GUIDLINE AMBIENT ENVIRONMENT STANDARDS FOR ETHIOPIA

Prepared By:

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PREFACE

The Federal Government of Ethiopia, through Proclamation 9/1995, established the Federal Environmental Protection Authority. The Authority is mandated to protect and preserve ecosystems of the Ethiopian environment.

It is in fulfilment of this mandate that these provisional standards for industrial pollution control are hereby presented. These are guideline standards, which will be periodically reviewed and updated in the light of additional information and knowledge.

It is now globally accepted that where there are threats of serious irreversible environmental damages, lack of scientific certainty should not be used as a reason for postponing measures to prevent environmental degradation.

The survival of man, and of any nation for that matter, depends on the ability to manage wastes in an environmentally sound manner. This can only be achieved through establishment and enforcement of appropriate standards and guidelines set to ensure that we do not destroy our environment and indeed the very basis of our existence.

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Contents

1 INTRODUCTION

Ambient environmental quality standards are set with a goal of safeguarding public health and protecting the environment. Both objectives have very high quality requirements which complement each other to a great extent. For example, in general terms, if a river or lake water meets the most stringent fishery requirements it will meet all or virtually all other environmental quality objectives.

It is appropriate then for the government of Ethiopia to set standards which will ensure that the ambient environment of the country is protected and ensure environmental quality is not degraded while also ensuring a healthy environment within people must live.

The government of Ethiopia has mandated the Environmental Protection Authority to set such standards and this document represent the Authorities guideline standards with respect to the ambient environment..

In practice, standards can be set from either first principles or based on existing national or international guidelines.

Deriving such standards from first principles requires classification, and prioritisation of pollutants, derivation of pollutant exposure processes and their ecological effects, determine. predicted environmental concentrations and predicted no effect concentration for the receiving environment.

Given the resources required to derive country specific standards from first principles, standards are generally derived based on existing published guidelines as is the case in this instance. The information upon which international guidelines are based are derived predominantly from extensive epidemiological and toxicological studies to determine the observed health and environmental effects of the compound in question. As such, there are a limited number of international sources who collate and interprets this data in order to prepare guideline for such parameters. The principle international and national guidelines used in the preparation of these guideline standards for Ethiopia are referenced throughout the document.

Where sufficient national baseline information is available, the guideline values prepared by international bodies may be further modified at to take account of particular national criteria prior to their implementation as a national standard. Additional baseline data collection is then undertaken to improve or adapt the initial standards to own country situation. Baseline data is important for the implementation of environmental quality standards particularly with regard to the following:

- forming a basis for zoning; where general or special standards should apply;
- assessing the assimilative capacity of the receiving environment;
- identifying the areas which require stringent or less stringent application of standards; and,
- formulating rehabilitation and/or conservation measures.

There is currently insufficient baseline data available within Ethiopia to allow modification of international guidelines for ambient environmental quality. As such many of the guideline standards have been adopted directly as recommended for developing countries.

These guideline standards are being introduced to be used all throughout the country subjected to amendment, as more information on the state or pollution is made available through the Ecologically Sustainable Industrial Development (ESID) project. The regional states can establish more stringent standards taking into consideration particular ecological conditions in their localities provided EPA's standards are used as the minimum. .

These guideline standards are primarily aimed at protection of ambient environmental quality within all components of the Ethiopian Environment. The guideline standards provided within this document with regard to water quality are not based on use related criteria e.g water for abstraction as a source of drinking water, or for example irrigation purposes. It is anticipated that such standards will be prepared by the Ministry of Water resources at a later date.

1.1 STRUCTURE OF THE DOCUMENT

The Guideline Standards are presented in summary form in the following section. Additional appendices are included which provides detailed information and background for the guideline standards in each area as follows.

Appendix 1: Air Quality Standards

Appendix 2: Water Quality Standards

Appendix 3: Soil and Groundwater Quality Standards

Appendix 4: Noise Standards

2 GUIDELINE AMBIENT ENVIRONMENTAL STANDARDS FOR ETHIOPIA

The guideline environmental standards for Ethiopia are presented below in summary form. Additional information is given on each parameter in a set of Appendixes attached to this document.

2.1 GUIDELINE AIR QUALITY STANDARDS

Guideline standards for priority ambient atmospheric pollutants are given below. Information on additional parameters is provided in Appendix 1.

Compound	Guideline Value [μg/m^3]	Averaging time
Sulphur dioxide	500	10 minutes
	125	24 hours
	50	1 year
Nitrogen dioxide	200	1 hour
	40	1 year
Carbon monoxide	100 000	15 minutes
	60 000	30 minutes
	30 000	1 hour
	10 000	8 hours
Ozone	120	8 hours
Suspended Particulate Matter		
PM_{10}	50	1 year
	150	24 hours
$PM_{2.5}$	15	1 year
	65	24 hours
Lead	0.5	1 year

2.2 GUIDELINE SURFACE WATER QUALITY STANDARDS

Guideline standards for priority surface water pollutants with regard to protection of aquatic species are given below. Detailed information on each parameter is provided in Appendix 2

Compound	Limit
Aluminium	200 μg/l Al;
Ammonium	20 μg/l NH_3 un-ionised
	25 μg/l NH_3 un-ionised
Antimony	20 μg/l Sb
Arsenic	50 μg/l As
Barium	100 μg/l Ba
Benzene	10.0 μg/l
Benzo(A)Pyrene	0.01 μg/l
BOD_5 [Biochemical oxygen demand]	$\leq$ 5 mg/l O_2
Cadmium	5.0 μg/l Cd [Total];
Chloride	250 mg/l Cl
Chlorine, Residual	5 μg/l as HOCl
Chromium	50 μg/l Cr
Conductivity	1000 μS/Cm (@ 20 °C)
Copper	5-112 μg/l dissolved Cu for hardness range 10-500 mg/l $CaCO_3$
Cyanide	50 μg/l CN
Dissolved oxygen	Game Fish - 50% samples $\geq$ 9 mg/l O_2[minimum 6 mg/l O_2]
	Course Fish - 50% samples $\geq$ 7 mg/l O_2[minimum 4 mg/l O_2]
Fluoride	1.0 mg/l F
Iron	1.0 mg/l dissolved Fe
Lead	50 μg/l Pb
Manganese	300 μg/l Mn
Mercury	1 μg/l Hg
Methylene Blue Active Substances[(Anionic) Detergents]	200 μg/l lauryl-SO_4
Nickel	100 μg/l Ni AM
Nitrate	50 mg/l NO_3

Compound	Limit
Nitrite	Game Fish - 200 μg/l NO_2
	Course Fish - 400 μg/l NO_2
Nitrogen, Kjeldahl	2 mg/l N
PCBs and PCTs	1 μg/l AM
Pesticides	
Aldrin	0.01 μg/l
Dieldrin	0.01 μg/l
Endrin	0.005 μg/l
Isodrin	0.005 μg/l
Atrazine	1.0 μg/l
Chloridazon	0.1 μg/l
2,4-D	0.005 μg/l
DDT (y-isomer)	10 μg/l
DDT (all isomers)	25 μg/l
Diazinon	5 μg/l
Dichlorbenil	10μg/l
Dichlorvos	0.001 μg/l
Diuron	25 μg/l
Endosulphan	0.001 μg/l
Fenitrothion	0.01 μg/l
Isoproturon	0.5 μg/l
Lindane	0.1 μg/l
Linuron	1.0 μg/l
Malathion	0.01 μg/l
MCPA	10 μg/l
Mecoprop	10 μg/l
Parathionethyl	0.01 μg/l
Pentachlorophenol	2.0 μg/l
Simazine	1.0 μg/l
Tributyltin oxide	0,001 μg/l
Trifuralin	0.1 μg/l
Triphenyltin acetate	0.01 μg/l
Triphenyltin hydroxide	0.01 μg/l

Compound	Limit
pH	6 to 9, but no change more than 0.2 units from natural level in 95% of samples
Phenols [non specific/total]	0.5 μg/l C_6H_5OH AM
Polycyclic aromatic hydrocarbons [PAH]	2 μg/l [Total for 6 specified compounds**] AM
Selenium	10 μg/l Se
Silver	10 μg/l Ag
Total Suspended Solids,	$\leq$ 25 mg/l [annual mean]
	50 mg/l [maximum value]
Sulphate	200 mg/l SO_4
Temperature	Game Fish - Discharge must not result in variation of more than 1.5^{o}C; temperature down stream of thermal discharge
	Course Fish - Discharge must not result in variation of more than 3^{o}C; temperature down stream of thermal discharge
Thallium	5 μg/l Tl AM
Toluene	10.0 μg/l AM
1,1,1-Trichloroethane	500 μg/l AM
Tetrachloroethylene	10 μg/l AM
Trichloroethylene	10 μg/l AM
Uranium	20 μg/l U AM
Vinyl chloride	10 μg/l AM
Zinc	30 μg/l to 500 μg/l Zn @ hardness 10 to 500 mg/l

2.3 GUIDELINE SOIL AND GROUNDWATER STANDARDS

Guideline standards for soil quality are provided below. These standards represent "clean-up" values for soils and groundwater's which have been contaminated as a result of anthropogenic activity. These values are based on a generic "risk assessment" and as such should be regarded as guideline values. A detailed risk assessment should be undertaken to obtain site specific values for the parameters in question. Additional information on this approach and the guideline standards is presented in Appendix 3.

2.3.1 Guideline Soil Quality Standards.

Substance	Guideline Standard (mg/kg dry weight)
Acetone	8
Arsenic	20[1(2)]
Benzene	1.5[2]
BTEX, total	10[2]
Cadmium	0.5[2]
Chloroform	50[2]
Chlorophenols, total	3[2]
Pentachlorophenol	0.15
Chromium, total	500
Chromium (VI)	20
Copper	500[1]
Cyanide, total	500
Cyanide, acid volatile	10[2]
DDT	1
Detergents, anionic	1,500[2]
1,2-dibromomethane	0.02[2]
1,2-dichloroethane	1.4[2]
1,1-dichloroethylene	5[2]
1,2-dichloroethylene	85[2]
Dichloromethane	8[2]
Fluorides, inorganic	20[1]
Gas oil (Total hydrocarbons (C_5–C_{35})[5])	100
Lead	40[2]
Mercury	1
Molybdenum	5

Substance	Guideline Standard (mg/kg dry weight)
MTBE	500[2]
Nickel	30[1]
Nickel	30[1]
Nitrophenols	
Mono-	125[2]
Di-	10[2]
Tri-	30[2]
PAH, total	1.5[2,3]
Benzo(a)pyrene	0.1[2]
Dibenzo(a,h) anthracene	0.1[2]
Petrol (C_5-C_{10})	25
Petrol (C_9-C_{16})	25
Phenols, total	70[1]
Phthalates, total	250[2]
DEHP	25[2]
Styrene	40[2]
Turpentine, mineral ($C_7 - C_{12}$)	25
Tetrachloroethylene	5[2]
Tetrachloromethane	5[2]
1,1,1-trichloroethane	200[2]
Trichloroethylene	5[2]
Vinyl chloride	0.4[2]
Zinc	500

[1]: Based on acute harmful effects

[2]: Based on chronic harmful effects

[3]PAH, total defined as the sum of individual components: fluoranthene, benzyl(b+j+k)fluoranthene, benzyl(a)pyrene, dibenzyl(a,h)anthracene, and ideno(1,2,3-cd)pyrene.

2.3.2 Guideline Standards for Groundwater Beneath Contaminated Sites

Substance	Groundwater Quality Standard µg/l
Acetone	10
Arsenic	8
Benzene	1
Boron	300

Butylacetates	10
Cadmium	0.5
Chlorinated solvents (not vinyl chloride)	1
Chloroform	As low as possible
Chromium, total	25
Chromium VI	1
Copper	100
Cyanide, total	50
DEHP	1
Detergents, anionic	100
1,2-dibromomethane	0.01
Diethylether	10
Isopropyl alcohol	10
PAH [1]	0.2
Lead	1
Methylisobutylketone	10
Methyl-tert-butylether (MTBE)	30
Mineral oil, total	9
Molybdenum	20
Naphthalene	1
Nickel	10
Nitrophenols	0.5
Pentachlorophenol	0.01
Pesticides, total	0.5
Pesticides	0.1
Pesticides, persistent chlorinated	0.03
Phenols	0.5
Phthalates (not DEHP)	10
Styrene	1
Toluene	5
Vinyl chloride	0.2
Xylenes	5
Zinc	100

[1] Sum of fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene.

2.3.3 Guideline Standards for Cations and Anions*

* It is not possible to assign a universal set of standards for groundwater due to the natural variation in hydrochemistry. Therefore, indicators can be used to assess groundwater status, which takes account of natural variation in quality. It should be noted that a guideline value may not be applicable in some cases due to the widely variable nature of groundwater bodies.

Parameter	Groundwater Guideline Value (mg/l)
Alkalinity	No abnormal change to background
Aluminium	0.2
Ammonia (as NH_4)	0.15
Barium	0.1
Bicarbonate/Carbonate	No abnormal change to background
Calcium	200
Chloride	30
Dissolved Oxygen	No abnormal change to background
Fluoride	1
Iron	0.2
Magnesium	50
Manganese	0.05
Mercury	0.001
Nitrate (as NO_3)	25
Nitrite (as NO_2)	0.1
Orthophosphate	0.03
Potassium	5
Silica	No abnormal change to background
Sodium	150
Sulphate	200

2.4 GUIDELINE STANDARDS FOR NOISE

The objective of these guidelines is to minimise the amount of noise to which people, living or working in sensitive locations, are exposed. Examples of such areas include domestic dwellings, hospitals, schools, places of worship, or areas of high amenity.

The sensitivity to noise is usually greater at night-time than it is during the day, by about 10dB(A). Ideally, if the total noise level from all sources is taken into account, the noise level at sensitive locations should be kept within the following values:

	Limits in dB (A) Leq

Area Code	Category of area	Day time[Note 1]	Night time[Note 2]
A	Industrial area	75	70
B	Commercial area	65	55
C	Residential area	55	45

Note-1: Day time reckoned in between 6.00 am to 9.00p.m

Note 2: Night time reckoned in between 9.00p.m. to 6.00am

Additional information on noise and vibration standards is provided in Appendix 4.

APPENDIX 1

GUIDLINE AIR QUALITY STANDARDS

1 SULPHUR DIOXIDE

Chemical Symbol or Formula: SO_2

Standard*:	*Averaging Time*
500 μg/m^3	10 minutes
125 μg/m^3	24 hours
50 μg/m^3	1 year

* The volume must be standardised at a temperature of 293 °K and a pressure of 101,3 kPa.

1.1 HEALTH EFFECTS[1]

1.1.1 Short-period exposures (less than 24 hours)

Most information on the acute effects of SO_2 comes from controlled chamber experiments on volunteers exposed to SO_2 for periods ranging from a few minutes up to one hour (WHO 1999a). Acute responses occur within the first few minutes after commencement of inhalation. Further exposure does not increase effects. Effects include reductions in the mean forced expiratory volume over one second (FEV1), increases in specific airway resistance (sRAW), and symptoms such as wheezing or shortness of breath. These effects are enhanced by exercise that increases the volume of air inspired, as it allows SO_2 to penetrate further into the respiratory tract.

A wide range of sensitivity has been demonstrated, both among normal subjects and among those with asthma. People with asthma are the most sensitive group in the community. Continuous exposure-response relationships, without any clearly defined threshold, are evident. To develop a guideline value, the minimum concentrations associated with adverse effects in asthmatic patients exercising in chambers have been considered.

1.1.2 Exposure over a 24-hour period

Information on the effects of exposure averaged over a 24-hour period is derived mainly from epidemiological studies in which the effects of SO_2, SPM and other associated pollutants are considered. Exacerbation of symptoms among panels of selected sensitive patients seems to arise in a consistent manner when the concentration of SO_2 exceeds 250 μg/m^3 in the presence of SPM. Several more recent studies in Europe have involved mixed industrial and vehicular emissions now common in ambient air. At low levels of exposure (mean annual levels below 50 μg/m^3; daily levels usually not exceeding 125 μg/m^3) effects on mortality (total, cardiovascular and respiratory) and on hospital emergency admissions for total respiratory causes and chronic obstructive pulmonary disease (COPD), have been consistently demonstrated. These results have been shown, in some instances, to persist when black smoke and SPM levels were controlled for, while in others no attempts have been made to separate the pollutant effects. In these studies no obvious threshold levels for SO_2 has been identified.

1.1.3 Long-term exposure

Earlier assessments examined findings on the prevalence of respiratory symptoms, respiratory illness frequencies, or differences in lung function values in localities with contrasting

[1] For further information on health effects see Guidelines for Air Quality, WHO, Geneva, 2000

concentrations of SO_2 and SPM, using data from the coal-burning era in Europe. The lowest-observed- adverse-effect level of SO_2 was judged to be at an annual average of 100 µg/m^3, when present with SPM. More recent studies related to industrial sources of SO_2, or to the changed urban mixture of air pollutants, have shown adverse effects below this level. But a major difficulty in interpretation is that long-term effects are liable to be affected not only by current conditions, but also by the qualitatively and quantitatively different pollution of earlier years. However, cohort studies on differences in mortality between areas with contrasting pollution levels indicate that mortality is more closely associated with SPM, than with SO_2.

1.2 MONITORING

As the main source of this pollutant is the combustion of fossil fuels containing sulphur, either in power stations or domestic/commercial space heating, the major local source types strongly influences monitoring and assessment strategies. Automatic analyzers need to be used if compliance against a short-term guideline is to be determined; a variety of active samplers are suitable for comparison with daily or annual guidelines. Passive samplers may be used to provide data for comparison with the long-term annual guideline.

1.2.1 Passive samplers

There are currently no national or international standards governing the application of SO2 diffusion tubes to ambient air monitoring, nor for their laboratory preparation and analysis.

Protocols for sample preparation and analysis by spectrophotometry and ion exchange chromatography have, however, been published in scientific literature (Bennett et al. 1992; Downing et al. 1994; Hargreaves and Atkins 1988).

A variety of passive sampling techniques are available (UNEP/WHO 1994b). The most widely used include:

- The triethanolamine (TEA)/glycol/spectrophotometry method (Hangartner et al. 1989).
- The potassium hydroxyde (KOH)/glycerol/spectrophotometry method (Hargreaves and Atkins 1988).
- The sodium carbonate (Na2CO3)/glycerine/ion-exchange chromatography method (Ferm 1991).

Hybridization of these techniques is widespread. In the UK, for instance, KOH or NaOH is used as absorbent, but with the tube membrane proposed by Ferm (1991) and using ion-exchange chromatography as the analysis method. In practice, the ion-exchange chromatographic technique has been informally accepted as the standard method for SO2 diffusion tube analysis. The typical sensitivity of this hybrid technique is ±8.5 mg/m 3 : some under-reading against automatic analysers has been observed (about 30%), although agreement with active samplers is better (Downing et al. 1994).

1.2.2 Active samplers

The equipment required for sampling gaseous sulphur compounds in ambient air is described in full in International Standard ISO 4219 (ISO 1979). This standard gives details of the equipment necessary to sample gaseous pollutants by absorption in a liquid bubbler. The standard also includes guidance for siting and installation of the apparatus. The principle of active-sampling methodologies is to draw ambient air through a collecting medium (typically a liquid bubbler), for a specified time, typically 24 hours. The volume of air is metered. The collecting medium is subsequently analysed and the concentration of pollutant in the sampled air determined. This proven method is well established, and has been used in many monitoring networks worldwide for

a number of years. In consequence, there is a long history of active sampler SO2 measurements available for trend assessment.

There are several methods of SO2 monitoring based on this principle, which can be carried out using the apparatus specified in ISO 4219. They differ with respect to the solutions used in the bubblers for SO2 absorption and the method of analysis. The four most widely used methods are described below.

Acidimetric (total acidity) method.

This method, given in ISO 4220 (ISO 1983), is used to determine a gaseous acid air pollution index. Although this method measures total acidity, and is not specific for SO2, it is adequate for general use. The simplicity of the method, and the fact that the reagents are relatively safe, makes it a popular choice for routine monitoring (AEA 1997). An accuracy of ±10% has been estimated for SO2 measurements using the total acidity method, taking account of all contributory factors. A precision of ±4 mg/m 3 is achievable for this widely-used method (AEA 1997).

Ion-exchange chromatography.

A variation on the above technique. The exposed peroxide solutions are analysed for sulphate ions by means of ion-exchange chromatography, rather than titration. This has the advantage of being sulphate-specific, but requires the use of an expensive ion-exchange chromatograph.

Tetrachloromercurate (TCM) method.

This is also known as the Pararosaniline method ISO 6767 (ISO 1990). This is the reference method specified in the EC Directive on SO2 and suspended particulate matter(EC 1980). However, the reagents used are very toxic, and for this reason the method is not widely used.

Thorin method.

This method is given in ISO 4221 (ISO 1980). The reagents used include perchloric acid, barium perchlorate, dioxane and thorin. These are hazardous and must be handled and disposed of with care. Accordingly, this method is not commonly used world-wide.

1.2.3 Automatic analysers

The measurement of SO2 in ambient air using automatic analysers is covered by ISO/DIS 10498 (ISO/DIS 1999). Well-established automatic monitoring techniques are available. The most widely used method for automatic SO2 measurement is ultraviolet fluorescence (UVF). SO2 molecules in the sample airstream are excited to higher, unstable energy states by UV radiation at 212 nm. These energy states decay, causing an emission of secondary fluorescent radiation with an intensity proportional to the concentration of SO2 in the sample.

The accuracy of data from automatic SO2 analysers depends on a range of factors encompassing the entire measurement chain. These include accuracy of calibration standards, analyser stability and sample losses in the measurement system. An accuracy of ±10% has been estimated for SO2 measurements in UK national automatic networks, taking account of all contributory factors. The precision of SO2 measurements, determined from long-term variations in baseline response of in-service analysers, is estimated to be ±3 mg/m^3 (AEA 1996).

1.2.4 Remote sensors

Remote optical sensor systems, such as the Differential Optical Absorption System (DOAS), use a long-path spectroscopic technique to make real-time measurements of the pollutant concentration by integrating readings along a path between a light source and a detector. Long-path monitoring systems can be used to measure SO2, but the methodology is less well established than that for automatic point monitors. The accuracy and precision of the data from these instruments are, therefore, much more difficult to determine. The method does not conform to ISO 7996 (ISO

1985b). Particularly careful attention needs to be paid to instrument calibration and quality assurance to obtain meaningful data from remote sensing instruments.

2 NITROGEN DIOXIDE

Chemical Symbol or Formula: NO_2

Standard*:	*Averaging Time*
200 μg/m^3	24 hours
40 μg/m^3	1 year

* The volume must be standardised at a temperature of 293 °K and a pressure of 101,3 kPa.

