Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 31

Behaviour of Trace Compounds in the Aquatic Environment

New Delhi, October 1999

CSMRS Building, 4th Floor, Olof Palme Marg, Hauz Khas,
New Delhi – 11 00 16 India
Tel: 68 61 681 / 84 Fax: (+ 91 11) 68 61 685
E-Mail: dhvdelft@del2.vsnl.net.in

DHV Consultants BV & DELFT HYDRAULICS

with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1. Module context

This module introduces the trace compounds, which are of concern in water quality. The compounds, their sources, and their effects will be presented.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1.	Basic water quality concepts	**WQ – 01**	• Discuss the common water quality parameters • List important water quality issues
2.	Basic chemistry concepts [a]	**WQ - 02**	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
3.	Oxygen Balance in Surface Waters	**WQ – 25**	• Explain the importance of oxygen in water • Identify the main processes of oxygen addition and depletion in surface waters
4.	Surface Water quality planning concepts	**WQ – 27**	• Understand principles of WQ monitoring and assessment • Know of simple data analysis methods.
5.	Advanced Aquatic Chemistry concepts[a]	**WQ – 29**	• Explain the principles of chemical equilibrium • Define solubility product and explain how this relates to water quality assessment • Explain oxidation-reduction equilibria • Define the octanol-water partition coefficient and explain how this relates to water quality assessment

a - prerequisite

2. Module profile

Title	:	Behaviour of Trace Compounds in the Aquatic Environment
Target group	:	HIS function(s): Q2, Q3, Q5, Q6, Q7, and Q8
Duration	:	1 session of 60 min
Objectives	:	After the training the participants will be able to: • Give examples of trace contaminants and explain their pollutant properties • Explain behaviour of trace contaminants in aquatic environment
Key concepts	:	• Classification of trace contaminants • Environmental effects • Degradation of trace organics • Adsorption of trace compounds
Training methods	:	Lecture and discussion
Training tools required	:	Board, OHS, flipchart
Handouts	:	As provided in this module
Further reading and references	:	• Chemistry for Environment Engineering, C. N. Sawyer, P.L. McCarty and C. F. Parkin. McGraw-Hill, 1994 • Water Quality Assessment, ed. D. Chapman, E&FN SPON, London

3. Session plan

No	Activities	Time	Tools
1	***Preparations***		
2	***Introduction***: • Introduce the topic of trace compounds • Explain the problems arising from trace compounds • Present the main categories of trace compounds	10 min	OHS
3	***Trace organic compounds*** • Identify the main types of organic compounds • Review sources and effects of the substances • Discuss any local examples of these compounds in the environment	10 min	OHS, discussion
4	***Trace Metals*** • Identify the main types of organic compounds • Review sources and effects of the substances • Discuss any local examples of these compounds in the environment	10 min	OHS, discussion
5	***Trace inorganics (non-metals***) • Identify the main types of organic compounds • Review sources and effects of the substances • Discuss any local examples of these compounds in the environment	10 min	OHS, discussion
6	***Fate of trace compounds*** • Decay /degradation in environment • Concentration in Food web • Partitioning onto sediment	10 min	OHS, discussion
7	***Wrap up and Evaluation***	10 min	Evaluation Sheets

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/ Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Trace Compounds in the Aquatic Environment

- Trace compounds of concern are contaminants
- Trace contaminants include:

  - *Organic compounds*
  - *Inorganic metals*
  - *Inorganic non-metals*

Trace organics

- *Pesticides*
- *Chlorinated solvents*
- *Aromatic hydrocarbons*

Pesticide types

- *organochlorines*
- *organophosphorus compounds*
- *carbamates*
- *triazines*

Chlorinated solvents

- *part of group of chemicals known as VOCs*
- *insoluble in water*
- *resistant to environmental degradation*

Aromatic hydrocarbons

- *can be soluble or insoluble in water*
- *many are carcinogenic*

Trace metals

- *‘heavy’ metals are often toxic but this often depends upon the chemical species*
- *heavy metals are often adsorbed onto suspended particles in water*
- *other metals such as antimony, beryllium and thallium can also be toxic*

