APPENDIX D

The Priority Pollutants and Indicators

Prepared by the Environmental Secretariat, National Research Council of Canada.

1. Airborne sulphur dioxide and sulphates
2. Suspended particulate matter
3. Carbon monoxide
4. Carbon dioxide
5. Airborne oxides of nitrogen
6. Ozone, photochemical oxidants atnd reactive hydrocarbons
7. Toxic metals:
   a) Mercury
   b) Lead
   c) Cadmium
8. Halogenated organic compounds
9. Petroleum hydrocarbons in water
10. Selected indicators of water quality
   a) BOD
   b) DO
   c) pH
   d) Coliform bacteria
   e) Ammonia
11. Nitrates, nitrites and nitrosamines
12. Environmental radioactivity

(Wherever the units ppm and ppb are mentioned, the phrase "by volume" is understood.)

D.I. AIRBORNE SULPHUR DIOXIDE AND SULPHATES

a) *Sources, environmental distribution, and sinks*

Robinson and Robbins (1972) have estimated the world sulphur cycle in 10^6 metric tons/year).

Sources	
Industry, space heating and transportation (mainly in the form of SO_2 and H_2S)	70
Fertilizer applications to soils (sulphates)	11
Rock weathering (sulphates)	14
Biological decay: Continents	68
Oceans	30
(H_2S and organic sulphur compounds including dimethyl sulphide)	
Sea spray (sulphates)	44
Volcanoes (SO_2, H_2S, sulphates)	small

Sinks

Precipitation and dry deposition:	Continents	90
	Oceans	71
Vegetation intake		26
Gaseous absorption by the oceans		25

The sinks listed above are mostly temporary, with considerable recycling through the biosphere and geosphere. The final sink, the deep ocean, is estimated to have a strength of 95×10^6 tons/year.

The gas SO_2 is associated mainly with human activities, and concentrations are highest in towns and near smelters and oil refineries (SO_2 values are sometimes greater than 0.05 ppm/yr, 0.20 ppm/day, 1 ppm/hr). Background levels (about 0.2 ppb) at remote sites are near or beyond the threshold of chemical detection.

The residence time of SO_2 varies widely, ranging from tens of minutes in a very polluted atmosphere to several days in a clean environment. On this account the mere measurement of SO_2 concentration alone gives no indication of the flux of sulphate pollutants. The gas oxidizes, particularly in the presence of sunlight or fog, to form sulphate aerosols and weak sulphuric acid droplets. The sulphate aerosols are removed from the atmosphere mainly by precipitation, so that the residence time is dependent on meteorological conditions. Within an anticyclone that remains stationary over an industrialized area for a few days, the assimilative capacity of the atmosphere can become impaired, and episode conditions may develop.

b) *Effects of SO_2*

Because SO_2 usually occurs concomitantly with other trace gases and particulates, and because atmospheric relative humidity is an additional relevant consideration, the effects of SO_2 are difficult to isolate. For example, the corrosion of metals is much more rapid in a humid than in a dry climate for the same concentrations of SO_2.

1. *Effects on materials*

Except in a very dry atmosphere, corrosion of metals becomes significant at SO_2 concentrations of about 0.03 ppm/yr. SO_2 also damages building materials such as limestone and marble, causes fading of fabric, dyes and paints, and reduces the life of textiles and leather (NATO, 1971).

2. *Effects on vegetation*

Linzon (1973) has examined the available literature on SO_2 damage to forests and epiphytic lichens. He concludes that there is ample evidence for effects at the following concentrations:

0.02 ppm/yr

0.35 ppm/4 hrs
0.10 ppm/4 hrs combined with 0.10 ppm/4 hrs of NO_2 or O_3
0.55 ppm/2 hrs

3. *Effects on animals*

Animals exhibit a higher resistance to SO_2 than does man. Animal toxicity is therefore not a limiting factor in deriving SO_2 criteria or standards (EPA, 1969).

4. *Effects on humans*

Epidemiological studies are not specific for SO_2. However, the following effects have occurred with the indicated concentrations of SO_2 and particulates.

Accentuation of symptoms in patients with chronic lung disease:
0.23 ppm/day of SO_2 and 300 ug/m^3 of smoke,
Rise in illness rates among elderly bronchitics:
0.27 ppm/day of SO_2 and 150 ug/m^3 of particulates,
Increased mortality (due to bronchitis and lung cancer):
0.04 ppm/yr of SO_2 and 160 ug/m^3 of particulates.

These values are representative of a large number of results summarized in EPA (1969) and NATO (1971).

5. *Effects on biota*

SO_2 is ultimately converted to H_2SO_4 and is removed from the atmosphere in precipitation. These "acid rains" cause acidification of lakes and rivers, leaching of cations from poorly buffered soils (podsols) and the disruption of soil and water ecosystems (Sweden's Case Study, 1971).

c) *Effects of Sulphates*

There is growing evidence to suggest that a number of sulphates may have a significant health effect (Junge and Scheich, 1969; Shy and Finklea, 1973; Brosset, 1973). Whereas SO_2 is largely absorbed in the nose and the upper respiratory tract, sulphate particles (which are mainly less than 0.5 u in diameter) may be inhaled into the lower respiratory tract and may be absorbed to form a weak solution of sulphuric acid.

d) *Feasibility of measurement*

Recommended methods for measuring SO_2 and sulphates are contained in WMO (1974). There are in fact many procedures for measuring SO_2; spectroscopy and flame photometry are probably the best for continuous and remote sensing. Those chemical methods depending on the reducing power of SO_2 may be adequate in the absence of interfering chemicals.

The sulphates, which are always found in the particulate phase, may be measured by titration, if they are acids, or by precipitation as barium sulphate, after collection by high-volume filters.

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D. 2. SUSPENDED PARTICULATE MATTER

a) *Introduction*

Suspended solids in water and particulate matter in the atmosphere both refer to the same physical phenomena, very small pieces of material supported against the forces of gravity in the medium, air or water, for lengthy periods of time by turbulent or molecular motions.

b) *Sources and Sinks of Suspended Solids in Water*

The natural erosion of soils and rocks by surface waters produces most of the suspended solids in water. Organic matter in the process of decomposition also comprises a significant fraction. Industrial and municipal waste waters often contain large quantities of suspended solids. Deposition, either temporarily in river beds and estuaries, or more permanently in the bottoms of eutrophying lakes and in the sea-bed constitute sinks. Normal levels of suspended solids in surface waters are a few milligrams per liter (mg/liter); in some turbulent rivers or highly polluted areas, suspended solids may reach 500 mg/liter.

c) *Biological Effects of Suspended Solids in Water*

The deposition of suspended solids on the bottom of rivers or lakes may blanket the habitat of bottom-dwelling form of life. In some cases, the pumping rate of oysters is reduced, the gills of fish are plugged, or the normal penetration of light into the water is prevented and aquatic photosynthesis is reduced. Of more importance, however, is the decomposition of excess organic material, such as the wood fibres from paper mills. This decomposition requires oxygen; in extreme conditions the oxygen content of the water may be reduced below that necessary to support aquatic life. Some suspended solids contain chemicals that are toxic to certain species, or else that can accumulate in edible species and thus represent a potential hazard to man.

