from fuels, smoke fires, metals from munitions, vehicles
Sports and leisure—Pb from gunshot and fishing, Cd, Ni, Hg from batteries, hydrocarbons from petrol

Derelict industrial sites
Gas works—phenols, tars, cyanides, As, Cd, combustibles
Electrical industries—Cu, Zn, Pb, PCBs, solvents
Tanneries—Cr
Scrapyards—metals, PCBs, hydrocarbons

Organic contaminants are widely varied in type and impact. Pesticides can remain in soils long after application or accidental spillages and there is a significant risk that their useful toxicity may also translate to harm beneficial plants and animals[35] and affect humans. Natural microbial activity can with time degrade many compounds to inactive residues, ultimately CO_2 and water. However, in some situations, degradation products may have significant toxicity or pollutants contain bonds, such as carbon–halogen bonds, which are not found in nature and are slow to degrade[9].

Insecticides include: organo chlorines, organo phosphates and carbamates, and herbicides including phenoxyacetic acids, toluidines, triazines, phenylureas, bipyridyls and glycines. A wide range of chlorinated compounds, such as dioxins and dibenzofurans are released from combustion sources, where they are synthesized at relatively high temperatures, have high stability and are slow to degrade[9]. Polychlorinated

Table 9.5 The hazards and effects of land contamination. Based on References 9 and 10

Hazard	*Examples of contaminants*
Direct ingestion by children, animals	Heavy metals, cyanides, phenols, coal tars
Inhalation of dusts, vapours, soil	Organic solvents, radon, volatile metals and metalloids (As, Hg)
Plant uptake and food chain transfer	Metals, PAHs
Phytotoxicity	SO_4^{2-}, CH_4, heavy metals
Degradation of construction materials	SO_3^{2-}, SO_4^{2-}, Cl^-, solvents, coal tars, phenols
Fires and explosions	High calorific wastes, organic solvents, CH_4
Contact with site clearance contractors	Coal tars, solvents, phenols, asbestos, radionuclides, PAHs
Aquatic pollution	Solvents, pesticides, cyanides, SO_4^{2-}

biphenyls (PCBs) are stable compounds, manufactured for use in electronic components and plastics and are found in a number of industrial processes. Sewage sludge which contains a wide variety of organic and inorganic compounds, is widely dumped on land as a means of disposal. The heavy metal, PAH and PCB content is of greatest concern. In practice, however, sludge amendment is of little hazard if used to landscape and encourage growth on recreational sites rather than on land used for food production[7,9].

The effects of land contamination are widespread and past industrial activity is the most significant factor. Soil transport and reaction processes are relatively slow compared to air and water, so contamination tends to persist at the point of deposition for a long period. Table 9.5 summarizes common hazards and examples of contaminants. These contaminants can affect humans by absorption into the body through oral, inhalation or skin adsorption pathways. For volatile compounds and dusts, inhalation is the most important pathway. This is of particular concern with young children playing on contaminated land. The re-use of derelict, industrial sites has emphasized many of these problems[9,10].

9.3
Options for the control and treatment of pollution and wastes from industrial sites

Having reviewed the key characteristics of major pollutants in the different compartments of the environment, it is appropriate to consider the options available for the control and for minimization of releases. Within this context, there is a need to consider waste management practices, as often the removal of a potential contaminant from the discharge, will provide a localized concentration of the material, which if not valuable for recycling, will have to be disposed of in another manner. Historically, discharges to air, water or land have only been subject to legislative control in the U.K. since the late 19th century[4].

The disposal of waste is one part of the waste management process. The minimization of waste production in turn reduces the potential for release of pollutants to the environment. Waste minimization can be viewed as a series of logical steps or objectives, which can be applied to any production process. The effects are felt not only in environmental impact, but it also has an impact on the economics of plant productivity. The effects are summarized as[39]:

(i) avoiding the creation of the waste products
(ii) re-using waste products
(iii) if a waste product is not re-usable, recover/reclaim the primary material for new manufactured products
(iv) if primary materials recovery is not practicable, recover, for a secondary material or if combustible use as fuel
(v) if none of the above is practicable, then choose the disposal option with the lowest environmental impact.

This approach can be carried through during the design of chemical processes such that they: afford maximum chemical conversion, have high energy efficiency; use minimum volumes and low hazard solvents; make minimum use of process water; ensure minimum dilution of carrier liquids; and ensure low inventories of liquids. It is outside the scope of this text to include detailed material relating to resource and energy recovery as a method of recycling and waste minimization. The nature of operations involved is dependent on the processes on site and therefore difficult to describe in general terms. However, there are numerous examples in the current literature of recycling routes for specific processes, including the recovery of sulphuric acid in monomer production, antimony recycling from polymer production[24], recovery and recycling of waste oils[40].

At the final stage, where disposal must proceed, there are two basic approaches. Firstly to *contain* the waste or pollutant, immobilized in a controlled manner. The pollutant is then localized and release is subject to the lifetime of the containment barriers, under the storage conditions used. This is relatively straightforward where the lifetime of the hazard is short but a major consideration in the longer term, where containment must perform adequately for many hundred and thousands of years. The management of radioactive waste from the nuclear fuel cycle is perhaps the most appropriate example here of the latter[30].

The second approach, *dilute and disperse*, is to allow discharge of the pollutant in liquid or gaseous forms, diluted to a level such that there is no direct risk to the local environment or that with prolonged releases, there is no likelihood of re-concentration under natural environmental processes close to or remote from the discharge point. This approach (whilst extremely cost effective) is philosophically questionable and the most difficult engineering challenge. Having been routinely used for most disposal solutions, it suffers from the fact that the only feedback to the practice is through the observation of adverse environmental effects. Obviously this is then too late to prevent and the environmental impact has occurred. This practice has driven the increased legislative control on industrial operations, characteristic of the mid to latter part of the 20th century. All waste management practices contain components of both approaches. In the design of containment, it is never possible to ensure complete integrity over time, the costs of this option rapidly escalating with complexity and construction effort and eventual release of the polluted or waste components, at some level, is certain. It is therefore ideal if the release of pollutants can be an integral part of the waste disposal option, which is able to tolerate variations in the physical and chemical characteristics of the waste.