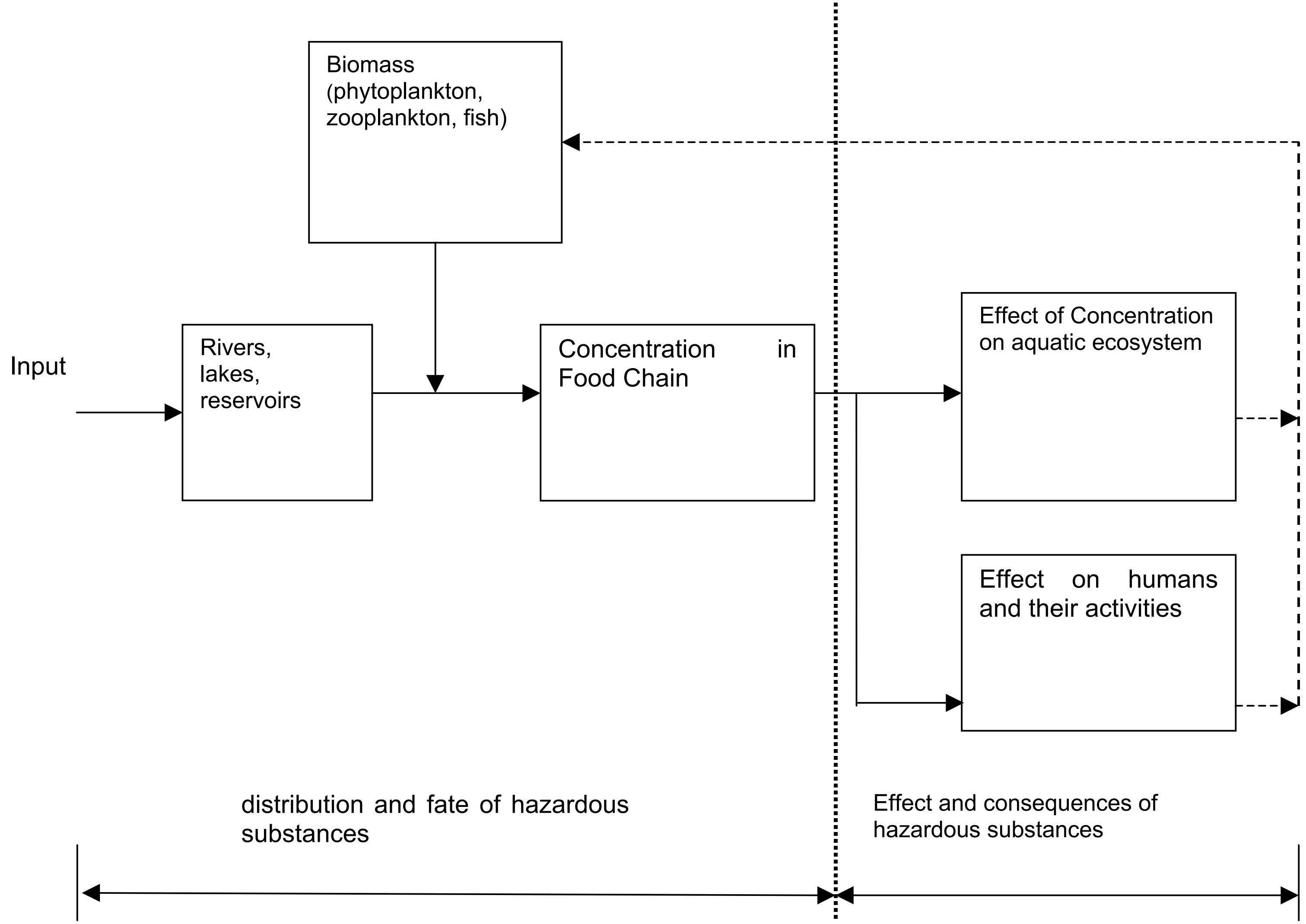
Trace non-metals

- *arsenic (variable toxicity)*
- *asbestos (carcinogenic)*
- *cyanide (highly toxic but degrades quickly)*

Fate in the Aquatic Environment (1)

- Accumulaiton at specific sites
  - *Bones*
  - *Fatty tissues*
  - *Selected organs*
- Bioconcentration
  - *Water ⟶ algae ⟶ zoo – plankton ⟶ fish ⟶ bird*
  - *concentration in net biomess produced at each level increases*

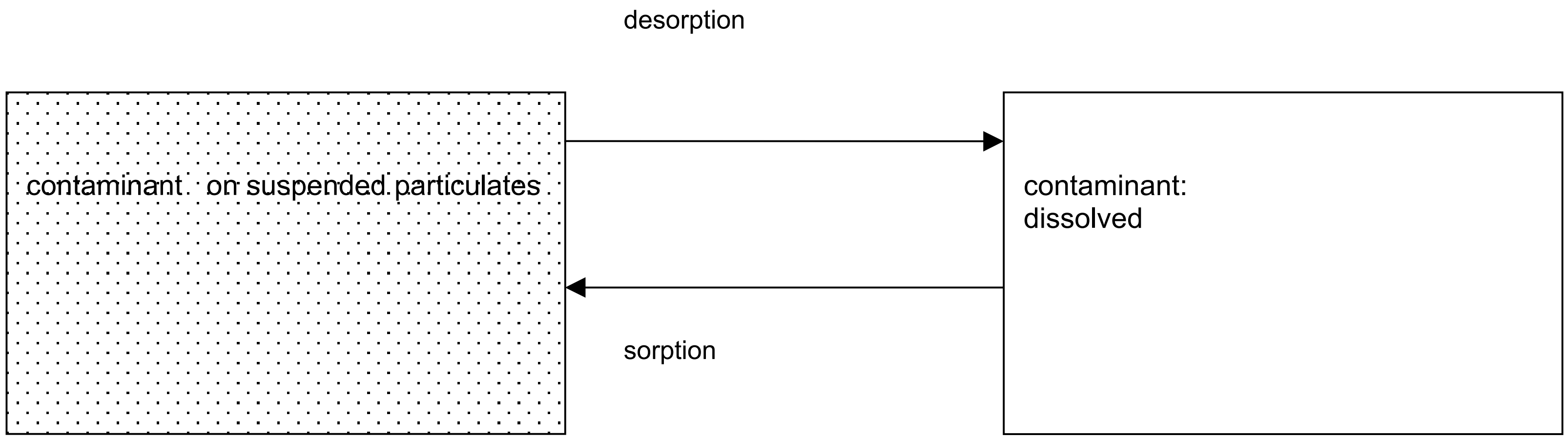
Fate in the Aquatic Environment (2)