Current ecological evidence indicates that inert, non-toxic suspended solids below 25 mg/liter are not harmful to fisheries, and levels in the range 80 to 400 mg/liter are unlikely to support good fisheries.

d) *Feasibility of Measurement in Water*

The analysis of the suspended solids concentration in water can be done easily by filtration, although characterization by size distribution or by chemical nature requires more elaborate equipment.

e) *Sources and Sinks of Airborne Particulates*

Particles in the air vary in size from 6×10^{-4} to 20 micrometers. Natural processes account for over 90% of the particulate matter in the atmosphere. Of most importance are sea spray, pollens and microorganisms, aerosols formed in the oxidation of naturally-produced chemicals such as hydrogen sulphide, sulphur dioxide and nitrogen oxides, and wind-blown dust. Man-made sources of most importance are combustion and industrial effluents, aerosols formed by oxidation of the gaseous effluents, sulphur dioxide, nitrogen oxides, hydrogen sulphides and ammonia, and hydrocarbon vapors. Precipitation and diffusion to the Earth's surface are the main sinks. Residence time varies from a few minutes for fly ash and large particles, to days and months for the smallest. Background levels are about 10 micrograms per cubic meter (ug/m^3); in some polluted areas, particulate daily averages reach $1000/ug/m^3$.

f) *Effects of Airborne Particulates*

1. *Climatic Effects*

Theoretical considerations suggest that the presence of particulates in the atmosphere lowers the quantity of solar radiation reaching the earth.

Studies of volcanic activity and global temperature indicate atmospheric cooling sometimes occurs for a year or so following intense volcanic eruptions. Direct sunlight is reduced noticeably, particularly in winter, at particulate concentrations averaging 100 to 150 ug/m³.

2. *Effects on Materials*

Corrosion of metals occurs at an accelerated rate of particulate concentrations of 60 to 180 ug/m³ in the presence of sulphur dioxide. In urban areas, rapid soiling rates from particulate deposition are a problem, often resulting in economic loss.

3. *Effects on Vegetation*

Excessive dust may block light needed for photosynthesis and plug stomates, interfering with oxygen and carbon dioxide exchange with the atmosphere. Ingestion of particles containing toxic material such as arsenic deposited on plants can subsequently be harmful to animal health.

4. *Effects on Humans*

Atmospheric particulate matter attenuates solar radiation, particularly in the ultraviolet. This may have a small effect on human health in populated areas, although no convincing epidemiological evidence has yet been presented.

Atmospheric particulates are correlated with the frequencies and severity of respiratory ailments. The size distributions of the particles as well as the total loading are important. A large proportion of particles having diameters from a few microns upwards is removed in the upper respiratory tract, and it is mainly those in the sub-micron range that can reach and be retained in the pulmonary air spaces (NATO, 1971). Unfortunately, monitoring of size distributions is laborious and relatively expensive. Most air quality networks include only observations of 24-hr. total suspended particulates or indirect indicators such as soiling index (which is sensitive to colour as well as to weight of particulates) or a measure of turbidity or solar radiation attenuation.

There is evidence from epidemiological studies that effects on health can be related to the available indices of suspended particulate matter, but equally they can be related to the concentrations of other pollutants that are present at the same time. Acute effects have been demonstrated in atmospheres containing coal smoke, together with other suspended and gaseous pollutants when the 24-hr. average concentration of parparticulates, inferred from a soiling index, has exceeded 250 ug/m³, and the accompanying sulphur dioxide concentration has exceeded 500 ug/m³ (Lawther *et al.*, 1970). Increased prevalence of respiratory illnesses has, however, been associated with extended exposures to lower concentrations than this. Because of the lack of specificity in these studies, results obtained in localities with one particular type of pollution cannot be applied to situations where the mixture is of a different character.

e) *Feasibility of measurement*

1. Atmospheric Turbidity

The sun photometer is a recommended instrument for the WMO air chemistry network (WMO, 1971). Recent US-Canada intercomparisons have revealed calibration drifts in the reference standards at the 0.38u wavelength although the 0.5u wavelength measurements seem to be satisfactory.

Alternatively, the pyrheliometer may be used, but as emphasized (WMO, 1974): "Experience suggests that under very clear conditions, use of pyrheliometers requires considerable detailed knowledge of the characteristics of the instrument (filter transmission factors, etc.) as well as precise information of other attenuating factors such as total ozone and water vapour."

2. Particle size distributions

WMO (1974) has published an authoritative account of methodologies for obtaining particle size distributions. No available method covers the full spectrum of atmospheric particle size.

3. Particulate concentrations

The high-volume sampler is a widely-used instrument in urban air-quality surveys, yielding a 24-hr. weight measurement. The volume of air sampled is determined from readings of a flow indicator and the mass is weighed, permitting calculation of the concentration. There is a risk with this instrument that particles well beyond the respirable size range will be collected.

Other measurements are made by drawing air at relatively low rates through filter paper, and estimating the amount of particulate matter from the reflectance or transmittance of the filter paper.

Further details of these and other methods are given in WHO (1974) and WMO 1974).

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D.3. CARBON MONOXIDE

(a) *Sources, environmental distribution, and sinks*

The world emissions of CO as follows: (in 10^6 tons/year)

Natural Sources	
Oxidation of methane and formaldehyde	3000
Decay and synthesis of cholorophyll	90
Photochemical oxidation of terenes	54
Oceans	220
Total	3364

Anthropogenic Sources (estimated for year 1970)	
Transportation	250
Coal and light	1
Other fuels (oil, gas, kerosene)	1
Industrial processes	41
Incineration (solid waste)	23
Miscellaneous (agricultural burning, etc.)	41
Total	360

The atmospheric residence time and the sink strengths for CO are not well established, and in fact, there has been mild controversy since the discovery in the late 1960's that the tropical oceans are often supersaturated with CO, indicating the presence of a marine biological source. Present estimates of the CO residence times range from 0.2 to 1-3 years.

Robinson and Robbins suggest that there are no proven significant oxidation reactions for CO in the troposphere. Possible sinks include upward diffusion into the stratosphere (believed to be very slow), absorption by the oceans (not proven), precipitation scavenging (Swinnerton *et al.* 1971), and biological uptake (proven but magnitude uncertain). CO as well as CO_2 are used by plants during photosynthesis, the former gas being largely overlooked in field experiments because it is such a small fraction of the latter. The other process that is now believed to be of significance is uptake by soil fungi.

Concentrations of CO as high as 50 ppm occur occasionally on busy urban expressways. Background concentrations are estimated to be 0.14 ppm in the Northern Hemisphere and 0.06 ppm in the Southern Hemisphere.

(b) *Biological Effects*

The affinity of haemoglobin for carbon monoxide is over two hundred times that for oxygen. The absorption of carbon monoxide is associated with a reduction in the oxygen-carrying capacity of blood due to the formation of carboxyhaemoglobin. Normal blood concentration of carboxyhaemoglobin in non-smokers is 0.5%, in smokers 5%. An exposure of eight or more hours to 10 ppm carbon monoxide will raise this level in non-smokers to over 2%. Impaired time-interval discrimination, visual acuity and brightness threshold are observed at levels above 2%.

Cardiovascular changes occur at carboxyhaemoglobin levels over 5%, reached by exposure for eight hours to 30 ppm carbon monoxide. Epidemiological studies indicate that mortality from heart failure may be increased by exposure to average weekly concentrations of about 10 ppm. Due to the time lag between exposure to carbon monoxide and the formation of carboxyhaemoglobin in the blood, short-term exposures to higher carbon monoxide levels are not considered to be as hazardous as long-term exposures to low levels.

Concentrations of carbon monoxide, needed to affect plant growth and microbial activity, are much higher than normally encountered in ambient air. Detrimental effects have not been detected at levels less than 100 ppm for durations of one to three weeks.