9.3.1 *The control of atmospheric discharges*

Historically, all industrial sites contain exhaust pipes, chimneys or stacks that release volatile gases and entrained particulates directly to the atmosphere. The dilution and natural scavenging and cleaning processes offered by this route take the emissions away from the site and generally ensure wide dispersal. Climatic conditions and stack height are the major factors and, as previously mentioned, dilution is at best a short-term measure, with many infamous examples[12,17,20].

The principles of pollution or waste minimization outlined above, if applied, ensure that minimal discharges occur. Control devices are designed as a secondary approach to destroy, counteract, collect or mask pollutants. Such devices are never effective for both particulate *and* gaseous emissions and are designed for either one or the other[17,41].

9.3.1.1 *Particulate discharges.* A varied range of industries release particulates into the atmosphere. Owing to their visibility, particulate control has received most attention, despite the greater volumes of gaseous components released[17]. Devices can be divided into five groups which, in principle, either alter the flow rate of gas stream or reduce the energy of particulates by impact. The key characteristics, advantages and disadvantages of each approach are summarized in Table 9.6. The devices used are dependent on particle characteristics: size distribution, shape, density, stickiness, hygroscopicity, electrical properties and the carrier gas properties of flow rate and particle loading. Additionally, the desired efficiency, nature of the source, intermittent or continuous, the space available, ultimate waste-disposal method and equipment tolerances to gas stream conditions (corrosion, temperature, pressure) must be compared to the costs of installation and operation. A summary of industrial process examples and control methods is given in Table 9.7. Details of designs for each type of device can be found elsewhere[41].

9.3.1.2 *Gaseous discharges.* From most industrial sites, the main gases of concern are oxides of sulphur, nitrogen and carbon, inorganic and organic

Table 9.6 Control devices available for particulates released from industrial processes. Based on References 17 and 41

Device	*Minimum particle size (μm, 90% efficiency)*	*Efficiency (%, mass)*	*Advantages*	*Disadvantages*
Gravitational settler	>50	<50	Low pressure loss; design simplicity and maintenance	Space; low collection efficiency
Centrifugal collector	5–25	50–90	Low–medium pressure loss; design simplicity and maintenance; space; continuous disposal of collected dusts; copes with large particles and high dust loadings; temperature independent	High headroom requirements; low collection efficiency of small particles; sensitivity to dust loadings and flow
Wet collector			Simultaneous gas and particle removal; cools and cleans high temperature, moisture laden gases; corrosive gas and mist recovery/neutralization; dust explosion risk minimized; efficiency can be varied	Problems with erosion and corrosion; costs of contaminated waste water treatment; low efficiency for small particles; freezing in cold weather; affects plume rise; can add water vapour to plume
spray tower	>10	<80		
cyclonic	$>2{\cdot}5$	<80		
impingement	$>2{\cdot}5$	<80		
venturi	$>0{\cdot}5$	<99		
Electrostatic precipitator	>1	95–99	$>99\%$ efficiency possible; small particles collected; wet or dry operation; low pressure drop and power requirements; few moving parts; can operate at high temperatures	Initial cost high; sensitive to loading and flow rates; low efficiency for high resistivity materials; electrical hazard; gradual, imperceptible reduction in collection efficiencies
Fabric filtration	<1	>99	Dry collection possible; degradation in performance obvious; high efficiencies and small particle collection possible	Sensitive to velocity; high temperature gases must be cooled; chemical degradation of filters; condensation effects

Table 9.7 Particle emission characteristics of industrial processes and control options. Based on References 17 and 41

Industry/process	*Emission source*	*Particulate composition*	*Control options*
Iron and steel mills	Blast and steel making furnaces	Oxides, dusts, smoke	cyc.; b.h.; e.p.; w.coll.
Iron foundries	Cupolas, shake-out making	Oxides, smoke, oil, metal fumes, dust	sc.; dry cent.
Nonferrous metallurgy	Smelters, furnaces	Smoke, metal fumes, oil, grease	e.p.; f.f.
Petroleum refineries	Catalytic regenerators, sludge incinerators	Catalyst dust, ash from sludge	cyc.; e.p.; sc.; b.h.
Portland cement	Kilns, driers, material handling	Alkali and process dusts	f.f.; e.p.; venturi sc.
Acid manufacture, phosphoric and sulphuric	Thermal processes, rock acidulating, grinding	Acid mist, dust	e.p.; mesh mist eliminators
Glass and fibreglass	Furnaces, forming/curing, handling	Acid mist, alkaline oxides, dust, aerosols	f.f.; afterburners

Abbreviations: cyc., cyclones; w.coll., wet collectors; b.h., baghouses; sc., scrubbers; cent., centrifuges; f.f., fabric filters; e.p., electrostatic precipitators.

acid gases, and hydrocarbons. Control methods available include: adsorption, absorption, condensation and combustion.

Adsorption of a gas stream passing through a bed of absorbent is by two discrete processes[41]. Physical adsorption involves intermolecular forces (van der Waals) and condensation of gases within the solid materials. The amount of material adsorbed depends on the amount of solid but it is not directly related to the surface area. The process is reversible and desorption can occur by raising temperature or lowering pressure. Chemisorption involves the reaction of the gas with the solid adsorbent to form a bond and is influenced by temperature and pressure. The process is usually irreversible and confined to a single layer of molecules on the solid surface.

Numerous adsorbents exist that are highly efficient at removing gaseous contaminants[42]. Examples are given in Table 9.8. The adsorbents and gas stream can be brought into contact through fixed, moving or fluidized beds of various designs. The adsorbents can be classified as *regenerative* or *non-regenerative* depending on the ease of removal of the collected gas. Chemisorption is naturally the most costly approach; where possible the regeneration processes require extremes of pressure, temperature or chemical treatment. Adsorption methods are an efficient way of material recovery and often valuable by-products are obtained[42].

