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ENVIRONMENTAL SCIENCE PART ONE

[NOISE , THERMAL ,AIR , WATER POLLUTION AND TYPES OF POLLUTANTS]

SYLLABUS

UNIT 1 -Multidisciplinary nature of environmental studies

Defination Scope and importance ;Need for public awareness

UNIT 2- Natural Resourses

UNIT 3 Ecosystems

UNIT 4 Biodiversity and its conservation

UNIT 5 Environmental Pollution Causes ,effects and control of -Air pollution,Water pollution , Soil Pollution, Marine Pollution,Noise Pollution,Thermal Pollution , Nuclear Hazards ,Solid waste management Disaster management ,Pollution control ,Pollution case studies

UNIT 6 Social Issues and Environmental Protection Act ;Environmental Ethics

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Chapter- 1- INTRODUCTION

ENVIRONMENTAL POLLUTION is normally taken to mean harm done to the natural environment by human activity. In fact, some environmental pollution can have natural sources, for example volcanic activity, which can cause major air pollution or water pollution and destroy flora and fauna. In terms of environmental issues, however, environmental pollution relates to human actions,especially in connection with energy resources. The demands of the industrialized nations for energy to power machines, provide light, heat, and so on are constantly increasing.The most versatile form of energy is electricity, which can be produced from a wide variety of other energy sources, such as the fossil fuels - coal, oil, and gas - and nuclear power produced from uranium.These are all non-renewable resources in addition,their extraction, transportation, utilization, and, and waste products, all give rise to pollutants of one form or another.The effects of these pollutants can have consequences not only for the local environment, but also at a global level.

Environmental issues

Matters relating to the detrimental effects of human activity on the biosphere, their causes, and the search for possible solutions Since the Industrial Revolution, the demands made by both the industrialized and developing nations on the Earth's natural resources are increasingly affecting the balance of the Earth's resources. Over a period of time, some of these resources are renewable - trees can be replanted,soil nutrients can be replenished – but many resources, such as fossil fuels and minerals, are non-renewable and in danger of eventual exhaustion. In addition, humans are creating many other problems which may endanger not only their own survival, but also that of other species. For instance,deforestation and air pollution are not only damaging and radically altering many natural environments, they are also affecting the Earth's climate by adding to the greenhouse effect and global warming, while water pollution is seriously affecting aquatic life,including fish populations, as well as human health.

WIDESPREAD EFFECTS OF POLLUTION

Many people think of air, water, and soil pollution as distinctly separate forms of pollution. However, each part of the global ecosystem - air,water, and soil - depends upon the others, and upon the plants and animals living within the environment.Thus, pollution that might appear to affect only one part of the environment is also likely to affect other parts.

For example, the emission of vehicle exhausts or acid gases from a power plant might appear to harm only the surrounding atmosphere. But once released into the air they are carried by the prevailing winds, often for several hundred kilometres, before being deposited as acid rain. This can produce an enormous range of adverse effects across a very large area, for example: increased acidity levels in lakes and rivers are harmful to fish stocks and other aquatic life;physical damage to trees and other vegetation results in widespread destruction of forest areas; increased acidity of soils reduces the range of crops that can be grown, as well as decreasing production levels; rocks such as limestone, both in the natural landscape and in buildings, are eroded - the effect of acid rain on some of the world's most important architectural structures is having disastrous consequences. In addition,acid rain in the form of aerosols or attached to smoke particles can cause respiratory problems in humans. Pollution of the Arctic atmosphere is creating Arctic haze- the result of aerosol emissions, such as dust, soot, and sulphate particles, originating in Europe.

ECOLOGY

Greek oikos `house´ Study of the relationship among organisms and the environments in which they live, including all living and nonliving components. The chief environmental factors governing the distribution of plants and animals are temperature, humidity, soil, light intensity, daylength, food supply, and interaction with other organisms. The term was coined by the biologist Ernst Haeckel in 1866. Ecology may be concerned with individual organisms (for example,behavioural ecology, feeding strategies), with populations (for example, population dynamics), or with entire communities (for example, competition between species for access to resources in an ecosystem, or predator-prey relationships).Applied ecology is concerned with the

management and conservation of habitats and the consequences and control of pollution.

HABITAT

Localized environment in which an organism lives, and which provides for all (oral most all) of its needs. The diversity of habitats found within the Earth's ecosystem is enormous, and they are changing all the time. Many can be considered inorganic or physical; for example, the Arctic ice cap, a cave, or a cliff face. Others are more
complex; for instance, a woodland or a forest floor. Some habitats are so precise that they are called microhabitats, such as the area under a stone where a particular type of insect lives. Most habitats provide a home for many species.Science of naming and identifying species, and determining their degree of relatedness. It
plays an important role in preserving biodiversity; only a small fraction of existing species have been named and described.

BALANCE OF NATURE

In ecology, the idea that there is an inherent equilibrium in most ecosystems, with plants and animals interacting so as to produce a stable,continuing system of life on Earth.The activities of human beings can,and frequently do, disrupt the balance of nature.Organisms in the ecosystem are adapted to each other - for example,waste products produced by one species are used by another and resources used by some are replenished by others; the oxygen needed by animals is produced by plants while the waste product of animal respiration, carbon dioxide, is used by plants as a raw material in photosynthesis. The nitrogen cycle,the water cycle, and the control of animal populations by natural predators are other examples.

The idea of a balance of nature is also expressed in the Gaia hypothesis, which likens the Earth to a living organism, constantly adjusting itself to circumstances so as to increase its chances of survival.

FOOD CHAIN

In ecology, a sequence showing the feeding relationships between organisms in a particular ecosystem.Each organism depends on the next lowest member of the chain for its food. A pyramid of numbers can be used to show the reduction in food energy at each step up the foodchain.Energy in the form of food is shown to be transferred from autotrophs, or producers, which are principally plants and photosynthetic microorganisms, to a series of heterotrophs, or consumers. The heterotrophs comprise the herbivores, which feed on the producers;carnivores, which feed on the herbivores; and decomposers, which break down the dead bodies and waste products of all four groups (including their own), ready for recycling.In reality, however, organisms have varied diets, relying on different kinds of foods, so that the food chain is an oversimplification.

The more complex food web shows a greater variety of relationships, but again emphasizes that energy passes from plants to herbivores to carnivores. Environmentalists have used the concept of the food chain to show how poisons and other forms of pollution can pass from one animal to another, threatening rare species.For example, the pesticide DDT has been found in lethal concentrations in the bodies of animals at the top of the food chain, such as the golden eagle Aquila chrysaetos.

CONSERVATION

In the life sciences, action taken to protect and preserve the natural world, usually from pollution,overexploitation, and other harmful features of human activity. The late1980s saw a great increase in public concern for the environment, with membership of conservation groups,such as Friends of the Earth, Greenpeace, and the US Sierra Club,rising sharply. Globally the most important issues include the depletion of atmospheric ozone by the action of chlorofluorocarbons (CFCs), the build-up of carbon dioxide in the atmosphere (thought to contribute to an intensification of the greenhouse effect), and deforestation.Conservation groups in Britain originated in the 1860s; they include the Commons Preservation Society 1865, which fought successfully against the enclosure of Hampstead Heath (1865) and Epping Forest(1866) in London; the National Footpaths Preservation Society 1844 ; and the National Trust 1895. In the UK the conservation debate has centred on water quality, road-building schemes, the safety of nuclear power, and the ethical treatment of animals.

Twelve coastal sites in Great Britain,including five Special Areas of Conservation, have been designated by the European Commission to be part of a network of Natura 2000 sites. The EC will provide funds to help preserve these sites from development,overfishing, and pollution, and to monitor rare plants.They include the North Northumber land Coast, with its sea caves, its breeding population of grey seals in the Farne Islands,and Arctic species such as the wolf fish; the Wash and North Norfolk Coast, with its population of common seals,waders, and wildfowl, and its extensive salt marshes; and Plymouth Sound and estuaries, with their submerged sandbanks.

A £10 million project, `Turning the Tide´ was launched 1997 by the Millennium Commission. It would fund coastal restoration of Britain's only magnesium limestone cliffs between Hartlepool and Sunderland.The area is rich in wild flowers, with grassland and denes (steep, wooded valleys). Intensive farming and the use of fertilisers damaged the flora and fauna of the area. The beaches are polluted as a result of over two centuries of coal mining along the Durham coast. Waste from the mines was dumped into the sea and onto the beaches, leaving heaps of spoil 12 to 15 ft high. The restoration project is aimed at removing spoil from the beaches and returning the cliffs to their natural grassland.

NATURE RESERVE

Area set aside to protect a habitat and the wildlife that lives within it,with only restricted admission for the public. A nature reserve often provides a sanctuary for rare species. The world's largest is Etosha Reserve, Namibia; area 99,520sq km/38,415 sq mi.

ENDANGERED SPECIES

Plant or animal species whose numbers are so few that it is at risk of becoming extinct. Officially designated endangered species are listed by the International Union for the Conservation of Nature (IUCN). Endangered species are not a new phenomenon; extinction is an integral part of evolution. The replacement of one species by another usually involves the eradication of the less successful form, and ensures the continuance and diversification of life in all forms. However, extinctions induced by humans are thought to be destructive, causing evolutionary dead-ends that do not allow for succession by a more fit species. The great majority of recent extinctions have been directly or indirectly induced by humans; most often by the loss, modification, or pollution of the organism's habitat, but also by hunting for `sport´ or for commercial purposes.

According to a 1995 report to Congress by the US Fish and Wildlife Service, althoughseven of the 893 species listed as endangered under the US Endangered

SpeciesAct 1968-93 have become extinct,40% are no longer declining in number. In February 1996, aprivate conservation group, Nature Conservancy, reported around 20,000 native US plantand animal species to be rare or imperilled.

According to the Red Data List of endangered species, published in 1996 by the IUCN,25% of all mammal species (including 46% of primates, 36% of insectivores, and 33% of pigs and antelopes), and 11% of all bird species are threatened with extinction.

An example of an endangered species is the Javan rhinoceros.There are only about 50 alive today and, unless active steps are taken to promote this species' survival, it will probably be extinct within a few decades.

Action by governments has been prompted and supplemented by private agencies, such as the World Wide Fund for Nature (formerly theWorld Wildlife Fund). In attempts to save particular species or habitats, a distinction is often made between preservation – that is, maintaining the pristine state of nature exactly as it was or might have been – and conservation, the management of natural resources in such a way as to integrate the requirements of the local human population with those of the animals, plants, or the habitat being conserved.

ECOTOURISM

Effects of tourism -The threat to conservationTourism is now the world's largest industry, generating over $2 billion every year. It isalso, potentially, one of the most damaging to the environment. Tourist developments often cause pollution, deplete scarce water resources, destroy natural habitats, and disturb wildlife.For example, marine turtles are currently threatened in some of their last European strongholds by beach developments; many national parks are now so heavily visited that people are threatening the very wildlife that the park is supposed to protect; sales of wildlife products to tourists is threatening some species with extinction; and producing host water in trekkers' accommodation in the Nepal Himalayas is causing serious timber shortages in places.

The cost to wildlife-The dusky seaside sparrow Ammodramus maritimus nigrescens,which lived in the Spartina bakerii-dominated salt marsh habitat on the east coast of Florida, became functionally extinct in the 1980s due mainly to habitat loss caused by tourist developments.Conservationists fear that African game parks are already suffering from overuse, and an industry representative is quoted as complaining that, at one time, 23 vehicles were surrounding one cheetah.

A possible solution Now, a new form of ecotourism is being developed, which aims to avoid the worst excesses of uncontrolled tourist development, and to play a positive role in conservation.Ecotourism is usually smaller-scale,relatively higher priced, and tailored specifically forpeople who want their holiday to be more than simply a laze on the beach. Ecotourism trips are designed to minimize the impact on the environment and, conversely, to provide local communities with a positive economic incentive for protecting wild habitats. A study in Cameroon, for example, showed that a standing natural forest would generate far more in terms of tourist earnings than it would if it were cut down for timber. Studies on `land value´ and tourism in the Monteverde Cloud Forest in Costa Rica have indicated a value of $1,250 perhectare. Ecotourism is already amajor industry in countries such as Costa Rica and Kenya.

SOCIAL CONCERNS

Most ecotourism initiatives also try to address social concerns. A sudden influx of tourists into a previouslyremote community can be culturally devastating, and ecotourists are usually encouraged to minimize these impacts by learning and respecting local cultural and religious norms, and by approaching communities in as sensitive a way as possible. Some national tourism authorities now publish posters or leaflets advising visitors of what to do or not to do,such as one advising on religious and cultural practices in Thailand. Well-designed ecotourism should also not conflict with sustainable land use, such as the collection of non-timber forest products in tropical rainforests,or local fishing activities.Real help for conservation efforts. Some holidays go even further, when tourists pay to go and work on conservation projects around the world. The visitor gets a great holiday, with the added excitement of taking part in activities aimed at protecting the natural environment .Local people have the chance to meet tourists in ways that are educative.

Chapter 2

WATER POLLUTION is the contamination of water bodies (e.g. lakes, rivers, oceans, aquifers and groundwater). Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds.

Water pollution affects plants and organisms living in these bodies of water. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities.

Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells). It has been suggested that it is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily. An estimated of 580 people in India die of diarrheal sickness every day. Some 90% of China's cities suffer from some degree of water pollution, and nearly 500 million people lack access to safe drinking water. In addition to the acute problems of water pollution in developing countries, developed countries continue to struggle with pollution problems as well. In the most recent national report on water quality in the United States, 45 percent of assessed stream miles, 47 percent of assessed lake acres, and 32 percent of assessed bays and estuarine square miles were classified as polluted.

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water.

Surface water and groundwater have often been studied and managed as separate resources, although they are interrelated. Surface water seeps through the soil and becomes groundwater. Conversely, groundwater can also feed surface water sources. Sources of surface water pollution are generally grouped into two categories based on their origin.

Surface water and groundwater have often been studied and managed as separate resources, although they are interrelated. Surface water seeps through the soil and becomes groundwater. Conversely, groundwater can also feed surface water sources. Sources of surface water pollution are generally grouped into two categories based on their origin.

Point source water pollution refers to contaminants that enter a waterway from a single, identifiable source, such as a pipe or ditch. Examples of sources in this category include discharges from a sewage treatment plant, a factory, or a city storm drain. The U.S. Clean Water Act (CWA) defines point source for regulatory enforcement purposes. The CWA definition of point source was amended in 1987 to include municipal storm sewer systems, as well as industrial stormwater, such as from construction sites.

NONPOINT SOURCES

Nonpoint source pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often the cumulative effect of small amounts of contaminants gathered from a large area. A common example is the leaching out of nitrogen compounds from fertilized agricultural lands. Nutrient runoff in stormwater from "sheet flow" over an agricultural field or a forest are also cited as examples of NPS pollution.

Contaminated storm water washed off of parking lots, roads and highways, called urban runoff, is sometimes included under the category of NPS pollution. However, this runoff is typically channeled into storm drain systems and discharged through pipes to local surface waters, and is a point source.

GROUNDWATER POLLUTION

Interactions between groundwater and surface water are complex. Consequently, groundwater pollution, sometimes referred to as groundwater contamination, is not as easily classified as surface water pollution.[7] By its very nature, groundwater aquifers are susceptible to contamination from sources that may not directly affect surface water bodies, and the distinction of point vs. non-point source may be irrelevant. A spill or ongoing releases of chemical or radionuclide contaminants into soil (located away from a surface water body) may not create point source or non-point source pollution, but can contaminate the aquifer below, defined as a toxin plume. The movement of the plume, called a plume front, may be analyzed through a hydrological transport model or groundwater model. Analysis of groundwater contamination may focus on the soil characteristics and site geology, hydrogeology, hydrology, and the nature of the contaminants.

CAUSES

The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens, and physical or sensory changes such as elevated temperature and discoloration. While many of the chemicals and substances that are regulated may be naturally occurring (calcium, sodium, iron, manganese, etc.) the concentration is often the key in determining what is a natural component of water, and what is a contaminant. High concentrations of naturally occurring substances can have negative impacts on aquatic flora and fauna.

Oxygen-depleting substances may be natural materials, such as plant matter (e.g.

leaves and grass) as well as man-made chemicals. Other natural and anthropogenic substances may cause turbidity (cloudiness) which blocks light and disrupts plant growth, and clogs the gills of some fish species.

Many of the chemical substances are toxic. Pathogens can produce waterborne diseases in either human or animal hosts. Alteration of water's physical chemistry includes acidity (change in pH), electrical conductivity, temperature, and eutrophication. Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases in the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations.

PATHOGENS

Coliform bacteria are a commonly used bacterial indicator of water pollution, although not an actual cause of disease. Other microorganisms sometimes found in surface waters which have caused human health problems include:

- Burkholderia pseudomallei ,Cryptosporidium parvum ,Giardia lamblia ,Salmonella ,Novovirus and other viruses Parasitic worms (helminths).

High levels of pathogens may result from inadequately treated sewage discharges. This can be caused by a sewage plant designed with less than secondary treatment (more typical in less-developed countries). In developed countries, older cities with aging infrastructure may have leaky sewage collection systems (pipes, pumps, valves), which can cause sanitary sewer overflows. Some cities also have combined sewers, which may discharge untreated sewage during rain storms.

Muddy river polluted by sediment. Pathogen discharges may also be caused by poorly managed livestock operations.

CHEMICAL AND OTHER CONTAMINANTS

Contaminants may include organic and inorganic substances.

Organic water pollutants include:

- Detergents ,Disinfection by-products found in chemically disinfected drinking water, such as chloroform
- Food processing waste, which can include oxygen-demanding substances, fats and grease. Insecticides and herbicides, a huge range of organohalides and other chemical compounds
- Petroleum hydrocarbons, including fuels (gasoline, diesel fuel, jet fuels, and fuel oil) and lubricants (motor oil), and fuel combustion byproducts, from stormwater runoff.· Tree and bush debris from logging operations
- Volatile organic compounds (VOCs), such as industrial solvents, from improper storage. ·Chlorinated solvents, which are dense non-aqueous phase liquids (DNAPLs), may fall to the bottom of reservoirs, since they don't mix well with water and are denser. ·Example Polychlorinated biphenyl (PCBs) ,Trichloroethylene
- Perchlorate ·Various chemical compounds found in personal hygiene and cosmetic products.

INORGANIC WATER POLLUTANTS INCLUDE:

- Acidity caused by industrial discharges (especially sulfur dioxide from power plants) ·Ammonia from food processing waste
- Chemical waste as industrial by-products
- Fertilizers containing nutrients--nitrates and phosphates—which are found in stormwater runoff from agriculture, as well as commercial and residential use[16]
- Heavy metals from motor vehicles (via urban stormwater runoff) and acid mine drainage · Silt (sediment) in runoff from construction sites, logging, slash and burn practices or land clearing sites.
- Toxic metals- Hg.Cr,Pb,Cu,Zn,Fe,Al,Cd,Ni,Co, As, Sn Fluoride

MACROSCOPIC pollution—large visible items polluting the water—may be termed "floatables" in an urban stormwater context, or marine debris when found on the open seas, and can include such items as:

- Trash or garbage (e.g. paper, plastic, or food waste) discarded by people on the ground, along with accidental or intentional dumping of rubbish, that are washed by rainfall into storm drains and eventually discharged into surface waters
- Nurdles, small ubiquitous waterborne plastic pellets
- Shipwrecks, large derelict ships.

THERMAL POLLUTION

Thermal pollution is the rise or fall in the temperature of a natural body of water caused by human influence. Thermal pollution, unlike chemical pollution, results in a change in the physical properties of water. A common cause of thermal pollution is the use of water as a coolant by power plants and industrial manufacturers. Elevated water temperatures decreases oxygen levels, which can kill fish, and can alter food chain composition, reduce species biodiversity, and foster invasion by new thermophilic species. Urban runoff may also elevate temperature in surface waters.

Thermal pollution can also be caused by the release of very cold water from the base of reservoirs into warmer rivers.

Example The Vermont Yankee Nuclear Power Plant discharges heated water to the Connecticut River.

TRANSPORT AND CHEMICAL REACTIONS OF WATER POLLUTANTS

Most water pollutants are eventually carried by rivers into the oceans. In some areas of the world the influence can be traced hundred miles from the mouth by studies using hydrology transport models. Advanced computer models such as SWMM or the DSSAM Model have been used in many locations worldwide to examine the fate of pollutants in aquatic systems. Indicator filter feeding species such as copepods have also been used to study pollutant fates in the New York Bight, for example. The highest toxin loads are not directly at the mouth of the Hudson River, but 100 kilometers south, since several days are required for incorporation into planktonic tissue. The Hudson discharge flows south along the coast due to coriolis force. Further south then are areas of oxygen depletion, caused by chemicals using up oxygen and by algae blooms, caused by excess nutrients from algal cell death and decomposition. Fish and shellfish kills have been reported, because toxins climb the food chain after small fish consume copepods, then large fish eat smaller fish, etc. Each successive step up the food chain causes a stepwise concentration of pollutants such as heavy metals (e.g. mercury) and persistent organic pollutants such as DDT. This is known as biomagnification, which is occasionally used interchangeably with bioaccumulation.

Example A polluted river draining an abandoned copper mine on Anglesey

Large gyres (vortexes) in the oceans trap floating plastic debris. The North Pacific Gyre for example has collected the so-called "Great Pacific Garbage Patch" that is now estimated at 100 times the size of Texas. Many of these long-lasting pieces wind up in the stomachs of marine birds and animals. This results in obstruction of digestive pathways which leads to reduced appetite or even starvation. Many chemicals undergo reactive decay or chemically change especially over long periods of time in groundwater reservoirs. A noteworthy class of such chemicals is the chlorinated hydrocarbons such as trichloroethylene (used in industrial metal degreasing and electronics manufacturing) and tetrachloroethylene used in the dry cleaning industry (note latest advances in liquid carbon dioxide in dry cleaning that avoids all use of chemicals). Both of these chemicals, which are carcinogens themselves, undergo partial decomposition reactions, leading to new hazardous chemicals (including dichloroethylene and vinyl chloride). Groundwater pollution is much more difficult to abate than surface pollution because groundwater can move great distances through unseen aquifers. Non-porous aquifers such as clays partially purify water of bacteria by simple filtration (adsorption and absorption), dilution, and, in some cases, chemical reactions and biological activity: however, in some cases, the pollutants merely transform to soil contaminants. Groundwater that moves through cracks and caverns is not filtered and can be transported as easily as surface water. In fact, this can be aggravated by the human tendency to use natural sinkholes as dumps in areas of Karst topography. There are a variety of secondary effects stemming not from the original pollutant, but a derivative condition. An example is silt-bearing surface runoff, which can inhibit the penetration of sunlight through the water column, hampering photosynthesis in aquatic plants.

CONTROL OF POLLUTION

Domestic sewage

Domestic sewage is typically 99.9 percent water with 0.1 percent pollutants. Although found in low concentrations, these pollutants pose risk on a large scale. In urban areas, domestic sewage is typically treated by centralized sewage treatment plants. Well-designed and operated systems (i.e., secondary treatment or better) can remove 90 percent or more of these pollutants. Some plants have additional systems to remove nutrients and pathogens. Most municipal plants are not specifically designed to treat toxic pollutants found in industrial wastewater.

Cities with sanitary sewer overflows or combined sewer overflows employ one or more engineering approaches to reduce discharges of untreated sewage, including:

- utilizing a green infrastructure approach to improve stormwater management capacity throughout the system, and reduce the hydraulic overloading of the treatment plant·repair and replacement of leaking and malfunctioning equipment
- increasing overall hydraulic capacity of the sewage collection system (often a very

expensive option).

A household or business not served by a municipal treatment plant may have an individual septic tank, which treats the wastewater on site and discharges into the soil. Alternatively, domestic wastewater may be sent to a nearby privately owned treatment system (e.g. in a rural community).

Example:Deer Island Waste Water Treatment Plant serving Boston, Massachusetts and vicinity.

MARINE POLLUTION

Marine pollution occurs when harmful, or potentially harmful, effects result from the entry into the ocean of chemicals, particles, industrial, agricultural and residential waste, noise, or the spread of invasive organisms. Most sources of marine pollution are land based. The pollution often comes from nonpoint sources such as agricultural runoff and wind blown debris and dust. Nutrient pollution, a form of water pollution, refers to contamination by excessive inputs of nutrients. It is a primary cause of eutrophication of surface waters, in which excess nutrients, usually nitrogen or phosphorus, stimulate algal growth.

Many potentially toxic chemicals adhere to tiny particles which are then taken up by plankton and benthos animals, most of which are either deposit or filter feeders. In this way, the toxins are concentrated upward within ocean food chains. Many particles combine chemically in a manner highly depletive of oxygen, causing estuaries to become anoxic.

When pesticides are incorporated into the marine ecosystem, they quickly become absorbed into marine food webs. Once in the food webs, these pesticides can cause mutations, as well as diseases, which can be harmful to humans as well as the entire food web.

Toxic metals can also be introduced into marine food webs. These can cause a change to tissue matter, biochemistry, behaviour, reproduction, and suppress growth in marine life. Also, many animal feeds have a high fish meal or fish hydrolysate content. In this way, marine toxins can be transferred to land animals, and appear later in meat and dairy products.

Although marine pollution has a long history, significant international laws to counter it were only enacted in the twentieth century. Marine pollution was a concern during several United Nations Conferences on the Law of the Sea beginning in the 1950s. Most scientists believed that the oceans were so vast that they had unlimited ability to dilute, and thus render pollution, harmless.

In the late 1950s and early 1960s, there were several controversies about dumping radioactive waste off the coasts of the United States by companies licensed by the Atomic Energy Commission, into the Irish Sea from the British reprocessing facility at Windscale, and into the Mediterranean Sea by the French Commissariat à l'Energie Atomique. After the Mediterranean Sea controversy, for example, Jacques Cousteau became a worldwide figure in the campaign to stop marine pollution. Marine pollution made further international headlines after the 1967 crash of the oil tanker Torrey Canyon, and after the 1969 Santa Barbara oil spill off the coast of California.

Marine pollution was a major area of discussion during the 1972 United Nations Conference on the Human Environment, held in Stockholm. That year also saw the signing of the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, sometimes called the London Convention. The London Convention did not ban marine pollution, but it established black and gray lists for substances to be banned (black) or regulated by national authorities (gray). Cyanide and high-level radioactive waste, for example, were put on the black list. The London Convention applied only to waste dumped from ships, and thus did nothing to regulate waste discharged as liquids from pipelines.

There are many different ways to categorize, and examine the inputs of pollution into our marine ecosystems. Patin notes that generally there are three main types of inputs of pollution into the ocean: direct discharge of waste into the oceans, runoff into the waters due to rain, and pollutants that are released from the atmosphere.

One common path of entry by contaminants to the sea are rivers. The evaporation of water from oceans exceeds precipitation. The balance is restored by rain over the continents entering rivers and then being returned to the sea. The Hudson in New York State and the Raritan in New Jersey, which empty at the northern and southern ends of Staten Island, are a source of mercury contamination of zooplankton (copepods) in the open ocean. The highest concentration in the filter-feeding copepods is not at the mouths of these rivers but 70 miles south, nearer Atlantic City, because water flows close to the coast. It takes a few days before toxins are taken up by the plankton[.

Pollution is often classed as point source or nonpoint source pollution. Point source pollution occurs when there is a single, identifiable, and localized source of the pollution. An example is directly discharging sewage and industrial waste into the ocean. Pollution such as this occurs particularly in developing nations. Nonpoint source pollution occurs when the pollution comes from ill-defined and diffuse sources. These can be difficult to regulate. Agricultural runoff and wind blown debris are prime examples.

Pollutants enter rivers and the sea directly from urban sewerage and industrial waste discharges, sometimes in the form of hazardous and toxic wastes.

INLAND MINING for copper, gold. etc., is another source of marine pollution. Most of the pollution is simply soil, which ends up in rivers flowing to the sea. However, some minerals discharged in the course of the mining can cause problems, such as copper, a common industrial pollutant, which can interfere with the life history and development of coral polyps. Mining has a poor environmental track record. For example, according to the United States Environmental Protection Agency, mining has contaminated portions of the headwaters of over 40% of watersheds in the western continental US. Much of this pollution finishes up in the sea.

SURFACE RUNOFF from farming, as well as urban runoff and runoff from the construction of roads, buildings, ports, channels, and harbours, can carry soil and particles laden with carbon, nitrogen, phosphorus, and minerals. This nutrient-rich water can cause fleshy algae and phytoplankton to thrive in coastal areas; known as algal blooms, which have the potential to create hypoxic conditions by using all available oxygen.

Polluted runoff from roads and highways can be a significant source of water pollution in coastal areas. About 75 percent of the toxic chemicals that flow into Puget Sound are carried by stormwater that runs off paved roads and driveways, rooftops, yards and other developed land.

Ships can pollute waterways and oceans in many ways. Oil spills can have devastating effects. While being toxic to marine life, polycyclic aromatic hydrocarbons (PAHs), found in crude oil, are very difficult to clean up, and last for years in the sediment and marine environment.[5]

Discharge of cargo residues from bulk carriers can pollute ports, waterways and oceans. In many instances vessels intentionally discharge illegal wastes despite foreign and domestic regulation prohibiting such actions. It has been estimated that container ships lose over 10,000 containers at sea each year (usually during storms). Ships also create noise pollution that disturbs natural wildlife, and water from ballast tanks can spread harmful algae and other invasive species.

Ballast water taken up at sea and released in port is a major source of unwanted exotic marine life. The invasive freshwater zebra mussels, native to the Black, Caspian and Azov seas, were probably transported to the Great Lakes via ballast water from a transoceanic vessel. Meinesz believes that one of the worst cases of a single invasive species causing harm to an ecosystem can be attributed to a seemingly harmless jellyfish. Mnemiopsis leidyi, a species of comb jellyfish that spread so it now inhabits estuaries in many parts of the world. It was first introduced in 1982, and thought to have been transported to the Black Sea in a ship’s ballast water. The population of the jellyfish shot up exponentially and, by 1988, it was wreaking havoc upon the local fishing industry. “The anchovy catch fell from 204,000 tons in 1984 to 200 tons in 1993; sprat from 24,600 tons in 1984 to 12,000 tons in 1993; horse mackerel from 4,000 tons in 1984 to zero in 1993. Now that the jellyfish have exhausted the zooplankton, including fish larvae, their numbers have fallen dramatically, yet they continue to maintain a stranglehold on the ecosystem.

Invasive species can take over once occupied areas, facilitate the spread of new diseases, introduce new genetic material, alter underwater seascapes and jeopardize the ability of native species to obtain food. Invasive species are responsible for about $138 billion annually in lost revenue and management costs in the US alone.

ATMOSPHERIC POLLUTION

Another pathway of pollution occurs through the atmosphere. Wind blown dust and debris, including plastic bags, are blown seaward from landfills and other areas. Dust from the Sahara moving around the southern periphery of the subtropical ridge moves into the Caribbean and Florida during the warm season as the ridge builds and moves northward through the subtropical Atlantic. Dust can also be attributed to a global transport from the Gobi and Taklamakan deserts across Korea, Japan, and the Northern Pacific to the Hawaiian Islands. Since 1970, dust outbreaks have worsened due to periods of drought in Africa. There is a large variability in dust transport to the Caribbean and Florida from year to year; however, the flux is greater during positive phases of the North Atlantic Oscillation. The USGS links dust events to a decline in the health of coral reefs across the Caribbean and Florida, primarily since the 1970s.

Climate change is raising ocean temperatures and raising levels of carbon dioxide in the atmosphere. These rising levels of carbon dioxide are acidifying the oceans. This, in turn, is altering aquatic ecosystems and modifying fish distributions, with impacts on the sustainability of fisheries and the livelihoods of the communities that depend on them. Healthy ocean ecosystems are also important for the mitigation of climate change.[18]

Deep sea mining

Deep sea mining is a relatively new mineral retrieval process that takes place on the ocean floor. Ocean mining sites are usually around large areas of polymetallic nodules or active and extinct hydrothermal vents at about 1,400 - 3,700 meters below the ocean’s surface. The vents create sulfide deposits, which contain precious metals such as silver, gold, copper, manganese, cobalt, and zinc. The deposits are mined using either hydraulic pumps or bucket systems that take ore to the surface to be processed. As with all mining operations, deep sea mining raises questions about environmental damages to the surrounding areas

Because deep sea mining is a relatively new field, the complete consequences of full scale mining operations are unknown. However, experts are certain that removal of parts of the sea floor will result in disturbances to the benthic layer, increased toxicity of the water column and sediment plumes from tailings. Removing parts of the sea floor disturbs the habitat of benthic organisms, possibly, depending on the type of mining and location, causing permanent disturbances. Aside from direct impact of mining the area, leakage, spills and corrosion would alter the mining area’s chemical makeup.

Among the impacts of deep sea mining, sediment plumes could have the greatest impact. Plumes are caused when the tailings from mining (usually fine particles) are dumped back into the ocean, creating a cloud of particles floating in the water. Two types of plumes occur: near bottom plumes and surface plumes. Near bottom plumes occur when the tailings are pumped back down to the mining site. The floating particles increase the turbidity, or cloudiness, of the water, clogging filter-feeding apparatuses used by benthic organisms. Surface plumes cause a more serious problem. Depending on the size of the particles and water currents the plumes could spread over vast areas. The plumes could impact zooplankton and light penetration, in turn affecting the food web of the area.

The oceans are normally a natural carbon sink, absorbing carbon dioxide from the atmosphere. Because the levels of atmospheric carbon dioxide are increasing, the oceans are becoming more acidic. The potential consequences of ocean acidification are not fully understood, but there are concerns that structures made of calcium carbonate may become vulnerable to dissolution, affecting corals and the ability of shellfish to form shells.

Oceans and coastal ecosystems play an important role in the global carbon cycle and have removed about 25% of the carbon dioxide emitted by human activities between 2000 and 2007 and about half the anthropogenic CO_2 released since the start of the industrial revolution. Rising ocean temperatures and ocean acidification means that the capacity of the ocean carbon sink will gradually get weaker, giving rise to global concerns expressed in the Monaco and Manado Declarations.

A report from NOAA scientists published in the journal Science in May 2008 found that large amounts of relatively acidified water are upwelling to within four miles of the Pacific continental shelf area of North America. This area is a critical zone where most local marine life lives or is born. While the paper dealt only with areas from Vancouver to northern California, other continental shelf areas may be experiencing similar effects.

A related issue is the methane clathrate reservoirs found under sediments on the ocean floors. These trap large amounts of the greenhouse gas methane, which ocean warming has the potential to release. In 2004 the global inventory of ocean methane clathrates was estimated to occupy between one and five million cubic kilometres. If all these clathrates were to be spread uniformly across the ocean floor, this would translate to a thickness between three and fourteen metres. This estimate corresponds to 500-2500 gigatonnes carbon (Gt C), and can be compared with the 5000 Gt C estimated for all other fossil fuel reserves.

EFFECT OF EUTROPHICATION ON MARINE BENTHIC LIFE

Eutrophication is an increase in chemical nutrients, typically compounds containing nitrogen or phosphorus, in an ecosystem. It can result in an increase in the ecosystem's primary productivity (excessive plant growth and decay), and further effects including lack of oxygen and severe reductions in water quality, fish, and other animal populations.

The biggest culprit are rivers that empty into the ocean, and with it the many chemicals used as fertilizers in agriculture as well as waste from livestock and humans. An excess of oxygen depleting chemicals in the water can lead to hypoxia and the creation of a dead zone.

Estuaries tend to be naturally eutrophic because land-derived nutrients are concentrated where runoff enters the marine environment in a confined channel. The World Resources Institute has identified 375 hypoxic coastal zones around the world, concentrated in coastal areas in Western Europe, the Eastern and Southern coasts of the US, and East Asia, particularly in Japan. In the ocean, there are frequent red tide algae blooms that kill fish and marine mammals and cause respiratory problems in humans and some domestic animals when the blooms reach close to shore.

In addition to land runoff, atmospheric anthropogenic fixed nitrogen can enter the open ocean. A study in 2008 found that this could account for around one third of the ocean’s external (non-recycled) nitrogen supply and up to three per cent of the annual new marine biological production. It has been suggested that accumulating reactive nitrogen in the environment may have consequences as serious as putting carbon dioxide in the atmosphere.

One proposed solution to eutrophication in estuaries is to restore shellfish populations, such as oysters. Oyster reefs remove nitrogen from the water column and filter out suspended solids, subsequently reducing the likelihood or extent of harmful algal blooms or anoxic conditions.Filter feeding activity is considered beneficial to water quality by controlling phytoplanton density and sequestering nutrients, which can be removed from the system through shellfish harvest, buried in the sediments, or lost through denitrification. Foundational work toward the idea of improving marine water quality through shellfish cultivation to was conducted by Odd Lindahl et al., using mussels in Sweden.

PLASTIC DEBRIS

Marine debris is mainly discarded human rubbish which floats on, or is suspended in the ocean. Eighty percent of marine debris is plastic - a component that has been rapidly accumulating since the end of World War II. The mass of plastic in the oceans may be as high as one hundred million metric tons.

Discarded plastic bags, six pack rings and other forms of plastic waste which finish up in the ocean present dangers to wildlife and fisheries Aquatic life can be threatened through entanglement, suffocation, and ingestion. Fishing nets, usually made of plastic, can be left or lost in the ocean by fishermen. Known as ghost nets, these entangle fish, dolphins, sea turtles, sharks, dugongs, crocodiles, seabirds, crabs, and other creatures, restricting movement, causing starvation, laceration and infection, and, in those that need to return to the surface to breathe, suffocation.

Many animals that live on or in the sea consume flotsam by mistake, as it often looks similar to their natural prey. Plastic debris, when bulky or tangled, is difficult to pass, and may become permanently lodged in the digestive tracts of these animals, blocking the passage of food and causing death through starvation or infection. Plastics accumulate because they don't biodegrade in the way many other substances do. They will photodegrade on exposure to the sun, but they do so properly only under dry conditions, and water inhibits this process. n marine environments, photodegraded plastic disintegrates into ever smaller pieces while remaining polymers, even down to the molecular level. When floating plastic particles photodegrade down to zooplankton sizes, jellyfish attempt to consume them, and in this way the plastic enters the ocean food chain. Many of these long-lasting pieces end up in the stomachs of marine birds and animals, including sea turtles, and black-footed albatross.

Plastic debris tends to accumulate at the centre of ocean gyres. In particular, the Great Pacific Garbage Patch has a very high level of plastic particulate suspended in the upper water column. In samples taken in 1999, the mass of plastic exceeded that of zooplankton (the dominant animal life in the area) by a factor of six. Midway Atoll, in common with all the Hawaiian Islands, receives substantial amounts of debris from the garbage patch. Ninety percent plastic, this debris accumulates on the beaches of Midway where it becomes a hazard to the bird population of the island. Midway Atoll is home to two-thirds (1.5 million) of the global population of Laysan Albatross. Nearly all of these albatross have plastic in their digestive system and one-third of their chicks die.

Toxic additives used in the manufacture of plastic materials can leach out into their surroundings when exposed to water. Waterborne hydrophobic pollutants collect and magnify on the surface of plastic debris, thus making plastic far more deadly in the ocean than it would be on land.[45] Hydrophobic contaminants are also known to bioaccumulate in fatty tissues, biomagnifying up the food chain and putting pressure on apex predators. Some plastic additives are known to disrupt the endocrine system when consumed, others can suppress the immune system or decrease reproductive rates. Floating debris can also absorb persistent organic pollutants from seawater, including PCBs, DDT and PAHs.[Aside from toxic effects, when ingested some of these are mistaken by the animal brain for estradiol, causing hormone disruption in the affected wildlife.[

TOXINS

Mercury in fish

Apart from plastics, there are particular problems with other toxins that do not disintegrate rapidly in the marine environment. Examples of persistent toxins are PCBs, DDT, pesticides, furans, dioxins, phenols and radioactive waste. Heavy metals are metallic chemical elements that have a relatively high density and are toxic or poisonous at low concentrations. Examples are mercury, lead, nickel, arsenic and cadmium. Such toxins can accumulate in the tissues of many species of aquatic life in a process called bioaccumulation. They are also known to accumulate in benthic environments, such as estuaries and bay muds: a geological record of human activities of the last century.

Specific examples

- Chinese and Russian industrial pollution such as phenols and heavy metals in the Amur River have devastated fish stocks and damaged its estuary soil.
- Wabamun Lake in Alberta, Canada, once the best whitefish lake in the area, now has unacceptable levels of heavy metals in its sediment and fish.
- Acute and chronic pollution events have been shown to impact southern California kelp forests, though the intensity of the impact seems to depend on both the nature of the contaminants and duration of exposure.
- Due to their high position in the food chain and the subsequent accumulation of heavy metals from their diet, mercury levels can be high in larger species such as bluefin and albacore. As a result, in March 2004 the United States FDA issued guidelines recommending that pregnant women, nursing mothers and children limit their intake of tuna and other types of predatory fish.
- Some shellfish and crabs can survive polluted environments, accumulating heavy metals or toxins in their tissues. For example, mitten crabs have a remarkable ability to survive in highly modified aquatic habitats, including polluted waters. The farming and harvesting of such species needs careful management if they are to be used as a food.
- Surface runoff of pesticides can alter the gender of fish species genetically, transforming male into female fish.
- Heavy metals enter the environment through oil spills - such as the Prestige oil spill on the Galician coast - or from other natural or anthropogenic sources.
- In 2005, the 'Ndrangheta, an Italian mafia syndicate, was accused of sinking at least 30 ships loaded with toxic waste, much of it radioactive. This has led to widespread investigations into radioactive-waste disposal rackets.

Since the end of World War II, various nations, including the Soviet Union, the United Kingdom, the United States, and Germany, have disposed of chemical weapons in the Baltic Sea, raising concerns of environmental contamination.

UNDERWATER NOISE

Marine life can be susceptible to noise or sound pollution from sources such as passing ships, oil exploration seismic surveys, and naval low-frequency active sonar. Sound travels more rapidly and over larger distances in the sea than in the atmosphere. Marine animals, such as cetaceans, often have weak eyesight, and live in a world largely defined by acoustic information. This applies also to many deeper sea fish, who live in a world of darkness. Between 1950 and 1975, ambient noise in the ocean increased by about ten decibels (that is a tenfold increase).

Noise also makes species communicate louder, which is called the Lombard vocal response.[83] Whale songs are longer when submarine-detectors are on. If creatures don't "speak" loud enough, their voice can be masked by anthropogenic sounds. These unheard voices might be warnings, finding of prey, or preparations of net-bubbling. When one species begins speaking louder, it will mask other species voices, causing the whole ecosystem to eventually speak louder.

According to the oceanographer Sylvia Earle, "Undersea noise pollution is like the death of a thousand cuts. Each sound in itself may not be a matter of critical concern, but taken all together, the noise from shipping, seismic surveys, and military activity is creating a totally different environment than existed even 50 years ago. That high level of noise is bound to have a hard, sweeping impact on life in the sea.

MARINE POLLUTION occurs when harmful, or potentially harmful, effects result from the entry into the ocean of chemicals, particles, industrial, agricultural and residential waste, noise, or the spread of invasive organisms. Most sources of marine pollution are land based. The pollution often comes from nonpoint sources such as agricultural runoff and wind blown debris and dust. Nutrient pollution, a form of water pollution, refers to contamination by excessive inputs of nutrients. It is a primary cause of eutrophication of surface waters, in which excess nutrients, usually nitrogen or phosphorus, stimulate algal growth.

Many potentially toxic chemicals adhere to tiny particles which are then taken up by plankton and benthos animals, most of which are either deposit or filter feeders. In this way, the toxins are concentrated upward within ocean food chains. Many particles combine chemically in a manner highly depletive of oxygen, causing estuaries to become anoxic.

When pesticides are incorporated into the marine ecosystem, they quickly become absorbed into marine food webs. Once in the food webs, these pesticides can cause mutations, as well as diseases, which can be harmful to humans as well as the entire food web.

Toxic metals can also be introduced into marine food webs. These can cause a change to tissue matter, biochemistry, behaviour, reproduction, and suppress growth in marine life. Also, many animal feeds have a high fish meal or fish hydrolysate content. In this way, marine toxins can be transferred to land animals, and appear later in meat and dairy products.

Although marine pollution has a long history, significant international laws to counter it were only enacted in the twentieth century. Marine pollution was a concern during several United Nations Conferences on the Law of the Sea beginning in the 1950s. Most scientists believed that the oceans were so vast that they had unlimited ability to dilute, and thus render pollution, harmless.

In the late 1950s and early 1960s, there were several controversies about dumping radioactive waste off the coasts of the United States by companies licensed by the Atomic Energy Commission, into the Irish Sea from the British reprocessing facility at Windscale, and into the Mediterranean Sea by the French Commissariat à l'Energie Atomique. After the Mediterranean Sea controversy, for example, Jacques Cousteau became a worldwide figure in the campaign to stop marine pollution. Marine pollution made further international headlines after the 1967 crash of the oil tanker Torrey Canyon, and after the 1969 Santa Barbara oil spill off the coast of California.

Marine pollution was a major area of discussion during the 1972 United Nations Conference on the Human Environment, held in Stockholm. That year also saw the signing of the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, sometimes called the London Convention. The London Convention did not ban marine pollution, but it established black and gray lists for substances to be banned (black) or regulated by national authorities (gray). Cyanide and high-level radioactive waste, for example, were put on the black list. The London Convention applied only to waste dumped from ships, and thus did nothing to regulate waste discharged as liquids from pipelines.

Pathways of pollution

There are many different ways to categorize, and examine the inputs of pollution into our marine ecosystems. Patin (n.d.) notes that generally there are three main types of inputs of pollution into the ocean: direct discharge of waste into the oceans, runoff into the waters due to rain, and pollutants that are released from the atmosphere.

One common path of entry by contaminants to the sea are rivers. The evaporation of water from oceans exceeds precipitation. The balance is restored by rain over the continents entering rivers and then being returned to the sea. The Hudson in New York State and the Raritan in New Jersey, which empty at the northern and southern ends of Staten Island, are a source of mercury contamination of zooplankton (copepods) in the open ocean. The highest concentration in the filter-feeding copepods is not at the mouths of these rivers but 70 miles south, nearer Atlantic City, because water flows close to the coast. It takes a few days before toxins are taken up by the plankton.

Pollution is often classed as point source or nonpoint source pollution. Point source pollution occurs when there is a single, identifiable, and localized source of the pollution. An example is directly discharging sewage and industrial waste into the ocean. Pollution such as this occurs particularly in developing nations. Nonpoint source pollution occurs when the pollution comes from ill-defined and diffuse sources. These can be difficult to regulate. Agricultural runoff and wind blown debris are prime examples.

DIRECT DISCHARGE

Inland mining for copper, gold. etc., is another source of marine pollution. Most of the pollution is simply soil, which ends up in rivers flowing to the sea. However, discharges, sometimes in the form of hazardous and toxic wastes .Some minerals discharged in the course of the mining can cause problems, such as copper, a common industrial pollutant, which can interfere with the life history and development of coral polyps. Mining has a poor environmental track record. For example, according to the United States Environmental Protection Agency, mining has contaminated portions of the headwaters of over 40% of watersheds in the western continental US. Much of this pollution finishes up in the sea.

LAND RUNOFF

Surface runoff from farming, as well as urban runoff and runoff from the construction of roads, buildings, ports, channels, and harbours, can carry soil and particles laden with carbon, nitrogen, phosphorus, and minerals. This nutrient-rich water can cause fleshy algae and phytoplankton to thrive in coastal areas; known as algal blooms, which have the potential to create hypoxic conditions by using all available oxygen.