(c) *Monitoring of Carbon Monoxide*

In view of its high urban levels and low threshold for physiological effects, the continuous measurement of carbon monoxide in urban areas is advisable. This may be accomplished with infrared analyzers, which are sensitive to carbon monoxide in the range 1 to 25 ppm. Non-urban data, requiring more sensitive detectors, may be acquired by gas chromatography or with a mercury vapor analyzer.

It is important that the significance of the oxidation of methane as a source of carbon monoxide be established.

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D.4. CARBON DIOXIDE

(a) *Sources, environmental distribution, and sinks*

Natural emissions of CO_2 include respiration by living matter and releases during decay of organic materials.

Man releases CO_2 into the atmosphere by burning organic fuels and by kilning of limestone. The emissions have been increasing steadily in recent years; Keeling (1973), for example, estimates an output rising from 1.2×10^9 metric tons in 1929 to 3.8×10^9 metric tons in 1968.

The average atmospheric CO_2 concentration around the world is about 330 ppm at the present time and it seems to be rising at the rate of about 1 ppm per year. The residence time in the atmosphere is about 2.5 years (Robinson and Robbins, 1972).

The principal sinks for CO_2 are the biosphere and the oceans. In the latter case, there is a strong dependence on sea temperature and on the pH of the surface mixed layer.

(b) *Biological effects*

At normal environmental concentrations, CO_2 has no harmful effects on biological systems. The gas is, in fact, essential for the growth of most plants.

(c) *Climatic effects*

Atmospheric CO_2 is one of many elements affecting world climate. Because CO_2 absorbs long-wave terrestrial radiation (in selected wavebands), consideration of the radiative transfer properties of the atmosphere must always include examination of the effects of a change in CO_2 concentrations, which could influence the vertical distributions of heat and temperature.

(d) *Feasibility of measurement*

1. *Atmosphere*

For biome studies, an instrumental sensitivity of 2 ppm is quite sufficient (the diurnal and annual ranges in CO_2 concentrations over vegetation are of the order of 10 to 30 ppm). This sensitivity is easily achieved with a number of commercially available instruments.

For climatic studies, a sensitivity of 0.2 ppm is required, and reference standards must maintain their stability over decades. Infra-red non-dispersive sensors are recommended (WMO, 1974), although there is still some doubt about their absolute calibrations.

(2) *Fresh and salt water*

Gas chromatography is recommended. Samples must be sealed, and analysis should be done immediately. If samples are stored, they must be maintained at the temperature of the water at the time of collection, to minimize loss of the gas to the atmosphere (Henry's Law).

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D.5. ATMOSPHERIC OXIDES OF NITROGEN

(a) *Sources, environmental distribution and sinks*

Nitrogen, which comprises almost 80% of the atmosphere, is a relatively inert gas not particularly soluble in water. Nitrogen *fixation* is the process by which nitrogen is incorporated into living tissues. This occurs through a variety of biochemical pathways.

Three oxides of nitrogen are of importance in environmental studies:

N_2O - nitrous oxide
NO - nitric oxide
NO_2 - nitrogen dioxide

Another nitrogen compound of significance is ammonia (NH_3), which is discussed in Section D. 10.e.

The major global sources for the nitrogen oxides are as follows (in 10^6tons per year, where the values have been converted to NO_2 equivalent) (Robinson and Robbins, 1972).

N_2O (bacterial action)		592
NO_2 (forest fires)		0.8
NO_2 (industrial)		
Burning of coal	26.9	
Burning of petroleum	22.3	
Burning of natural gas	2.1	
Incineration	0.5	
Burning of wood	0.3	
Total	52.1	

Lightning is not believed to contribute significantly to the fixation of nitrogen on the world scale. Hahn (1974) has recently suggested that the North Atlantic is super-saturated with N_2O and therefore must be an additional source.

NOx emissions are associated chiefly with combustion processes, occurring whenever the temperature exceeds 1000° C. and whenever the combustion gases are quenched so rapidly that dissociation back to nitrogen and oxygen is prevented. The major oxide in combustion emissions is NO but a small fraction is converted to NO_2 by reaction with oxygen during the exhaust dilution process.

NO and NO_2 are active photochemically, contributing to the production of oxidants (See Section D.6). NO may be oxidized to NO_2 during such periods. The resulting particulate biproducts are then scavenged, usually in a few days, by precipitation.

The other oxide, N_2O, has a very large natural cycle. Small fractions are lost to the stratosphere but the major portion is used by vegetation, and is, in fact, an important nutrient.

Global background concentrations of the 3 oxides are as follows:

N_2O	0.25 ppm
NO	6 ppb or less
NO_2	6 ppb or less

The residence times are 3-4 years for N_2O and about 4 days for NO and NO_2.

(b) EFFECTS

(1) *Effects on Humans*

At normal atmospheric concentrations, nitrous oxide has no known adverse effects.

Due to the rapid conversion of nitric oxide to nitrogen dioxide, the two are often combined as NOx when discussing their effects. Acute exposure to NOx causes nasal and eye irritation at 12 ppm, pulmonary discomfort at 50 ppm, bronchiolitis at 50 to 100 ppm, bronchiolitis fibrosa at 150 to 200 ppm, and bronchopneumonia at 500 ppm. Chronic exposures at NOx levels of 10-40 ppm cause lung damage, leading to fibrosis, reduced breathing capacity and increased respiratory resistance. An epidemiological study showed that people living in an atmosphere with annual average NOx concentrations of 0.08 ppm exhibited reduced respiratory performance and a larger frequency of acute respiratory illnesses, compared with controls elsewhere in the same city.

2. *Effects on Vegetation*

Chronic exposures to 0.15 ppm NOx and acute exposures to 2.5 ppm cause obvious damage to tomato plants. Many other species of commercial value are similarly affected.

3. *Effects on Climate*

An increase in tropospheric N_2O could cause an increase in stratospheric NOx, which in turn would affect the radiation balance of the atmosphere,

c) *Feasibility of measurement*

1. N_2O: A gas chromatography method is recommended (WMO, 1974).
2. NO, NO_2, and NOx: A recommended procedure has been given by WMO (1974), using the principle of the chemiluminescent reaction of ozone with NO. To monitor NOx, the NO_2 is converted to NO before the gas stream reaches the sensor. The concentration of NO_2 is then obtained by subtraction. A laser florescent technique has also been proposed (Birnbaum *et al.*, 1974). For baseline observations, Nash (1974) has used a modified Saltzman reagent and subsequent colorimetric determination, with a sensitivity of about 0.2 ppb.

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D. 6. OZONE, PHOTOCHEMICAL OXIDANTS AND REACTIVE HYDROCARBONS

a) *Sources, environmental distribution, and sinks*

Oxidants are highly-reactive gases formed photochemically, usually in the presence of NOx and hydrocarbons. One of the well-known oxidants is ozone (O_3), which is also generated during lightning, and in the stratosphere due to photolysis of O_2 to atomic oxygen with subsequent conversion to O_3.

The hydrocarbons may be of natural origin, e.g., forest terpenes, or may be released by man into the atmosphere. Hydrocarbons are classified according to their molecular structure; acyclic, alicyclic and aromatic. The third type is believed to have the most direct link with human health but it cannot be monitored operationally as yet. There is, of course, a wide range of hydrocarbons, many of which are volatile and occur as gases in the atmosphere.