Absorption (or scrubbing) involves liquid absorbent (solvent) so that one or more of the effluent gases are removed, treated or modified. This may be

Table 9.8 Applications of adsorbents in the treatment of gaseous waste streams. Based on References 41 and 42

Adsorbent	*Applications*
Activated carbon	Odour removal; gas purification; solvent recovery
Alumina	Drying air, gases and liquids
Bauxite	Treating petroleum fractions, drying gases and liquids
Bone charcoal	Decolorizing sugar solutions
Fuller's earth (mineral)	Refining animal oils, lubrication oils, fats, waxes
Magnesia	Treating petrol and solvents, removing metallic impurities from caustic solutions
Molecular sieves	Controlling and recovering Hg, SO_2 and NO_x
Silica gel	Drying and purifying gases
Strontium sulphate	Removing iron from caustic solutions

through chemical reaction of simple dissolution. The amount of gas removed depends on the gas and solvent properties. A general guide is that solvents with similar properties to effluent components are suitable. So alkaline solvents are suitable for acidic gases and hydrocarbon solvents for organic molecules. Gases commonly controlled in this manner include sulphur dioxide, oxides of nitrogen, hydrogen sulphide, hydrogen chloride, chlorine, ammonia and light hydrocarbons. Other solvent characteristics must include: low freezing point, low toxicity, chemical stability and very low volatility and flammability. Absorption units usually mix a spray of droplets with the effluent gas in a turbulent manner, to maximize gas/solvent contact area and time.

Condensation methods of air pollution control involve the cooling of the effluent stream by either contact with a cooled solid surface (surface condenser) or by mixing with the coolant itself (contact condenser). Applications of condenser systems are not widespread, being restricted mainly to hydrocarbons, and are usually used as a pretreatment step for other control techniques. Incineration has wide application in the conversion of contaminants such as CO or hydrocarbons to carbon dioxide and water. The main parameter controlling efficiency include: oxygen—concentrations must be such that combustion can continue to completion; temperature—this must be as close to the ignition temperature as possible; turbulence—to allow sufficient mixing of oxygen and combustible components; time—to allow reactions to complete. A range of combustion techniques is available. These include direct flame combustion, in which waste gases are burnt directly in a combustor, with or without the addition of extra fuel. Gas flames in petrochemical plants and refineries are examples. Thermal combustion (after burner), for gas streams with low combustibility, involves preheating the gas stream prior to injection into a combustion zone, containing an independent burner. Design is crucial here, to ensure complete combustion. In catalytic combustion a preheated gas stream is passed over a catalyst, which accelerates the rate of oxidation. This process can be highly efficient and catalytic material from platinum group metals, transition metals and oxides have been used to treat SO_2, NO_xs, hydrocarbons and carbon monoxide. Potential disadvantages include poisoning of the catalyst and the relatively high capital cost of the catalyst. This method has widespread application in automotive emission control, where transportation accounts for >50% of all major air contaminants[41].

9.3.2 *The control of aquatic discharges*

The range of toxic substances present in industrial waste waters is diverse. Tables 9.3 and 9.4 have indicated examples of the types of potential pollutants present. From the preceding section, aqueous effluents from industry include primary process waters and liquids contaminated by secondary processes to treat atmospheric discharges and other on site operations including cleaning and occasionally fire control. Discharges to water courses during firefighting operations can be catastrophic and result in the release of vast quantities of contaminated water into site and local drainage systems[43]. The major problem being the large water volumes used to combat the fires. The company is liable for any pollution effect. Site design, which involves the equipping of drainage systems to cope with estimated volumes of water and changes in firefighting procedures through the use of containment booms and absorbent pads are being developed.

The most convenient and economical treatment of routine aqueous discharges is to mix industrial wastes with domestic waste waters. This practice is limited only in the situations where: the site is in a rural area with no convenient sewerage system; recycling is feasible (although there will still be a final discharge); domestic effluent is used in irrigation; industrial waste water does not meet the consent conditions for discharge to the sewer[44]. Examples of specific water treatment methods that have been applied to waste streams include the removal of dissolved hydrocarbons with polymer particles[24]; the treatment of mine waters by adding lime to increase pH and the use of reed beds to reduce and precipitate metals[45].

The consequence of the treatment on site allows both the recycling of components and the use of more extreme treatment conditions in addition to the avoidance of contamination of a much larger waste water stream. Toxic contaminants may inhibit routine sewage treatment processes and can be overcome relatively easily with the more specific site treatment processes. In many situations however, on-site treatment may be obviated by simple dilution to acceptable levels prior to discharge. This is especially advantageous if there is not enough space on site, personnel are not experienced enough in treatment or the localization of waste during treatment may cause an odour nuisance[44]. The philosophy of waste minimization has already been described and a number of techniques are available. The decision to treat or not will be a result of the factors outlined above. However, even employing simple physical methods can improve effluent quality con-

Table 9.9 Physical methods of pre-treatment applicable to aqueous waste streams. Based on References 32, 44 and 46

Process	*Objective*	*Typical examples*
Screening	Removal of coarse solids	Paper mills, vegetable canneries
Centrifuging	Concentration of solids	Sludge dewatering in chemical plants
Filtration	Concentration of fine solids	Final stages (in above)
Sedimentation	Removal of settleable solids	Coal, clay ore processing
Flotation	Removal of low specific gravity solids	Oil, grease and solids separation in chemicals and food industry
Freezing	Condensation of liquids and sludges	Non-ferrous metal and process liquids recovery
Solvent extraction	Recovery of specific metals and organics	Coal carbonizing, plastics manufacture, metal processing
Ion exchange	(as above)	Metal processing
Adsorption	Trace impurities	Pesticides, dye stuffs
Reverse osmosis	Dissolved solids	Desalination of industrial waters, waste waters with dissolved contaminants

siderably. Generally this involves some form of screening to reduce solid content, balancing of concentration flow, pH and traps to prevent oil and grit escape[32,44,46]. A brief summary of physical methods commonly used is given in Table 9.9. Further pre-treatment may involve the reduction of organic matter content by biological oxidation methods, particularly if the discharge is to go straight to a water course. These methods are varied at the pre-treatment stage and all biological methods are particularly prone to poisoning by toxin concentrations, especially where levels vary. Ultimately, problematic industrial wastes with high organic matter content are usually subject to conventional primary and secondary treatment. Chemical methods are used either to oxidize particular compounds or to aid in the physical treatment process by adjusting pH and/or removing solids and some dissolved species by flocculation and precipitation.