Bioconcentration factor

- Conc. in fish (mg//kg) = Conc. in water (mg/L) X BCF (L/kg)
- BCF examples
  - *Aldrin – 28, Chlorodane – 14000, DDT – 54,000*
  - *PCBs – 100,000*
  - *Cd – 81, Cr – 16, Cu – 200*
- If DDT in water = 0.001 mg/L,
  in fish = 0.001 X 54,000 = 54 mg/kg fish

Adsorption (1)



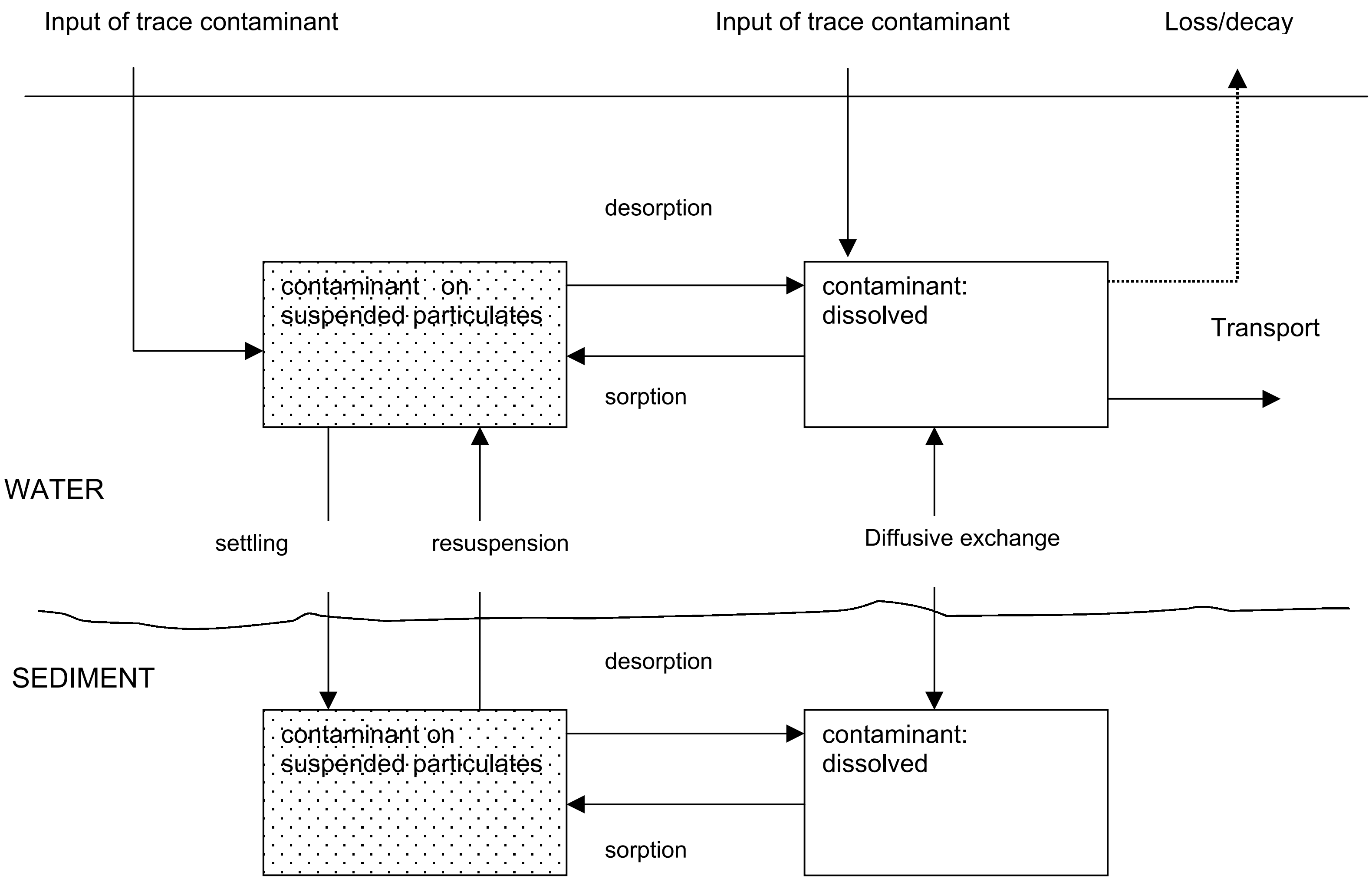
$$K_d = Partition\ Coefficiet = \frac{Particulate\ Conc.}{Dissolved\ Conc.} = \frac{\mu g / kg}{\mu g / \ell} = \frac{\ell}{kg}$$