2.1 HEALTH EFFECTS[2]

2.1.1 Short-term exposure effect

Available data from animal toxicology experiments indicate that acute exposure to NO_2 concentrations of less than 1880 μg/m^3 (1 ppm) rarely produce observable effects. Normal healthy humans, exposed at rest or with light exercise for less than two hours to concentrations above 4700 μg/m^3 (2.5 ppm), experience pronounced decreases in pulmonary function; generally, normal subjects are not affected by concentrations less than 1880 μg/m^3 (1.0 ppm). One study showed that the lung function of subjects with chronic obstructive pulmonary disease is slightly affected by a 3.75-hour exposure to 560 μg/m^3 (0.3 ppm).

A wide range of findings in asthmatics has been reported. Asthmatics are likely to be the most sensitive subjects, although uncertainties exist in the health database. The lowest concentration causing effects on pulmonary function was reported from two laboratories that exposed mild asthmatics for 30-110 minutes to 565 μg/m^3 (0.3ppm) NO2 during intermittent exercise. However, neither of these laboratories was able to replicate these responses with a larger group of asthmatic subjects. One of these studies indicated that NO_2 can increase airway reactivity to cold air in asthmatic subjects. At lower concentrations, the pulmonary function of asthmatics was not changed significantly.

NO_2 increases bronchial reactivity, as measured by the response of normal and asthmatic subjects following exposure to pharmacological bronchoconstrictor agents, even at levels that do not affect pulmonary function directly in the absence of a bronchoconstrictor. Some, but not all, studies show increased responsiveness to bronchoconstrictors at NO_2 levels as low as 376-565 μg/m^3 (0.2 to 0.3 ppm); in other studies, higher levels had no such effect. Because the actual mechanisms of effect are not fully defined and NO_2 studies with allergen challenges showed no effects at the lowest concentration tested (188 μg/m^3; 0.1 ppm), full evaluation of the health consequences of the increased responsiveness to bronchoconstrictors is not yet possible. Recent studies have shown an increased reactivity to natural allergens in the same concentration range. The results of repetitive exposures of such individuals, or the impact of single exposures on more severe asthmatics, are not known.

2.1.2 Long-term exposure effects

Studies with animals have clearly shown that several weeks to months of exposure to NO2 concentrations of less than 1880 μg/m^3 (1ppm) causes a range of effects, primarily in the lung, but also in other organs such as the spleen and liver, and in blood. Both reversible and irreversible lung effects have been observed. Structural changes range from a change in cell type in the

[2] For further information on health effects see Guidelines for Air Quality, WHO, Geneva, 2000.

tracheobronchial and pulmonary regions (at a lowest reported level of 640 µg/m^3), to emphysema-like effects. Biochemical changes often reflect cellular alterations, with the lowest effective NO_2 concentrations in several studies ranging from 380-750 µg/m^3.

NO_2 levels of about 940 µg/m^3 (0.5ppm) also increase susceptibility to bacterial and viral infection of the lung. There are no epidemiological studies that can be confidently used to quantify a long-term NO_2 exposure or concentration likely to be associated with the induction of unacceptable health risks in children or adults. Homes with gas cooking appliances have peak levels of NO2 in the same range as levels causing effects in some animal and human clinical studies. Epidemiological studies evaluating the effects of NO_2 exposures in such homes have been conducted. In general, epidemiological studies of adults and infants (less than 2years old) show no significant effect of the use of gas cooking appliances on respiratory illness; nor do the few available studies of infants and adults show any associations between pulmonary function changes and gas stove use. However, children 5-12 years old are estimated to have a 20% increased risk for respiratory symptoms and disease for each increase of 28 µg/m^3 NO_2 (2-week average), where the weekly average concentrations are in the range of 15-128 µg/m^3 or possibly higher. However, the observed effects cannot clearly be attributed to either the repeated short-term high level peak, or to long-term exposures in the range of the stated weekly averages (or possibly both).

The results of outdoor studies consistently indicate that children with long-term ambient NO2 exposures exhibit increased respiratory symptoms that are of longer duration, and show a decrease in lung function. However, outdoor NO_2 epidemiological studies, as with indoor studies, provide little evidence that long-term ambient NO_2 exposures are associated with health effects in adults. None of the available studies yields confident estimates of long-term exposure-effect levels, but available results most clearly suggest respiratory effects in children at annual average NO2 concentrations in the range of 50-75 µg/m^3 or higher.

2.2 MONITORING

Automatic analysers must be used for the direct determination of compliance against the hourly guideline, although much useful information can be inferred using passive samplers (see section 4.5). Either technique is applicable for comparing ambient levels against the annual guideline.

2.2.1 Passive samplers

Monitoring ambient NO2 concentrations using passive diffusion tube samplers is now well established. This method provides an integrated, average concentration for the pollutant over the exposure period (typically 2-4 weeks) and is particularly well suited to baseline and screening studies for assessing the spatial distribution of NO2 concentrations in an urban environment. The most widely used techniques are variants on the Palmes-type sampler, originally developed for the assessment of occupational exposure. This uses a tube sampler, employing TEA as absorbent. Sample analysis, after thermal desorption, is by spectrophotometry or ion-exchange chromatography (Palmes et al. 1976). Very large scale mapping surveys are possible using diffusion tubes, but careful attention both to the harmonization of analytical procedures and to the outputs from different analytical laboratories is essential for the success of large-scale passive sampler surveys.

Although extensively used throughout the UK and Europe there are, at present, no national or international standards governing the application of diffusion tubes for ambient air quality monitoring, nor for the laboratory preparation and analysis of diffusion tubes. Protocols for sampler preparation and analysis by spectrophotometry have, however, been published in the scientific literature (Palmes et al. 1976; Atkins et al. 1986); these have been informally accepted as standard procedures for NO2 diffusion tube preparation and analysis.

Recent comparisons of NO2 diffusion tube measurements with co-located chemiluminescent NOx analysers show good agreement (Smith et al. 1997; Gerboles and Amantini 1993). Over the range of concentrations generally encountered in urban areas (20-80 mg/m 3), it was found that on average NO2 diffusion tubes, exposed for one month, tended to overestimate ambient NO2 by approximately 10% compared with a chemiluminescent NOx analyser. Precision estimates of the diffusion tube technique have been quoted as 5-8% in similar studies.

2.2.2 Active samplers

A variety of active sampler technologies are available (UNEP/WHO 1994b). The best known of these is the Griess-Saltzman method, covered by ISO 6768 (ISO 1985a). Although this method is sensitive and requires a relatively simple, inexpensive sampling apparatus, there are a number of disadvantages. It is a relatively skilled and labour-intensive technique, uses corrosive chemicals and is not readily applicable to sampling periods longer than 1-2 hours. There also remain doubts about calibration methods, collection efficiency and possible side-reactions. In consequence, this method cannot be recommended for general baseline monitoring applications.

2.2.3 Automatic analysers

The reference method for automatic measurement of nitrogen oxide concentrations, as defined for compliance with EC Directive 85/203/EEC (EC 1985), is the automatic chemiluminescence method described in ISO standard 7996 (ISO 1985b). This method is widely used world wide. The method is based on the chemiluminescence energy emitted when NO in the sample airstream reacts with O3 in an evacuated chamber to form an excited energy state of NO2. The chemiluminescent reaction is:

$$NO + O_3 = NO_2^* + O_2$$

Emitted light from the excited NO_2^* is converted to an output voltage by a photomultiplier tube and amplifier.

Automatic NO2 analysers based on liquid-phase chemiluminescence, produced by reacting NO2 with a chemical solution, are also available. These highly sensitive but relatively fragile instruments are mostly employed for research applications and are not generally regarded as being suitable for routine baseline monitoring purposes.

The accuracy of data from automatic NO2 analysers depends on a range of factors encompassing the entire measurement chain. These include the accuracy of calibration standards, analyser stability and sample losses in the measurement system. Final accuracy can therefore vary from network to network. An accuracy of ± 8% has been estimated for NO2 measurements in well-run automatic networks, taking account of all contributory factors (AEA 1996). The precision of NO2 measurements is estimated to be ±6.5 mg/m 3 , determined from long-term variations in the baseline responses of in-service analysers.

2.2.4 Remote sensors

Long-path monitoring systems are available for the measurement of NO2, but the methodology is less well established than that for automatic point monitors. The accuracy and precision of the data from these instruments are, therefore, much more difficult to determine. The method does not conform to ISO 7996 (ISO 1995b) and, as noted previously, careful attention needs to be given to instrument calibration and quality assurance to obtain meaningful data.

3 CARBON MONOXIDE

Chemical Symbol or Formula: CO

Standard*:		*Averaging Time*
	100,000 μg/m^3	15 minutes
	60,000 μg/m^3	15 minutes
	30,000 μg/m^3	1 hour
	10,000 μg/m^3	8 hours

* The volume must be standardised at a temperature of 293 °K and a pressure of 101,3 kPa.

3.1 HEALTH EFFECTS[3]

CO diffuses rapidly across alveolar, capillary and placental membranes. Approximately 80-90 % of the absorbed CO binds with hemoglobin to form carboxyhemoglobin (COHb), which is a specific biomarker of exposure in blood. The affinity of hemoglobin for CO is 200-250 times that for oxygen. During exposure to a fixed concentration of CO, the COHb concentration increases rapidly at the onset of exposure, starts to level off after 3 hours, and reaches a steady-state after 6-8 hours of exposure. It is noted that the elimination half-life in the fetus is much longer than in the pregnant mother. The binding of CO with hemoglobin to form COHb reduces the oxygen-carrying capacity of the blood and impairs the release of oxygen from hemoglobin. These are the main causes of tissue hypoxia produced by CO at low exposure levels. At higher concentrations, the rest of the absorbed CO binds with other heme proteins such as myoglobin and with cytochrome oxidase and cytochrome P-450. The toxic effects of CO first become evident in organs and tissues with high oxygen consumption, such as the brain, heart, exercising skeletal muscle and the developing fetus. Severe hypoxia due to acute CO poisoning may cause both reversible, short-lasting, neurological deficits and severe, often delayed, neurological damage. The neurobehavioural effects include impaired coordination, tracking, driving ability, vigilance and cognitive performance at COHb levels as low as 5.1-8.2%. In apparently healthy subjects, the maximal exercise performance decreases at COHb levels as low as 5%. The regression between the percentage decrease in maximal oxygen consumption and the percentage increase in COHb concentration appears to be linear, with a fall in oxygen consumption of approximately 1% for each 1% rise in COHb level above 4%.

In controlled studies involving patients with documented coronary artery disease, mean pre-exposure COHb levels of 2.9-5.9% (corresponding to post-exercise COHb levels of 2.0-5.2%) have been associated with a significant shortening in the time to onset of angina, with increased electrocardiographic changes and with impaired left ventricular function during exercise. In addition, ventricular arhythmias may be increased significantly at the higher range of mean post-exercise COHb levels. Epidemiological and clinical data indicate that CO from smoking and environmental or occupational exposures may contribute to cardiovascular mortality and to the early course of myocardial infarction. Current data from epidemiological studies and experimental animal studies indicate that common environmental exposures to CO in the developed world would not have atherogenic effects on humans (WHO 1999a).

During pregnancy, endogenous production of CO is increased so that maternal COHb levels are usually about 20% higher than the non-pregnant values. At steady-state, the fetal COHb levels are

[3] For further information on health effects see Guidelines for Air Quality, WHO, Geneva, 2000.

as much as 10-15% higher than the maternal COHb levels. There is a well-established and probably causal relationship between maternal smoking and low birth weight at fetal COHb levels of 2-10%. In addition, maternal smoking seems to be associated with a dose-dependent increase in perinatal deaths and with behavioural effects in infants and young children.

3.2 MONITORING

CO in urban areas results almost entirely (typically ~90%) from road traffic emissions. Since CO is a primary pollutant, its ambient concentrations closely follow emissions. In urban areas, concentrations are therefore highest at the kerbside and decrease rapidly with increasing distance from the road. Mostly automatic analysers are being used for the direct assessment of ambient levels against guidelines.

3.2.1 Passive samplers

A passive sampler has been developed for CO, utilizing a zeolite absorber and a narrow filamental diffusion passage to optimize uptake, and involving GC/FID analysis after thermal desorption (Lee et al. 1992). This technique may be useful for screening, mapping and 'hot-spot' identification. Its use does not, however, appear to be widespread at the present time. Active samplers

Grab samples may be collected for subsequent laboratory analysis. However, this technique is not known to be widely used.

3.2.2 Automatic analysers

The measurement of CO in ambient air is covered by international standards ISO/FDIS 4224 (ISO/FDIS 1999a) and ISO 8186. (ISO 1989) .

Baseline ambient CO monitoring is normally carried out using IR analysers. A number of electrochemical CO analysers are available, but these are generally of low sensitivity and not suitable for routine ambient monitoring. However, they may have application in areas of high concentrations. A version of this sensor is incorporated in a commercially available roadside pollution monitoring system.

CO analysis is based on the absorption of IR radiation at wavelengths of 4.5-4.9 micrometres. Since other gases and particles can also absorb IR, the analyser must distinguish between absorption by CO and absorption by interferences. In the most common analyser type, this is done using a gas filter correlation wheel containing a cell of pure nitrogen and a cell of nitrogen plus CO. The cell containing CO removes the CO-sensitive wavelengths before the IR signal enters the absorption chamber, whilst all wavelengths are transmitted by the other cell. The difference in the intensity of the two absorption signals, divided by the intensity of the IR source, provides a measure of the ambient CO concentration.

The accuracy of data from automatic CO analysers depends on a range of factors encompassing the entire measurement chain. These include accuracy of calibration standards, analyser stability and sample losses in the measurement system. An accuracy of ± 8% and a precision of ±0.5 mg/m 3 may be achieved using this technique in well-managed and quality-assured programmes.

4 OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

Chemical Symbol or Formula: O_3

Standard*:	***Averaging Time***
120 µg/m^3	8 hours

* The volume must be standardised at a temperature of 293 °K and a pressure of 101,3 kPa.

4.1 HEALTH EFFECTS[4]

O_3 toxicity occurs in a continuum in which higher concentrations, longer exposure duration, and greater activity levels during exposure cause greater effects. Short-term acute effects include pulmonary function changes, increased airway responsiveness and airway inflammation, and other symptoms. These health effects are statistically significant at 160 µg/m^3 (0.08 ppm) for 6.6 hour exposures in a group of healthy exercising adults, with the most sensitive subjects experiencing a more than 10% functional decrease within 4-5 hours. Controlled exposure of heavily exercising adults, or children to an O_3 concentration of 240 µg/m^3 (0.l2 ppm) for 2 hours, also produced decreases in pulmonary function. There is no question that substantial acute adverse effects occur during exercise with one hour exposure to concentrations of 500 µg/m^3 or higher, particularly in susceptible individuals or subgroups.

Field studies in children, adolescents, and young adults have indicated that pulmonary function decrease can occur as a result of short term exposure to O3 concentrations in the range 120-240 µg/m^3 and higher. Mobile laboratory studies have observed changes in pulmonary function in children or asthmatics exposed to O3 concentrations of 280-340 µg/m^3 (0.14-0.17 ppm) for several hours. Respiratory symptoms, especially coughing, have been associated with O3 concentrations as low as 300 µg/m^3 (0.15 ppm). O3 exposure has also been reported to be associated with increased respiratory hospital admissions and exacerbation of asthma. The effects are observed with exposures to ambient O3 (and co-pollutants) and with controlled exposures to O3 alone. This demonstrates that the functional and symptomatic responses can be attributed primarily to O3.

A number of studies evaluating animals (rats and monkeys) exposed to O_3 for a few hours or days have shown alterations in the respiratory tract, in which the lowest-observed-effect levels were in the range of 160-400 µg/m^3 (0.08-0.2 ppm). These included the potentiation of bacterial lung infections, inflammation, morphological alterations in the lung, increases in the function of lung enzymes active in oxidant defenses, and increases in collagen content. Long-term exposure to O3 in the range of 240-500 µg/m^3 (0.12 to 0.25 ppm) causes morphological changes in the epithelium and interstitium of the centri-acinar region of the lung, including fibrotic changes.

4.2 MONITORING

O3 is not emitted directly from man-made sources in any significant quantities, but is formed in the atmosphere by sunlight-driven chemical reactions involving NOx and VOC (see Section 2.1.2). These reactions are not immediate, but may take from hours to days to complete. O3 is chemically scavenged by primary NOx emissions from traffic, and is also removed from the atmosphere by deposition to the ground.

[4] For further information on health effects see Guidelines for Air Quality, WHO, Geneva, 2000

Both spatial and temporal distributions of O3 differ markedly from those of other pollutants. In particular, significant impacts may occur in areas up to hundreds of kilometres downwind of the original precursor emissions, as a result of long-range as a result of long-range transport. Ambient concentrations and population exposure may often be maximized in suburban and rural areas. This has important implications for monitoring system design.

4.2.1 Passive samplers

A variety of techniques are available (UNEP/WHO 1994b). These include:

1,2,di-(4-pyridyl) ethylene absorbent- spectrophotometry (Monn and Hangartner 1990).

KI –spectrophotometry (Grosjean and Hisham 1992).

NaNO2/Na2CO3/glycerine -ion chromatography (Koutrakis et al. 1990).

Indigo carmine-reflectance (Alexander et al. 1991).

These methods are not as widely used or validated as corresponding samplers for NO2 and no clear consensus as to a standard technique has yet emerged.

4.2.2 Active samplers

The most widely used active sampler technique was the Neutral Buffered Potassium Iodide (NKBI) method. Although relatively simple and inexpensive, there are practical problems with deterioration of the iodine complex and interference (most notably from NO2 and SO2). These issues have reduced its use to the extent that the technique may now be regarded as obsolete.

4.2.3 Automatic analysers

ISO 10313 (ISO 1993a) is not of real relevance, as the chemiluminescence detection technique it describes is no longer widely used. The most commonly used technology is now that of UV absorption; this is specified as the reference method for the purposes of EC Directive 92/72/EEC (EC 1992). An ISO standard is being developed for the UV method.

UV absorption is a robust, well-developed technique. Ambient O3 concentrations are calculated from the absorption of UV light at 254 nm wavelength. The sample passes through a detection cell of known length (l). An O3-removing scrubber is used to provide a zero reference light intensity, I0. The analyser alternately measures the absorption of air in the cell with no O3 present and the absorption in the experimental sample cell, Is. The ambient O3 concentration, c, may be simply calculated using the Beer-Lambert equation:

$$I_s = I_0 e^{-alc}$$

where a is the relevant absorption coefficient at 254 nm.

Given appropriate attention to system design, calibration and equipment support a typical measurement accuracy of ±11% and a precision of ±4 mg/m 3 should be readily achievable in well-run automatic networks.

4.2.4 Remote sensors

Open-path optical remote sensing techniques such as DOAS are available for O3, although the associated practical issues noted in previous sections are applicable.

5 SUSPENDED PARTICULATE MATTER

Chemical Symbol or Formula:	Not Applicable	
Standard:		***Averaging Time***
PM_{10}	**50 μg/m^3**	1 Year
	150 μg/m^3	24 hours
$PM_{2.5}$	**15 μg/m^3**	1 Year
	65 μg/m^3	24 hours

5.1 HEALTH EFFECTS[5]

Health effects of SPM in humans depend on particle size and concentration, and can fluctuate with daily fluctuations in PM_{10} or $PM_{2.5}$ levels. They include acute effects such as increased daily mortality, increased rates of hospital admissions for exacerbation of respiratory disease, fluctuations in the prevalence of bronchodilator use and cough and peak flow reductions. Long-term effects of SPM refer also to mortality and respiratory morbidity, but only few studies on the long-term effects of SPM exist. Air pollution by particulate matter has been considered to be primarily an urban phenomenon, but it is now clear that in many areas of developed countries, urban-rural differences in P_{M10} are small or even absent, indicating that PM exposure is widespread. This is not to imply that exposure to primary, combustion-related PM may not be higher in urban areas.

A variety of methods exist to measure different fractions of particulate matter in air, with different health significance. This evaluation has tended to focus on studies in which PM exposure was expressed as PM_{10} and $PM_{2.5}$. Health effect studies conducted with various TSP and BS as exposure indicators have provided valuable additional information. However, they are less suitable for deriving exposure-response relationships for PM because TSP includes particles that are too large to be inhaled, or because the health significance of particle opacity as measured by the Black Smoke method is uncertain.

The current time-series epidemiological studies are unable to define a threshold below which no effects occur. Recent studies suggest that even at low levels of PM (less than 100 μg/m^3), short-term exposure is associated with health effects. At low levels of PM_{10} (0 - 100 μg/m^3), the short-term exposure-response curve fits a straight line reasonably well. However, there are indications from several studies that at higher levels of exposure (several hundreds of μg/m^3 of PM10), at least for effects on mortality, the curve is flatter than at low levels of exposure. This is discussed later in this section.

Although many studies have obtained acute effect estimates for PM_{10} that are reasonably consistent, this does not imply that particle composition or size distribution within the PM_{10} fraction is unimportant. Limited evidence from studies on dust storms indicates that such PM_{10} particles are much less toxic than those associated with combustion sources. Recent studies in which PM_{10} size fractions and/or constituents have been measured suggest that the observed effects of PM_{10} are largely associated with fine particles and not with the coarse fraction (PM_{10} minus $PM_{2.5}$). In some areas strong aerosol acidity or sulphate may be the cause of the effects associated with $PM_{2.5}$.

[5] For further information on health effects see Guidelines for Air Quality, WHO, Geneva, 2000

Evidence is also emerging that long-term exposure to low concentrations of PM in air is associated with mortality and other chronic effects, such as increased rates of bronchitis and reduced lung function. Two cohort studies conducted in the U.S.A. suggest that life expectancy may be 2-3 years shorter in communities with high PM than in communities with low PM. This is consistent with earlier cross-sectional studies, which compared age-adjusted mortality rates across a range of long-term average PM concentrations. The results showed that long-term average exposures to low PM levels, starting at about 10 $\mu g/m^3$ of fine particulate matter, were associated with a reduction in life expectancy. Whilst such observations require further corroboration, preferably also from other areas in the world, these new studies suggest that the public health implications of PM exposure may be large.

5.2 MONITORING

SPM is a generic term embracing all airborne particulate matter. This therefore encompasses a wide range of size fractions, morphologies and chemical compositions, as discussed in Chapter 2. Although coarse particle size ranges may cause significant local nuisance or soiling, it is the finer fractions, such as PM2.5, that are capable of deep lung/airway penetration. Concern about the potential health impacts of fine particulate matter has increased rapidly over recent years.

SPM monitoring is fundamentally different from the measurement of gaseous pollutants, and the methods are generally less precise. A wide variety of different sampling and detection methodologies is available, including the Tapered Element Oscillating Microbalance (TEOM), b-ray analysis, gravimetric sampling (low or high-volume) and a number of indirect optical, particle counting and light-scattering methods. The sampling system strongly affects the measurement process and appropriate aerodynamically designed inlets are essential for proper sample-fractionated determinations (UNEP/WHO 1994c).