The use of pre-treatment methods is waste stream dependent, as is the resulting effluent quality. Should further processing be required, standard sewage treatment is frequently used[44,47]. The stages involved in this process are summarized in Figure 9.6. Preliminary screening is needed to remove large suspended solids, metals and rags. Grit removal occurs prior to the sedimentation of as much of the suspended solids as possible. Biological (*secondary*) treatment is one of two types: (i) percolating filter, comprising a packed bed of clinker or stones, with a high surface area, that allows aerobic oxidation; and (ii) activated sludge, in which the sewage is aerated in agitated tanks to expose the waste to as much oxygen as possible. Sludge is recycled to seed raw sewage and speed up the process.

Aerobic oxidation should produce low BOD material unless the plant is overloaded. Further settling occurs prior to discharge of the liquid and the disposal or further treatment of the sludge. Tertiary treatment may still be

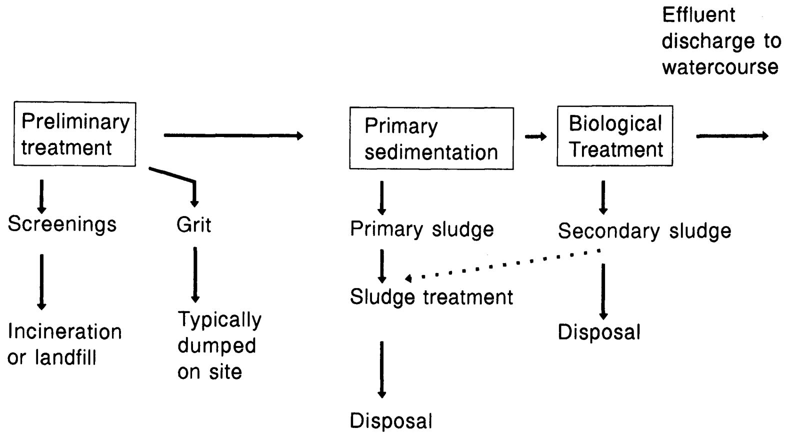

Figure 9.6 A schematic diagram of the sewage treatment process. Most industrial aqueous wastes are introduced to domestic treatment plants. Where the process justifies costs, a purpose built system, with similar operations is used. Based on Reference 47.

required for further solids reduction and various types of filter, lagoons for settling or reverse osmosis processes are used. The treatment of sewage sludge and its subsequent disposal can account for 40% of the operating costs of a sewage treatment plant[47]. Sludge has a water content of 95%, is odorous and a major waste management problem. Four methods are used to deal with sewage sludges depending on relative costs and legislative controls.

(i) Conversion to methane by anaerobic digestion in a variety of tank-based systems. This approach can produce enough gas to burn for energy. It removes pathogens and odours from the sludge and provides a solid residue for use as a soil amendment. The raw sludge must have a high enough organic content, so unless mixed with high organic streams, such as sewage, some industrial effluents may not be suitable. Anaerobic digestion is now routinely used to treat organic rich liquid wastes from a range of industries such as paper mills, breweries, dairies, and distilleries[48]. The technology has been developed from sewage sludge treatment processes and allows relatively rapid processing.

(ii) Incineration can be relatively high cost, requiring additional fuels. Once de-watered, sludge can be burnt (in self-sustaining incinerators at 850°C) in fluidized bed processes, with useful excess heat production[49,50]. The process destroys most toxic organic compounds. Flue gas scrubbing is required to remove acidic gases.

(iii) Disposal directly on land is an option that is attractive where heavy metal, organic pollutants and pathogen levels are low[9,44]. Restrictions on the amounts used, land use and fallow periods are dependent on factors relating to transmission of disease and accumulation of toxins. The sludge can be applied wet—as such it is a valuable source of moisture—or dry. Where agriculture is intensive or soil quality low, the practice can be highly beneficial to crop growth.

(iv) Dumping at sea, for coastal communities, has been a traditional disposal route. Sea dumping can both dilute and treat wastes, provided no re-accumulation occurs under current action and loading rates allow time for processes to complete. In the U.K. this practice has been abandoned under European Union guidelines[49].

9.3.3 *The disposal of solid wastes*

In the discussion of atmospheric and aqueous discharges, the underlying principles of waste minimization, in terms of volume reduction, includes recycling, and treatment. This leads to the removal or minimization of hazards from effluents and results in the production of a solid residue. This must be disposed of along with any other solid material produced on site.

Further treatment options by incineration and biological composting or digestion depend on the total carbon and organic matter content of the solid waste and payback from direct heat and methane generation, which may be used to offset costs of the process[49]. The environmental impact of incineration has recently been reviewed[49,51] and there exists a wide range of technological options in incinerator design that optimize the process, minimizing environmental effects. Incineration produces atmospheric emissions—CO_2, CO, H_2S, HX, NO_xs, SO_xs, dioxins, vapours, heavy metals, inorganic salts; high temperatures; acidity/alkalinity; contaminated waste water and ash. Whilst physically stabilizing the original waste, in some cases it may serve to concentrate a number of potential pollutants. The ash can contain relatively high levels of heavy metals and residual organic compounds, some of high toxicity or carcinogenicity[52].