Polluted runoff from roads and highways can be a significant source of water pollution in coastal areas. About 75 percent of the toxic chemicals that flow into Puget Sound are carried by stormwater that runs off paved roads and driveways, rooftops, yards and other developed land.[4]

SHIP POLLUTION

Ships can pollute waterways and oceans in many ways. Oil spills can have devastating effects. While being toxic to marine life, polycyclic aromatic hydrocarbons (PAHs), found in crude oil, are very difficult to clean up, and last for years in the sediment and marine environment.[5] A cargo ship pumps ballast water over the side.

Discharge of cargo residues from bulk carriers can pollute ports, waterways and oceans. In many instances vessels intentionally discharge illegal wastes despite foreign and domestic regulation prohibiting such actions. It has been estimated that container ships lose over 10,000 containers at sea each year (usually during storms).[6] Ships also create noise pollution that disturbs natural wildlife, and water from ballast tanks can spread harmful algae and other invasive species.[7]

Ballast water taken up at sea and released in port is a major source of unwanted exotic marine life. The invasive freshwater zebra mussels, native to the Black, Caspian and Azov seas, were probably transported to the Great Lakes via ballast water from a transoceanic vessel.[8] Meinesz believes that one of the worst cases of a single invasive species causing harm to an ecosystem can be attributed to a seemingly harmless jellyfish. Mnemiopsis leidyi, a species of comb jellyfish that spread so it now inhabits estuaries in many parts of the world. It was first introduced in 1982, and thought to have been transported to the Black Sea in a ship’s ballast water. The population of the jellyfish shot up exponentially and, by 1988, it was wreaking havoc upon the local fishing industry. “The anchovy catch fell from 204,000 tons in 1984 to 200 tons in 1993; sprat from 24,600 tons in 1984 to 12,000 tons in 1993; horse mackerel from 4,000 tons in 1984 to zero in 1993.”[Now that the jellyfish have exhausted the zooplankton, including fish larvae, their numbers have fallen dramatically, yet they continue to maintain a stranglehold on the ecosystem.

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DEEP SEA MINING

Deep sea mining is a relatively new mineral retrieval process that takes place on the ocean floor. Ocean mining sites are usually around large areas of polymetallic nodules or active and extinct hydrothermal vents at about 1,400 - 3,700 meters below the ocean’s surface. The vents create sulfide deposits, which contain precious metals such as silver, gold, copper, manganese, cobalt, and zinc. The deposits are mined using either hydraulic pumps or bucket systems that take ore to the surface to be processed. As with all mining operations, deep sea mining raises questions about environmental damages to the surrounding areas

Because deep sea mining is a relatively new field, the complete consequences of full scale mining operations are unknown. However, experts are certain that removal of parts of the sea floor will result in disturbances to the benthic layer, increased toxicity of the water column and sediment plumes from tailings. Removing parts of the sea floor disturbs the habitat of benthic organisms, possibly, depending on the type of mining and location, causing permanent disturbances. Aside from direct impact of mining the area, leakage, spills and corrosion would alter the mining area’s chemical makeup.

Among the impacts of deep sea mining, sediment plumes could have the greatest impact. Plumes are caused when the tailings from mining (usually fine particles) are dumped back into the ocean, creating a cloud of particles floating in the water. Two types of plumes occur: near bottom plumes and surface plumes. Near bottom plumes occur when the tailings are pumped back down to the mining site. The floating particles increase the turbidity, or cloudiness, of the water, clogging filter-feeding apparatuses used by benthic organisms. Surface plumes cause a more serious problem. Depending on the size of the particles and water currents the plumes could spread over vast areas. The plumes could impact zooplankton and light penetration, in turn affecting the food web of the area.

Water treatment describes those industrial-scale processes used to make water more acceptable for a desired end-use. These can include use for drinking water, industry, medical and many other uses. Such processes may be contrasted with small-scale water sterilization practiced by campers and other people in wilderness areas. The goal of all water treatment process is to remove existing contaminants in the water, or reduce the concentration of such contaminants so the water becomes fit for its desired end-use. One such use is returning water that has been used back into the natural environment without adverse ecological impact.

The processes involved in treating water for drinking purpose may be solids separation using physical processes such as settling and filtration, and chemical processes such as disinfection and coagulation.

Biological processes are employed in the treatment of wastewater and these processes may include, for example, aerated lagoons, activated sludge or slow sand filters.

Water purification is the removal of contaminants from untreated water to produce drinking water that is pure enough for the most critical of its intended uses, usually for human consumption. Substances that are removed during the process of drinking water treatment include suspended solids, bacteria, algae, viruses, fungi, minerals such as iron, manganese and sulfur, and other chemical pollutants such as fertilisers.

Measures taken to ensure water quality not only relate to the treatment of the water, but to its conveyance and distribution after treatment as well. It is therefore common practice to have residual disinfectants in the treated water in order to kill any bacteriological contamination during distribution.

World Health Organisation (WHO) guidelines are generally followed throughout the world for drinking water quality requirements. In addition to the WHO guidelines, each country or territory or water supply body can have their own guidelines in order for consumers to have access to safe drinking water.

Combination selected from the following processes is used for municipal drinking water treatment worldwide:

- Pre-chlorination - for algae control and arresting any biological growth
- Aeration - along with pre-chlorination for removal of dissolved iron and manganese
- Coagulation - for flocculation
- Coagulant aids, also known as polyelectrolytes - to improve coagulation and for thicker floc formation
- Sedimentation - for solids separation, that is, removal of suspended solids trapped in the floc
- Filtration - removing particles from water
- Desalination - Process of removing salt from the water
- Disinfection - for killing bacteria.

There is no unique solution (selection of processes) for any type of water. Also, it is difficult to standardise the solution in the form of processes for water from different sources. Treatability studies for each source of water in different seasons need to be carried out to arrive at most appropriate processes.

Technologies for potable water treatment are well developed, and generalised designs are available that are used by many water utilities (public or private). In addition, a number of private companies provide patented technological solutions.Automation of water and waste-water treatment is common in the developed world. Capital costs, operating costs available quality monitoring technologies, locally available skills typically dictate the l Sewage treatment

Sewage treatment is the process that removes the majority of the contaminants from wastewater or sewage and produces both a liquid effluent suitable for disposal to the natural environment and a sludge. To be effective, sewage must be conveyed to a treatment plant by appropriate pipes and infrastructure and the process itself must be subject to regulation and controls. Some wastewaters require different and sometimes specialized treatment methods. At the simplest level, treatment of sewage and most wastewaters is carried out through separation of solids from liquids, usually by sedimentation. By progressively converting dissolved material into solids, usually a biological floc, which is then settled out, an effluent stream of increasing purity is produced.

In developing countries as of 2006, waterborne diseases are estimated to have caused 1.8 million deaths each year. These deaths are attributable to inadequate public sanitation systems and in these cases, proper sewerage (or other options as small-scale wastewater treatment) need to be installed.

Appropriate technology options in water treatment include both community-scale and household-scale point-of-use (POU) designs. Such designs may employ solar water disinfection methods, using solar irradiation to inactivate harmful waterborne microorganisms directly, mainly by the UV-A component of the solar spectrum, or indirectly through the presence of an oxide photocatalyst, typically supported TiO_2 in its anatase or rutile phases. Despite progress in SODIS technology, military surplus water treatment units like the ERDLator are still frequently used in developing countries. Newer military style Reverse Osmosis Water Purification Units (ROWPU) are portable, self-contained water treatment plants are becoming more available for public use.

In order for the decrease of waterborne diseases to have long term effects, water treatment programs implemented by research and development groups in developing countries must be sustainable by their citizens. This can ensure the efficiency of such programs after the departure of the research team as monitoring is difficult because of the remoteness of many locations.

Industrial water treatment

Two of the main processes of industrial water treatment are boiler water treatment and cooling water treatment. A lack of proper water treatment can lead to the reaction of solids and bacteria within pipe work and boiler housing. Steam boilers can suffer from scale or corrosion when left untreated leading to weak and dangerous machinery, scale deposits can mean additional fuel is required to heat the same level of water because of the drop in efficiency. Poor quality dirty water can become a breeding ground for bacteria such as Legionella causing a risk to public health.

With the proper treatment, a significant proportion of industrial on-site wastewater might be reusable. This can save money in three ways: lower charges for lower water consumption, lower charges for the smaller volume of effluent water discharged and lower energy costs due to the recovery of heat in recycled wastewater.

Corrosion in low pressure boilers can be caused by dissolved oxygen, acidity and excessive alkalinity. Water treatment therefore should remove the dissolved oxygen and maintain the boiler water with the appropriate pH and alkalinity levels. Without effective water treatment, a cooling water system can suffer from scale formation, corrosion and fouling and may become a breeding ground for harmful bacteria such as those that cause Legionnaires' Disease. This reduces efficiency, shortens plant life and makes operations unreliable and unsafe.

Disinfectants Ozone is a gas that can be found in the stratosphere due to the fact that ultraviolet (UV) radiation is emitted by the sun on oxygen molecules. Accordingly, it provides protection against harmful UV radiation. Ozone is made up of three atoms of oxygen as its chemical formula O_3 indicates. Ozone, as a very strong oxidant, is one of the main disinfectants when purifying water. As ozone breaks down in the water, a complex chain reaction mechanism occurs under the effect of the various solutes in the water or released during purification treatment. Ozone is known to be the most powerful chemical disinfectant used in water purification treatment. Ultraviolet(UV) radiation is produced using ultraviolet lamps with quartz covers. UV produces a minimum of by-products when treating the water.

An advanced oxidation process (AOP) is a system to purify water by chemical oxidation to deactivate residual organic pollutants. AOPs are capable of generating a more powerful and less selective secondary oxidant in the reaction medium by activating an available primary oxidant. AOP has been only gradually used in the water treatment industry. One of the many AOP systems, the combined O_3/H_2O_2, is the most widely used one especially for the purpose of destroying pesticides in order to produce water for human consumption.

Any chemical used in farming,gardening, or indoors to combat pests. Pesticides are of three main types: insecticides (to kill insects), fungicides (to kill fungal diseases), and herbicides (to kill plants, mainly those considered weeds). Pesticides cause a number of pollution problems through spray drift onto surrounding areas, direct contamination of users or the public, and as residues on food.

In the United States, pesticides were found to pollute every stream and over 90% of wells sampled in a study by the US Geological Survey. Pesticide residues have also been found in rain and groundwater. Studies by the UK government showed that pesticide concentrations exceeded those allowable for drinking water in some samples of river water and groundwater.

There are four major routes through which pesticides reach the water: it may drift outside of the intended area when it is sprayed, it may percolate, or leach, through the soil, it may be carried to the water as runoff, or it may be spilled, for example accidentally or through neglect. They may also be carried to water by eroding soil.

Factors that affect a pesticide's ability to contaminate water include its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop, and the method used to apply the chemical. Many of the chemicals used in pesticides are persistent soil contaminants, whose impact may endure for decades and adversely affect soil conservation.The herbicide PARAQUAT, when sprayed onto bird eggs, causes growth abnormalities in embryos and reduces the number of chicks that hatch successfully, but most herbicides do not directly cause much harm to birds. Herbicides may endanger bird populations by reducing their habitat.The USDA and USFWS estimate that over 67 million birds are killed by pesticides each year in the US. Fish and other aquatic biota may be harmed by pesticide-contaminated water. Pesticide surface runoff into rivers and streams can be highly lethal to aquatic life, sometimes killing all the fish in a particular stream. For example, in Montague on Prince Edward Island in Canada, nine "fish kills" happened in one year: every fish, snake, and snail was killed in a river called Sutherland's Hole near potato farms from which herbicides, insecticides, and fungicides ran off after heavy rains.

Application of herbicides to bodies of water can cause fish kills when the dead plants rot and use up the water's oxygen, suffocating the fish. Some herbicides, such as copper sulfite, that are applied to water to kill plants are toxic to fish and other water animals at concentrations similar to those used to kill the plants. Repeated exposure to sublethal doses of some pesticides can cause physiological and behavioral changes in fish that reduce populations, such as abandonment of nests and broods, decreased immunity to disease, and increased failure to avoid predators.Application of herbicides to bodies of water can kill off plants on which fish depend for their habitat.Pesticides can accumulate in bodies of water to levels that kill off zooplankton, the main source of food for young fish. Pesticides can kill off the insects on which some fish feed, causing the fish to travel farther in search of food and exposing them to greater risk from predators.

The faster a given pesticide breaks down in the environment, the less threat it poses to aquatic life. Insecticides are more toxic to aquatic life than herbicides and fungicides. Direct contact of sprays of some pesticides (either by drift from nearby applications or accidental or deliberate sprays) can be highly lethal to amphibians. A Canadian study showed that exposing tadpoles to ENDOSULFAN, an organochloride pesticide at levels that are likely to be found in habitats near fields sprayed with the chemical kills the

tadpoles and causes behavioral and growth abnormalities.

PYRETHRUM and DERRIS

The safest pesticides include those made from plants, such as the insecticides. Pyrethrins are safe and insects do not develop resistance to them. Their impact on the environment is very small as the ingredients break down, harmlessly.More potent are synthetic products,such as chlorinated hydrocarbons.These products, including DDT and DIELDRIN, are highly toxic to wildlife and often to human beings, so their use is now restricted by law in some areas and is declining. Safer pesticides such as malathion are based on organic phosphorus compounds, but they still present hazards to health. The aid organization Oxfam estimates that pesticides cause about 10,000 deaths worldwide every year. Pesticides were used to deforest SE Asia during the Vietnam War, causing death and destruction to the area's ecology and lasting health and agricultural problems. Many pesticides remain in the soil,since they are not biodegradable, and are then passed on to foods.In the UK, more than half of all potatoes sampled 1995 contained residues of a storage pesticide; seven different pesticides were found in carrots, with concentrations up to 25 times the permitted level; and 40% of bread contained pesticide residues.There are around 4,000 cases of acute pesticide poisoning a year in the UK.The situation arises frequently because some pesticides banned in the developed world may be bought by agricultural operations or companies in the Third World, perhaps unaware of any health implications. The policy was adopted by the FAO in 1989,and has since been made binding by the EC on its member states.

Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including nontarget species, air, water, bottom sediments, and food.

Pesticide contaminates land and water when it escapes from production sites and storage tanks, when it runs off from fields, when it is discarded, when it is sprayed aerially, and when it is sprayed into water to kill algae. The amount of pesticide that migrates from the intended application area is influenced by the particular chemical's properties: its propensity for binding to soil, its vapor pressure, its water solubility, and its resistance to being broken down over time. Factors in the soil, such as its texture, its ability to retain water, and the amount of organic matter contained in it, also affect the amount of pesticide that will leave the area.

Pesticides can contribute to air pollution . Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. Pesticides that are applied to crops can volatilize and may be blown by winds into nearby areas, potentially posing a threat to wildlife. Also, droplets of sprayed pesticides or particles from pesticides applied as dusts may travel on the wind to other areas, or pesticides may adhere to particles that blow in the wind, such as dust

particles. Ground spraying produces less pesticide drift than aerial spraying does. Farmers can employ a buffer zone around their crop, consisting of empty land or non-crop plants such as evergreen trees to serve as windbreaks and absorb the pesticides,preventing drift into other areas.

METHYL BROMIDE ,ALDICARB ,CHLORPYRIFOS

Pesticides contribute to global warming and the depletion of the ozone layer.Pesticides that are sprayed onto fields and used to fumigate soil can give off chemicals called volatile organic compounds, which can react with other chemicals and form a pollutant called ozone, accounting for an estimated 6% of the total ozone production.

The use of pesticides decreases the general biodiversity in the soil. Not using the chemicals results in higher soil quality, with the additional effect that more organic matter in the soil allows for higher water retention. This helps increase yields for farms in drought years, when organic farms have had yields 20-40% higher than their conventional counterparts. A smaller content of organic matter in the soil increases the amount of pesticide that will leave the area of application, because organic matter binds to and helps break down pesticides Pesticides inflict extremely widespread damage to biota, and many countries have acted to discourage pesticide usage through their Biodiversity Action Plans.Animals may be poisoned by pesticide residues that remain on food after spraying, for example when wild animals enter sprayed fields or nearby areas shortly after spraying.

Widespread application of pesticides can eliminate food sources that certain types of animals need, causing the animals to relocate, change their diet, or starve. Poisoning from pesticides can travel up the food chain; for example, birds can be harmed when they eat insects and worms that have consumed pesticides. Some pesticides can bioaccumulate, or build up to toxic levels in the bodies of organisms that consume them over time, a phenomenon that impacts species high on the food chain especially hard. The USDA and USFWS estimate that about 20% of the endangered and threatened species in the US are jeopardized by use of pesticides. There is evidence that birds are continuing to be harmed by pesticide use. In the farmland of Britain, populations of ten different species of birds have declined by 10 million breeding individuals between 1979 and 1999,

a phenomenon thought to have resulted from loss of plant and invertebrate species on which the birds feed. Throughout Europe, 116 species of birds are now threatened. Reductions in bird populations have been found to be associated with times and areas in which pesticides are used. In another example, some types of fungicides used in peanut farming are only slightly toxic to birds and mammals, but may kill off earthworms, which can in turn reduce populations of the birds and mammals that feed on them.Some pesticides come in granular form, and birds and other wildlife may eat the granules, mistaking them for grains of food. A few granules of a pesticide is enough to kill a small bird.Nitrogen fixation, which is required for the growth of higher plants, is hindered by pesticides in soil. The insecticides DDT, METHYL PARATHION, AND ESPECIALLY PENTACHLOROPHENOL have been shown to interfere with legume-rhizobium chemical signaling. Reduction of this symbiotic chemical signaling results in reduced nitrogen fixation and thus reduced crop yields. Root nodule formation in these plants saves the world economy $10 billion in synthetic nitrogen fertilizer every year.

Pesticides can kill bees and are strongly implicated in pollinator decline, the loss of species that pollinate plants, including through the mechanism of Colony Collapse Disorder, in which worker bees from a beehive or Western honey bee colony abruptly disappear. Application of pesticides to crops that are in bloom can kill honeybees, which act as pollinators. The USDA and USFWS estimate that US farmers lose at least $200 million a year from reduced crop pollination because pesticides applied to fields eliminate about a fifth of honeybee colonies in the US and harm an additional 15%.Persistent organic pollutants POPs

Compounds that resist degradation and thus remain in the environment for years. Some pesticides, including ALDRIN, CHLORDANE, DDT, DIELDRIN, ENDRIN,HEPTACHLOR, HEXACHLOROBENZENE, MIREX, and

TOXAPHENE, are POPs,have the ability to volatilize and travel great distances through the atmosphere to become deposited in remote regions. The chemicals also have the ability to bioaccumulate and biomagnify, and can bioconcentrate (i.e. become more concentrated) up to 70,000 times their original concentrations. POPs may continue to poison non-target organisms in the environment and increase risk to humans by disruption in the endocrine, reproductive,and immune systems; cancer; neurobehavioral disorders, infertility and mutagenic effects, although very little is currently known about these chronic effects.

Some POPs have been banned, while others continue to be used

DDT [dichloro-diphenyl-richloroethane(ClC6H5)2CHC(HCl2)]insecticide discovered in1939 by Swiss chemist Paul Müller. It is useful in the control of insects that spread malaria, but resistant strains develop.Its use is now banned in most countries, but it continues to be used on food plants in Latin America.

US scientists have found that some pesticides used in farming disrupt the nervous systems of frogs, and that use of these pesticides is correlated with a decline in the population of frogs in the Sierra Nevada. In the past several decades, decline in amphibian populations has been occurring all over the world, for unexplained reasons which are thought to be varied but of which pesticides may be a part. Being downwind from agricultural land on which pesticides are used has been linked to the decline in population of threatened frog species in California. Mixtures of multiple pesticides appear to have a cumulative toxic effect on frogs. Tadpoles from ponds with multiple pesticides present in the water take longer to metamorphose into frogs and are smaller when they do, decreasing their ability to catch prey and avoid predators. In Minnesota,pesticide use has been causally linked to congenital deformities in frogs such as eye,mouth, and limb malformations. Researchers in California found that similar deformities in frogs in the US and Canada may have been caused by breakdown products from pesticides which themselves did not pose a threat. The herbicide ATRAZINE has been shown to turn male frogs into hermaphrodites, decreasing their ability to reproduce.

The RAINBOW HERBICIDES are a group of chemicals used by the United States military in Southeast Asia during the Vietnam War. Success with Project AGILE field tests with herbicides in South Vietnam in 1961 led to the formal herbicidal program Trail Dust (1961 - 1971). Herbicidal warfare is a form of chemical warfare, in which the objective is to destroy the plant-based ecosystem of an area for the purpose of disrupting agricultural food production and/or destroying plants which provide cover to an enemy.

AGENT ORANGE is the code name for a powerful herbicide and defoliant used by the U.S. military in its Herbicidal Warfare program during the Vietnam War. During the Vietnam War, an estimated 80 000 m^3 of Agent Orange were deployed in South Vietnam.

Agent Orange's usage from 1961 to 1971 was by far the most used of the so-called "Rainbow Herbicides" used during the program. Degradation of Agent Orange (as well as Agents Purple, Pink, and Green) released dioxins, which have caused health problems for those exposed during the Vietnam War. Agents Blue and White were part of the same program but did not contain dioxins.Studies of populations exposed to dioxin, though not necessarily agent orange, indicate increased risk of various types of cancer and genetic

defects; the effect of long-term low-level exposure has not been established.Since the nineteen-eighties, several lawsuits have been filed against the companies which produced agent orange,among them; Dow Chemical, Monsanto, and Diamond Shamrock (which produced 5%. U.S. veterans obtained a $180 million settlement in 1984, with most affected veterans receiving a one-time lump sum payment of $1,200.American veterans of the Vietnam war were seeking recognition of agent orange syndrome, compensation and treatment for diseases that they and their children suffered from; many exposed to agent orange have not been able to receive promised medical care through the Veterans Administration medical system, and only with rare exception have their affected children received healthcare assistance from the government. They alleged that most of those still alive would succumb to the effects of toxic exposure before the age of 65.In Australia, Canada and New Zealand, veterans obtained compensation in settlements that same year.

In 1999, South Korean veterans filed a lawsuit in the Korean courts. In January 2006, the Korean Appeal Court ordered Monsanto and Dow to pay US$62 million in compensation. However, no Vietnamese have received compensation, and on March 10, 2006, Judge Jack B. Weinstein of the United States District Court for the Eastern District of New York dismissed the lawsuit filed by the Vietnamese victims of agent orangeagainst the chemical companies which produced the defoliants and herbicides.

AGENT PURPLE is the code name for a powerful herbicide and defoliant used by the U.S. military in its Herbicidal Warfare program during the Vietnam War. The name comes from the purple stripe painted on the barrels to identify the contents. It was one of the so-called "rainbow herbicides" that included the more infamous Agent Orange.Agent Purple is chemically similar to Agent Orange, consisting of a mixture of the herbicides 2,4-D and 2,4,5-T. It was later discovered that Agents Orange and Purple had been contaminated with varying levels of tetrachlorodibenzodioxin (TCDD), a dioxin that is a toxic and persistent substance, as a side-effect of the manufacturing process of 2,4,5-T. Agent Purple is reputed to have three times the dioxin levels of Agent Orange, 45 parts per million as opposed to 13 parts per million in Agent Orange.

ORGANOPHOSPHORUS PESTICIDES BY WHITE ROT FUNGI

Organophosphorus and carbamate pesticides are widely used in agricultural and residential applications. OPPs are esters of phosphoric acid in some cases containing thioether groups. There are also amides, fluor and cyanophosphoric compounds This family of chemicals replaced the organochlorine pesticides banned for use in the United States since the 1970's. Unlike organochlorine pesticides, which are persistent inthe environment and cause biological damage as they accumulate in an organism over time, OPPs and carbamate pesticides are short-lived in the environment and fast-acting on their "target pest". OPPs primarily affect the nervous system by inhibiting acetylcholinesterase whose main function is the break down of theneurotransmitter acetylcholine. When acetylcholinesterase is inhibited, acetylcholine accumulates leading to an increase of the nerve impulse transmission then to nerveexhaustion and, ultimately, to general failure of the nervous system. The respiratory muscles are the most critical group affected and respiratory paralysis is often the immediate cause of death Some OPPs are degraded by bacteria, such as Pseudomonas, Flavobacterium, Altermonas, and Bacillus, harboring the organophosphorus hydrolase ororganophosphorus acid anhydrolase activities involved in the cleavage of P-O bonds.

However, these enzymes showed a limited capacity to cleave the thioether bond present in several OPPs On the other hand, the ligninolytic fungus Phanerochaetechrysosporium has been shown to be able to mineralize chlorpyrifos, fonofos, and terbufos, and the contribution of extracellular ligninolytic enzymes has been suggested . In a previous work we demonstrated that chloroperoxidase from the fungus Caldariomyces fumago was able to oxidize 7 of 10 OPPs assayed, although no oxidationwas detected when other heme proteins such as lignin peroxidase, horseradish peroxidase or cytochrome c were used The enzymatic product for the transformation of organophosphorus pesticides (OPPs) by microsomal fraction of Pleurotus ostreatus 7989 was studied. The microsomal fraction was found able to degrade three OPPs with the following rates: 10 µmol mg prot $^{-1}$ h $^{-1}$ for phosmet, 5.7 µmol mg prot $^{-1}$ h $^{-1}$ for terbufos, and 2.2 µmol mg prot $^{-1}$ h $^{-1}$ for azinphos-methyl. The products from these reactions and from the transformation of trichlorfon and malathion, were identified by mass-spectrometry. These results, supported by specific inhibit ion experiments and the stringent requirement for NADPH during the in vitro assays suggest the involvement of a cytochrome P450

BIOREMEDIATION OF A PESTICIDE FORMULATION PLANT

Stauffer Management Company (SMC), a subsidiary of the AstraZeneca Group PLC, has been evaluating and developing remedial technologies for the treatment of pesticide contaminated soil for a number of years to remediate its own properties.

Pesticide formulation plants receive active agents which are then formulated with variousadditives, such as carriers, stickers, surfactants and dye stuffs, to produce a product for a number of various markets. Over the life of a typical plant, it could deal with 30 to 50 actives, as well as several hundred additives. This product and by-product heterogeneity offers many challenges to the remedial process.

In the past the company has used low temperature thermal desorption and/or capping technologies to remediate sites. Both of these technologies/approaches do not destroy the contaminants, but either partition them into a smaller matrix or reduce the overall risk by separating the soil from potential receptors. Bioremediation, the utilization of the indigenous microflora associated with the historically contaminated soil, has beenfound to be a cost-effective, destructive technology to treat pesticide contaminated soils.

An enhanced composting technology was developed, utilizing anaerobic and aerobic phases to treat chlorinated and non-chlorinated pesticides. This technology, now called Xenorem TM , was developed in a step-wise manner, from laboratory studies (e.g.radio-labelled biodegradation studies, fate studies, microbial screening etc.), through to lab and pilot studies (14, 60 and 100 yd 3), a commercial scale-up study (1,000 yd 3), and full-scale operations (4,000 and 8,000 yd 3). Full-scale operations are now underway,treating 30,000 yd 3 of pesticide contaminated soil in 4,000 to 5,000 yd 3 batches at a

former pesticide formulation plant.The soil is contaminated with chlorinated (e.g. DDT, DDD, DDE, toxaphene, chlordane)and non-chlorinated (e.g. molinate) pesticides. The bioremediation process, an enhanced composting technology using anaerobic and aerobic cycling, utilizes the indigenous microflora of the contaminated soil. Controlling the redox and temperature conditions by using organic amendments was found to be very important in the process. Organic amendments such as dairy cattle manure, chicken litter, straw and wood-chips were evaluated in the field. Once advantage of using organic amendments is that they can be used to consume oxygen within the windrow, to create the anaerobic phases of thetreatment. Mechanical mixing was then employed to create a set of aerobic phases. The first batch was completed in 2001, with greater than 90% degradation being achieved for the chlorinated and non-chlorinated pesticides. A second batch was completed in March 2002 with very similar results, even though the level of contaminants was higher.

The anaerobic and aerobic phases of the process are controlled by the addition of organic amendments (up to 40% of the final amended soil volume) and the use of mechanical mixing equipment. The amendments (manures and woodchips) were added to the top of the excavated soil windrow, and incorporated into the soil using a self-propelled SCAT 4932 windrow unit. This machine mixes in such a fashion that the soil

is also aerated at the same time. The presence of high levels of available nutrients,increases the overall metabolic activity of the amended soil, leading to an increase intemperature and a reduction in the oxygen level within the soil, giving rise to an anaerobic phase The prescribed length of this phase, as well as the follow-up aerobic phase, is determined by the earlier microcosm studies. For each batch, a study iscarried out to ensure that to create the process decision-tree used in treating that particular batch of contaminated soil.

The SCAT unit is also used to mix the amended windrow at prescribed times to create the aerobic phase, as well as to apply moisture to the soil, if needed. This action increases the amount of oxygen entrapped in the soil, stimulating the indigenous microflora, creating another increase in soil temperature, leading to a secondary anaerobic phase. With time, the organic amendments are consumed in the process,reducing the ability of the windrow to enter additional anaerobic phases; therefore, you see an increase in the duration of the aerobic phase. Typically, by the end of 14 weeks the organic amendment is spent. If the target levels for the individual pesticides have not

been reached, the windrow would be reamended with additional organics.This bioremediation process was first piloted at 1000 yd 3 , using soil from theSMC Tampa site. The chemicals of concern (CoC) are those listed in the Record of Decision (ROD) for the Tampa site (Table 1). The overall objective was to remediate the site contaminated soil to the acceptable clean-up standards.

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With a successful 1,000 yd 3 commercial trial, it was decided to use the technology to remediate the SMC Tampa site. The amount of soil that can be treated in each batch is limited by the capacity of the enclosure being used. Before each batch begins, the data from the previous batch is reviewed, site logistics are considered, and any improvementswhich can be made to the operation are implemented.

Chlordane	2.3	3.8	<MDL	<MDL	ROD
DDD	12.6	26	9.3	65	ROD
DDE	8.91	6.6	2.1	68	ROD
DDT	8.91	82	9.8	88	ROD
Dieldrin	0.19	2.4	<MDL	<MDL	ROD
Molinate	0.74	0.2	<MDL	<MDL	ROD
Toxaphene	2.75	129	7.8	94	>94%

The degradation curve for DDT is very similar for the pilot-scale and the two batches. Inall cases, there is a quick degradation of the parent compound; even thought in the case of Batch 2, the T0 value is more than double the T0 value for Batch 1, no inhibition was seen.

In all cases, toxaphene was the main CoC, typically in levels 2-3 times higher than that of DDT. toxaphene was also found to be highly degradable.After 12 weeks, all of the CoC have been degraded significantly, in some cases to ROD levels. At 20 weeks, the windrow will be reamended (10-20% by volume) in order to achieve the required end-points. One major difference between the soils used in the pilot study and the full-scale operations, was the level of sulphur; in the full-scale operations, high sulphur levels were noted (ca. 3%), which was converted during thebiological process to hydrogen sulphide.

During mixing operations, the hydrogen sulphide would be released in bursts and challenged the efficiency of the original odor abatement system. It was at this time an R & D program evaluated various recipes for a biofilter. One unit (120 yd 3) was piloted and proved so successful, that a full-scale system was built (1,200 yd 3) to treat the exhausted air from Batch 2. first two full-scale batches (4,000-4,500 yd 3 each) at the SMC Tampa site, a former pesticide formulation plant.

BIOREMEDIATION OF PHENOLS ON SOILS –

INSECTICIDE REMEDIATION RAPID REMOVAL OF TOXAPHENE USING ANAEROBIC BIOREMEDIATION TECHNOLOGY

Toxaphene is a broad spectrum insecticide which is primarily used to control pests on crops and ectoparasites on livestock (Korte, Scheunert, and Parlor, 1979). The pesticide has been shown to be highly toxic to fish and mammals as well as having mutagenic and carcinogenic properties. Moreover, it is highly stable and can persist in the environment for years. Due to its persistence and toxicity, toxaphene was taken off the market in 1982. Fifty-eight sites, contaminated with toxaphene, were identified and included on the National Priority List by the United States Environmental Protection

Agency (U.S. EPA). Investigations have shown that toxaphene is biodegradable by anaerobic processes (Mirsatari et al., 1987; Parr and Smith, 1976; Smith and Willis,1978). The U.S. EPA Environmental Response Team Center (U.S. EPA ERTC) and Response Engineering and Analytical Contract (REAC) personnel have successfully developed an anaerobic process for removal of toxaphene from soil (Camacho et al.,1997; Allen et al., 1999). Results of three site cleanup operations are summarized below.The objective of these studies was to remove toxaphene from contaminated soil using anaerobic bioremediation technology. Composite soil samples, collected from each site, were screened for toxaphene-degradative activity in bench-scale studies using standard recipes. Once activity was identified, plans for site cleanup were initiated.

Site Description. Studies were conducted at three sites: (1) Laahty Family Dip Vat (LDV), (2) Henry O Dip Vat (HDV), and (3) Gila River Indian Community (GRIC) sites.

The two dip vat sites were cleaned up under a joint collaborative effort between thePueblo Office of Environmental Protection (POEP), the U.S. EPA (Region VI), and the U.S. EPA/ERTC. Both sites were former locations of livestock dip vat facilities withinthe Pueblo of Zuni near Gallup, New Mexico. Each site consisted of a holding corral, a concrete dipping trench having a capacity of 2,500-5,000 gallons (9,464-18,927 liters) of pesticidal formulation, a drip pad, and a pesticide disposal area. On an annual basis,livestock were herded into the holding corral, driven through the dipping trench, and held in the drip pad area to dry. After the livestock had been treated, the formulation was drained from the trench to an area used for disposal. Over time, the pesticide disposal area became extensively contaminated with toxaphene and other pesticides. Dip vat sites were prioritized for cleanup based on their proximity to human habitation and to streams and wetlands. Toxaphene levels in soil samples were as high as 800 mg/kg. Contaminated soil at both sites was dug up and stockpiled.

During construction of a trench on Gila River Indian Community (GRIC) property near Chandler, Arizona, workers detected a strong chlorine odor and evacuated thearea. Evaluation of old aerial photographs indicated that the area was the former location of an airstrip used by crop dusters. It was believed that soil became contaminated due to crop dusters and pesticide transport trucks emptying and rinsing their storage tanks on or near the runway. High levels of toxaphene were found in site soil samples with contamination levels ranging from 15,000 to 24,000 mg/kg. Contaminated soil was dug up and transported to a designated area for temporary storage pending treatment.

Soil samples were extracted for 16 hours in a Soxhlet apparatus using 1:1 (v:v)hexane:acetone as extracting solvent. Toxaphene was analyzed in solvent extracts using a modified gas chromatography/electron capture (GC/ECD) method developed by ERTC/REAC laboratories (ERTC/REAC, 1994).

Bench-Scale Studies. Composited soil samples were initially screened through a #10 stainless steel sieve to remove large particulates, extensively mixed, and then analyzed for toxaphene content. Soil was screened for toxaphene-degradative activity in bench-scale anaerobic reactors using standard recipes. Reactors consisted of 125 mL serum bottles with 100 mL working volumes. Reactors were charged with 25 grams of soil (dryweight) and with varying amounts of dried blood meal. The soil and blood meal were suspended in sodium phosphate buffer to 100 mL. The starting pH ranged from 6.5-7.3.Reactors were incubated at room temperature for up to 56 days with samples collected at Days 0, 28, or 56. At each sampling time, duplicate or triplicate reactors were harvested,analyzed for toxaphene content, and values averaged.

Field-Scale Studies (LDV site). Soil at the LDV site was dug up and stockpiled with a total soil volume of 253 yd 3 (193 m 3). The soil pile was turned over with a backhoe to mix the soil. The anaerobic cell was then constructed with dimensions of 73 ft (22.3 m) by 30 ft (9.1 m) by 4 ft (1.2 m) and then lined with a plastic liner. The soil was added to Field-scale studies were conducted to remove toxaphene from soil at two abandoned livestock dip vat sites and at an abandoned air strip using anaerobic bioreme-diation technology. The dip vat cleanup studies were a joint collaboration between the Pueblo Office of Environmental Protection (POEP) and the United States Environmental Protection Agency/Environmental

Response Team Center (U.S.EPA/ERTC). Composite samples, collected from the Laahty Family Dip Vat (LDV), Henry O Dip Vat (HDV), and Gila River Indian Community (GRIC) sites, were screened for toxaphene-degradative activity in bench-scale studies and found to be active. In field-scale studies, results showed that initial toxaphene levels decreased from 29 mg/kg to 4 mg/kg (86% removal) in 31 days at the LDV site using a standard recipe consisting of blood meal and phos-phate buffer. At the HDV site, toxaphene levels in two anaerobic cells decreased from 17-29 mg/kg to 6-9 mg/kg in 61-76 days, the extent of removal ranging from 65-69%.

Using a modified phosphate buffer-blood meal recipe for cleanup at the GRIC site,toxaphene levels decreased from 29-34 mg/kg to 4-5 mg/kg in approximately 190 days,with removal levels ranging from 83-88%. Cleanup costs ranged from \$149-\$337/m 3 .

BIODEGRADATION OF SYNTHETIC PYRETHROID DIP INSECTICIDES:

Synthetic pyrethroids (SP) are a class of insecticide used in many domestic,industrial and agricultural applications (Extoxnet PIP, 1994). Those SPs commonly used possess high toxicity to their targets, but also to some non-target species, particularly waterborne invertebrates (Extoxnet PIP, 1994, Tomlin, 1997). Many pollution incidents arising from the use of SP based formulations have been reported with sheep dips (Virtue and Clayton, 1997), mostly where there has been a route to the aquatic environment(Armstrong and Phillips, 1998). Whilst the number of incidents is low, the toxicity of an SP in water means that as little as 10 ng/L can cause the destruction of the local aquatic ecosystem (Pearce, 1997, Virtue and Clayton, 1997). Thus the disposal of SPs and the wastes arising from their usage (such as used sheep dip and carpet mill washings) has attracted attention from Environment Agencies around the world. The problem is also compounded by the increase in SP use over the traditional organophosphate (OP) based sheep dips due to health concerns (Stephens et al., 1995) and OP banning in several countries.

This reseacrch project investigates the use of novel isolated SP-degrading bacteria in removing the synthetic pyrethroid active ingredient in used SP-based sheep dips, and the factors associated with this for in-situ and ex-situ treatments.

Technical grade cypermethrin was obtained from Zeneca Agrochemicals (Kent UK). Ecofleece ® Non-OP sheep dip (contains 10% cypermethrin) was provided by Bimeda (Liverpool, UK). Bayticol ® Scab & Tick dip (contains 6% flumethrin) was provided by Bayer (Leverkusen, Germany). The mineral medium used was Bushnell Haas broth (BHB), composed of (L of deionized water) K2HPO4, 1 g; KH2PO4, 1 g; NH4NO3, 1 g; CaCl2, 0.02 g; MgSO4, 0.2 g; FeCl3, 0.05 g; adjusted to pH7 with NaOH.Synthetic pyrethroid (SP)-degrading bacteria were isolated from soil previously exposed to SP sheep dips and identified as a Pseudomonas and a Serratia species. The Ps. sp. grew best in the lower temperatures whereas the Ser. sp. grew better (Armstrong and Phillips, 1998). Whilst the number of incidents is low, the toxicity of an SP in water means that as little as 10 ng/L can cause the destruction of the local aquatic

ecosystem (Pearce, 1997, Virtue and Clayton, 1997). Thus the disposal of SPs and the wastes arising from their usage (such as used sheep dip and carpet mill washings) has attracted attention from Environment Agencies around the world. The problem is also compounded by the increase in SP use over the traditional organophosphate (OP) based sheep dips due to health concerns (Stephens et al., 1995) and OP banning in several countries.

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previously exposed to SP sheep dips and identified as a Pseudomonas and a Serratia species. The Ps. sp. grew best in the lower temperatures whereas the Ser. sp. grew better affected by the culture temperature. Studies into the metabolism of the isolates showed that both organisms grew best and degraded the most SP in the mineral and sucrose cultures. However the limiting factors were different depending on the organism, with the Ps sp. limited by the lack of minerals whereas the Ser. sp. was limited by the carbon source availability. With environmental samples it was found that the isolated organisms were significantly better at removing the SP from used sheep dip, but only by a few percent in comparison to the control.

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Chapter 4 - INORGANIC POLLUTANTS

Study of groundwater degradation by inorganic pollutants and various removal techniques

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4A DEGRADATION OF GROUND WATER DUE TO FLOURIDE, RELATION TO FLUOROSIS IN HUMAN POPULATION AND DEFLUORIDATION TECHNOLOGIES-

The presence of disease causing micro-organisms and/or excessive dissolved compounds and salts of fluorides, nitrates,metals like iron, arsenic, lead, chromium, mercury, cadmium, copper in surface and ground water sources leads to contamination of potable drinking waters. Ground water is severely threatened by pollution due to industrial wastes and excessive inputs of population. River water pollution is mainly through industrial waste waters from paint, pigment, chrome and leather tanning, electroplating ,textile dyeing andpulp and paper industry ,cotton textile , steel industry , ceramic industries ,galvinisation of iron products , iron ore mining . Drinking water is one of the basic necessities of life. It has been observed that water is a major source of pollutants and contaminants which cause several ailments. Large number of people run the risk of suffering the adverse affects when water is unsafe to drink. WHO estimates indicate that 80% of the diseases are associated with contaminated water The common diseases are dental and skeletal fluorosis and methaemoglobinemia hepatitis A, polio, typhoid, cholera, dysentery

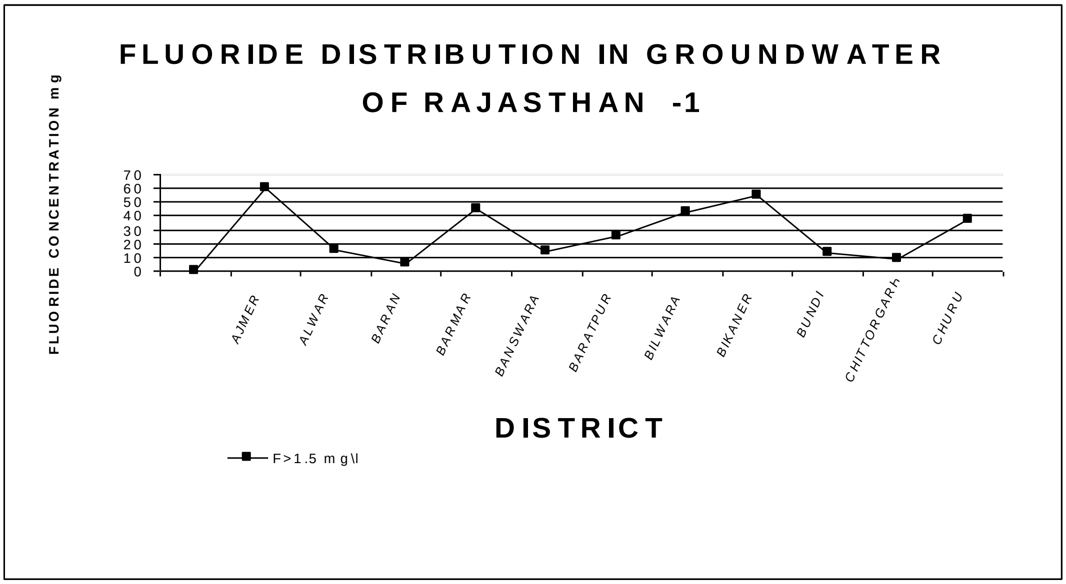
FLUOROSIS

Fluorosis is a crippling disease affecting nearly 25 million population in the country. Fluorosis problem is wide spread all over the country the endemic states are Andhara Pradesh, Karnataka, Tamil Nadu, Uttar Pradesh, Haryana, Punjab, Maharastra, Gujarat, Rajasthan, Jammu Kashmir, Delhi, Kerala. Table 1 give a summarized information on the occurrence of fluoride in ground water in some districts in different states of India. The fluoride distribution in the ground water of various towns of Rajasthan are shown in Figure 1&2 ,where fluoride exceeds 1.5 mg\l permissible limit .