Adsorption (2)

Partition Coefficients for some chemicals

Chemical	Partition Coefficient (K_d) (L/kg)
Heavy metals	10^4 - 10^5
Benzo(a)pyrene	10^4 - 10^5
PCB	10^5 - 10^6
Methoxychlor	10^4
Napthalene	10^3

General Processes



Analysis

- Present in low concentrations
- Care in sampling, preservation, extraction
- Advanced level equipment

  - *AAS, Metals*
  - *GC, Organics*
  - *Expertise and practice*

5. Evaluation sheets

6. Handout

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Pesticide types

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- *organophosphorus compounds*
- *carbamates*
- *triazines*

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- *other metals such as antimony, beryllium and thallium can also be toxic*

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- *arsenic (variable toxicity)*
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- Care in sampling, preservation, extraction
- Advanced level equipment

    - *AAS, Metals*
    - *GC, Organics*
    - *Expertise and practice*

Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8. Main text

Contents

Behaviour of Trace Compounds in the Aquatic Environment

1. Introduction

There is general agreement that the term 'trace' contaminants in water refers to substances which are present at a concentrations below approximately 5 mg/L. Of course, many trace contaminants can be measured as present at considerably lower concentrations; certain pesticides for example are now routinely measured in tenths of nanograms per litre (10^{-10} g/L) in a number of countries.

The fact that contaminants are only present in trace quantities means that their detection is often difficult and expensive, frequently requiring specialised techniques and equipment. It is important therefore that any monitoring exercise targeted at trace pollutants is well planned and has clear objectives so that unnecessary costs are minimised.

Even though they are only present in very small quantities, many of the trace compounds can be highly toxic. These compounds in water can effect human health, both directly and indirectly:

- Directly: if the compound is ingested from the drinking water supply
- Indirectly: if the compound is ingested from contaminated aquatic foodstuffs (fish or shellfish)

When ingested in too high amounts over a long term, many of these substances may cause health problems ranging from cancers, tumours, and birth defects.

Trace compounds can also have a strong effect on ecosystems, disrupting reproduction capability of organisms, and also causing tumours, or other abnormalities.

Essentially, trace contaminants can be split into a number of different classes of materials as follows:

- Trace organics
- Trace inorganic metals
- Trace inorganic non-metals

These three categories are dealt with in greater detail in the sections that follow.

2. Trace organic contaminants

Trace organic pollutants fall into a number of distinct classes of compounds – the most important of which are:

- Pesticides – a large group of substances, including sub-groups such as herbicides, insecticides and fungicides, which are specifically designed to be toxic to living organisms
- Chlorinated solvents – a group of chemicals, normally toxic, which can be a particular problem when a contaminant of groundwater although in surface waters they tend to be eventually released to the atmosphere.
- Aromatic hydrocarbons – a group of organic chemicals, many of which are carcinogenic, including such substances as benzene, toluene, styrene and phenol

In addition to the above there are many thousands of other organic chemicals which are potentially polluting including the products which are produced as a result of environmental degradation of the above groups of compounds.

In order to give some idea of the pollution problems posed by organic contaminants the groups of pollutants referred to above, and any other individual compounds of interest, will be discussed below.

Pesticides

The term pesticide actually represents a very large number of chemicals (approximately 10,000) including the classes:

- organochlorine pesticides,
- organophosphorus pesticides,
- carbamate pesticides,
- triazine pesticides and
- others.

Organochlorine pesticides are generally chemically stable and have been in widespread use for a number of years. They are, therefore, present in many environments (including the Arctic and Antarctic regions) at elevated concentrations. These compounds tend to be insoluble in water but highly soluble in hydrocarbons and fats. This means that when they are absorbed from the environment they are often concentrated within living tissue and this, combined with their toxicity, makes many organochlorine pesticides particularly hazardous to animals and humans.

In the aquatic environment, organochlorine pesticides tend to adsorb onto suspended material and are thus often found at higher concentrations in bottom sediments.

Examples of organochlorine pesticides are insecticides, e.g. DDT (dichlorodiphenyltrichloro ethane) and lindane (□-benzene hexachloride) and herbicides, e.g. 2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid).

The organophosphorus pesticides were developed towards the end of World War II as a by-product of nerve gas research. They can be highly toxic to man and higher animals, although tend to be much less toxic to fish and birds than the organochlorines.

Unlike organochlorines, organophosphorus pesticides are relatively unstable and tend to decompose in the environment. These types of compounds also have an affinity with solid particles and are often found in higher concentrations in aquatic sediments than in the water column itself.