Biological treatment has been reviewed in section 9.3.2 and depends on the organic content of the waste. It can include aerobic or anaerobic processes. The anaerobic system supplying potentially useful methane is the most difficult to control efficiently, with operational problems that relate to the handling of solids and leachate, and the harnessing of gas yields.

Unless alternative uses can be found (for example as road/construction fill or soil amendment) the solid waste residues require a final disposal route. Ultimately this is through landfilling. The pretreatment methods above serve an important role in stabilizing and reducing the volumes required for landfill. Currently, landfilling is the most economic (and consequently most used) form of disposal in the U.K., U.S.A. and Europe. In the U.S.A. and U.K. this route takes approximately 90% of controlled and 80% of hazardous wastes[7,53,54].

A landfill site should be on inexpensive ground, within economical transport distance from the main waste producers, have year-round access and be a suitable distance from neighbours. The area should be clear, level and well drained, with adequate capacity for the intended use. The surrounding soil should be of low permeability and the site should be isolated from the water table, either through distance and/or design characteristics.

Two approaches are used in landfill design[53,54].

(i) *Containment* in which the waste is isolated from the environment, the generation of aqueous leachate in the waste is minimal, and waste management is more straightforward. Barriers between the landfill waste and the environment are engineered, with designed tolerances. A wide range of materials is available for barrier constructions including polymer membranes and inorganic clays[53,54,58].

(ii) *Disperse and attenuate:* natural sites with materials of known properties are used to alter the composition of leachate and reduce potential environmental damage through physical, biological and chemical processes. There is a net loss of leachate to the groundwater through design[53,54].

A suitable understanding of the site hydrogeology must be gained before operation. Figure 9.7 summarizes many of the key characteristics of a landfill site.

The landfill can be operated in a number of ways to receive both

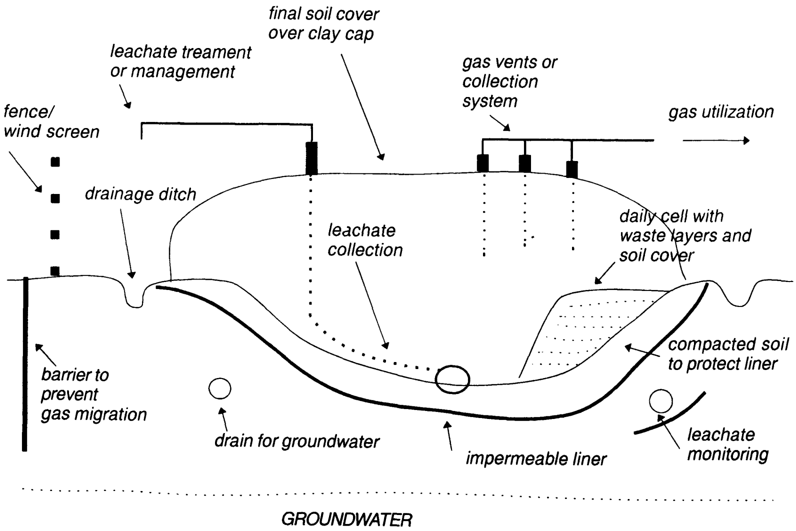

Figure 9.7 A sketch of a typical landfill site, showing leachate and landfill gas management options and cellular filling practices. Based on References 7, 53, 54 and 55.

municipal and industrial wastes, providing waste properties are understood[7]. Co-disposal, in which toxic wastes are added to mature (6 months–2 years) domestic wastes and multi-disposal where, for example, an inert solid may be used to stabilize a slurry, are two options available for industrial wastes[56]. Key factors to consider are waste density on deposition; waste compaction; biodegradability; odour; the variation physical/chemical properties with time, and the compatibility of various wastes (i.e. mixing solid nutrients with biological wastes is unwise!)

The main environmental effects of landfills include:

(i) The generation of landfill gas from the biological degradation of organic components. Landfill gas (LFG) is a general term for a varied mixture of gases, primarily CO_2 and CH_4, that are produced by the wastes commencing immediately after deposition and lasting for many decades, long after the site has been closed[53]. The amount of methane produced can be sufficiently high to 'farm' and be used as a fuel source. The profile of gas composition changes to reflect aerobic and anaerobic activity. They key factors to consider in LFG generation are summarized in Table 9.10. The major LFG hazard is through migration off site and build-up to toxic or explosive levels in enclosed spaces such as residences or site buildings[57,59,60].

(ii) The production of landfill leachate. During the degradation process, moisture from within the waste, the ingress of groundwater, rainfall and surface water runoff can percolate through the site, producing an often noxious liquid, known as leachate[61]. This is a coloured liquid (light yellow, through to red and black) with high levels of organic matter, dissolved and particulate iron and sulphides, and varying levels of heavy metals and organic pollutants[55]. It can be up to 100 times more polluting than raw sewage and contains dissolved LFG. Leachate quality varies greatly between sites and with time. The important factors influencing its production are summarized in Table 9.10.

Table 9.10 Key factors influencing the generation of landfill gas and landfill leachate in solid waste disposal. Based on References 7, 53, 54, 56 and 58

Landfill leachate	*Landfill gas*
Surface water ingress	Site dimensions
Ground water ingress	Waste composition and variation
Absorbing capacity of waste	Waste input rate
Weight of waste deposited	Site operations
Evaporation losses	Waste density
Cellular filling practice	Moisture content
Capping and landscaping	pH
Waste composition and variation	Temperature
	Ingress of oxygen

The production of LFG and leachate at a landfill, must be minimized, monitored (unless CH_4 production is desired) and controlled if environmental impacts are to be minimized. Some of the uncertainties in landfill operation include: the selection criteria for containment or open site management; consequences of co-disposal; moisture input rates; and gas recovery[53].