TABLE 1 : SUMMARISED INFORMATION ON THE OCCURENCE OF FLUORIDE IN GROUNDWATER IN VARIOUS STATES OF INDIA

STATE	DISTRICT	FLUORIDE mg|litres
Andhra Pradesh	Ananthapur	0.8-3.5
	Nalgonda,Prakasam	
	Visakhapatnam	
	Hyderabad	0.3-1.9
Bihar	Palamu	2.24-7.54
	Jamui	2.96-8.16
	Gadhwa	1.60-4.8
	Bhabhna	1.80-3.0
	Rohtas	2.50-3.0
	West Champaran	1.60-2.0
	Gopalganj	1.60-2.5
Gujarat	Mehsana	1.58-9.9
Haryana	Gurgaon	0.17-24.5
Jammu&Kashmir	Doda	0.05-4.21
	Ghat ,Monkhil, Malwas ,Bhagwa Khastigarh ,Bharat, Chamalwas, Batroo	
Karnataka	Dharwad	0.40-18.0
	Gulbarga	0.20-5.60
	Raichur	0.40-8.5
Maharastra	Jalgoan	0.11-3.0
	Bhandara	

1.50-10.2
Nagpur
0-4.4
M.P. Shivpuri&Jabua
1.50 –4.2
Punjab Sangrur
0.28-4.0
Tamil Nadu Madurai 0-0.27
Dindigul 0.2-1.03
Tuticorin of
Chidambarar above 0.5
U.P Unnao
0.12-19.0
Agra
0.28-22.0
Allahabad
1.00-1.50
Dehradun
0.02-0.10


FLUORIDE DISTRIBUTION IN GROUNDWATER OF RAJASTHAN -1
FLUORIDE CONCENTRATION mg
70
60
50
40
30
20
10
0
AJMER
ALWAR
BARAN
BARMAR
BANSWARA
BARATPUR
BILWARA
BIKANER
BUNDI
CHITTORGARh
CHURU
DISTRICT
F>1.5 mg\l

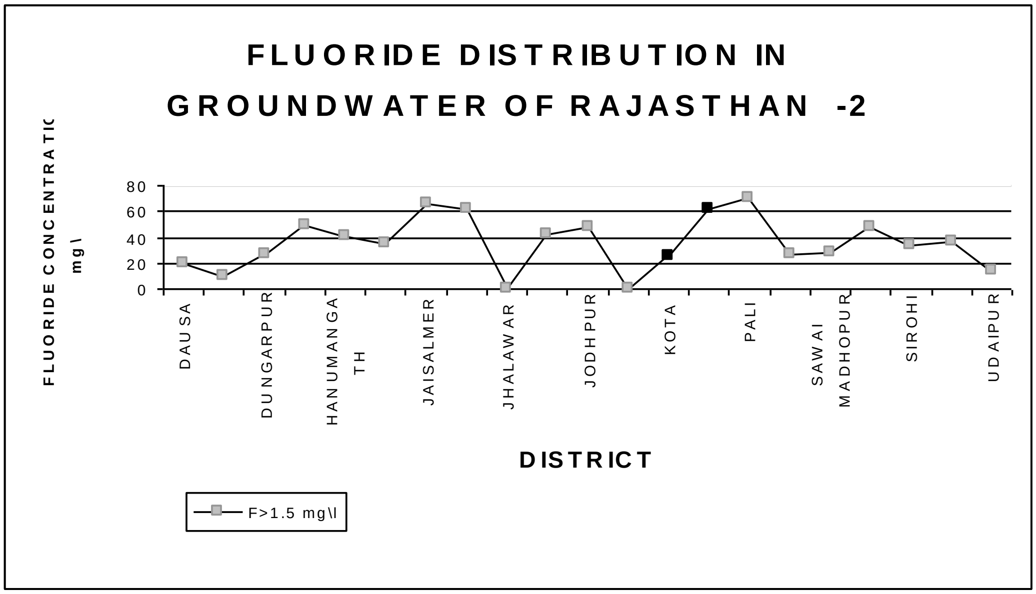

FLUORIDE DISTRIBUTION IN GROUNDWATER OF RAJASTHAN -2
FLUORIDE CONCENTRATIO
mg\
80
60
40
20
0
DAUSA
DUNGARPUR
HANUMANGA TH
JAISALMER
JHALAWAR
JODHPUR
KOTA
PALI
SAWAI MADHOPUR
SIROHI
UDAIPUR
DISTRICT
F>1.5 mg\l

FIGURE 2 a FLUORIDE DISTRIBUTION IN INDUSTRIAL AREAS OF KANPUR

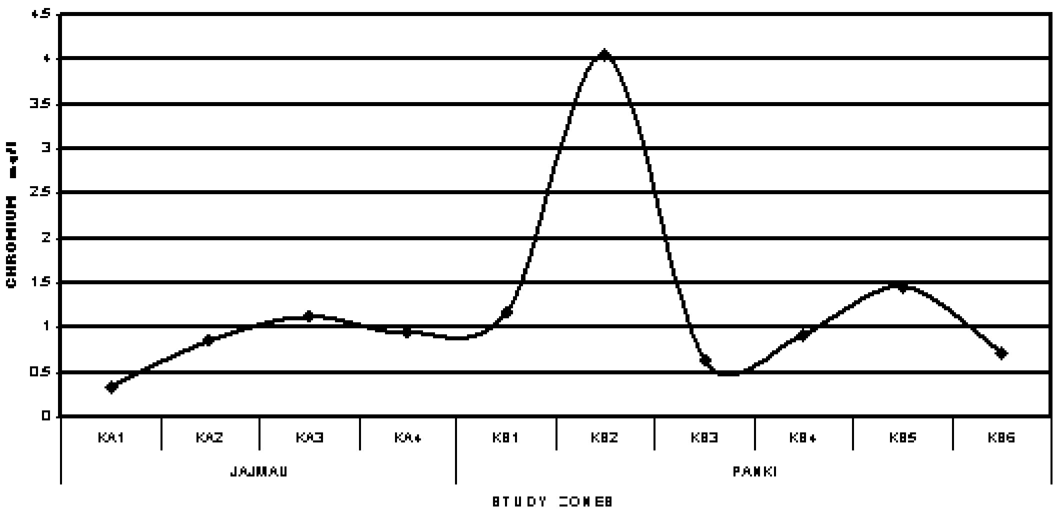
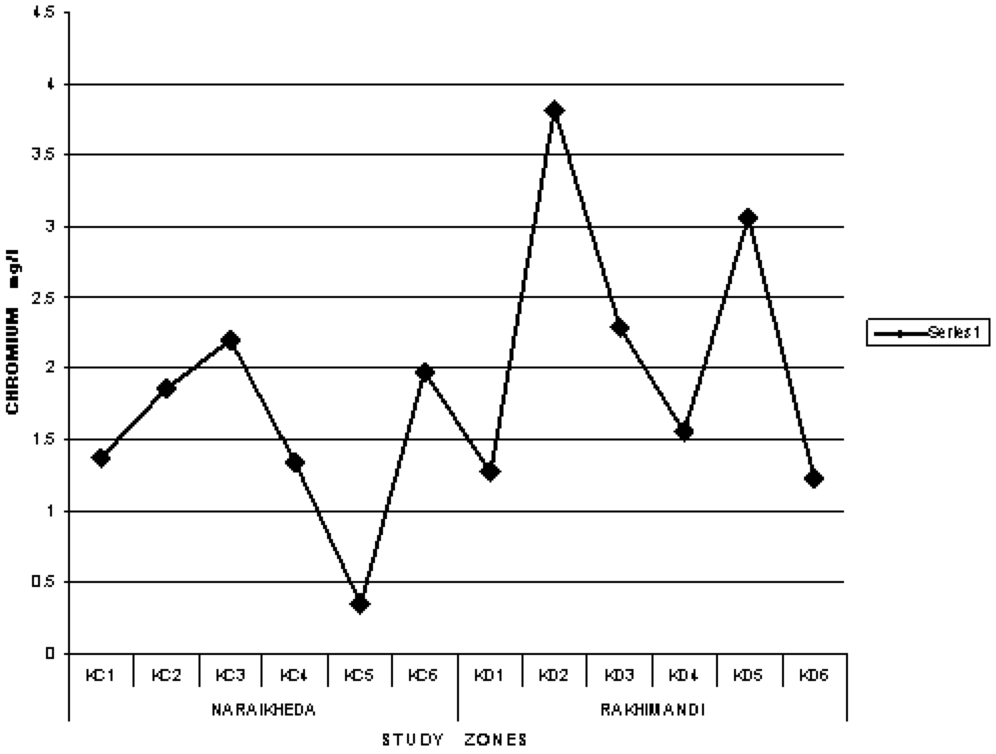


FIGURE 2 b FLUORIDE DISTRIBUTION IN INDUSTRIAL AREAS OF KANPUR



The fluoride problem in Bihar is acute where around 30% districts have excess fluoride in ground water as per survey , these districts are Palamu ,Jamui, Gadhwa, Bhabhna, Rohtas, West Champaran, Gopalganj .Due to high fluoride concentration in water almost all children in the affected villages are suffering from dental fluorosis and a large number of adults are suffering from skeletal fluorosis .[Table 2]

TABLE 2 : THE OCCURENCE OF FLUORIDE IN GROUNDWATER OF BIHAR

DISTRICT	PANCHAYATS AFFECTED	FLUORIDE RANGE	WATER SOURCE BIHAR DEPTH 100-250 Ft
Palamu	Daltangnj,Chai	2.24-7.54	Tubewell\openwell
Jamui	Soni.JhajhaJam	2.96-8.12	Tubewell\openwell
Gadhwa	Durki,Ranka	1.60-4.80	Tubewell\openwell
Bhabhna	Bhagwanpur,Ramgarh	1.80-3.00	Tubewell\openwell
Rohtas	Sasaram,Bhaghwanpur	2.50-3.00	Tubewell\openwell
West Champaran	Bagha,Sitka,Munjholia Bettiah, Chopatia	1.60-2.00	Tubewell\openwell
Gopalganj	Bhor, Gopalganj	1.60-2.54	Tubewell\openwell

FLOURIDE RELEASING INDUSTRIES

Large scale of industrial growth has caused serious concern regarding the suscepility of ground water due to heavy metals . Waste materials near the factories are subjected to reaction with percolating rain water and reaches the groundwater level . The permissible limit for fluoride in drinking water 1.5mg\l [.Industries using hydrofluoric acid or fluoride salts in their technology i.e.aluminium industries,steel and enamel, pottery and glass industries,oil refineries , pharmaceuticals and cosmetic industries which liberate flourous gases to the atmosphere and are the main cause of industral induced Fluorosis.Certain beverages like dry tea leaves contain 39.8 –68.6 ppm fluoride Chewing items like supari ,tobacco,pan contain 3.8-38.0 ppm fluoride . Use of fluoride bearing toothpaste and mouth wash lead to Fluorosis .[Table 3]

TABLE 3: FLUORIDE CONTENT OF SOME FOOD ITEMS

FOOD ITEMS	FLUORIDE CONTENT ppm
Cereals	1.71 -14.03
Pulses	2.4 -21.2
Leafy vegetables	1.8 –6.3
Fruits	1.7 –5.7
Tea dry leaves	39.8 –68.6
Supari, Tobacco, Pan	3.8 –38.0
Nuts & Oil seeds	4.0 –5.7

RELATION OF HIGH FLUORIDE INTAKE TO FLUOROSIS

There are. two types of fluorosis ,dental and skeletal fluorosis Dental fluorosis occurs when the level of fluoride in water exceeds 1.5 mg/l. Teeth due to their high calcium content easily take up fluoride. Prolonged intake of water having fluoride levels exceeding 3 mg/l leads to skeletal fluorosis leads to bow legs and knock knees which affects children as well as adults symptoms of this disease tingling knees. sensation in the legs followed by pain, stiffness of the back.

SYMPTOMS OF SKELETAL FLUOROSIS

In patients showing effects of skeletal fluorosis ,the medical reports suggest accumulation of fluoride ion more in cancellous bones than in cortical bone ,because of porosity ,copious blood supply,presence of trabecular bone surfaces and bone engulfing bone marrow

The fluorosed bone shows characteristic structural changes viz.

*increased bone mass and density.

*exostosis(bone outgrowth) at bone surfaces

*increased osteoid seam and resorption surfaces.

*increased trabecular bone volume,cortical porosity and periosteocytic lacunar surface.

*formation of unminneralizid cartilaginous loci within the trabeculae of the cacellous bone

*maximum ill effects are detected in the neck spine knee pelvic and shoulder joints and

. small joints of hands and feet

*severity of skeletal flurosis ,increases pain which is associated with rigidity and restricted

movement of cervical and lumber spine ,knee,pelvic and shoulder joints .

*further severity results stiff spine i.e. Bamboo spine , immobile knee ,pelvic and shoulder

joints.

*cripplingdeformityfurther results :Kyphosis,Scoliosis,Hexion deformity,Paraplegia.

Quadriplegia and Osteophytes

MECHANISM OF FLUORIDE ACCUMULATION IN THE SOIL

Fluoride in lithosphere and soil found chemically in compound forms i.e. flouraphite ,fluorite and other rock forming minerals in order of 0.06% -0.09% of the earth crust . Salt deposists of marine orgin also contribute fluoride to the soil. The fluoride accumulation in soil is governed by (i) natural solubility of fluoride compounds (ii) acidity of the soil (iii) presence of other minerals & chemical compounds (iv) amount of water present . The fluoride accumulation in soil is also depth factor .

ACCUMULATION OF FLUORIDE IN THE HUMAN BODY

The accumulation of fluoride in the human body is due to the high reactivity of fluoride ion with calcium of teeth bones ,resulting to form calcium flourphosphate (florapatite) crystals and leaving unbound calcium in certain locations in the same tissue,which gets calcified and in turn results in stiffness of tissues & joints causing skeletal fluorosis in late stages .the chemical substitution of fluoride ions replacing hydroxl ions and calcium hydroxy - apatite in bones is due to strong affinity between fluoride and biological apatite of the body .once the apatite/fluorhydrxyapatite forms ,it remains chemically stable until the tissue is reabsorbed or metabolized .A little of fluoride increase in the body by diffusion and absorbtion .Nearly 90% of fluoride in the body is associated with calcified tissues . The fluoride effects on proteins and on DNA molecules are also possible

DEFLUORIDATION METHODS

It has been observed that, there is a pressing need for development and introduction of simple and inexpensive methods of water treatment. Water Treatment technologies and purification methods are being tested, several pilot projects have been set up by Department of Science and Technology in rural Rajasthan . Inexpensive defluoridation units have been tested in laboratory and field. application .

Ion exchange , Nalgonda technology,and Absorption on activated alumina have been reviewed in this light . Fishbone charcoal has been used for fluoride removal Alum treated fly ash as low cost adsorbent as deflouridation material Ion exchange is such a process ,that removes unwanted ions from raw water by trans ferring them to a solid material called an ion-exchanger ,which accepts while giving back an equivalent number of a desirable species stored on the ion-exchanger skeleton.

The ion –exchanger has a limited capacity for storage of ions on its skeleton called its ion-exchange capacity ,because of this the ion-exchanger eventually depleted of its desirable ions and saturated with unwanted ions. It is then washed with a strong ,regenerating solution containing desirable ions ,and then these replace the accumulated undesirable ions,returning the ion-exchanger to usable condition.[Patterson et al 1988] This operation is a cyclic chemical process.Ion Exchange technology is a defluoridation method where 30,000 litres\day can be treated, the contact bed consists of a strong base anion exchange resin with an exchange capacity for fluoride ions filled in a pressure vessel.The water from the bore well is pumped into the pressure vessel and the water treated is collected in an overhead tank.Ion Exchange defluoridation unit was installed at Methsana village near Sidhpur town in Gujarat in 1997 In Table 4 Nalgonda technology and Ion Exchange technology have been compared .

Nalgonda technology is a chemical pretreatment method for defluoridation of well waters , electicity is required to operate this technology and the treatment capacity of water is about 10,000litres\day. Water is stored in tank and alum and lime are added for precipitation of dissolved impurities , followed by flocculation and sedimentation \ filteration , later treated with bleaching powder . Water treated by Nalgonda technology contains residual aluminium in the range of 2.1 - 6. 8 mg\ l under various operating conditions . Al in concentration of 80 µ g \ l or more results in Dialysis dementia and risk of Alzheimer' s disease .

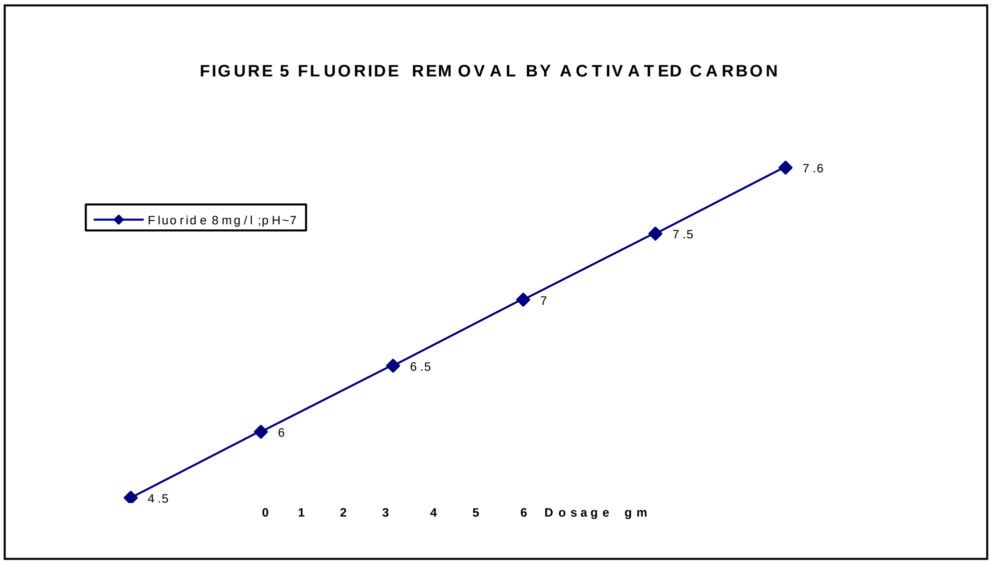
Activated alumina has been extensively used both for laboratory and field application. Activated alumina is widely used as deflouridation material in developed countries. The main component of Activated alumina is Al_20_3 ,Which is prepared by dehydration of aluminium hydroxide in temperature range of 300-600 0 C . Alcoa F-1 grade of Activated alumina is a stable crystalline form with a particle size of 28-48 mesh ,high acid resistance . Flouride uptake capacity of activated alumina depends upon physical and chemical properties of alumina [Table 4] Aloca F-1 exhibted maximum absorbtion at pH 5 . AAG-87 grade of Activated alumina has been screened for domestic defluoridation in Makkar village U.P. in the year 1993

A domestic water filter was fitted with alumina casket for defluoridation of drinking water in the kitchen.[Karthikeyan,G et al 1994] This deflouridation unit is a modified model of the original house filter containing two chambers , a detachable alumina casket in the place of the silica candle in the upper chamber below it , is the water collecting chamber. Total cost of the defluoridation unit including activated alumina cost Rs 650 = 00 and the frequency of regeneration is three months .

UNICEF sponsored the development of domestic and hand pump attachable defluoridation units using activated alumina. The study area for field performance was Unnao district near Kanpur city inU.P

Some low cost adsrbents have been tested for fluoride removal , results have shown in

Figure 3 Aloe vera , Figure 4 water hyscinth root , Figure 5 activated carbon



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CONCLUSION

Based upon the above literature survey the following conclusion can be drawn

(i) factors responsible for spread and severity of fluorosis

*population over growth ,consumption of more water for daily use

*unplanned and indiscrimination in digging of wells

*increase in rate of industrialization

*high level of fluoride intake through drinking water and fluoiride bearing food stuff like tea and chewing items supari , tobacco, pan .

*unawareness towards fluorosis

(ii) Several defluoridation technologies have been studied and the process of absorption on alumina has an edge other methods due to its simplicity and sludge free operation. Activated alumina has been widely recommended as a defluoridating material in developed countries.

(iii) Alum based defluoridation technologies should be avoided It has been observed that, there is a pressing need for development and introduction of simple and inexpensive methods of water treatment.

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Chapter 4

4BTOXIC EFFECT OF MERCURY

Mercury is known to be one of the most toxic metals. Many areas in the world are contaminated by small-scale gold mining and industrial use of mercury, constituting serious environmental problems. Removal of mercury from industrial wastewater has been achieved by means of ion-exchangeable resin or other chemical processes. However,such chemical processes are generally expensive and sensitive to environmental conditions, and they require enormous quantities of chemicals. Therefore, new cost-effective, non-sensitive and sustainable technologies for the removal of mercury are needed

DEVELOPMENT OF A BIOLOGICAL MERCURY REMOVAL SYSTEM

.Several studies on processes for biological mercury removal mainly investigated sorption, accumulation and reduction. In particular, mercuric reduction processes are more efficient because that can transform highly toxic water-soluble ionic mercury to insoluble metallic mercury. It is important that active bacterial cells are maintained at high concentration during mercuric reduction processes. In present study, the removal of mercuric chloride by immobilized cells of mercury-volatilizing bacterium,*Pseudomonas putida* PpY101/pSR134 was examined The mercury removal activity of bacterial cells immobilized on various carriers was investigated..

Materials and methods

A genetically engineered mercury-volatilizing bacterium, P. *putida* PpY101/pSR134 was used throughout this study. Removal of mercuric chloride was examined by immobilized cells of genetically modified *Pseudomonas putida* PpY101/pSR134 which was endowed with mercury volatilizing activity. The immobilized cells on calcium alginate exhibited the highest mercury volatilization activity in various carriers. Immobilized cells have highly stability of mercury removal activity against high temperatures and storage than free cells, and maintained mercury removal activity after four times of removal experiments. The experiment using the mercury removal-reactor system demonstrated that about only 80-85% of the added mercury was recovered in the Hg-trapping solution while about 95% of added mercury

was removed from reaction mixture. Electron micrographs of the immobilized beads and electron dispersive x-ray spectroscopy (EDS) analyses showed that part of the volatilized mercury was entrapped in gel matrix of immobilized beads.

Removal of mercuric chloride by various immobilized cells.

The calcium alginate immobilized cells and free cells exhibited the almost same mercury removal rate at 5 and 10 mg/L of mercuric chloride. The free cells removed almost of 20 mg/L of mercuric chloride for 1 hr,

while about 75% and 40% of added mercury were removed by calcium alginate and strontium alginate immobilized cells. Mercury removal rates of the cells immobilized by agar and the photo-cross-linkable resin prepolymer were lower than those of calcium alginate and strontium alginate immobilized cells. Thefree cells and immobilized cells could remove mercury up to 100 mg/L. There was no removal or sorption of mercury by the gel beads without cells. . Immobilization on calcium alginate demonstrated the most effective removal rate in all the carriers. However, the mercury removal rates and the affinity for mercury of free cells were higher than those of all immobilized cells. These results indicated that immobilization decreased the mercury removal rate and affinity for mercury of this mercury-volatilizing bacterium.

Removal of mercuric chloride by immobilized cells using a mercury removal-recovery system.Removal of mercuric chloride by calcium alginate and strontium alginate immobilized cells was examined using a mercury removal-recovery system can collect bacterial volatilized-mercury. Free cells removed 20 mg/L of mercuric chloride after 2 hrs . Calcium alginate and strontium alginate immobilized cells removed all mercuric chloride after 6 hrs, however, there was no mercury removal in the control flask without cells.Almost all of the added mercury was recovered in the mercury-trapping solution by free cells. Although about 95% of the added mercury was removed from the flasks, only approximately 85% and 80% of the added mercury were recovered by calcium alginate and strontium alginate immobilized cells, respective*ly* Residual Hg (%)

ANAEROBIC/AEROBIC BIOREMEDIATION OF CHLORINATED ORGANIC- AND MERCURY-POLLUTED SITES

Pesticides (DDT), *po*ly-chlorinated benzenes (CBs) and heavy metals such as As and Hg are common contaminants responsible for the environmental toxicity and health hazard of petrochemical industrial sites.

Many chlorinated hydrocarbons are considered in the US EPA priority list of hazardous pollutants . The commercially available soil remediation technologies are thermal desorption of chlorinated aromatics, pesticides and Mercury and hydraulic ligant stabilization or soil washing of heavy metals other than Hg. A not invasive and low-impacting (environmentally friendly) process technology for achieving CBS and DDT biodegradation (dechlorination) coupled with metal inertization (metal sulfides precipitation) is based on the metabolic diversity of specific soil microbial communities (sulfate-reducing bacteria, SRB) and individual populations (dehalorespiratory bacteria, DB). This process involves a first step of reductive biotransformation under anaerobic sulfidogenic conditions with sulfates, chlorinated aromatics and pesticides as terminal electron acceptors Anaerobic dehalogenating processes show encouraging activity levels towards higher halogenated aromatics (and aliphatics) (Drzyzga et al., 2001). For instance, DDT can be reductively dechlorinated to DDD (2,2' - Bis (p-chlorophenyl)- 1,1-dichloroethane) and dehydrochlorinated to DDE (2,2' - Bis (p-chlorophenyl)- 1,1-dichloroethylene) . Recently, further dechlorination of DDE and dehydrochlorination of DDD to DDMU (1-chloro-2,2-bis (p-chlorophenyl) ethylene) mechanisms have beenproved in both methanogenic and sulfidogenic marine sediments The biogenic SRB-mediated sulfide salts precipitation results in the stabilization of metals in less exchangeable and less toxic insoluble form Due to both halo-aromatics dechlorination and metal sulfides generation the toxicity of the treated soil decreases markedly . Studies have been conducted on the use of indigenousmicrobes for the bio-detoxification of xenobiotics in sequential anaerobic-aerobic systems . These studies demonstrated a faster degradation of dechlorinated compounds under subsequent aerobic oxidizing conditions.Little research has been performed on the remediation and detoxification of heavy metals/xenobiotic-containing soils. Our purpose was to study at a lab-scale the sequential process of the degradation/ detoxification of inorganic and organic soil pollutants based on autochthonous subsurface environment anaerobic and aerobic *microflora* with a low cost electron donor.

In this work a soil contaminated with toxic and persistent chlorinated aromatic hydrocarbons (DDT (1,1,1-trichloro-2-2-bis(p-chlorophenyl)ethane), chlorinated benzenes (CBs)) and heavy metals, (mainly Hg and As) has been studied at the laboratory scale. In particular, a process consisting of a sequential anaerobic-aerobic soil treatment has been investigated. Experiments with soil samples highly contaminated with DDT isomers (2600 mg/kg dwb) and based on enrichment of indigenous anaerobic soil *microflora* with discontinuous addition of nutrient (electron donor) showed good dechlorination levels of DDT and CBs. At the same time, a sizeable decrease of the exchangeable/available Hg and As fractions, and a corresponding increase of more stable metal species (sulfides and silicates) were obtained. This resulted in a strong reduction of the whole soil toxicity (solid phase Microtox TM toxicity assay). Further degradation of halo-aromatic intermediates occurred in the aerobic step where natural heterotrophs have been stimulated by sparging air into the soil. The results confirmed the technical feasibility of the sequential bioremediation process. According to the results of a preliminary technical-economical assessment, the process shows favourable economical perspectives (estimated costs 78 Euro/t).

Site background

Soil samples collected from a 250000 m 2 petrochemical site located in a valley in northern Italy were used. Since the early twenties the plant was used for the production of a variety of chemicals such as chlorine, explosives, sulfuric acid from pyrite, ammonia, carbon tetrachloride, chlorinated aromatics and pesticides (DDT). The plant is located on alluvial, permeable soil consisting of gravel and sand with a depth of 40 m below groundsurface (bgs). The water table is located at a depth fluctuating between 5 and 7 m bgs.Environmental data from a previous general site characterization estimated an average soil DDT concentration of 250 mg/kg dwb.

Conclusions

The technical feasibility of the sequential process for the petrochemical polluted soil bioremediation by stimulating matrix autochthonous anaerobic (SRB and DB trophic groups) and aerobic (heterotrophic) specific *microbiota* was demonstrated at lab scale. Efficient dehalogenation of *po*ly-chlorinated hydrocarbons (DDT and CBs) and heavy metal (Hg and As) inertization as sulfides were accomplished by anaerobic treatment of the soil as submerged and flooded slurry. The effectiveness of the anaerobic treatment were confirmed by a decrease of the whole soil toxicity. The subsequent aerobictreatment yielded further degradation of most residual halo-aromatics in mixed anaerobic/anoxic/aerobic conditions. According to preliminary economical evaluations this on site applicable biotechnology results cost effective in comparison to available .

REMEDIATION OF MERCURY-CONTAMINATED SLUDGE AND MINE WASTE USING SILICA MICRO ENCAPSULATION

Mercury (Hg) is a classical poison, with a complex chemistry that often makes remedial treatment of contaminated solids technically difficult and expensive. Consequently, containment or landfilling of wastes remains dominant. However, these are increasingly out of step with the concepts of sustainable development. KEECO has developed the *Silica Micro Encapsulation* (SME) process as an alternative approach. Hg-contaminated sludge from a chloralkali plant waste lagoon in British Columbia (containing 2,250 _g g -1 total recoverable Hg) and mine waste from Sulfur Bank Mercury Mine (a Superfund site) (containing _ 2,000 _g g -1 total Hg) were successfully treated during independently verified studies using the SME process. Both in situ and ex situ treatment approaches were assessed using column studies and field trials and data demonstrated that encapsulation of these contaminated wastes significantly reduced the concentration of leachable Hg (up to 75% reduction for the sludge and 88% for the mine waste). Operating costs per metric ton treated were estimated at $15.00 for the sludge, and $18.26 for the mine waste). In the case of the mine waste study, technical and economic performance of the SME process exceeded that of the two competing approaches being assessed (sulfide and phosphate-based treatments)

Silica micro encapsulation

The focus of this paper is the treatment of Hg-contaminated wastes using the SME process. Results from the treatment of two waste types are reported: contaminated sludge (from a lagoon at a former chloralkali facility in British Columbia, Canada – CASE STUDY A) and a contaminated mine waste (from the Sulfur Bank Hg

Mine Superfund site – CASE STUDY B).

SME is a technology specifically developed for the removal and stabilization of heavy metals in contaminated liquids and solids. The process has been subjected to close regulatory, technical and economic scrutiny in North America and Europe by regulators, private and publicly owned corporations,

NGOs and other potential stakeholders. It has consistently demonstrated its ability to meet stringent regulatory requirements at a price competitive with established and alternative technologies. The process is also capable of treating 'difficult' metals such as chromium, arsenic, Hg, molybdenum and selenium in a wide range of liquid and solid materials, including waters, soils and industrial residues. These are 'difficult' metals because there are few effective, economic alternatives to 'dig and dump'. SME is unique in that ituses silica to minimize the bioavailability and toxicity of heavy metals in waters, soils, sediments and other solid and liquid phases.

Column study methodology.

Two samples of waste material were collected from the SBMM site for testing; one served as the primary test material and the other as secondary. This paper focuses only on results from the primary test sample, labeled 'white material'. In addition to KB-SEA TM , the test included the use of a proprietary inorganic sulfide treatment chemical and a generic phosphate treatment. Four-kilogram sub-samples of the raw material were loaded into 3-foot long, 3" diameter PVC columns and treated with the vendor-supplied chemical reagents. Low flow leaching was performed for twelve weeks with weekly sampling for leachable Hg and other metal contaminants. KEECO performed thetreatment using both in situ chemical application and an ex situ application. KB-SEA TM slurry was prepared by mixing the dry chemical with deionized water. For the ex situ column samples, the chemical slurry was evenly broadcast over the test material and mixed by hand turning. For the in situ column samples, the untreated materials were loaded into the columns prior to chemical amendment. A pre-determined volume of chemical slurry was then applied to each column and allowed to infiltrate through the pore spaces. In addition to the kinetic column leach testing, a series of secondary tests were also conducted. They included the Synthetic Precipitation Leaching Procedure (SPLP), humidity cell testing and humic/fulvic acid leaching as well as

SEM/EDM and XRD analysis to evaluate mineralogical changes arising from treatment (full results of these tests have been published elsewhere (EPA, 2001)). In addition to the technical evaluations, each technology vendor was also asked to conceptualize a treatment system for full-scale technology application and provide cost estimates for treatment based on the laboratory-scale data.

Column study results and conclusions.

Testing conducted on untreated samples indicated that leachable Hg was primarily associated with particulates and was correlated with turbidity. Therefore, the remedial solution would require a technology that can minimize the release of particulates as well as dissolved Hg from the material. For purposes of these tests, mobile Hg was defined as the Hg associated with the <25_m filtered fraction. The success of each treatment was measured versus untreated control columns and each column was prepared in triplicate. Each technology was evaluated for the reduction in the total mass of Hg leached from the columns as compared to the untreated control columns with a target goal of achieving 90% reduction.

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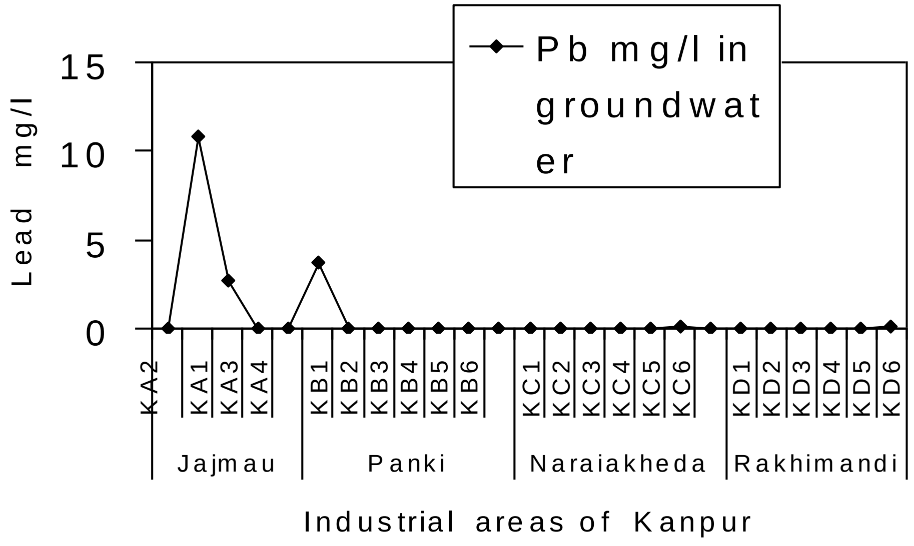
Chapter 4c
REMEDIATION OF LEAD BY LOW COST ADSORBENTS

Lead is a toxic heavy metal with cumulative effects Figure 1 shows the presence of lead in the ground water of Kanpur city [1] The presence of lead in drinking water above the permissible level (0.05mg/l) causes various types of diseases anemia and CNS syndrome also gastric disorders, kidney and liver problems , changes in endocrine glands like thyroid and adrenal glands. Lead is deposited on the bones as a cumulative poison and is stored in teeth ,soft tissues including brain. The main anthropogenic pathway through which lead enters into the aquatic environment is via waste waters from industrial process such as storage batteries, paper and pulp, lead smelting ,mining, petroleum refinery, ammunition , ceramic and glass industries. Lead is also used in storage batteries, insecticides, food,beverages,ointments and medicinal concoction for flavouring and sweetening . Lead accumulation in the environment causes serious ecological problems and requires the application of cheap and effective methods for its removal from contaminated aqueous systems .Water treatment methods suitable for developed countries and urban areas is often inappropriate for villages and small industries of developing countries because of limitation of funds and skilled man power .Among the well-known methods for wastewater treatment , the most frequently used methods are chemical precipitation and electrochemical methods for high lead concentration and for relatively low lead concentrations are adsorption and ion-exchange. The author wishes to direct interest towards low cost adsorbents due their simple and sludge free operation . The adsorption studies on the removal of lead from aqueous solutions by six low cost adsorbents prepared from locally available waste material , Iron dust obtained from cast iron finishing operations, sawdust a raw material from saw mills , mustard husk from agricultural waste , two low cost adsorbents were prepared by impregnating bituminous coal with ferric hydroxide and manganese dioxide , also a cheap carbon was prepared from sawdust . The removal of Pb (II) by these six low cost adsorbents was explored in the laboratory using batch adsorption process and Column technique . The effect of pH, concentration, contact time, dosage, kinetics of adsorption and breakthrough behaviour have been studied . The author wishes to highlight the fact that these adsorbents show promise as a medium for use in small systems and or home–treatment units for removing relatively low concentrations of lead.

FIGURE 1 LEAD IN GROUNDWATER OF INDUSTRIAL AREAS OF KANPUR



.HEALTH HAZARDS DUE TO HIGH LEAD INTAKE-

Lead poisoning causes damage to liver, kidney, and reduction in heamoglobin formation mental retardation,infertility and abnormalties in pregnancy.[Table1].Chronic lead poisoning may cause three general disease syndromes:Gastrointestinal disorder, Neuromuscular effects (lead lapsy) weakness, fatigue muscular atrophy, Central nervous system effects or CNS syndrome that may result to coma and death. Lead poisoning also causes constipation,abdominal pain,etc.

TABLE 1 LEAD IN THE GROUNDWATER OF INDUSTRIAL AREAS OF INDIA

Area	mg /l	Industry
Visakhapatnam	0.040 – 0.06	zinc smelter
	0.016- 0.927	steel
Goa	0.16- 0.54	ore-mining
Himachal Pradesh	0.011-0.12	ore-mining
Rourkela ,Bihar	0.0 - 0.41	steel
Maharastra	0.0 - 1.0	distisllery
Haryana	0.012-0.45	Tanneries
Uttar Pradesh	0.006-0.036	“ “

Madhaya Pradesh	0.0 - 0.006	
Kerala	0.003-0.006	“ “

Lead is one of the toxic metal present in environment and microorganisms in lake sediments can transfer certain inorganic and organic lead compounds to volatile lead tetra methyl. During investigation,. It is found that, some lead containing sediments generates $Pbme_4$ and that the process is purely biological.
Biomethylation reaction of Pb is given $Pb(NO_3)_2 + CH_3I$ à $PbMe_4$ .Methylocobalamine reacted with lead dioxide to give $PbMe_4$. Methylocobalamine transferring a methyl group as a carbanion. Tetramethyl lead are detected by reaction of the dioxide with Methylocobalamine. Lead is deposited on the bones as a cumulative poison and teeth, soft tissue including brain. Lead creates a many blood anamias in the body. The presence of lead , the entry of Iron into photoporphirine PPF rising circulating erythrocyte porphirine lead coproporphirine 3 levels in urine . Lead causes Iron deficiency in children and so rise many side effects psychological and neurological as depends upon the dosages. It also affects on the behavioural changes. Also affects on nervous system kidney problems, liver problems, changes in endrocrine glands are thyroid and adrenal glands, carcinogenic ,teratogenic effects as still births and genetic effects causes chromosomal aberration in man that is lead creats physical, mental, social, behavioral changes in man .Lead is used in the petrol as a antiknocking agent [Table2]

TABLE 2 CONCENTRATION OF LEAD IN BLOOD SAMPLES OF CHILDREN OF DIFFERENT AGE GROUPS

Age group	No of samples	Pb [µg/dL]
3M-1Y	48	6.0-8.7
1Y-2Y	36	2.2-4.9
2Y-3Y	15	3.0- 5.4
3Y-4Y	17	4.4-10.2
4Y-5Y	12	2.9-5.9
5Y-6Y	32	7.0-12.6

METHOD AND MATERIALS

Preparation of adsorbents

Iron saving were obtained from cast iron finishing operations. It was washed with (D M W) deionised distilled water, dried and sieved to a geometric mean size (0.425-0.6mm) and dessicated

To remove lignin raw sawdust was treated by alternately immersing in 2N NaOH and 2N H_2SO_4 for 8 hr approximately, later washed repeatedly with DMW dried and dessicated.

Crushed Mustered husk raw material was used as adsorbent material without any pre-treatment.

For manganese dioxide impregnation, the reported method [4] was used. Crushed and washed coal having geometric mean size 0.102 mm (24g) was added to a solution of potassium permanganate (26.675 g in 325 ml distilled water) at 90 C in a water bath. The slurry was stirred for 10 minutes, followed by slow addition of 300 ml of 2 N hydrocloric acid in 10 minutes with constant stirring. Stirring was continued for another 10 minutes followed by washing of excess precipitate with distilled waternand 0.05 M perchloric acid till the supertant liquor becomes clear. The adsorbent following pretreatment / impregnation was removed, washed several times with distilled water, dried at 60 + 1 C and dessicated.

Iron (III)hydroxide impregnation on coal was done by reported method[5[Crushed and washed coal having geometric mean size 0.102 mm (20g) was slurried in100ml distilled water to which 2gm of iron(III)chloride was added Using 2 N sodium hydroxide solution the pH of the slurry was then adjusted to ~11.5 and the total volume made upto 200ml ,the slurry was allowed to settle for 24 hr. The adsorbent following pretreatment / impregnation was removed, washed several times with distilled water, dried at 60 + 1 C and dessicated.

All solutions were prepared using analytical grade chemicals . Stock lead solutions were prepared from lead nitrate.Batch adsorption studies were carried out in stoppered conical flasks using a mechanical shaker. pH was adjusted by a digital pH meter.Lead was analysed in solution using EDTA complexometric titration and spectrophotometrically

RESULTS AND DISCUSSION

iron shavings removes 40.8 mg /g at pH~5.5 and 16.8 mg/g pH~4 .[6]

Tea leaves treated with 10ml of 39% HCHO-0.2N H2SO4 removed 100.9 Pb mg/g while Tea leaves treated with 2.5ml of 39% HCHO-0.4N H2SO4 Pb(II) 117mg/g Chemically treated tealeaves 100mgsorbent, Pb(II)20mg/l at pH~6. In Figure 3 the percentage sorption increases steadily with increases with contact time 60 minutes and becomes constant Mustard husk shows 96% removal by 0.6 gm and 100% removal by 1.2gm adsorbent at pH 5-6 which increases gradually with contact time with 100% removal at 72 hr . Sawdust does not show much variation and there is 100% removal at 72 hr with 0.5 gm at pH 5-6. The adsorption of Pb[11] by activated carbon from an aqueous solution of 50 and 100 mg/L at various pH shows that percentage adsorption of Pb {II} increases as pH and reached a maximum at pH~6 90.6% , 80.2 %respectively and at pH~9 only 57.9 % and 47.9%. Earlier studies on the adsorption of metals on the solid surface have shown that adsorptive uptake of the metals exhibit a strong dependence on the formation of highly soluble metal species. Activated carbon surface behaves as a diprotic acid

Coal impregnated with manganese dioxide shows 100% removal per 1.3 gm dosage and coal impregnated with ferric hydroxide 97 % removal per 1 gm dosage at pH~4 33.07 mg/gm [Figure 5]

Phytoremediation by Eichhornia crassipes or water hyacinth has been done [Figure 6] Water hyacinth absorbs 70-80 % Pb from water within half and maximum absorption occurs after 4 hr. The water hyacinth was collected from artificial ponds of wastewater of thermal power station. Phytoremediation of hazardous lead from the environment ,researchers have studied accumulation of Pb by high biomass plants like Brassica juncea , B.rapa ,Helianthus annus , Vicia faba, Pissum sativum , Phaseolus vulgaris on application of lead Brassica juncea could accumulate more than 1.5% of lead of its shoot dry weight on EDTA application . It has been designated as best lead Phytoremediator plant as it is nonedible plant and poses no health hazards for the public. It is also a high biomass plant and has a short life cycle. However there are concerns about side effects associated with chelate application. Pb-EDTA easily percolates through soil profile and causes ground water pollution . studies are going on to find a better biodegradable organic chelate.Once inside the plant ,the metal needs to be detoxified .Detoxification of lead occurs by its binding to cell wall,to polyphosphates bodies in some cyanobacteria and in most cases by binding to specific peptides called phytochelatins. Phytochelatins are low molecular weight peptides having the general formula (-Glu-Cys)n-Gly where n=2-11, these are sythesised by the enzyme phytochelatin synthase (PC synthase)and their synthesis is induced by entry of metal.Inductionn of PCs by lead has been reported in algae ,lichens , aquatics and cell cultures. Phytochelatins responses to lead have been extremely sensitive and these detoxifing peptides are synthesized even at 1nM Pb2+ levels in a marine algae Thalassiosira weissflogii.PCs bind Pb via hiolate coordination PC 2 and PC 3 can bind one Pb molecule per peptide molecule wheras PC 4 forms two distinct species with stoichiometries for binding one or two Pb ions per peptide molecule respectively.Scientists have tried to genetically engineer high biomass non edible plants for better hyperaccumulation of lead.There is report of transfer of PC synthase gene (TaPCS1) of Wheat to Nicotiana glauca (shrub tobacco) where it doubled the accumulation of lead.

CONCLUSION

Use of adsorbents derived from plant biomass sawdust , mustard husk, tealeaves are cheap and effective for lead removal similarly coal based adsorbent CFe and CMnO2 can be used for lead though the kinetics need to be studied . Phytoremediation of lead by Eichhornia crassipes from water and Brassica juncea , B.rapa ,Helianthus annus , Vicia faba, Pissum sativum , Phaseolus vulgaris Nicotiana glauca (shrub tobacco) from soil offer good alternatives.

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CHAPTER 4D

Health Hazards Due To High Nickel Intake- And Removal Of Nickel [Ii] By Low Cost Adsorbents

There are a number of toxic trace metals found in natural and waste waters , some of these are essential at low levels of concentrations serving as nutrients for animals and plants but toxic at higher levels . These metals may originate from a variety of sources including the nuclear power , defence and fuel reprocessing industries ; surface finishing processes in the aerospace industry ; and silk –screening processes in the computer industry. In addition , ground waters at many sites are contaminated with these metals ions making their removal and concentration a neccessary step in the restoration of these areas. Table1 Nickel in groundwater of industrial area of India The industrial town of Kanpur has a many cotton textiles , chrome leather tanning , chemical manufacturing industries . A survey was conducted and found that in comparision to other industrial areas of India the ground water of kanpur city contains a very high concentration Ni Table 2. [Ground Water Quality Series 1996-97] The process of adsorption has a an edge over other methods ,due to its simplicity and sludge free clean operation Activated carbons are widely used as adsorbents for purification of aqueous solutions . of heavy metals .The author wishes to draw attention toward the various low cost technologies are available for removing Ni from water

TABLE 1 NICKEL IN THE GROUNDWATER OF INDUSTRIAL AREAS OF INDIA

Area	mg /l	Industry
Rourkela ,Bihar	0.0 - 0.66	steel
Goa	0.10- 0.34	ore-mining
Himachal Pradesh	0.013-0.14	
Uttar Pradesh	0.01-0.033	“ “
Kerala	0.002-0.004	“ “

TABLE 2 NICKEL IN GROUNDWATER OF INDUSTRIAL AREA OF KANPUR CITY .UP . INDIA

	block	mg/l
JAJMAU	KA1	0.05
	KA2	0.04
	KA3	0.05
	KA4	0.05
PANKI	KB1	0.09
	KB2	0.04
	KB3	0.05
	KB4	0.07
	KB5	0.04
	KB6	0.04
NARAIKHEDA	KC1	0.04
	KC2	0.03
	KC3	0.06
	KC4	0.09
	KC5	0.06
	KC6	0.16

RAKHIMANDI	KD1	0.09
	KD2	0.09
	KD3	0.11
	KD4	0.09
	KD5	0.11
	KD6	0.06

HEALTH HAZARDS DUE TO HIGH NICKEL INTAKE-

Table 3 Nickel status in soils of Haryana state India
Table 4 effect of Nickel [20- 80mg/kg] contaminated soil on plant growth [Hisar . Haryana] Heavy metals Ni , As , Hg , Pb , Cd act as effective enzymes inhibitors . The virons or carcinogenic metals with their tendency for chelation are associated with vitamins; protein and nucleic acid .These metals ions may replace the (ZnII, MgII)from the normal enzyme system or nucleic acid and may alter the structure and function of genetic material resulting in the formation of cancer. It has been shown that specific metals are required for genetic regulation and wrong metal ions,even the essential metal ions in wrong concentrations can lead to errors resulting in metal carcinogenesis. The fashioned DNA molecule require only deoxy nucleotides and not ribonucleotide be incorporated in to the nucleic acid .The ability of DNA polymerase 1 to distinguish between these two monomers types has been shown to depend on the nature or the metals used to activate the enzyme thus the presence of Mg(II) insure incorporation of deoxynucleotides,but Ni (II), Mn(II) and Cr(VI) permits the concurrent incorporation of ribonucleotides Thus the presence of Ni (II), Mn(II) and Cr(VI) lead to incorporation of the wrong sugar (Ribonucleotidees) in place of deoxynucleotides in to the nucleic acid with both type of enzyme (RNAand DNA polymerase) carcinogenic metals are suppose to cause error.[Chakrawarti.2003]

TABLE 3 NICKEL STATUS IN SOILS OF HARYANA STATE

Range of Ni mg/kg	Total area km 2	% Area
< 0.75	25083.83	56.79
0.75- 1.25	8837.0	20.00
1.25-1.75	5711.1	12.93
1.75-2.25	2596.3	05.88
>2.25	1940.3	04.39

TABLE 4 EFFECT OF NICKEL [20- 80mg/kg] CONTAMINATED SOIL

ON
PLANT GROWTH [HISAR . HARYANA]

Crops	% age reduction
Brassica juncia	19.70
Brassica carinata	19.40
Green gram	5.0
Pegion pea	12.0
Black gram	20.8
Wheat grain	37.4
Barley grain	5.30

METHOD AND MATERIALS

Preparation of adsorbents

For manganese dioxide impregnation, the reported method [KiranKumar1984] was used. Crushed and washed coal having geometric mean size 0.102 mm (24g) was added to a solution of potassium permanganate (26.675 g in 325 ml distilled water) at 90 C in a water bath. The slurry was stirred for 10 minutes, followed by slow addition of 300 ml of 2 N hydrocloric acid in 10 minutes with constant stirring. Stirring was continued for another 10 minutes followed by washing of excess precipitate with distilled waternand 0.05 M perchloric acid till the supertant liquor becomes clear. The adsorbent following pretreatment / impregnation was removed, washed several times with distilled water, dried at 60 + 1 C and dessicated.

Iron (III)hydroxide impregnation on coal was done by reported method [Jyotsna Lal 1992] Crushed and washed coal having geometric mean size 0.102 mm (20g) was slurried in100ml distilled water to which 2gm of iron(III)chloride was added Using 2 N sodium hydroxide solution the pH of the slurry was then adjusted to ~11.5 and the total volume made upto 200ml ,the slurry was allowed to settle for 24 hr. The adsorbent following pretreatment / impregnation was removed, washed several times with distilled water, dried at 60 + 1 C and dessicated.