5.2.1 Active samplers

Gravimetric samplers collect particulate matter onto a filter using high-volume (about 100 m 3 /hour) or low-volume (about 1 m 3 /hour) pumped sample flows. The weight of particulate matter deposited on the filter is used to calculate a 24-hour average mass concentration. No ISO or CEN standards have yet been promulgated for ambient measurement of PM10 particulate matter using gravimetric samplers, although these are under development at the present time. An ISO standard for evaluating PM10 inlet heads is, however, available (EN 1999). A United States Environmental Protection Agency procedure for PM10 using the high-volume sampler is given in Federal Register 40 CFR Part 50 (CFR 1993). However, compliance with this procedure does not ensure consistency with the anticipated CEN standards.

The various SPM monitoring techniques may not necessarily produce comparable measurements. Different sampling systems, operating temperature, filter media and filter history may also potentially affect measurement equivalence. The accuracy and precision of any measured mass concentration is, therefore, liable to a wide margin of error. A target accuracy of <10 µg/m 3 and a precision of <5 µg/m 3 (for daily average concentrations <100 µg/m 3) are given for PM10 measurements by EN 12341 (EN 1999).

Medium- or low-volume gravimetric samplers are more portable and less noisy than high-volume samplers, making them more suitable for use in urban areas. However, the mass of particles collected is far less than with high-volume samplers, giving a greater potential for errors due to filter weighing. According to a recent large-scale instrument comparison, a number of commercially available high- and medium-volume samplers are equivalent to a reference Wide Ranging Aerosol Collector (WRAC) (EN 1999).

Correct filter handling, documentation and analysis is fundamental for obtaining valid data. The filters must be conditioned in a temperature- and humidity-controlled environment, typically 20 o C

and 50% relative humidity, for at least 24 hours before and after exposure. The filters must be accurately weighed using a suitable balance, that has been calibrated using an accredited method.

5.2.2 Automatic analysers

Instruments are commercially available using the following techniques:

Tapered Element Oscillating Microbalance (TEOM).

Beta-ray absorption analysers (ISO/FDIS 1999b).

Light scattering systems.

Of the automatic instrument types available, the TEOM and b-ray systems have been operated widely for many years and are well tested in the field. The light scattering type of instrument has been developed more recently, and is therefore less well proven in service. Operating experience and co-located measurement campaigns indicate that measurements from the different instruments are not always equivalent or comparable

For traceable and robust measurements, samplers must be fitted with a tested PM10 inlet head and an accurate flow control system. The PM10 sampling inlet should be tested to ISO Standard 7708 (ISO 1995) to ensure accurate size fractionation at the point of sampling. A target accuracy figure of <10µg/m 3 and precision of <5µg/m 3 (for daily average concentrations <100 µg/m 3) are given in EN 12341 (EN 1999). Tests on in-service TEOM analysers deployed in UK networks demonstrate these figures to be realistic and achievable.

6 LEAD

Chemical Symbol or Formula: Pb.

Standard:	***Averaging Time***
0.5 μg/m^3	1 Year

6.1 HEALTH EFFECTS[6]

The level of lead in blood is the best available indicator of current and recent past environmental exposure and, with stable exposures, may also be a reasonably good indicator of lead body-burden. The biological effects of lead can therefore be related to blood lead levels as an indicator of internal exposure. The relationship between blood lead concentrations and exposure to lead in air exhibits downward curvilinearity where the range of exposures is sufficiently large. At low levels of exposure the deviation from linearity is negligible and linear models of the relationship between intake and blood lead levels are satisfactory approximations.

The LOAEL for hematological and neurological effects of lead in adults and children can be summarized as follows. Frank anemia is exhibited in adults at blood lead levels above 800 μg/l, and in children above about 700 μg/l. Hemoglobin production is reduced in adults at blood lead levels above 500 μg/l and in children above 250-300 μg/l. The presence of lead in the blood also inhibits delta-aminolaevulinic acid dehydrase (ALAD), an enzyme involved in heme biosynthesis, resulting in an accumulation of its substrate, ALA, in blood, plasma and urine (WHO 1987). Urinary ALA and coproporyphyrin are elevated in both adults and children above blood lead levels of about 400 μg/l. Erythrocyte protoporphyrin is found to increase in male adults at blood lead levels above 200-300μg/l, and in female adults and children above 150-200 μg/l. A reduction in vitamin D3 occurs in children at blood lead levels above 100-150 μg/l. Consequently, inhibition of ALAD in adults and children is likely to occur at blood lead levels of about 100 μg/l. However, because of its uncertain biological significance for the functional reserve capacity of the heme biosynthetic system, ALAD inhibition is not treated as an adverse effect here. Encephalopathic signs and symptoms appear not to occur in adults at lead concentrations in blood below 1000-1200 μg/l, and in children below 800-1000 μg/l.

Cognitive effects in lead workers have not been observed at blood lead levels below 500 μg/l, although reductions in nerve conduction velocity were found at concentrations as low as 300 μg/l. Elevation of free erythrocyte protoporphyrin has been observed at blood lead levels of 200- 300 μg/l. Central nervous system effects, as assessed by neurobehavioural endpoints, appear to occur in children at levels below 200 μg/l. Consistent effects have been reported for global measures of cognitive functioning, such as the psychometric intelligence quotient, at blood lead levels between 100-150 μg/l. Some epidemiological studies have indicated effects such as hearing impairment at blood lead levels below 100 μg/l. Animal studies provide qualitative support for the claim that lead is a causative agent for hearing impairment.

6.2 MONITORING

The main sources of lead in air are the combustion of petrol containing lead-based additives and industrial emissions.

[6] For further information on health effects see Guidelines for Air Quality, WHO, Geneva, 2000

6.2.1 Active samplers

These are based on pumped sampling of large quantities of ambient air, capturing fine ambient particulate matter on a filter for subsequent analysis. Analysis of filters for lead is covered by ISO 9855 (E), which specifies atomic absorption spectroscopy as the standard analytical method (ISO 1993b). There is no standard sampling method, although the EC Directive does specify some relevant sampling and filter criteria (EC 1982).

A variety of sampling methods are used, including high-, medium-, and low-volume samplers. There is no standard or reference sampling method. The UK method is broadly typical: this utilises an "M Type" sampler designed specifically for this purpose. Its flow rate is controlled to 5.4-7.1 m 3 /day, and Millipore Aerosol Field Monitor filters are exposed and changed weekly. Passive sampling methods are not applicable.

7 GUIDELINES FOR AIR QUALITY: COMPOUNDS WITH NON-CARCINOGENIC HEALTH ENDPOINTS

Compound	Guideline Value (GV) or Tolerance Concentration (TC) $\mu g/m^3$	Averaging Time
Acetaldehyde	2 000 (TC)	24 hours
	50 (TC)	1 year
Acrolein	50 (GV)	30 min
Acrylic acid	54 (GV)	1 year
2-Butoxyethanol	13100 (TC)	1 week
Cadmium	5×10^{-3}(GV)	1 year
Carbon disulphide	100 (GV)	24 hours
	20 (GV) odour annoyance	30 min
Carbon Tetrachloride	6.1 (TC)	1 year
1,4 Dichlorobenzene	1000 (TC)	1 year
Dichloromethane	3000 (GV)	24 hours
Diesel exhaust	5.6 (GV)	1 year
Ethylbenzene	22 000 (GV)	1 year
Fluorides	1 (GV)	1 year
Formaldehyde	100 (GV)	30 min
Hydrogen sulphide	150 (GV)	24 hrs
	7 (GV) Odour annoyance	30 min
Manganese	0.15 (GV)	1 year
Mercury, inorganic	1 (GV)	1 year
Methyl Methacrylate	200 (TC)	1 year
Monochlorobenzene	500 (TC)	1 year
Styrene	260 (GV)	1 week
	7 (GV) Odour annoyance	30 minutes
Tetrachloroethylene	250 (GV)	24 hours
	8000 (GV) Odour annoyance	30 minutes
Toluene	260 (GV)	1 week
	1000 (GV) Odour annoyance	30 minutes
1,3,5 Trichlorobenzene	200 (TC)	1 year
1,2,4 Trichlorobenzene	50 (TC)	1 year
Vanadium	1 (GV)	24 hours
Xylenes	4800 (GV)	24 hours
	870 (GV)	1 year

Compound	Tolerable Daily Intake (TDI or ADI) μg/kg bw d	Averaging Time (Over lifetime)
Chloroform	15 (TDI)	24 hours
Cresol	170 (ADI)	24 hours
Di-n-butyl Phthalate	66 (ADI)	24 hours
Dioxin-like compounds	1-4 (TDI) [TEQ/kg bw d]	24 hours

8 GUIDELINES FOR AIR POLLUTANTS WITH CARCINOGENIC HEALTH ENDPOINTS

See Table 8.1

Table 8.1 8 Guidelines For Air Pollutants With Carcinogenic Health Endpoints

Compound	Average ambient air concentration $\mu g/m^3$	Health endpoint	Unit risk $[\mu g/m^3]^{-1}$	IARC classification
Acetaldehyde	5	Nasal tumours in rats	$(1.5\text{-}9) \times 10^{-7}$	2B
Acrylonitrile	0.01-10	Lung cancer in workers	2×10^{-5}	2A
Arsenic	$(1\text{-}30) \times 10^{-3}$	Lung cancer in exposed humans	1.5×10^{-3}	1
Benzene	5.0-20.0	Leukaemia in exposed workers	$(4.4\text{-}7.5) \times 10^{-6}$	1
Benzo[a]pyrene		Lung cancer in humans	8.7×10^{-2}	1
Bis(chloromethyl)ether	No data	Epitheliomas in rats	8.3×10^{-3}	1
Chloroform	0.3-10	Kidney tumours in rats	4.2×10^{-7}	2B
Chromium VI	$(5\text{-}200) \times 10^{-3}$	Lung cancer in exposed workers	$(1.1\text{-}13) \times 10^{-2}$	1
1,2-Dichloroethane	0.07-4	Tumour formation in rodents	$(0.5\text{-}2.8) \times 10^{-6}$	2B
Diesel exhaust	1.0-10.0	Lung cancer in rats	$(1.6\text{-}7.1) \times 10^{-5}$	2A
ETS	1-10	Lung cancer in exposed humans	10^{-3}	
Nickel	1-180	Lung cancer in exposed humans	3.8×10^{-4}	1
PAH (BaP)	$(1\text{-}10) \times 10^{-3}$	Lung cancer in exposed humans	8.7×10^{-2}	1
1,1,2,2-Tetrachloroethane	0.1-0.7	Hepatocellular carcinomas in mice	$(0.6\text{-}3.0) \times 10^{-6}$	3
Trichloroethylene	1-10	Cell tumours in testes of rats	4.3×10^{-7}	2A
Vinychloride	0.1-10	Hemangiosarkoma in exposed workers. Liver cancer in exposed workers	1×10^{-6}	1

9 INFORMATION SOURCES

The following information sources were utilised in the preparation of these standards:

- Guidelines for Air Quality, WHO, Geneva, 2000
- DEAT Guideline Values for Ambient Air Quality in South Africa
- The United Kingdom National Air Quality Strategy (March 1997 - Command no. 3587)
- USEPA National Ambient Air Quality Standards
- European Union, Directive 1999/30/EC relating to limit values for sulphur dioxide, nitrogen dioxide, and oxides of nitrogen, particulate matter and lead in ambient air.

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APPENDIX 2

WATER QUALITY STANDARDS

(Surface Waters)

PRESENTATION OF THE DATA

For convenience in reference each parameter included in this volume is covered in a standard format consisting of a template in which important explanatory and background information is summarised. The parameters are dealt with in one alphabetical. The elements of the template are as follows, in the order in which they appear:

Chemical Symbol or Formula: These are in the conventional chemical notation, e.g. Antimony is Sb, Silver is Ag, Zinc is Zn, and so on. In many cases the entry is "Not Applicable" as there is either no chemical formula at all, as for microbiological parameters, or else the parameter, although chemical, is a bulk one, e.g. Pesticides, so that the use of formulae is precluded on practical grounds.

Units used for Analytical Results: For several key parameters the results of analysis may be reported in terms other than those of the chemical formulae of the entities being determined. Examples are nitrate, NO_3^-, reported often as N, and phosphate, PO_4^{--} commonly reported as P.

Reference Methods of Analysis: Reference methods are specified for the parameter in question. The references given relate to *Standard Methods for the Examination of Water and Wastewater, 1998, (prepared and published jointly by A.P.H.A., A.W.W.A & W.E.F) 20th Ed., American Public Health Association, 1015 Fifteenth Street, N.W., Washington DC 20005, USA*, a standard text used in most water laboratories.

As a guide, to the complexity of the method specified the following letters [A], [B], [C] and [D] have been used throughout to indicate, respectively, an increasing degree of sophistication of the technique and/or of the equipment used. Thus, [A] indicates a method suitable for use in a more basic water laboratory, [B] implies a method more demanding of staff expertise or equipment, [C] implies an elaborate laboratory set-up, with advanced instrumentation, and [D] denotes a specialist laboratory with state-of-the-art equipment. A dual designation, e.g. [B/C], is used for those methods which may be practicable at different levels of instrumentation or expertise. It may be noted that these designations are quite in for mat and are offered for guidance only. In reality, there may often be no clear gradations between the capabilities of different laboratories.

With regard to sampling, a sample should be collected such that the sample is representative of the condition being investigated and in a manner consistent with the collection, handling and preservation principles enunciated in the above publication section 1060.

Introduction: This section contains adequate detail to set the significance of each parameter in perspective. In some important cases, notably " Biochemical Oxygen Demand," "Hardness" and " Dissolved Oxygen," the entries are fairly lengthy, but this is in line with one of the primary aims of this volume, namely to act as a "free-standing" reference for the engineer, environmentalist or scientist.

Occurrence: A brief indication is given as to whether substances covered by the parameter occur in rock, are constituents of sewage or industrial wastes, or are synthetic materials. It is assumed throughout that substances attributed to industrial wastes could equally well arise from tiphead leachates, this is not always specified.

Effect: Brief reference is made to known toxic or physiological effects - or the lack of them - of each parameter. It must be stressed that such references are not in any way exhaustive, but are merely indicative. This volume does not purport in any way to deal with medical matters or with any material connection between a given parameter and the health of the user/consumer of a water containing it.

1 ALUMINIUM

Chemical Symbol or Formula: Al.

Standard: **0.2 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard**.**

Units Used for Analytical Results: mg/l Al.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Colorimetry	B	**3500-Al-D**
Atomic Absorption Spectrometry Method	B/C.	**3500-Al-B**
Inductively Coupled Plasma Method	D	**3500-Al-C**

Introduction

Aluminium is the third most abundant element in the earth's crust. It occurs primarily as aluminosilicate minerals which are too insoluble to participate readily in bio-geochemical reactions. Aluminium is a strongly hydrolysing metal and is relatively insoluble in the neutral pH range. Under acidic (pH < 6.0) or alkaline (pH > 8.0) conditions, or in the presence of complexing ligands, elevated concentrations may be mobilised to the aquatic environment.

The solubility of aluminium in water is strongly pH dependent. Under acid conditions, it occurs as soluble, available and toxic hexahydrate (aquo) species. At intermediate pH values, it is partially soluble and probably occurs as hydroxy- and polyhydroxo- complexes. At alkaline pH values, aluminium is present as soluble but biologically unavailable hydroxide complexes or as colloids and flocculants.

Aluminium is described as a non-critical element, though there is growing concern over the effects of elevated concentrations of aluminium in the environment, primarily that mobilized as a result of acid mine drainage and acid precipitation. Studies of the environmental chemistry and toxicity of aluminium provide a limited understanding of the processes regulating the aqueous concentration, speciation and bio-availability of this element. Clearly, the toxicity of aluminium depends on the chemical species involved.

Occurrence

Aluminium can be mobilised from soils and sediments by both natural weathering and accelerated acidification processes, resulting in detectable concentrations in surface waters. Although aluminium is found in waters made naturally acidic by humic and fulvic acids, it usually adsorbs onto these and is therefore not available in soluble form in such waters, even at low pH.

Aluminium is found in soluble forms mainly in acid mine drainage waters and is also of concern in natural waters affected by acid rain. Aluminium is one of the principal particulates emitted from the combustion of coal, and aluminium fluoride is emitted from aluminium smelters. Industries using aluminium in their processes or in their products include the following:

- the paper industry,
- the metal construction industry,
- the leather industry, and

- the textile industry.

In addition to liquid effluents that may be generated from the above industries, alum or aluminium sulphate is used in most water treatment processes as a flocculating agent for suspended solids, including colloidal materials, micro-organisms and "humic rich" dissolved organics.

Effects

Elevated concentrations of bio-available aluminium in water are toxic to a wide variety of organisms. There is, however, uncertainty as to the form(s) of bio-available aluminium as well as to the mechanism(s) of toxicity. The toxic effects are dependent on the species and life stage of the organism, the concentration of calcium in the water, and pH. The pH may not only affect the chemistry of aluminium but may also determine how the organism responds to dissolved aluminium. In acidic waters, aluminium is generally more toxic over the pH range of 4.4 - 5.4, with maximum toxicity occurring about pH 5.0 - 5.2.

The mechanism of toxicity in fish seems to be related to interference with ionic and osmotic balance and with respiratory problems resulting from coagulation of mucus on the gills. It has also been suggested that aluminium interferes with calcium metabolism, thereby altering the functioning of the calcium regulating protein, calmodulin. Aluminium has been shown to interfere with ion exchange sites, in particular those involved in sodium homeostasis. This in turn may lead to neuromuscular dysfunction.

2 AMMONIA

Chemical Symbol or Formula: NH_3

Standard:

Game Fishing:	**0.02 mg/l NH_3 (Non-ionised Ammonia)**
Game Fishing:	**0.04 mg/l NH_4 (Total Ammonia)**
Coarse Fishing:	**0.025 mg/l NH_3 (Non-ionised Ammonia)**
Coarse Fishing:	**0.2 mg/l NH_4 (Total Ammonia)**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l N.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Preliminary Distillation Step	B	**4500 NH_3 B**
Titrimetric Method	B	**4500 NH_3 C**
Ammonia – Selective Electrode Method	B	**4500 NH_3 D**
Colorimetric Method (Phenate)	B	**4500 NH_3 F**

Introduction

Un-ionized ammonia (NH_3) is a colourless, acrid-smelling gas at ambient temperature and pressure. It is produced naturally by the biological degradation of nitrogenous matter and provides an essential link in the nitrogen cycle.

Ammonia may be present in the free, un-ionized form (NH_3) or in the ionized form as the ammonium ion (NH_4^+). Both are reduced forms of inorganic

nitrogen derived mostly from aerobic and anaerobic decomposition of organic material. They exist either as ions, or can be adsorbed onto suspended organic and inorganic material.

The toxicity of ammonia is directly related to the concentration of the un-ionized form (NH_3), the ammonium ion (NH_4^+) having little or no toxicity to aquatic biota. The ammonium ion does, however, contribute to eutrophication. Modifying factors may alter the acute toxicity by altering the concentration of un-ionized ammonia in the water through changes in the ammonia-ammonium ion equilibrium, or may increase the toxicity of the un-ionized ammonia to organisms.

Occurrence

Ammonia is present in small amounts in air, soil and water, and in large amounts in decomposing organic matter. Natural sources of ammonia include gas exchange with the atmosphere; the chemical and biochemical transformation of nitrogenous organic and inorganic matter in the soil and water; the excretion of ammonia by living organisms; the nitrogen fixation processes whereby dissolved nitrogen gas enters the water and ground water. Ammonia, associated with clay minerals enters the aquatic environment through soil erosion. Bacteria in root nodules of legumes fix large amounts of nitrogen in the soil and this may be leached into surrounding waters.

Ammonia is a common pollutant and is one of the nutrients contributing to eutrophication. Commercial fertilizers contain highly soluble ammonia and ammonium salts. Following application of fertilizer, if the concentration of such compounds exceeds the immediate requirements of the plant, transport via the atmosphere or irrigation waters can carry these nitrogen compounds into aquatic systems. Other sources of ammonia include:

- fish-farm effluent (un-ionized ammonia);
- sewage discharge;
- discharge from industries that use ammonia or ammonium salts in their cleaning operations;
- manufacture of explosives and use of explosives in mining and construction; and
- atmospheric deposition of ammonia from distillation and combustion of coal, and the biological degradation of manure.

Effects

The most significant factors that affect the proportion and toxicity of un-ionized ammonia in aquatic ecosystems are water temperature and pH. An increase in either results in an increase in the relative proportion of un-ionized ammonia in solution, and hence an increase in toxicity to aquatic organisms, as given in Table 1.

Contribution of Un-ionised Ammonia to Total Ammonia (expressed as percentage) as function of pH Value and Water Temperature

	Water Temperature °C							
pH	0	5	10	15	20	25	30	35
6.0	0.0083	0.012	0.019	0.027	0.039	0.056	0.079	0.11
6.5	0.026	0.039	0.059	0.086	0.12	0.18	0.25	0.35
7.0	0.083	0.12	0.18	0.27	0.39	0.56	0.79	1.1
7.5	0.26	0.39	0.58	0.85	1.2	1.7	2.4	3.4
8.0	0.82	1.2	1.8	2.6	3.8	5.3	7.3	9.9
8.5	2.6	3.8	5.5	7.9	11	15	20	26
9.0	7.6	11	16	21	28	36	44	52
9.5	21	28	37	46	55	64	71	78

Ammonia toxicity is also affected by the concentrations of dissolved oxygen, carbon dioxide and total dissolved solids, and the presence of other toxicants, such as metal ions. The acute toxicity of ammonia to fish increases as dissolved oxygen decreases. Ammonia is oxidized to nitrate in well oxygenated waters. Ammonia may also be adsorbed onto suspended and bed sediments and to colloidal particles.

Un-ionized ammonia affects the respiratory systems of many animals, either by inhibiting cellular metabolism or by decreasing oxygen permeability of cell membranes. Acute toxicity to fish may cause a loss of equilibrium, hyper-excitability, an increased breathing rate, an increased cardiac output and oxygen intake, and in extreme cases convulsions, coma and death.

Chronic effects include a reduction in hatching success, reduction in growth rate and morphological development, and pathological changes in tissue of gills, liver and kidneys. An increased ventilation of the gills following exposure to ammonia indicating a respiratory effect has been observed in mayfly larvae *Ecdyonurus dispar*.

3 ANTIMONY

Chemical Symbol or Formula: Sb

Standard: **20 μg/l.**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l Sb.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometry Method	B/C	**3500-Sb-B**
Inductively Coupled Plasma Method	D	**3500-Sb-C**

Occurrence Naturally occurring trace element used in metal industry and in flame retardant materials. Antimony can occur naturally in water from weathering of rocks but is more likely to arise from effluents.

Effects Significance: Although the health effects of antimony have not been established definitively, there is evidence of actual or potential carcinogenicity of some antimony compounds. Accordingly, concentrations are limited in drinking water.