9.4
Health and safety at work and hazards of the chemical industries

9.4.1 *Hazards and historical evidence*

There is a requirement for releases to the environment to be monitored and prevented, where appropriate. By default, the releases will originate on site, in a localized area with potential exposure for site personnel. Industry, worldwide, has a requirement, enforced by various legal systems to provide: clean air at work, safe working practices, well-being at work (which includes occupational health factors) and the control of noise and vibration[62]. Through the manufacture and processing of materials, individuals are exposed to elevated concentrations of chemicals, high energy sources or an elevated risk of injury from physical manipulations. Historically, we have a lot of data relating to the hazards of the modern chemical and process industries[63]. The toxicity of metals and metalloids, extracted from the surface of the earth, the initial development of extraction processes, by smelting, etc., has provided abundant evidence in the history books of detrimental health effects on the exposed workers[63]. Societies have an inbuilt limitation in this respect, with lessons from the past having a relatively short period of prominence before becoming relegated to the annals of history. As a result of the human perception of risk and other socioeconomic factors, such incidents tend to have a habit of repeating themselves. This is particularly true in developing countries, when viewed from a developed, industrial society. Through education and legislation, developed society has evolved a management system to minimize risks at various levels. This system results from past experiences and the effective communication of the results. In developing societies, with poorer communication, higher reliance on primary resource exploitation, this is not the case. A good example of this is the mining of gold in the Amazon Basin, Brazil[64,65]. The extraction of gold has a history of over 20 years, at various levels of activity. Informal sector miners, known as garimpeiros, use vast quantities of liquid mercury to form an amalgam with the gold particles. During the mining process, mercury is sprinkled onto crushed rock, mixed and washed, then separated from the tailings. The mercury is then collected and burnt, releasing the amalgamated gold. The process is summarized in Figure 9.8.

Mercury losses during the process are considerable and the environmental impact of the mining, above and beyond the effects of erosion and deforestation, is enormous. There is evidence of mercury pollution of the

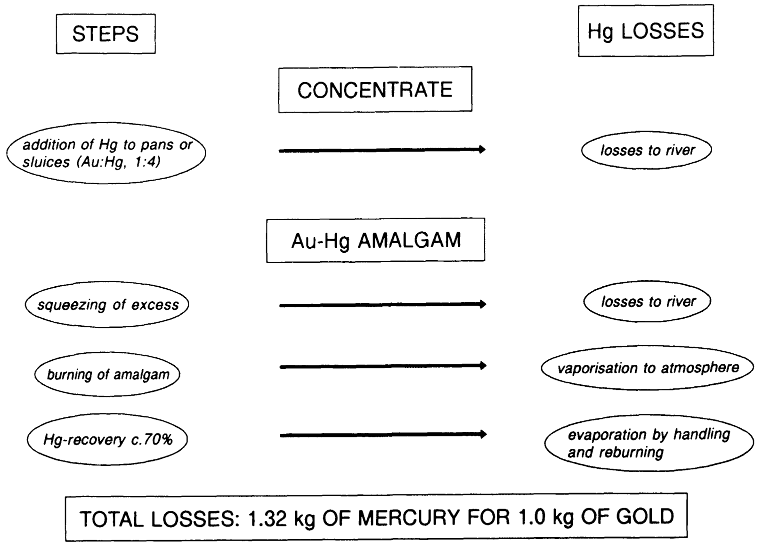

Figure 9.8 A flow diagram showing the losses of mercury during the extraction of gold using the mercury amalgam technique. Based on Reference 66.

local terrestrial and aquatic ecosystems, health effects in the miner and local Indian populations from the high levels of mercury released during amalgam processing and the contamination of local foodstuffs[64]. From a distance this seems quite a remarkable situation. Mercury has long been known to have toxic properties[67–69]. The phrase 'as mad as a hatter' referring to the mercury-induced medical conditions prevalent in the felt-making industry where mercuric nitrate was used to treat furs[68]. More recent examples include the mass poisonings of the fishing community in Minimata Bay, Japan during the 1950s. This occurred through the release of mercury-containing catalysts from a chemical plant manufacturing a vinyl chloride monomer[22].

Further historical lessons include the fact that any detrimental effects from the manufacture and use of chemicals and hazardous materials can only truly be appreciated *after* their introduction into society. There are numerous examples from the pharmaceutical industry, where drugs are produced with the object of providing a beneficial impact on society in treating or alleviating a detrimental aspect of life. With most drugs, there are always additional risks of known 'side effects' and the possibility of unknown effects. In general, there is a degree of general risk to be considered. The effect of a symptom or illness continuing through not taking the drug must be balanced with the known risks from the chemical. One of many tragic examples is the thalidomide episode in the U.K. in the late 1950s[22], where the use of a non-addictive alternative to barbiturates, when administered to pregnant mothers as a sedative, had a major effect on foetus development. This side effect was only appreciated from birth defect statistics, post-administration. The results of such incidents, which still continue today, serve as a salutary reminder of the importance of the holistic approach to the production and use of materials. The testing of toxicity and environmental impact is complex and now statutory for all new chemicals. However, it should never be considered that all hazards have been evaluated. Time, economics and current scientific knowledge can never guarantee future safety.

Turning to the hazards and the impact of industrial processes. Many disasters such as Flixborough, Seveso and Bhopal[22,63] (see section 1.6) have ably illustrated the environmental impact of human errors and the need for rigorous safety controls. The capacities and productivity of chemical plants are driven upwards as are the magnitudes of losses in terms of economic cost and fatalities. Analysis of the major causes of accidents in the U.S. chemical industry in the 1978–1980 period[63] highlighted that:

(i) most frequent and severe losses were from fire and explosion
(ii) explosions were more severe than fires
(iii) accidental and uncontrolled reactions were the main causes of explosions
(iv) most explosions occurred in buildings and with batch processes
(v) vessel and pipe failure was the major contributory factor
(vi) fires were caused by flammable gas and liquid releases

The wide variety of chemicals produced and very poor overall health and safety statistics, make the assessment of occupationally determined disease and ill-health particularly difficult. Taking this a stage further, other than disasters or accidents, where the effect on workers and the environment can be relatively easy to observe, the long-term impact, particularly from low levels of new or poorly studied materials, is a particular problem. Epidemiology, (the study of social groups and patterns of disease as a means of determining causes[70]) is difficult due to the varied exposure conditions and the varied significance of other factors. Exposure to chemicals at work is one hazard that can be controlled.