Sunlight has no appreciable effect on hydrocarbons alone. In the presence of NOx, however, intermediate and secondary products are formed, some of which do have detrimental effects on materials, vegetation and man. The reactivity of hydrocarbons varies greatly, methane being the least reactive although the most ubiquitous—with large natural sources due to bacterial decomposition processes in swamps and marshes.

Robinson and Robbins (1972) have made the following estimates of global total and reactive hydrocarbons.

Sources	*Total hydrocarbons* 10^6 tons/yr	*Reactive hydrocarbons* 10^4 tons/yr
Burning coal	2.9	40.8
Burning oil	40.6	1594
Evaporation losses from oil	7.8	156
Evaporation of solvents	10	150
Incinerators	25	750
Wood burning	0.7	10.5
Forest fires	1.2	25
Terpene-type releases from vegetation	170	?
Methane from swamps	310	small

The photochemical products of present interest are:

1. ozone (O_3),
2. nitrogen dioxide (NO_2), formed primarily by the photo-oxidation of nitric oxide (NO),
3. aldehydes, particularly formaldehyde,
4. peroxyacyl nitrates, particularly peroxyacetyl nitrate (PAN).

No doubt, related substances will become important when detection methods improve and when the photochemical processes are better understood. The term *total oxidants* usually means the gases O_3, NO_2, and the peroxyacyl nitrates.

Global background concentrations of methane (CH_4) are about 1-2 ppm. The residence time is about 1 to 4 years, in contrast to the residence times of a few hours to a few days for the reactive species. Total hydrocarbons in urban areas have yearly average concentrations of from 5 to 15 ppm (as carbon). The reactive components are generally in the ppb range.

Total oxidants in forests, resulting from terpene photochemical reactions, may reach 0.06 ppm, as compared with global background values of about 0.01 ppm. In Los Angeles during smoggy days, concentrations can exceed 0.50 ppm. In this connection, note should be made of the fact that because the photochemical process requires several hours to complete, the highest concentrations of oxidants and of other products may occur downwind of a city, rather than in the Central Business District.

b) *Effects*

1. *Effects on Humans and Animals*

a) *Ozone*. Nasal irritation occurs at ozone levels of 0.05 ppm, headaches are experienced at 1 ppm for exposures over 30 minutes, changes in several visual parameters have been observed at 0.2 to 0.5 ppm, pulmonary congestion and changes in respiratory efficiency occur at 1 ppm. At levels of 0.25 ppm, increases in attacks among asthmatic patients were observed. Lung tumor incidence doubled in mice exposed to 1 ppm ozone daily for 15 months.

b) *PAN.* Peroxyacetyl nitrate induces an increase in uptake of oxygen at 0.3 ppm, eye irritation is detected at 0.5 ppm.

c) *Reactive Hydrocarbons.* Throat and eye irritation at 0.5 ppm is reported. Brief exposures of guinea pigs at 1 ppm formaldehyde caused temporary changes in respiratory efficiency.

2. *Effects on Vegetation*

a) *Ozone.* Tobacco is injured by exposure to 0.05 ppm ozone for four hours; 0.1 ppm for two hours damages spinach, corn and beans. Synergistic effects with sulphur dioxide reduce the threshold for injury to some plants.

b) *PAN.* PAN is the primary phytotoxicant generated in photochemical smog. A four-hour exposure to 15 ppb of PAN causes injury to tomato and lettuce plants.

c) *Reactive Hydrocarbons.* Ethylene concentrations of 1 ppm are sufficient to injure sunflower, tomato and potato plants.

c) *Feasibility of Measurement*

The chemiluminescent reactions of ozone with ethylene or nitric oxide may be used to measure ozone very accurately, without interferences. Colormetric and coulometric techniques are available for the determination of total oxidant concentrations. Gas chromatography is suitable for monitoring hydrocarbons and PAN levels; flame photometric detectors are most suitable for the former, electron capture detectors for the latter. The aldehydes can be measured with colorimetric techniques using a bisulphite reagent, but the method is only moderately sensitive.

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D. 7. TOXIC METALS

a) *Mercury*

The chemical and toxicological properties of inorganic mercury ions, elemental mercury and organic mercury derivatives are so different that they must be discussed separately.

Elemental Mercury

Mercury vapour is present in air due to degassing of the earth and industrial contamination. Past exposures in industrial workplaces indicate that 0.1 to 1 mg Hg/m^3 air is toxic. Mercury values in San Francisco were a few nanogram/m^3. One gram of liquid mercury can be taken by mouth with no observable effect.

Inorganic Mercury

Mercury is a normal constituent of many rocks and soils and thus of plants used as food. About 1 g of mercuric chloride will produce severe acute poisoning in humans. About 50 mg/kg is needed continuously in the diet to produce chronic toxic symptons in rats.

Methyl mercury

General: Methyl mercury is completely absorbed from the gastro-intestinal tract into the blood. About two months after ingestion starts in humans, neurological symptoms of toxicity appear. The first symptom is paresthesia-numbness of the extremities. Later symptoms are ataxia (loss of control of limbs) and constriction of vision. Severe cases are fatal. After ingestion ceases, there is often slight improvement but the brain damage is largely irreversible, even though the methyl mercury content of the body falls back no normal.

Methyl mercury is excreted largely via the faeces. The concentration in the blood is a good indication of total body burden. The half-life varies greatly with species, being about two weeks in the rat, 70 days in humans, and several hundred days in some species of fish. From the half-life and blood concentration, the daily intake needed to produce a given body burden can be calculated.

Release of Synthetic Mercury to the Environment:

A derivative of methyl mercury is used as a fungicide on cereal grains to be used as seed. Birds that eat the grain accumulate excessive methyl mercury. There have been many tragedies where treated grain has been unknowingly ingested by humans. In the latest of these in Iraq, the death toll has been estimated at several hundred.

In two locations in Japan, methyl mercury was discharged in factory effluents into the sea. Fish can concentrate methyl mercury several thousand fold from the surrounding water. The contaminated and dead fish were eaten by local fishermen and their families. Many deaths and disabilities resulted. The methyl mercury blood concentration and total body burden were measured on survivors of these tragedies. The body burden for the mildest symptoms (paresthesia) is estimated to be 30 mg for an adult and the daily intake needed to produce this burden is 1% of the burden or 300 ug/day. Blood levels were about 200 ng/m*l* for the mildest cases and several thousand ng/m*l* for severe ones.

People who do not eat fish have total blood mercury values of 2-5 ng m*l* and "normal" fish eaters about 10 ng/m*l*.

Biosynthesis of Methyl Mercury in the Environment:

In streams and lakes, where large amounts of inorganic mercury have been dumped into the sediments, the fish have concentrations of methyl mercury in the flesh, of a few ug/g and as high as 25 ug/g, The mercuric ion is methylated by bacterial action and the methyl mercury accumulated by the fish in some way. Many areas have been closed to fishing as a result. As the mercury is strongly absorbed by the sediments and the sediments are often only slowly moved or covered up, the situation can be expected to last many years.

There are as yet no human poisonings from "biosynthetic" methyl mercury but a few individuals in Sweden and Canada who continuously eat fish from contaminated areas have blood mercury levels near the expected toxic value without showing any symptoms.

Mercury in Food

Total mercury in food comprises both inorganic and methyl mercury and might average 10 ug/person/day. An approximation which is not strictly true is that all mercury in fish is methyl mercury and in other foods inorganic mercury. The mercury values in most foods are so low that the analysis for methyl mercury becomes difficult. Fish with more than 0.5 ug/g of total mercury are not sold in North America. Most fish in commerce are much below this and an average might be 0.1 ug/g.