All solutions were prepared using analytical grade chemicals . Stock nickel solutions were prepared from nickel sulphate .Batch adsorption studies were carried out in stoppered conical flasks using a mechanical shaker. pH was adjusted by a digital pH meter.

nickel was analysed in solution using EDTA complexometric titration and spectrophotometrically

RESULTS AND DISCUSSION

5 low cost adsorbents tested for ni [ii] removal from water . Table 5 low cost adsorbents tested for NI [II] removal from water

Metal accumulation by micro organisms environmental scientists and engineers try to utilize this property of bio accumulation for monitoring metal pollution as well as removal \ recovery of property of bio accumulation for metals from natural and waste waters . table 6 microorganisms which can bind nickel in their biomass

TABLE 4 LOW COST ADSORBENTS TESTED FOR Ni [II] REMOVAL FROM WATER

	Sorption capacity mg /gm
Natural clay	12.5
Clay-HCl	10.93
Clay-NaCl	14.54
Red mud	15.0
Dye treated rice hull	6.16
Na OH treated rice hull	12.31
Rice hull	5.58
Fly Ash	0.683
Polymerized onion skin	7.55
Peanut hull carbon	53.65
Granualar AC	1.49
Fe [III]/Cr[III] hydroxide	22.94
Sphagnum peat	14.69
Bituminous coal	6.47
Chemically treated coal	7.29
H202 treated coal	8.12
Melon seed husk	5.9
Pea moss	9.18
Coir pith carbon	62.5
A C Cloth CS -1501	8.82
A C Cloth CS- 1301	7.36
Blast furnace slag	55.75
Coconut tree sawdust carbon	133.5
Soyabean hull	89.52
Cotton seed hull	46.57

TABLE 5 MICROORGANISMS WHICH CAN BIND NICKEL IN THEIR BIOMASS

Microorganism		Site of binding
Candida sp	Ni	cell wall [mannan-protein layer & inner glucan -chitin layer]
Cyano bacteria	“ “	
Anabena ,Nostoc sp		
Arthro bacter ,Klebsilla		
Consortia of bacteria ,		
Staphylococcus aureous		
Bacillus lichencforms	Ni , Cu, Fe [III] , Mn , Au .	Cell wall [Teichoic acids]
Bacillus subtilus	Ni Fe ,Mn ,Cu , Zn , Mg , Pb	Cell wall [Peptidoglyan]

FIGURE 4 Ni REMOVAL BY EICCHORNIA CRASSIPES

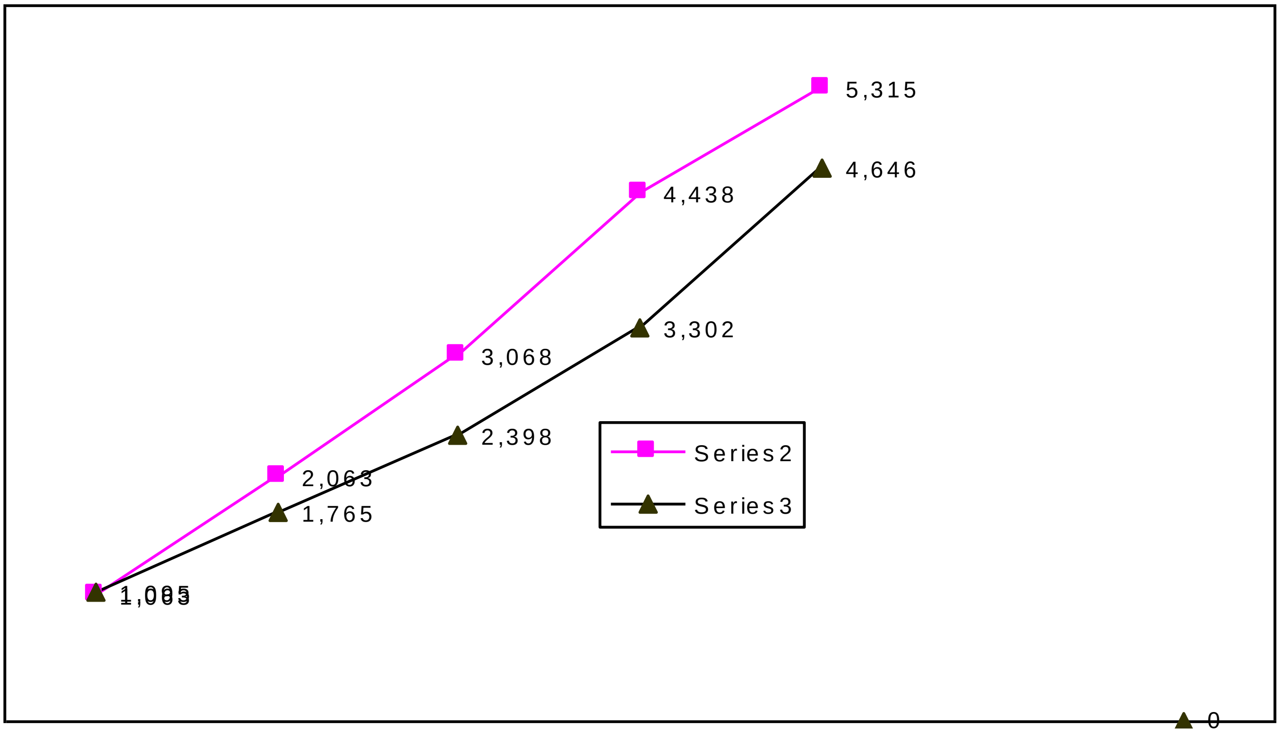
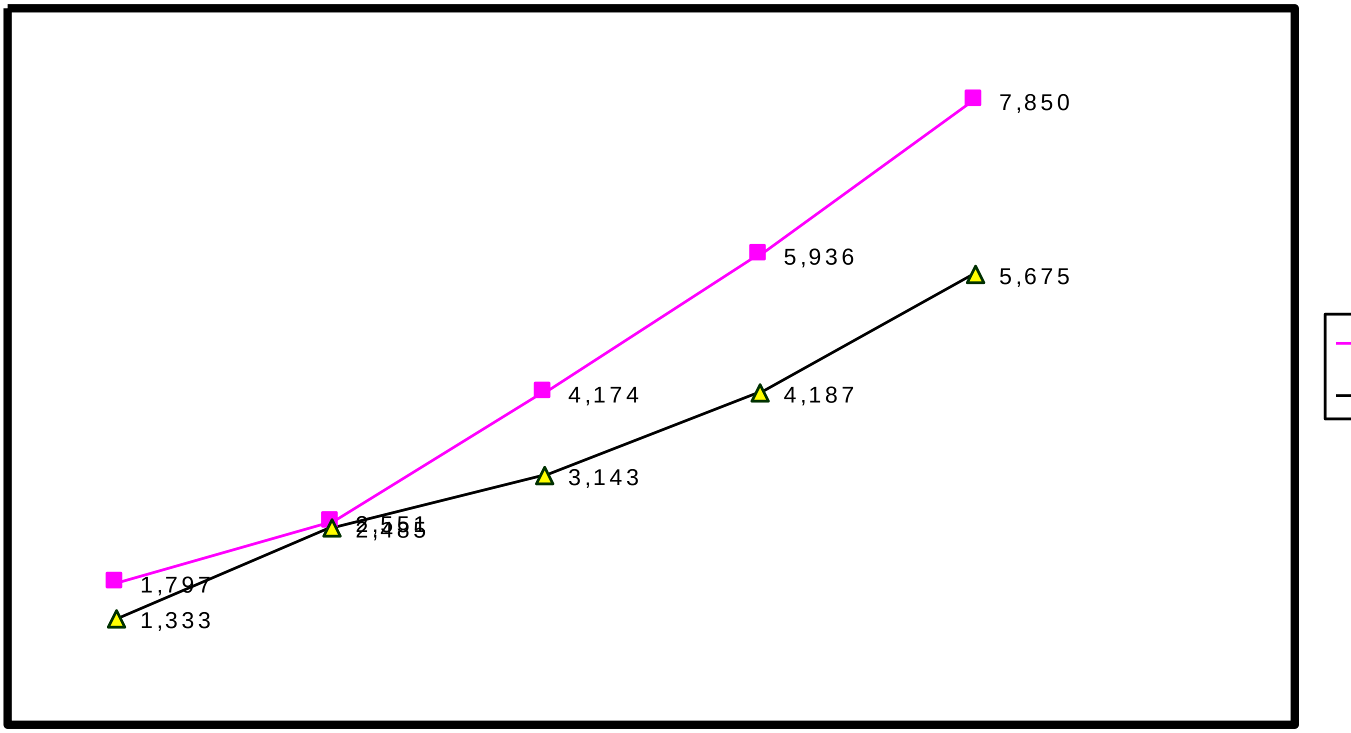


FIGURE 5 NICKEL REMOVAL BY WATER LETTUCE
AND PISTIA STRATIOTES



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Chapter 4

4F Degradation Of Groundwater By Nitrate And Remediation

High levels of nitrate (permissible limit 45 mg/l as NO_3^-) are a serious Problem in different regions of the country, excessive use of nitrgenous fertilizers in agriculture has been primary source of high levels of nitrate . The excessive concentration of nitrates in drinking water could be du e to intensive animal operation, over application of animal wastes, soil induced mineralization of soil organic nitrogen , septic tank systems and land fills. Apart from nitrate ,nitrogen is applied in ammonium NH_{4+} and amide NH_{2-} forms , which generates nitrates in soil system through mineralization which is fairly rapid in tropical and subtropical soils .Due to its high solubility in water and low retention by soil particles ,nitrate is prone to leaching to the subsoil layers and ultimately to the ground water ,if not taken up by plants or denitrified to N_2O and N_2

TABLE 1 SUMMARISED INFORMATION ON THE OCCURENCE OF NITRATE IN THE GROUNDWATER

STATE DISTRICT	nitrate mg / l
Andhra Pradesh	
Hyderabad	11.8.7
Secunderabad	63.3
Visakhapatnam	1.12 –28.9
Assam	16
districts	0.35-3.2
Harayana	
Mahendragarh	>100
Karnataka	
Bangalore	>50
Maharastra	Nagpur
>45	
Orissa	Ganjain
3.6-800	
Rajasthan	Barmar
>11.3	
	Bikaner
..	
	Jaipur
..	
Jaisalmer	..
	Udaipur
	Jodhpur
45-613	
Tamil Naidu	Chennai
15-45	
Uttar Pradesh	
Lucknow	0.0- 650
	Jaunpur
65-1250	
	Varanasi
59-284	

[FertilizerStatistics,1997-98]

In Table 1 The fertilizer consumption in some states of india

HEALTH HAZARDS DUE TO NITRATE

Nitrate itself is not toxic .The presence of excessive quantity of nitrate in drinking

water causes infantile methaemoglobinemia in babies under 3 months of age. Nitrate becomes a problem only when it is converted to nitrite in the human body and causes methemoglobinemia, alternately called Blue Baby Disease or Blue baby Syndrome . Several studies have correlated nitrate in drinking water with gastric cancer. Nitrite produced from nitrate in drinking water enters the bloodstream mainly through the the upper gastrointestinal tract .Almost all nitrate is taken but the efficiency of the process depends on the food matrix . Nitrate excretion in saliva and urine reaches a peak 3-6 hours after nitrate ingestion Excretion mainly occurs through urine ,sweat and faeces Bacteria in the mouth and gastric mucus transform part of NO_3- to NO_2- . Urine is mainly sterile but nitrate can form due to urinary infections .
For haemoglobin to act as a oxygen carrier , the iron atom within the molecule has to be in the reduced [FeII] state. When nitrite is absorbed in bloodstream, it oxidizes haemoglobin to methaemoglobin , a [FeIII] compound with reduced oxygen transport capacity, as this compound contains iron in its highest oxidation state which is incapable of binding oxygen .In this way nitrate reduces the total oxygen carrying capacity of blood .As different parts of the body get deprived of oxygen , clinical symptoms of oxygen starvation start to appear ,the skin stars to take a blue colouration wherefrom the disease derives its name, the Blue Baby Syndrome. In infants ,where the diet is normally carbohydrates, coliform organisms are thought to be primarily responsible for conversion of NO_3- to NO_2- in the digestive tract . In adults , as the stomach fluid is more acidic , the nitrate reducing bacteria live in the lower intestine ,wherefore absorption of nitrite to the blood stream doesnot occur . Gastro intestional illness and Diarrhoea may allow the bacteria responsible for conversion of of NO_3- to NO_2- to migrate from lower intestine to upper intestine and stomach, and increase the chances of nitrite formation prior to absorption in the small intestine

EX SITU ABIOTIC TREATMENT OF SOILS TO REMOVE HIGH AMMONIA CONCENTRATIONS

Soils can become impacted with ammonia (distributed as ammonia and ammonium) from a number of sources including fertilizers, manure, industrial products,
and municipal and industrial wastes. An environmental assessment at the site of a decommissioned sour natural gas processing plant found elevated concentrations of
ammonia. Previous studies on this material have shown that the ammonia is present as a
microbial degradation product of amine compounds which were used at the site to strip
hydrogen sulfide gas from produced natural gas. The amines in site soils have been
shown to degrade both aerobically and anaerobically (Mrklas et al, 2001; Lunn et al,
1999). The microbial degradation pathways for amine are described by Mrklas et al,
2001. Ammonia (NH3) is a gas under ambient environmental conditions. However,

ammonia gas is extremely soluble (89.9g / 100 mL, Weast, 1985) and is a weak base which may protonate to form its conjugate acid ammonium (NH_4^+). The pKa of ammonium is 9.3 (e.g. Snoeyink and Jenkins, 1980) and ammonium is therefore the dominant form under typical environmental conditions ($6<pH<8.5$). The ammonium ion interacts strongly through cation exchange with the negative charges associated with clay mineral surfaces, and hence is not very mobile in the subsurface. Under anaerobic conditions, the ammonium is generally stable and immobile, although it interacts physically with soil as described and may serve as a nutrient in anaerobic metabolism.

Under aerobic conditions, however, the ammonium may undergo additional biological conversion to nitrate (NO_3^-) through nitrification. Nitrate is much more mobile and may contribute to groundwater contamination (Cantor, 1997). The affected soils contained about 1400 mg/Kg ammonium and only nominal nitrate (4 mg/Kg). Although redox values were not taken, the sampled soils had standing water and was likely under anaerobic conditions. The site soils typically have a high clay content (30%). Under these conditions, the ammonium was mostly bound to the clay soils and was unlikely to nitrify. However, this material also contained hydrocarbons which if aerobically bioremediated would result in concurrent or sequential nitrification of the ammonium to nitrate. On a mass per mass basis, 1400 mg/Kg ammonium would be converted to _ 4800 mg/Kg nitrate which, exceeds regulatory targets.The premise behind the study presented here was to find a treatment method which would remove the excess ammonia prior to (or concurrent with) the bioremediation of the hydrocarbons. Little is reported in the literature regarding the treatment of excess ammonia in soils. In general, ammonia is deficient in soils rather than in excess. Treatment of ammonia by sequential nitrification and denitrification is one option but requires careful control of oxygen to provide the necessary aerobic and anaerobic steps. Calcium hydroxide is a known treatment for ammonium in wastewater (Viessman and Hammer, 1985) but not for treatment of ammonium in soils. For wastewater, added calcium hydroxide elevates pH, shifting the dominant form to dissolved ammonia. Subsequent air stripping removes the ammonia from the water. The stripped ammonia is either vented to the atmosphere or collected into a more concentrated form for disposal or possibly beneficial re-use. The remaining high pH water is neutralized with carbon dioxide to remove excess hydroxide and calcium as calcium carbonate.

The removal of ammonium from soil is not as straightforward as in water treatment because the reactions are typically slower due to mixing and mass transfer constraints. In addition, it may is also be difficult to recover added substances if they interact with the solid matrix. Thus an ideal treatment technique involving the addition of a substance should achieve target compound treatment goals while leaving the soil in an acceptable condition for the long term.The objective of the study presented here was to determine if calcium hydroxide could be used to remove ammonium, preventing nitrate formation, and ultimately achieve regulatory requirements for soil pH ($6.0<pH<8.5$) and electrical conductivity EC (2 dS/m) (Alberta Environment, 1994). Ammonium, which is often applied to soil as a fertilizer, is not regulated in soil in Alberta and does not have a numerical remediation standard. The treatment objective used here for ammonium is a final concentration of less than 125 mg/Kg which is sufficiently high to provide the nitrogen requirements for subsequent biological metabolism of hydrocarbons in the soil.

The governing reactions for the process are presented in equation 1-4 below. This is a simplified scheme and does not include concurrent reactions that might occur in the complex soil mixture.

When calcium hydroxide is added to the soil in the solid form, some dissolves in soil moisture and dissociates into calcium and hydroxide ions. The hydroxide ions increase the pH. The calcium ions have a large affinity for the negatively charged mineral surfaces that hold exchanged ammonium ions. The calcium ions displace ammonium ions which results in dissolved ammonium (equation 2). Ammonium, as discussed previously is in equilibrium with ammonia depending on the pH. Equation 3 shows that the hydroxide ions present due to the dissociation of calcium hydroxide react with ammonium to form dissolved ammonia gas. In a high pH environment the dissolved ammonia will partition to the gas phase as ammonia gas (equation 4) and will dissipate from the soil in much the same way as ammonia gas is stripped during water treatment.

These experiments demonstrate that treatment of ammonium impacted soil with the addition of modest amounts of calcium hydroxide is effective at removing between 90% and 100% of the ammonium while meeting criteria for soil pH and electrical conductivity. Without lime treatment, nitrification of ammonium was observed (>4000 mg/Kg nitrate) along with low pH, and high EC. Target ammonium values were achieved within 56 days under laboratory conditions using between 1.5% and 2.5% w/w calcium hydroxide. Calcium hydroxide was the most effective when added in two applications of 1.0% and was more effective than a single application at meeting ammonium and pH targets while reducing the rate of ammonia gas emissions. Plans to implement a field demonstration at the pilot scale are underway.Soils containing high concentrations of ammonia distributed as both ammonium (NH_4^+) and ammonia (NH_3) species may, under certain circumstances,require treatment. Under normal environmental conditions, the ammonium ion is the dominant form and is relatively immobile because of cation exchange onto clay minerals.

However, under aerobic conditions, ammonium will nitrify to nitrate in a 1:3.4 $NH_4^+:NO_3^-$ mass ratio, resulting in mobile nitrate, which could impact water resources. Soils from a decommissioned natural gas treatment plant containing hydrocarbons (C6-C34) and approximately 1400 mg/Kg total ammonia were treated with calcium hydroxide (hydrated lime) to eliminate the ammonia and prevent the accumulation of nitrate during biodegradation of the hydrocarbons. The treatment provides an elegant solution by releasing the ammonia from the soils without generating any unwanted by-products. The process begins with the addition of lime to the soil. The lime partly dissociates in soil water to calcium and hydroxide ions with a concurrent increase in soil pH. The calcium ions cation exchange for ammonium on clay minerals, resulting in available ammonium for reaction with the hydroxide ion to form dissolved ammonia and water. Because of the increased soil pH due to excess calcium hydroxide, the dissolved ammonia is released as a gas from the soil. As the calcium hydroxide reacts and the ammonia is released, the soil pH drops. Even after the majority of the ammonium is released, the soil pH continues to drop and the pH returns to acceptable levels (Canadian Alberta Tier 1,$6.0<pH<8.5$). The residual soil end products of the treatment are water, cation exchangedcalcium which benefits the soil structure, and low solubility calcium salts. In laboratory experiments, greater than 90% removal of total ammonia was observed for relatively low lime additions. In contrast, control soils that did not receive the treatment generated over 4000 mg/Kg nitrate, resulting in soils that would not meet regulatory criteria for EC or pH.

TABLE 2 FERTILIZER CONSUMPTION [Kg/ha] IN SOME STATES OF INDIA

STATE	CONSUMPTION[Kg/ha]
Delhi	347.5
Pondicherry	260.9
Punjab	130.6
Haryana	109.0
Chandigarh	105.0
Uttar Pradesh	91.0
Andra Pradesh	84.1
Tamil Nadu	72.2
Bihar	65.4
Gujarat	62.8
West Bengal	62.7
Karnataka	50.4
Maharastra	45.7
Jammu Kashmir	43.0
Manipur	40.7
Madhya Pradesh	30.3
Rajasthan	29.3
Kerala	28.5

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Section 4G

Toxic Effect Of Arsenic [Iii] And Arsenic [V], Removal From Aqueous Solutions By Different Adsorbents .

The traditional reputation of arsenic as a poison is largely due to the higher toxicity of As(III) ion whereas elemental As , As(V), organic arsenic compounds are commonly considered less toxic. Arsenic is well known for its toxic and carcinogenic properties (class A carcinogen).

The normal amount of As in hair is 0.08-0.25 mg/kg wheras 1mg/kg is an indication of toxicity . The normal amount of As in nails 0.043 –1.08 mg/kg The normal amount of As in urine range 0.005-0.40 mg/kg [1.5 D] Maximum permissible limit of As for drinking water is 0.05 mg/l . Arsenic contamination has been found wide spread in different regions of West Bengal is due to dissolution of arsenic containing bedrock. The high arsenic content of the drinking water has become a major public health issue in 6 districts of West Bengal in India, where an estimated 30 million people dependent on tube well water sources have been adversely affected. The district are in the eastern sector of West Bengal, extending 450 km. From north to south bordering Bangladesh.The severely affected districts are Malda, Mursshidabad, Nadia, Bardhaman, 24 Parganas (North) and 24 Parganas (South). The arsenic content in the ground water ranges from 0.01 to 0.59 mg/l in as many as 830 villages in this area.Tubewells have been dug to a depth of 120 to50 feet.able 1a shows the arsenic levels in drinking water in West Bengal. Table 1b shows a study of arsenic level in the tissue and body fluid of the people of West Bengal

TABLE 1 a OCCURENCE OF ARSENIC IN THE GROUNDWATER OF WEST BENGAL

8 districts /830 villages in 58 blocks	Conc of As in water mg\l		
Total samples of analysed	<0.01	>0.05	> 0.01
34900	43.5	38.7	56.5

TABLE 1 b STUDY ARSENIC LEVEL IN THE HUMAN TISSUE [mg/kg] AND BODY FLUID [ug/1.5D] OF THE PEOPLE OF WEST BENGAL

	Total samples of analysed	% of samples above normal level
HAIR	3530	74.0
NAIL	3620	74.0
SKIN	163	[1.2-29.3]
URINE	7240	83.6

In the last decade, the contamination of soil and groundwater by arsenic compounds has been getting more and more attention. The seriousness of the problem can be seen in Florida where over 2600 sites were found contaminated with arsenic compounds 1 . Similarly, thousands of additional sites exist throughout the U.S. Typical sources of arsenic contamination include mining and processing operations, leakage from natural rocks, and usage of arsenic based herbicides and pesticides. Arsenic in the form of arsenates is one of the common elements uniformly distributed in major rocks types.Under standard conditions, arsenate migration is limited due to the strong sorption by clays, hydroxides and organic matter 2 . However, the change of redox potential, pH and oxygen can trigger desorption. Also, several strains of bacteria were found to be involved in oxidation as well as in methylation and alkilation of arsenic compounds.The overall toxicity of arsenic depends on the concentration and the ionic form of arsenic salts. Unfortunately, the active components of the arsenic based herbicides; pesticides and wood preservatives were soluble forms, such as sodium arsenate and arsenic trioxide. Also, organic arsenical pesticides pose a danger of releasing toxic inorganic derivatives of arsenic via biotransformation. In general, most of the arsenic-contaminated sites are the result of common application of arsenic based herbicides and pesticides.Until 1960, calcium arsenate was used for boll weevil and cotton leaf worms 10 ; lead arsenate and arsenic trioxide have been used for pest and termite control, and sodium arsenite solutions have been utilized for dipping cattle and sheep. Agriculture utilizes arsenic in the form of methyl arsenate (MSMA), disodium methyl arsenate (DSMA), cacodylic acid and arsenic acid. The MSMA, DSMA and cacodylic acid are used to control Johnson and nusedge grass and weeds in cotton fields. Arsenic acid is used as a desiccant for the defoliation of the cotton ball before harvesting 3 , and arsenic trioxide was widely used as herbicide from the early 1950's to early 1970's to eliminate weeds at industrial facilities and on railroads.

Most water treatment technologies suitable for the developed countries are expensive for towns and small industries of the developing countries because of limitation of funds and lack of skilled man power . The process of adsorption has a an edge over other methods,,due to its simplicity and sludge free clean operation . There is a increasing search for low cost adsorbent material made from locally available waste material and plant substrata [Table 2] Some low cost adsorbents selective for As (III), As(IV) have been tested in the laboratary by batch and column technique , pH , concentration and flow rate , break- through capacity have been investigated .

The objective of this chapter is to review the existing methods that are or could be applied to remove arsenic compounds from the soil and groundwater. Some of those technologies could be used for soil and groundwater treatment as well. However, because of a different matrix (soil or water), even the same application will carry different limitations, costs and overall effectiveness. For these reasons we are presenting separate reviews of the methods used for the soil treatment and for groundwater clean up

TABLE 2 ADSORBENTS FOR REMOVAL OF As [III] , As[V] FROM WATER

ADSORBENT	REFERENCE

Ferric Sulphide bed	Lee et al 1972
Bauxite sample	Balient Ambro 1974
Chitin mixture	Elson CM et al 1980
Amorphous iron oxide	Pierce et al 1982
Manganese Dioxide soil	D.W Huang 1983
Lake sediments	Takamastsu 1985
Coal fly Ash	Sen AK and Arnab K.De 1987
Coral limestone	Shigeru 1992
Activated carbon impregnated with metallic Ag,Cu	Rajakovic 1992
Ganga sand	Vaishaya RC 1993
Synthetic Birnessite	Scott 1995
Basic Yttrium carbonate	Warsy SA 1996
Iron coated spent catalyst	Liu JC ;Huang 1997
Chemically treated sawdust	Nag A 1998
Manganese Dioxide coated sand	Sanjeev Bajpai 1999
Lanthanum impregnated Sawdust carbon	Raji .C; Anirudhan1999
Ferric oxide impregnated carbon	Brian Reed 2000

INDUSTRIES RELEASING ARSENIC

Arsenic is used in metallurgical industry ,glassware and ceramic industrues, dye and pesticide manufacturing industries petroleum refineries . Chemicals containing Arsenic are used in manufacture of herbicides and pesticide In West Bengal, a factory manufacturing acetocopper arsenite , an pesticide polluted drinking water in the southern part of Calcutta Arsenic is released into the surface water through mining and burning of coal as well as copper smelting. Rivers flowing through the coal fields of Bihar have been reported to carry large amounts of arsenic, responsible for downstream arsenic poisoning in West Bengal. According to studies the arsenic contamination of the Damodar in West Bengal is mainly due to dumping wastes from the coal mines along the river bed.

HEALTH HAZARDS DUE TO HIGH ARSENIC INTAKE

As (III) ion causes arsenicosis in human beings . Symptoms of arsenic poisoning are abdominal pains vomiting,, diarrhoea and pain in the extremities followed later by numbers and tingling of the extremities palmoplatar hyper keratosis, Mees lines on the finger nails, deterioration in motor and sensory responses, , chronic arsenicalism include dermal lesion, peripheral neuropathy, skin cancer, peripheral vascular disease. Bony fishes and fresh water mussels contain a high content of As [Table 3] Non-cancerous effects of arsenic exposure might show up as skin lesions such as hyperkeratosis, hyperpigmentation and depigmentation. Prolonged exposure could cause central nervous dysfunction, cardiovascular diseases, digestive and respiratory system diseases, liver and spleen swelling and liver cirrhosis

TABLE 3 ARSENIC CONTENT OF SOME FOOD ITEMS

Food items	Arsenic content [ppm]
Bony fish	2-8
Oyster	3-10
Mussels	120
Shrimps	42
Prawns	174
Cows milk	0.03-0.06
Vegetables	0.001

As , Hg, Pb , Cd are highly toxic even at low concentrations. Zn (II) in some metallo- enzymes is substituted by Cd (II) . Arsenic acts on the biological system in the following ways Trivalent toxic As inhibts enzyme activity by reacting with ligands containing sulphydryl ligands . As (III) attacks -SH groups of an enzyme i.e inactivation of pyruvic dehydrgenase by complexation with As (III) preventing the generating of ATP in citric acid cycle . pyruvic dehydrgenase is highly sensitive to As because of its interaction with two –SH groups of of lipoic acid ,leading to pyruvate accumulation . As (III) ion readily crosses the placental barrier and causes foetal damage . Arsenic when absorbed in the biological system can undergo bio-transformation under in vivo conditions As (V) ion or arsenate can be reduced into As (III) ion or arsenite The half life of this bio-transformed arsenite is three to five days , when it can cause harm to the system .

Arsenicosis is a chronic disease with a significant latency period for non-cancer and cancer effects. There appears to be discrepancy in the literature regarding latency, with some reports of 2 years being the minimum for hyperpigmentation and keratosis. Researchers in Bangladesh suggest that 5 years is the minimum latency, whilst some other estimates suggest that this is 9 years. Latency for cancers is also unknown, but it is estimated to be of the order of 20 years. The proportion of a population exposed to elevated arsenic that will develop arsenicosis is uncertain, but may be significant. Medical treatments for arsenicosis are not fully developed. There is indication that switching to arsenic-safe water and anti-oxidants may reverse symptoms in early stages. The proportion of a population exposed to elevated arsenic from drinking-water that will go on to develop arsenicosis is unknown.WHO have modelled the progression of arsenicosis using data from Samta, Bangladesh. The range of those affected over 30 years was 15.75% in the lowest estimate scenario to 29.25% in the highest estimate scenario. Variation in the estimates of mortality from cancers was between 5.0 and 6.5%. This implies a significant overall health burden for those affected.It is not clear whether early removal of arsenic- contaminated water would reduce the onset of cancers, but it is assumed that it would have some impact because of the cumulative nature of the risk. More recent work suggests that anti-oxidants within vitamins A, C and E and possibly compounds containing zinc and selenium also work to reverse symptoms. A recent controlled trial was performed in Bangladesh, but this remains to be published and may require further controlled clinical trials. However, this does indicate the necessity of combining both environmental and medical interventions for arsenicosis.

PREPARATION OF ADSORBENTS

Washed and dried river Ganga sand [geometric mean size 0.49mm] sand was washed with distilled water until the runoff was clear , dried stored Manganese dioxide coated sand was prepared by forming manganese dioxide by oxidation of manganous ion by permanganate in presence of sand .Washed and dried river sand [geometric mean size 0.49mm]250g was added to 250 ml 0.1 M KMnO4 solution , to this 250 ml of 0.4 M NaOH to make the pH alkaline thereafter 250ml 0.3m MnCl2 was added dropwise while the mixture was mixed in magnetic stirrer .dried in oven for 24 hr The coated sand was washed with distilled water until the runoff was clear , dried stored .

The method adopted for iron III hydroxide impregnation on coal. Bituminous coal crushed to geometric mean size of 0.102 mm was washed several times with distilled water and dried in the oven The proximate analysis of coal was moisture at [60% RH] 4.7%,ash 18.2% , volatile 32.0% and fixed carbon 45.1% coal 20 g was slurried in 100ml distilled water to which 2 g of iron III chloride was added ,using 2N sodium hydroxide solution the pH was then adjusted to 11.5 and the volume made upto 200ml .The slurry was allowed to settle for 24 hrs . The adsorbent following pretreatment /impregnation was removed, washed several times with distilled water dried and dessicated.

METHODS AND MATERIALS

Stock solutions were prepared using AR grade Sodium Arsenate and Sodium Arsenite in distilled and tap water . 0.1 MKOH and 0.2 M HCl used to adjust the pH . Batch adsorption studies were performed in glass stoppered conical flasks at room temperature in rotary shaker. Column studies were done using 1.25 ID glass column loaded with adsorbent ,and As (III) and (V) was percolated downward at flow rate ~5ml/minute .The operation was stopped when As was detected in effluent [break-through point] Arsenic was determined in the test solutions spectrophotometrically using Perkin Elmer Spectrophotometer.

RESULTS AND DISCUSSION

Ganga sand can be used as low cost adsorbent for treating As (III) at low levels . The removal of As (III) was determined to be 85 µg /g for initial concentration of 1.6 mg/l at an adsorbent dose of 20g/l, adsorption of As (III) on ganga sand is pH dependent and maximum percent removal of occurs between pH 7-9.followed by a marginal decrease at pH range 9-12 [Figure 1] The is that As (III) is found in aqueous in form of arsenious acid .Being undissociated weak acid with no charge the uptake of As (III) may be due to combination of electrostatic attraction between sorbate and sorbents and Vander Waals attraction .Column studies were done at 0.8mg As (III)/l concentration in tap water which produced arsenic levels below WHO guideline value for As .Sodium hydroxide is a efficient regenerant chemical for removing As from ganga sand.

Manganese dioxide coated sand [Figure 2] Arsenite is oxidized to arsenate by manganese dioxide [$H_3AsO_3 + Mn O_2 = HAsO_4{}^{2-} + Mn^{2+} + H_20$] ; the released Mn^{2+} adsorb on the manganese dioxide ,giving it a positive surface and leading to an enhancement in the removal/adsorption of arsenate present initially or produced as a result of arsenite oxidation The performance of manganese dioxide coated sand in As removal in 10 cycles in column experiment was good [0.5mgAs(III)/l , 0.5mg As (V) /l influent] no As (III) or Mn (II) leaching in the effluent Breakthrough volume was at WHO guideline 0.01mg/l ,85% As was recovered during regeneration .

On Iron III hydroxide impregnated coal.[Figure 3] , For anionic As (V) removal decreased with increasing pH while As(III) removal is not a strong function of pH ,increased to maximum at pH~7. Arsenic (V) and (III) form inner shere complexes with iron hydroxide . As (V) speciation between pH 4-10 H_2AsO_4-= $HAsO_4{}^{2-}$ + H^+ pKa =7 ,at this pH range the net surface is negative , producing a repulsive electrostatic force between $HAsO_4{}^{2}$ and adsorbent .The chemical interaction force must be greater Than the repulsive electrostatic force for removal to occur . As (III) in pH range 3-11, $H_3AsO_3 = H_2AsO_3^- + H^+$ pKa= 9.2 , the predominant species is H_3AsO_4 ,the electrostatic force is zero the removal is attributed to chemical interactions [inner shere complexation] at pH ~ 8.5 about 20 % of the the aqueous As (III) exists as H_2AsO_4- , a repulsive electrostatic force exists ,this repulsive electrostatic force contributes to the decrease in removal with increasing pH

Iron (III) hydroxide loaded coral was used as an adsorbent for Arsenic (V) and (III) Iron (III) coexisted in the aqueous solution , no effect of presence of Cl, NO_2 , SO_4 ,CH_3COO but PO_4 greatly decreased the adsorption.

As (III) adsorption on Lanthanum impregnated saw dust carbon .[Figure 4 increased 10.3 %-- 86.0 % by increasing the pH from 1.0-12 for the initial concentration of 50 mg/l .The anionic forms H_2AsO_3-and $HAsO_3$ are the predominant species in this pH 12. It seems that the chemical reaction and the less soluble precipitates La $HAsO_3$ or La(OH) H_2 As O_3 on the carbon surface was most likely adsorption process , the predominant species is H_3AsO_3 in this acid range .

-C-O-La(OH)$_2$ + H_2 As O_3 = La(OH) H_2 As $O_3{}^{2-}$ + OH –
-C-O-La(OH)$_2$ + H As $O_3{}^{2-}$ = -C-O- La(H As O_3) + 2 OH –

Impregnation of activated carbon by metallic Cu improves the sorption process for As (III) in pH range 4 - 9 which is the optimum pH for apparent affinity between the carbon surface and the arsenic species H_3AsO_3 and H_2AsO_4 predominant at this pH

A strong anion exchange resin DOWEX -1X8 can be used to separate a mixture of Arsenic (V) and (III) anions at pH 7.7 [Table 4a]. As (III) is as unionized H_3AsO_3 while As (V) is present as H_2AsO_4-, $HAsO_4$ anions which are retained on the resin bed which is eluted from the column with 0.1M Hcl The toxic As (III) can be oxdised to As(V) by Chlorine water and removed [Table 4 b].

TABLE 4a RECOVERY OF ARSENIC FROM A MIXTURE OF As(III), As(V) IN DIFFERENT RATIO AFTER SEPARATION THROUGH ANION EXCHANGE COLUMN

As (III)	As(V)	As (III)	As(V)
Taken µg		Recovered µg	
2 .0	0	1.8	0.01
0 .0	1.8	0.01	1.9
1.0	0.45	0.95	0.5
1.4	0.35	1.4	0.35
0.4	0.25	0.3	0.35
0.2	0.35	0.1	0.35
0.2	0.2	0.15	0.2
0.1	0.09	0.1	0.1
0.04	0.04	0.04	0.05
0.02	0.02	0.015	0.015

TABLE 4b RECOVERY OF As (V) FROM As (III) AFTER OXIDATION WITH OXIDATION WITH Cl_2 WATER AND PASSING ION EXCAHANGE COLUMN

Amount of As (III) µg	Amount of Cl_2 water (ml)added	Amount of As(V) µg recovery	% Recovery
100	nil	0	- -
100	2.0	92	92
100	4.0	90	90
100	8.0	89	89

A study indicated that Al in concentration of 80 µ g\ L or more results in Dialysis dementia and risk of Alzheimer' s disease[Gupta AB et al 1999] .Activated alumina could achieve over 95% Arsenic (V) and (III) removal twice as effectively as activated bauxite and 12 times more effectively than activated carbon Activated alumina removed As (V) over 20 times more effectively than As (III) along with Fluoride at pH 5.0 The adsorption of As (V) on alumina is governed by the diffusion within the particles better adsorption capacity can be achieved by standing the adsorption process for over a period of more than 12 hr .The smaller the particle size the better will be the kinetic performance .Activated alumina can be regenerated by 4-5% NaOH , 70% capacity can be regenerated after first use Ganga sand and Manganese dioxide coated sand are better low cost adsorbents than others . Both show promise for cheap and effective removal of Arsenic (V) and (III) from water .

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SOIL TREATMENT METHODS

There are number of known technologies that could be used for the treatment of soil contaminated with arsenic. These techniques allow for either physical removal of the arsenic compounds from the soil matrix, or permanent or temporary “lock” of arsenic compound on site. The second group of technologies focuses on stopping migration of arsenic through soil and leaching to groundwater. In the last decade, the contamination of soil and groundwater by arsenic compounds has been getting more and more attention.

1. Excavation.

a. Description: Soil, removed from the contaminated site, is hauled to landfill or treated ex-situ.

b. Advantages: Permanent removal from the site; no future leaching.

c. Disadvantages: Transfer of contaminated soil to other location.

d. Cost (with disposal): $46 – 70/ton 1 .

2. Capping.

a. Description: This technique utilizes an impermeable surface barrier for stopping or reducing possible infiltration of the precipitation or stormwater runoff collected at the contaminated land surface. Caps are designed to either redirect rainfall/stormwater or eliminate infiltration.

b. Advantages: No percolation through contaminated site.

c. Disadvantages: High groundwater table, or high fluctuation in groundwater will make this method useless.

d. Cost: $54.00/ton 5 .

3. Soil Solidification/Stabilization.

a. Description: Uses cement or other binder for solidification of contaminated soil by chemical fixation or encapsulation.

b. Advantages: (1) Encapsulated contaminated soil stays on-site; (2) Soil permeability is reduced below 1 x 10 -7 cm/s and (3) Possibility of leachate is substantially reduced.

c. Disadvantages: (1) Not feasible in residential setting, and (2) Required monitoring for the changing conditions that could lead to the leachate in the future.

d. Cost: $72-348/ton 5 .

4. Vitrification.

a. Description: The contaminated soil is melted into glass. The technology is based on generating high temperatures on site (1600 – 2000 o C) by high amperage current deliver through electrodes inserted into contaminated area 6 .

b. Advantages: (1) Contamination is trapped in the glass; (2) Possible leachate is eliminated.

c. Disadvantages: (1) Air could be contaminated by vapor from the heated site, therefore air above melted area should be collected and treated; (2) Maximum depth of treatment is 6 m; (3) Possible safety hazard because of high voltage and potential splashing of melted medium; (4) High costs.

d. Cost: $480-1044/ton 5 .

5. Containment (barrier walls).

a. Description: Construction of the walls to inhibit migration of contaminants from the site. Several used options include sheet pile walls, grout curtains and bentonite slurry walls.

b. Advantages: (1) Simple solution; (2) Decreases permeability from surrounding sediments.

c. Disadvantages: (1) Required monitoring for the changing conditions that could lead to leachate in the future; (2) Possible contamination from the wall's material; (3) Not effective without lower clay or confining unit.

6. Soil Flushing.

a. Description: Contaminated soil is purged with a mixture of reagents with addition of co-solvents or surfactants. Soil flushing could be done in the continuous, slug or pulsed mode. By using different extraction solutions, arsenic could be extracted in ionic form, but also as a (1) aluminum bound-, (2) iron bound- or (3) calcium bound- complex. It was found that flushing soil with phosphate solution under controlled pH (4–6) can remove up to 80% of adsorbed arsenic compounds 7,8 .

b. Advantages: Permanent removal from contaminated site.

c. Disadvantages: (1) Possible contamination of site by extraction solution, and (2) additional treatment or disposal of the sludge is required. d. Cost: Depending on technique: Reported: (1) $8/ton, including ancillary costs such as mixing chemicals and groundwater pump and treat (1), but also $72-348/ton 5 .

7. Electrokinetics.

a. Description: Method uses low intensity direct current applied to anode and cathode inserted into contaminated soil. Direct current initiates electroosmosis and ion migration to the appropriate electrode.

b. Advantages: Method could be used in fine-grained geologic materials.

c. Disadvantages: (1) Soil need to be saturated with water; (2) No commercial uses yet.

d. Cost: Estimated <$120/ton 1 .

8. Phytoremediation.

a. Description: Removal through plant's uptake. Studies shows that water hyacinth (Eichhornia crassipes)7 , saw palmetto (S. repens) and plant moss verbena (V. tenuisecta)9 can accumulate arsenic. It was reported that phytoextraction by edenfern TM could attain bioaccumulation factor of through uptake and bioaccumulation from the 38.9 mg As/kg of soil to7526 mg As/ kg fern fronds 10 . b. Advantages: Depending on the plant used for phytoextraction, it is possible to achieve considerably high bioaccumulation (ratio of plant over soil concentration).

c. Disadvantages: (1) Limited to the growing season; (2) Requires properbiomass disposal/treatment; (3) Litter from plants could be a problem; (4)Uptake possible only up to the depth of root penetration.

TOXIC EFFECT OF HIGH CHROMIUM INTAKE ON THE HUMAN BODY AND CHROMIUM REMOVAL FROM WATER WITH LOW COST ADSORBENTS

INTRODUCTION

Large scale industrial growth in India has caused serious concern regarding the susceptibility of ground water contamination due to heavy metals . Waste materials near the factories which is subjected to reaction to percolating rain water and reaches the ground water level . This percolating water picks up a large number of heavy metals and reaches the aquifer system and degrades the ground water quality The most important factor which distinguishes metals from other pollutants is that they are not biodegradable once they enter the environment .These metals [Al(III), Cr(VI),Fe(III),Ni(II),Mn(II),Mg(II),have cumulative effects at low levels when present in drinking water and ground water .The adsorbtion of these metals in the body system is high and excretion is slow . Studies on the relationship between the carcinogenicity of a metal and its ability to decrease the fidelity of RNA synthesis with DNA polymerase.The genetic toxicity of metals have shown levels of some metals [in blood serum , plasma nucleic acid and tissues] increase with tumour initiation and development .

INDUSTRIES RELEASING CHROMIUM

The heavy metal Chromium is emitted from various sources for example electroplating industry , paint and pigement waste , cotton textiles dyeing , glass chrome leather tanning industries . [Table 1] More than 80% of tanneries in India and other asian countries adopt chrome tanning practice In traditional chrome tanning practice only 50-60% of the chromium applied is taken up byleather and the balance is discharged as waste.Indian tanneries numbering more than 3000 use annually 45 ,000 metric tons of basic chromium sulphate [BCS] out of this quantity 20,000 tons of chromium salt is discharged in wastewater streams. These discharges cause pollution, waste costly chemicals , and complicate effluent treatment particularly anaerobic biological treatment and disposal of chromium containing sludge

The industrial town of Kanpur in Uttar Pradesh has a many cotton textiles , chrome leather tanning , chemical manufacturing industries . A survey was conducted and found that in comparision to other industrial areas of India the ground water of this area contains a very high concentration Cr (VI) [Figure 1.] With regard to the study zone of Rakhmandi in Kanpur is of particular significance which is mainly due to subsurface disposal of chromium- rich sludge ,indiscriminately disposed (along with municipal garbage) by units manufacturing basic chrome suphate ,the chromium leacheates acidic in nature imparts a moderately yellow hue and supports leaching of cationic sulphates The study zone of Jajmau housing a cluster of tanneries presents altogether a contrasting sceneario on account of its situation being hydrodynamically upstream of the river the basic ascribable reason is the possible wash out of the pollutants percolating through the ground and ultimately reaching the river in the proximity

TABLE 1 CHROMIUM IN THE GROUNDWATER OF INDUSTRIAL AREAS OF INDIA

AREA	mg/L	INDUSTRY
Rourkela Bihar	0- 0.01	steel plant
Cochin ,Kerala	0.008- 0.019	Tanneries
Jharia Bihar	0.01- 0.09	Ore -mining
Himachal Pradesh	0.001- 0.019	Ore -mining

Harayana	Bi cycles
Punjab	wollen garments

HEALTH HAZARDS DUE TO HIGH CHROMIUM INTAKE

Trace amounts of Cr is considered essential for normal metabolic processes (metallo-enzymes), however intakes at higher levels have been found toxic mainly kidneys and liver Hepato and nephrato toxic effects have been reported in rats .

Cr is highly toxic to fish and other aquatic life ,causes changes in oxygen uptake and blood parameters in the fish Sarotherodan mossambicus (Peters) [4] Hexavalent form of Chromium is more toxic than trivalent form , Cr (VI) causes bronchial cancer in man .The maximum permissible limit of Cr in drinking water ,as recommended by WHO is 0.05 mg\l Chromium has been widely used in industry for many years with the toxicity of Cr (VI) being well recognized as a health related problem .The virons [carcinogenic metals, organic compound] in their first phase of activity interact with the host cell and then within the host cell and then with the nucleotides resulting in alteration in the structures and functions of genetic materials .It is proposed that these carcinogens are considered to link with the nucleotides through the metal ions.Carcinogenic metals with their pronounced tendency for chelation are associated with vitamins; protein and nucleic acid .These metals ions may replace the essential metal ions (ZnII MgII;)from the normal enzyme system or nucleic acid and thus may alter the structure and function of genetic material resulting in the formation of cancer. It has been shown that specific metals are required for genetic regulation and the wrong metal ions or even the essential metal ions in the wrong concentrations can lead to errors resulting in metal carcinogenesis. The fashioned DNA molecule require of course, that only deoxy nucleotides and not ribonucleotide be incorporated in to the nucleic acid .The ability of DNA polymerase 1 to distinguish between these two monomers types has been shown to depend on the nature or the metals use ed to activate the enzyme thus the presence of Mg(II) insure incorporation of deoxynucleotides,but Mn(II) andCr(VI) permits the concurrent incorporation of ribonucleotides Thus the presence of Mn(II) andCr(VI) lead to incorporation of the wrong sugar (Ribonucleotidees) in place of deoxynucleotides in to the nucleic acid with both type of enzyme (RNAand DNA polymerase) carcinogenic Metal are suppose to cause error.

EXISTING METHODS FOR CR(VI) REMOVAL

The author wishes to draw attention toward the fact that various technologies are available for removing Cr (VI), including reduction and precipitation, ion-exchange ,precipitation of chromate with barium or lead, ion-flotation , electrodialysis , liquid– liquid extraction and reverse osmosis , the process of adsorption has a an edge over other methods ,due to its simplicity and sludge free clean operation. The most widely used method is to first detoxify Cr (VI) by reducing to the Cr (III) form , which is about 100 times less toxic . This can be accomplished with reducing agents such as SO_2 , ferrous-sulphate , sodium bisulphite or other sulphite . Then precipitation of chromium is induced by the addition of a base . A major problem with this type of treatment is the disposal of precipitated chromium hydroxide . Metal hydroxides tend to be highly hydrated and voluminous stable colloids contaning as much as 80 % water by volume due to the slower replacment of coordinate water for hydroxide ions .Ion-exchange treatment does not present a sludge disposal problem and has the advantage of reclaimation of Cr (VI) . However , Ion-exchange treatment does have disadvantages of being expensive , being poorly selective for chromate over foreign anions and of having a critical flow rate neccesary for efficient removal

Biological removal of toxic Cr was tried using an Enterobactor cloaca strain that reduces under anaerobic conditions . The bacteria Enterobactor cloaca removes toxic Cr VI by reducing it to Cr III , this trivalent Cr forms $Cr(OH)_3$ which can be separated using negetively charged materials . This method may also create sludge problems .