4 ARSENIC

Chemical Symbol or Formula: As.

Standard: **0.05 mg/l**

Percentage Compliance Required: All monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l As.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometry Method	C/D.	**3500-As-B**
Inductively Coupled Plasma Method	D	**3500-As-D**

Introduction Arsenic is a metalloid element which is toxic to marine and freshwater aquatic life and is a known carcinogen. Elemental arsenic is insoluble in water, but many of its compounds are highly soluble. Arsenic occurs in several oxidation states, namely, III, IV, V and III, -depending on the pH and redox potential of the water. The two most common forms are arsenic (III) and arsenic (V), both of which form stable compounds with carbon, resulting in numerous organo-arsenical compounds. Elemental arsenic also combines readily with many metals to form arsenide salts, which are toxic to organisms.

Most forms of arsenic, including the arsenical gases arsine (AsH_3) and trimethyl arsine, are very toxic. The USEPA has classified arsenic as "very toxic and relatively accessible" to aquatic organisms.

Occurrence

Elemental arsenic is found to a limited extent in nature, mostly as a result of weathering of arsenic-containing rocks and of volcanic activity. Arsenic most commonly occurs as arsenides of metals or as arsenopyrite. Inorganic arsenic occurs in aquatic ecosystems primarily as arsenic (III) and as arsenic (V), depending on pH and redox potential. Arsenic readily adsorbs onto sediments and suspended solids, and is lipid-soluble.

Arsenic may occur at high concentrations in water bodies subject to industrial pollution, or in the vicinity of industrial activities utilising or discharging arsenic or arsenal compounds.

Manufacturers that use arsenic in their processes, or in their products, include:

- the mining industry,
- the metal processing industry,
- producers of pesticides and fertilizers,
- producers of glass and ceramics,
- tanneries,
- dye manufacturers,
- producers of wood preservation products,
- the chemical industry,
- producers of detergents.

Effects

Arsenic has been reported to have a variety of adverse effects on both vertebrate and invertebrate aquatic organisms; the type and severity of adverse effects being dependent on the life stages of the organisms concerned. Exposure to arsenic results in reduced growth and reproduction in both fish and invertebrate populations. Arsenic also causes behavioural changes such as reduced migration in fish.

Organic arsenal compounds have been shown to be less toxic than inorganic forms of arsenic to fish. In fresh water, there is little evidence to suggest that different inorganic forms of arsenic vary significantly in their toxicity to aquatic biota. Arsenic (V) is more toxic to plants than arsenic (III). Arsenates, although not particularly toxic, interfere with energy metabolism, whereas arsenites inhibit the activity of a variety of essential enzymes.

Increased duration of exposure to arsenic at a given concentration leads to a reduction in adverse effects experienced by aquatic organisms, and they have been shown to develop tolerance. The response of organisms to arsenic is reduced by pre-exposure, and organisms may become gradually acclimated to high concentrations of arsenic in aquatic ecosystems.

Although inorganic arsenic does not accumulate in aquatic organisms, various forms of arsenic are lipid-soluble and therefore accumulate, in fatty tissue. Arsenic accumulation is usually higher in algae and invertebrates than in fish, though bottom-feeding fish are most likely to accumulate arsenic. Humans are more sensitive to arsenic than are aquatic organisms; therefore, consumption of contaminated products can pose a health risk to humans. Arsenic can be bio-concentrated in aquatic organisms because it has a high affinity for organic substances.

Many of the toxic effects of arsenic on aquatic organisms can be reversed if arsenic concentrations are reduced and maintained at very low levels.

5 BARIUM

Chemical Symbol or Formula: Ba.

Standard: **0.1 mg/l**

Percentage Compliance Required: All monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l Ba.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometry Method	B/C	**3500-Ba-B**
Inductively Coupled Plasma Method	D	**3500-Ba-C**

Occurrence Naturally occurring mineral (e.g. in barytes. According to the WHO Guidelines, while food is the main source of barium intake by humans, where barium occurs in drinking water supplies the latter can contribute a significant proportion of total intake.

In normal surface waters levels are likely to be low as traces of barium will react with sulphate present to form the highly insoluble barium sulphate.

Effects Significance: Excessive amounts of barium can cause muscular, cardiovascular and renal damage. Although not markedly toxic, barium in excess quantities is clearly undesirable.

6 BENZENE

Chemical Symbol or Formula: C_6H_6

Standard: **10 μg/l**

Percentage Compliance Required: All monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l compound.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Purge and Trap Gas Chromatographic Method I	C	**6220-B**
Purge and Trap Gas Chromatographic Method II	C	**6220-C**
Purge and Trap Gas Chromatographic/Mass Spectrometric Method	D	**6220-D**

Background: Emissions from motor vehicles account for most of the benzene in the air, which can in due course reach the aquatic environment. Pollution from industrial sources can also introduce benzene to water.

Benzene is not a naturally-occurring constituent of water.

Occurrence Constituent of some petroleum products; industrial raw material; solvent.

Effects Carcinogenic substance which also affects the central nervous system adversely.

7 BENZO(A)PYRENE

Chemical Symbol or Formula: $C_{20}H_{12}$

Standard: **0.01 µg/l**

Percentage Compliance Required: All monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l compound.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method	D	**6410-B**
Liquid-Liquid Extraction Gas Chromatographic Method	C	**6431-B**

Occurrence Synthetic complex aromatic organic compound formed by pyrolysis or combustion of organic materials.

Effects Benzo(a)pyrene is a carcinogenic and mutagenic substance which is considered to be highly undesirable in drinking water, even though the WHO Guidelines indicate that food is the main source of human exposure to this type of substance.

8 BENZENE

Chemical Symbol or Formula: C_6H_6

Standard: **10 µg/l**

Percentage Compliance Required: All monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l compound.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Purge and Trap Gas Chromatographic Method I	C	**6220-B**
Purge and Trap Gas Chromatographic Method II	C	**6220-C**
Purge and Trap Gas Chromatographic/Mass Spectrometric Method	D	**6220-D**

Background: Emissions from motor vehicles account for most of the benzene in the air, which can in due course reach the aquatic environment. Pollution from industrial sources can also introduce benzene to water.

Benzene is not a naturally-occurring constituent of water.

Occurrence Constituent of some petroleum products; industrial raw material; solvent.

Effects Carcinogenic substance which also affects the central nervous system adversely.

9 BIOCHEMICAL OXYGEN DEMAND (BOD_5)

Chemical Symbol or Formula: Not applicable [Bulk parameter]

Standard: **≤ 5 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l O_2.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
5-Day BOD Test	B	**5210-B**

Background When organic matter is discharged into a watercourse it serves as a food source for the bacteria present there. These will sooner or later commence the breakdown of this matter to less complex organic substances and ultimately to simple compounds such as carbon dioxide and water. If previously unpolluted, the receiving water will be saturated with dissolved oxygen (DO), or nearly so, and the bacteria present in the water will be aerobic types. Thus the bacterial breakdown of the organic matter added will be an aerobic process - the bacteria will multiply, degrading the waste and utilising the DO as they do so. If the quantity of waste present is sufficiently large, the rate of bacterial uptake of oxygen will outstrip that at which the DO is replenished from the atmosphere and from photosynthesis, and ultimately the receiving water will become anaerobic.

Bacterial degradation of the waste will continue but now the products will be offensive in nature -for example, hydrogen sulphide. Even if the uptake of oxygen is not sufficient to result in anaerobic conditions there will be other undesirable effects as the DO level falls, notably damage to fisheries and, ultimately, fish deaths. Where levels are around 50 per cent saturation for significant periods there may be adverse, though non-lethal, effects on game fish. Coarse fish will be likewise affected if levels are regularly around 30 per cent saturation.

Because of the potential danger to the oxygen levels in receiving waters from waste discharges considerable emphasis is placed in the laboratory on the estimation of the oxygen demand of wastes: i.e. the amount of oxygen which will be required in their breakdown. This is done chemically and biologically, by a variety of tests which are also employed to assess the actual effects of waste discharges on receiving water, as discussed below. As in most cases the oxygen demand of a waste on the DO level of a receiving water results from biological action, it follows that the most important analytical method should

also depend on a biological process, to measure the biochemical oxygen demand or BOD. The principle of this test, which was devised some 85 years ago, is straightforward. The (five-day) BOD of a water is the amount of dissolved oxygen taken up by bacteria in degrading oxidisable matter in the sample, measured after 5 days incubation in the dark at 20°C. The BOD is simply the amount by which the DO level has dropped during the incubation period. This technique is the basis of BOD analyses for all types of sample even though considerable extensions of procedure are necessary in dealing with wastewaters and polluted surface waters.

Current scientific opinion is that waters with a BOD failing within the range of 0 - 4 mg/l O_2 are of satisfactory quality for sensitive species such as salmonid fish and thus for other beneficial uses. If an upper limit for BOD of 4 mg/l O_2 is adopted as a criterion of satisfactory quality then it is possible to assess the degree to which waters are polluted by reference to this datum. It is most important to remember, however.. that a BOD figure for a receiving water indicates the maximum extent to which the oxygen level may be depleted by the organic matter present. In reality, no appreciable deoxygenation may occur because of factors such as low temperatures, reaeration at weirs or shallows, dilution by tributaries and so on. Conversely, in some waters which do not have high BOD levels, but which are eutrophic, there may be severe night-time DO depletions caused by algal respiration. Notwithstanding the many often contradictory considerations which govern the interpretation of BOD data the analysis is one of the most important elements in river quality surveillance and it seems unlikely to be superseded for a long time yet.

Somewhat different considerations apply to the BOD analysis of effluents. BOD data are normally required for one of two purposes. Firstly, it is necessary to know the strength of a waste which is to be treated by biological means, as in an oxidation ditch or percolating filter. This is essential so that adequate treatment capacity may be provided for in the design of the plant. Secondly.. where wastes are being discharged to receiving waters a knowledge of their strength and the magnitude of the river discharge will permit the dilution to be calculated and hence the maximum potential change in the river BOD at the boundary of the mixing zone. A factor which must be borne in mind in obtaining and in assessing BOD results is nitrification. This is the oxidation of ammonia to nitrate by suitable micro-organisms and if the process is occurring under test conditions high oxygen uptake values will be recorded. For normal river waters the onset of nitrification under BOD test conditions does not occur within the 5-day period of the analysis but in the case of waters or wastewaters containing nitrifying organisms this phenomenon will take place much more promptly. Unless suitable precautions are taken the result is an apparently very high BOD level which, if the analysis is being used to check the performance of a waste treatment works (with respect to the removal of organic matter), for example, may lead to serious errors in the interpretation and use of the data.

Occurrence Natural or introduced organic matter in water.

Effects An indicator of overall water quality.

10 CADMIUM

Chemical Symbol or Formula: Cd.

Standard: **5 µg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l Cd.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Cd-B**
Inductively Coupled Plasma Method	D	**3500-Cd-C**
Dithizone Method	B	**3500-Cd-D**

Introduction

Cadmium is a metal element which is highly toxic to marine and fresh water aquatic life. Elemental cadmium is insoluble in water though many of its organic and inorganic salts are highly soluble. Cadmium occurs primarily in fresh waters as divalent forms including free cadmium (II) ion, cadmium chloride and cadmium carbonate, as well as a variety of other inorganic and organic compounds.

Cadmium is defined by the United States Environmental Protection Agency as potentially hazardous to most forms of life, and is considered to be toxic and relatively accessible to aquatic organisms.

Occurrence

Cadmium is present in the earth's crust at an average concentration of 0.2 mg/kg, usually in association with zinc, lead and copper sulphide ore bodies.

Due to its abundance, large quantities of cadmium enter the global environment annually as a result of natural weathering processes. Cadmium is found at trace concentrations in fresh waters and mostly a result of industrial activity.

The main sources of cadmium in the environment are due to:

- emissions to air and water from mining, metal (zinc, lead and copper) smelters, and industries involved in manufacturing alloys, paints, batteries and plastics;
- agricultural use of sludges, fertilizers and pesticides containing cadmium;
- burning of fossil fuels (very limited effect); and
- the deterioration of galvanized materials and cadmium-plated containers.

Effects

Cadmium is easily absorbed by mammals, where it is concentrated by binding with the protein metallothionein. Many plant and animal tissues contain cadmium, but there is no evidence that cadmium is biologically essential or beneficial. Cadmium is chemically similar to zinc, and its physiological effects are often due to its replacement of zinc in some enzymes, thereby impairing enzyme activity. Cadmium is known to inhibit bone repair mechanisms, and is teratogenic, mutagenic and carcinogenic.

Bioavailable cadmium may be accumulated by macrophytes, phytoplankton, zooplankton, invertebrates and fish. Bioavailability is dependent on cadmium speciation; for example, the free ion, Cd , is readily taken up by aquatic plants,

whereas organo-cadmium complexes are 2+ not absorbed. Lethal concentrations of cadmium also vary depending on the test animal, water hardness and temperature, and time of exposure. The level of bio-accumulation is dependent on the species and age of the organism. Cadmium bio-accumulates in the food chain due to its tendency to bind strongly to sulphydryl groups.

Bio-concentration factors range from 10 to 10 for both invertebrates and fish. However, 2 5 there is no evidence for cadmium bio-magnification through the aquatic food web.

11 CHLORIDE

Chemical Symbol or Formula: Cl^-.

Standard: **250 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l Cl.

Normal Method(s) of Analysis: Titration (Mohr Method: Silver Nitrate) [A]

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Mercuric Nitrate Method	B	**4500-Cl^--C**
Potentiometric Method	B	**4500-Cl^--D**
Ion Chromatographic Method	B/C	**4500-Cl^--F**

Introduction At levels above 250 mg/l Cl water will begin to taste salty and will become increasingly objectionable as the concentration rises further. However, external circumstances govern acceptability and in some arid areas waters containing up to 2,000 mg/l Cl are consumed, though not by people unfamiliar with such concentrations. High chloride levels may similarly render freshwater unsuitable for agricultural irrigation.

Because sewage is such a rich source of chloride, a high result may indicate pollution of a water by a sewage effluent. Natural levels in rivers and other fresh waters are usually in the range 15-35 mg/l Cl - much below drinking water standards. What is normally important to note in a series of results from a river, for example, is not the absolute level, but rather the relative levels from one sampling point to another.

An increase of even 5 mg/l at one station may give rise to suspicions of a sewage discharge, especially if the free ammonia levels (q.v.) are also elevated. Normal raw water treatment processes do not remove chloride.

Occurrence Chloride exists in all natural waters, the concentrations varying very widely and reaching a maximum in sea water (up to 35,000 mg/l Cl). In fresh waters the sources include soil and rock formations, sea spray and waste discharges. Sewage contains large amounts of chloride, as do some industrial effluents.

Effect Chloride does not pose a health hazard to humans and the principal consideration is in relation to palatability

12 CHLORINE

Chemical Symbol or Formula: Cl_2.

Standard: **5 µg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l Cl.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Iodometric Method I	B	**4500-Cl-B**
Amperometric Titration Method	B/C	**4500-Cl-D**
DPD Colorimetric Method	A	**4500-Cl-G**

Introduction Elemental chlorine (Cl_2) is a greenish-yellow gas that dissolves readily in water. It is not normally a constituent of natural waters since chlorine is too reactive to persist in the aquatic environment..

Occurrence Free forms of chlorine such as HOCl and OCl^-, or combined available chlorine (chloramines), occurs in aquatic ecosystems as a result of:

- chlorination of drinking water (to remove unwanted tastes and odours, and for the purposes of disinfection);
- the textile industry (bleaching, slimicide);
- the pulp and paper industry (bleaching, slimicide);
- sewage treatment (reduce odour, algicide, bactericide);
- cooling waters (slimicide); and
- swimming pools (disinfection).

Effluents containing ammonia, organic matter or cyanides convert chlorine into substances such as chloramines, which may be less toxic but more persistent than chlorine, thereby posing a long-term threat to aquatic life..

Effects The toxic effects of chlorine are usually irreversible. Free chlorine is more toxic but less persistent than combined chlorine. Diatoms are more sensitive to chlorine than are green algae, which, in turn, are more sensitive than blue-green algae. Newly hatched fish larvae are more sensitive to chlorine than are fish eggs.

Avoidance behaviour, adverse changes in the blood chemistry, damage to gills, decreased growth rate, restlessness preceding loss of equilibrium and death have been observed for fish exposed to chlorine. Invertebrates become immobile, and exhibit reduced reproduction and reduced survival on exposure to chlorine. Aquatic plants may become chlorotic, whilst reduced rates of photosynthesis and respiration are observed for phytoplankton.

Acclimation to sublethal chlorine concentrations leads to increased resistance. Chlorine itself does not accumulate, but chlorinated organic substances may bio-concentrate in aquatic organisms.

13 CHROMIUM

Chemical Symbol or Formula: Cr.

Standard: **50 μg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l Cr.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Cr-B**
Inductively Coupled Plasma Method	D	**3500-Cr-C**
Colorimetric Method	B	**3500-Cr-D**
Ion Chromatographic Method	B	**3500-Cr-E**

Introduction

Chromium is a relatively scarce metal, and the occurrence and amounts thereof in aquatic ecosystems are usually very low. Chromium ions occur in a variety of forms:

- chromium (II) - chromous ion (Cr^{2+}),
- chromium (III) - chromic ion (Cr^{3+}, trivalent),
- chromium (III) - chromite ion (CrO_3^{3-}, trivalent),
- chromium (VI) - chromate ion (CrO_4^{2-} , hexavalent),
- chromium (VI) - dichromate ion ($Cr_2O_7^{2-}$, hexavalent)

Chromium(VI) is a highly oxidized state and occurs as the yellow dichromate salt in neutral or alkaline media, and as the orange chromate salt in acid medium. Both of these chromium(VI) salts are highly soluble at all pH values. The reduced forms, chromium(II) and chromium(III) are reported as being less toxic and therefore less hazardous than chromium(VI)..

Occurrence

The most common ore of the metal chromium is chromite, in which chromium occurs in the trivalent state. Other minerals containing chromium do occur, but are not common. Most elevated levels of chromium in aquatic ecosystems are a consequence of industrial activity.

In the aquatic environment chromous compounds tend to be oxidized to chromic forms, whilst the chromium(VI) form can be reduced to chromium(III) by heat, in the presence of organic matter and by reducing agents.

Of the trivalent chromium salts, the chloride, nitrate and sulphate salts are readily soluble, whereas the hydroxide and carbonate salts are relatively insoluble. Of the hexavalent chromate salts only the sodium, potassium, and ammonium chromates and dichromates are soluble.

Hexavalent chromium salts are used extensively:

- in metal pickling and plating;
- in the leather industry as tanning agents; and
- in the manufacture of paints, dyes, explosives, ceramics and paper.

Trivalent chromium salts are used much less frequently, but are important as:

- fixatives in textile dye manufacture;
- in the ceramic and glass industry; and
- in photography.

Chromium compounds may also be discharged in chromium-treated cooling waters where chromium has been used as a corrosion inhibitor.

Effects Chromium exerts a toxic effect at different concentrations in different groups of aquatic organisms. Fish are the most resistant, and in some cases the toxicity of chromium(VI) is no greater than for chromium(III). A temporarily reduced growth phase has been reported for young fish at low chromium concentrations. Invertebrates are usually at least an order of magnitude more sensitive, with daphniids showing the greatest sensitivity to chromium. Green algae are also more sensitive than fish, whilst bacterial responses to chromium are variable.

14 CONDUCTIVITY

Chemical Symbol or Formula: Not Applicable [Physical parameter].

Standard: **1000 µS/Cm (@ 20°C)**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µS/cm

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Field Method (Electrometric)	A	-
Laboratory Method	B	**2510**

Introduction Also referred to as electrical conductivity and, not wholly accurately, as specific conductance, the conductivity of a water is an expression of its ability to conduct an electric current. As this property is related to the ionic content of the sample which is in turn a function of the dissolved (ionisable) solids concentration, the relevance of easily performed conductivity measurements is apparent. In itself conductivity is a property of little interest to a water analyst but it is an invaluable indicator of the range into which hardness and alkalinity values are likely to fall, and also of the order of the dissolved solids content of the water. While a certain proportion of the dissolved solids (for example, those which are of vegetable origin) will not be ionised (and hence will not be reflected in the conductivity figures) for many surface waters the following approximation will apply: Conductivity (µS/cm) x 2/3 = Total Dissolved Solids (mg/l).

In samples from a source which is regularly tested a rapid conductivity analysis may be an adequate replacement for other, longer determinations.

It is important to note that there is an interrelationship between conductivity and temperature, the former increasing with temperature at a rate of some 2 per cent per degree C rise. There is a regrettable lack of uniformity in the terms in which

conductivity is reported. Some UK methods manuals report the results at 20°C while the standard US reference manual uses 25°C. A difference of 10 percent can therefore arise depending on how the results are quoted. An error of this magnitude could not be tolerated, especially where conductivity readings are being used to estimate salinity.

Occurrence Reflects mineral salt content of water.

Effect No direct significance.

15 COPPER

Chemical Symbol or Formula: Cu.

Standard:

Copper (μg/l)	Hardness (mg/l $CaCO_3$)
5	10
22	50
40	100
112	500

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l Cu.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Cu-B**
Inductively Coupled Plasma Method	D	**3500-Cu-C**
Neocuproine Method	B	**3500-Cu-D**

Introduction Copper is one of the world's most widely used metals. Although copper occurs naturally in most waters, it is regarded as potentially hazardous by the USEPA.

Copper occurs in four oxidation states, namely, 0, I, II and III. The two most common forms are cuprous copper(I) and cupric copper(II). Cuprous copper is unstable in aerated aqueous solutions and will normally be oxidized to cupric copper..

Occurrence Copper is a common metallic element in the rocks and minerals of the earth's crust, and is commonly found as an impurity in mineral ores. Chalcopyrite ($CuFeS_2$) is the most abundant of the copper minerals. Crustal (igneous) rocks contain more copper (23 - 55 mg/kg) than sedimentary rocks (4 - 45 mg/kg).

The occurrence of natural sources of copper in the aquatic environment is due to weathering processes or from the dissolution of copper minerals and native copper. Metallic copper is insoluble in water, but many copper salts are highly soluble as cupric or cuprous ions. Anthropogenic sources account for 33 - 60 % of the total annual global input of copper to the aquatic environment.

The main anthropogenic sources of copper in the aquatic environment are:

- corrosion of brass and copper pipes by acidic waters;

- sewage treatment plant effluents;
- copper compounds used as aquatic algicides;
- runoff and ground water contamination from the use of copper as fungicides and pesticides in the treatment of soils; and
- liquid effluents and atmospheric fallout from industrial sources such as mining, smelting and refining industries, coal-burning, and iron- and steel-producing industries.

Effects

Copper is a micronutrient and an essential component of enzymes involved in redox reactions and is rapidly accumulated by plants and animals. It is toxic at low concentrations in water and is known to cause brain damage in mammals. Copper exerts its effect by forming stable co-ordinate bonds in proteins, where it functions as a catalyst in redox reactions. Metabolically, copper interacts with zinc, molybdenum, arsenic and selenium.