Analysis of Mercury in the Environment

Mercury in the air is so low as to be of no concern. Mercury in soil is bound, is a natural constituent and again is of no concern. Total mercury in waters is of the order of 1 ug/litre and is easily measured. Few separate measurements of the more important methyl mercury have been made. Because of the great concentration of methyl mercury by fish and because they probably represent the largest source of methyl mercury in food, monitoring of fish probably represents the easiest way to monitor mercury in the environment.

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D.7. (b). LEAD

a) *Sources, environmental distribution and sinks*

Lead is a natural constituent of all soils and plants. The concentration in plants varies, depending on the plant species, time of year, soil properties, and concentrations in the soil. Lead concentration in soil is generally highest in the surface few centimetres.

Significant sources of lead in the environment include that emitted in engine exhausts as a result of the combustion of tetraethyl lead in gasoline, liquid and airborne particulate wastes from coal burning and metal smelting and lead arsenate pesticides.

The particles from gasoline combustion are emitted in two size ranges. The smaller ones are about 0.2 um in diameter, formed by direct condensation as the combustion gases cool. This size of particle remains suspended in the atmosphere by air movements and thus may be transported long distances. Lead has been found in Greenland glacier cores. The particles are removed only by precipitation or by agglomeration into larger particles. Moreover, these particles are in the size range most likely to be deposited in the alveoli of the lungs. The larger particles emitted, which are approximately 5 um in diameter, are formed when lead deposited on the inside of the exhaust system flakes off due to mechanical vibration. These particles are dense and only travel short distances (typically up to 200 m from the point of emission). If inhaled, they are deposited in the upper respiratory tract and swept upwards by ciliary action and subsequently swallowed. The lead in one cubic metre of air is 5 - 25 ug at busy city intersections 2 m above the curb, 0.5 - 3 ug in suburban gardens and 0.1 to 0.5 ug in rural areas away from roads. Particle size-distribution measurements are rarely performed. Concentrations in buildings when the windows are closed are about half of those outside.

Lead in the dustfall from air is retained in the surface soil and accumulates together with that derived from decaying vegetation. High lead contents (up to 1 g/kg or more) have been found in soils near industrial sources and in roadside dust in the vicinity of heavy traffic. In water, lead is partially absorbed by sediments and transported with them. Lead concentrations in natural waters are about 10 ug/litre.

b) *Effects of Lead*

Plants: Lead is not toxic to plants at any concentration normally found in soils.

Domestic Animals: The most sensitive domestic animals are young horses. The estimated lethal dietary level is 100 mg lead/kg dry weight of feed or 2 mg lead/kg live weight of animal per day, when fed at this level over many weeks. Some deaths of colts have been reported near lead smelters.

Aquatic Animals: The toxicity of lead to aquatic animals varies with the temperature, pH and hardness of the water, in particular. The most sensitive species (e.g., salmon and trout) die after 4 days exposure to 0.14 - 1.0 mg lead/litre in soft water.

Man: Adults—The often-heard statement that "lead is a cumulative poison" is only true for intakes above normal. For most people, the lead absorbed from the alimentary tract and lungs (the uptake) is balanced by excretion via hair, sweat, gastro-intestinal tract and by way of the urine. If lead uptake rises, the rate of excretion follows this trend, but it may require many months or years to achieve a new equilibrium. The excess uptake, if limited, will be stored in the bones where it is largely inert and does not produce the symptoms of lead intoxication (95% of total body burden is located in the bones). Only if the excess rate of lead uptake exceeds the rate at which the element can be laid down in the bones will the soft tissue concentration rise to give the typical symptoms of lead poisoning. This is a reversible process and most adults who suffer from lead poisoning recover without permanent harm when excess uptake terminates. The half-life of lead in adult bones is estimated to be several years. Clinical symptoms of poisoning do not occur in the adult until the blood lead values rises to at least 80 ug/100 g whole blood. Clinical effects include anemia, basophil stippling of red blood cells, kidney damage with aminoaciduria, tiredness, gastro-intestinal distress with constipation or diarrhoea, and nausea. Permanent neurological consequences may occur in 25% of those cases of acute lead encephalopathy occurring in children.

Criteria are required to relate the uptake (the total amount of lead absorbed by the body) to the above stages. The uptake is not measured directly, but calculated from the intake and adjusted using an absorption factor.

Most lead uptake is derived from food in which the lead content varies greatly. Older estimates in North America and present estimates in Britain suggest that the average person ingests about 300 ug/day with great variation from day to day according to the food selected. More recent estimates from diet studies in Canadian cities and on convicts in New York prisons, together with faecal analyses of American women, indicate the intake to be 120 - 140 ug/day. Most authors agree that only about 10% of the lead in the diet is "digested", so that uptake from food will be from 12 to 30 ug/day.

Drinking water has an average lead concentration of approximately 10 ug/litre. With an intake of 2 *l*/day, the intake from water would be 2 ug lead/day.

The calculation of lead uptake from air for an urban dweller is more difficult to estimate. First, the concentration of lead in air varies according to location, from bedroom to city street to office. Second, the deposition of lead in the lungs has never been measured in a normal urban atmosphere. Instead, the figure of 36%, measured by Kehoe on lead sesquioxide particles at a concentration of 150 ug/m^3, is assumed to be a reasonable estimate. Recent electron micrographs of urban air particulates by Lawther *et al.* seem to show very small, dense particles aggregated on less dense carbon particles. The behaviour of these aggregates in the lung is unknown and may well be very different from the action of lead sesquioxide. Lead particles, once deposited in the alveoli, are assumed to be completely absorbed since *post mortem* analyses of lungs have shown the same lead concentration as that found in other soft tissues. Daily lead uptake from lungs may be roughly estimated by multiplying the following factors:

> 15 m^3 of air inhaled/day; 1 ug lead/m^3 air averaged for 24 hours; 36% deposition inhaled lead in alveoli; 100% absorption of deposited lead for a total of 5 ug/day.

The total normal lead uptake from all sources is then in the range of 19 to 37 ug/day.

Epidemiological surveys in the United States show no correlation between the blood lead values of suburban women (mean about 16 ug/100 g) and exposure to air lead concentrations in the range 1 to 3.5 ug/m^3 (annual means). Kehoe showed that a subject whose total lead ingestion was 600 ug/day (60 ug uptake) was still in equilibrium. Ingestion of 3000 ug/day (300 ug uptake) resulted in a net accumulation, although the experiment was not carried for a sufficient time to determine if a new equilibrium could be established before toxicity symptoms ensued. Present-day industrial hygiene standards (299 ug lead/m^3 of air for an 8-hour day) suggest that an uptake of roughly 600 ug/day may be sustained without producing clinical symptoms, but causing blood lead values to rise to about 80 ug/100 g blood.

Children—Comparable figures for lead metabolism in children are not known. Extrapolations on the basis of body weight corrections are likely to be unreliable and the capacity for storage in bone is most certainly very different. The symptoms of lead poisoning in children differ from those of adults. Those who survive a severe case of encephalopathy may be permanently impaired. The fact that some cases have blood lead values slightly above 40 ug/100 g is sometimes stated as evidence that children are more susceptible to lead poisoning than adults. This may be so, but the uptake of lead per kg body weight required to produce these blood levels is unknown. It should be borne in mind that blood only acts as a carrier of lead and is not necessarily closely related to lead concentration in the brain.