Activated carbons are widely used as adsorbents for purification of aqueous solutions of chromium as adsorption has an edge over other methods ,due to its simplicity and sludge free clean operation. Activated carbons are used in full scale operations in developed countries,however their use is not suitable for developing countries due to their high manufacturing cost . Most water treatment technologies suitable for the developed countries are expensive for towns and small industries of the developing countries because of limitation of funds and lack of skilled man power .There is a increasing search for low cost adsorbent material made from locally available waste material and plant substrata The Table 2 lists some of low cost adsorbents which have been earlier reported .

TABLE 2 LOW COST ADSORBENTS FOR Cr(VI) REMOVAL FROM WATER

ADSORBENTS	REFERENCE
Baggase	M.Rao 1999
Baggase carbon	GM Shantha1993
Bituminous coal	Narayan,N 1989
Brick kiln ash	AK Rai 1999
Charred waste of oxalic acid plant	N.Shukla 1990
Chitosan	P.Udaybhaskar 1990
Feldspar	DB Singh etal 1991
Fly ash	Haribabu 1992
Fly ash-china clay	K K Pandey 1984
Fly ash –Wollasonite	K K Pandey 1984
Groundnut husk carbon	K.Peraswamy 1991
Human hair	TC Tani 1985
Haematite	D B Singh 1994
Iron coated sand	R P Bailey 1992
Leaf powders	M. Vasanthy 1993
Magnifera indica leaves	D K Singh 1993
Peat Moss	B Coupal 1996
Peat	T.Liang 1987
Pinus slyvestris bark	M M Alves 1993
Rice straw	Nandita Deo 1992
Rice husk ash	T K Bansal 1992
Rice husk carbon	K Srinivasan 1988
Sawdust	DK Singh 1990
Tea leaves carbon	J . Lal 1992

4.Methods

Reagents and Methods : Solutions of Cr (VI) were prepared in tapwater using $K_2Cr_2O_7$ (BDH,India) pH was adjusted with HCl .Presence of Cr (VI) in the effluent was determined by Diphenyl Carbazide All the reagents used were analytical grade .

Locally available sawdust was sieved (60-100 mesh) was treated with water to remove the impurities ,then the water was filtered off using cloth bag .

Waste tea leaves (TL)were treated hot dimineralised water ,dried at 100 oC . A pseudo activated carbon was prepared by reacting 10 gm TL/10ml H_2SO_4 The carbonised material was washed with DMW and dried at 100 oC , sieved (60-100 mesh) gave the

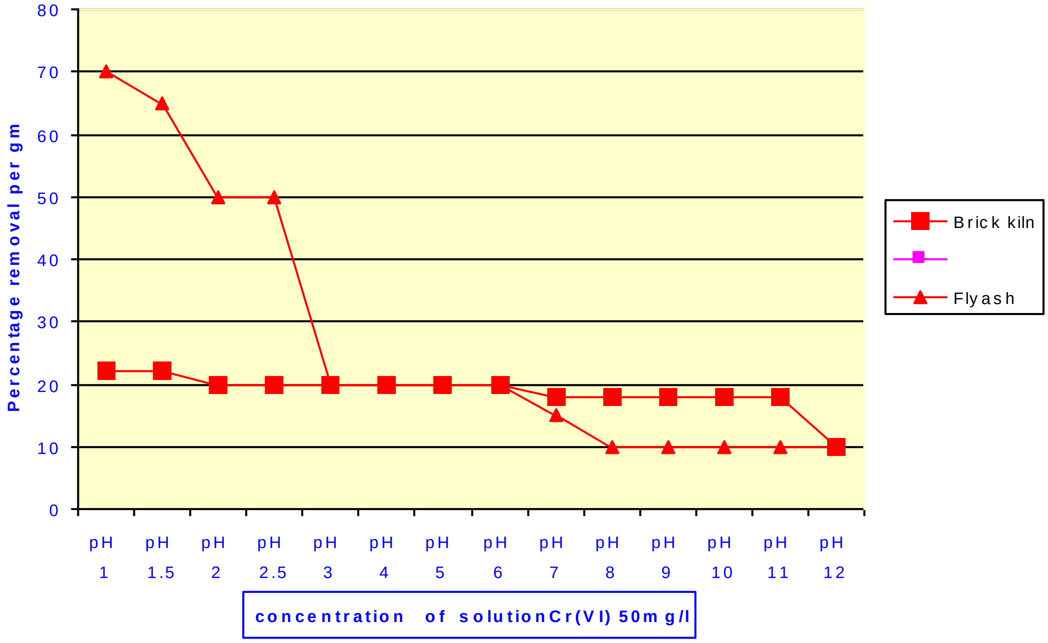
Adsorbent waste tealeaves carbon .

Rice straw was procured from the fodder of the local market cut 1cm long size ,soaked in water overnight ,washed free of colored impurities and dried. Sieved (60-100 mesh)

Adsorption Capacity by column and batch technique

Breakthrough capacity of Cr (VI) was determined by passing Cr (VI) solution through a glass column (i.d.1.25cm) packed with 5gm adsorbent on a glasswool support The flow rate was maintained at 125 ml/h .Batch studies were carried out in glass stoppered conical flasks containing 100ml solution with different dosage and contact time in a mechanical shaker.

FIGURE 2 Cr (VI) REMOVAL BY ADSORPTION ON BRICK KILN ASH AND FLY ASH



RESULTS AND DISCUSSION

Some low cost adsorbents selective for Cr (VI) have been tested in the laboratary by batch and column technique pH , concentration and flow rate on break- through capacity have been investigated The author compared some adsorbents which are available through out the year Human Hair was a poor adsorbent at pH range 1-5 removed 1.1mg Cr/ gm Similarly Brick kiln ash showed only 50% removal as compared to Fly ash at pH 1.3 from chromeplating wastewater as shown in Figure 2 Bituminous coal at pH 2 removed 2.5mg/gm Adsorbent made from a mixture Fly ash – Chinaclay showed 100% removal at pH 2 from solution 4.3mg Cr (VI)/L .Columns packed with Sawdust a natural inexpensive material , available everywhere can be utilized as low cost adsorbent for the removal of CrVI from aqueous solution ,the adsorption capacity was determined as 97.5 mg/5gm or 19.5mg/gm at pH~2 Break through capacity as a function of pH is plotted in Figure 3 . Rice straw a inexpensive material can be utilized as low cost adsorbent for the removal of CrVI from aqueous solution [Figure 4] ,the adsorption capacity was determined 25mg Cr /gm Baggase is reported to remove 80.80% at pH 6-7 from solution 3.5gm Cr (VI)/L Tea leaves carbon [TLC] can play an important role in treatment processes of metal bearing industrial effluents, a cheap carbonaceous adsorbent made from waste tea leaves Break through capacity 39.3mg/gm . In Figure 5 , Cr(VI) removal as as function of pH and carbon dosage can be seen .The amount of TLC required for 100% Cr(VI) removal 433mgCr (VI)/L carbon dosage 1200mg/L at pH 1.5 –2.0 Author compares TLC to Groundnut husk carbon GHC It can be seen that ,Activated Groundnut husk carbon at pH range 0.5-1.7 showed 100% removal from 10mg Cr (VI)/L solution , carbon dosage 2400mg /L in Figure 6 Presence of holocellulose and lignin on sawdust and rice straw can be explained for removal of CrVI from aqueous solution .

Sigworth and Smith have proposed the possibility of heavy metal precipitation on the carbon surface by nucleation as one of the pathways for heavy metal removal by activated carbon .

The adsorption of Cr (III) on red mud is highly dependent on pH=5 -6 Cr(III)adsorption on red mud also depends the upon contact time, sorbent dose and initial concentration of Cr(III) Figure7 Red mud showed 99.6%Cr (III) removal from a solution containing 150 mg Cr (III)/ 100 ml .Iron hexamine modified sawdust removed 19.53 mg Cr VI /gm in presence of other ions in pH range 2-6 Figure 8

Alternative low cost method is removal of Cr(VI) from tannery effluent using waterweeds , water weeds Salvinia molesta and Spirodela polyrhiza were allowed to grow in the tannery effluents from Tanneries .

CONCLUSION

Rice straw , Baggase and Sawdust are natural inexpensive materials ,which are easily available and do not require chemical pretreatment .Exhibit exceptionly high degree of Cr(VI) adsorption , thus can be utilized for treatment of industrial waste effluents containing Cr(VI).Red mud may serve as economic and effective fixing agent for Cr(III) removal from chromium laden wastewater. On the other hand Tea leaves carbon TLC and Groundnut husk carbon GHC are excellent cheap carbonaceous adsorbents showing high degree of Cr(VI) adsorption. Iron hexamine modified sawdust is another cheap adsorbent These adsorbents can easily prepared in any laboratory of a tannery , chrome plating or paint industry All these adsorbents offer a good alternative to expensive activated carbons and other water treatment technologies .

This paper has been limited to a study of adsorption capacities at different pH for some low cost asorbents . There is a need to describe the mechanisms responsible for removal of CrVI from aqueous solution by low cost asorbents , CrVI adsorption and reduction to C r III by these Adsorbents.

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Chapter 5

INDUSTRIAL WASTEWATER TREATMENT

Dissolved air flotation system for treating industrial wastewater.

Some industrial facilities generate ordinary domestic sewage that can be treated by municipal facilities. Industries that generate wastewater with high concentrations of conventional pollutants (e.g. oil and grease), toxic pollutants (e.g. heavy metals, volatile organic compounds) or other nonconventional pollutants such as ammonia, need specialized treatment systems. Some of these facilities can install a pre-treatment system to remove the toxic components, and then send the partially treated wastewater to the municipal system. Industries generating large volumes of wastewater typically operate their own complete on-site treatment systems.

Some industries have been successful at redesigning their manufacturing processes to reduce or eliminate pollutants, through a process called pollution prevention. Heated water generated by power plants or manufacturing plants may be controlled with:

- cooling ponds, man-made bodies of water designed for cooling by evaporation, convection, and radiation
- cooling towers, which transfer waste heat to the atmosphere through evaporation and/or heat transfer
- cogeneration, a process where waste heat is recycled for domestic and/or industrial heating purposes.

AGRICULTURAL WASTEWATER TREATMENT

NONPOINT SOURCE CONTROLS

Sediment (loose soil) washed off fields is the largest source of agricultural pollution in the United States. Farmers may utilize erosion controls to reduce runoff flows and retain soil on their fields. Common techniques include contour plowing, crop mulching, crop rotation, planting perennial crops and installing riparian buffers.

Nutrients (nitrogen and phosphorus) are typically applied to farmland as commercial fertilizer; animal manure; or spraying of municipal or industrial wastewater (effluent) or sludge. Nutrients may also enter runoff from crop residues, irrigation water, wildlife, and atmospheric deposition. Farmers can develop and implement nutrient management plans to reduce excess application of nutrients and reduce the potential for nutrient pollution.

To minimize pesticide impacts, farmers may use Integrated Pest Management (IPM) techniques (which can include biological pest control) to maintain control over pests, reduce reliance on chemical pesticides, and protect water quality. Example Riparian buffer lining a creek in Iowa

POINT SOURCE WASTEWATER TREATMENT

Farms with large livestock and poultry operations, such as factory farms, are called *concentrated animal feeding operations* or *feedlots* in the US and are being subject to increasing government regulation. Animal slurries are usually treated by containment in anaerobic lagoons before disposal by spray or trickle application to grassland. Constructed wetlands are sometimes used to facilitate treatment of animal wastes. Some animal slurries are treated by mixing with straw and composted at high temperature to produce a bacteriologically sterile and friable manure for soil improvement.

CONSTRUCTION SITE [STORMWATER[

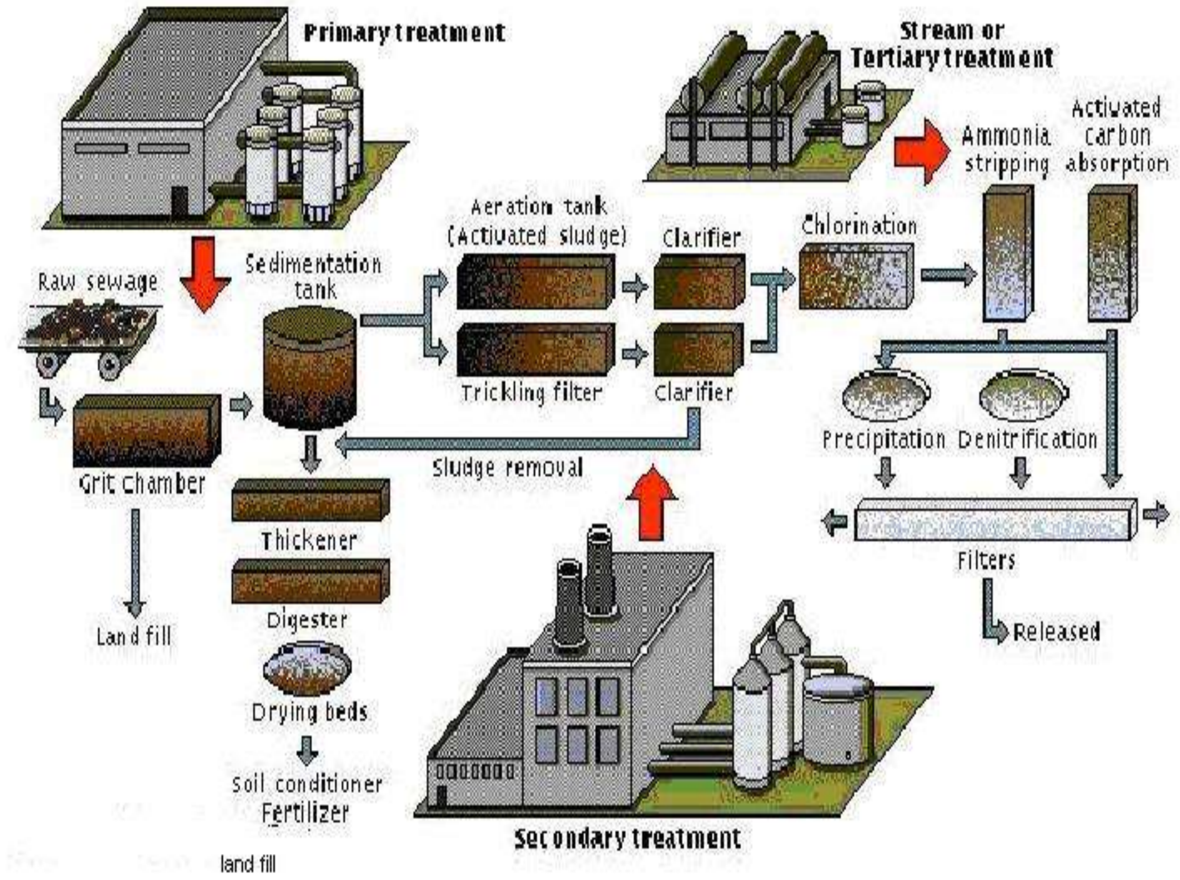
Sediment from construction sites is managed by installation of: erosion controls, such as mulching and hydroseeding, and sediment controls, such as sediment basins and silt fences. Discharge of toxic chemicals such as motor fuels and concrete washout is prevented by use of:spill prevention and control plans, and · specially designed containers (e.g. for concrete washout) and structures such as overflow controls and diversion berms.

URBAN RUNOFF (STORMWATER)

Retention basin for controlling urban runoff. Effective control of urban runoff involves reducing the velocity and flow of stormwater, as well as reducing pollutant discharges. Local governments use a variety of stormwater management techniques to reduce the effects of urban runoff. These techniques, called best management practices (BMPs) in the U.S., may focus on water quantity control, while others focus on improving water quality, and some perform both functions. Pollution prevention practices include low-impact development techniques, installation of green roofs and improved chemical handling (e.g. management of motor fuels & oil, fertilizers and pesticides). Runoff mitigation systems include infiltration basins, bioretention systems, constructed wetlands, retention basins and similar devices.

Thermal pollution from runoff can be controlled by stormwater management facilities that absorb the runoff or direct it into groundwater, such as bioretention systems and infiltration basins. Retention basins tend to be less effective at reducing temperature, as the water may be heated by the sun before being discharged to a receiving stream.

INDUSTRIAL WASTE WATER TREATMENT PLANT



chapter 6

BIOSORPTION—A VIABLE TECHNOLOGY

It has long been known that many biological materials will accumulate metals This phenomenon tends to exacerberate the environmental impact of various metals that are released in the environment because they become concentrated in the flora and \or fauna and ultimately get into the food chain . How ever , the same phenomena potentially can be used in a controlled environment to remove dissolved metal from processing streams either for recovery of valuable resources or to remove pollutants . The interaction between microbes and metals has been studied by scientists of different disciplines. Agricultural scientists are primarily interested in the microbicidal action of metals , bio inorganic chemists basically look at the metal coordinating geometry and their environment in metallo proteins and biological functions Scientists in life sciences study the toxicological effects , its bio accumulation and bio magnification while the environmental scientists and engineers try to utilize this property of bio accumulation for monitoring metal pollution as well as removal \ recovery of metals from natural and waste waters . There is an increasing interest in investigating such biological adsorbents for variety of applications , as biologically derived material can be produced at low cost , yet have adsorbtion capacities near those of commercial ion-exchange resins . Adsorbtion of the metal ions on to materials of biological origin is now regarded as one of the most promising technologies for treating wastes economically . In this paper the author wishes to direct attention towards the application of micro organisms for metal reclaimation and recovery It has been observed that many microbial species exhibit metal binding properties the adsorption capacities of microbial biomass are comparable to or can exceed those of inorganic adsorbents . The use of bio adsorbents .for removal and recovery of dissolved metals has been demonstrated on a laboratory scale or with small pilot plants [1,2] Biosorption has emerged as a viable alternative to conventional metal scavenging techniques . To make this technology economically viable, however the dynamics of this reaction must be enhanced significantly Some mechanisms have been proposed by reseachers for metal accumulation by micro organisms

BIO SORPTION BY MICROBIAL BIOMASS

Use of yeast cells *Saccharomyces* sp for starch fermentation in ethanol production is well known Research in use of mixed culture of *Saccharomyces diastaticus* and *Zymomonas mobilis* in ethanol production has been reported [3] Biosorption , is the process in which live or dead microbes are used for removal of metals from their dilute solutions In recent years investigation of various types of micro organisms for metal adsorption has been reported Heavy metals , which can be toxic to living organisms are present in many industrial aqueous waste streams . These metals may originate from a variety of sources including the nuclear power defence and fuel reprocessing industries ; surface finishing processes in the aerospace industry ; and silk –screening processes in the computer industry. In addition , ground waters at many sites are contaminated with these metals ions making their removal and concentration a neccessary step in the restoration of these areas. Large scale industrial growth has caused serious concern regarding the suscepility of ground water due to heavy metals , waste materials near the factories are subjected to reaction with percolating rain water and reaches the ground water level [4] There are a number of toxic trace elements found in natural and waste waters , some of these are essential at low levels of concentrations serving as nutrients for animals and plants but toxic at higher levels . [5] Zn essential in many metallo-enzymes toxic to plants at high levels , Cu essential trace element ,non to animals but toxic to plants and algae while As ,Hg Pb Cd are highly toxic even at low concentrations . These metals attack the active sites of enzymes , inhibiting essential enzyme activity . Heavy metals act as effective enzymes inhibitors . Zn (II) in some metallo - enzymes is substituted by Cd (II) .

As (III) attacks -SH groups of an enzyme i.e inactivation of pyruvate dehydrogenase by complexation with As (III) preventing the genaration of

ATP in the citric acid cycle . As (III) ion causes arsenicosis , widely prevalent in regions of rural West Bengal . Pb inhibits sevaral key enzymes involved in process of heme synthesis in humans Hg came into the limelight with the incidence of the Minamata disease

Many microbial species exhibit metal binding properties Most research in this area has been associated with heavy metals , such as Pb, Cd, Cu , Cr ,and radio nuclide accumulation. Intra cellular accumulation of many metals has been observed in bacteria , fungi and algae . It has been shown [Table 1] by several researchers[7] that for some types of microbial biomass , most of the metal adsorption occurs in the cell or membrane wall , this included microbial biomass from fungi such as *Ganoderma lucidum* which adsorbs Cu[17] , bacteria such as *Micrococcus luteus* for adsorption of Sr[18] and yeast *Saccharomyces cerevisae* for U , Zn , Mg , Co[19] Bioaccumulation of Ni, Cu by non pathogenic yeast Candica sp[23] Copper was accumulated by *Pseudomonas* sp[34] Artificial ponds and streams contain filamentatous algae and cyanobacteria can greatly reduce levels Pb ,Cu , Zn and Mn from waste waters

The live cyano bacteria *Anabena cylindrica* , *Anabena flos-aquae* and *Nostoc* sp accumulates Ni [11] *Arthrobacter* has high Ni uptake [12] *Chlorella vulgaris* has affinity for Au ,Ag Hg [9, 33] *Oscillatoria perornata var attenate* and *Scenedesmus quadricauda var longispuia* are able to accumulate Fe Zn , Cu and also affected by high concentrations of heavy metals In Table 2 the toxicity and uptake of heavy metals on Algae are given [6] Blue green algae [35] *Westiellopsis prolifica* has significantly reduced high levels of Na , K , Ca , Cl , SO_4^{2-} , PO_4^{3-} from Paper mill waste waters . *Thiobacillus* species are involved in oxidation of sulphide minerals *Aspergillus niger* and *Trichoderma harzianum* oxidises sulphides of Cu , Pb , Zn , Co , Mg . *Bacillus sp and Vibrio* sp reduce Ferromanganese nodules [7] Escheria coli can be used to accumulate Ni [10]Bacterium such as *Enterobacter cloacae* will reduce chromate to trivalent chromium which can then be removed using other bioadsorption technology. [8]

Zooglea ramigera , common in natural water have been used to accumulate Ni , Fe , Cr from waste waters [19] Micro organisms involved in bio reduction and bio oxidation of minerals [7] are given in Table 3 & 4 *Citrobactor* sp immobilised in poly acrylamide gel scavenged large quantities of Cd [16]

Most research in this area has been associated with heavy metals such as of Cd Cu , Pb , Cr, but a broad range of micro organisms has been shown to effectively remove metals like Sr from a typical waste water containing radioactive pollutants As seen in Table 5 the distribution coefficients for Sr adsorbtion (quantity of Sr adsorbed per unit mass of dry biosorbent divided by

equilibrium concentration of the metal within the bulk solution) [14]

IMMOBILIZED MICRO ORGANISMS

The immobilization of micro organisms can be defined as any technique which limits the free migration of cells There are two types of immobilization

(i) attachement , micro organisms and other cellular materials have a natural inclination to adhere to surfaces and in this way become immobilised (ii) entrapment where micro organisms are caught in the interstices of fiberous \porous material or physically restrained within solid or porous matrix such as a stabilized gel or a membrane To concentrate large quantities of bio mass , the microbial biomass is entraped into gel matrix like carragenan , alginate , modified bone gel in the form of beads .The gel is generally formed into useful biocatalyst beads by adding the cells as a sus pension to the aqueous solution of the gelling material . This material is formed into droplets either by forcing it dropwise through a nozzle or orifice or by dispersing into a non-interacting liquid medium . Immobilization or entrapment of micro organisms is done for various applications like ethanol fermentation , production of antibiotics and therapeutics . Micro organism *Cephalosporium acremonium* was immobilized in poly acrylamide gel, used for the production of Cephalosporin ß lactam antibiotic .[27] *Citrobactor* sp immobilised in poly acrylamide gel scavenged large quantities of Cd[16] L.K Jang et al dispensed green algae *Microcystis* in sodium alginate to form a biopolymer gel for the recovery of Cu^{2+} and Co^{2+} ions .[25] Researchers[14, 15 29] have discussed the use of various types of bioadsorbent materials plant tissue and microbial mass for immobilization in gel matrix for removal of dissolved metals A unique columnar system has been proposed for the use of crosslinked bone gel beads Significant quantities of heavy metal ions will adsorb on bone gel beads in a Fluidized - bed contactor. The loaded beads can easily be removed and regenerated[36]

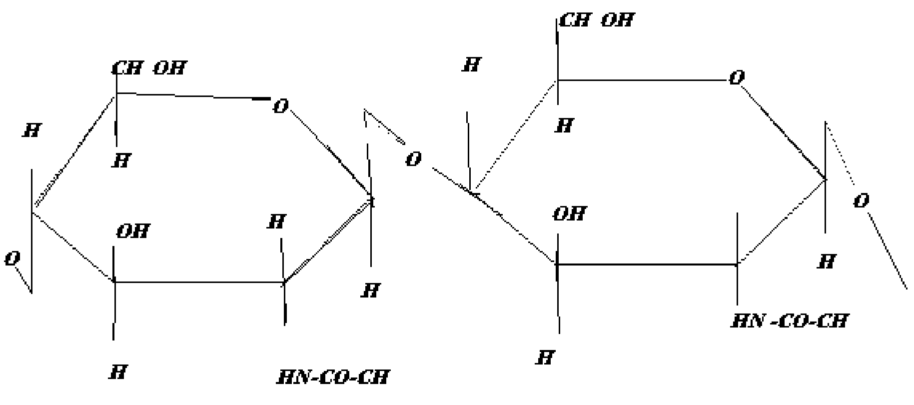


FIGURE 1 STRUCTURE OF CHITIN MOLECULE

MECHANISM OF BIO ACCUMULATION

Mechanisms by which micro organisms remove metals from solution are (i) extracellular accumulation \ precipitation (ii) cell – surface sorption

\complexation
(iii) Intracellular accumulation ; process (ii) can occur whether the micro organism is living or dead (i) may be facilitated by micro bial viabilty (iii) process requires micro bial activity

Both active and passive mechanisms are employed by living cells to accumulate dissolved metals Since , high concentration of heavy metals tend to adversely affect phsiological processes living cells that adsorb such materials must use [Table 2] mechanisms that ensure that only a limited amount of the metal actually reaches in the interior of the cell where it is most toxic . Many cellular mechanisms result in depositing the metals in cell wall or membrane *Citrobactor* sp in presence of a suitable phosphate donor is able to immobilise large quantities of Cd , Cu ,Pb ,U by forming insoluble metal phosphates on the cell surface [16] Sulphate reducing bacteria may produce H_2S gas which will react with metal ions to form an insoluble precipitate . [14] Phytochelatins , a class of peptides found in plants are apparently effective in metal binding These peptides are in the range of 5-17 amino acids in length with a carboxyl terminal glycine that apparently binds metals by thiolate coordination . The Phytochelatins are generated in the living plant tissue that is exposed to metal ions thus providing a means of enhancing the metal adsorption capacity of the biomass

Living cells are affected by metal toxicty and they require the addition of necessary nutrients , maintenance of specific operating conditions . On the other hand nonliving or inactive microbial biomass does not have these requirements and in many cases can be a very effective bioadsorbent for dissolved metals . The cell walls and internal materials within biomass offer abundant sites for metal complexation or micro precipitation .

Biological components have amounts of poly saccharides , protiens and lipids that are replete with metal binding functional groups including carboxylate , hydroxy , sulfate , phosphate and amino groups [14]

It has been shown by several researchers that for some types of microbial biomass ,most of the metal adsorption occurs in the cell or membrane wall , this included microbial biomass from fungi such as *Ganoderma lucidum* which adsorbs Cu [17] , bacteria such as *Micrococcus luteus* for adsorption of Sr [18] and yeast *Saccharomyces cerevisae* for U , Zn , Mg , Co .

Strandberg et al studied *Saccharomyces cerevisae* for U [20] . suggested the role of phosphomannans carboxylic groups of cell wall protein of yeasts in metal binding Yeast cells [23] have been shown to accumulate heavy metals such as Cu , Ni via two distinct process .There is an initial rapid accumulation step that is metabolism and temperature independent ,involves cation binding to negetively charged sites on the cell wall .The outer mannan protein layer of the yeast cell wall as well as the inner glucan - chitin layer are important for heavy metal accumulation Second process is metabolism dependent much slower can accumulate large quantieties of cations .

Researchers have shown that nine species of genus *Penicillum* had no significant difference in their ability to accumulate metal ions , this accumulation property is associated with a microbial species rather than genus . [21]

Chitin , an amino polysaccaride with a molecular structure shown in

Figure 1 has been postulated as the cell wall component responsible for metal coordination

Tsezos and Volesky have reported results of a systematic study carried out to delineate the mechanism of biosorption of uranium by *Rhizopus arrhizus*[22].Based on electron microscopy ,X-ray energy dispersion analysis ,and infrared spectrascopic studies , they proposed three processes responsible for metal scavenging :

(i) The first process is complex formation between dissolved uranium ionic species and chitin present in the cell wall of *Rhizopus arrhizus* . Uranium coordinates to the amino nitrogen of the chitin crystallates and is retained within the cell wall of the mycellium .

(ii) The second process is adsorption of additinal uranium by chitin network close
to that complexed by chitin nitrogen .

(ii) The third process is hydrolysis of uranium chitin complex formed by the first process and the precipitation of the hydrolysis product on the cell wall upon which the chitin nitrogen relieved wil re engage further uranium untill accumulation of the hydrolysis product inhibits the cycle
.

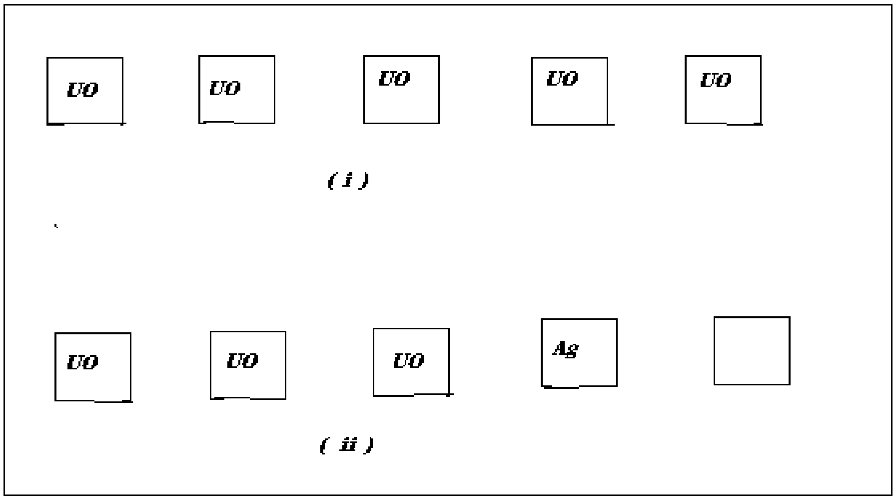
TABLE MICRO-ORGANISMS INVOLVED IN BIO-REDUCTION

ORGANISMS	ORE
Vibrio sp	Ferro manganese nodules
Clostridium sp	Goethite , Haematite
Entero bactor sp	Goethite , Haematite, Cr(IV) to Cr (III)
Bacillus sp	Ferro manganese nodules
Pseudomonas sp	“ “
Chromatiphilia sp	Chromium ore
Sulphate reducers	Sulphates of Fe(II),Ni(II) ,Cu(II) ,Co(II)
Bacteria and Fungi	SeO , SeO

Free radicals are highly unstable species which are traped in the very stable cell wall matrix , this free radical has been attributed to chitin nitogen Muraleedharan et al [17] have concluded that the free radical present consistently in the biosorbents is not taking part in the metal uptake . However the cell wall matrix which has encampassed and trapped this free radical opens up upon metal uptake indicating its role in metal uptake . The exposed cell wall matrix thus freely interacts with the metal resulting in high removal rates , the free radical can be used to probe for further identification of the stable cell wall components responsible for metal sorption .

Tsezos observed that at pH 4 , uranly uptake by *Rhizopus arrhizus* was inhibited by competing cations ,while pH 2 no effect was evident J.M..Tobin et al [24] studied the effects of cation competition on the uptake of a range of different metals on the fungus *Rhizopus arrhizus* , They have reported ,the displacement of Ag^+ ions by UO_2^{2+} , indicates that the sites of uptake of these metals are the same . In studies where Ag^+ was in excess the results support the presence of multiplicity of binding sites in the biomass .In the UO_2^{2+} - Ag^+ system it appears that at less than saturation concentrations UO_2^{2+} ions bind preferentially to certain sites, leaving others partially unoccupied and available for Ag^+ binding even at low $[Ag^+] \backslash [UO_2^{2+}]$ ratios . As this ratio increases ,Ag^+ ions may increasingly displace the UO_2^{2+} ions from the latter type sites .Conversely , at higher UO_2^{2+} concentrations UO_2^{2+} ions occupy all the sites and Ag^+ is not absorbed

Figure 2 A Diagrammatic model of the multiciplicity of uptake sites on *Rhizopus arrhizus* .[Suggested by J .M . Tobin and coworkers]



L.K Jang and coworkers dispensed green algae *Microcystis* in sodium alginate to form a biopolymer gel for the recovery of Cu^{2+} and Co^{2+} ions .[25] The algin contained 4.356 mmol\g uronate residues or repeating monomer units According to the egg box model of gelatin mechanism , each cavity formed in the alginate gel to trap a divalent metal ion has to involve two carboxyl groups from participating uronate residues . Bone gelatin based gel beads are able to accumulate large quantities of Cu and Sr and thus enhance capacity of immobilized biosorbent [31]

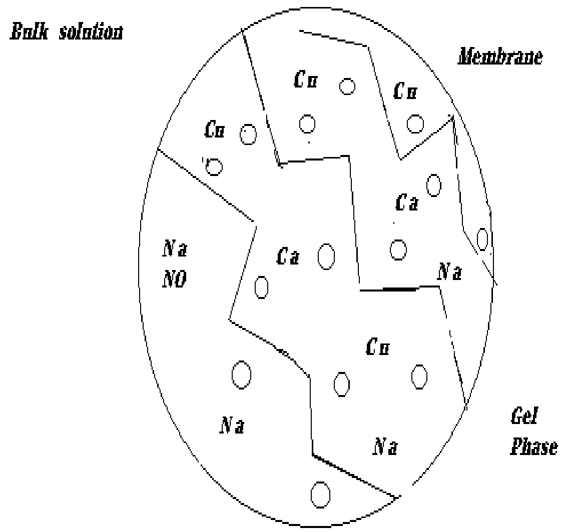


Figure Egg Box Model of Gelatin mechanism

CONCLUSION

The preceeding discussion shows that many microbial species exhibit metal binding

properties The major potential use for immobilized cells is in biomedical area for production of antibiotics and therapeutics Waste water treatment is one of the significant application for immobilized cells To evaluate the suitability of a biosorbent for field application in the treatment of metal rich waste waters, it is neccessary to determine the maximum sorption capacity, kinetics of sorption, recovery of the metal and physical state of the biosorbent.

However, not all of them may be suitable, it is better to select the microbial mass which can fulfil the following criteria : (i) the bio sorbent should be produced at low cost and be reusable (ii) uptake and release of the metal should be efficient and rapid (iii) regeneration of the biosorbent should be possible

An understanding of the mechanisms by which organisms accumulate metals is important to the developement of microbial processes for the concentration, removal and recovery of the metal from aqueous solutions .A knowledge of the chemical and physiological reactions during metal uptake might enable the specification and control of process parameters to increase the rate of metal accumulation

TABLE MICRO- ORGANISMS INVOLVED IN BIO-OXIDATION

ORGANISM	ORE
Thio bacillus ferro oxidans 2- 40 C pH 1.4 –4.8	Metal sulphides, Uranite Rock phosphate,
T . thiopains	Sulphide

	minerals
T .cupriums	“ “
T .acidophilus	Pyrite Chalcopyrites
Sulfolobus acido caldarium Optimum Temp 80 - 85 C	Sulphide minerals
S .brierleyi Optimum Temp 70 C	Sulphide minerals
Sulphobacillus thermo sulkfido oxidans 20 –60 C	Sulphide minerals
Archae bacteria [un identified]	Mn (II) minerals
Thio microspria crunogen	Sulphur oxidizing
Arthro bacter Optimum Temp 88 C	Mn (II)
Hypho microbium sp	Mn (II)
Gallionella	Fe 2+ -----> FeO OH
Aspergillus niger	Sulphides of Cu Pb , Zn ,Co , Mg
Trichoderma harzianum	“ “
Leptothrix discophora	Mn (II)

TABLE 5 ADSORPTION OF STRONTIUM BY VARIOUS MICRO-ORGANISMS

Micro organism	2 Days	7 Days

Rhizopus arrhizus	1,470	85,533
Micro coccus lutes	24,943	12,010
Anaebaena	5.554	10,304
Streptomyces viridochromogenes	4,147	3,949
Penicillium chrysogenum	7,181	3,625
Escherichia coli	967	1,961
Chlorella pyrenoidosa	734	1,915
Zooglea ramigera	493	1,858
Chlamydomonas reinhardtii	1,639	1,785
Candida sp	764	1,139
Caulobactor fusiformis	619	1,055
Pseudomonas aeruginosa	6,	1,

Paecilomyces marquandii	3211,808	003656

Discussion of geochemical data

To provide an anaerobic state to support the development of anaerobic microorganisms, all oxygen and other electron acceptors (such as nitrate and sulfate) have tobe consumed.This condition can be achieved by providing substrates such as lactic acid to the saturated zone. HRC is a source of lactic acid. Anaerobic microorganisms metabolize lactic acid to carbon dioxide and water depleting electron acceptors. Subsequently, the oxidation reduction potential (ORP) shifts from a positive to a negative value. Fermentative microorganisms and the HRC-derived lactic acid, in conjunction, form pyruvic acid and acetic acid. This decomposition process provides the hydrogen required for reductive dechlorination (replacing the chlorine in the COCs with hydrogen). Naturally occurring microorganisms capable of reductive dechlorination then use the hydrogen to progressively remove chlorine atoms from chlorinated hydrocarbon contaminants (i.e., in a simplistic sense, to convert PCE to TCE to DCE to VC to ethane or ethane) (Wiedemeier et al., 1996). Pertinent groundwater geochemical data collected from MW-3 and10 since May 1, 2000 (immediately prior to the HRC injection event). Analysis of perchedgroundwater samples in and around the source area indicate that the saturatedzone is now in an anaerobic condition, which has been promoted by the injection of HRC. ORPmeasurements range from –307 millivolts (mV) in source well MW-3 to -39 mV in MW-10, and ORP has reduced significantly in MW-3 and MW-10 since the application of HRC. An ORP of less than 50 mV is required for effective reductive dechlorination, with values of less than –100 mV being optimal (Wiedemeier et al., 1996). In general, the ORP will reduce only when the electron acceptors (nitrates and sulfates, for example) are consumed. Furthermore, the presence of low quantities of methane in monitoring wells in and around the source area indicates that the aquifer is slightly methanogenic (indicative of anaerobic conditions). Elevated levels of HRC-derived metabolic acids (lactic, propionic, pyruvic, butyric, and acetic acids) in MW-3 and MW-10 indicate that these acids have been effectively released into the shallow aquifer and are being utilized to generate hydrogen within the aquifer to stimulate reductive dechlorination. Permanent gases ethane and ethene have been detected in source well MW-3. The presence of ethane and ethene indicates that the reductive dechlorination pathway has proceeded through DCE and VC to the end-product ethene and/or ethane. Geochemical sampling results indicate conclusively that the HRC injection has been successful in stimulating the reductive dechlorination process.

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Chapter 7

POLLUTION BY COLOR / DYE AND THEIR REMOVAL

Water pollution due to release of industrial waste water has already become a serious problem. Almost every industry uses dyes to color their products and the residual and unspent dyes are discharged into the environment, particularly aquatic environment. Color is the most obvious indicator of water pollution. The discharge of colored waste into streams not only affects their aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic action. Effluents from the dye manufacturing industry, the textile industry and the pulp and paper industry are highly colored. The American dye-manufacturing institute showed that the basic dyes are generally more toxic than acid or direct dyes. Considerable research has been done on color removal from wastewater. The adsorption process provides an attractive treatment, especially if the adsorbent is inexpensive and readily available.

Parthenium Hysterophorus L. As An Adsorbent

In this case study Parthenium hysterophorus L. is used as an adsorbent for the removal of dye from waste water. Parthenium is an unwanted weed growing throughout the country without any input/effort.This is likely to serve basically two purposes, one it will help in protecting the environment from pollution and secondly, ever increasing unwanted weed, parthenium would be put to some use. Adsorbents prepared from Parthenium hysterophorus L. were successfully used to remove the methylene blue from an aqueous solution in a batch reactor. The adsorbents included sulphuric acid treated parthenium carbon (SWC) and phosphoric acid treated parthenium carbon (PWC). The effect of adsorbent surface change, initial pH, initial dye concentration, adsorbent dose and.contact time on dye removal have been studied. Similar experiments were carried out with commercially available activated carbon (AC) for comparison. The adsorption efficiency of different adsorbents were in the order AC>PWC>SWC. Initial pH had negligible effect on the adsorption capacity. Maximum dye was sequestered from the solution within 60-90 min. after the start of every experiment. After that, the concentration of methylene blue in liquid phase remained almost constant. The optimized dosage of biomass and initial dye concentration was found to be 0.4g/100 mL and 100ppm (mg/L) respectively for both the adsorbents under the optimized condition of pH and contact time. At equilibrium, the maximum total uptake by these adsorbents was 47.05 mg per g and 26.1 mg per g respectively. Kinetic of removal has been found to follow the first order rate equation and fit the Lagergren equation well. Langmuir and Freundlich isotherm models were applied to check the efficiency of these adsorbents. The study indicated that these adsorbents can be effectively and efficiently used for the removal of methylene blue from dilute synthetic solution.

A Beer-Waste Biosorbent

Textile industries consume large volumes of water and chemicals for the wet processing of textiles. The presence of very low concentrations of dyes in effluent discharged from these industries is highly visible and undesirable . Due to their chemical structure, dyes are resistant to fading when exposed to light, water and chemicals . Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and difficult to biodegrade. Various physical, chemical and biological methods have been used for the treatment of dye-containing wastewater. Some chemical oxidations, such as Fenton reagent, ozone, UV plus H2O2 or NaOCl, result in aromaticring cleavage, which may generate chemical sludge or by-products that are likely to be even more toxic Physical adsorption technology, i.e. by activated carbons, has recently gained favor as its high efficiency in the removal of highly stable dyes, and is economically feasible compared to other methods . However, activated carbons are expensive and not easily regenerated Although ion exchange resins can be regenerated easily, the high cost hinders their wide application for the treatment of dye-bearing wastewater. Consequently, various types of (bio)sorbents, which are able to bind dye molecules and be easily regenerated, have been extensively searched and tested. The beer waste is generated in a great quantity from the beer plant in China. After an aerobic treatment at wastewater treatment process, this 1/6.waste is currently reclaimed. Thus, the main objective of this work is to utilize beer wastes as a low-cost sorbent for adsorption of a reactive dye, specifically Reactive Red 4 from aqueous solution, and to discuss the application of kinetic and isotherm models to the sorption.

Preparation of the protonated coke waste

The bio waste was collected from an aerobic waste water treatment in a China beer plant and treated with 1 M HNO3 solution for 24 h, replacing the natural mix of ionic species with protons. The acid-treated waste was washed several times with deionized distilled water to remove the excess of acid. It was then dried in an oven at 60 o C to yield protonated bio waste for 24 h. The resulting dried waste was stored in a desiccator and used as biosorbent in the sorption experiments. The protonated beer waste was used as a new type of adsorbent for the removal of Reactive Red 4.

Various experimental parameters were investigated. Adsorption reached equilibrium in 18 hours. Asthe solution pH decreased the dye uptake increased, and in alkaline conditions desorption was dominating. The pseudo-second-order model and Langmuir isotherm model provided a high degree of correlation with the experimental data for the biosorption processes. The rate constant, theequilibrium sorption capacity and the initial sorption rate were calculated. The maximum adsorptioncapacities of the beer waste were 82.23 ±8.67 and 72.50 ±6.45 mg/g at pH 1 and 2, respectively.Kinetic study showed a pseudo-second-order rate of adsorption with respect to the solution. These results of adsorption performance indicate the beer waste as a potentially economical adsorbent for dye removal.

ADSORPTION OF DYES AND PHENOLS ONTO CARBONS PREPARED FROM BAMBOO

Most bamboos contain large amounts of ligneous fiber and can therefore be carbonized into chars, which can be used in decoration, in purifying drinking water, for indoor air filtering, dehumidifying, thermal insulation, electromagnetic wave shielding, etc. However, bamboo is rarely used as the raw material for activated carbon. Meso bamboo is grown profusely in Taiwan. Its stem diameter can reach up to 15 cm. In earlier days, itwas commonly used for building, furniture, eating and cooking utensils, foods, and food processes. Lately, there only use that seems to have remained, is that of using bamboo shoots for food. It is regrettable that the mature bamboo does not seem to have many uses any more. Since the utility value of bamboo has greatly dropped, bamboo-growing has mostly been abandoned reducing the number of plants. The reduction in the number of bamboos grown has caused severe ecological damage to the environment and to water-soil conservation. Bamboo grows fast, absorbing, CO2 from the atmosphere at great speed,so it effectively helps to slow down global greenhouse effect. In previous studies, oak, bamboo, coconut shell, and cedar were activated with steam to obtain activated carbons. The results showed that physical properties (BET surface area and pore volume) and adsorption capacities (chloroform adsorption) of the activated carbons derived from bamboo were lower than those from the other three raw materials Furthermore, studies have shown that of the carbons derived from bamboodust, coconut shells, groundnut shells, rice husks, and straw, straw carbon has the highest adsorption capacity being 5.9 times that of bamboo dust carbon, which is the lowest . From this evidence it is clear that it is not easy to make good activated carbon from bamboo.The aim of this work was to prepare porous carbons from Meso bamboo using KOH etchingand CO2 gasification processes. The physical properties of the carbons, namely the BETsurface area, pore size distribution, and the total pore volume were compared. Theircapacities for the adsorption of basic blue 1, methylene blue, p-cresol, p-chlorophenol, p-nitrophenol, and phenol from water were systematically investigated.

ADSORPTION OF DYES ONTO LDH-MODIFIED BENTONITE

Large amounts of aqueous waste generated by textile, paper, carpet and printing industries contain high concentration of coloured organic, often toxic compounds which has posed severe damage on the environment. It has been reported that there is a large amount of unused dyes existing in wastewaters discharged from dyeing process,especially for reactive dyes,because their hydrolysed form has no affinity for textile fabrics . Due to the toxic nature of most dyes to plants and micro-organisms, coloured wastewater can not be discharged directly without adequate treatment. Toremove dyes from wastewater, a number of physical, chemical and biological wastewater treatment techniques have been developed, such as membrane separation, flocculation-coagulation, adsorption, ozonatioin and aerobic or anaerobic treatment . Among these processes, adsorption has been found to be an effective and cheap process for removing dyes and having wide potential applicationsIt has been reported that many different types of adsorbents are effective to remove dyes from aqueous effluents Clay minerals, such as bentonite, have the potential as alternative low-cost adsorbents becausethey possess unique physiochemical properties. Bentonite is a clay with net negative charges in its lattice structure due to the isomorphous substitution. In order to maintain the electrical neutrality, some cations external to the lattice, like sodium or calcium ions, are commonly present in the interlayer region acting as offset cations. In general, these charge-compensating cations can be exchanged and replaced by others .present in the bulk of the suspension. The application of bentonite as an adsorbent is largely based on its cation exchange ability. It is this property that makes bentonite unable to adsorb anionic species. In order to remove the contaminants in effluent that normally contain both cationic and anionic materials,modification of bentonite is needed. We chose layered double hydroxides (LDHs), the anionic clay materials as the modifier.LDHs consist of positively charged metal hydroxide layers and interlayer anions. These anions together with water presented on the surface or the interlayer space can be exchanged with other anionic species . More particularly, the derived mixed oxides can be transferred back to the LDH structure by adsorbing anions present in water. In this work, bentonite was modified with Mg2Al-Cl-LDH and then calcined so that the composite is able to adsorb anionic species. The work aims to determine whether the LDH modified bentonite composite adsorbent hold the promise for the removal of two anionic dyes, acid red 18(AR18) and direct blue 1(DB1).