The effect of elevated copper concentrations on aquatic organisms is also related to factors such as the duration of exposure and life stage of the organism. Studies have shown that species richness and species composition of invertebrate communities and changed as copper concentrations increased. Early life stages of organisms appear to be more sensitive than adults to copper pollution.

Nitrogen fixation by blue-green algae is reduced by the addition of trace amounts of copper. Although bio-concentration factors range from 100 - 26 000, there is no evidence to suggest that copper is bio-magnified.

16 CYANIDE

Chemical Symbol or Formula: CN^-.

Standard: **50 µg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l CN

Normal Method(s) of Analysis: Colorimetric (after distillation) [B];

Specific Ion Electrode (after distillation) [B].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Preliminary Treatment of Samples	B	**4500-CN^--B**
Total Cyanide after Distillation	B	**4500-CN^--C**
Titrimetric Method	B	**4500-CN^--D**
Colorimetric Method	B	**4500-CN^--E**
Cyanide Selective Electrode Method	B	**4500-CN^--F**

Introduction

Hydrocyanic acid (HCN) which is the most toxic form of cyanide reacts with water to release cyanide ions (CN^-).

Occurrence Most of the cyanide in water is in the hydrocyanic acid form which is largely undissociated at pH values of 8 or less. Cyanide in the environment is usually found complexed with metals. Cyanides are present in effluents from gas works and coke ovens, scrubbing of gases at steel plants, metal cleaning, electroplating and chemical industries. Cyanide is a common reagent in gold extraction processes and large quantities of cyanide are found in gold mine tailing dams. Cyanide is sometimes present in phenolic wastes..

Effects Cyanide interferes with aerobic respiration and is therefore toxic only to aerobic organisms. Cyanide is thus not as toxic to "lower" organisms (invertebrates) as it is to fish and other vertebrates. There is a greater variability in sensitivities of invertebrates than there is in fish species. Embryos, sac larvae and warm-water-adapted species of fish are more resistant to cyanide than are other life stages or species of fish. The gills of fish suffering from cyanide poisoning are bright red in colour.

17 DISOLVED OXYGEN

Chemical Symbol or Formula: O_2.

Standard:

Game Fish	**50% Samples ≥ 9 mg/l**
	Minimum 6 mg/l
Course Fish	**50% Samples ≥ 7 mg/l**
	Minimum 4 mg/l

Units Used for Analytical Results: mg/l O_2

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Iodometric (Winkler) Method	B	**4500-O-B**
Azide Modification	B	**4500-O-C**
Permanganate Modification	B	**4500-O-D**
Membrane Electrode (may be modified for filed work)	A	**4500-O-G**

Introduction Gaseous oxygen (O_2) from the atmosphere dissolves in water and is also generated during photosynthesis by aquatic plants and phytoplankton. Oxygen is moderately soluble in water. Equilibrium solubility, termed the saturation solubility, varies non-linearly with temperature, salinity and atmospheric pressure, and with other site-specific chemical and physical factors.

The maintenance of adequate dissolved oxygen (DO) concentrations is critical for the survival and functioning of the aquatic biota because it is required for the respiration of all aerobic organisms. Therefore, the DO concentration provides a useful measure of the health of an aquatic ecosystem. Measurement of the biochemical oxygen demand (BOD) or the chemical oxygen demand (COD) are inappropriate for aquatic ecosystems, but are useful for determining water quality requirements of effluents discharged into aquatic systems, in order to limit their impact.

Occurrence

In unpolluted surface waters, dissolved oxygen concentrations are usually close to saturation. Typical saturation concentrations at sea level, and at TDS values below 3 000 mg/l, are: 12.77 mg/l at 5 °C; 10.08 mg/R at 15 °C; 9.09 mg/l at 20 °C.

There is a natural diel variation (24 hour cycle) in dissolved oxygen associated with the 24-hour cycle of photosynthesis and respiration by aquatic biota. Concentrations decline through the night to a minimum near dawn, then rise to a maximum by mid afternoon. Seasonal variations arise from changes in temperature and biological productivity.

Reduction in the concentration of dissolved oxygen can be caused by several factors:

- Resuspension of anoxic sediments, as a result of river floods or dredging activities.
- Turnover or release of anoxic bottom water from a deep lake or reservoir.
- The presence of oxidizable organic matter, either of natural origin (detritus) or originating in waste discharges, can lead to reduction in the concentration of dissolved oxygen in surface waters. The potential for organic wastes to deplete oxygen is commonly measured as biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The COD is used as a routine measurement for effluents, and is measure of the amount of oxygen likely to be used in the degration of organic waste. However, in aquatic ecosystems it is unlikely that all organic matter will be fully oxidised.
- The amount of suspended material in the water affects the saturation concentration of dissolved oxygen, either chemically, through the oxygen-scavenging attributes of the suspended particles, or physically through reduction of the volume of water available for solution.

Dissolved oxygen concentrations can be increased by natural diffusion of gaseous oxygen from the atmosphere into water. Diffusion continues until the saturation concentration is reached. The rate of increase of dissolution of oxygen can be accelerated if turbulence of the water increases, causing entrainment of air from the atmosphere.

Effects

Aerobic organisms are dependent for respiration on the presence of dissolved oxygen in water. Anoxic or hypoxic conditions may be lethal within short time scales (minutes to hours).

The sensitivity of many species, especially fish and invertebrates, to changes in dissolved oxygen concentrations depends on the species and the life stages (eggs, larvae or adult) and behavioural changes (feeding and reproduction) Juveniles of many aquatic organisms are more sensitive to physiological stress arising from oxygen depletion, and in particular to secondary effects such as increased vulnerability to predation and disease. Where possible, many species will avoid anoxic or oxygen-depleted zones.

Cold-water-adapted species such as salmonids (e.g., trout) are especially sensitive to depletion of dissolved oxygen. Reproduction and growth in these species is reduced under continuous exposure to oxygen concentrations less than 100 % saturation.

Oxygen concentrations above saturation may cause gas bubble disease in fish. Super-saturated conditions also tend to inhibit photosynthesis in green algae, favouring instead blue-green algae, which are more tolerant of super-saturation, but which may become a nuisance to other water users.

The reversibility of toxic effects on organisms depends on the duration, frequency and timing of the occurrence of oxygen depletion. Physiological stress effects in adult or less sensitive life stages may be rapidly reversed if oxygen depletion is short-lived. Prolonged exposure of aquatic communities to dissolved oxygen concentrations less than 50 % of saturation can cause significant changes in community composition, as more tolerant species are favoured.

18 FLORIDE

Chemical Symbol or Formula: F^-.

Standard: **1 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l F.

Normal Method(s) of Analysis: Colorimetric (after distillation) [B];

Specific Ion Electrode [B].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Preliminary Distillation Step	B	**4500-F⁻-B**
Ion Selective Electrode Method	B/C	**4500-F⁻-C**
SPADNS Method	B	**4500-F⁻-D**

Introduction Fluoride is a halogen gas which is highly reactive with a variety of substances. It is seldom found as free fluorine gas in nature, but occurs either as the fluoride ion or in combination with calcium, potassium and phosphates.

Occurrence Fluoride occurs in the earth's crust at an average concentration of 0.3 g/kg, most often as a constituent of fluorite (CaF_2), often known as fluorspar or calcium fluoride, in sedimentary rocks. Other important occurrences of fluoride are cryolite and fluorapatite in igneous rocks. Traces of fluoride (< 1 mg/l) occur in many aquatic ecosystems, whilst higher concentrations (often > 10 mg/l) can be found in ground waters derived from igneous rocks.

Fluoride is used in:

- the manufacture and use of insecticides;
- disinfecting brewery apparatus;
- fluxes used in the manufacture of steel;
- wood preservatives;
- glass and enamel manufacture;
- chemical industries;
- water treatment, where fluoride may be added for dental purposes; and
- other minor uses.

Effects Low concentrations of fluoride (< 1 000 μg/l) strengthen tooth enamel and bones in mammals. Skeletal fluorosis may occur if exposure to intermediate fluoride concentrations occurs over long periods.

19 HYDROCARBONS, DISSOLVED & EMULSIFIED

Chemical Symbol or Formula: Not Applicable [Bulk parameter].

Standard: **10 μg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l material.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Hydrocarbons (followed by Gas chromatography)	C	**5520-F**

Introduction This heading includes petroleum, oil, grease and related materials. Problems caused by these substances include interference with such vital processes as the mass transfer of oxygen from air to water (essential in river reaeration, for example), blockage of pipes, fouling of plant and animal life, odour and taste problems, and the like

It is worth reiterating that this parameter as herein defined is an overall aggregate (or bulk) parameter which is nonetheless limited in its scope by the generalised nature of the relevant analytical methods. A large number of specific (and potentially undesirable) hydrocarbon compounds are thus excluded from its coverage

Occurrence Effluent discharges, oil spillages etc.

Effect The main implications are organoleptic in the context of this parameter, but many complex hydrocarbon materials are carcinogenic (e.g. polycyclic aromatic hydrocarbons, q.v.).

20 IRON

Chemical Symbol or Formula: Fe.

Standard: **1 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l Fe Dissolved.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Fe-B**
Inductively Coupled Plasma Method	D	**3500-Fe-C**
Phenanthroline Method	B	**3500-Fe-D**

Introduction

Iron is the fourth most abundant element in the earth's crust and may be present in natural waters in varying quantities depending on the geology of the area and other chemical properties of the water body. The two common states of iron in water are the reduced (ferrous, Fe^{2+}) and the oxidised (ferric, Fe^{3+}) states. Most iron in oxygenated waters occurs as ferric hydroxide in particulate and colloidal form and as complexes with organic, especially humic, compounds. Ferric salts are insoluble in oxygenated waters, and hence iron concentrations are usually low in the water column. In reducing waters, the ferrous form, which is more soluble, may persist and, in the absence of sulphide and carbonate anions, high concentrations of ferrous iron may be found.

The toxicity of iron depends on whether it is in the ferrous or ferric state, and in suspension or solution. Although iron has toxic properties at high concentrations, inhibiting various enzymes, it is not easily absorbed through the gastro-intestinal tract of vertebrates. On the basis of iron's limited toxicity and bio-availability, it is classified as a non-critical element.

Iron is an essential micronutrient for all organisms, and is required in the enzymatic pathways of chlorophyll and protein synthesis, and in the respiratory enzymes of all organisms. It also forms a basic component of haeme-containing respiratory pigments (for example, haemoglobin), catalyses, cytochromes and peroxidases. Under certain conditions of restricted availability of iron, photosynthetic productivity may be limited.

Occurrence

Iron is naturally released into the environment from weathering of sulphide ores (pyrite, FeS_2) and igneous, sedimentary and metamorphic rocks. Leaching from sandstones releases iron oxides and iron hydroxides to the environment. Iron is also released into the environment by human activities, mainly from the burning of coke and coal, acid mine drainage, mineral processing, sewage, landfill leachates and the corrosion of iron and steel. Various industries that also use iron in their processes, or in their products, include:

- the chlor-alkali industry,
- the household chemical industry,
- the fungicide industry,
- the petro-chemical industry.

Streams may be negatively impacted by high levels of iron in acid mine drainage. Pyrite, iron sulphide, is often found in close association with coal deposits. Upon exposure to moisture and atmospheric oxygen, the ferrous iron is oxidised to the ferric state, a reaction which is frequently accelerated by bacteria of the Thiobacillus-Ferrobacillus group. If the mine drainage results in acid conditions in the stream, the rate of oxidation will be slow. If, however, the acid is neutralized (the rate of neutralization depends on the surface geology) and pH rises to between 7 and 8, the rate of oxidation will increase and ferric hydroxide will precipitate. A layer of ferric hydroxide precipitate, so-called "yellowboy", on stream bottoms and structures is a common sight in areas affected by acid mine drainage. The receiving water is often also oxygen deficient.

Effects Data on the acute and chronic toxicity of iron to both invertebrates and vertebrates are rather limited.

21 LEAD

Chemical Symbol or Formula: Pb.

Standard: **0.05 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l Pb.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Pb-B**
Inductively Coupled Plasma Method	D	**3500-Pb-C**
Dithiozone Method	B	**3500-Pb-D**

Introduction Lead exists in several oxidation states, that is, 0, I, II and IV, all of which are of environmental importance. Lead occurs as metallic lead, inorganic compounds, and organometallic compounds. The divalent form, lead (II), is the stable ionic species present in the environment and is thought to be the form in which most lead is bio-accumulated by aquatic organisms. In fresh waters lead is generally present as $PbCO_3$ and as lead-organic complexes, with a small proportion in the form of free lead ions. Lead may also be complexed with organic ligands, yielding soluble, colloidal and particulate compounds. Lead is defined by the USEPA as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms.

Occurrence Lead is principally released into the aquatic environment through the weathering of sulphide ores, especially galena. Since metallic lead and common lead minerals such as sulphides, sulphates, oxides, carbonates and hydroxides are almost insoluble, levels of dissolved lead (acetate and chloride salts) in aquatic ecosystems are generally low. Most of the lead entering aquatic ecosystems is associated with suspended sediments, while lead in the dissolved phase is usually complexed by organic ligands.

The photolysis of lead compounds is an important process in the removal of lead from the atmosphere. The products of this photo-degradation are lead oxides and halides, which enter the aquatic ecosystems via direct deposition or surface runoff.

The major sources of lead in the aquatic environment are anthropogenic, these include:

- precipitation, fallout of lead dust and street runoff (associated with lead emissions from gasoline-powered motor vehicles);
- industrial and municipal wastewater discharge;
- mining, milling and smelting of lead and metals associated with lead, e.g. zinc, copper, silver, arsenic and antimony; and
- combustion of fossil fuels.

Effects

Lead is a common and toxic trace metal which readily accumulates in living tissue. Metabolically, lead interacts with iron and therefore interferes with haemoglobin synthesis. It also affects membrane permeability by displacing calcium at functional sites, and inhibits some of the enzymes involved in energy metabolism. Lead that has been absorbed by vertebrate organisms is largely deposited in the bony skeleton, where it does not usually exhibit toxic effects. If stress results in decalcification or deossification, lead deposits may result in toxic effects. It has been shown that rainbow trout develop spinal deformities after exposure to lead in soft water, while no deformities were evident in hard water.

Low concentrations of lead affect fish by causing the formation of a film of coagulated mucous over the gills and subsequently over the entire body. This has been attributed to a reaction between lead and an organic constituent of the mucous. Death of fish is due to suffocation brought about by the mucous layer since insoluble lead is apparently not toxic to fish.

Lead is bio-accumulated by benthic bacteria, freshwater plants, invertebrates and fish. Bio-concentration factors for four species of invertebrates and two species of fish ranged from 42 - 1 700, though lead does not appear to bio-magnify through the aquatic food web.

22 MANGANESE

Chemical Symbol or Formula: Mn.

Standard: **0.3 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l Mn.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Mn-B**
Inductively Coupled Plasma Method	D	**3500-Mn-C**
Persulphate Method	B	**3500-Mn-D**

Introduction

Manganese is an essential micronutrient for plants and animals. It is a functional component of nitrate assimilation and an essential catalyst of numerous enzyme systems in animals, plants and bacteria. When manganese is not present in sufficient quantities, photosynthetic productivity may be limited and plants may exhibit chlorosis (a yellowing of the leaves) or failure of leaves to develop properly. A deficiency in manganese in vertebrates leads to skeletal deformities and reduced reproductive capabilities.

High concentrations of manganese are toxic, and may lead to disturbances in various metabolic pathways, in particular disturbances of the central nervous system caused by the inhibition of the formation of dopamine (a neurotransmitter).

Occurrence

Manganese is the eighth most abundant metal in nature, and occurs in a number of ores. In aquatic ecosystems, manganese does not occur naturally as a metal but is found in various salts and minerals, frequently in association with iron compounds. It may exist in the soluble manganous (Mn^{2+}) form, but is readily oxidised to the insoluble manganic (Mn^{4+}) form. The Mn^{2+} ion occurs at low redox potentials and low pH. Permanganates (Mn^{7+}) do not persist in the environment. They rapidly oxidise organic materials and are therefore reduced. Nitrate, sulphate and chloride salts of manganese are fairly soluble in water, whereas oxides, carbonates, phosphates, sulphides and hydroxides are less soluble.

Soils, sediments and metamorphic and sedimentary rocks are significant natural sources of manganese. Industrial discharges also account for elevated concentrations of manganese in receiving waters. Various industries use manganese, its alloys and manganese compounds in their processes, or in their products, examples of which are given below:

- the steel industry, in the manufacture of dry cell batteries;
- the fertilizer industry (manganese is used as a micro-nutrient fertilizer additive); and
- the chemical industry in paints, dyes, glass, ceramics, matches and fireworks.

Acid mine drainage also releases a large amount of the manganese. Iron and steel foundries release manganese into the atmosphere, where it is then redistributed through atmospheric deposition.

Effects Information on the acute and chronic toxicity effects of manganese to algae, invertebrates and vertebrates are very limited..

23 MERCURY

Chemical Symbol or Formula: Hg.

Standard: **1 µg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l Hg.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Cold-Vapor Atomic Absorption Spectrometric Method	C	**3500-Hg-B**
Inductively Coupled Plasma Method	D	**3500-Hg-C**
Dithizone Method	B	**3500-Hg-D**

Introduction Mercury is a heavy metal that is of quite rare geological occurrence, and its concentration in the environment is normally very low. Mercury occurs in three oxidation states in the natural aquatic environment, namely: as the metal, as mercury(I), and as mercury(II). The dissolved forms of mercury and those adsorbed onto particulate material are included in the guideline since they are both available for uptake by aquatic organisms. Mercury is also found as organo-mercurial salts, the most important of which is methyl mercury.

Mercury and mercury-organic complexes are of concern in the natural aquatic environment because of their extreme toxicity to aquatic organisms and the potential to bio-accumulate in the food chain. Intake of mercury can occur via air, food and water.

Occurrence Mercury may occur at high concentrations in water bodies subject to industrial pollution, or in the vicinity of industrial activities utilising or discharging mercury or compounds thereof. Important industries that use mercury in their processes, or in their products, include:

- the chlor-alkali industry,
- the paint industry,
- the fungicide industry,
- the paper and pulp industry,
- medical and dental industries, and
- the electrical equipment industry.

Mercury has a strong affinity for sediments and suspended solids. Under anaerobic conditions, bacteria readily transform inorganic mercury into methyl

mercury. Dissolved mercury salts are also easily absorbed by aquatic organisms and can be bio-accumulated.

Methyl mercury, the most common form of mercury found in aquatic organisms, is lipid soluble (readily passes through plant and animal membranes) and is stored within the bodies of organisms. In aquatic animals, bio-accumulated mercury is stored in fatty tissues, whilst in aquatic plants, mercury is usually stored in roots and stems.

Effects

Because of its neuro- and renal toxicity, mercury is severely poisonous to mammals. Poisoning by mercury takes the form of neurological disturbances, particularly in the case of organo-mercurial salts such as methyl mercury, and of renal dysfunction in the case of inorganic mercury. The kidneys are the main route of excretion of inorganic mercury. De-methylation is a slow process, and methyl mercury is only excreted over a long period.

Methyl mercury accumulated in fatty tissue or storage organs can be mobilized rapidly into the nervous and reproductive systems. This bio-accumulated mercury increases the risk of mercury toxicity to aquatic and terrestrial organisms in the food chain.

Organic forms of mercury are approximately ten times more toxic than inorganic forms because they pass rapidly through biological membranes. Solid inorganic forms of mercury have relatively low toxicity to vertebrates since solids are not easily absorbed by the gastrointestinal tract. In contrast, dissolved mercury salts are easily absorbed by aquatic organisms and can be bio-accumulated.

The toxic effects of mercury on aquatic organisms cannot be reversed.

24 METHYLENE BLUE – ACTIVE SUBSTANCES

Chemical Symbol or Formula: Not applicable [Bulk parameter].

Standard: **0.2 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l reference material (Lauryl sulphate).

Normal Method(s) of Analysis: Methylene Blue/Solvent Extraction [B]

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Anionic Surfactants as MBAS	B	**5540-C**

Introduction

Often abbreviated to MBAS, the designation of this parameter is the chemically correct term for the group of compounds commonly known as anionic detergents. To cloud the issue further, the non-specific terms surf octants (surface active agents) and syndets (synthetic detergents) are also used on occasion, the former more frequently. Synthetic detergents fall into three groups - anionic, cationic and non-ionic. The last-mentioned are all substituted polymers of ethylene oxide which do not ionise in water. They are more expensive than the anionic type but are coming into greater use. The cationic

types are salts of quaternary ammonium hydroxide and are known for their properties of disinfection. The major group comprises the anionic detergents which are all sodium salts of organic sulphates or sulphonates. Such entities form ion pairs with the reagent methylene blue, a property which forms the basis of their estimation. The results are quoted as mg/l standard reference material. Some authorities specify lauryl sulphate which is used increasingly as a standard.

It is worth noting that other terms have been used in connection with synthetic detergents. "Hard" and "soft" detergents are those which are biodegraded with difficulty and with ease, respectively. The designations have nothing to do with the hardness of the waters in which they are used. Some of the original anionic detergents were very hard; structurally they were of the "ABS" (alkylbenzenesulphonate) type. Later, there was a move towards the much more biodegradable ("soft") linear alkylate sulphate/sulphonate ("LAS") detergents. This was to help eliminate the major problem of foaming. In the US very severe foaming problems were encountered in the days of first use of synthetic detergents. Other disadvantages associated with them include interference with the reaeration of water which is low in dissolved oxygen, and the synergistic foaming effects which can arise when waters containing sub-foaming concentrations of different types of detergents are mixed. Most detergent preparations contain around 20 per cent surface active agent (which is all that is determined in this test): the rest of the formulation consists of so-called "builders" which enhance the properties of the active constituent. Chief among these are phosphates which are of major environmental significance (see below).

It should be noted that, as there may be some extraneous matter which will also react with methylene blue, the analysis is more correctly designated as "methylene blue active substances" than as anionic detergents, even though the latter may in fact represent 100 per cent of levels found

Occurrence Synthetic materials in domestic and industrial wastes.

Effect No immediate implications as other problems will prevent consumption of waters with these materials present.

25 NICKEL

Chemical Symbol or Formula: Ni.

Standard: **0.1 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l Ni.

Normal Method(s) of Analysis: Atomic Absorption Spectrometry [B/C]

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Ni-B**
Inductively Coupled Plasma Method	D	**3500-Ni-C**

Introduction This is another metallic element which is of moderate concern because of possible carcinogenicity as far as humans are concerned; it also has variable harmful effects on aquatic life. It is toxic to plant life, too, and is a hazard to fish (generally in the mg/l concentration range).

Occurrence Principal sources are minerals and industrial wastes.

Effect Very limited.