Lead poisoning is most often induced in children by eating old lead paint (a habit called pica) or in the general population by drinking soft waters that have passed through lead pipes or by consuming contaminated, illegally-distilled whiskey. None of these causes would seem to have a place in environmental monitoring. Lead in the air is not as yet contributing to ill-health.

c) *Feasibility of Measurement*

Lead in air is easily assayed using filters and high-volume samplers. Particle sizing is more difficult. The lead in biological samples (as small as a drop of blood) can be measured fairly easily by atomic absorption or anodic stripping voltemetry, although reproducibility may suffer by using such small samples. The total amount of lead released to air in any area can be calculated from gasoline consumption figures and, as gasoline is the main source, large changes in air concentrations will only follow changes in gasoline consumption or its lead content.

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D. 7. (c) CADMIUM

1. *Sources*

Cadmium is universally distributed in the natural environment at low levels. Local concentrations are found in association with zinc, and most cadmium production is a by-product of zinc smelting. Major uses include electro-plating, pigments and electrical uses.

Some rivers carry substantial quantities of cadmium: it is not yet clear whether this 'is derived primarily from natural sources or from leaching or mine tailings. Effluents from electroplating industries can also contain cadmium.

Smelters can release cadmium into the air but air transport of the particles is usually short-range and significant contamination only occurs within a few kilometres of the source.

Cadmium is taken up from soils by plants and from water by aquatic plants and animals. Highest concentration factors (10^3 - 10^5) have been reported for plankton and shellfish. Cadmium levels do not appear to increase in passage up food chains, but relatively high levels have been reported in some long-lived marine birds and mammals. Among animals used for human food, highest concentrations are found in shell fish (often 1 ppm and up to 20-50 ppm in some polluted areas).

Effects

Some adverse biological effects have been reported in highly polluted areas near smelters, but these cannot be uniquely associated with cadmium in the presence of other pollutants. Adverse effects on reproduction of fish have been reported in the laboratory at levels (1-10 ug/litre) similar to those found in many natural fresh waters. However, no unequivocal adverse effects on natural populations have been demonstrated.

An outbreak of cadmium poisoning occurred in Japan in the 1940's and was called "itai-itai" disease. It was restricted to women over 40 who had borne several children and lived in one polluted area. Obviously other factors than cadium were involved and the complete explanation is now unlikely to be known as new cases no longer arise.

Cadmium is potentially one of the most dangerous toxic elements as it is truly accumulated in the human body. Estimations of the half-life of cadmium in humans are imprecise, but are around 20-30 years. The greater part of the total body burden is stored in the liver and kidney cortex which is the most sensitive organ. When cadmium concentration reaches 200 mg/kg in the kidney cortex, symptoms of kidney damage (protein in the urine) appear. Cadmium in the body rises to a maximum at about age 50. Cadmium in the kidney cortex of normal populations is about 25-50 mg/kg. It has also been suggested that higher exposures to cadmium are statistically associated with renal ischaemic hypertension and elevated death rates. Although this is not universally accepted, the safety margin is small and concern should be expressed for high exposure groups such as habitual shellfish eaters.

Estimates of human intake from all sources (mainly from food) range from 15 to 70 ug/day. Locally significant intakes may occur from drinking water. Absorption from the gut is low, about 5%, but absorption through the lungs is much more efficient and there is some evidence that cigarette smokers ingest significantly larger quantities (up to 3 times larger) than non-smokers. It can be calculated that an intake of 62 ug/day will produce a kidney cortex concentration of 50 mg/kg by age 50.

The relative proportion of the present cadmium intake derived from "natural" cadmium always present in the environment compared with "pollutant" cadmium released by man's activities is unknown.

Monitoring

A number of methods are available for estimating cadmium levels in environmental samples. Although these have given good results when carefully calibrated, interlaboratory comparisons have often shown poor agreement. Efforts to improve standardization of techniques are needed before a large-scale monitoring scheme can be set up. Food, especially shellfish from polluted areas, should be the main concern.

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D. 8. HALOGENATED ORGANIC COMPOUNDS

Residues of chlorinated hydrocarbons, particularly DDT, its metabolite, DDE, polychlorinated biphenyls (PCB's) and dieldrin, have been identified in man and wildlife from even isolated regions of the world. Chemists initially developed halogenated organic chemicals for their inherent stability against physical and biological degradation. They have been used widely in a number of industrial applications. Some are biologically active and used extensively as persistent pesticides. Generally, compounds identified as having significant environmental effects contain chlorine.

There is strong evidence that DDT and its metabolite DDE, dieldrin and polychlorinated biphenyls (PCB's) have significantly contributed, singularly or in combination with other pollutants, to population declines in a number of fish and fish eating birds.

DDT and its metabolites, dieldrin and PCB's are concentrated from water into the fatty tissues of fish and other aquatic organisms by up to one hundred thousand times. Thus, the exposure of aquatic organisms to seemingly insignificant levels of these pollutants can result in levels which are of biological significance. Chlorinated hydrocarbons tend to accumulate in large lakes and oceans which act as sinks. It is thus not surprising that high residues and populations demonstrated to be affected by chlorinated hydrocarbons are associated with fish and fish-eating birds.

The deleterious effects of dieldrin and other chlorinated hydrocarbons have also been linked to population declines in terrestrial organisms exposed through the application of these insecticides in agricultural and forest pest control programs.

Is man affected by chlorinated hydrocarbons?

Generally, chlorinated hydrocarbons are not particularly toxic to mammals. At the present levels found in the environment, dieldrin, PCB's or DDT are not expected to produce significant effects in the general population. Of course the diet of the general population does not include large quatntities of food such as fish, containing the higher levels of chlorinated hydrocarbons. However, breast-fed infants do receive relatively high exposure to chlorinated hydrocarbons including PCB's, dieldrin and DDT and its metabolites. Levels of aldrin and dieldrin in human milk (locally exceeding 0.1 ppm) approach levels which affect laboratory animals.

An outbreak of mass human poisoning through consumption of rice oil containing PCB's was reported in Japan. The lowest exposure causing effects is estimated to be about 200 ug/kg/day. It is likely that the observable effects were related to extremely toxic contaminants, chlorinated dibenzofurans (CDBF's) found in some commercial mixtures of PCB's.

What are the demonstrated effects of PCB's dieldrin, DDT and DDE?

The reproductive success of both mammals and birds can be severely decreased upon continued exposure of laboratory animals to these compounds. Some of the effects which lead to a decerased reproductive success include decreased hatchibility, increased egg production, delayed increased susceptibility to disease, decreased egg production, delayed breeding, the production of thin-shelled eggs and decreased litter size. Both aquatic invertebrates and vertebrates are affected at low levels of these chlorinated hydrocarbons in the water. Dieldrin is more toxic than either DDT or PCB's upon a short exposure. Some of the other effects include induction of microsomol enzymes, porphyria, immunosuppression and decreased resistance to stress. Combined effects of the chlorinated hydrocarbons have been observed and total residues of chlorinated hydrocarbons at the higher trophic levels do exceed those which can produce effects in laboratory animals.

What are the effects of the declining production of DDT, PCB's and dieldrin?

Models indicate that the atmospheric cycling of these persistent pollutants throughout the world is accompanied by a significant lag before the ocean sink will reflect this decline or other changes in the use patterns of persistent chlorinated hydrocarbons.