9.4.2 *Toxicity and exposure to chemicals*

9.4.2.1 *Hazard and toxicity.* Any material is a poison if the dose is large enough and the study of the effects of substances on the human body through, dose–response relationships, known as toxicology, is an advanced discipline. It is at the centre of occupational health activities in industry. Exposure can result in a number of effects depending on the levels of substance[63,71].

The major hazards are: *carcinogenicity*, cancer causing or incidence increasing; *teratogenicity*, the induction of non-heriditable birth defects in offspring; and *mutagenicity*, the increase of the risk of hereditary genetic defects. These effects may be *acute*, a rapid response over a matter of hours; or *chronic*, over a matter of months.

Exposure pathways, in particular their relative significance for different substances, are varied[71]. In an industrial context, these are: by swallowing, by absorption through the skin and by breathing. Once in the bloodstream, toxins may attack one or more organs, causing harm.

Dermal (skin) absorption is a significant hazard for a number of volatile substances[72]. These include: aromatic compounds such as benzene and toluene; nitro-compounds such as nitrobenzene, trinitrotoluene and nitropropane; several insecticides and herbicides; hydrogen cyanide and organo phosphates. Protective clothing can minimize risks except where splashing and adsoprtion into cloth concentrates exposure to the skin.

The inhalation pathway is the major route for chemicals into the body[71]. Gases and vapours can penetrate deep into the lungs where, as the penetration of particles is strongly dependent on size, the general rule being the finer (smaller) the further they penetrate. Deposition in the lungs of very fine (1–2 μm) particles is of greatest concern. The action of asbestos is well known[73].

Measures of toxicity are from two routes. Firstly, data from laboratory testing on animals by direct injection, oral or chemical administration and is usually expressed as an LD_{50} value. This is the dose that causes death to 50% of the population after 14 days[71,74], expressed as mg or μg of substance per kg body weight. Tests are performed under standard conditions and subject to rigorous statistical analysis. The lethal concentration (LC_{50}) unit is used for hazardous airborne concentrations and is defined as the 4-hour inhalation of which causes death of 50% of the test group within the 14 day observation period.

The results from this type of study are coupled with the second, very limited, source of toxicity data from previous chemical exposure records of workers. Chemicals are then classified in terms of their inferred, relative toxicity[72]. The two extremes being *practically non-toxic* (probable lethal dose for a 70 kg human ~15 g/kg) to *supertoxic* (probable lethal dose for a 70 kg human <5 mg/kg)[72,75,76].

The derivation of these levels and more importantly the dose–response relationships for particular chemicals, incorporates considerable uncertainty when translating experimental data which are often derived from a different species, to the workplace environment[72,75]. Generous safety margins must be incorporated to minimize the risk, and the shape of the dose–response curve is important. The dose–response curve allows the relative effect of increased exposure to a substance to be evaluated. Whether it is linear or non-linear, with or without threshold concentrations has important consequences for exposure. The presence or absence of a threshold concentration is critical in the consideration of levels present in the environment and the potential to increase or decrease with time. One situation that receives detailed attention in this respect, is the effect of low levels of ionizing radiation in the environment from nuclear weapons testing, accidents such as the Chernobyl disaster and discharges from the nuclear fuel cycle[30,77]. The effect of small additional radiation doses to a population that has evolved within a naturally radioactive environment is continually debated. Concern centres on the extrapolation of a dose response relationship based on data from high doses to the low environmental doses.

9.4.2.2 *Occupational exposure.* Within the workplace environment, occupational exposure limits (OELs) have been established by several countries[74]. These are the maximum concentrations in air of substances that should not be exceeded in the breathing zone of workers. They apply to single substances only and it must always be considered, that where there are mixtures, effects may be neutralized or enhanced (synergism). As the amount of information on the effects of exposures increases, there is a tendency to reduce these levels. Vapour and gas limits are represented as ppm (volume) or mg per m^3 in air and for solids as mg per m^3.

In the U.K., the Health and Safety Executive (HSE) publish recommended levels for occupational exposure[78] as: maximum exposure limits (MEL), which are reasonably practicable for all work activities; and *occupational exposure standards* (OES) which cover realistic plant design, engineering and control of exposure and can be used to help in the selection of personal protective equipment. Further subdivision of limits occurs into long-term (usually 8-hour) and short-term (10-minute). Short-term limits are of use where brief exposure may cause acute effects. Both levels are expressed as time-weighted average concentrations (TWAs) over the specified period. Studies of OELs in other countries reveal that there are some differences, but generally they fall close to each other in industrial societies[72].

Exposure sources for workers can be divided into two categories:

(i) periodic emissions—short-term releases associated with planned manipulative operations or accidental releases. In these situations, acute exposure effects are common.

(ii) Fugitive emissions—small, but continuous escape of liquids, vapours in general, that tend to arise from dynamic seals and can lead to chronic effects in workers.

Monitoring the working environment is a complex task and advice is available in the U.K. from the HSE, and in the U.S.A. from occupational health authorities, the Occupational Health and Safety Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH). The primary objectives of monitoring are to estimate personal exposure and the effectiveness of engineering and process control measures, as well as to monitor epidemiological and environmental impacts[72]. The approach is complicated by the varied type and number of emission sources and dispersion processes, but should include the following steps:

(i) Initial assessment, including: the substances present; their physical form; likely health hazards; exposure potential–severity, duration, location; evidence from comparative situations elsewhere.

(ii) Preliminary survey: this will include sampling and analysis. A complex stage, that usually involves the capture of substances by reaction, dissolution or filtration from a known volume of air over a suitable time period prior to chemical, physical or even biological analysis.

(iii) A detailed survey to back up major exposure indications; to evaluate highly variable preliminary results; where previous survey indicated levels that were close to OELs, requiring a more accurate picture of exposure, before the decision to act.