26 NITRATE

Chemical Symbol or Formula: NO_3^-

Standard: **50 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l NO_3^-.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Ultraviolet Spectrophotometric Screening Method	B	**4500-NO_3^--B**
Ion Chromatographic Method	B/C	**4500-NO_3^--C**
Nitrate Electrode Method	B/C	**4500-NO_3^--D**
Titanous Chloride Reduction Method	B	**4500-NO_3^--G**

Introduction Relatively little of the nitrate found in natural waters is of mineral origin, most coming from organic and inorganic sources, the former including waste discharges and the latter comprising chiefly artificial fertilisers. However, bacterial oxidation and fixing of nitrogen by plants can both produce nitrate. Interest is centred on nitrate concentrations for various reasons. Most importantly, high nitrate levels in waters to be used for drinking will render them hazardous to infants as they induce the "blue baby" syndrome (methaemoglobinaemia). The nitrate itself is not a direct toxicant but is a health hazard because of its conversion to nitrite [see also below] which reacts with blood haemoglobin to cause methaemoglobinaemia.

Of increasing importance is the degree to which fertiliser run-off can contribute to eutrophication problems in lakes. Sewage is rich in nitrogenous matter which through bacterial action may ultimately appear in the aquatic environment as nitrate. Hence, the presence of nitrate in ground waters, for example, is cause for suspicion of past sewage pollution or of excess levels of fertilisers or manure slurries spread on land. (High nitrite levels would indicate more recent pollution as nitrite is an intermediate stage in the ammonia-to-nitrate oxidation). In rivers high levels of nitrate are more likely to indicate significant run-off from agricultural land than anything else and the parameter is not of primary importance per se. However, it should be noted that there is a general tendency for nitrate concentrations in rivers to increase as a result of enhanced nutrient run-off; this may ultimately lessen their utility as potential sources of public water supply. Nitrite concentrations in rivers are rarely more than 1 - 2 per cent of the nitrate level so that it may therefore be acceptable to carry out the

analytically convenient determination of nitrate + nitrite at the same time. This determination is correctly referred to as total oxidised nitrogen

Occurrence Oxidation of ammonia: agricultural fertiliser run-off.

Effect Hazard to infants above 50 mg/l NO3.

27 NITRITE

Chemical Symbol or Formula: NO_2^-

Standard: **0.1 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l NO_2^-.

Normal Method(s) of Analysis: Manual or Automated Colorimetry [A/B]

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Colorimetric Method	B	**4500-NO_2^--B**
Ion Chromatographic Method	B/C	**4500-NO_2^--C**

Introduction Nitrite exists normally in very low concentrations and even in waste treatment plant effluents levels are relatively low, principally because the nitrogen will tend to exist in the more reduced (ammonia; NH3) or more oxidised (nitrate; NO3) forms

Because nitrite is an intermediate in the oxidisation of ammonia to nitrate, because such oxidation can proceed in soil, and because sewage is a rich source of ammonia nitrogen, waters which show any appreciable amounts of nitrite are regarded as being of highly questionable quality. Levels in unpolluted waters are normally low, below 0.03 mg/l NO_2. Values greater than this may indicate sewage pollution.

The significance of nitrite (at the low levels often found in surface waters) is mainly as an indicator of possible sewage pollution rather than as a hazard itself although, as mentioned above under "Nitrate" (q.v.), it is nitrite rather than nitrate which is the direct toxicant. There is, accordingly, a stricter limit for nitrite in drinking waters. In addition, nitrites can give rise to the presence of nitrosamines by reaction with organic compounds and there may be carcinogenic effects.

Occurrence Generally from untreated or partially treated wastes.

Effect Methaemoglobinaemia-causing agent [cf. Nitrate]..

28 NITROGEN (KJELDAHL)

Chemical Symbol or Formula: Not Applicable [Bulk parameter]

Standard: **1 mg/l**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l N.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Macro-Kjeldahl Method	B	**4500-N_{org}-B**
Semi-Micro- Kjeldahl Method	B	**4500-N_{org}-C**

Introduction

This determination is for organically-bound nitrogen and, under the normal test conditions (without ammonia removal), it includes ammonia. However, the results do not include oxidised nitrogen. The sum of the organically-bound nitrogen and ammonia figures is the "Kjeldahl nitrogen" value; if the ammonia has been excluded the result is "organic nitrogen." The term "total nitrogen" refers to the sum of the Kjeldahl and total oxidised nitrogen figures.

In past years much reliance was placed on the so-called albuminoid nitrogen determination which was frequently carried out in conjunction with the manual distillation technique for measuring ammonia. In this test the ammonia-free residue from the initial distillation is treated with alkaline potassium permanganate and then distilled again to give a further quantity of ammonia which is derived from proteinaceous matter and is a reflection of the organic content. Although alternative procedures have superseded the albuminoid nitrogen determination, it may still be found useful especially in assessing water with possible sewage contamination. While high values are themselves indicative of pollution, the albuminoid nitrogen results are most often considered in conjunction with the figures for ammonia. This is because in natural waters the ratio of free/saline ammonia nitrogen to albuminoid nitrogen is normally significantly less than unity (frequently of the order of 0.2-0.4), being a reflection of the fact that albuminoid nitrogen sources (principally vegetable) occur with a natural frequency. When the ratio approaches or exceeds unity an extraneous source of free ammonia is indicated and in many cases this is a sewage discharge. Thus, by scrutinising this nitrogen ratio the analyst can get an early indication of possible sewage contamination of a water, an indication which may be reinforced by elevated chloride values (q.v.).

In the Kjeldahl nitrogen determination the sample is subjected to quite severe digestion conditions which break down proteins and other organic matter and convert the nitrogen to ammonia, in which form it is actually measured.

Occurrence

Principally from organic matter naturally present (e.g. falling leaves etc.) or added in discharges.

Effects

Site-specific conditions, especially the availability of phosphorus, are critically important in modifying the influence of inorganic nitrogen on eutrophication. Inorganic nitrogen toxicity is not considered to be important for setting inorganic nitrogen water quality guidelines for protection of aquatic ecosystems.

Total nitrogen concentrations below 0.5 mg N/l are considered to be sufficiently low that they can limit eutrophication and reduce the likelihood of nuisance growths of blue-green algae and other plants. However, in the presence of sufficient available phosphorus, nitrogen-fixing organisms will be able to fix atmospheric nitrogen, thereby compensating for any deficit caused by low total nitrogen concentrations.

The information given in the table below illustrates typical symptoms associated with selected ranges of total nitrogen concentrations, if all other nutrients and environmental conditions are within favourable ranges for the organisms concerned.

Average Summer Inorganic Nitrogen Concentration(mg/l)	***Effects***
<0.5	***Oligotrophic*** conditions; usually moderate levels of species diversity; usually low productivity systems with rapid nutrient cycling; no nuisance growth of aquatic plants or the presence of blue-green algal blooms.
0.5 – 2.5	***Mesotrophic*** conditions; usually high levels of species diversity; usually productive systems; nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms seldom toxic.
2.5 – 10	***Eutrophic*** conditions; usually low levels of species diversity; usually highly productive systems, nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms may include species which are toxic to man, livestock and wildlife.
>10	***Hypertrophic*** conditions; usually very low levels of species diversity; usually very highly productive systems; nuisance growth of aquatic plants and blooms of blue-green algae, often including species which are toxic to man, livestock and wildlife.

29 PESTICIDES

Chemical Symbol or Formula: Not applicable [Bulk parameter].

Standard:

Aldrin	**0.01 μg/l**	**Fenitrothion**	**0.01 μg/l**
Dieldrin	**0.01 μg/l**	**Isoproturon**	**0.5 μg/l**
Endrin	**0.005 μg/l**	**Lindane**	**0.1 μg/l**
Isodrin	**0.005 μg/l**	**Linuron**	**1.0 μg/l**
Atrazine	**1.0 μg/l**	**Malathion**	**0.01 μg/l**
Chloridazon	**0.1 μg/l**	**MCPA**	**10 μg/l**
2,4-D	**0.005 μg/l**	**Mecoprop**	**10 μg/l**
DDT (y-isomer)	**10 μg/l**	**Parathionethyl**	**0.01 μg/l**
DDT (all isomers)	**25 μg/l**	**Pentachlorophenol**	**2.0 μg/l**
Diazinon	**5 μg/l**	**Simazine**	**1.0 μg/l**
Dichlorbenil	**10μg/l**	**Tributyltin oxide**	**0,001 μg/l**
Dichlorvos	**0.001 μg/l**	**Trifuralin**	**0.1 μg/l**
Diuron	**25 μg/l**	**Triphenyltin acetate**	**0.01 μg/l**
Endosulphan	**0.001 μg/l**	**Triphenyltin hydroxide**	**0.01 μg/l**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l specified compound

Normal Method(s) of Analysis: Chromatographic techniques (GLC/HPLC) [C]

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Carbamate Pesticides		
High Performance Liquid Chromatographic Method	C/D	**6610-B**
Organochlorine Pesticides		
Liquid-Liquid Extraction Gas Chromatographic Method	C/D	**6630-B**
Liquid-Liquid Extraction Gas Chromatographic Method II	C/D	**6630-C**
Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method	D	**6630-D**
Acidic Herbicide Compounds		
Micro Liquid-Liquid Extraction Gas Chromatographic Method	C/D	**6640-B**
Glyphosate Herbicides		
Liquid Chromatographic Post-Column Florescence Method	D	**6651-B**

Introduction This broad designation encompasses a large group of compounds with either related uses or similar chemical composition. The substances covered comprise insecticides (organo-chlorine and organo-phosphorus), herbicides, fungicides, PCBs (polychlorinated biphenyls) and PCTs (polychlorinated terphenyls). Compounds such as pesticides are among those which cause mortality or severe reproductive or genetic problems in fauna and which also qualify for inclusion under the broad heading of substances which possess carcinogenic, mutagenic or teratogenic properties. As such, they are highly undesirable in waters of virtually any type. Even if levels in, say, a river water are very low there is the probability of bioaccumulation in fish or other living tissue and, to compound the matter, of retention on the in-situ sediments..

Occurrence Synthetic compounds - agricultural discharges, spillages or runoff, industrial waste discharges

Effect Compounds of great acute or chronic toxicity.

30 PH (ACIDITY AND ALKALINITY)

Chemical Symbol or Formula: Not applicable [Physical parameter].

Standard: **6-9** (but no change of more than 0.2 units from natural level)

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: pH units.

Normal Method(s) of Analysis: Electrometry [pH electrode] [A/B]

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Electrometric Method	B	**4500-H^+-B**

Introduction The pH value is a measure of the hydrogen ion activity in a water sample. It is mathematically related to hydrogen ion activity according to the expression: $pH = -\log_{10} [H^+]$, where $[H^+]$ is the hydrogen ion activity. The pH of pure water (that is, water containing no solutes) at a temperature of 24 °C is 7.0, the number of H^+ and OH^- ions are equal and the water is therefore electrochemically neutral. As the concentration of hydrogen ions $[H^+]$ increases, pH decreases and the solution becomes more acid. As $[H^+]$ decreases, pH increases and the solution becomes more basic.

The equilibrium between H+ and OH^- ions is influenced by reactions with acids and bases introduced into the aqueous system. In general, acidity is the number of OH^- ions that have reacted over a given pH range during a base titration, that is, a measure of the water's ability to neutralise base. Similarly, alkalinity is a measure of the number of H^+ ions that have reacted over a given pH range during an acid titration, that is, a measure of the water's ability to neutralise acid.

Alkalinity is primarily controlled by carbonate species and is therefore usually expressed in terms of equivalence to calcium carbonate ($CaCO_3$). Briefly,

carbon dioxide dissolves in water to form carbonic acid (H_2CO_3) which, depending on pH, dissociates to form carbonate, bicarbonate and hydrogen ions:

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \leftrightarrows HCO_3^- + H^+ \leftrightarrows CO_3^{2-} + 2H^+$$

At a pH value of less than 4.0, carbonate species are mostly in the form of H_2CO_3 , whilst between pH values of 6.4 and 8.6 they are in the form HCO_3^-. As the pH increases to greater than 8.6, so the proportion of CO_3^{2-} increases, and above pH 10.3 CO_3^{2-} predominates.

The rate of change of pH, on addition of a given quantity of an acid or base, depends on the buffering capacity of the water. The most important buffering system in fresh waters is the carbonate-bicarbonate one, and between pH values of 6.4 - 10.3 the hydrogen carbonate ion predominates. In naturally acid waters, complex polyphenolic organics and their salts may form the major buffering system, while aluminium and its salts become effective buffering agents in waters subject to acid precipitation.

Occurrence

For surface water, pH values typically range between 4 and 11. The relative proportions of the major ions, and in consequence the pH, of natural waters, are determined by geological and atmospheric influences. Most fresh waters, are relatively well buffered and more or less neutral, with pH ranges between 6 and 8. Very dilute sodium-chloride-dominated waters are poorly buffered because they contain virtually no bicarbonate or carbonate. If they drain catchments containing certain types of vegetation (for example, fynbos), the pH may drop as low as 3.9 owing to the influence of organic acids (for example, humic and fulvic acids).

The pH may also vary both diurnally and seasonally. Diurnal fluctuations occur in productive systems where the relative rates of photosynthesis and respiration vary over a 24- hour period, because photosynthesis alters the carbonate/bicarbonate equilibrium by removing CO from the water. Seasonal variability is largely related to the hydrological 2 cycle, particularly in rivers draining catchments with vegetation such as fynbos, where the concentration of organic acids is consistently lower during the rainy season.

Industrial activities generally cause acidification rather than alkalinization of rivers. Acidification is normally the result of three different types of pollution, namely:

- low-pH point-source effluents from industries, such as pulp and paper and tanning and leather industries;
- mine drainage, which is nearly always acid, leading to the pH of receiving streams dropping to below 2; and
- acid precipitation resulting largely from atmospheric pollution caused by the burning of coal (and subsequent production of sulphur dioxide (SO_2)) and the exhausts of combustion engines (nitrogen oxides). Both sulphur oxides (SO_x) and nitrogen oxides (NO_x) form strong mineral acids when dissolved in water. When acid rain falls on a catchment, the strong acids leach calcium and magnesium from the soil and also interfere with nutrient availability.

Elevated pH values can be caused by increased biological activity in eutrophic systems. The pH values may fluctuate widely from below 6 - above 10 over a 24-hour period as a result of changing rates of photosynthesis and respiration.

Effects

A change in pH from that normally encountered in unimpacted streams may have severe effects upon the biota. The extent of acidification or alkalinization

is important in determining the severity of the effects, which do not vary linearly either with pH or over time. When assessing the potential effect of a change in pH, it is important to note that some streams are naturally more acidic than others and their biotas are often adapted to these conditions.

Direct effects of pH changes consist of alterations in the ionic and osmotic balance of individual organisms, in particular changes in the rate and type of ion exchange across body surfaces. This requires greater energy expenditure, with subsequent effects such as slow growth and reduced fecundity becoming apparent. Aquatic organisms, however, generally have well developed mechanisms for maintaining ionic and osmotic balance. Impacts of indirect pH changes include changes in the availability of toxic substances such as aluminium and ammonia.

Acidic pH

Gradual reductions in pH may result in a change in community structure, with acid-tolerant organisms replacing less tolerant organisms.

Streams with acidic pH values have different periphyton (micro flora and fauna living on solid surfaces) communities and lower overall production compared with less acidic streams.

The discharge of acid wastes into water containing bicarbonate alkalinity results in the formation of free carbon dioxide. If the water is alkaline, free CO_2 may be liberated and be toxic to fish even though the pH does not drop to a level normally considered toxic.

Alkaline pH

Limited information is available on the effects of elevated pH.

31 PHENOLS

Chemical Symbol or Formula: Not applicable [Physical parameter].

Standard: **0.5 μg/l.**

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l C_6H_5OH [Phenol].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Liquid-Liquid Extraction Gas Chromatographic Method	B	**6420-B**
Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method	B	**6420-C**

Introduction Phenol itself is an organic compound consisting of a hydroxyl group attached to a benzene ring.

Occurrence In unimpacted water systems phenols are only found in very low concentrations, usually in the μg/l range or less. Phenols are produced as by-products in many industrial processes where organic chemicals are used. Phenols are also used as a disinfectant, and as a starting material for a wide

variety of synthetic organic processes. Phenolic wastes arise from the distillation of wood and coal, from oil refineries, chemical plants, pulp and paper industries, livestock dips and human and animal wastes. Phenol is often present in sewage at levels between 0.07 - 0.1 mg/l. Phenols are generally biodegraded in water.

Effects

Phenols are thought to be a nerve poison which gives rise to an increased blood supply to the gills and heart cavities. Fish exposed to phenol become excited, swim more rapidly, become more sensitive to stimuli and show increased respiratory rates, colour changes and increased secretion of mucus. Death may occur quickly or follow a period of depressed activity and loss of equilibrium, with occasional convulsions. Fish surviving long-term exposure to low phenol concentrations show general inflammation and necrosis of tissues. This is possibly due to irreversible changes in protein structure. Histopathological changes in the blood, liver, heart, skin and spleen may also occur. Reduction in growth and sexual activity and a loss of balance and co-ordination have been observed in some fish species. Phenol affects some aquatic organisms directly by increasing their demand for oxygen.

Reduction in oxygen consumption occurs in some invertebrates. Avoidance behaviour has been observed in leeches. Phenols have also been shown to reduce rates of photosynthesis in aquatic plants.

32 PHOSPHATES

Chemical Symbol or Formula: $PO4^{-}$

Standard

The inorganic phosphorus concentration for a specific system must be based on the existing trophic status of the system. It is undesirable to allow inorganic phosphorus concentrations to rise to a level which will change the trophic status of the system. A standard for each water body should be derived only after case- or site-specific studies.

- Inorganic phosphorus concentrations should not be changed by > 15 % from that of the water body under local, unimpacted conditions at any time of the year; and
- The trophic status of the water body should not increase above its present level, though a decrease in trophic status is permissible (see Effects); and
- The amplitude and frequency of natural cycles in inorganic phosphorus concentrations should not be changed.

Percentage Compliance Required: 95% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l P.

Normal Method(s) of Analysis: Manual or Automated Colorimetry [B/C].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Sample Preparation	B	**4500-P-B**
Vanadomolybdophosphoric Acid Colorimetric Method	B	**4500-P-C**
Stannous Chloride Method	B	**4500-P-D**
Ascorbic Method	B	**4500-P-E**

Introduction

Phosphorus can occur in numerous organic and inorganic forms, and may be present in waters as dissolved and particulate species. Elemental phosphorus does not occur in the natural environment. Orthophosphates, polyphosphates, metaphosphates, pyrophosphates and organically bound phosphates are found in natural waters. Of these, orthophosphate species H_2PO_4 and HPO_4^{2-} are the only forms of soluble inorganic phosphorus directly utilizable by aquatic biota. Soluble Reactive Phosphate (SRP), or orthophosphate, is that phosphorus which is immediately available to aquatic biota which can be transformed into an available form by naturally occurring processes.

The forms of phosphorus in water are continually changing because of processes of decomposition and synthesis between organically bound forms and oxidised inorganic forms. The phosphorus cycle is influenced by the exchange of phosphorus between sedimentary and aqueous compartments. In turn this is affected by various physical, chemical and biological modifying factors such as mineral-water equilibria, water pH values, sorption processes, oxygen-dependent redox interactions, and the activities of living organisms.

Phosphorus is an essential macronutrient, and is accumulated by a variety of living organisms. It has a major role in the building of nucleic acids and in the storage and use of energy in cells. In unimpacted waters it is readily utilized by plants and converted into cell structures by photosynthetic action. Phosphorus is considered to be the principle nutrient controlling the degree of eutrophication in aquatic ecosystems.

Occurrence

Natural sources of phosphorus include the weathering of rocks and the subsequent leaching of phosphate salts into surface waters, in addition to the decomposition of organic matter. Spatial variation is high and is related to the characteristics of regional geology. Phosphorus levels are generally lowest in mountainous regions of crystalline rocks and levels increase in lowland waters derived from sedimentary deposits.

Phosphorus is seldom present in high concentrations in unimpacted surface waters because it is actively taken up by plants. Concentrations between 10 and 50 μg/l are commonly found, although concentrations as low as 1 μg/l of soluble inorganic phosphorus may be found in "pristine" waters and as high as 200 mg/l of total phosphorus in some enclosed saline waters.

Elevated levels of phosphorus may result from point-source discharges such as domestic and industrial effluents, and from diffuse sources (non-point sources) in which the phosphorus load is generated by surface and subsurface drainage.

Non-point sources include atmospheric precipitation, urban runoff, and drainage from agricultural land, in particular from land on which fertilizers have been applied.

Effects

The most significant effect of elevated phosphorus concentrations is its stimulation of the growth of aquatic plants. Both phosphorus and nitrogen limit plant growth, and of these, phosphorus is likely to be more limiting in fresh water. The effect is dependent on the form of phosphorus present in the water, since not all forms are available for uptake by plants. Other factors, such as water temperature, light and the availability of other nutrients, also play an important role in limiting plant growth.

Inorganic phosphorus concentrations of less than 5 μg P/l are considered to be sufficiently low to reduce the likelihood of algal and other plant growth.

The information given in the table below illustrates typical symptoms associated with selected ranges of inorganic phosphorus concentrations, if all other nutrients and environmental conditions are within favourable ranges for the organisms concerned.

Average Summer Inorganic Phosphorous Concentration (μg/l)	***Effects***
<5	***Oligotrophic*** conditions; usually moderate levels of species diversity; usually low productivity systems with rapid nutrient cycling; no nuisance growth of aquatic plants or blue-green algae.
5-25	***Mesotrophic*** conditions; usually high levels of species diversity; usually productive systems; nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms seldom toxic.
25-250	***Eutrophic*** conditions; usually low levels of species diversity; usually highly productive systems, nuisance growth of aquatic plants and blooms of blue-green algae; algal blooms may include species which are toxic to man, livestock and wildlife.
>250	***Hypertrophic*** conditions; usually very low levels of species diversity; usually very highly productive systems; nuisance growth of aquatic plants and blooms of blue-green algae, often including species which are toxic to man, livestock and wildlife.

33 POLYCHLORINATED BIPHENYLS & TERPHENYLS

Chemical Symbol or Formula: Not applicable [Physical parameter].

Standard: **1 µg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l reference PCB/PCT (mixture) used.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Liquid-Liquid Extraction Gas Chromatographic Method	C/D	**6431-B**
Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method	D	**6431-C**

Introduction Commonly termed PCBs/PCTs, this parameter covers those chlorinated compounds which have been used as mixtures in transformer coolant oils. The mixtures are normally designated by a proprietary name, for example "Aroclor," to which is suffixed a number, e.g. 1254 or 1260. The first two digits represent the number of carbon atoms in the molecule and the second two the percentage by weight of chlorine. The basic molecules present are biphenyl, which is $C_{12}H_{10}$ and comprises two benzene rings joined together, or terphenyl ($C_{18}H_{14}$, consisting of three fused benzene rings).