Examples of organophosphorus pesticides are parathion (O,O-diethyl-O-p-nitrophenylthiophosphate) and malathion (S-(1,2-dicarbethoxyethyl)-O,O-dimethyldithiophosphate)

Carbamate pesticides generally have a low toxicity to animals and degrade relatively easily. Isopropyl N-phenylcarbamate (IPC) is an example of this type of pesticide.

Triazines are mostly used as herbicides. Generally, they do not degrade easily and have low toxicity to fish and birds. Probably the best known pesticide of this group is the herbicide atrazine. Because it does not degrade easily it is often detected in surface water and groundwater in agricultural areas.

Chlorinated solvents

Chlorinated solvents and related compounds are part of a larger group of chemicals known as volatile organic compounds (VOCs). Because of their volatility, these compounds are normally released into the atmosphere even when they are originally discharged to surface water bodies. This does not occur when they are released to groundwater, however, with the result that, due to their toxicity and carcinogenic properties, they can be problematic pollutants.

Generally chlorinated solvents are insoluble in water and resistant to environmental degradation. As with chlorinated pesticides, many chlorinated solvents tend to be adsorbed onto solid particles within water bodies so that their concentration is often greater in the sediment than it is in the water column.

Examples of chlorinated solvents are carbon tetrachloride, chloroform, trichloroethane, vinyl chloride and bromoform.

Aromatic Hydrocarbons

These are a large group of organic chemicals with a variety of different properties and it is these properties that determine their polluting nature.

Certain of these compounds are used widely and are soluble in water, which means that they can often be found in surface waters, and groundwater. Of particular note in this regard are compounds such as benzene, toluene and xylene which are present in petrol and phenol which is highly water soluble and widely used in industry. Such compounds tend to stay in the water column rather than migrate to the sediment when released to the aquatic environment.

Other aromatic hydrocarbons, particularly the ones containing chlorine, bromine and fluorine atoms, are insoluble in water and tend to be adsorbed onto solid particles within water bodies or, as they are often less dense than water, float on the water's surface. These chemicals would also have a tendency to be concentrated within living organisms as many of them will be soluble in fat.

Many aromatic organic compounds have been found to be human and animal carcinogens, which are resistant to environmental degradation. They can be, therefore, hazardous pollutants.

3. Trace inorganic metals

Normally, when trace inorganic metals are referred to it is taken to mean the so-called 'heavy metals' such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg) and nickel (Ni). Other metals can also be problematic pollutants, however, and these and the heavy metals will be discussed below.

Heavy Metals

The heavy metals can be problematic pollutants because they are generally toxic either to higher animals or plants or both. The toxicity of these elements is, however, very dependent upon the chemical species in which they exist in the environment as this will, in turn, affect their physical properties (e.g., solubility). It can be important, therefore, when analysing metals in the environment, to know in what form they exist in addition to their concentration. The determination of the form of the chemical species is known as speciation. Speciation can be carried out via laboratory studies, by using models based on stability constants or by analysis of environmental samples.

The table below provides a summary of the type of effects normally associated with the heavy metals referred to above. Generally, as can be seen from the table, ionic forms of the heavy metals are more toxic than complexed varieties although certain organic-metal compounds can also be highly toxic (e.g., methyl mercury)

In the aquatic environment, metals can exist as dissolved species or as suspended or colloidal material. Normally it can be expected that more than 50% of the total metal present will be absorbed onto suspended particles in the water.

Heavy metal	Use	Toxic compounds	Effects
Cadmium	Batteries, paints, plastics, metal finishing	Most compounds of cadmium are toxic – Cd (II) is particularly toxic	Humans and animals, kidney effects
Chromium	Metal production, metal finishing, tanning	Cr (VI) is the most toxic form	Humans, animals (liver / kidney effects) and plants
Copper	Metal and alloy production, metal finishing, electrical items, pipes	Copper tends to form non-toxic complexes in natural waters – the free ionic forms can be toxic	Plants and fish – less harmful to higher animals
Lead	Batteries, solder, anti-knock additive in petrol	Most compounds of lead are toxic but organic lead compounds tend to be more toxic then inorganic compounds	Higher animals: central and peripheral nervous system damage; kidney effects; highly toxic to infants and pregnant women.
Mercury	Dentistry, batteries, lamps, scientific instruments	Organic (particularly methyl) mercury compounds are the most toxic	Higher animals: Central nervous system disorders; kidney effects
Nickel	Electroplating , metal and alloy production	Ionic forms tend to be more toxic	Plants

Other Metals

Metals other than the traditional heavy metals referred to above can cause aquatic pollution problems. A short description of the main species in this regard is given below:

- Antimony – a metal used in a variety of industrial processes which is toxic to higher animals affecting the heart, liver, skin and respiratory and gastrointestinal tracts
- Barium – used in the manufacture of paints, paper and drilling muds, it can be toxic to higher animals affecting the muscles, heart and kidneys
- Beryllium – a rare metal used in some industrial and nuclear processes it is an animal, and possibly a human, carcinogen
- Selenium – an essential element for humans, it can occur naturally in waters; toxic to animals and humans at higher concentrations which can be achieved through accumulation in plants
- Thallium – salts of thallium are extremely toxic to humans and higher animals where they affect the nervous system, skin, and respiratory and digestive tracts