Materials and methods

Materials.s supplied by the IntegratedMineral Technology Holdings Ltd, Australia. It was used without any further purification. Its cation exchange capacity (CEC) is 75 meq/100g. LDH, the modifying clay, with a designed formula of $Mg_2Al(OH)_6Cl\cdot 2H_2O$ was synthesised in laboratory by coprecipitation of $AlCl_3\cdot 6H_2O$ and $MgCl_2\cdot 6H_2O$ in NaOH solution under vigorous stirring.The solid material was then collected via centrifugation and washed before being dispersed into a Teflon-lined action.Adsorbent.

LDH-modified bentonite was obtained by mixing the delaminated bentonite

Chapter 8

REMOVAL OF ORGANIC POLLUTANT TETRACHLOROETHYLENE(PCE) FROM GROUNDWATER

A significant percentage of commercial properties requiring environmental cleanup have been contaminated by releases of the chlorinated solvent tetrachloroethylene(PCE) by dry cleaning operations. Dry cleaning facilities have been ubiquitous in commercial properties, particularly strip shopping centers, since the 1940s.

A significant percentage of these facilities have released PCE into the soil and groundwater beneaththese properties, and a significant percentage of these releases will display contaminant levels above applicable state regulatory standards. Therefore, some form of environmental cleanup will be required for many of these properties. Due to the physical characteristics (particularly its density being greater than water) and the health-based risks associated with PCE, this contaminant and its degradation products have proven to be difficult and expensive to remediate.The case study documented herein involves a typical strip center property contaminated by a PCE release from a small dry cleaning operation located in Arlington, Texas. In our professional experience, the release history, subsurface conditions,contaminant types and concentrations at this site are typical of these properties in Texasas well as other states. Hydrogen Release Compound (HRC) developed by Regenesis offers a viable option for the remediation of groundwater at these PCE contaminated sites. Contaminant concentration and geochemical data clearly indicates that the injection of HRC at the subject dry cleaner facility greatly accelerated the reductive dechlorination of PCE and its degradation products and has allowed the site to achieve a Conditional Certificate of Completion from the Texas Natural Resource Conservation Commission (TNRCC) Voluntary Cleanup Program.

Case Study

Site Background and History. The site is located in Arlington, Texas and is approximately 7 acres and contains two one-story multi-tenant strip shopping centers constructed in 1979. A former dry cleaner was situated in the small suite and conducted dry cleaning operations on site between approximately 1982 and 1992.

Phase I and II Environmental Site Assessments were conducted at the site in 1996,and the site was admitted into the TNRCC Voluntary Cleanup Program in November of 1996. A release of an unknown amount of chlorinated solvents (apparently PCE) had occurred at the dry cleaners and had affected soil and groundwater beneath the site.Based on the results of these investigations, PCE and degradation products [trichloroethylene(TCE), cis-1,2,-dichloroethylene (cis-DCE), trans-1,2-DCE (trans-DCE), and vinyl chloride(VC)] were identified as the chemicals of concern (COCs) for the subsequent SiteInvestigation Report (SIR) and Conceptual Environmental Assessment Model (CEAM;i.e.,health-based risk assessment) required by the Voluntary Cleanup Program. The SIRand CEAM were completed in 1996 and 1997, respectively.

The SIR has documented the installation of 11 groundwater monitoring wells and 18 soil borings at the site. The CEAM was prepared to identify potential human health risks associated with the historic release and identified potential receptors (construction workers and on site commercial workers) and exposure pathways (inhalation of vapors and dermal contact with perched groundwater). The CEAM also established site target cleanup concentrations for soil and groundwater. Site target concentrations for groundwater are,asfollows: PCE (500 ug/L), TCE (500 ug/L), cis-DCE (7,000 ug/L), VC (200 ug/L). In the contaminant source area located directly beneath the dry cleaner’s building, the COCs had affected subsurface soils in excess of site target concentrations below the building foundation to a depth of approximately 8 feet (ft) [2.4 meters (m)] bgs. This source area was excavated [excavation size approximately 10 ft (3.0 m) by 10 ft (3.0 m)by 10 ft (3.0 m) deep] in 1998, and all soils exceeding site target concentrations were removed.

Removal of this highly contaminated soil, which was located in close proximity to and in contact with the shallow aquifer, was crucial to the overall success of this project, as a continuing source of contaminants to the shallow aquifer was permanently removed by excavation.

Site investigations revealed that the perched groundwater with COC concentrations above site target concentrations occupied an area of approximately 3,500 ft 2 (330.5 m 2) directly beneath and downgradient of the source area. Groundwater modeling performed in 1998 indicated that unassisted natural attenuation would require approximately 20 to 25 years to reduce contaminant concentrations at the site to target concentrations.

Geology and Hydrogeology. Topography in the site vicinity slopes very gently toward the north; however, the surface relief is probably not sufficiently pronounced to definitively affect shallow groundwater gradient. The site is located on the outcrop of the Eagleford Group (Bureau of Economic Geology, 1972). This formation is generallycharacterized as predominantly medium to dark gray shale which readily weathers to a thick, clayey soil horizon.Two TNRCC- designated aquifers exist beneath the Eagleford Group at the site; the
Woodbine and Trinity Aquifers (Texas Water Development Board, 1994). Thehydrogeologic setting is not considered sensitive based on the depth and distance to the recharge zones for these beneficial use aquifers. Shallow, perched groudwater in the site vicinity is definitely hydrologically separated from these deeper aquifers by aquicludes formed by unweathered shales of the Eagleford Group.

There is no known beneficial use of shallow, perched groundwater within a 0.5 mile (0.8 Km) radius of the site, and the total dissolved solids concentration is 3,170milligrams/liter (mg/l) in the shallow aquifer. encountered; commonly causing auger refusal at or near the top. Cores taken from this shale aquiclude had a vertical intrinsic permeability of approximately 7.72 X 10 -16 centimeters (cm 2). This layer effectively limits the vertical migration of contaminants. Water levels in the aquifer perched in the weathered clays above this aquiclude occur at approximately 4 to 7 ft (1.2 to 2.1 m) bgs at the site. Local groundwater gradient in this perched aquifer has consistently been toward the southeast in the vicinity of the on site
source area . Slug tests have demonstrated conclusively that this shallow aquiferhas a very low permeability and is not capable of producing 150 gallons/day [567.8 liters (l)/day] (TNRCC benchmark for consideration as a potentially beneficial use aquifer). This fact has allowed the application of the site specific target contaminant concentrations.

HRC Application

As an alternative to natural attenuation alone as a response action, injection of HRC]hydrogen elease release compound] material into the saturated zone was chosen as the means of enhancing and expediting the biodegradation process, thus reducing dissolved-phase COC concentrations more rapidly. Utilizing site specific geological, hydrogeological, and geochemical data in conjunction with software provided by Regenesis, it was estimated that approximately 7,000 pounds (3,171 kg) of HRC should be sufficient for achieving target concentrations at the site, and the time required to achieve target concentrations was estimated at two years or less.

The HRC was injected into the shallow aquifer near the source area at the site from May 1 through May 12, 2000, and a total of approximately 7,000 pounds (3,171 kg) of HRC was injected. The injection area [approximately 3,000 ft 2 (283 m 2)] encompassed the majority of the area with dissolved-phase COC concentrations greater than established target concentrations, which was estimated to be approximately 3,500 ft 2 (330.5 m 2)located beneath and southeast of the former dry cleaners suite. The HRC was injectedinto 45 injection borings within this area, and each boring was injected with HRC from approximately 7 ft to 22 ft in (2.1 to 6.7 m) depth. Twenty nine injection borings were advanced perpendicular to the ground surface, and 16 additional borings were advanced at angles of 15 and 30 degrees from vertical to extend beneath the building's
foundation. Each of the 45 injection borings were advanced using a Stratoprobe boring unit. A "top-down"injection system was utilized by advancing two ft (0.6 m) into the target interval and pumping the HRC material into the formation through a 2-ft (0.6 m) by 1.5-inch(3.81 cm) perforated injection body. The overlying interval was sealed off from the injection zone by a 2-ft (0.6 m) by 2-inch (5.1 cm) sealing packer, and the section below the perforated target interval was sealed by a 6-inch (15.2 cm) by 1.75-inch (4.4 cm) pre-probe.

After pumping the proportionate amount of HRC material [approximately 10 pounds (4.5 kg) per vertical, saturated foot] into the formation, the probe was driven another two feet (0.6 m) and the process repeated. The injection was accomplished by use of a hydraulically-powered, progressive cavity, Moyno pump with a flowrate of 1 to 2gallons per minute (3.8 to 7.8 liters per minute) at a pressure ranging from 200 to 300 lbs.per square in. (14.1 to 21.2 Kg per square cm). This method of injection, while a time consuming process, assures an even injection of the HRC material over the entire thickness of the target subsurface interval. We believe that this even HRC distribution is crucial to the success of the overall HRC injection project, particularly in low
permeability aquifers.HRC material costs were approximately $31,200. Direct push boring costs,concrete cutting and coring, site cleanup, field supervision, consulting oversight and design, and report writing costs were approximately $28,500. No future operating expenses, other than the expense of field collection and field and laboratory analysis of geochemical parameters, were anticipated as a result of the HRC injection.

Cost effective remediation of chlorinated solvents in groundwater is a significant challenge for retail dry cleaner facilities across the United States. The toxicity and distribution of the contaminants coupled with the proximity of nearby businesses and residential areas limits the applicability of many conventional groundwater remediation technologies. This paper presents results from a full scale, in situ groundwater remediation application at a Texas dry cleaner facility. Hydrogen Release Compound (HRC ®) was injected into groundwater to serve as a slow release electron donor in order to enhance the reductive dechlorination of the chlorinated solvents. Primary groundwater contaminants at the site include tetrachloroethylene (PCE),trichloroethylene (TCE), cis-1,2-dichloroethylene (cis-DCE), and vinyl chloride (VC).

Near the source area, groundwater contaminant concentrations for PCE (4,500micrograms/liter, ug/l), TCE (1,000 ug/l), cis-DCE (7,300 ug/l), and VC (870 ug/l) wererecorded in MW-3 immediately prior to HRC injection. The treatment area wasapproximately 3,000 square feet (ft 2) [283 square meters (m 2)] - a portion of which underlies the former dry cleaner's building foundation. In May of 2000, HRC was injected into 45 borings within the contaminated area. All 45 direct push borings were installed to approximately 22 ft (6.7 m) below ground surface (bgs), and the HRC was injected evenly over the interval from approximately 7 to 22 ft (2.1 to 6.7 m) bgs.Sixteen of the borings were installed at angles of 15 and 30 degrees from vertical in order to access contaminated groundwater beneath the building's foundation. A total of approximately 7,000 pounds [3,171 kilograms (Kg)] of HRC were injected at the site. HRC material costs were approximately $31,200. Direct push boring costs, concrete coring and cutting, site cleanup, field supervision, consulting oversight and design, and report writing costs were approximately $28,500. These one-time expenditures compare very favorably to the initial and recurrent operating costs anticipated for other remedial options. Approximately 18 months after HRC injection, PCE, TCE, cis-DCE, and VC levels had decreased to 408, 87, 438, and 132 ug/l, respectively. As of May 2001, all contaminant levels at the site were below site target concentrations established within the Texas Voluntary Cleanup Program.Injection of HRC into shallow aquifers utilizing direct push technology can be a cost effective remedial technology for dry cleaner facilities contaminated by PCE and its degradation products.

Contaminant and geochemical data presented from this case study of a dry cleaner facility in Arlington, Texas clearly demonstrate that the HRC injected into this shallow, perched aquifer aided in creating the requisite anaerobic subsurface environment and provided the hydrogen required for efficient reductive dechlorination which has significantly reduced contaminant concentrations within a year of application. As a direct result of HRC application, this site has received a Conditional Certificate of Completion from the TNRCC Voluntary Cleanup Program, as all contaminant concentrations are below site target concentrations.

The successful use of HRC is dependent upon its effective injection over the affected zone in the shallow aquifer. The "top-down" injection methods employed in this project achieved even subsurface distribution of the HRC over a 15 ft (4.6 m) interval in a very low permeability aquifer. Other, less stringent, methods will undoubtedly decrease required field time; however, poor treatment distribution can compromise the overall success of the injection project. Furthermore, removal of the source area contaminated soils (completed in 1998 by excavation under the dry cleaner's building) has also been important in the subsequent remedial success of this project. If allowed to remain in place, these highly contaminated source area soils provide a continuing source of contaminants leaching into the shallow aquifer.

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Chapter 9

ORGANIC COMPOUNDS NITROAROMATIC AND NITROAMINE COMPOUNDS (NACS)

Nitroaromatic and nitroamine compounds (NACs) are major groundwater and soil contaminants at military ammunition fabrication and demilitarization facilities. NACs in groundwater can disperse widely and undergo microbial transformation to additional hazardous products. A promising remedy is Fenton's reagent in-situ chemical oxidation (FRISCO). Fenton's reagent produces a hydroxyl free radical (OH•) by reaction of $H2O2$ and Fe(II). Oxidative systems (in addition to Fenton's reagent) that generate OH•($H2O2$/ozone, $H2O2$/UV, or ozone/UV) rapidly destroy NACs via side-chain oxidation and ring cleavage .
Fenton's reagent oxidation of 2,4-DNT generates intermediate products including 1,3-DNB, benzaldehyde, benzoic acid,and nitroaniline . Fenton's reagent oxidation of TNT and RDX in soil results in formation of NO 3-2and oxalic acid (from TNT), and ammonia, NO 3-2 formic acid, and methylene dinitramine (from RDX)
Formation of these compounds indicates that side-chain oxidation and ring cleavage also occur with Fenton's reagent. Fenton's reagent also oxidizes 2-A-4,6-DNT and 4-A-2,6-DNT (natural TNT degradation products) with rate constants approaching diffusion-controlled limits (>1.6 x 10 9 M -1 s -1)
The source of NACs in groundwater at PCD was a drainage ditch and leach bed at a former TNT Washout Facility and Discharge System. Contaminated soil from the leach bed, drainage ditch, and associated areas was removed in 1997-1998. A groundwater plume follows paleochannels and around a bedrock high The shallow aquifer is a heterogeneous deposit of sand with sporadic clay, silt, and gravel (eolian, alluvial and colluvial origin), which unconformably overlies Pierre Shale bedrock. Average hydraulic conductivity is 2 x 10 -2 cm/sec.
Two existing monitoring wells (TNTMW04 and CSPDPW171) were located in Area 1.
The depth to groundwater and bedrock were 3.4 m and 4.0 m, respectively. Area 1 had
the highest NAC concentration. Baseline samples yielded NACs (and their maximumconcentrations) as follows: TNB (1,160 ug/L), TNT (678 ug/L), 2-A-4,6-DNT (212ug/L), 4-A-2,6-DNT (164 ug/L), TNX (56.0 ug/L), 2,4-DNT (33.6 ug/L), 1,3-DNB (16.1ug/L), MNX (5.94 ug/L), RDX (4.90 ug/L), and HMX (1.51 ug/L). Soil sampling for preliminary bench tests detected TNT (1.73 mg/kg) and TNB (3.14 mg/kg) in soil. NO 3-2 in groundwater ranged from 1.9 to 15 mg/L.

Area 1. The field pilot test was conducted from September 6-7, 2000. Approximately 1,500 L of 25% $H2O2$ and 4,200 L of catalyst solution were injected to IW-1 and IW-2, and 2,700 L of 25% $H2O2$ and 5,800 L of catalyst were injected to IW-3.Groundwater pH, Fe, and H2O2 concentrations in monitoring wells adjacent to the injectors were analyzed to determine radius of influence (. The difference between potential and observed NO 3 -2 production represents destruction of soil-sorbed NACs.

The size of the treatment area was estimated at approximately 204 m 2 from the observed ROI and distribution of injectors. Assuming an aquifer thickness of 0.9 m and 30% porosity, the water volume within the treatment area was approximately 55,000 L.

The total injectate volume (H2O2 plus catalyst) was approximately 20,000 L, hence themaximum total volume over which the NO 3 -2 increase was integrated was 75,000 L. This is a minimum estimate that assumes that advection and dispersion were negligible.

The mean baseline concentration of total NACs was 888 ug/L, with weighted average nitrogen content (incorporating the contribution of each compound to the total NAC concentration) of 19.8%. The corresponding mass of nitrogen that could be produced by 100% mineralization of the dissolved explosives, therefore, is approximately 9.7 g (as N) or 43 g (as NO3 -). The mean total NAC concentration in the first post-test sampling event was 853 ug/L with weighted average nitrogen content of 19.2%.Incorporating the total volume of groundwater plus injected reagents (75,000 L), the corresponding mass within the treatment area is, therefore, 12 g (as N) or 54 g (as NO3 -). Thus there is a net negative NO 3 -2balance within the treatment area (i.e., post-test NO 3-2 mass is greater than pre-test mass), indicating release of NO 3-2from sources (e.g., soil-sorbed explosives) other than the dissolved NACs.

The average NO 3-2concentration was 5.8 mg/L prior to the pilot test and 34.3 mg/L during the first post-test sample round, for an average increase of 28.5 mg/L. A28.5 mg/L increase integrated through 55,000 L of groundwater yields a minimum production of 1.6 kg of NO 3-2. The maximum production for 75,000 L (groundwater plus injected reagents) corresponds to 2.1 kg of NO 3-2. Thus the increase in NO 3-2 concentration is far greater than expected from 100% mineralization of the dissolved NACs, further indicating that soil-sorbed NACs were oxidized during the pilot test.

TheNAC mineralized mass was estimated from the observed NO 3-2increase of 1.6-2.1 kg (equivalent to 0.4-0.5 kg as N). The weighted average nitrogen content of the dissolved NACs was 19.8%, thus approximately 2.0-2.5 kg of NACs were mineralized to generate the observed NO 32increase. The conclusion from the NO 3-2mass balance is that the observed NO 32increase is too large to be explained by mineralization of NACs in groundwater. Treatment must have also oxidized soil-sorbed explosives. 1,3-DNB is formed as an intermediate Fenton oxidation product of 2,4-DNT (and possibly other NACs) by side-chain oxidation). The concentration of 1,3-DNB in Area 1 groundwater increased following treatment , which could be interpreted as either an intermediate oxidation product or soil desorption. 1,3-DNB is not a known contaminant disposed at PCD, thus formation as an intermediate oxidation product is most likely. Theincrease in 1,3-DNB concentrations was, therefore, also used to estimate corresponding NAC destruction, assuming all of the1,3-DNB was a 2,4-DNT oxidation product. Theaverage concentration of 1,3-DNB in Area 1 groundwater during baseline sampling was4.1 ug/L. The average 1,3-DNB concentration in the first post-injection sampling round was 43 ug/L, for an average increase of 38.9 ug/L. Integrating a 38.9 ug/L increase through a 55,000-75,000 L treatment area volume yields an estimated 1,3-DNB mass increase of 2.1-2.9 kg. The formula weight of 1,3-DNB is 168.1 g per mole, thus the increased mass corresponds to production of 12.5-17.3 moles of 1,3-DNB. Assuming that 1,3-DNB is derived only from 2,4-DNT, then 12.5-17.3 moles of 2,4-DNT were oxidized. The formula weight of 2,4-DNT is 182.2 g per mole, thus 2.3-3.2 kg of 2,4-DNT were oxidized.

The estimate of NAC contaminant mass destruction from 1,3-DNB production has greater uncertainty than estimates derived from NO 32production, because more than one compound may produce 1,3-DNB as an oxidation product, the 1,3-DNB is itself subject to oxidation, and the possible pre-treatment presence in the soil-sorbed fraction is unknown. However, the large (10-fold) increase in 1,3-DNB during treatment, coupled with the known susceptibility of 1,3-DNB to Fenton reagent oxidation and production as an oxidation product, support the interpretation of 1,3-DNB formation as an intermediate product.

Significance for Explosives Remediation. The Area 1 results demonstrate that FRISCO is an effective remedy for dissolved RDX, HMX, 2-A-4,6-DNT, 4-A-2,6-DNT, 2,4-DNT,MNX, and TNX. Due to enhanced soil desorption, dissolved concentrations of strongly-sorbedNACs such as TNT and TNB may not decrease following treatment, despiteevidence (such as NO 32or 1,3-DNB production) of significant mass destruction.

Effectiveness of FRISCO cannot be evaluated from only dissolved NAC concentrations if a soil-sorbed phase exists. Such application requires evaluation of soil NAC concentrations and oxidation products to determine effectiveness. Soil-sorbed NACs will supply groundwater plumes as the NACs and their degradation products are slowly desorbed, and effectiveness of any groundwater remedy will be reduced if the soil-sorbed source is addressed. FRISCO can be applied as a source-area remedy to address soil-sorbed NACs. Coupling FRISCO with other technologies may also improve performance.

Increased desorption of TNB and TNT following FRISCO (in addition to the overall contaminant mass destruction) may enhance performance of existing pump-and-treat systems or other remediation technologies, thus reducing time and cost for site cleanup.

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Chapter 10

POLLUTION BY DNAPL [DENSE NONAQUEOUS PHASE LIQUID]

The Components Clean Facility (CCF) site at the National Aeronautics and Space Administration's (NASA's) Kennedy Space Center near Titusville, Florida was selected for this study. The CCF site encompasses nearly 17 acres and has been used since the early 1960's for cleaning and refurbishing of predominantly stainless steel hardware in support of space exploration operations. Cleaning operations typically included pre-cleaning of parts in ultrasonic vats and vats of cleaning agents (predominantly chlorinated solvents). The most prevalent solvents used at this facility have been 1,1,2 trichloro 1,2,2 trifluoroethane (Freon 113), as well as other freon products, and trichloroethene (TCE).

Obtaining direct evidence of DNAPL is difficult in the field. A field study was recently performed comparing several approaches to DNAPL characterization at a site where indirect and limited direct evidence of DNAPL exists.

The techniques evaluated included:a three-dimensional (3-D) high-resolution seismic survey, field screening of soil cores with a flame ionization detector (FID)/organic vapor analyzer (OVA), hydrophobic dye (Sudan IV)-impregnated reactive Flexible Liner Underground Technologies (Flute_)membrane used in combination with Rotasonic drill cores, centrifuged soil with Sudan IV dye, ultraviolet light (UV) fluorescence, a Geoprobe Membrane Interface Probe (MIP_), and phase equilibrium partitioning evaluations based on laboratory analysis of soil samples.

Sonic drilling provided continuous cores from which minor soil structures could be evaluated and the OVA provided reliable preliminary data for identifying likely DNAPL zones within the cores. The Flute_membrane provided direct evidence for the presence of DNAPL. The MIP_ probe provided rapid identification of probable DNAPL areas as well as soil conductivity data .

The 3-D seismic survey was of minimal benefit to this study and the centrifuging of samples with Sudan IV dye and the use of UV fluorescence provided no benefit. Results of phase equilibrium partitioning calculations to infer the presence of DNAPL were in good agreement with the site screening data.

CHLORINATED SOLVENT AND HEAVY METALS SOURCE

Site Description. The subject site is a former metal plating facility located within the boundaries of the South Mesa Water Quality Assurance Revolving Fund (Arizona State Superfund) Registry Site (SMWRS). In 1983, PCE was detected in an irrigation well located approximately 500 ft (152 m) downgradient of the site. This well was immediately taken off-line, though it was periodically sampled. This well was also operated as a containment pump-and treat well from 1994 to 1997, after which time the well was permanently taken off-line. In 1985, a sample collected from the irrigation well contained 780 mg/L of PCE. A second irrigation well, located approximately 1.5 mi (2.4 km) downgradient of the site, was also detected with PCE. Preliminary investigation, involving sampling of production wells and the installation of 10 monitoring wells,identified an approximate 1.5 mi long (2.4 km) by 0.5 mi (0.8 km) wide PCE groundwater plume apparently originating from the subject site site plan of the former metal plating facility. PCE and metal wastes were discharged to an on-site injection well from approximately 1979-1988. Other possible on-site sources of contamination were a septic system and leakage from processing equipment. While the metal plating facility was in operation, groundwater was as deep as 200 ft (61 m) bgs. However, due to decreased groundwater usage in the Effective source characterization is an important component in remedial alternative evaluation and selection. Arizona has unique hydrogeological conditions (deep groundwater, very dense and coarse sediments) that often result in dense non-aqueous phase liquids (DNAPL) released at source areas migrating several hundred feet vertically before they encounter a finer-grained interval that may impede or retard further migration. These conditions can make source characterization challenging and potentially costly. Characterization costs are a factor of drilling depth, number of samples collected and analyzed, and the number of monitoring wells installed. Therefore, the consultant must utilize innovative tools to reduce the number of borings that are drilled, the number of samples that are collected, and the number of wells that are installed while still collecting enough data to evaluate risks and remedial alternatives.Law Engineering and Environmental Services, Inc (LAW) is currently characterizing a deeply impacted chlorinated solvent and heavy metals source area and has utilized an innovative source characterization approach to minimize the number of borings and samples and thus costs. Data will be used to evaluate risks, determine achievable cleanup goals, and select/design potential future remedies.

REMEDIATION OF A DNAPL SOURCE ZONE AT CAPE CANAVERAL

To meet the objectives of this study, it is sufficient to estimate the overall mean TCE concentration across an entire test plot, rather than estimating TCE concentrations at various spatial locations within a test plot. In geostatistical terms, this is known as global estimation. One approach, and in fact the simplest approach, for calculating a global mean estimate is to calculate the simple arithmetic average (i.e., the equally weighted
average) across all available TCE concentrations measured within the plot. However, this approach is appropriate only in cases where no correlation is present in the measured data. Unfortunately, this is a rare situation in the environmental sciences.

A second approach, and the approach taken in this analysis, is to use a spatial statistical procedure called kriging to take account of spatial correlation when calculating the global average. Kriging is a statistical interpolation method for analyzing spatiallyvarying data. It is used to estimate TCE concentrations (or any other important parameter) on a dense grid of spatial locations covering the region of interest, or as a global average across the entire region. At each location, two values are calculated with the kriging procedure: the estimate of TCE concentration (mg/kg), and the standard error of the estimate (also in mg/kg). The standard error can be used to calculate confidence intervals or confidence bounds for the estimates. It should be noted that this calculation of confidence intervals and bounds also requires a serious distributional assumption, such as a normality assumption, which is typically more reasonable for global estimates than
for local estimates.

The kriging approach includes two primary analysis steps:

1. Estimate and model spatial correlations in the available monitoring data
using a semivariogram analysis.
2. Use the resulting semivariogram model and the available monitoring data
to interpolate (i.e., estimate) TCE values at unsampled locations; calculate
the statistical standard error associated with each estimated value. This paper presents the
results of a statistical analysis of data collected
before and after remediation of trichloroethylene (TCE) in subsurface soil at Cape Canaveral, Florida. The primary objective of this analysis was to determine whether different remediation alternatives were effective at significantly reducing TCE in soil.

The geostatistical analysis approach was to utilize kriging, a statistical spatial interpolation procedure, to estimate the overall average TCE concentration in soil before and after remediation, and then determine if those concentrations were significantly different.approach

THE ROLE OF MICROORGANISMS ON DNAPL INTERFACIAL PROPERTIES AND TRANSPORT

PCE (tetrachloroethene) is a chlorinated solvent and suspected carcinogen, and is also a contaminant frequently present in groundwater. As a dense nonaqueous phase liquid(DNAPL), PCE migrates with relative ease through regions of high conductivity in the subsurface. However, regions of lower conductivity (smaller pore spaces) inhibit migration of PCE. It has also been observed that once regions of low conductivity are occupied by PCE, it becomes very difficult to extract from these smaller pore spaces.The overall distribution and migration of DNAPLs in a natural system is affected by a number of variables. The most critical of these variables include the complexities of the porous matrix, and the corresponding interfacial properties of this matrix. These proper-ties affect the capillary forces that define fluid and solid phase interactions, and ulti-mately the DNAPL migration.

Microorganisms have been observed to affect such interfacial properties in aerobic systems through the production of biosurfactants (Dohse and Lion, 1994). The goal of this research is to define the role of anaerobic microorganisms on PCE migration and interfacial properties in the subsurface. Research has shown that anaerobic microorgan-isms can survive in PCE-contaminated environments, and furthermore have the ability to reductively dechlorinate tetrachloroethene completely to ethene. Such organisms have the ability to derive energy directly from PCE dechlorination, using it as a respiratory electron acceptor (Gossett et al., 1997). These organisms were chosen for their obvious
ability to survive and even thrive at PCE concentrations toxic to most organisms. Research has shown that a number of organisms have the ability to an-aerobically dechlorinate PCE and other chlorinated solvents However, the extent to which the presence of these organisms affects the interfacial properties and mobility of the DNAPL is largely unknown. Conversely, aerobic organisms have been studied and observed to change their adhesion properties, and to also produce extracellular compounds, or biosurfactants, under stressed conditions . The environmental conditions of anaerobic PCE-degrading cultures have been varied in an attempt to either stimulate similar changes in adhesion properties, or stimulate biosurfactant production. Either of these mechanisms may significantly impact the interfacial properties of PCE, thereby increasing its effective mobility in the subsurface. To date, research has shown that culture media ionic strength, nitrogen concentrations, and varying carbon sources have little effect on these mechanisms. However, it has been observed that extremely high concentrations of PCE, as well as the presence of low concentrations of DO, may have a significant impact on the properties of the organisms, thereby affecting the interfacial properties of the DNAPL, and its mobility.

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Chapter 11

CONSTRUCTED WETLAND FOR WATER TREATMENT

Case Study-Treating Wastewater From Dairy Parlors

During the 1970s-80s in Italy, among constructed wetland systems used in the livestock production sector, attention was focussed primarily on surface flow systems, in which floating macrophytes such as duckweed (Lemna spp.) or water hyacinth (Eichhornia crassipes) were grown over broad surfaces submerged by wastewater, also those particularly rich in organic substance and nutrients The hope was to accumulate energy and large quantities of nutrients in the plants, whose biomass could be profitably reused for energy purposes (methane fermentation) or for animal feed;unfortunately this was not possible due to operational difficulties and unsustainable costs.Over the last ten years, there has been increasing use of subsurface flow systems for treatment of municipal wastewater of small villages that are far from the sewage mains (These systems consist of wetlands impermeabilised and filled with inert material of different particle size (crushed stone, gravel, sand), on which plants are grown, such as reed (Phragmites), cattail (Typha), and rush (Scirpus).This type of system can be constructed so that the wastewater to be treated runs through the filling substrate in a direction that is prevalently horizontal (SFS-h) or prevalently vertical (SFS-v). While in the former case the movement of the wastewater is more or less continuous, in vertical flow wetlands it is intermittent, and therefore the bed can be periodically re-oxygenated, with important implications on the purification processes that take place there.

On livestock farms, as other experiences have demonstrated, the application of subsurface flow systems can only be conceived for wastewater with a lower load of organic matter and nutrients, similar to municipal wastewater, as are those deriving from washings of the milking areas not trod on by the cows In the dairy sector, loose housing barn with the milking operation in a dedicated parlour has become more and more common. This operation gives rise to considerable volumes of wastewater with a low content of fertilising elements, for which storage and spreading along with other livestock effluents are problematic and uneconomic. For this type of wastewater, it could be more appropriate the use of purification treatments which, in respect to the laws parameters, enable wastewater re-use or disposal in the sewage systems or in surface waters. Due to its low environmental impact, reduced or nil energy consumption, and simplicity of operation, the technique of horizontal subsurface flow constructed wetland may constitute an interesting solution While in the tie-stall barn the quantity of wastewater produced during milking operations normally does not exceed 10-15

L/day per lactating cow (washing of the pipes, milking units, and milk room), in loose housing barn the production of wastewater is generally higher. In fact, in addition to the washing water of the milking system and the milk room, wastewaters deriving from the holding area and the milking parlour must be considered.Optimising the sizing of the various areas as well as the washing operations and water consumption, it would be reasonable to estimate wastewater production in the milking center of 50-55 L/day per cow under production, which tends to decrease when the herd size increases (Rossi and Betti, 1999).

Methods

A demonstration horizontal subsurface flow constructed wetland was set up at the Santa Lucia farm in Casina (682 m a.s.l., province of Reggio Emilia, Italy) in 1999. The wetland treats the wastewater coming from the washing of the milking pit, stalls, milking system, and bulk milk tank of a milking center with a herring-bone parlour with 5+5stalls. The system was sized considering the presence of 80 lactating cows and the opportunity to include in the treatment the domestic sewage coming from farm inhabitants.

Plant Description. The plant (is essentially composed of: (1) a well for inspection of the inflowing wastewater to the plant; (2) an Imhoff type septic tank and a plastic filter for the removal of sedimentable suspended solids; (3) two SFS-h constructed wetlands (reed beds) parallel to each other, sizing 12 x 6 x 1 m each, and planted with reed (Phragmites australis); (4) wells at the outflow of the reed beds; (5) a system for recirculation of the waters coming out of the wetlands.Immediately upstream from the area of the reed beds, a drainage channel filled with gravel was built to collect the rainwater run-off that could flow into the two wetlands from the surrounding areas. The bottom of the two reed beds was suitably impermeabilised using a synthetic covering in PVC protected on both ends with geotextile. One wetland was filled with washed pea gravel of 3-6 mm diameter, and the other with washed gravel of 8-12 mm diameter. Near the wastewater inflow and outflow points of both beds a layer of coarse gravel (diameter 8-35mm) was put to favour the flow of water at the bottom of each section. Perforated tubes for inspecting the water flow that crosses each of the two beds were placed vertically at 1/4, halfway, and 3/4 of the length of each wetland. The homogeneous distribution of the wastewater at the head of each wetland is guaranteed by special channels whose discharge points onto the gravel beds can be regulated separately. The height of the wastewater outflow pipes in the wells at the outflow of the reed beds can be regulated; also the water level inside each reed bed can be controlled. The recirculation system includes a centrifugal pump with a float that makes it possible to redirect the outgoing wastewater from one wetland to another through a plastic pipe.

A minimal colonisation by weeds (Solanum nigrum, Taraxacum officinale, Rumex conglomeratus, Populus nigra, Salix caprea, Anagallis arvensis) occurred, and no intervention of any type was necessary for controlling them.

Results and discussion

The average values and the range of fluctuation for each of the parameters measured at the inflow and outflow of the plant (sampling points 1 and 5), the average percentage reductions found and, for purposes of comparison, the limits of the current regional laws of the Emilia-Romagna Region for discharging these wastewater into the surface water (Table III Regional Law no. 7 of 29 January 1983).

Although the organic and nutrient load of the wastewater flowing into the plant are higher than those of the typical municipal wastewater, the percentages of removal obtained with the whole system are high, allowing to respect the regional limits imposed by the legislation.

For the first reed bed, the cleaning efficiency was greater than for the second bed. The total reduction of suspended solids and organic load was consistently maintained at levels above 90%; those of the nutrients nitrogen and phosphorous were over 40% and 50%, respectively.

The comparison between the first period of operation, spring-summer, and the second, autumn-winter, made it possible to verify the increase in purification capacities of the second reed bed, probably due to the progressive plant and microbial colonisation, which occurred with a certain delay with respect to the first one (not shown). During the autumn-winter period, this condition, as well, made it possible to keep at high levels the overall purification capability of the plant.(*) Values calculated as weighted average according to the incidence of the type of wastewater sampled (domestic, from milking, from washings) on the total inflow value.

The evolution of the concentrations of the various forms of nitrogen through the constructed wetland highlights conditions of diffuse anoxia that do not allow significant nitrification inside the wetlands; this phenomenon happened despite the fact that there were good levels of mineralisation of the organic nitrogen and elimination of total nitrogen.

In the second year, the reduction percentages for COD, BOD, TSS, total N, total P attained the same levels of the first year (data not shown).

The data collected on the development of Phragmites australis showed uniform propagation of the reeds and greater biomass of the epigeal and radical parts, especially in the first bed This is probably due to the larger amount of nutrients reaching the first wetland with respect to the second. n the search for mycorrhizae, only endomycorrhizae were identified, with a clear prevalence of vesicular over arbuscular, without, however, significant differences between the two reed beds (not shown).

Considering the results of the analyses of copper and zinc, with total concentration levels in the plants (culms + rhizomes + roots) in wetlands 1 and 2, respectively, of 10.9 and 6.1 mg/m^2 for copper and 62.7 and 17.8 mg/m^2 for zinc, it was possible to conclude that the two metals were accumulated more by the reeds of the first wetland. Moreover, it can be argued that insignificant percentages (0.5-1%) were assimilated in the plant tissues with respect to the quantity of metals on entry to the wetland from the beginning of the vegetative period.

Microanalysis with SEM/EDX has been carried out on root, rhizome and culm samples. Typically, the most abundant elements in all plant tissues are K, Ca and P. Dot maps of element localization (data not shown) illustrate an interesting feature of

Phragmites roots: Fe accumulates at the surface of the periderm, creating a sort of plaque due to oxidation. Tanton and Crowdy (1971) and Peverly et al. (1995) report that this plaque of Fe oxide would determine the accumulation of other metals, such as Cu and Pb,acting as a barrier and preventing their entry into plant tissues. Semiquantitative analyses carried out on cells within plant tissues evidenced that Si is very abundant in the periderm of roots and rhizomes. On the contrary, Ca, P and K are particularly abundant in parenchymatic cells. Cr, Cu, Ni and Pb are more concentrated in ipogeal parts as compared with culms, without specific tissue localization.

A comparison between plants from the two lagoons did not evidence significant differences in the distribution of elements among tissues. Pb was significantly higher in plants from the first lagoon,whereas Cr, K and P were higher in plants from the second one.

Conclusions

Over the last several years, the rediscovery of the environmental qualities of constructed wetland systems have favoured their rapid diffusion, with applications aimed mainly at the treatment of municipal wastewater (Pergetti et al, 1995).

In the livestock production sector, constructed wetland systems can find application in the treatment of wastewater produced during milking operations in the parlour, offering a solution to the problem, still often unresolved, of correct disposal of these wastewater with acceptable costs (such systems can be created for the most part with on-farm work). In perspective, the widespread application of this clean up technique could also respond to the problem of domestic sewage from rural dwellings not connected to the public sewage mains and situated on and/or near farms, particularly on the hills or in mountain zones.

A constructed wetland consisting in two horizontal sub-surface flow beds to treat dairy parlor wastewater and domestic sewage was built in a mountain agricultural settlement in Northern Italy. The beds were planted with Phragmites australis. Wastewater inflows and outflows were sampled throughout two years of the trial. The efficacy of the wetlands was maintained also during the winter months. The wetland operation brought to significant reduction in BOD5, COD, nitrogen, copper and zinc.SEM/EDX analyses evidenced the precipitation of iron on the outside surface of the root,reported to be acting as a barrier towards uptake of other metals.

The creation of the horizontal subsurface flow constructed wetland operating on the wastewater of the Santa Lucia farm not only serves as a demonstration plant but also velops a technique that is well-known though rarely applied to wastewater of this type.

This, along with the monitoring of the operating conditions and the purification performance of the plant, has provided important indications, in particular regarding the most suitable criteria of design, construction, and management of constructed wetland systems serving dairy cattle farms equipped with milking parlours.

The plant monitoring allowed to verify good purification performance, with high percentages of pollutant removal.

The application of SEM/EDX lead to the identification of the heavy metals and macronutrients distribution in plant organs and tissues. These data can help to understand the role of Phragmites in the wastewater clean up process.

What is yet to be verified are the possible applications of this treatment scheme in other important production sectors, first of all that of the agro-food industry related to milk production (wastewater from cheese-making) (Ferrari and Piccinini, 1989), and the possible system developments that could lead to an improvement in purification efficiency (vertical flow).

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CHAPTER 12

REMEDIATION OF METAL-CONTAMINATED GROUNDWATER USING APATITE

For several years MSE Technology Applications, Inc. has studied the material ApatiteII™ (Patent Number 6,217.775; PIMS NW, Inc.; Drs James Conca and Judith Wright, developers) for the removal of metals, metalloids and radionuclides. Apatite II™ is a form of apatite that appears to have higher reactivity than natural apatite and is lower cost than commercially available bone char. ApatiteII™ is very effective in removing uranium. Several mechanisms for uranium removal by apatite are possible: uranium exchange for the calcium anions in the apatite matrix, non-specific adsorption to the apatite material, or the dissolution of apatite will create condi-tions at the boundary layer that exceed the Ksp for autunite (Ca(UO2)2(PO4)2 _ 10H2O) and this U-bearing crystalline phase will form. Laboratory batch studies observed the presence of meta-autunite (Ca(UO2)2(PO4)2 _ 6H2O) within the apatite material, suggesting the formation of autunite. Meta-autunite formation was due to the drying step before analysis by X-ray Powder Diffraction.Additionally, investigated the removal of soluble cadmium from syn-thetic and authentic contaminated groundwater. Cadmium removal by apatite is probably due to one or all of three mechanisms: ion exchange, nonspecific adsorption, and pre-cipitation of cadmium phosphate minerals. Previous studies have observed a cadmium phosphate mineral, otavite. However, the removal of cadmium only occurs at about 5 wt.% of the apatite added, as opposed to 10 to 20 wt.% in the case of uranium and lead. initial studies with this material showed that uranium was rapidly removed from solution in batch shake flasks. Bacterial growth was associated with the incubation of this material at room temperature however, sterilized controls vs. unsterilized flasks did not show significant difference in the rate of uranium uptake by the apatite. Subse-quently, batch studies were undertaken to determine whether surface area had an effect on uranium removal. Previous studies had used a very fine (surface area = 2.75 m 2 /g) powdered apatite that would not be as easily implemented in a canister or barrier situationin the field. Various crushed sizes were tested and it was shown that for the range tested (0.425 to 4.75 mm) there was no significant difference in the rate of uranium uptake.The object of these studies was to follow up the batch studies with column studies to determine if the apatite material could be used in permeable reactive barrier systems or canister type configurations for removal of uranium and cadmium from contaminated groundwater

Most recently we have begun studies to determine if apatite can be added in a soil-mixing scenario to remove metals from contaminated soils. Batch and column studies have been performed by MSE to determine the efficacy of metal cation removal from aqueous solutions by an organic apatite material. results have shown that the Apatite II™ media rapidly removes uranium ($C0=5$mg/L) from solution to below detection levels, and moderately removes cadmium.

The mechanism of uranium removal appears to be by reprecipitation as the uranium phosphate autunite. Cadmium removal appears to be via several mechanisms including adsorption and phosphate mineral precipitation. Currently, a soil-mixing study is being carried out to test immobilization of metal cations in contaminated soils.

HEAVY METAL REMOVAL BY ZERO-VALENT IRON

Zero-valent iron Fe(0) has been investigated as a potential remediation agent for the removal of a whole series of heavy metals. Possible removal mechanisms, depending on the metal of interest, are reduction, cementation, surface complexation and (co)precipitation The basis for any of these reactions is the corrosion of iron. The first corrosion product is amorphous ferrous hydroxide, which is predicted thermodynamically to convert to magnetite ($Fe3O4$) . Mixed valent iron salts, known as green rusts may also form. Their subsequent oxidation can lead to the formation of magnetite, maghemite, goethite and lepidocrocite . As a result of these reactions, the iron surface is coated by a layer of iron oxides and oxyhydroxides, similar to natural oxide solid phases, where heavy metals may interact.The chemistry of metal ions in natural waters strongly depends on the formation of complexes. Complexes reduce the concentration of the free metal species in solution, and affect the solubility, the toxicity, and the mobility of the metal . Polluted groundwaters, especially in the case of landfill leachate contaminated groundwater, contain elevated concentrations of inorganic and organic ligands. Three possible scenarios in aqueous systems containing both humic acids and heavy metals, in contact with hematite. Firstly, the binding of humic acids to the oxide surface may block the binding sites and compete with metal removal. Alternatively, complexes between metals and humic acids may remain in solution and prevent the metal from adsorbing to the oxide. Thirdly, metal adsorption can be enhanced by the formation of ternary humic acids-metal-surface complexes. The enhanced metal binding can result from the adsorption of metal-humic acid complexes, or through metal complexation by the sorbed humic acids. The overall effect from addition of humic acids on metal binding depends on the stability of the numerous interactions involved.

The results of this study indicate that zero-valent iron is a promising reactive agent for the in-situ removal of mixed heavy metals (i.e. Ni, Zn and Cr(VI)) from contaminated groundwater. Humic substances bind heavy metals and influence their fate and mobility. We found that humic acids formed metal-humate complexes remaining in solution, which prevented the removal of Zn and Ni in batch kinetic experiments.Chromate removal was not affected. Sorption of humic acids to the iron surface hindered the metal removal reactions in a longer-term column test, especially for Ni, probably through blocking of reactive sites.

Humic acids impact the efficiency and lifetime of a reactive iron barrier for in-situ

removal of heavy metals.
The presence of dissolved organic matter in groundwater should therefore be considered in the design of a permeable barrier.A laboratory study was set-up to investigate the effects of Aldrich humic acids on the removal of zinc, nickel and chromate in zero-valent iron systems. The rate and the extent of zinc and nickel removal were negatively impacted by the presence of the humic acids in batch kinetic experiments. Chromate removal was not affected. It was hypothesized that the formation of humic acid–heavy metal complexes prevented the removal reactions at the iron surface. Two parallel column systems were set-up with the mixed heavy metals (5 mg/l each). The first system acted as reference without humic acids, while the second system was fed with humic acids (20 mg/l). Both column systems efficiently (> 90%) removed the heavy metal mixture during the first 27 weeks. When the input heavy metal concentration was increased to 8-10 mg/l, a significant breakthrough of nickel and zinc occurred in the column system with humic acids. Conversely, chromate and humic acids did not significantly break through. The accumulated humic acids on theiron surface (approx. 5 mg/g) probably hindered the nickel and zinc removal. After 60 weeks, the effect of humic acids on leaching of the accumulated metals (approx. 2 mg/g) was investigated. No significant leaching was observed. The results of present study indicate that the impact of dissolved organic matter on the efficiency and lifetime of a reactive iron barrier for in-situ removal of heavy metals should be considered in the design of the barrier.

Chapter 13

CARBONS PREPARED FROM BAMBOO

Most bamboos contain large amounts of ligneous fiber and can therefore be carbonized into chars, which can be used in decoration, in purifying drinking water, for indoor air filtering, dehumidifying, thermal insulation, electromagnetic wave shielding, etc. However, bamboo is rarely used as the raw material for activated carbon. Meso bamboo is grown profusely in Taiwan. Its stem diameter can reach up to 15 cm. In earlier days, it was commonly used for building, furniture, eating and cooking utensils, foods, and food processes. Lately, there only use that seems to have remained, is that of using bamboo shoots for food. It is regrettable that the mature bamboo does not seem to have many uses any more. Since the utility value of bamboo has greatly dropped, bamboo-growing has mostly been abandoned reducing the number of plants. The reduction in the number of bamboos grown has caused severe ecological damage to the environment and to water-soil conservation.