Methods of Measurement:

DDT, PCB's and dieldrin can be measured qualitatively in environmental samples by means of gas-liquid chromatography with electron-captive detection. Because of the large number of organochlorine and other interfering substances, periodic confirmation of identification with mass spectrometry is necessary. Techniques are relatively standardized and some international agreement on methods has already been reached. The Codex Alimentarius (1972) recommends monitoring methods for biological materials and water. However, the required equipment is relatively sophisticated, analyses are slow and time-consuming and considerable efforts in training and standardization would be needed before a large-scale monitoring system can be set up. Thus, it will be necessary to choose indicator species with extreme care if a meaningful and economically-realistic program is to be developed. Since fish or mollusks concentrate chlorinated hydrocarbons, they can serve as better monitors than direct sampling of drinking water. For most of the other chlorinated hydrocarbons, adequate analytical methods are at present in the development stage.

The monitoring program must contain provisions for the periodic review and inclusion of other chlorinated hydrocarbons which may be recognized in the future as having deleterious environmental effects. Particularly, the program should consider the inclusion of chlorinated dibenzofurans and chlorinated dibenzo-p-dioxins in the future. These compounds have been identified as extremely toxic contaminants in mixtures of PCB's and derivatives of chlorophenols. Analytical techniques are not presently capable of detecting these compounds in environmental samples at the lowest levels where toxic effects are expected to occur. They are powerful mutagens or teratogens and the most common effect of human exposure is chloracne.

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D. 9. PETROLEUM HYDROCARBONS IN WATER

a) *Sources, environmental distribution, and sinks*

Crude oils are developed in nature by the decomposition of animals and plants in sediments laid down mainly under estuarine and marine conditions of rapid sedimentation. They are usually found in Tertiary formations and collect in geological reservoirs from which they are abstracted by drilling.

Oils vary greatly in their composition and physical properties. The principal component hydrocarbons are straight and branched chain paraffins, naphthenes and aromatics. Impurities are mainly sulphur compounds, nickel and vanadium, usually in low concentrations. The quantities spilled during the production, transport or handling of oils either by accident or design have been estimated to be well in excess of 10^6 tons per year. Almost all oil spills occur at sea, the greatest quantities resulting from tanker accidents, of which the 'Torrey Canyon' spill of 1967 of more than 100,000 tons is the largest so far recorded. Blow outs from exploratory and production wells account for a smaller proportion but include the Santa Barbara Californian spill of 10-20,000 tons. Smaller but more persistent seepages are common from pipe lines at production platforms and at terminals.

Petroleum hydrocarbons are not particularly biodegradable, although microbial activity is believed to be effective in some instances and is the subject of continuing study at the present time.

b) *Effects*

The hazards caused by escaping oils are in part due to their viscous nature when on the surface of the sea. Numerous and well authenticated reports record the deaths of birds (sometimes in thousands) alighting or diving through the surface of oil slicks, and of mammals (whales, porpoises, seals, etc.) which break the surface periodically, and are in part due to the toxicity of some oils.

There is substantial evidence that hydrocarbons of low carbon number are more toxic than those of high carbon number and that the order of toxicity of hydrocarbons of like carbon number is in descending order of aromatic hydrocarbons, napthenes and paraffins. Most oils are toxic on first release through the solution and emulsification of the lighter fractions, but dependent upon water temperature and wind conditions, the greater part of the lighter fractions are lost rather quickly to the air by evaporation. Weathered oil of 2 or more days in the sea is remarkably non-lethal to marine organisms.

The main hazards of oil pollution to marine organisms are probably due to long-term, low concentrations, but there is a need for continuing and more intensive research on the sublethal effects of oils, expressed as lowered viability to other environmental stresses, and in lowered growth rates and reproductive capacity.

The oceans have a rather large assimilative capacity, of course. In estuaries, inland lakes and marshes, on the other hand, oil can accumulate in bottom sediments, resulting ultimately in the death of micro-organisms and the impoverishment of bottom fauna. Bengtsson and Berggren (1972) have described a lake near Stockholm that is in this condition, while Ehrhardt (1972) has found petroleum hydrocarbons, including aromatics, in oysters in Galveston Bay, Texas.

c) *Feasibility of measurement*

Oil presence in the oceans can be monitored as visible sheens, by infrared photography, by gas chromatography analyses (Ehrhardt and Blumer, 1972) and by the abundance of tar balls and residues which are relatively resistent to evaporation and biodegradation. The measurement of Total Organic Carbon (TOC) may be convenient for use on the global scale. Also, it must be emphasized the hydrocarbon-type effluents exert an oxygen demand (on receiving waters) that is mostly of the *chemical* rather than the *biochemical* type; for this reason, measurement of *Chemical Oxygen Demand* will give more meaningful information than Biochemical Oxygen Demand (BOD).

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D. 10. SELECTED INDICATORS OF WATER QUALITY

a) *Biochemical oxygen demand (BOD):*

This is a test that measures the amount of oxygen (in milligrams per liter) required for the biological degradation of organic matter in water. It is a relatively simple test to perform, and is usually done on a 5-day basis during which the sample is incubated at 20°C, with results expressed as a "BOD$_5$" value. As such, the test is also a measurement of the rate of oxygen requirement in a 5-day period, and this information is important because too high an oxygen demand can deplete the dissolved oxygen concentration in receiving waters (as discussed in the next section). However, it must be understood that the BOD test is not a measurement of the *total* oxygen demand; instead, it provides an estimate of the short-term oxygen demand. Recent research indicates that BOD$_5$ tests should be supplemented by measurements of concomitant Chemical Oxygen Demand (COD), which is a much more rapid test that provides a measurement of the oxygen demand arising from strictly chemical (i.e., non-biological) reactions. BOD_5 measurements are of particular significance in grossly polluted waters; otherwise, the BOD_5 values will usually be below 5 milligrams per liter, and below 2 milligrams per liter in relatively uncontaminated waters. Another method for potential oxygen demand is coming into use: this is a measurement of Total Organic Carbon (TOC) which is even more rapid to perform than the COD test; however, TOC measurements require special instrumentation and, therefore, may not be as convenient.

b) *Dissolved oxygen (DO):*

This is undoubtedly one of the most important indicators of water quality, in terms of ecological evaluation. Just as human beings are dependent on the oxygen present in the air they breathe, so fish and other aquatic life are dependent on the dissolved oxygen content of the water. The saturation-point of oxygen in water is temperature-dependent: at 20°C, the solubility of oxygen in water is 9.1 milligrams per liter; at 25°C, it is 7.5 milligrams per liter. When large quantities of waste-materials are discarded into waterways, they can require more oxygen (for their decomposition) than can be supplied by the receiving waters; this can be a long-term process, especially when some wastes settle and accumulate on the bottom where they undergo gradual decomposition. The consequence of this can be a reduction, and even depletion, of the water's dissolved oxygen. Not only does this impose a stress on aquatic life, but it can eventually eliminate many species that are valuable to man. Furthermore, the depletion of dissolved oxygen can mean that the accumulated wastes will then undergo decomposition by anaerobic (i.e., non-oxidative) processes, with concomitant production of malodorous gases such as hydrogen sulfide. The end-result can be a stagnant, putrid body of water. As a mere illustration of extremes, a dissolved oxygen concentration of greater than 7 milligrams per liter can be termed desirable, but concentrations below 2 milligrams per liter are viewed as undesirable. In so saying, it must be remembered that, in large bodies of water such as lakes, the "natural" distribution of dissolved oxygen will vary according to depth; in comparison, a turbulent stream will have a more uniformly-mixed distribution of oxygen. Dissolved oxygen is easily measured by titration or continuous recorders.