Water Quality Standards Specified by Bureau of Indian Standards (Tolerance Limits)

Substance	Water Use		
	A	B	C
Mercury (as Hg) mg/l	0.001		
Cadmium (as Cd) mg/l	0.01		0.01
Lead (as Pb) mg/l	0.1		0.1
Zinc (as Zn) mg/l	15		15
Chromium (as Cr^{+6}) mg/l	0.05	0.05	0.05
Copper (as Cu) mg/l	1.5		1.5
Silver (as Ag) mg/l	0.05		
Selenium (as Se) mg/l	.01		.05

A = Drinking water sources without conventional treatment but after disinfection
B = Outdoor bathing
C = Drinking water sources with conventional treatment followed by disinfection

4. Trace inorganic non-metals

There are a large number of trace inorganic species, which can cause water pollution problems. Some of the more important ones are listed below:

- Arsenic – released to the environment through mining, insecticide application and fossil fuel combustion. Arsenic can be highly toxic to some individuals, causing dermal and nervous system toxicity. Certain arsenic compounds are suspected carcinogens.
- Asbestos – naturally occurring fibrous material which was extensively used in the past for its fire and chemical resistant properties; less used now due to its potent carcinogenic properties many countries worldwide have drinking water standards to protect their population from the possible effects of drinking asbestos contaminated water
- Cyanide – released from electroplating, refining and coking operations, cyanide is highly toxic although it is usually broken down quickly in the environment

Water Quality Standards Specified by Bureau of Indian Standards (Tolerance Limits)

Substance	Water Use		
	A	B	C
Arsenic (as As) mg/l	0.05	0.2	0.2
Cyanides (as Cn) mg/l	0.05	0.05	0.05

5. Fate of trace compounds in the environment

Once trace compounds enter into a water system, they can have several different outcomes. Those compounds that can degrade will eventually disappear given enough time. However, many trace compounds are not degradable, and they will accumulate in the environment.

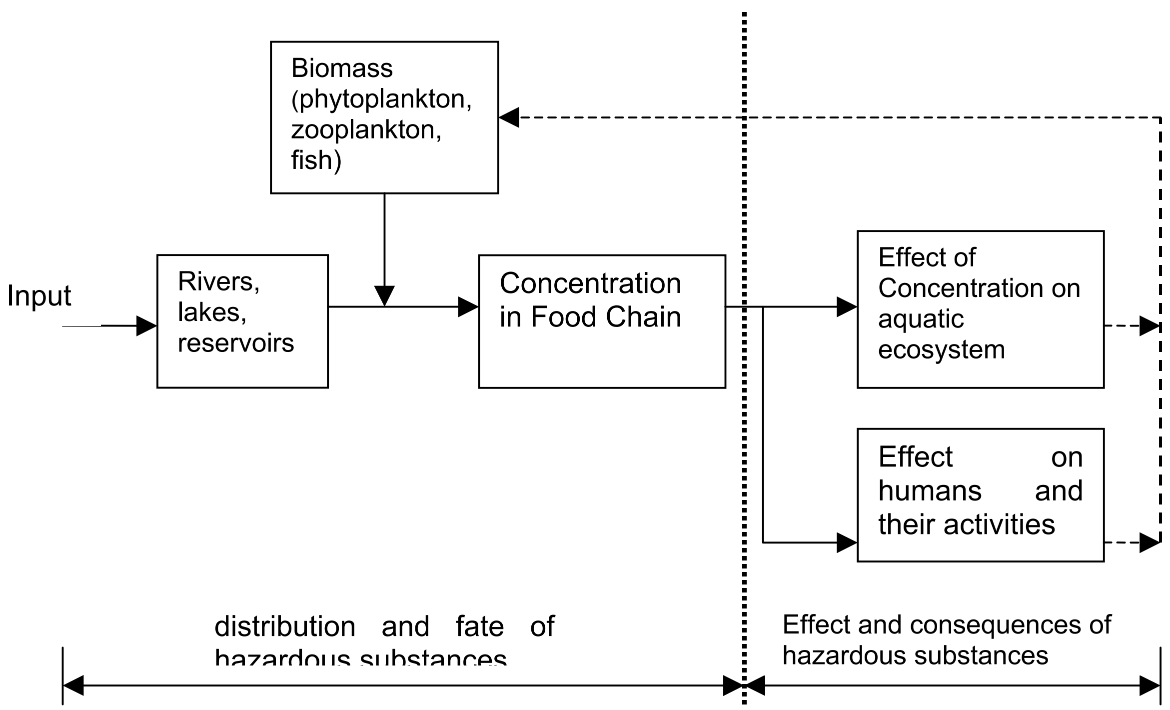
Three features of toxic substances are characteristic and separate them from other pollutants:

1. Certain chemicals can become concentrated by aquatic organisms and can be transferred upwards in the food chain
2. Certain chemicals adsorb to particulate matter in the water
3. Certain chemicals are toxic at low water concentrations.