When these are chlorinated a whole range of polychlorinated compounds is produced and the mixtures are of such complexity that no effort is made to identify the individual components. The mixtures are dense and extremely stable, resisting biodegradation and conventional incineration procedures.

The best process currently available for their destruction is very high temperature "flash" incineration. It is not without significance that, according to current estimates, about 90% of the total world production of these materials since the 1940s, when they were introduced, is still extant.

Occurrence Synthetic components of transformer coolant oils which gain access to water by spillages or industrial discharges.

Effect Compounds of marked chronic toxicity; they are actual or potential carcinogens. PCBs/PCTs are toxic, causing genetic effects and mortality to fauna. They are accumulated to a very great extent by fauna and there are many literature references to concentration factors of over 100,000 - in other words, an infinitesimal concentration in a water may be matched by 100,000 times that amount in the tissue of fish or animals normally resident in that water. When these toxicants enter the food chain, through consumption of fish for example, there is a health risk to man.

34 POLYCYCLIC AROMATIC HYDROCARBONS

Chemical Symbol or Formula: Not applicable [Physical parameter].

Standard: **2 μg/l (Total of 6 specified).**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l PAH [or specific PAH compound(s)].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Liquid-Liquid Extraction Chromatographic Method	D	**6440-B**
Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method	D	**6440-C**

Introduction

This term, while strictly applicable to very many substances, has been defined as applying to six specific compounds:

- Fluoranthene
- 3,4-benzofluoranthene [benzo(b)fluoranthene]
- 11,12-benzofluoranthene [benzo(k)fluoranthene]
- 3,4-benzopyrene [benzo(a)pyrene]
- 1,12-benzoperylene [benzo(ghi)perylene]
- indeno(l,2,3-cd)pyrene

The compounds covered are the six originally identified by the WHO.

It may be useful to comment on the nomenclature of these compounds and related materials. They are so-called aromatic compounds, the term being used for those substances containing the "aromatic ring" (i.e. the cyclic molecular structure of benzene) a basic element of their composition. As the substances contain more than one such ring, they are termed polycyclic (or sometimes, poly- aromatic compounds). The compounds are hydrocarbons - i.e. they consist of the elements carbon and hydrogen only.

The alternative often-used designation - "polynuclear aromatic hydrocarbons" • arises from the (inaccurate) use by organic chemists of the word "nucleus" to refer to the benzene ring structure. As there is more than one such ring in these compounds they are termed "polynuclear."

All of these materials are complex organic molecules which originate typically in the combustion of organic compounds. Their analysis, like that of many other so-called micropollutants, is difficult, but the procedures are justified because of the potential health hazards posed by the PAH. The listed compounds can be determined relatively easily, albeit with advanced instrumental techniques, and their presence is also taken as indicative of the possible occurrence of other undesirable aromatic compounds. While all have been regarded previously as carcinogens, the six listed compounds comprising the most widely found such group in the environment, by far the most hazardous compound among them is benzo(a)pyrene [3,4-benzopyrene].

Occurrence Synthetic compounds occurring in soot, tar, vehicle exhausts, combustion products of hydrocarbon fuels

Effect Carcinogens of greater or lesser potency.

35 SELENIUM

Chemical Symbol or Formula: Se.

Standard: **10 μg/l (Total of 6 specified).**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l Se.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Sample Preparation	B	**3500-Se-B**
Atomic Absorption Spectrometric Method	C	**3500-Se-C**
Inductively Coupled Plasma Method	D	**3500-Se-I**
Colorimetric Method	B	**3500-Se-D**

Introduction Selenium is a non-metallic element similar to sulphur. Selenium occurs in five oxidation states, namely, -II, 0, II, IV and VI, of which the tetravalent state is the most common. Small quantities of selenium are essential to animals and bacteria, where it is important in certain enzyme systems, but selenium is apparently not essential for plants.

Occurrence Selenium occurs naturally as ferric selenite, calcium selenate, as elemental selenium and in organic compounds derived from decayed plant tissue. Although selenium occurs in some natural waters, it is usually in nanogram quantities.

Selenium may occur at increased concentrations in water bodies subject to industrial pollution, or in the vicinity of industrial activities utilising or discharging selenium or selenium compounds. Industries that use selenium in their processes, or in their products, include:

- the paint industry;
- the food processing industry;
- the steel industry;
- vehicle and aircraft plating industries;
- the pesticide industry;
- the glass and ceramics industries;
- the dye manufacturing industry;
- the rubber industry; and
- the metal alloy and electrical apparatus industries.

Effects

Because these are chemical similarities between selenium and sulphur, selenium can replace sulphur in some biologically important substances and thereby cause toxic effects. The toxic effects are similar in cold- and warm-water adapted fish.

Selenium toxicity effects observed in fish include changes in feeding behaviour and equilibrium, pathological changes, deformities, haematological (blood) changes and death. Fish are generally less sensitive to selenium than are invertebrates. Toxic effects of selenium that have been recorded in invertebrates include immobilisation, reduced survival and reduced reproduction.

Selenium is passed up through the aquatic food chain and accumulates in the liver of mammals and fish; it may therefore pose a threat to predators. Selenium undergoes biological methylation in sediments, a process similar to mercury methylation. Selenomethionine is ten times more toxic than inorganic selenium.

36 SILVER

Chemical Symbol or Formula: Ag.

Standard: **10 μg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: μg/l Ag..

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Ag-B**
Inductively Coupled Plasma Method	D	**3500-Ag-C**
Dithizone Method	B	**3500-Ag-D**

Introduction

This metal is toxic, especially to micro-organisms, and its soluble salts are excellent disinfectants. It is not considered particularly toxic to humans and, as it is likely to be found only in very low levels (such that it would be practically impossible to reach hazardous levels through consumption of water and food), few limits have been set. However, it has been reported that restrictions on its use were introduced to discourage the use of silver as a disinfectant because of possible health effects if used unduly liberally. Nowadays, economic considerations are likely to restrict the discharge of silver.

Occurrence Ores, industrial wastes (e.g. photographic effluents).

Effect Metal of varying toxicity.

37 SULPHATE

Chemical Symbol or Formula: SO_4^{--}

Standard: **200 mg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l SO_4

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Ion Chromatographic Method	C	**4500-SO_4^{--}-B**
Turbidimetric Method	B/C	**4500-SO_4^{--}-E**

Introduction Sulphates exist in nearly all natural waters, the concentrations varying according to the nature of the terrain through which they flow. They are often derived from the sulphides of heavy metals (iron, nickel, copper and lead). Iron sulphides are present in sedimentary rocks from which they can be oxidised to sulphate in humid climates; the latter may then leach into watercourses so that ground waters are often excessively high in sulphates. As magnesium and sodium are present in many waters their combination with sulphate will have an enhanced laxative effect of greater or lesser magnitude depending on concentration. The utility of a water for domestic purposes will therefore be severely limited by high sulphate concentrations, hence the limit of 250 mg/l SO_4.

Occurrence Rocks, geological formations, discharges and so on .

Effect In polluted waters in which the dissolved oxygen i.e. zero, sulphate is very readily reduced to sulphide causing noxious odours.

38 TEMPERATURE

Chemical Symbol or Formula: Not applicable [Physical parameter]

Standard:

Game fish	**Discharge must not result in variation of more than 1.5 °C temperature down stream of the thermal discharge**
Coarse fish	**Discharge must not result in variation of more than 3 °C temperature down stream of the thermal discharge**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: Degrees Celsius [°C].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Laboratory and Field Method	A	**2550-B**

Introduction

Temperature may be defined as the condition of a body that determines the transfer of heat to, or from, other bodies. As temperature increases viscosity, surface tension, compressibility, specific heat, the ionization constant and the latent heat of vaporization decrease, whereas thermal conductivity and vapour pressure increase. The solubilities of the following gasses, H_2, N_2, CO_2 and O_2 decrease with increasing temperature.

Temperature plays an important role in water by affecting the rates of chemical reactions and therefore also the metabolic rates of organisms. Temperature is therefore one of the major factors controlling the distribution of aquatic organisms. Natural variations in water temperature occur in response to seasonal and diel cycles and organisms use these changes as cues for activities such as migration, emergence and spawning. Artificially-induced changes in water temperature can thus impact on individual organisms and on entire aquatic communities.

Occurrence

The temperatures of inland waters generally range from 5 - 30 °C. Thermal characteristics of running waters are dependent on various features of the region and catchment area, including:

- the latitude and altitude of the river;
- hydrological factors such as the source of water, the relative contribution of ground water, and the rate of flow or discharge;
- climatic factors such as air temperature, cloud cover, wind speed, vapour pressure and precipitation events; and
- structural characteristics of the river and catchment area, including topographic features, vegetation cover, channel form, water volume, depth and turbidity.

Surface waters exhibit daily and annual periodicity patterns, in addition to longitudinal changes along a river course, and vertical stratification in deeper waters. The minimum and maximum temperatures, and temperature ranges vary depending on the factors mentioned above.

Anthropogenic sources which result in changes in water temperature include:

- discharge of heated industrial effluents;
- discharge of heated effluents below power stations;
- heated return-flows of irrigation water;
- removal of riparian vegetation cover, and thereby an increase in the amount of solar radiation reaching the water;
- inter-basin water transfers; and
- discharge of water from impoundments.

Effects

The effects of temperature on aquatic organisms have been the subject of a number of literature reviews, predominantly conducted in the northern hemisphere. There is however, little information on the thermal tolerances of the African aquatic organisms, or their responses to temperature change.

Aquatic organisms have upper and lower thermal tolerance limits, optimal temperatures for growth, a preferred temperature range in thermal gradients, and temperature limitations for migration, spawning and egg incubation. All organisms associated with freshwater, excluding birds and mammals, are poikilothermic. In other words, they are unable to control their body temperatures and are therefore highly dependent on ambient water temperature and very susceptible to changes in water temperature. Consequently, rapid changes in temperature may severely affect aquatic organisms and lead to mass mortality. Causes of thermal mortality in fish from acute exposure to elevated temperatures are basically the result of metabolic malfunctions (including fluid-electrolyte imbalance, alterations in gaseous exchange and osmoregulation, hypoxia of the central nervous system and inactivation of enzyme systems).

Less severe temperature changes in water bodies may have sub-lethal effects or lead to an alteration in the existing aquatic community. The qualitative and quantitative composition of the biota can change as a result of population shifts caused by the disappearance of stenothermal species (organisms adapted to a very narrow range of temperatures) from heated waters, and replacement by heat-tolerant species which increase in number and supplant the original species in the ecosystem.

Many organisms have life cycles in which temperature acts as a cue for the timing of migration, spawning or emergence. Artificial changes in temperature can interfere with temperature cues, thereby altering normal development.

39 TOTAL DISSOLVED SALTS/SOLIDS

Chemical Symbol or Formula: Not applicable [Bulk parameter].

Standard: **TDS concentrations should not be changed by > 15 % from the normal cycles of the water body under unimpacted conditions at any time of the year; and**

The amplitude and frequency of natural cycles in TDS concentrations should not be changed.

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l solids (Dried at stated temperature).

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Total Dissolved Solids Dried at 180 °C	A	**2540-C**

Introduction

The total dissolved solids concentration , is a measure of the quantity of all compounds dissolved in water. The total dissolved salts concentration is a measure of the quantity of all dissolved compounds in water that carry an electrical charge. Since most dissolved substances in water carry an electrical

charge, the TDSalts concentration is usually, used as an estimate of the concentration of total dissolved solids in the water.

The TDSalts concentration is directly proportional to the electrical conductivity (EC) of water. Because EC is much easier to measure than TDSalts, it is routinely used as an estimate of the TDSalts concentration. Therefore, it has become common practise to use the total dissolved salts concentration, as a measure for the total dissolved solids.

Electrical conductivity (EC) is a measure of the ability of water to conduct an electrical current. This ability is a result of the presence in water of ions such as carbonate, bicarbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium, all of which carry an electrical charge. Many organic compounds dissolved in water do not dissociate into ions (ionise), and consequently they do not affect the EC.

Occurrence

Natural waters contain varying quantities of TDS as a consequence of the dissolution of minerals in rocks, soils and decomposing plant material, the TDS concentrations of natural waters therefore being dependent at least in part on the characteristics of the geological formations which the water has been in contact with. The TDS concentration also depends on physical processes such as evaporation and rainfall.

The TDS concentrations are generally

- Low in rainwater, less than 1 mg/l;
- Low in water in contact with granite, siliceous sand and well-leached soils, less than 30 mg/l;
- Greater than 65 mg/l in water in contact with precambrian shield areas; and
- In the range of 200 - 1100 mg/l in water in contact with palaeozoic and mesozoic sedimentary rock formations.
- High as a result of evapoconcentration, usually greater than 1100 mg/ml.

Salts accumulate as water moves downstream because salts are continuously being added through natural and anthropogenic sources whilst very little is removed by precipitation or natural processes. Domestic and industrial effluent discharges and surface runoff from urban, industrial and cultivated areas are examples of the types of sources that may contribute to increased TDS concentrations. Evaporation also leads to an increase in the total salts.

Effects

Plants and animals possess a wide range of physiological mechanisms and adaptations to maintain the necessary balance of water and dissolved ions in cells and tissues. This ability is extremely important in any consideration of the effects of changes in total dissolved solids on aquatic organisms.

The individual ions making up the TDS also exert physiological effects on aquatic organisms.

Changes in the concentration of the total dissolved solids can affect aquatic organisms at three levels, namely:

- effects on, and adaptations of, individual species;
- effects on community structure; and
- effects on microbial and ecological processes such as rates of metabolism and nutrient cycling.

The rate of change of the TDS concentration, and the duration of change, appears to be more important than absolute changes in the TDS concentration, particularly in systems where the organisms may not be adapted to fluctuating levels of TDS. Seasonal timing of the change in TDS concentration may also have important synergistic effects with water temperature on the total community composition and functioning. Organisms adapted to low-salinity habitats are generally sensitive to changes in the TDS concentration.

40 TOTAL SUSPENDED SOLIDS

Chemical Symbol or Formula: Not applicable [Physical parameter].

Standard: **≤ 25 mg/l (annual mean)**

50 mg/l (maximum value)

Units Used for Analytical Results: mg/l solids (Dried at stated temperature).

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Total Suspended Solids Dried at 103-105 °C	A	**2540-D**

Introduction

The total suspended solids (TSS) concentration is a measure of the amount of material suspended in water. This definition includes a wide range of sizes of material, from colloids (0.1 μm) through to large organic and inorganic particulates.

The concentration of suspended solids increases with the discharge of sediment washed into rivers due to rainfall and resuspension of deposited sediment. As flow decreases the suspended solids settle out, the rate of which is dependent on particle size and the hydrodynamics of the water body.

Water turbidity in the southern hemisphere is generally considered to be equivalent to some measure of the concentration of suspended solids. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through a water sample. The scattering of light is caused by suspended matter such as clay, silt and finely divided organic material, while the absorption of light is caused by inorganic matter, plankton and other microscopic organisms and soluble coloured organic compounds, such as fulvic, humic and tannic acids.

Correlation of turbidity with the concentration of suspended solids (mass/unit volume) is difficult because the size, shape and refractive index of particulates affects the light scattering properties of the suspension. The relationship between turbidity and suspended solids may however, be determined on a site-specific basis. A turbidimeter, calibrated with consideration of the site-specific characteristics, may then potentially be used to monitor suspended solids.

Occurrence

Natural variations in rivers often result in changes in the TSS, the extent of which is governed by the hydrology and geomorphology of a particular region. In general, all rivers become highly turbid and laden with suspended solids during the rainy season. The major part of suspended material found in most natural waters is made up of soil particles derived from land surfaces. Erosion of land surfaces by wind and rain is a continuous and natural process. However,

land use practices such as overgrazing, non-contour ploughing, removal of riparian vegetation and forestry operations accelerate erosion and result in increased loads of suspended solids in rivers.

Increases in total suspended solids may also result from anthropogenic sources, including:

- discharge of domestic sewage,
- discharge of industrial effluents (such as the pulp/papermill, china-clay, and brick and pottery industries),
- discharge from mining operations,
- fish-farm effluents (mostly organic suspended solids) and
- physical perturbations from road, bridge and dam construction.

Effects

In turbid waters light penetration is reduced, leading to a decrease in photosynthesis. The resultant decrease in primary production reduces food availability for aquatic organisms higher up the food chain. Suspended solids may interfere with the feeding mechanisms of filter-feeding organisms such as certain macroinvertebrates, and the gill functioning, foraging efficiency (due to visual disturbances) and growth of fish.

Suspended solids that settle out may smother or abrade benthic plants and animals, and may result in changes to the nature of the substratum. This may then lead to changes in the structure of the biotic community by the decline of these organisms, through the replacement with organisms which burrow in soft sediments. Sensitive species may be permanently eliminated if the source of the suspended solids is not removed.

The recovery of a stream from sediment deposition is dependent on the elimination of the sediment source and the potential for the deposited material to be flushed out by stream flow.

41 TETRACHLOROETHYLENE

Chemical Symbol or Formula: C_2Cl_4.

Standard: **10 µg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l C_2Cl_4.

Normal Method(s) of Analysis: Gas Chromatography [B/C].

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Purge and Trap Packed-Column Gas Chromatographic/Mass Spectrometric Method I	C	**6210-B**
Purge and Trap Packed-Column Gas Chromatographic/Mass Spectrometric Method II	C	**6210-C**
Purge and Trap Capillary Column Gas Chromatographic/Mass Spectrometric Method	C	**6210-D**
Purge and Trap Packed-Column Gas Chromatographic Method I	C	**6230-B**
Purge and Trap Packed-Column Gas Chromatographic Method II	C	**6230-C**
Purge and Trap Capillary Column Gas Chromatographic Method	C	**6230-D**

Introduction Information: Synonyms for tetrachloroethylene are tetrachloroethene and perchloroethylene. It is the most commonly used dry-cleaning solvent. As with all chlorinated solvents, this substance should be handled with care, and in well-ventilated areas.

Occurrence Synthetic solvent used extensively in dry-cleaning industry; also used to a significant extent for degreasing metals.

Effect Toxic solvent which can cause narcosis, dermatitis and ultimately fatal intoxication. However, when handled according to proper procedures and with adequate ventilation, tetrachloroethylene may be used without problems.

42 THALLIUM

Chemical Symbol or Formula: Tl.

Standard: **5 µg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l Tl.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Tl-B**
Inductively Coupled Plasma Method	D	**3500-Tl-C**

Introduction The metal is used at 2-3% concentration in rodent poisons, and is also used in the electrical components industry.

Occurrence Minerals, but more often from discharges.

Effect Causes a wide variety of effects including nausea, vomiting, pain and, ultimately, death.

43 TRICHLOROETHYLENE

Chemical Symbol or Formula: C_2HCl_3.

Standard: **5 µg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l C_2HCl_3.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Purge and Trap Packed-Column Gas Chromatographic/Mass Spectrometric Method I	C	**6210-B**
Purge and Trap Packed-Column Gas Chromatographic/Mass Spectrometric Method II	C	**6210-C**
Purge and Trap Capillary Column Gas Chromatographic/Mass Spectrometric Method	C	**6210-D**
Purge and Trap Packed-Column Gas Chromatographic Method I	C	**6230-B**
Purge and Trap Packed-Column Gas Chromatographic Method II	C	**6230-C**
Purge and Trap Capillary Column Gas Chromatographic Method	C	**6230-D**

Introduction Trichloroethylene is used in the manufacture of organic chemicals and pharmaceuticals, and it also has some medical uses.

Occurrence Synthetic solvent used in various industrial and manufacturing processes (e.g. solvent for paints, varnishes, resins etc); used in dry-cleaning and in metals degreasing.

Effect Potential carcinogen. Causes narcosis and effects similar to alcohol inebriation. See also "Tetrachloroethylene," which is a very similar compound.

44 URANIUM

Chemical Symbol or Formula: U.

Standard: **5 µg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: mg/l U.

Normal Method(s) of Analysis: Radiometric or Fluorometric techniques [D]

There are atomic absorption spectrometric procedures for uranium analysis but (ICP analysis excepted) their sensitivity is generally inadequate for very low levels.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Radiochemical Method	D	**7500-U-B**

Introduction This radioactive element is used in the nuclear industry and is thus far from being universally encountered.

Occurrence Rare natural occurrence; equally rare in effluents

Effect Highly toxic, with a variety of effects leading ultimately to death.

45 VINYL CHLORIDE

Chemical Symbol or Formula: C_2H_3Cl.

Standard: **5 µg/l.**

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l C_2H_3Cl.

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Purge and Trap Packed-Column Gas Chromatographic/Mass Spectrometric Method I	C	**6210-B**
Purge and Trap Packed-Column Gas Chromatographic/Mass Spectrometric Method II	C	**6210-C**
Purge and Trap Capillary Column Gas Chromatographic/Mass Spectrometric Method	C	**6210-D**
Purge and Trap Packed-Column Gas Chromatographic Method I	C	**6230-B**
Purge and Trap Packed-Column Gas Chromatographic Method II	C	**6230-C**
Purge and Trap Capillary Column Gas Chromatographic Method	C	**6230-D**

Introduction Although a very reactive monomer which forms plastic polymers very easily, it is almost inevitable that in some cases the resultant polymer - the most common of which is polyvinyl chloride or PVC - will contain vestigial amounts of vinyl chloride itself. Thus, in the first use, in particular, of vessels made of PVC there is the possibility of residual monomer gaining access to water..

Occurrence Synthetic gaseous compound which polymerises very readily and is an important raw material in the manufacture of plastics. It is also used as a refrigerant.

Effect It is a suspected causative agent of liver cancer.

46 ZINC

Chemical Symbol or Formula: Zn.

Standard:

Zinc (µg/l)	Hardness (mg/l $CaCO_3$)
30	10
200	50
300	100
500	500

Percentage Compliance Required: 100% of all monitoring data must comply with the standard.

Units Used for Analytical Results: µg/l Zn

Reference Method(s) of Analysis:

Method Type	Complexity	APHA Reference
Atomic Absorption Spectrometric Method	B/C	**3500-Zn-B**
Inductively Coupled Plasma Method	D	**3500-Zn-C**
Dithizone Method II	B	**3500-Zn-E**
Zincon Method	B	**3500-Zn-F**

Introduction

Zinc, a metallic element, is an essential micronutrient for all organisms as it forms the active site in various metalloenzymes. Zinc occurs in two oxidation states in aquatic ecosystems, namely as the metal, and as zinc(II).

In aquatic ecosystems the zinc(II) ion is toxic to fish and aquatic organisms at relatively low concentrations.

Occurrence

Zinc occurs in rocks and ores and is readily refined into a pure stable metal. It can enter aquatic ecosystems through both natural processes such as weathering and erosion, and through industrial activity.