c) *pH:*

The term "pH" refers to the negative logarithm of the free hydrogen ions present in water. Accordingly, this means that a low pH refers to high acidity, whereas a high pH is indicative of high alkalinity. The discharge of wastes that are either highly acid or highly alkaline can have a severe impact, particularly in receiving waters that have a low mineral content (and thus, will have low "buffering capacity"), because there are not enough chemicals in the water to permit "neutralization" of the acids or alkalis. If the pH of the receiving waters becomes too low or too high, the water can have a corrosive quality and can adversely affect aquatic life. For instance, extreme pH values such as a low pH of 3 or a high pH of 11 can kill all fish species within a few hours, whereas there is fairly general agreement that a desirable pH range is within 6.5 to 8.5. Variations above or below this optimum range can, if sustained, impose severe stress on some species of aquatic life. It is also important to mention that some toxic substances that may be released in water can have enhanced toxic properties in certain regions of the pH scale; with metallic pollutants, this is because of their generally greater solubility in acidic waters (i.e., low pH). The pH of water can be easily measured by inexpensive field methods as well as continuously-recording apparatus.

d) *Coliform bacteria:*

The measurements of these organisms in water are extremely important from the point of view of safeguarding human health. They arise from contamination of water by fecal wastes, and can contaminate shellfish or other forms of aquatic life used by man as a food-source, in addition to contaminating drinking water and bathing areas. This type of organism is measured by means of a bacteriological test, and can be done using a rapid filter-membrane technique. In Canada, the Province of Ontario has set a "Recommended" level which must not exceed 100 *total* coliforms, nor exceed 10 *fecal* coliforms, nor exceed 1 fecal streptococcus (all values given in "Most Probable Numbers per 100 milliliters of water", as derived from actual counting of cultures grown on bacteriological plates).

e) *Ammonia:*

This substance can be very toxic to aquatic life, especially when present in the "free ammonia" (i.e., NH_3) form. The proportion of total ammonia that exists in water as "free ammonia" depends on pH and water temperature, with higher pH and/or temperature resulting in a greater proportion of "free ammonia" in water. For long-term conditions, "free ammonia" concentrations greater than 0.025 milligrams per liter can adversely affect aquatic life-forms. Ammonia measurements can be done easily by means of classic laboratory techniques.

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D. 11. NITRATES, NITRITES AND NITROSAMINES

The consumption of food and water containing nitrite or nitrate can lead to impairment of oxygen transport in the blood (methemoglobinemia or "blue baby disease"). There have been indications of an interaction between nitrate and hypertension patterns in man, including increased heart rate, decreased blood pressure and circulatory collapse. Nitrite may react with amines to form nitrosamines which are known to have carcinogenic, mutagenic and teratogenic effects in experimental animals, often at very low exposure levels. Animals have become ill or died after consuming feed or water containing large amounts of nitrate or nitrite, especially in drought-affected areas. Animals receiving nitrate or nitrite over long periods of time may suffer abnormalities leading to reduced productivity. Such chronic toxicity is most likely to be seen in the very young, the old, the sick and the poorly-fed animal and most frequently in cold weather. In very cold environments, nitrate can function as an antithyroid substance by "washing out" iodine. High nitrate or nitrite levels in feed and water may lead to Vitamin A deficiencies by destroying carotene or interfering with the utilization of Vitamin A. In addition, reproduction and lactation in animals, as well as digestibility of feed are adversely affected.

Vegetables such as beets, spinach, broccoli, celery, lettuce, radishes, kale, mustard greens and collards may accumulate large quantities of nitrate. Factors leading to such accumulation include the level of applied fertilizer, nutrient deficiencies, low light intensity, drought and insect damage. Nitrite accumulates in plants as the result of bruising or processes involving bacterial fermentation, such as ensilage. Concern is rising over the accumulation of nitrate in some surface water, groundwater and well-water; where concentrations are beyond recommended levels, removal from drinking water may become necessary.

Some recent studies have linked esophageal cancer in humans to dimethylnitrosamine derived from natural sources. While mixtures of nitrate and nitrite used to preserve and cure meat and fish are usually subject to legal tolerances, nitrosamines, which can be toxic to man and animals, are found to occur most frequently in such processed foods. Monitoring is required to estimate the hazard this poses to man and to establish whether nitrosamines are found in soil or natural bodies of water which contain appreciable amounts of nitrate or nitrite.

Although nitrogen is abundant and essential for all living things, supplies of the forms available to plants and needed for crop production are inadequate in many parts of the world. Man has compensated for this by using animal and human manure, by cultivating legumes and by applying chemical fertilizers. This expanded use of nitrogen, together with releases from feedlots, municipal and industrial wastes, refuse dumps and emissions from internal combustion engines, has tended to enrich the supply of available nitrogen in water bodies. Although phosphorous has received particular attention in efforts to maintain water quality by limiting growth of weeds and algae, it is nitrogen that controls algal growth and eutrophication in coastal waters and estuaries. The measurement of nitrate and nitrite in various media presents no particular difficulty from the viewpoint of methods of chemical analysis. However, present methods utilizing colorimetry, thin-layer chromatography, gas chromatography, and mass spectrometry are inadequate for monitoring the occurrence and quantity of nitrosamines in foods. Thus, there is a critical need for an accurate and reliable method to fill vital gaps in this area of growing concern.

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D. 12. ENVIRONMENTAL RADIOACTIVITY

Radioactive materials are present in the environment both as a result of natural processes and man's activities. These radioactive materials emit ionizing radiations which are a potential hazard to those exposed to them. The numerical estimates of the risks of damage from such exposures constitute the criteria on which safety standards may be based.

The release of man-made radioactivity to the environment has in the past resulted mainly from nuclear weapon testing and, to a lesser extent, from the operation of nuclear power plants. The radioactive materials are either released to the atmosphere or to waterways and, from there, can be transported to the food chain of man. Some radioactive material in the atmosphere will be absorbed directly by inhalation. The ingestion of contaminated food and the inhalation of contaminated air results in internal exposure of the population to radioactivity. Furthermore, man can be exposed directly to ionizing radiation emitted by radioactive materials in the atmosphere or on the earth; this is termed external exposure. The redionuclide that presents the greatest hazard soon after an environmental release is radioactive iodine and those that give the greatest exposure at later times are radioactive strontium and caesium. Radioactive materials and ionizing radiation can be measured down to lower levels than any other environmental contaminants. In order to assess adequately the dose commitment to human populations from environmental radioactivity, air, water, and foodstuffs (for different types of diets) should be surveyed at least four times a year.

The harmful effects of ionizing radiation are divided into two main categories: genetic and somatic. Genetic effects of ionizing radiation are those which are transmitted to future generations by the exposed individuals. Such hazards result from radiation-induced changes in the cells involved in reproduction. Genetic risks have been evaluated but the estimates cover a wide range. Somatic effects of ionizing radiation are those which are expressed in the exposed individuals themselves. The main somatic hazard from low levels of radiation are the development of leukaemia and of cancers. Present risk estimates indicate that if all members of a population of one million received a dose of one rad, there would result a lifetime risk among the exposed persons of approximately:

40 fatalities from leukaemia
100 fatalities from cancer
40 cases of thyroid cancer (usually non-fatal)

plus 300-6000 genetic defects in the next generation. Since the numerical estimates of risk are based on grossly incomplete knowledge, the greatest caution is needed in drawing quantitative conclusions, especially where protection of human health and life is involved.

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