Bioconcentration

Many trace compounds, especially the organic contaminants, are especially harmful because they become concentrated in the food chain.

Once a substance is input to the aquatic environment (rivers, lakes, reservoirs, etc.), different organisms can ingest the substance. The substances tend to accumulate in the tissues of organisms, where they can have an effect on proper functioning. The substance can move up the food chain, from phytoplankton, zooplankton, to fish and higher predators. With each step up in the food chain, the substance becomes more concentrated, i.e. the concentrations in the tissues become higher. This process is known as 'bioaccumulation' or 'bioconcentration'.



The bioconcentration factor (BCF) is a measure of the tendency for a substance to accumulate in fish tissue. The equilibrium concentration of a chemical in fish can be estimated by multiplying its concentration in water by the bioconcentration factor:

Concentration in fish = (Concentration in water) x (Bioconcentration factor)

Where the following units are used:

Concentration in fish = mg/kg
Concentration in water = mg/L
BCF = L/kg

Some BCF values are given in the table below:

Chemical	Bioconcentration Factor (L/kg)
Aldrin	28
Arsenic and compounds	44
Benzene	5.2
Cadmium	81
Chlorodane	14,000
Chromium III, VI and compounds	16
Copper	200
DDT	54,000
PCBs	100,000
Trichloroethylene (TCE)	10.6

The chlorinated hydrocarbons pesticides, like chlordane and DDT, have especially high bioconcentation factors, as do PCBs. These high bioconcentration factors have been an important part of the decision to reduce or eliminate use of these chemicals in many countries.

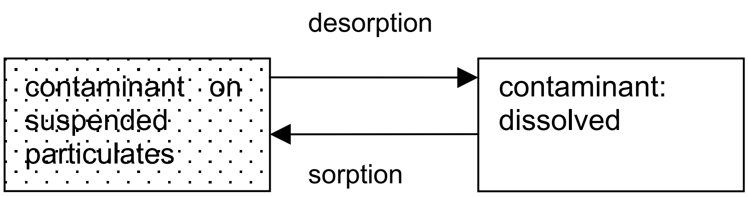
Example:
The concentration of TCE in water is 150 ppb. What is the concentration of TCE in fish that live in this water?

The bioconcentration factor for TCE is 10.6 L/kg. The expected concentration in fish is:

Concentration in fish = 0.15 mg/L x 10.6 L/kg = 1.59 mg TCE / kg fish

Adsorption to Particles

Many trace contaminants have the characteristic that they preferentially adsorb to particulate matter in the water (suspended particulates). This process is known as 'sorption' or 'adsorption'.



In the opposite reaction, contaminants adsorbed to suspended particulates can 'desorb', and once again become dissolved in water.

The sorption/desorption reactions occur very quickly and can be considered as equilibrium reactions. The ratio between the amount of contaminant adsorbed to particles and the amount which is dissolved in water is known as the 'Partition Coefficient' (K_d).

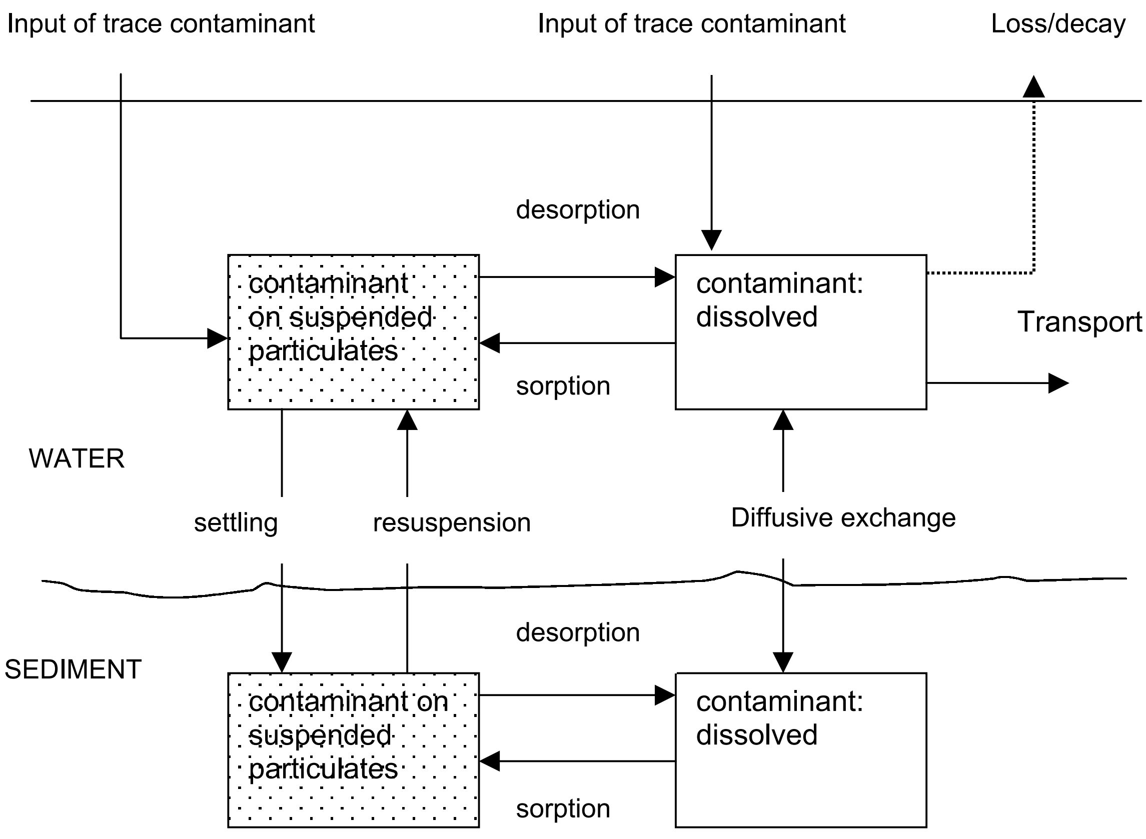
$$K_d = Partition\ Coefficiet = \frac{Particulate\ Conc.}{Dissolved\ Conc.} = \frac{\mu g / kg}{\mu g / \ell} = \frac{\ell}{kg}$$