In aqueous solutions zinc is amphoteric, that is, it dissolves in acids to form the hydrated cations Zn^{2+} and in strong bases it forms zincate anions (probably of the form $Zn(OH^{2-})_4$). Organozinc complexes and compounds can also be formed. In most natural waters zinc exists mainly as the divalent cation, which is the potentially toxic form. The proportion of other forms such as inorganic compounds like $ZnCO_3$; stable organic complexes like Zn-cysteinate; or colloids like Zn^{2+} -clay or Zn^{2+} -humic acid, depends on the chemistry of the water. The greatest dissolved zinc concentrations will occur in water with low pH, low alkalinity and high ionic strength. Chemical speciation of zinc is affected primarily by pH and alkalinity.

Soluble zinc salts (for example, zinc chloride and zinc sulphate) or insoluble precipitates of zinc salts (for example, zinc carbonate, zinc oxide and zinc sulphide) occur readily in industrial wastes. The carbonate, hydroxide and oxide forms of zinc are relatively resistant to corrosion and are used extensively in the following industries:

- metal galvanising;
- dye manufacture and processing;
- pigments (paints and cosmetics);
- pharmaceuticals; and
- fertilizer and insecticide.

Effects

Zinc is a trace metal which is also an essential micronutrient in all organisms. The requirement for trace elements frequently varies substantially between species, but the optimal concentration range is generally narrow. Severe imbalances can cause death, whereas marginal imbalances contribute to reduced fitness.

The lethal effect of zinc on fish is thought to be from the formation of insoluble compounds in the mucus covering the gills. Sub-lethal concentrations at which

toxic effects are evident depend on the concentration ratio of zinc to copper, since zinc interferes with copper absorption. Observed symptoms include depressed white blood cell-thrombocyte counts. Observed effects of prolonged exposure to sublethal concentrations of zinc in fish fry include oedema and liver necrosis.

Although invertebrate responses to zinc toxicity vary, molluscs are generally more resilient than are other organisms. Sub-lethal effects include reduced rates of shell growth, oxygen uptake and larval development. Algal photosynthesis can be inhibited by zinc.

47 INFORMATION SOURCES

The following information sources were utilised in the preparation of these standards:

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- Standard Methods for the Examination of Water and Wastewater, 1998, (prepared and published jointly by A.P.H.A., A.W.W.A & W.E.F) 20th Ed., American Public Health Association, 1015 Fifteenth Street, N.W., Washington DC 20005, USA.

APPENDIX 3

SOIL AND GROUNDWATER QUALITY STANDARDS

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1 RISK ASSESSMENT

A risk assessment is an evaluation of environmental and health-related effects of contamination. The purpose is to assess the need for remediation or protective measures. If contamination is found to pose a significant risk to human health or the environment, remedial work or other protective measures should be put in place.

Risk assessments appraise the specific circumstances of the contaminants in question, transport and exposure pathways and potential receptors at risk in each given situation. This is the source-pathway-receptor model. The risk assessment must be based on:

- The results of the investigations, including the nature and extent of contamination as well as prevailing geological, hydrogeological and hydrological conditions.
- A hazard assessment pertaining to the contaminants of interest.
- A survey of possible ways of transport and exposure pathways
- Knowledge of the potential receptors exposed.
- Conceptual Model of the site.

A conceptual model of the site is an essential component of a risk assessment and gives a representation of the environmental processes at a contaminated site including details of the source of contamination and the potential pathways and receptors at risk. A specific risk assessment will highlight interconnected ways and effects that may constitute a hazard to the receptor. It may also be necessary to take ecotoxicological aspects into consideration.

A hazard assessment is a review of the inherent characteristics of a potential contaminant. Qualitatively, a hazard may be described as carcinogenic, corrosive, toxic, etc. and effects may be characterised as acute and more long term (chronic effects). Whenever possible, the hazard is quantified by determining the concentration level at which harmful effects arise. Determining the inherent hazard of a given contamination incident entails a comprehensive assessment of toxicity, biodegradability, bioavailability, and mobility.

Risk is also assessed by considering the possible transport and exposure pathways. Three of the most important considerations include; health considerations in connection with land use, groundwater protection considerations and considerations regarding surface-water recipients and soil.

It is important that the risk assessment is planned as an integral part of the site investigation work.

Soil contamination cannot be clearly distinguished from soil gas or groundwater contamination. In the saturated zone, the space between soil particles is filled with groundwater. The contaminants are in a state of dynamic equilibrium between soil particles and groundwater. Similarly, there is air and water between the soil particles in the unsaturated zone and the volatile substances will reach a dynamic equilibrium between soil, soil gas, and water. Thus, while distinction between the contamination of soil, groundwater and soil gas may be difficult in a purely physical sense, it may still be useful to carry out separate risk assessments in connection with land use, groundwater and evaporation.

Criteria for soil quality have been established to be used in risk assessments in relation to land use. Sites where the soil fully lives up to these criteria can be used without restriction for all purposes including those that are highly sensitive to contamination. Furthermore, cut-off criteria have been established for several contaminants. These criteria state the level at which it is necessary to prevent all contact with the soil. It should be noted that compliance with soil quality criteria does not necessarily ensure compliance with evaporation and groundwater criteria.

At contaminated sites, indoor air in buildings as well as outdoor air may be unacceptably affected by underlying contamination of soil or groundwater. The effect on the indoor and outdoor air should be assessed in stages by various methods that have been constructed. In several stages, theoretical calculation models are included. Risk assessment should be based on evaporation to the overlying air and must not exceed the acceptable contamination contribution.

The risk of methane gas explosions in buildings on or in the immediate proximity of landfill sites can also be assessed in stages.

Risk assessment of groundwater should be used to assess whether contamination of either soil or groundwater contributes unacceptably to the contamination of groundwater resources. Groundwater quality criteria have been established for use in risk assessments. Risk assessments should be based on the aquifer complying with groundwater criteria at all points. Risk assessment can be carried out in stages, starting with a simple assessment. If this assessment does not provide enough evidence of the lack of risk, a more detailed risk assessment should be carried out taking sorption, dispersion and degradation of the contaminants into account. Furthermore, the assessment of the effect on the groundwater should be used to perform a risk assessment for surface water receptors where groundwater discharges to or is hydraulically connected to surface waters.

It should be emphasised that the soil and groundwater criteria do *not* represent a risk analysis. A specific risk analysis should take account of the local geological conditions and the sensitivity of land use (site and adjacent land).

If the risk assessment establishes a risk to human health or the environment, residents on or in the proximity of the site should be advised as to how to act until remediation can be implemented.

2 SOIL QUALITY STANDARDS

Standards for soil have been identified for a range of contaminants. In addition, cut-off criteria have been identified for ten contaminants (metals, total PAH and Benxzo(a)pyrene). The Soil Quality Standard (SQS) values and cut-off values are largely based on human toxicological data. Most values have been determined by means of a risk assessment process which assumes a two year old child,consuming 0.2g of soil a day as a target. Ecotoxicologial data has been taken into consideration for 16 of the compounds assessed. Soil quality standard (SQS), cut-off values and background values (based on total soil concentrations) are listed in Table 1 and 2.

Remediation is required if the concentration of contaminants exceeds the cut-off value. If the concentration is between the SQS and the cut-off values, remediation is not required however measures to reduce exposure may have to be implemented. Cut-off values have been identified for ten compounds due to their low mobility, making it relatively easy to implement measures to reduce exposure. They are also the contaminants most frequently encountered in topsoil from both point sources and non-point sources.

When interpreting analytical data against the SQS values, data from distinguishable soil horizons should be assessed separately to prevent data from contaminated soil horizons becoming diluted. Similarly data from hot spots should also be considered separately to data from other parts of the site.

For compounds that can lead to adverse chronic health effects average concentrations need to meet the SQS in order to avoid risk of contamination. In the case of compounds with acute health effects such as arsenic, the average concentration should not exceed the SQS and no more than 10% of the samples analysed should exceed the SQS by more than 50%. If these criteria are not met the area represented by the samples could pose an unacceptable risk and further investigation is required to determine if remedial work or other isolation or protective measures are required.

2.1 APPLICATION IN RELATION TO LAND USE.

Three categories of land use are identified:

- Very sensitive e.g. home with gardens, playgrounds, allotments
- Sensitive e.g. parks
- Non sensitive e.g. industrial areas

In the case of the very sensitive land uses there is considered to be no risk from exposure to contamination provided that SQS are not exceeded up to 3m below ground level (bgl). If the SQS are only met to a depth of 1m bgl there is considered to be no risk to site users under ordinary conditions. If SQS are exceeded beyond 1m, any activities such as construction work should be controlled to take the contaminated soil into account. Sensitive land uses can take place even if the SQS are only met within the top 0.3m of soil provided the underlying soil in which the criteria are exceeded is isolated. For sensitive and non-sensitive land uses SQS must be met in the depth of utilisation, which is determined on a site by site basis. For parkland and other areas of open space the depth of utilisation is generally considered to be 0.5m. For grassed and built up areas it is set at 0.25m.

Table 1 Soil Quality Standards. All units are in mg/kg dry weight (DW).

Substance	Soil quality criteria	Substance	Soil quality criteria
Acetone	8	Molybdenum	5
Arsenic	20[1(2)]	MTBE	500[2]
Benzene	1.5[2]	Nickel	30[1]
BTEX, total	10[2]	Nickel	30[1]
Cadmium	0.5[2]	Nitrophenols	
Chloroform	50[2]	Mono-	125[2]
Chlorophenols, total	3[2]	Di-	10[2]
Pentachlorophenol	0.15	Tri-	30[2]
Chromium, total	500	PAH, total	1.5[2,3]
Chromium (VI)	20	Benzo(a)pyrene	0.1[2]
Copper	500[1]	Dibenzo(a,h) anthracene	0.1[2]
Cyanide, total	500	Petrol (C_5-C_{10})	25
Cyanide, acid volatile	10[2]	Petrol (C_9-C_{16})	25
DDT	1	Phenols, total	70[1]
Detergents, anionic	1,500[2]	Phthalates, total	250[2]
1,2-dibromomethane	0.02[2]	DEHP	25[2]
1,2-dichloroethane	1.4[2]	Styrene	40[2]
1,1-dichloroethylene	5[2]	Turpentine, mineral (C_7 – C_{12})	25
1,2-dichloroethylene	85[2]	Tetrachloroethylene	5[2]
Dichloromethane	8[2]	Tetrachloromethane	5[2]
Fluorides, inorganic	20[1]	1,1,1-trichloroethane	200[2]
Gas oil (Total hydrocarbons (C_5–C_{35})[5])	100	Trichloroethylene	5[2]
Lead	40[2]	Vinyl chloride	0.4[2]
Mercury	1	Zinc	500

[1]: Based on acute harmful effects

[2]: Based on chronic harmful effects

[3]PAH, total defined as the sum of individual components: fluoranthene, benzyl(b+j+k)fluoranthene, benzyl(a)pyrene, dibenzyl(a,h)anthracene, and ideno(1,2,3-cd)pyrene.

Table 2 Criteria for necessary contamination cut-off, mg/kg, dry weight (DW)

Substance	Level where contamination cut off is necessary
Arsenic	20[1]
Cadmium	5[2]
Chromium	1,000
Copper	500[1]
Lead	400[2]
Mercury	3
Nickel	30[1]
Zinc	1,000
PAHs	15[2]
Benzo(a)pyrene	1[2]
Dibenzo(a,h)anthracene	1[2]

[1]: Based on acute harmful effects
[2]: Based on chronic harmful effects

3 GROUNDWATER QUALITY STANDARDS

Groundwater Quality Standards (GQS) have been set with the objective of protecting groundwater for the purposes of abstraction. They should be applied irrespective of whether there are any abstractions in the area under consideration. Values have been set for a range of substances and are listed in Table 3. Effectively the GQS values are concentrations of contaminants which can be reduced to those of drinking water quality by means of standard water treatment processes (oxidation and filtration).

The interpretation of analytical data against the GQS values is a staged process. If an initial study indicates the values are being exceeded, a more detailed site specific risk assessment is required to determine the contribution of soil contamination at a particular site to the groundwater. The risk assessment can comprise up to three stages:

1. Mixing model close to source area which comprises a simple calculation of contaminant concentrations in groundwater directly below the affected area. If these calculated values exceed the GQS, remedial action needs to be taken or Step 2 needs to be carried out.
2. Mixing model downgradient of source area which is based on compliance with the GQS at a point in the aquifer located within 100m downgradient or at a distance equalling one years groundwater flow. The width of the mixing zone in the aquifer is determined as vertical dispersion. If these calculated values exceed the GQS, remedial action needs to be taken or Step 3 needs to be carried out.
3. Downgradient model based on sorption and natural degradation is based on compliance with the GQS at the same distance as in Step 2 but the concentrations of the contaminants are reduced due to degradation in the aquifer. If the concentrations of contaminants are below the GQS, the specific degradation rate shall be determined either by field

measurements or in the laboratory, and samples from monitoring wells must confirm that degradation is actually taking place at the site.

Table 3 Standards for groundwater beneath contaminated sites.

Substance	Groundwater Quality Standard µg/l
Acetone	10
Arsenic	8
Benzene	1
Boron	300
Butylacetates	10
Cadmium	0.5
Chlorinated solvents (not vinyl chloride)	1
Chloroform	As low as possible
Chromium, total	25
Chromium VI	1
Copper	100
Cyanide, total	50
DEHP	1
Detergents, anionic	100
1,2-dibromomethane	0.01
Diethylether	10
Isopropyl alcohol	10
PAH [1]	0.2
Lead	1
Methylisobutylketone	10
Methyl-tert-butylether (MTBE)	30
Mineral oil, total	9
Molybdenum	20
Naphthalene	1
Nickel	10
Nitrophenols	0.5
Pentachlorophenol	0.01
Pesticides, total	0.5
Pesticides	0.1
Pesticides, persistent chlorinated	0.03
Phenols	0.5
Phthalates (not DEHP)	10
Styrene	1
Toluene	5
Vinyl chloride	0.2
Xylenes	5
Zinc	100

[1] Sum of fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene.

3.1 CATIONS/ANIONS

This section presents proposals for the setting of environmental quality objectives and standards for groundwater through the use of 'guideline values'. It is not possible to assign a universal set of standards for groundwater due to the natural variation in hydrochemistry. Therefore, indicators can be used to assess groundwater status, which takes account of natural variation in quality. It should be noted that a guideline value may not be applicable in some cases due to the widely variable nature of groundwater bodies. This variability in groundwaters, in pristine condition, is due to the influence exerted by the particular geology of the area. Where a guideline value is not applicable the natural background quality of the groundwater should be taken into consideration instead. Where there is interaction between groundwater and surface water and more sensitive standards exist for the receiving water body, these should then apply. The guideline values can be used to assist with the characterisation of groundwater bodies and to establish the need for additional investigations or further action in the event of guideline values being exceeded.

Table 4 Standards for Cations and Anions.

Parameter	Groundwater Guideline Value (mg/l)
Alkalinity	No abnormal change to background
Aluminium	0.2
Ammonia (as NH_4)	0.15
Barium	0.1
Bicarbonate/Carbonate	No abnormal change to background
Calcium	200
Chloride	30
Dissolved Oxygen	No abnormal change to background
Fluoride	1
Iron	0.2
Magnesium	50
Manganese	0.05
Mercury	0.001
Nitrate (as NO_3)	25
Nitrite (as NO_2)	0.1
Orthophosphate	0.03
Potassium	5
Silica	No abnormal change to background
Sodium	150
Sulphate	200

4 SAMPLING

Soil and water sampling is carried out in the investigation phase and as part of monitoring strategies to demonstrate compliance with an agreed remedial plan. The objective of sampling is to obtain representative samples to describe the nature and extent of contamination, the soil and groundwater. This enables a risk assessment to be carried out so that there is an adequate foundation for managing the contamination.

A written sampling strategy should be agreed and should include provision for the following:

- Sample locations
    - Targeted sampling of hot spots on the basis of knowledge of the historical activities at the site.
    - Near boundaries of known contaminated areas to identify the extent of contamination.
    - In areas of a contamination-sensitive land use.
    - Non-targeted sampling at the rest of the site. In order to reveal unknown contamination and to achieve the best statistical coverage of the site, it may be beneficial to locate investigation points according to specific rules. In such cases, sample fields/grids/nets can be defined.
- Sampling depth

Guidance on soil and groundwater sampling is provided in BS ISO 10175:2001 Investigation of Potentially Contaminated Sites.

4.1 - SOIL SAMPLING

Two soil samples are recommended to provide for geological descriptions and for chemical analyses. Surface samples can be taken in the top 0.15m for direct ingestion and inhalation risks. Sample sets are usually collected every 0.5m and one should be taken per soil layer or to reflect any strata/contamination changes as a minimum. Depths should also take into account proposed activities at the site e.g. removal of topsoil, main sewer services etc. Three or four samples should be taken through the soil profile with the deepest sample being natural strata. If contamination has penetrated the natural strata sampling should continue to depths where contamination is at background concentrations or it is not physically possible to sample.

4.2 - METHODS OF INVESTIGATION FOR SAMPLING

- Shallow investigations using hand augers
- Trial pits/trench excavations for depths up to 3m
- Percussion hammer probehole for depth up to 10m
- Shell and auger/rotary cored or open boreholes for deeper samples

Shallow investigations up to 1m may be backfilled with the excavated material. Deeper investigations should be sealed with a low permeability material to prevent possible cross contamination.

BS ISO 10381:2 Soil Quality – Sampling Techniques specified standard methods of sampling.

4.3 WATER SAMPLING

The objective of sampling is to obtain a water sample from the well which is representative of the groundwater in the aquifer with regard to the parameters to be investigated. A monitoring well should be screened at the depth of interest in the aquifer and an impermeable seal installed through any low permeability layers penetrated by the borehole to prevent cross contamination. After installation a well is developed to clear the screen and to achieve the best possible well efficiency.

A minimum of three wells should be installed in a triangular patter to provide an estimate of groundwater flow direction. The depth to the water level and depth of the well should be taken prior to sampling using a dip meter. The thickness of any dense non-aqueous phase liquids (DNAPL) and light non-aqueous phase liquids (LNAPL) should be taken prior to purging.

Prior to sampling, a well should be purged to ensure that water from the aquifer surrounding the monitoring well is sampled. As a general rule, the amount purged is a minimum of three well volumes or until groundwater quality measurements (electrical conductivity, pH, temperature, Eh, DO) have stabilised. In cases where a borehole is purged dry, the sample may be taken from the groundwater that subsequently enter the borehole.

BS ISO 5667:11 Water Quality – Groundwater Sampling details standard methods of sampling.

Bailers or pumps can be used to take a sample. Low flow methods are particularly appropriate where general parameters (e.g.Eh, DO) are important to the overall assessment of biogeochemical conditions. Samples should be carefully transferred from the bailer or pump to the sample container (appropriate to the contaminant). Samples should be filtered or preserved where relevant (e.g. metals).

Methods of sampling, packing, handling, and storage should be adapted to the types of contaminants being investigated e.g volatile organics, to ensure that there is no loss of contaminant during the sampling and analysis procedure. Water samples should be stored in the dark at $4^{O}C$. The time from sampling to analysis should be kept to a minimum and in any case should not exceed the recommended duration as specified in Standard Methods for the Examination of Water and Wastewater, 1998. As far as possible, samples should be delivered to the laboratory on the same day they are collected. If this is not possible, it should be noted on the analysis form. Sampling field sheets and chain of custody forms should be completed, dated and signed and should accompany the samples.

Three important considerations that should be taken into account when sampling include the following:

- The equipment should not contaminate the sample.
- The equipment should not be made of materials which ad/absorb substances.
- The method should not bias the contaminant content of the sample.

It is good practice to take field measurement of general water quality parameters on site at the time of sampling (O_2, CO_2, Eh (redox potential) and pH), as these may change with time.

5 INFORMATION SOURCES

The following information sources were utilised in the preparation of these standards:

- BSI (1999) BS 5930. Code of Practice for Site Investigations. BSI, London.
- BSI (2002) BS 15176. Characterisation of excavated soil for reuse. BSI, London.
- BSI (2001) BS 10175. Investigation of Potentially Contaminated Sites. Code of Practice. BSI, London.

- BSI (2002) BS 10381-2 Soil Quality – Sampling – Part 2 Guidance on Sampling Techniques. BSI, London.
- ISO (1993) 5667-11 Water Quality – Sampling – Part 11 Guidance on the sampling of groundwaters.
- Nathanail, J., Bardos, P. and Nathanail, P, 2002, Contaminated Land Management, Ready Reference, Land Quality Press and EPP Publications. [ISBN 1 900995 06 9].
- Aspinwall & Co. for Scottish Environment Protection Agency, 1999, Review of International Guideline and Intervention Values (Contaminated Land) Report.
- Standard Methods for the Examination of Water and Wastewater, 1998, (prepared and published jointly by A.P.H.A., A.W.W.A & W.E.F) 20th Ed., American Public Health Association, 1015 Fifteenth Street, N.W., Washington DC 20005, USA.

APPENDIX 4

NOISE STANDARDS

1 NOISE STANDARDS TO BE ACHIEVED AT NOISE SENSITIVE LOCATIONS

The generation of excessive noise in the community can have undesirable effects on the population. It can cause annoyance and disturbance to people at work or during leisure activities, disturbance to sleep and possibly a deleterious effect on general physical and mental well being. All people are not equally sensitive to the disturbing aspects of noise. There is a small but significant minority which is more sensitive than others.

The objective of these guidelines is to minimise the amount of noise to which people, living or working in sensitive locations, are exposed. Examples of such areas include domestic dwellings, hospitals, schools, places of worship, or areas of high amenity.

The sensitivity to noise is usually greater at night-time than it is during the day, by about 10dB(A). Ideally, if the total noise level from all sources is taken into account, the noise level at sensitive locations should be kept within the following values:

		Limits in dB (A) Leq	
Area Code	**Category of area**	**Day time**[Note 1]	**Night time**[Note 2]
A	Industrial area	75	70
B	Commercial area	65	55
C	Residential area	55	45

Note-1: Day time reckoned in between 6.00 am to 9.00p.m

Note 2: Night time reckoned in between 9.00p.m. to 6.00am

In some particularly quiet areas, such as pastoral, rural settings, where the background noise levels are very low, lower noise limits may be more appropriate. Audible tones and impulsive noise at sensitive locations at night should be avoided, irrespective of the noise level. Because of the variability in sensitivity to noise from one area to the next, it may be desirable to establish formal noise zoning criteria under the planning code.

2 VIBRATION AND AIR OVERPRESSURE

In the case of quarrying and mining operations, the vibration levels from blasting should not exceed a peak particle velocity of 12 mm/sec, measured in any three mutually orthogonal directions at a receiving location when blasting occurs at a frequency of once per week, or less. For more frequent blasting the peak particle velocity should not exceed 8mm/sec. These levels are for low frequency vibration, i.e., less than 40 Hertz.

Blasting should not give rise to air overpressure values at sensitive locations which are in excess of 125 dB (Lin)max peak.*Ambient Noise Standards