Bamboo grows fast, absorbing, CO2 from the atmosphere at great speed, so it effectively helps to slow down global greenhouse effect. In previous studies, oak, bamboo, coconut shell, and cedar were activated with steam to obtain activated carbons. The results showed that physical properties (BET surface area and pore volume) and adsorption capacities (chloroform adsorption) of the activated carbons derived from bamboo were lower than those from the other three raw materials Furthermore, studies have shown that of the carbons derived from bamboo dust, coconut shells, groundnut shells, rice husks, and straw, straw carbonhas the highest adsorption capacity being 5.9 times that of bamboo dust carbon, which is the lowest . From this evidence it is clear that it is not easy to make good activated carbon from bamboo. The aim was to prepare porous carbons from Meso bamboo using KOH etching and CO2 gasification processes. The physical properties of the carbons, namely the BET surface area, pore size distribution, and the total pore volume were compared. Their capacities for the adsorption of basic blue 1, methylene blue, p-cresol, p-chlorophenol, p-nitrophenol, and phenol from water were systematically investigated.

1. Meso bamboo char was removed, crushed, and sieved to a uniform size ranging from 0.83 to 1.65 mm. These powders were well mixed with water and KOH in stainless steel beakers with water/KOH/char weight Meso bamboo was first carbonized for 1.5 h at 450 o C, then soaked in KOH solutions with KOH/char ratios of 0.5, 1, 2, and 3. Three kinds of activation processes, no, low, and high CO2, were used. Carbons activated under high CO2 conditions exhibited high BET surface areas ranging from 1627 to 2444 m 2 g -1 .

The adsorption of methylene blue, basic brown 1, p-nitrophenol, p-chlorophenol, p-cresol and phenol from water at 30 o C on the activated carbons was studied. All adsorption equilibrium isotherms were in agreement with the Langmuir equation, and were used to compare the adsorption of covered areas (Sc/Sp) of the activated carbons with the different combinations of CO2 gasification and KOH/char ratios. In this research, activated carbons with high surface area were obtained from Meso bamboo having excellent adsorption capacity for dyes and phenols ratios of 1/0.5/1, 1/1/1, 2/2/1, and 2/3/1.

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Effect of humic acids on heavy metal removal by zero-valent iron

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Competitive sorption and desorption of phenols in surfactant-modified clays, *Won Sik Shin* and Young Kyu Kim, Ji-Hoon Kim, Young-HunKim, Young Woong Jeon and Dong-Ik Song

Adsorption of dyes and phenols onto high surface Area carbons prepared from bamboo using koh Etching and co2 gasification,Feng-chin wu, wei-feng chang ru-ling tseng

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CHAPTER 14

BIOREMEDIATION OF PERCHLORATE-CONTAMINATED GROUNDWATER

Perchlorate, an oxyanion extensively used by the aerospace industry in the production of solid rocket fuel, potentially contaminates the drinking water of 12 million people in the United States Even at concentrations in the low part-per-billion range, perchlorate is suspected of affecting hormone production in humans Current methods of remediating perchlorate-contaminated groundwater involve extracting the groundwater and treating it above ground. In situ remediation of perchlorate (that is, remediation that occurs in place, without the need to pump perchlorate-contaminated groundwater to the surface) has the potential for large cost and safety benefits.

In this study, a model for in situ biodegradation of perchlorate in an aquifer in which horizontal flow treatment wells (HFTWs) are used to mix an electron donor into perchlorate-contaminated groundwater to stimulate perchlorate reduction by indigenous microorganisms.

HFTWs have been used effectively for the in situ remediation of chlorinated ethene-contaminated groundwater, and their potential applications have been the subject of a number of studies For example, McCarty et a*l*. (1998) demonstrated that trichloroethene (TCE) could be successfully destroyed in situ using a pair of HFTWs to inject toluene and oxygen into contaminated groundwater at Edwards Air Force Base, CA. The in situ addition of these compounds stimulated cometabolic destruction of TCE by indigenous toluene-oxidizing bacteria.), which depicts an operating concept similar to that applied at the Edwards site, shows a dual screened treatment well pumping in a downflow mode alongside a treatment well pumping in an upflow mode. In the upflow treatment well, water is extracted through the lower screen and reinjected through the upper screen. The flow path is reversed in the downflow well. In the aquifer around the injection screens, bioactive zones form where indigenous bacteria degrade the target contaminant. As shown in Figure 1 (right), the pattern of recirculation created by the HFTW system results in multiple passes of the contaminated groundwater through the bioactive zones. This recirculation, which can be adjusted by modifying the pumping rates in the well pairs, significantly increases the effectiveness of the treatment process. In addition to providing high levels of treatment, HFTWs also reduce risk and costs by treating contaminants in the subsurface, without the need to pump contaminant aboveground.

METHODOLOGY

The model developed during this project simulates advective/dispersive transport of the electron donor (acetate, in this case), perchlorate, and competing electron acceptors (oxygen and nitrate) in the groundwater flow field induced by operation of the HFTW well pair. Microorganisms are assumed to be immobile. The rate of perchlorate reduction is modeled using Monod kinetics, with the rate dependent on both perchlorate and electron donor concentrations. The presence of competing electron acceptors (oxygen and nitrate) serves to decrease the rate of perchlorate reduction. This is modeled using an inhibition coefficient that slows the rate of nitrate reduction if oxygen is present and slows the rate of perchlorate reduction if either oxygen or nitrate are present. The rate of microbial growth is a result of the consumption of the growth substrate (electron donor) less biomass decay, which is modeled as a first-order decay process. The biodegradation model was developed through the Strategic

Environmental Research and Development
Program (SERDP Project CU-1163). Kinetic parameters for the model were estimated using batch and column studies in the laboratory .A finite difference code was implemented that solves the partial differential equations describing steady-state flow, electron donor and acceptor transport, and reduction of the acceptors by microorganisms that use the electron donor for growth and energy, as described above. By solving these equations for given initial and boundary conditions, the code estimates concentration of donor, acceptors, and biomass at any Groundwater contamination by perchlorate has been recognized as a significant environmental problem across the United States.

In this study, a numerical model was developed to evaluate the potential for an innovative in situ bioremediation
technology, horizontal flow treatment wells (HFTWs), to manage perchlorate-contaminated groundwater. The HFTW technology employs paired, dual-screened injection and extraction wells to distribute and mix an electron donor into perchlorate-contaminated groundwater. The HFTW delivery system is designed to promote the reduction of perchlorate by indigenous microorganisms in subsurface bioactive zones, as well as to recirculate the contaminated water between treatment well pairs to achieve multiple passes of contaminated water through the bioactive zones. The numerical model used in this study couples a three-dimensional fate and transport model, which simulates advective/dispersive transport of solutes induced by regional groundwater flow and operation of the HFTWs, with a biodegradation model that simulates perchlorate reduction, and the reduction of competing electron acceptors, by indigenous microorganisms. The model was applied to an example site to demonstrate how in situ perchlorate biotreatment might be implemented in the field. A sensitivity analysis using the model was also conducted to evaluate which engineered and environmental parameters most affect technology performance. Model simulation results demonstrate that this technology is potentially an effective approach for delivering electron donor and stimulating perchlorate biodegradation in contaminated groundwater. The recirculation induced by the HFTW system results in increased treatment efficiency, as compared to treatment that would be achieved by a single pass of contaminated water through a bioactive zone. The model presented in this study is an important tool that may be used to design field evaluations of the technology and ultimately to help transition the technology for commercial application at sites with perchlorate-contaminated groundwater.

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Modeling In Situ Bioremediation Of Perchlorate-Contaminated Groundwater

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CHAPTER 15

PHYTOREMEDIATION OF INDUSTRIAL WASTEWATER

Water is one of the ultimate sinks for various pollutants. The domestic and industrial wastes are discharged in surface water bodies in increasing quantities beyond the natural treatment/buffering potential of fresh water. These wastes include large quantities of organic matter, inorganic nutrients, heavy metals and a variety of organic chemicals, all of which not only lower the water quality but also are toxic to living organisms. Heavy metal pollution of natural water resources is a major environmental problem faced by the modern world. The disposal of heavy metal rich effluents/sewage poses a problem to every large and small scale industry in the country. Several physical, chemical, and biological methods are employed by various industries for waste water treatment such as ion exchange, use of resins, electrodeposition, reverse osmosis etc, but these techniques are much sophisticated and at times costly too, and can not be taken up by small scale/low budget industries. High capital and regeneration cost in these technologies have resulted in increasing search for low cost and efficient systems. Modern researches are emphasizing a shift towards clean, ecofriendly environment, low cost and efficient technology Treatment of effluents/sewage is necessary to bring the concentration of toxic metals to desirable limits before they are discharged or utilized. Recently there has been some research in the use of living and non-living bacteria and algae for the bioremedation and recovery of heavy metals from aqueous streams

In addition, live or dead cultured cells of *Datura innoxi*a, a higher plant can be used to remove Ba +2 from solutions Commercial application of this research is hampered by the high cost of growing pure cultures of cells and microorganisms and by the need of their immobilization or separation from the aqueous stream . The phytoremedation concept is based on the well known ability of plants and their associated medium to concentrate and/or degrade higher contaminants. These have capability of bioaccumulation. Aquatic plants have the capability to move large amounts of solution in to the plant body through the root and evaporate this water out through transpiration. Nutrients move along with the water uptake. These plants consume a large range of contaminants, mobilize them and accumulate them in the body. The process of bioaccumulation enable the plants to concentrate the toxicant thousand time higher in them than in the soil or waste water. Such plant biomass can further be ashed to reduce its volume and the resulting small volume of material can be processed as an “ore” to recover the contaminant. If recycling the metals is not economically feasible, the relative small amount of ash could be used as a fertilizer in nutrient deficient soils or can be disposed off in an appropriate manner. In case of aquatic plants a regular harvesting can be done and, biomass can be used for making pulp and further processed, for small scale hand paper industries or can also be used for biogas generation.

Phytoremediation is the process of the removal of hazardous substances from soil or ground water contaminated with municipal and industrial wastes by plants. In a study, phytoremediation of copper (Cu), Zinc (Zn) and Iron (Fe) was observed.The purpose of the research work was to remove copper, iron and zinc from industrial wastewater (effluent) by aquatic plants. Aquatic plants have been regarded biofilters and purifiers of small and large water bodies. They are capable of accumulating various contaminants to a concentration several order of magnitude higher than in the surrounding medium. The need for better and efficient system for remediation of wastewater led to the present investigation.

An attempt to use few aquatic weeds for wastewater remediation was made.Aquatic higher plants eg. Water hyacinth *(Eichhornia crassipe*s) Water velvet *(Azolla pinnat*a) and *(Lemna mino*r). Have also been regarded as bio-filters and purifiers of ponds and lakes.

Owing to the importance of aquatic plants in the present study an attempt to evaluate the potential for removal of heavy metals from effluents by different aquatic plants, was made. In macrophyte based system shallow ponds, the water flow as surface, or as subsurface. The pollutants are reduced by a complex variety of physical, chemical and biological processes . The macrophytes remove pollutants by;

1. Directly assimilating them into their tissue and
2. Providing surface and suitable environment for microorganism to transform pollutants and reduce their concentration. Oxygen transfer by aquatic plants into the rhizosphere is also a requirement for certain microbial pollutant removing processes to function effectively .In the present study all the test plants that were selected did show a significant removal ability for various heavy metals (Graph: 6-8). The response of various aquatic plant species to different effluent concentration varied. All the plants studied were effective in the effluent treatment, but best resultswere obtained only at lower concentration (10 to 25%). At higher dilution trough the plants could manage to reduce the contamination load but their growth retarted to a great extent. All the test plants showed their differential uptake and were efficient enough to remove considerable amount metals.

The heavy metals Fe and Zn were found to be accumulated more in *Hydrodictyon reticulat*a, followed by *Wolffia arrhiza* than *Hydrilla verticillat*a. While for Cu, Hydrillawas more effective. All the plants efficiently removed Fe even at 50% effluent dilution, suggesting of its low toxicity. Waste water (effluent) pH, after treatment with plants in all the cases shifted towards alkalinity, which is evident from the decrease in chloride ions. The total dissolved solids decreased significantly in *Hydrilla verticillata* and *Wolffi*a, followed by *Hydrodictyon reticulata* sets. The alkalinity also increased after phytoremedation treatment with maximum increase in *Hydrilla* followed by *Wolffia* and *Hydrodictyon*). The chloride removal was observed in all the plant sets, and the trend was maximum in *Hydrill*a, *Wolffia* and *Hydrodictyon.*The important parameter like oxygen content in the waste-water was found to increase with phytoremedation treatment, the dissolved oxygen of higher dilution after treatment increased significantly. The change in DO was maximum in *Hydrodictyon reticulata* followed by *Wolffia arrhiza* and *Hydrilla verticillata* at 10% effluent concentration . The chemical oxygen demand (COD) reduced significantly in *Hydrodictyon reticulata* treated sets and efficiently followed by the *Wolffia* and *Hydrilla.* It was interesting to note that *Hydrodictyon reticulata* could decrease COD maximum at higher dilutions . Most of the domestic sewage and small scale industry effluent is poured into some stabilization lagoons. These treatment systems are economical and sufficiently efficient but have their own problems. Use of plant system together with these stabilization lagoons can prove to be far economical and effictive. , *Wolffia* could be effectively used for waste water treatment. It can bring down the chemical oxygen demand (COD), and Total dissolved solids (TDS), Similar results were obtained in the present investigation too, *Wolffia, Hydrodictyon* and *Hydrilla* were sufficiently effective for various metal removal.

According to wetland plants show good phytoremedation potential for trace elements and this could be seen in the present study as well, further the growth rates and harvest potential of the aquatic plants, make them fit for phytoremedation activities. water hyacinth *(Eichhornia crassipe*s) can remove radio active 137 cs, 90 U from radioactive wastes. It has been reported that phytoremedation is far cheaper, easier and safer than many of the conventional engineering techniques. Even though phytoremedation appears to be quite a promising process for the removal of various contaminants from soil and waste water, but still its scope is limited. More research and an integrated approach is required. A better understanding of the
process involved in uptake, transport, acclimatization and reuse is needed.
At this juncture of study it can be said that, more such studies with different effluent and waste water taking various test plants, be done. In order to select a properand efficient system further genetic studies and molecular manipulation be made for improvement in efficiently.

DEVELOPING PHYTOREMEDIATION FOR CHLOROFORM IN A TROPICAL AREA

The study area is an industrial plant situated in the State of São Paulo, Brazil. The groundwater in the area is contaminated with chlorinated solvents, basically chloroform. The remediation approach used different techniques depending the concentration of chloroform. At the source area chemical oxidation with Fenton's reagent and at the nearby plume, in situ reductive action with molasses and
as a polishing system. A phytoremediation system was implemented as a barrier for the eventual contamination of an artificial lake. The goal of the study was to evaluate the effectiveness of the phytoremediation system as a polishing remediation technique and the use of tropical native species to do this. The objective of the phytoremediation system was to create a last barrier for a chloroform contamination plume (up to 16mg/l of chloroform) before the groundwater discharge reaches an artificial lake. The activities started in September of 2000 with 179 plants of 10 native species introduced in a 2175 m 2 area. Four species are from seasonal (mesophytic) and/or tropical rain forests (wet areas) and the other six, from *Cerrado* (Brazilian savanna). Most of the species are deciduous or semi-deciduous pioneer and secondary species that grow fast and with relatively deep root systems. It were estimated that this system will evapotranspirate in a range from 4 to 170 m 3 /day. The specie with the highest growth rate, *Peltophorum dubium* (Leguminosa*e),* has grown 1,24 m in 10 months. In August/2001 it was observed an average reduction of 0,15 m of the level of groundwater at the treatment area. The groundwater depth varies from 5,6 m in the upper parts to 1,0m nearby the lake. The groundwater in the area presented a growth in the concentration of dissolved carbon after 6 months, as well as the Fe 2+ concentration. The results for chloroform are preliminary and not yet conclusive, even though a 43% reduction was observed at the wells within the treatment area, and also a metabolite, methylene chloride, appeared in the wells indicating biodegradation.
Phytoremediation acts through two fundamental remediation processes, enhancement of saturated zone in situ biodegradation and phytoextraction .The rhizosphere is the zone in the subsurface Occupied by plants root system. Within therhizosphere plants contribute to enhanced in situ biodegradation through the

supply ofcarbonaceous substrate and oxygen transfer. Rhizodeposition is partially the result of thedecay of dead roots and root hairs. Also important are carbonaceous root exudations such as leakage from epidermal cells, secretions resulting from metabolic activity, mucilages from root tips (which act as lubricants for root penetration), and lysates from sloughed cells. Exudates are composed of a wide range of chemicals that include sugars, aminoacids, organic acids, fatty acids, and numerous other compounds. It is estimated that 7% to 27% of the total plant mass is annually deposited as carbonaceous material in the rhizosphere. This carbonaceous material stimulates overall bacterial activity as well as providing substrate to support cometabolic degradation of xenobiotic hydrocarbons. The primary in situ remediation potential of plants for hydrocarbons lies in their capacity to enhance oxidation rates in the subsurface and provide cometabolic substrate.However, plants also have the ability to remove compounds, a process termed
phytoextraction, which can be applied to organic or metal contaminants. In the case of hydrocarbons, the compound must be water solubility and have a moderate degree of lipid solubility. Lipid solubility is a function of the octanol-water partition coefficient (Kow) for the compound. The compounds most readily mobilized by plants have log Kow values in the range of 1 to 3. Compounds with values of Kow in this range include BTEXhydrocarbons, chlorinated solvents. (the logKow for chloroform is 1,97). , and other short chain aliphatic hydrocarbons. Once in the interior of the plant the adsorbed hydrocarbons may be: stored via lignification; volatilized; partially degraded through metabolization; orcompletely mineralized. Compounds with values of log Kow higher than 3 such as PNA's are incapable of entering the root, those with log Kow values lower than 1 are rejected by the root membranes.

Site description

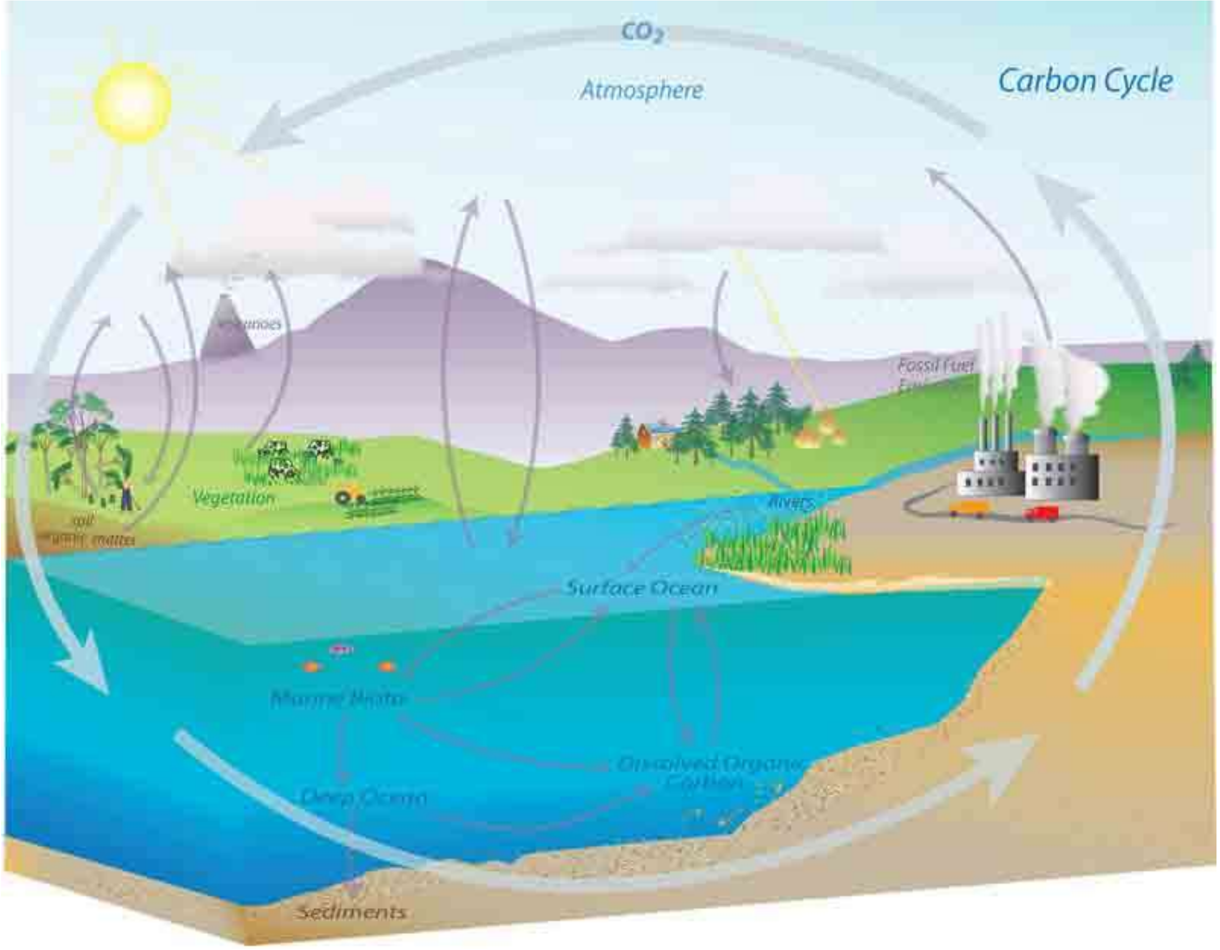
The site is near the 22 o S latitude. The phytoremediation system is located downhill between the contamination source area and an artificial lake, where the groundwater discharges . The slope has a 11% gradient, covered only with grass. All the phytoremediation area is within the plant limits, so there is no direct recipients of contamination nearby. According to IAC, 2002, the average monthly temperature in area ranges from 17 o C to 24 o C, and the monthly precipitation from 37 mm rain in July to 238 mm in January. The evaporation ranges from 46,1 mm in June up to 125 mm in January. Geological substratum is characterized by the palaeozoic sediments of the Itararé Group and the mesozoic basalts of the Serra Geral Group. Those rocks originate interbeded soils of silt and sand layers. Based on the above studies , concluded that: There is a mortality of 15% of total plantings, which indicated that at the concentrations (10 mg/L of chloroform) found there is no observed toxicity._ The most adequate species among those used in this study were canafístula *(Peltophorum dubiu*m, Leguminosae) and angico-do-cerrado *(Anaderanthera falcat*a, Leguminosae) that showed higher growth and lower death rates. _ The less adequate were manduirana *(Senna macranthera, Leguminosa*e), pau-terra-mirim *(Qualea dichotom*a, Vochysiaceae), and ipê-amarelo-do-brejo*(Tabebuia umbellat*a, Bignoniaceae)._ canafístula *(Peltophorum dubiu*m, leguminosae) growth 1,24 m in 8 months._ Even with a small period of study, the effect in the groundwater was alreadyobserved with an average drop in groundwater depth of 0,15 m _ The pumping effect was observed also in the change of the soil moisture profile _ Considering the wells in the middle and downstream of the area, it was observed an average reduction of 44% in the chloroform concentration, even though the results are not very conclusive, _ The effect of the plants seems to increase in the dissolved organic carbon which increase the conditions for a reductive decomposition of the chloroform. The increase of TOC, Fe 2+ and the show up of metabolites as methylene chloride are the evidence lines that this could be happening.

FAST-GROWING TREES FOR HEAVY METAL AND CHLORINATED SOLVENT PHYTOREMEDIATION

Recent studies with fast-growing trees in Florida have identified their potential for metal and hydrocarbon phytoremediation Greenhouse studies suggest that 1) baldcypress and castor bean are promising candidates for Cu remediation, accumulating over 15mg/kg in stem biomass, 2) a leaf disk immersion technique may indicate differences among PD clones for As, Cu, and Cr uptake, and 3) of synthetic and biological chelating agents, the combination of EDTA plus histidine increased As concentration in PD by 97% without significantly affecting growth or survival Field studies identify that silvicultural and genetic options impact phytoremediation potential. At a CCA contaminated site near Quincy, FL, although 11 of
97 *PD* clones had above-average growth and one clone exhibited good growth and high As tissue concentration, growth and survival were low, due primarily to poor site preparation. *PD* growth and As uptake at a CCA contaminated site in Archer, FL, was superior to that at Quincy but varied with season, plant tissue, and clone (CardellinoEffective phytoremediation of heavy metal or chlorinated solvent contaminated sites by fast-growing trees such as *Eucalyptus amplifolia (E*A), E. *grandis (E*G), eastern cottonwood *(Populus deltoides, P*D), and *Salix* spp. depends on tree-contaminant interactions and on tree growth as influenced by silvicultural and genetic factors. *E*A, *P*D, poplars, and willows tolerated trichloroethylene (TCE) more than baldcypress, and variation within willows was significant. *PD* growth and arsenic (As) uptake in Archer, FL, varied with season, tissue, and clone. For toluene phytoremediation near St. Augustine, FL, 6" diameter tubes inhibited *PD* and *EA* growth, *PD* and *EA* were similar in vigor, but an *EA* progeny was the most productive genotype.

At a TCE contaminated site in Orlando, FL, *PD* whips stuck 6' into sandy soil rooted to the base and were up to 18' tall in six months, with locally adapted clones surpassing a clone widely planted for phytoremediation in more temperate regions. Due to climatic stress at LaSalle, IL, unrooted willow cuttings survived poorly, but several rooted poplar clones all survived and grew rapidly in perchloroethylene (PCE) contaminated clay soil. Non-hyperaccumulating eucalypts, poplars, and willows may phytoremediate while providing an income from energywood, mulchwood, and/or pulpwood.

Effective phytoremediation of heavy metal or chlorinated solvent contaminated sites by fast-growing trees depends on tree-contaminant interactions and on tree growth as influenced by silvicultural and genetic factors. A greenhouse study suggests that young EA, PD, poplars, and willows have similar TCE tolerance, with perhaps useful variation among willow clones. Field studies identified silvicultural and genetic options that impact phytoremediation potential. *PD* growth and As uptake varied with season, plant tissue, and clone. Small diameter "training" tubes were ineffective in promoting *PD* and *EA* root growth, *PD* and *EA* were equal in vigor, but an *EA* progeny was the most productive genotype. *PD* whips deep planted 6' into sandy soil effectively rooted to the base of the whip, unless impacted by fluctuating groundwater, and averaged 18’ in height in six months. Locally adapted clones grew more rapidly than a well documented clone planted for phytoremediation purposes in more temperate regions. Unrooted willow cuttings survived poorly compared to rooted poplar cuttings due to late spring freezes, while several poplar clones all survived and grew rapidly in PCE contaminated clay soil. Fast-growing eucalypts, poplars, and willows have phytoremediation potential when superior genotypes are matched with the necessary silvicultural options. As non-hyperaccumulators, they may provide an income to offset cleanup costs.



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Chapter-16 THERMAL POLLUTION

Thermal pollution is the accumulation of unwanted heat energy in rivers, lakes and estuaries due to human activities. Thermal inefficient energy conversion processes are responsible for heat pollution. That part of the energy content of the fuel input which is not converted into useful work appears in the form of heat and must somehow be dissipated. Quantitatively, the most significant thermal polluters are the relatively fuel-inefficient energy converters in the generation of electricity by conventional and nuclear power plants, which are estimated to account for over 70 per cent of thermal plants.

Causes of Thermal Pollution

There are different sources of thermal pollution:

1. Working of Thermal Stations:

The thermal power stations are the backbone of power generation. But these power stations are contributing to enormous environmental degradation problems due to the use of poor quality of coal in underdeveloped countries. Discharge from thermal power stations include solid and gaseous pollutants like suspended particulate matter (SPM), oxides of sulphur, and carbon oxides of sulphur and nitrogen. When mixed with air and moisture, they result in formation of sulphuric and nitric acid and may result in formation of acid rain under certain adverse conditions.

2. Nuclear Power Stations:

Radioactivity is not the only waste that nuclear power plants produce. There is another unseen waste. For cooling purposes, nuclear reactors and thermal power stations use large quantities of water. Many times, water from the source of lower temperature is taken and the hot water is let into the river causing rise in temperature.

3. Industrial Power Wastes:

Similarly, industries generating electricity require huge amounts of cooling water for removal of heat. Industries release gases and high ash content. They not only create ash disposal problems but also cause many hazardous diseases like asthma and tuberculosis etc.

Effects of Thermal Pollution

The following are the main effects of thermal pollution:

(i) Changes in temperature have a disastrous effect on aquatic life, plants and animals. It is estimated that a rise of 3.6°c in the earth temperature would make ice caps to melt in the Antarctic and Arctic.

(ii) It reduces the dissolved oxygen content of water.

(iii) It influences reproductive cycle, digestion rate, respiration rate and enzymatic activities of living organisms.

(iv) It favours the growth of certain bacteria and pathogens

(v) Toxicity of pesticides and chemicals in the effluents increases with increase in temperature.

(vi) The composition of flora and fauna changes because of the species sensitive to increased temperature due to thermal shocks.

(vii) Many species may move towards suitable temperature to avoid hot conditions.

Slowing of Metabolism

Water temperatures usually change gradually as the seasons change. During cold seasons, when fewer food sources are available, fish metabolisms slow. When industrial discharges heat up the water, fish metabolisms also speed up, causing malnutrition due to insufficient food sources. Mass fish kills can occur as a result.

Oxygen Depletion

Organic matter decomposes faster in warmer temperatures, depleting dissolved oxygen from the water and increasing bacteria levels. This causes an overabundance of organic nutrients. Aquatic plants grow at a faster rate in warmer waters, resulting in overpopulation and shorter life spans. Algae blooms occur, choking fish gills and clouding the water. As the algae growth increases, other aquatic plants are unable to perform photosynthesis because of a lack of light. Corals and other marine life may die because of oxygen depletion.

Forced Migration

When water temperatures change, local marine life may be forced to migrate from the area, relocating to a more suitable location. Aquatic life from other areas may move into the vacated waters, giving rise to changes in biodiversity in both locations.

Cool Water Discharges

Most thermal pollution is caused by the discharge of warmer water, but cooler water discharges also have a detrimental effect on aquatic life. Cold waters from the bottoms of deep reservoirs are emptied into warmer rivers. Plankton cannot survive the cooler temperatures. Many fish, their eggs and their fry may die. As some organisms die, others reproduce and take over, potentially changing the area's ecosystem.

Industrial wastewater

In the United States, thermal pollution from industrial sources is generated mostly by power plants, petroleum refineries, pulp and paper mills, chemical plants, steel mills and smelters.

Some facilities use once-through cooling (OTC) systems which do not reduce temperature as effectively as the above systems. For example, the Potrero Generating Station in San Francisco, which uses OTC, discharges water to San Francisco Bay approximately 10° C (20° F) above the ambient bay temperature.

Urban runoff

During warm weather, urban runoff can have significant thermal impacts on small streams, as stormwater passes over hot parking lots, roads and sidewalks. Stormwater management facilities that absorb runoff or direct it into groundwater, such as bioretention systems and infiltration basins, can reduce these thermal effects. Retention basins tend to be less effective at reducing temperature, as the water may be heated by the sun before being discharged to a receiving stream.

Measures to Control Thermal Pollution

The following measures are suggested to control thermal pollution:

First, for controlling thermal pollution, factories and power houses should make their own cooling towers and spray ponds. This way the water can be used again and again and the thermal pollution can be eliminated.

Heated water from these sources may be controlled with:

1- cooling ponds, man-made bodies of water designed for cooling by evaporation, convection, and radiation

2-cooling towers, which transfer waste heat to the atmosphere through evaporation and/or heat transfer

3- cogeneration, a process where waste heat is recycled for domestic and/or industrial heating purposes.

Second, alternative sources of energy should be used.

Third, minimize the use of electricity so that thermal and nuclear power plants can use less amount of water.

Fourth, the techniques used in the industrial sector should be those which reduce the generation of hot water. Last, there should be complete ban on the discharge of heated water directly into water sources.

Chapter-17 Noise Pollution

Noise Pollution:

Noise is a disturbance to the human environment that is escalating at such a high rate that it will become a major threat to the quality of human lives. In the past thirty years, noise in all areas, especially in urban areas, have been increasing rapidly. There are numerous effects on the human environment due to the increase in noise pollution. In the following paper, the cause and effects of noise pollution

All sounds are not noise. Noise is any sound that is unwanted and goes beyond its certain limit, i.e., above 80 decibels Harsh sounds of lightening and thunder, noise produced by machines, automobiles, railways, aero planes and the blaring sound of loudspeakers and some musical instruments come under the category of noise pollution.

More and more noise is the creation of modern civilization and has now become a major environmental pollutant, specially in urban areas. The most notable effect of noise pollution is on hearing. It may cause total loss of hearing that may result in the reduction of worker’s efficiency.

At the higher levels, it may lead to physical and psychological damage. There is evidence that noise is one of the major causes of stress and anxiety. It also causes headaches and irritability. It may also affect blood pressure and heart beat. Air, water and noise pollutions are very common which are creating havoc for all types of life. They have disastrous transnational consequences.

There are two types of hearing loss: conductive and sensorineural (see fig.1 for anatomy of the ear). In conductive deafness sound-pressure waves never reach the cochlea, most often as a consequence of a ruptured eardrum or a defect in the ossicles of the middle ear (Bugliarello, et al., 1976).

The three bones form a system of levers linked together, hammer pushing anvil, anvil-pushing stirrup. Working together, the bones amplify the force of sound vibrations. Taken together, the bones double, often treble the force of the vibrations reaching the eardrum (Bugliarello, et al., 1976).

Mitigation of potentially harmful amplification occurs via muscles of the middle ear. These muscles act as safety device protection the ear against excessive vibrations from very loud noises, very much like an automatic damper or volume control.

When jarring sounds with their rapid vibrations strike the eardrum; the muscles twist the bones slightly, allowing the stirrup to rotate in a different direction. With this directional shift, less force is transmitted to the inner ear: less, not all

The human ear is a delicate and fragile anatomical structure on the other hand it s a fairly powerful physical force. These muscles act quickly but not always as in examples of when the ear catches the sound of gun being shot unexpectedly. The muscles of the ear were relaxed and were unprepared for such a blast, because of this damage was done.

Conductive hearing loss can be minimized, even overcome by use of the familiar hearing aids. The most common is worn over the mastoid bond behind the pinna. It picks up sound waves and transmits them through the skull to the cochlea.

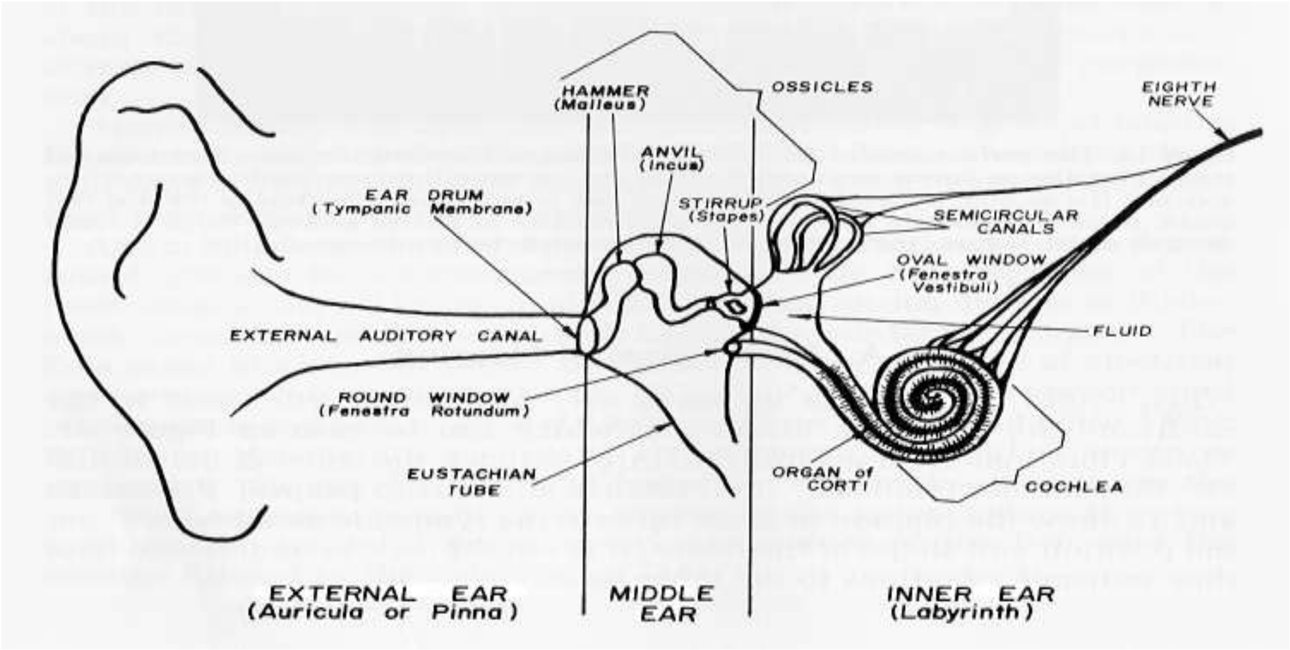
Sensorineural hearing loss, the most common form in the United States, occurs as a result of advancing age as well as exposure to loud noises. In both instances there is a disruption of the organ of Corti. The organ serves two functions: converting mechanical energy to electrical and dispatching to the brain a coded version of the original sound with information bout frequency, intensity, and timbre. The hair cells of the organ of Corti send their electrochemical signals into the central nervous system, where the signals are picked up by thousands of auditory nerve fibers and transmitted to the brain. It is the decoding of all the information that enables a person to distinguish the unique ant separate sounds of a violin, trumpet, and clarinet, even all three are playing the same note.

The Occupational Safety and Health Agency (OSHA) has set the danger level at 95 decibels (dB) and above for 4 or more hours per day as likely to induce permanent hearing impairment

The organ of corti, a gelatinous mass, is on of the best protected parts of the body, encased as it is within the cochlea which in turn is deeply embedded in the temporal bone, perhaps the hardest of the 206 bones (Bugliarello, et al., 1976). None the less, loud noise can damage the hair cells and the auditory nerve, producing at times, depending on the type of noise, sudden and often total deafness.

Sustained noise over a period of time can also engender sensorineural deafness in the form of gradual losses in hearing. This is the most common loss in teenagers today listening to loud rock music (Bugliarello, et al., 1976).

Until a few years ago, sensorineural deafness could not be helped by hearing aids. However, with advances in electronic wizardry and miniaturization, devices for insertion into the auditory canal are available.



Cause and Effects of Noise Pollution

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Chapter-18 AIR POLLUTION

What is outdoor air pollution?

Air lets our living planet breathe—it's the mixture of gases that fills the atmosphere, giving life to the plants and animals that make Earth such a vibrant place. Broadly speaking, air is almost entirely made up of two gases (78 percent nitrogen and 21 percent oxygen), with a few other gases (such as carbon dioxide and argon) present in absolutely minute quantities. We can breathe ordinary air all day long with no ill effects, so let's use that simple fact to define air pollution, something like this:

Air pollution is a gas (or a liquid or solid dispersed through ordinary air) released in a big enough quantity to harm the health of people or other animals, kill plants or stop them growing properly, damage or disrupt some other aspect of the environment (such as making buildings crumble), or cause some other kind of nuisance (reduced visibility, perhaps, or an unpleasant odor).

As with water pollution and land contamination, it's the quantity (or concentration) of a chemical in the air that makes the difference between "harmless" and "pollution." Carbon dioxide (CO2), for example, is present in the air around you at a typical concentration of less than 0.05 percent and breathing it in usually does no harm (you breathe it out all day long); but air with an extremely high concentration of carbon dioxide (say, 5–10 percent) is toxic and could kill you in a matter of minutes. Since Earth's atmosphere is very turbulent—many of us live in windy countries—air pollution will often disperse relatively quickly. In less enlightened times, factory operators thought that if they built really high smokestacks, the wind would simply blow their smoke away, diluting and dispersing it so it wouldn't be a problem. The only trouble was, Earth is a much smaller place than we think and pollution doesn't always disappear so conveniently.

NATURAL AIR POLLUTION

When we think of pollution, we tend to think it's a problem that humans cause through ignorance or stupidity—and that's certainly true, some of the time. However, it's important to remember that some kinds of air pollution are produced naturally. Forest fires, erupting volcanoes, and gases released from radioactive decay of rocks inside Earth are just three examples of natural air pollution that can have hugely disruptive effects on people and the planet.

Forest fires (which often start naturally) can produce huge swathes of smoke that drift for miles over neighboring cities, countries, or continents. Giant volcanic eruptions can spew so much dust into the atmosphere that they block out significant amounts of sunlight and cause the entire planet to cool down for a year or more. Radioactive rocks can release a gas called radon when they decay, which can build up in the basements of buildings with serious effects on people's health.

All these things are examples of serious air pollution that happen without any help from humans; although we can adapt to natural air pollution, and try to reduce the disruption it causes, we can never stop it happening completely.

Primarily air pollutants can be caused by primary sources or secondary sources. The pollutants that are a direct result of the process can be called primary pollutants. A classic example of a primary pollutant would be the sulfur-dioxide emitted from factories

Secondary pollutants are the ones that are caused by the inter mingling and reactions of primary pollutants. Smog created by the interactions of several primary pollutants is known to be as secondary pollutant.

UNNATURAL " types of air pollution

Anything people do that involves burning things (combustion), using household or industrial chemicals (substances that cause chemical reactions and may release toxic gases in the process), or producing large amounts of dust has the potential to cause air pollution.

Traffic

There are something like a half billion cars on the road today—one for every two people in rich countries such as the United States. Virtually all of them are powered by gasoline and diesel engines that burn petroleum to release energy. Petroleum is made up of hydrocarbons (large molecules built from hydrogen and carbon) and, in theory, burning them fully with enough oxygen should produce nothing worse than carbon dioxide and water. In practice, fuels aren't pure hydrocarbons and engines don't burn them cleanly. As a result, exhausts from engines contain all kinds of pollution, notably particulates (soot of various sizes), carbon monoxide (CO, a poisonous gas), nitrogen oxides (NOx), volatile organic compounds (VOCs), and lead—and indirectly produce ozone. Mix this noxious cocktail together and energize it with sunlight and you get the sometimes brownish, sometimes blueish fog of pollution we call smog, which can hang over cities for days on end.

TOXIC GASES

Sulfur dioxide: Coal, petroleum, and other fuels are often impure and contain sulfur as well as organic (carbon-based) compounds. When sulfur (spelled "sulphur" in some countries) burns with oxygen from the air, sulfur dioxide ($SO2$) is produced. Coal-fired power plants are the world's biggest source of sulfur-dioxide air pollution, which contributes to smog, acid rain, and health problems that include lung disease.

Carbon monoxide: This highly dangerous gas forms when fuels have too little oxygen to burn completely. It spews out in car exhausts and it can also build up to dangerous levels inside your home if you have a poorly maintained gas boiler, stove, or fuel-burning appliance. (Always fit a carbon monoxide detector if you burn fuels indoors.)

Carbon dioxide: This gas is central to everyday life and isn't normally considered a pollutant: we all produce it when we breathe out and plants such as crops and trees need to "breathe" it in to grow. However, carbon dioxide is also a greenhouse gas released by engines and power plants. Since the beginning of the Industrial Revolution, it's been building up in Earth's atmosphere and contributing to the problem of global warming and climate change.

Nitrogen oxides: Nitrogen dioxide ($NO2$) and nitrogen oxide (NO) are pollutants produced as an indirect result of combustion, when nitrogen and oxygen from the air react together. Nitrogen oxide pollution comes from vehicle engines and power plants, and plays an important role in the formation of acid rain, ozone and smog. Like carbon dioxide, nitrogen oxides are also greenhouse gases (ones that contribute to global warming).

Volatile organic compounds (VOCs): These carbon-based (organic) chemicals evaporate easily at ordinary temperatures and pressures, so they readily become gases. That's precisely why they're used as solvents in many different household chemicals such as paints, waxes, and varnishes. Unfortunately, they're also a form of air pollution: they're believed to have long-term (chronic) effects on people's health and they also play a role in the formation of ozone and smog.

Particulates: These are the sooty deposits in air pollution that blacken buildings and cause breathing difficulties. Particulates of different sizes are often referred to by the letters PM followed by a number, so PM10 means soot particles of less than 10 microns (10 millionths of a meter or 10µm in diameter). In cities, most particulates come from traffic fumes.

Ozone: Also called trioxygen, this is a type of oxygen gas whose molecules are made from three oxygen atoms joined together (so it has the chemical formula $O3$), instead of just the two atoms in conventional oxygen ($O2$). In the stratosphere (upper atmosphere), a band of ozone ("the ozone layer") protects us by screening out harmful ultraviolet radiation (high-energy blue light) beaming down from the Sun. At ground level, it's a toxic pollutant that can damage health. It forms when sunlight strikes a cocktail of other pollution and is a key ingredient of smog (see box below).

Chlorofluorocarbons (CFCs): Once thought to be harmless, these gases were widely used in refrigerators and aerosol cans until it was discovered that they damaged Earth's ozone layer. We discuss this in more detail down below.

Unburned hydrocarbons: Petroleum and other fuels are made of organic compounds based on chains of carbon and hydrogen atoms. When they burn properly, they're completely converted into harmless carbon dioxide and water; when they burn incompletely, they can release carbon monoxide or float into the air in their unburned form, contributing to smog.

Lead and heavy metals: Lead and other toxic "heavy metals" can be spread into the air either as toxic compounds or as aerosols (when solids or liquids are dispersed through gases and carried through the air by them) in such things as exhaust fumes and the fly ash (contaminated waste dust) from incinerator smokestacks.

SMOG

Smog isn't the stuff that pumps from a car's tailpipe or drifts from a factory smokestack—it's the nasty brown or blue haze that builds up over a city as a result.

Smog (a combination of the words "smoke" and "fog") forms when sunlight acts on a cocktail of pollutant gases such as nitrogen and sulfur oxides, unburned hydrocarbons, and carbon monoxide; that's why it's sometimes called photochemical smog (the energy in light causes the chemical reaction that makes smog). One of the most harmful constituents of smog is a toxic form of oxygen called ozone, which can cause serious breathing difficulties and even, sometimes, death. When smog is rich in ozone, it tends to be a blueish color, otherwise it's more likely to be brown.

Although smog can happen in any busy city, it's a particular problem in places such as Los Angeles where the local climate (influenced by the ocean and neighboring mountains) regularly causes what's known as a temperature inversion. Normally, air gets colder the higher up you go but in a temperature inversion the opposite happens: a layer of warm air traps a layer of cold air nearer the ground. This acts like a lid over a cloud of smog and stops it from rising and drifting away. Largely because of their traffic levels, smog afflicts many of the world's busiest cities, including Athens, Beijing, Mexico City, Milan, and Tokyo.

Effects of Air pollution

1. Respiratory and heart problems: The effects of Air pollution are alarming. They are known to create several respiratory and heart conditions along with Cancer, among other threats to the body. Several millions are known to have died due to direct or indirect effects of Air pollution. Children in areas exposed to air pollutants are said to commonly suffer from pneumonia and asthma.

2. Global warming: Another direct effect is the immediate alterations that the world is witnessing due to Global warming. With increased temperatures world wide, increase in sea levels and melting of ice from colder regions and icebergs, displacement and loss of habitat have already signaled an impending disaster if actions for preservation and normalization aren’t undertaken soon.

INDOOR AIR POLLUTION

Numerous forms of indoor air pollution are possible in the modern home. Air pollutant levels in the home increase if not enough outdoor air is brought in to dilute emissions from indoor sources and to carry indoor air pollutants out of the home. In addition, high temperature and humidity levels can increase the concentration of some pollutants. Indoor pollutants can be placed into two groups, biologic and chemical.