The higher the value of the partition coefficient, Kd, the more larger the proportion of the contaminant will be sorbed to particulates.

Partition Coefficients for some chemicals

Chemical	Partition Coefficient (Kd) (L/kg)
Heavy metals	10^4 - 10^5
Benzo(a)pyrene	10^4 - 10^5
PCB	10^5 - 10^6
Methoxychlor	10^4
Napthalene	10^3

The figure below shows many of the general processes which effect the fate of trace contaminants in a (surface) water body, including sorption/desorption.



Processes controlling the fate and transport of contaminants in water:

1. The contaminant is input into the water body, either as a dissolved substance or associated with particulate matter.
2. Sorption and desorption of the contaminant occurs between the dissolved and particulate forms. This happens in both the water column and the bottom sediment
3. Settling and resuspension of the particulate matter with contaminant occurs. This distributes the contaminant in the water column and the bottom sediment.
4. The dissolved contaminant is also distributed between the water column and the bottom sediment by diffusive exchange
5. The chemical can be lost due to processes of decay (biodegradation, volatilisation, photolysis, and other chemical reactions.)
6. Transport of the contaminant by advective flow and dispersive mixing
7. Net deposition of contaminant in bottom sediment

Not all processes are relevant for all chemicals. Some chemicals can be highly volatile, or will break down quickly in the environment. Others will stay mostly dissolved, and be carried by the water flow. Others will sorb strongly to particles and may settle and accumulate in the bottom sediment.

Because trace contaminants tend to adsorb to particulate matter, when sampling and analysing for trace contaminants it is very important to collect a 'whole' sample, i.e. including suspended particulate matter. Once the sample is in the laboratory, and ready for analysis, it is again important to thoroughly mix and shake the sample, and digest a representative sub-sample. It is incorrect to filter the sample, because then only the dissolved fraction of the contaminant will be analysed. Such filtering should only be conducted if the goal of the analysis is to measure the dissolved fraction of the contaminant.

Toxicity: Acute and Chronic Effects

Effects of toxic contaminants on the ecosystem or directly to humans are distinguished between Acute and Chronic:

- Acute effects: coming speedily to a crisis, i.e. several hours to a few days
- Chronic effects: continuing for a long time, lingering, i.e. months - years

Exposure to high concentrations of a toxic trace compound may cause acute effects, or even death in organisms.

Exposure to low concentrations of a toxic trace compound may cause chronic effects in organisms.

6. Analysis of Trace contaminants

Analysis of trace contaminants and other pollutant substances must be made with sophisticated analytical equipment. Their analysis is often difficult due to the low concentration levels, and interference from other substances, often present at higher concentrations.

Inorganic contaminants: metals and non-metals

Metals such as cadmium, chromium, copper, lead, mercury, zinc, selenium, etc, as can be analysed with Atomic Absorption Spectrophotometer (AAS). In this method, a sample is aspirated into a flame, and a light beam is directed through the flame to a detector that measures the amount of light that is absorbed by the atomised element in the flame. A different source lamp emitting a specific wavelength has to be used for each element. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.

Detection of arsenic requires AAS with graphite furnace, or the inductively coupled plasma method. Measurement of cyanide can be made by titration, calorimetric procedures or cyanide specific electrode, depending on the concentrations involved.

Organic contaminants

Trace organic contaminants are generally measured with gas chromatograpy (GC). This procedure is based upon the principle of separation and then detection and quantification. The analyses can be used to detect pesticides, aromatic hydrocarbons, and others.