(iv) Routine monitoring to ensure that control measures perform continuously.

Table 9.11 Control techniques of use in chemical plants. Based on Reference 79

Type and explanation	*Examples*
Substitution—less hazardous chemicals and equipment	Low toxicity solvents, heat transfer through water rather than oil, high flash point chemicals
Attenuation—use chemicals under conditions that are less hazardous	Use vacuum to reduce boiling point, reduce temperature and pressure, dissolve in safe solvents, prevent reactor run away
Isolation—isolate equipment and hazards	Controls distant from operations, strengthen control rooms and tanks
Intensification—reduce quantities of chemicals	Use small continuous reactors, reduce raw material inventories, improve control to minimize hazardous intermediates
Enclosures—enclose equipment/room and use negative pressures	Seal rooms, sewers vents, shielding, remote and continuous monitors
Local ventilation—contain and exhaust hazardous substances	Fume hoods, extractors
Dilution ventilation—control low level toxicity through air dilution	Ensure all work areas adequately ventilated
Wet processes—to control dusts	Water sprays, clean frequently with solvents
Good housekeeping—contain toxic materials, dusts	Place dykes around pumps and tanks, cleaning and flushing lines, sewer systems
Personal protection—last resort	Safety glasses, face masks, protective clothing appropriate to hazards

Throughout this assessment process, the sampling strategy employed requires careful consideration of exposure, and hazards and should be established to cope with the statistical variability of each step.

There exists a wide range of methods for the control of chemical plant hazards which have implications not only for occupational exposure, but by default, the environmental impact. A few basic approaches are summarized in Table 9.11. Personal protection should always be considered as a last line of defence, for use in short-term situations where there is a risk of acute exposure. Environmental control should always be the primary objective.

9.5

Conclusions—legislative controls affecting the environmental impact of the chemical industry

The control and management of environmental pollution has become the domain of complex legal frameworks, evolving from a number of specific acts at various governmental levels. The variety and nature of controls varies between countries, but most industrial societies have generally similar structures. This section presents a brief outline of the roles and responsibilities in the U.S.A., E.U. (European Union) and U.K. Ultimately, the objectives of these controls are to minimize environmental impact of any operation.

Within the U.S.A. environmental protection and occupational health has derived from federal administrative agencies through inspection. The U.S. Environmental Protection Agency (EPA), the OSHA and NIOSH establish occupational exposure standards that have the force of law[80]. Ambient standards are defined to minimize risks to the health of humans, animals or the environment. The European approach has been through the issue of Directives and Regulations in a more coherent manner than in the U.K.[62] They concentrate on placing specific duties on employers by laying down quantifiable and minimum standards. Increasingly this will have an impact on U.K. law. Directives have been established to control certain industrial hazards through a central, European Environment Agency (in Copenhagen) and a European Environment Information and Observation Network. The European Union thereby driving member countries to harmonize systems and fill any gaps in procedures. At the time of writing a similar approach to the integrated pollution control principles of the U.K. regulations, is under consideration[81].

Within the U.K., the 1990 Environment Protection Act established a new approach to U.K. environmental law[81,82]. It brings together air framework directives, dangerous substance directives (responsible for the definition of black and grey list substances, see section 9.2.2) and waste disposal directives, as a total emissions management system. Sections are defined that include integrated pollution control and air pollution control. The objectives are: pollution prevention at source; risk minimization; the application of advanced technological solutions appreciating the integrated nature of the environment; a critical loads assessment approach to highlight sensitive environments; and the principle that the polluter pays for the necessary controls.

This has resulted in a system of authorization, the enforcement of pollution control under certain (prescribed) processes and the control and monitoring of the release of certain (prescribed) substances. These are enforced by HM Inspectorate of Pollution (HMIP), river agencies, local authorities and the HSE with a series of registration fees and penalties for meeting authorization.

There are a number of objectives to be met for authorization:

(i) To ensure that the *best available techniques not entailing excessive costs* (BATNEEC) will be used to prevent release of prescribed substances, minimizing release or rendering harmless;

(ii) Compliance with E.U. law;

(iii) Compliance with environmental quality standards (EQSs) or objectives (EQOs) prescribed by the Secretary of State;

(iv) Compliance with emission standards or quotas;

(v) Where releases are likely into one or more environmental media, the principle of BATNEEC will be applied to minimize pollution to the *best practical environmental option* (BEPO). Waste disposal on land is covered in detail and contains improved consideration of the waste disposal process from importing, producing, carrying, keeping, treating and disposing of or controlling waste in a true cradle-to-grave manner. This is through the ability of new Local Authority Waste Disposal Companies to amend contractors' disposal contracts and ensure that the waste contractor is a fit and proper person. An imposed 'Duty of Care' clause proposes to prevent escape of wastes and that the waste is transferred to an authorized person.

The details of the act are widespread and implications to pollution and environmental impact of any industrial operation wide-ranging. This highlights the more recent issues in the environmental impact of industrial processes. In the U.K., past policies on bringing disused/derelict land back into productive use, highlighted the terrestrial environmental effects of industry (see section 9.2.3). In addition a number of disasters, such as Love Canal in the U.S.A., prompted legislative responses such as the Comprehensive Environmental Response and Liability Act 1980 (CERCLA)[83]. This allowed the US-EPA to investigate and clean up contamination and to recover costs from past and present owners, transporters of hazardous waste, previous occupiers and anyone connected with the waste. The UK-EPA 1990 containing the duty of care approach follows similar lines. Today, site investigation techniques[10,84,85], methods for the remediation of contamination[86], which include biological[87], as well as physical and chemical techniques[86], has generated considerable academic and consultancy research, driven primarily by industry. From the above description, worldwide, the drive continually is towards the principle that the polluter pays. Either to operate a plant in which discharges and waste products are minimized, offering safe conditions for the workforce and to ensure that ultimately the releases have minimal environmental impacts. There are economic considerations at all stages, where the cost versus risk analysis of operations (to the workforce and environment) must be balanced by industry and by law.

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