Biologic Pollutants

Biologic pollutants include bacteria, molds, viruses, animal dander, cat saliva, dust mites, cockroaches, and pollen. These biologic pollutants can be related to some serious health effects. Some biologic pollutants, such as measles, chickenpox, and influenza are transmitted through the air. However, the first two are now preventable with vaccines. Influenza virus transmission, although vaccines have been developed, still remains of concern in crowded indoor conditions and can be affected by ventilation levels in the home.

Common pollutants, such as pollen, originate from plants and can elicit symptoms such as sneezing, watery eyes, coughing, shortness of breath, dizziness, lethargy, fever, and digestive problems. Allergic reactions are the result of repeated exposure and immunologic sensitization to particular biologic allergens.

Although pollen allergies can be bothersome, asthmatic responses to pollutants can be life threatening. Asthma is a chronic disease of the airways that causes recurrent and distressing episodes of wheezing, breathlessness, chest tightness, and coughing Asthma can be broken down into two groups based on the causes of an attack: extrinsic (allergic) and intrinsic (nonallergic). Most people with asthma do not fall neatly into either type, but somewhere in between, displaying characteristics of both classifications. Extrinsic asthma has a known cause, such as allergies to dust mites, various pollens, grass or weeds, or pet danders. Individuals with extrinsic asthma produce an excess amount of antibodies when exposed to triggers. Intrinsic asthma has a known cause, but the connection between the cause and the symptoms is not clearly understood. There is no antibody hypersensitivity in intrinsic asthma. Intrinsic asthma usually starts in adulthood without a strong family history of asthma. Some of the known triggers of intrinsic asthma are infections, such as cold and flu viruses, exercise and cold air, industrial and occupational pollutants, food additives and preservatives, drugs such as aspirin, and emotional stress. Asthma is more common in children than in adults, with nearly 1 of every 13 school-age children having asthma

AIR POLLUTION BY ENVIRONMENTAL TOBACCO SMOKE

Burning tobacco is the main source of indoor pollution in the developed world. Tobacco smoke contains about 4,000 chemicals including carcinogens, irritants and toxic gases. The health impact of breathing environmental tobacco smoke is well documented. Many potentially toxic gases are present in higher concentrations in sidestream smoke than in mainstream smoke and nearly 85% of the smoke in a room results from sidestream smoke. The particulate phase includes tar (itself composed of many chemicals), nicotine, benzene and benzo(a)pyrene. The gas phase includes carbon monoxide, ammonia, dimethylnitrosamine, formaldehyde, hydrogen cyanide and acrolein. Some of these have marked irritant properties and some 60 are known or suspected carcinogens (cancer causing substances). The Environmental Protection Agency

(EPA) in the USA has classified environmental tobacco smoke as a class A (known human) carcinogen along with asbestos, arsenic, benzene and radon gas.[Lee Jong-wook,2004 ,WHO]
Breathing other people's smoke is called passive, involuntary or secondhand smoking. The non-smoker breathes "sidestream" smoke from the burning tip of the cigarette and "mainstream" smoke that has been inhaled and then exhaled by the smoker. Secondhand smoke (SHS) is a major source of indoor air pollution..Aldicarp,chlorpyrifos and methyl bromide are highly toxic pestisides and commonly used to fumigate the soil prior to planting tobacco seedling. In 1997, over 5.5 million pounds of methyl bromide were applied to tobacco fields worldwide. The effects of these chemicals are not monitored generally but it is known that they leach into the soil and find their way into streams, rivers, and food chains. These substances may indirectly cause the genetic selection of pesticide-resistant mosquitoes or flies, making the control of diseases such as malaria much more difficult.[Lee Jong-wook,2004,WHO]

In 1998, a report by the Independent Scientific Committee on Smoking and Health (SCOTH) reviewed the evidence on passive smoking and concluded that: “Smoking in public places should be restricted on the grounds of public health.” The report added that “Wherever possible, smoking should not be allowed in the work place.” A BMA(British medical association) report, “Towards smoke-free public places” published in December 2002, also called for a ban on smoking in public places. A survey by Action on Smoking and Health(ASH) in April 1999 revealed that about 3 million people in the UK are exposed to passive smoking in their places of work. A national survey commissioned by SmokeFree London found that over half of non-smoking employees (51%) are still exposed to tobacco smoke at work, with almost a third (31%) being exposed every day or most days. A survey commissioned by ASH found that 80% would support a law to require all enclosed workplaces to be smokefree. Public opinion surveys have shown widespread support for smoking restrictions in public places and this has been growing steadily in recent years.
The 2002 British government commissioned survey of smoking attitudes found that 86% of respondents (including 70% of smokers) agreed that smoking should be restricted at work and a similar proportion favoured smoking restrictions in restaurants. The survey also revealed that a majority of people supported smoking restrictions in pubs.

The WHO Framework Convention on Tobacco Control, which was adopted in May 2003 by WHO’s 192 member States, is intended as a common framework in which countries can work together to address the challenge that tobacco use represents at the global level. Tobacco use has also a development dimension..Tobacco causes around 13 500 deaths per day .Half of children are exposed to tobacco smoke at home. 47.5% of men smoke and 10.3% of women smoke. A cigarette is the only legally available consumer product that kills through normal use 2000: Business: market share: World's largest tobacco companies: 1. China national tobacco company 31% [china has 385 million smokers] 2. Philip Morris 17% 3. British American tobacco (bat) 13% 4. Rjr reynolds 6% 1999: consumption: China annual cigarette volume: around 1.6 trillion cigarettes US: around 415 billion sticks.Japan: 327 billion russia: 257 billion Germany: 140 billion India: just under 100 billion. Brazil: 97 billion

1999: consumption: about 10 million americans smoke cigars. In the year 2004 the Central Govt of India passed a legislation on advertisement, production, trade and sale of tobacco and tobacco products .banning the advertisement of tobacco & tobacco products on Tv, newspapers and media from 01 May 2004 Reason tobacco leaves contain an alkaloid nicotine which is lethal ,carcinogen and causes addiction. Table 1 Indoor air standards of nicotine; Table2 Toxic levels of nicotine. [Encyclopedia of Clinical Toxicology & Handbook of Environmental Data on Organic Clinical Data Vol 2] .

GREEN TOBACCO SICKNESS **(GTS)**

Tobacco growers are susceptible to an occupational illness known as green tobacco sickness. This is caused by the absorption of nicotine through the skin from contact with wet tobacco leaves. Symptoms of green tobacco sickness include nausea, weakness, dizziness and abdominal cramps, and fluctuations in blood pressure and heart rates. It is not known exactly now many tobacco workers are affected by green tobacco sickness but one study of migrant workers in North Carolina USA suggests that 41% of the workers get the illness at least once during harvest season. [SCOTH 1998].

EFFECT OF CHEWING TOBACCO ON THE HUMAN BODY

Tobacco use is a major preventable cause of premature death and of several general diseases. In addition to cigarette, pipe, cigar and bidi smoking, betel quid chewing (pan), guhtka use and other traditional forms of tobacco have several effects in the mouth. Tobacco is a risk factor for oral cancer, oral cancer recurrence, adult periodontal diseases and congenital defects such as cleft lip and palate in children. Tobacco suppresses the immune system's response to oral infection, compromises healing oral surgical and accidental wounding, promotes periodontal degeneration in diabetics and adversely affects the cardiovascular system. Moreover, tobacco greatly increases the risk when used in combination with alcohol or areca nut. Most oral consequences of tobacco use impair quality of life be they as simple as halitosis, as complex as oral birth defects, as common as periodontal disease or as troublesome as complications during wound healing.

EFFECT OF PASSIVE SMOKING ON THE HUMAN BODY

Some of the immediate effects of passive smoking include eye irritation, headache, cough, sore throat, dizziness and nausea. Adults with asthma can experience a significant decline in lung function when exposed, while new cases of asthma may be induced in children whose parents smoke. Short term exposure to tobacco smoke also has a measurable effect on the heart in non-smokers. Just 30 minutes exposure is enough to reduce coronary blood flow. [Otsuka R., 2001]
In the longer term, passive smokers suffer an increased risk of a range of smoking-related diseases. Non-smokers, who are exposed to passive smoking in the home, have a 25 per cent increased risk of heart disease and lung cancer.] A major review by the Government-appointed Scientific Committee on Tobacco and Health (SCOTH 1998) concluded that passive smoking is a cause of lung cancer and ischaemic heart disease in adult non-smokers, and a cause of respiratory disease, cot death, middle ear disease and asthmatic attacks in children. A more

recent review of the health impacts of passive smoking by the International Agency for Research on Cancer (IARC) noted that "the evidence is sufficient to conclude that involuntary smoking is a cause of lung cancer in never smokers".[UNCTAD, 2004]

Whilst the relative health risks from passive smoking are small in comparison with those from active smoking, because the diseases are common, the overall health impact is large. The British Medical Association has conservatively estimated that secondhand smoke causes at least 1,000 deaths a year in the UK. However, the true figure is likely to be much higher. Professor Konrad Jamrozik of Imperial College London estimated that domestic exposure to secondhand smoke causes at least 3,600 deaths annually from lung cancer, heart disease and stroke combined, while exposure at work leads to approximately 700 deaths from these causes. Jamrozik also estimates 49 deaths – or about 1 a week – from exposure at work in the hospitality trades. In the population aged 65 or older, passive smoking is estimated to account for 16,900 deaths annually. 9,700 are due to stroke, where current evidence of health effects is weakest.
.[Jamrozik Konrad (2004)].

Almost half of all children in the UK are exposed to tobacco smoke at home. Passive smoking increases the risk of lower respiratory tract infections such as bronchitis, pneumonia and bronchiolitis in children. One study found that in households where both parents smoke, young children have a 72 per cent increased risk of respiratory illnesses. Passive smoking causes a reduction in lung function and increased severity in the symptoms of asthma in children, and is a risk factor for new cases of asthma in children. Passive smoking is also associated with middle ear infection in children as well as possible cardiovascular impairment and behavioural problems.

Infants of parents who smoke are more likely to be admitted to hospital for bronchitis and pneumonia in the first year of life. More than 17,000 children under the age of five are admitted to hospital every year because of the effects of passive smoking. Passive smoking during childhood predisposes children to developing chronic obstructive airway disease and cancer as adults. Exposure to tobacco smoke may also impair olfactory function in children. A Canadian study found that passive smoking reduced children's ability to detect a wide variety of odours compared with children raised in non-smoking households. Passive smoking may also affect children's mental development. A US study found deficits in reading and reasoning skills among children even at low levels of smoke exposure.[Hackshaw AK et al.,1997]

Scientists from Canada reported finding evidence of cigarette smoke in fetal hair, the first biochemical proof that the offspring of non-smoking mothers can be affected by passive cigarette smoke. Smoking during pregnancy can harm the baby .[Fielding, JE and Phenow ,KJ,1998].

There is a rise in impotency in men with a nicotine addiction .Women with smoking husbands are unable to conceive .number of still births are more in cases of smoking fathers . Exposure to passive smoking during pregnancy is an independent risk factor for low birth weight. A recent study has also shown that babies exposed to their mother's tobacco smoke before they are born grow up with reduced lung function Parental smoking is also a risk factor for sudden infant death syndrome (cot death).

Lung cancer, which was rare before the 20th century, increased dramatically by the 1930s. The American Cancer Society and other organizations initiated studies comparing deaths among smokers and nonsmokers over a period of several years. All such studies found increased mortality among smokers, both from cancer and other causes The American Cancer Society estimates that cigarettes are responsible for about 431,000 deaths in the United States each year. Lung cancer accounts for about 30 percent of all cancer deaths in the United States, and smoking accounts for nearly 90 percent of lung cancer deaths. The risks of dying from lung cancer are 23 times higher for male smokers and 13 times higher for female smokers than for nonsmokers. Additionally, smokers are at increased risk for many other types of cancer. The National Cancer Center (NCC) South Korea officially confirmed that smoking causes lung cancer .[UNCTAD,2004]

In addition to the health risks posed by using pesticides[aldicarb and chlorpyrifos, Methyl bromide,an ozone-depleting chemical A study published in the British Medical Journal suggests that previous studies of the effects of passive smoking on the risk of heart disease may have been under-estimated. The researchers found that blood cotinine levels among non-smokers were associated with a 50-60% increased risk of heart disease. [EPA,1992]

Nicotine causes thickening of blood. nicotine increases chlorestrol deposistion. [Law Mr et al.(1997)]

For those who do not inhale, tobacco smoke does not reach the lungs in the same quantity as it does in cigarette smokers. Therefore, the risk of death from lung cancer is not as high as it is for cigarette smokers, but is still several times higher than the risk for non-smokers.

PATERNAL SMOKING AND CHILDHOOD CANCERS

A putative association between cancer in children and paternal smoking at the time of their conception has been proposed in studies based on the Oxford Survey of Childhood Cancers and a large case-control investigation from Shanghai. The Committee examined the published papers and certain limitations were noted, but it was agreed that there were plausible hypothetical mechanisms whereby paternal smoking at the time of conception could induce an increase in cancers in the offspring.

There are many changes found in the histological type of lungs which causes the changes in lung cancer incidences in the several part of the world. Squamous and small cell carcinomas, arising from the larger bronchi, are traditionally associated with smoking, but relative and absolute increases in the incidence of adenocarcinomas of the lung have been increasingly recognised. A recent study from Switzerland demonstrates rising incidence rates for adenocarcinomas in both younger men and women in the early 1990s, the rates being more than 3-fold higher than for squamous carcinomas in the same groups. This alteration in histological pattern almost certainly reflects changes in the pattern of exposure of bronchial tissues to tobacco-associated carcinogens. Smokers of modern low-tar filtered cigarettes tend to compensate by increasing the number and depth of puffs, the peripheral parts of the lung are thus more exposed to larger amounts of tobacco-associated carcinogens, and it is in the peripheral parts of the lung that adenocarcinomas develop. The diagnostic and therapeutic implications of an increase in lung adenocarcinomas are likely to be considerable. [EPA(1999) California].Table 3[analysis of lower respiratory illness in children]

CIGARS AND CIGARETTES

A cigar is defined, as "any roll of tobacco wrapped in leaf tobacco or in any substance containing tobacco," while a cigarette is "any roll of tobacco wrapped in paper or any substance not containing tobacco." Most cigars are made up of a single air-cured or dried burley tobacco. Cigar tobacco leaves are first aged for about a year and then fermented in a multi-step process that can take from 3 to 5 months. Fermentation causes chemical and bacterial reactions that change the tobacco and give cigars a different taste and smell from cigarettes. Cigars come in different sizes, some as small as a cigarette (called a cigarillo), others much larger. Large cigars typically contain between 5 and 17 grams of tobacco. It is not unusual for some premium brands to have as much tobacco in 1 cigar as in a whole pack of cigarettes. Large cigars can take between 1 to 2 hours to smoke.While the reasons people smoke cigars are varied, the fact is, like cigarettes, cigars can become addictive. Nicotine is the substance in tobacco that causes addiction. Most cigars have as much nicotine as several cigarettes. If cigar smokers inhale, nicotine is absorbed as rapidly as it is with cigarettes. For those who do not inhale, it is absorbed more slowly through the lining of the mouth. People who use smokeless tobacco absorb nicotine the same way. Both inhaled and non-inhaled nicotine are highly addictive. [Table 4 Ingredients of a cigarette]

Cigar smoking increases your risk of death from several cancers, including cancer of the lung, oral cavity (lip, tongue, mouth, throat), oesophagus (the tube connecting the mouth to the stomach), and larynx (voice box). If you inhale, cigar smoking appears to be linked to death from cancer of the pancreas and bladder, as well. Carcinogens in cigar smoke include the following: benzene , aromatic amines (especially carcinogens such as 2-naphthylamine and 4-minobiphenyl) ,vinyl chloride ,ethylene oxide,arsenic ,chromium ,cadmium ,nitrosamines ,polynuclear , aromatic hydrocarbons . [NIDA FACTS 2006]

THE CIGARETTE TEST METHOD

Cigarette ratings for "tar," nicotine and carbon monoxide are currently determined by machine testing conducted in accordance with a methodology adopted by the Commission in 1967. The "tar" and nicotine testing program was intended to provide smokers seeking to switch to lower "tar" cigarettes with a single, standardized measurement with which to choose among the then-existing brands.

Over the past 30 years that the current system has been in place, there have been dramatic decreases in the machine-measured "tar" and nicotine yields of cigarettes. Since 1968, the average sales-weighted machine-measured "tar" yield has fallen from 21.6 mg. to 12.0 mg. Today, nearly 82% of all cigarettes sold have machine-measured "tar" yields of 15 mg. or less.Despite these substantial decreases in machine-measured yields, the Commission has been concerned for some time that the current test method may be misleading to individual consumers who rely on the ratings it produces as indicators of how much "tar" and nicotine they actually get The concentration of CO will be reported as milligrams per

cigarette;
The present method for "tar" and nicotine determination by[Wagner (1978)]

1. Smoke cigarettes to a 23mm. butt length, or to the length of the filter and overwrap plus 3mm. if in excess of 23mm.;
2. Base results on a test of 100 cigarettes per brand, or type;
3. Cigarettes to be tested on a random basis, as opposed to "weight selection,
4. Determination of "tar" yield after subtracting moisture and alkaloids (as nicotine) from particulate matter;
5. Determination of particulate matter [Sloan C.H. 1965]

Table 5 gives mean values of nicotine, total moisture and pH of six moist snuff tobacco products of USA[National centre for chronic disease prevention and health promotion 1999]

NICOTINE ADDICTION

Nicotine is the primary chemical responsible for smoking addiction. Nicotine stimulates the production of dopamine in the nucleus accumbens, the brain's "pleasure centre dopamine and norepinephrine – neurotransmitters within the regions of the brain responsible for feelings of pleasure,which causes a sudden release of glucose .

Stimulation is followed by depression and fatigue leading the abuser to seek more nicotine. Addiction to nicotine results in withdrawal symptoms when a chronic smoker tries to stop smoking for 24 hours they had increased anger , hostility and aggression and loss of social cooperation ,take longer to regain emotional eguilibrium following stress. [NIDA FACTS 2006]

In a study, it was assessed whether long-term nicotine exposure would result in the loss of mature cerebellar Purkinje cells in an adult rat model system. At present,the information available with regard to the clinical correlation linking chronic tobacco use with the cerebellar dysfunctionsis limited. However, nicotine is reported to cause postural imbalance in nonsmokers and occasional smokers showing that nicotine may be affectin g a circuitry involving the cerebellum .The findings support the notion that the cerebellar Purkinje cells are the targets for nicotine and that the function of these neurons may be modified by nicotine. Therefore, It has been hypothesized that the number of mature Purkinje cells would be reduced following a long-term nicotine exposure regimen in a manner similar to the nicotine-induced developing Purkinje cell loss. The rationale for selecting the longterm exposure regimen and the Purkinje cells was based on the fact that most smokers are exposed to nicotine for a long period and the cerebellum is a vulnerable target for neurotoxins.[Russell B.Edwards,Roland D. Romeo,2002]

In a study it was observed that second hand smoke stimulates the tumor growth in mice.second hand smoke (SHS) significantly increases tumor size, weight, and vascularity. SHS, the tobacco combustion products inhaled by nonsmokers in the proximity of burning tobacco, is dangerous because it contains high concentrations of nicotine, benzene, polycyclic aromatic hydrocarbons, fine particles ($PM_{2.5}$), and many other carcinogens and irritants.It has been observed that nicotine induces angiogenesis and accelerates the growth of tumor and atheroma in association with increased lesion vascularity, these effects mediated by nicotinic acetylcholine receptors.The current results are consistent with the hypothesis that nicotine activates an endogenous angiogenic pathway mediated by endothelial nACh receptors. Furthermore,the observations indicate that nicotine absorbed from SHS can exert a substantial effect on tumor angiogenesis and growth at levels of exposure experienced by people in smoky environments. In conclusion, exposure to SHS at levels observed in smoky environments stimulates tumor growth, tumor angiogenesis, and an increase in growth factors and cells known to contribute to tumor angiogenesis. These effects were reduced by mecamylamine, a nicotinic receptor antagonist, and cerivastatin, an inhibitor of isoprenoid synthesis.[William W. Parmley , Stanton A. Glantz**]**

SMOKING CESSATION

Nicotine was the first pharmacological agent approved by the Food and Drug Administration (FDA) for use in smoking cessation therapy. Nicotine replacement therapies, such as nicotine gum, the transdermal patch, nasal spray, and inhaler, have been approved for use in the United States. They are used to relieve withdrawal symptoms, because they produce less severe physiological alterations than tobacco-based systems, and generally provide users with lower overall nicotine levels than they receive with tobacco. An added benefit is that these forms of nicotine have little abuse potential since they do not produce the pleasurable effects of tobacco products. Nor do they contain the carcinogens and gases associated with tobacco smoke.[Henningfield JE,Radzius A,1995]

The FDA's approval of nicotine gum in 1984 marked the availability (by prescription) of the first nicotine replacement therapy on the U.S. market. In 1996, the FDA approved gum (Nicorette®) for over-the-counter sales. Whereas nicotine gum provides some smokers with the desired control over dose and ability to relieve cravings, others are unable to tolerate the taste and chewing demands. In 1991-1992, FDA approved four transdermal nicotine patches, two of which became over-the-counter products in 1996, thus meeting the needs of many additional tobacco users.[Tomar SL ,1997]

A popular treatment for nicotine addiction can also cut cravings among crystal meth addicts, a US study suggests.Crystal meth – the commonly used term for methamphetamine – is a cheap and addictive drug that has become a massive problem in the US in recent years. It increases alertness and creates sensations of euphoria in users by stimulating the generation of dopamine and norepinephrine – neurotransmitters within the regions of the brain responsible for feelings of pleasure.Bupropion – the active chemical ingredient found in the nicotine addiction drug, Zyban, as well as the anti-depressant Wellbutrin – was found to reduce the drug-induced high experienced by methamphetamine users and also to lessen their urge to take the drug in response to visual cues, in a study by researchers at the University of California Los Angelos.[Hoffmann D,Connolly GN, 1995]

CYP2A6 GENE

Two new studies of smokers have yielded new insight into a gene linked to cigarette addiction. The findings could lead to more personalised – and ultimately more effective – treatments that help people to quit smoking.Both groups examined the numerous forms of a gene called *CYP2A6*, which codes for an enzyme that acts mostly in the liver and regulates nicotine metabolism in the body. Previous research revealed that people with an ineffective form of the gene are less likely to become addicted to smoking.

Experts think that nicotine levels remain elevated for longer in these individuals, delaying the craving for the next cigarette. Nicotine is the primary chemical responsible for smoking addiction. People carry different forms of the *CYP2A6* gene, and this is more pronounced in particular parts of the world. “It seems that there’s more variation in this gene in Asian populations,” says Sharon Murphy of the University of Minnesota in Minneapolis, US, who has studied nicotine metabolism.Researchers in Tokyo decided to compare how different forms of the gene influenced the cigarette consumption of 200 Japanese people aged 50 or over who smoked 20 cigarettes (one pack) or more each day.[NIDA FACTS (2006)]

The scientists found that roughly one-quarter of the participants carried two copies of the normal form of the gene, *CYP2A6*1* and that these people smoked the most – almost two packs a day on average.Smokers who carried two copies of the *CYP2A6*4* gene, which results in slower nicotine metabolism, smoked the least. The study also provided new details about the role of other forms of the gene – *CYP2A6*7* and *CYP2A6*9* – suggesting these also reduce cigarette consumption.Another new study has found that variation in the *CYP2A6* gene can affect the nicotine levels people receive from nicotine patches often used to help quit smoking. Rachel Tyndale of the University of Toronto, Canada, found that slow metabolisers of nicotine had higher levels of nicotine in their blood when using the patches compared with faster metabolisers. Both genes alter the function of the brain neurotransmitter dopamine, which is associated with reward. The interaction of a form of *SLC6A3*, a dopamine transporter gene, and a variant of *DRD2*, a dopamine receptor gene, appears to ease the difficulty of kicking the habit, says the team.Previous work has shown that the same form of *SLC6A3* is associated with higher levels of dopamine in the brain, suggesting a mechanism for the effect.

A simple genetic test could help doctors tailor anti-smoking treatments to patients' needs, making it easier for them to quit. The test allowed an Oxford University team to successfully predict which smokers would respond well to nicotine patches, and which wouldn't. The test is for common mutations in genes that control the metabolism of dopamine. Nicotine stimulates the production of dopamine in the nucleus accumbens, the brain's "pleasure centre".People with these mutations metabolise dopamine more quickly. They would therefore benefit from anti-smoking treatments that are designed to boost dopamine levels. The team found that a person's genotype affects not only whether they are likely to smoke or not, but how many cigarettes they consume. Between 30 and 40 per cent of people have mutations in genes that code for two enzymes involved in dopamine metabolism: dopamine-hydroxylase and monoamine oxidase.

Heavy smokers are two to three times as likely to have mutations in these genes as non-smokers, says Robert Walton, one of the Oxford researchers. People with these mutations need to smoke more to maintain normal dopamine levels, so should be targeted with dopamine-boosting drugs such as buproprion, Walton says. Smokers without the mutations are more likely to be fast metabolisers of nicotine, and could be given nicotine patches.

Nicotine replacement therapy is currently the most popular form of anti-smoking treatment, [National Institute on Drug Abuse; National Institute of Health DHHS 2004]."In one study, the team found they could predict which of 800 smokers would respond to the patches. A University of Minnesota study indicates that the nicotine vaccine NicVax, which is now being tested in humans, appears safe, well-tolerated, and a potentially effective method for helping smokers kick the habit. Dorothy Hatsukami, Ph.D., director of the University of Minnesota Cancer Center's Transdisciplinary Tobacco Use Research Center (TTURC), is the lead author on this study. The 38-week study included 68 active smokers who were randomly assigned to receive one of three different doses of the vaccine or a placebo. The findings are published in the current issue of the journal Clinical Pharmacology and Therapeutics. "The vaccine works by producing antibodies that specifically bind to nicotine and thereby prevent much of the nicotine from entering the brain," Hatsukami said. "This process potentially reduces the pleasurable effects from smoking and reduces the addiction to nicotine.The vaccine may become a new option for helping the approximately 45 million people in the United States who smoke. In 2004, the rate for smoking in Minnesota was about the same as the national average of 20.9 percent. [European respiratory journal]

In a study it was found that The level of 8-oxoguanine (8-oxoG), a general marker of oxidative DNA damage, in DNA is the result of both an equilibrium between the rates of its formation and removal from DNA by DNA repair enzymes and the removal of 8-oxodGTP from the cellular nucleotide pool by hydrolysis to 8-oxodGMP, preventing its incorporation into DNA. Cellular DNA and its deoxynucleoside-5 . -triphosphate (dNTP)
precursors are continuously exposed to reactive oxygen species that are generated by mitochondrial respiration and inflammation and by environmental exposures to ionizing radiation and certain chemicals. Oxidative stress increases the level of oxidative damage to cellular components, including DNA. . Because cells, in response to oxidative DNA damage, can repair the damage, replicate it, or activate cell death pathways, oxidative DNA damage has been implicated to play a role in various diseases, including cancer.
Increased DNA damage resulting from oxidative stress has been suggested to play an important role in the induction and progression of many types of human cancers. The etiology of lung cancer has been linked to tobacco smoking. Cigarette smoke contains many carcinogens, including polycyclic aromatic hydrocarbons, which can form DNA adducts in lung tissue , and reactive oxygen species, which can induce oxidative damage in human lung tissue . Cigarette smoke can also cause chronic lung inflammation, which increases the oxidative stress in lung tissues .[*Agnieszka Siomek, Kowalewski,2005]*

CONCLUSION

Tobacco is the second major cause of death in the world. It is currently responsible for the death of one in ten adults worldwide (about 5 million deaths each year). If current smoking patterns continue, it will cause some 10 million deaths each year by 2025. Half the people that smoke today -that is about 650 million people- will eventually be killed by tobacco. Tobacco is the fourth most common risk factor for disease worldwide. The economic costs of tobacco use are equally devastating. In addition to the high public health costs of treating tobacco-caused diseases, tobacco kills people at the height of their productivity, depriving families of breadwinners and nations of a healthy workforce. Tobacco users are also less productive while they are alive due to increased sickness. A 1994 report estimated that the use of tobacco resulted in an annual global net loss of US$ 200 thousand million, a third of this loss being in developing countries.Tobacco and poverty are inextricably linked. Many studies have shown that in the poorest households in some low-income countries as much as 10% of total household expenditure is on tobacco. This means that these families have less money to spend on basic items such as food, education and health care. In addition to its direct health effects, tobacco leads to malnutrition, increased health care costs and premature death. It also contributes to a higher illiteracy rate, since money that could have been used for education is spent on tobacco instead. Tobacco's role in exacerbating poverty has been largely ignored by researchers in both fields.The WHO Oral Health Programme aims to control tobacco-related oral diseases and adverse conditions through several strategies. Within WHO, the Programme forms part of the WHO tobacco-free initiatives, with fully integrated oral health-related programmes. Externally, the Programme encourages the adoption and use of WHO tobacco-cessation and control policies by international and national oral health organizations. Primary partners are WHO Collaborating Centres in Oral Health and NGOs who are in official relations with WHO, i.e. the International Association for Dental Research (IADR) and the FDI World Dental Federation. [Table 6] There are several ethical, moral, and practical reasons why oral health professionals should strengthen their contributions to tobacco-cessation programmes The most cost-effective strategies are population-wide public policies, like bans on direct and indirect tobacco advertising, tobacco tax and price increases, smoke-free environments in all public and workplaces, and large clear graphic health messages on tobacco packaging [Lee Jong-wook, WHO 2004]

Table 1 INDOOR AIR POLLUTION FACTORS

A] LEVELS OF NICOTINE IN INDOOR AIR

Billiard parlour	19.4	µg/m3
Home	12.1- 14.4	
Departmental store	0.6	
Automobile	0.4	

B] INDOOR AIR QUALITY

	Nicotine	µg/ m3
Restaurents	0.5- 37	average 5.4
	7.1 -37	average 15
Offices	3- 48	
	9-32	
	6-20	average 5
Public common areas	2-36	
	1-3	
Smoking sections of airplanes	6-29	average 15
	0-112	average 9
Non smoking sections of airplanes	0-40	average 6
Food counters of shopping malls	1.6- 3.1	average 2.3

B] Mothers Smoking - 20 cigarettes
Babies receive 9.3 µg/kg/day Nicotine
Breast milk ~ 200-500 ppb

Encyclopedia of clinical Toxicology (pp 744-45)

TABLE 2HARMFUL INGREDIENTS OF CIGARETTE

Acetone [Nail Polish Remover]	Hydrogen Cyanide [Gas Chamber Poison]

Acetic Acid [Vinegar]
Ammonia [Floor/Toilet Cleaner]
Arsenic [Poison]
Butane [Cigarette Lighter Fluid]
Cadmium [Rechargeable Battery]
Carbon Monoxide [Car Exhaust]
DDT/ Dieldrin [Insecticides]
Ethanol [Alcohol]
Formaldehyde [Preservative - Body Tissue & Fabric]
Hexamine [Barbecue Lighter]

Methane [Swamp Gas]
Methanol [Rocket Fuel]
Naphthalene [Mothbals]
Nicotine [Insecticide/ Addictive Drug]
Nitrobenzene [Gasoline Additive]
Nitrous Oxide
Phenols [Disinfectant]
Stearic Acid [Candle Wax]
Toluene [Industrial Solvent]
Vinyl Chloride [Makes PVC2]

American cancer society (2006)

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Chapter 20 PARTICULATE MATTER

Particulate matter is the sum of all solid and liquid particles suspended in air, many of which are hazardous. This complex mixture contains for instance dust, pollen, soot, smoke, and liquid droplets.

These particles come in many different size ranges such as coarse, fine and ultrafine. They also vary in composition and origin.

Particles are either directly emitted into the air by sources such as combustion processes and windblown dust, or formed in the atmosphere by transformation of emitted gases such as SO2.

Extensive research indicates that exposure to outdoor PM 10 and PM 2.5 levels exceeding current air quality standards is associated with increased risk of hospitalization for lung and heart-related respiratory illness, including emergency room visits for asthma. PM exposure is also associated with increased risk of premature deaths, especially in the elderly and people with pre-existing cardiopulmonary disease. In children, studies have shown associations between PM exposure and reduced lung function and increased respiratory symptoms and illnesses. Besides reducing visibility, the acidic portion of PM (nitrates, sulfates) can harm crops, forests, aquatic and other ecosystems.

In Europe, sulphate and organic matter are the main components of particulate air pollution in terms of the mass of the particles. Mineral dust, nitrate, and soot can also be major components under certain conditions.

In Europe, long-term exposure to current ambient particulate matter concentrations may affect the lungs of both children and adults and may reduce life expectancy by a few months, mainly in subjects with pre-existing heart and lung diseases.

Ambient particulate matter is responsible for harmful effects on health, even in the absence of other air pollutants. Both fine and coarse particles have been shown to affect health, in particular the respiratory system.

Fine particles are more dangerous than coarse particles. Apart from the size of the particles, other specific physical, chemical, and biological characteristics that can influence harmful health effects include the presence of metals, PAHs, other organic components, or certain toxins.

When particulate matter is combined with other air pollutants, the individual effects of each pollutant are cumulated. In certain cases, especially for combinations of particulate matter with ozone or allergens, effects were shown to be even greater than the sum of the individual effects. When particulate matter interacts with gases, this interaction changes its composition and, therefore, its effects.

Certain groups of people are more susceptible to suffer health effects due to ambient particulate matter. These include elderly people, children, people with a pre-existing heart and lung disease, asthmatics, and socially disadvantaged and poorly educated populations.

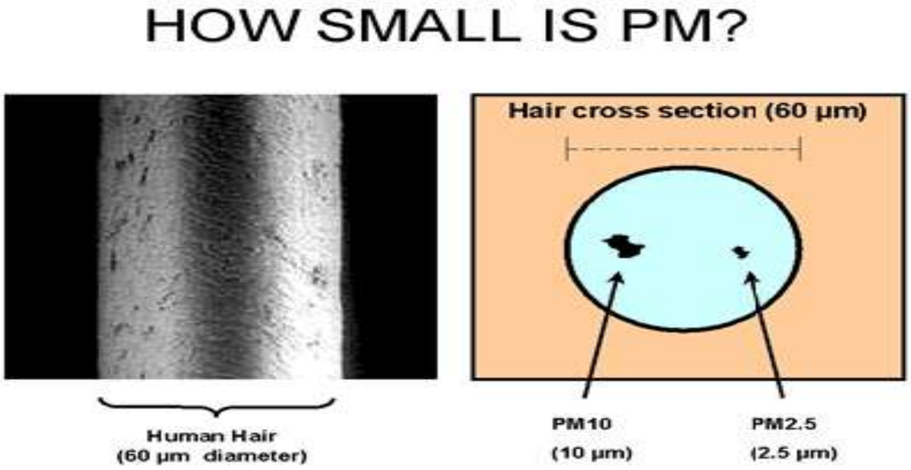
Some persons are vulnerable even at low concentrations of ambient particular matter, no threshold has been identified below which nobody's health is affected

In June 2002, the ARB adopted new ambient air quality standards for PM 10 and PM 2.5, resulting from an extensive review of the health-based scientific literature.

California Ambient Air Quality Standards for PM

Averaging Time	PM 10	PM 2.5
Annual *	20 µg/m3	12 µg/m3
24 Hours	50 µg/m3	

PM may be divided into many size fractions, measured in microns (a micron is one-millionth of a meter). ARB regulates two size classes of particles - particles up to 10 microns (PM10) and particles up to 2.5 microns in size (PM2.5). PM2.5 particles are a subset of PM10.

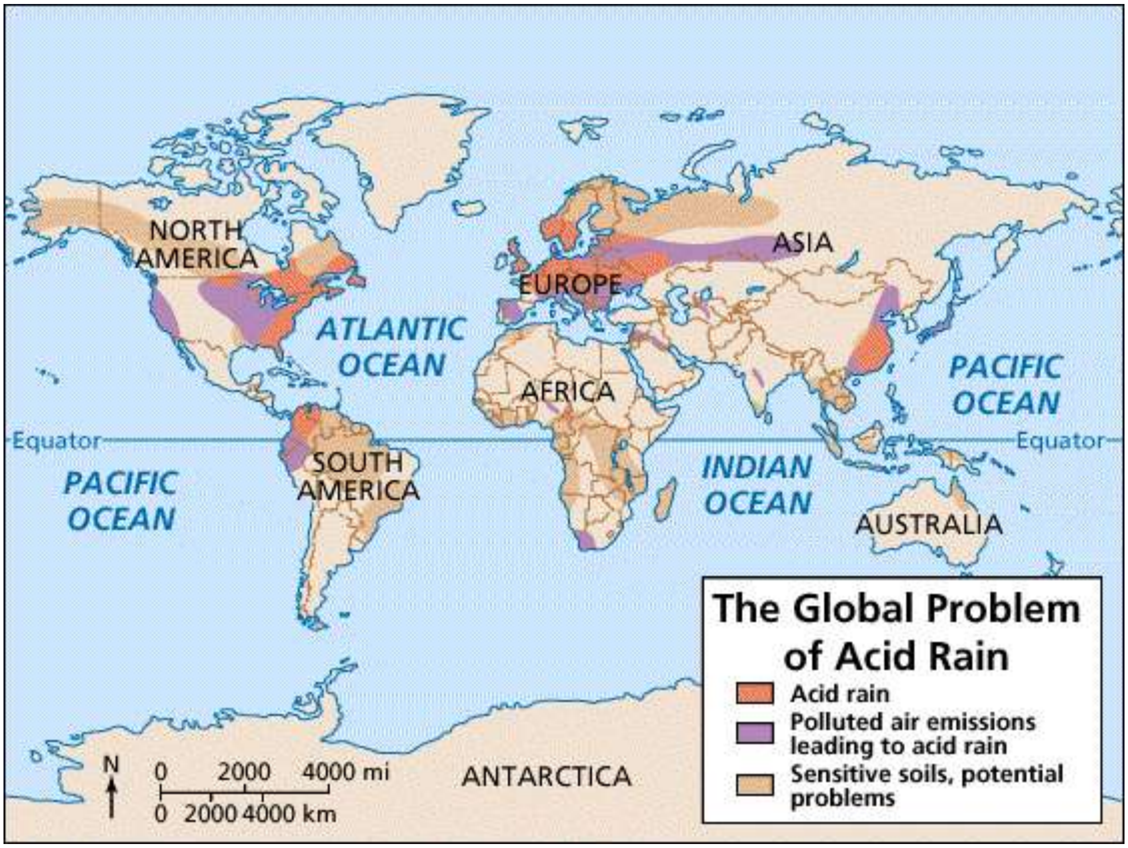


A picture of a human hair compared to the relative sizes of PM 10 and PM 2.5 particles PM10 and PM2.5 are each measured and expressed as the amount (in micrograms) of particles contained in a cubic meter of air, expressed as micrograms per cubic meter (µg/m3).

REFERENCE

California Environmental Protection Agency Air Resources BoardAmbient Air Quality Standards (AAQS) for Particulate Matter, November 24, 2009

Chapter 20 ACID RAIN



Acid rain is a rain or any other form of precipitation that is unusually acidic, i.e. elevated levels of hydrogen ions (low pH). It can have harmful effects on plants, aquatic animals, and infrastructure through the process of wet deposition.Acid rain is caused by emissions of compounds of ammonium, carbon, nitrogen, and sulphur which react with the water molecules in the atmosphere to produce acids. The various gases like sulphur dioxide and nitrogen dioxide react with water vapours in presence of sunlight and form sulphuric acid and nitric acid mist. The reaction takes place in the following manner.

SO2 + H2O = H2SO3 (Sulphurous acid)

SO2 + O3 (Ozone) = SO3 + O2

SO3 + H2O = H2SO4 (Sulphuric acid)

2NO + O2 = 2NO2

2NO2 + H2O = HNO3 (Nitric acid) + HNO2(Nitrous acid)

The sulphuric acid and nitric acid remain in a vapour state when the temperature is high. The condensation begins with the fall of temperature and it mingles with the rain, fog or snow and this increases its acidity

Causes of Acid Rain:

The oxides of nitrogen, or NOx, and sulphur dioxide, or S02, are the two main sources of acid rain. Sulphur dioxide, which is a colourless gas, is given off as a by-product when fossil fuels that contain sulphur are burned.

This gas is produced due to various industrial processes, like the processing of crude oil, utility factories, and iron and steel factories. Natural means and disaster can also result in sulphur dioxide being released into the atmosphere, such as rotting vegetation, plankton, sea spray, and volcanoes, all of which emit about 10% sulphur dioxide.

On the whole, industrial combustion is responsible for 69.4% sulphur dioxide emissions into the atmosphere, and vehicular transportation is responsible for about 3.7%.Nitrogen oxide is the other chemical that acid rain is made up of. Any nitrogen compound that contains oxygen atoms of any amount is known as oxides of nitrogen. For example, nitrogen dioxide and nitrogen monoxide are oxides of nitrogen.

These gases are produced in firing processes which involve extremely high temperatures, e.g., utility plants and automobiles, as well as in chemical industries, such as in the production of fertilizers.

Five per cent of nitrogen oxide is emitted by natural processes like lightning, volcanic eruptions, forest fires, and action of bacteria in the soil. Industrial processes emit 32% and vehicular transportation is responsible for 43%.

Nitrogen oxide, which is a dangerous gas in itself, causes damage to the respiratory organs by attacking the membranes in them, thus increasing the chances of respiratory diseases. It also causes smog and is a contributory factor for the damage of the ozone layer in the atmosphere. When there is acid rain, the nitrogen oxide can be carried far away from the original location of the rain.

Effects of Acid Rain:

Acid rain has serious implications for continuation of life on this planet. The main acid rain problems are:

i. Effects on Water Bodies:

Most rivers and lakes have a pH that ranges between 6 and 8. Acid rain that may fall directly in these water bodies or may be washed into them as surface runoff, alter their chemical environment. The flora and fauna in these water bodies are adapted for life in the original pH value of the water.Altered acidity of their environment may be a threat to their survival. Although, some soils are capable of buffering increase in acidity, water bodies that have soil with poor buffering capacity may release aluminium ions from the soil which is toxic for aquatic life forms. Read more on water pollution.

ii. Effects on Soil and Forests:

Acid rain is being cited as one of the major causes of degradation of the forests at higher altitudes of the Appalachian Mountains from Maine to Georgia. Forests are affected directly as well as indirectly by acid rain. When leaves are frequently exposed to acid rain they are stripped off the essential nutrients present in them.

Acid rain falling on the soil, change soil acidity. In its bid to neutralize this change in pH, soil releases substances that are toxic for trees growing on it. Acidic water also dissolve nutrients in the soil and as it runs off the surface, it carries these essential minerals away with it, before they can be absorbed by flora growing on the forest floor.

iii. Acid Rain Effects on Aquatic Flora and Fauna:

Acid rain has a long term can directly effect on the aquatic life, as the high amount of sulphuric acid and nitric acid levels in acid rains are directly consumed by aquatic animals and plants. The harmful acids affect the ability of fish to take in nutrients, salt, and oxygen.

Aquatic animals intake oxygen from the water through their gills, but harmful acids leads to mucus formation in the gills, which hinders their ability to respire. Acid rains affect the pH level of the water which reduces the absorption capacity of essential nutrients of the aquatic life. This also hampers the reproduction process in fish leading to weak or brittle eggs.

iv. Effects of Acid Rain on Humans:

Most of all, acid rain affects human health adversely. It has the ability of harming us via the atmosphere as well as the soil where the food we eat is grown. Acid rain results in toxic metals breaking loose from the chemical compounds they occur in naturally.While toxic metals may be dangerous, but as long as they exist in combination with other elements, they are not harmful. Once acid rain causes these toxic metals to be released they can infiltrate into the drinking water, and the animals or crops that humans use as sources of food.

This contaminated food can damage the nerves in children, or result in severe brain damage, or even death. Scientists suspect that aluminum, one of the toxic metals affected by acid rain, is associated with Alzheimer’s disease.

Another adverse health effect of acid rain on humans is the respiratory problems it causes. The emissions of nitrogen oxide and sulfur dioxide cause respiratory problems like throat, nose and eye irritation; headache; asthma; and dry coughs. Acid rain is particularly harmful for those who have difficulty in breathing or suffer from asthma. In fact, even the lungs of healthy people can be damaged by the pollutants in acid air.

v. Acid Rain Effects on Historical Monuments:

Acid rain destroys stained glass windows, corrodes metal and also ruins the paint colour. Acid rain reacts with calcium to form calcium bicarbonate, which can be easily washed away. One drastic effect of acid rain can be seen on one of the Seven Wonders of the World, Taj Mahal in India.

The marble walls and pillars of this great man-made monument are found to be getting eroded by acid rains. Even St. Paul’s Cathedral in London, and the Statue of Liberty in New York are few such examples.

3. Control Measure:

The numbers of possible solutions for acid rain that are available to us are aplenty:

i. One of the most fundamental acid rain solutions is to utilize fuels that burn more cleanly, or to burn coal more efficiently. This will greatly reduce the possibilities of acid rain developing in the atmosphere.

ii. As fast as industrial power plants are concerned, the best solution is to attach devices known as ‘scrubbers’ in the chimneys of these plants. These scrubbers reduce the amount of sulfur produced in the smoke by 90 – 95%.

iii. Vehicles and cars must be mandatory required to comply with very tight and efficient emission standards. Fitting catalytic converters into the exhaust pipes of vehicles also reduces the amount of sulfur dioxide produced by the vehicles.

iv. For industrial power plants, there are many more acid rain solutions that must be enforced, as they are clearly the biggest contributors to the formation of acidified water droplets in the atmosphere. Industries must regularly inspect and clean all their emission equipment and chimneys and pipes.

v. All these acid rain solutions will be pointless unless people are informed and educated about the ill-effects and harms of acid rain. A widespread and nationwide effort must be made to make people aware. Only after that is done will all the acid rain solutions actually make a difference.

Acid rain is one of the biggest environmental hazards that we are facing today, and strong measure must be taken to prevent it, before it is too late. Governments need to sit up and take notice, and do much more than what they are already doing.

Acid rain adversely affects plants, animals and human beings, and as a result it is not something that we can afford to ignore. It is our duty towards ourselves and towards our fellow human beings to do all we can to prevent and reduce the presence and increase of acid rain in our environment

Chapter 21

The OXYGEN CYCLE is the biogeochemical cycle that describes the movement of oxygen within and between its three main reservoirs: the atmosphere (air), the biosphere (living things), and the lithosphere (Earth's crust). The main driving factor of the oxygen cycle is photosynthesis, which is responsible for the modern Earth's atmosphere and life.

Reservoirs and fluxes

By far the largest reservoir of Earth's oxygen is within the silicate and oxide minerals of the crust and mantle (99.5%). Only a small portion has been released as free oxygen to the biosphere (0.01%) and atmosphere (0.36%). The main source of atmospheric oxygen is photosynthesis, which produces sugars and oxygen from carbon dioxide and water:

$6CO_2 + 6H_2O + \text{energy} \rightarrow C_6H_{12}O_6 + 6O_2$

Photosynthesizing organisms include the plant life of the land areas as well as the phytoplankton of the oceans. The tiny marine cyanobacterium Prochlorococcus was discovered in 1986 and accounts for more than half of the photosynthesis of the open ocean.[1]

An additional source of atmospheric oxygen comes from photolysis, whereby high energy ultraviolet radiation breaks down atmospheric water and nitrite into component atoms. The free H and N atoms escape into space leaving O_2 in the atmosphere:

$2H_2O + \text{energy} \rightarrow 4H + O_2$
$2N_2O + \text{energy} \rightarrow 4N + O_2$

The main way oxygen is lost from the atmosphere is via respiration and decay, mechanisms in which animal life and bacteria consume oxygen and release carbon dioxide.

Because lithospheric minerals are oxidised in oxygen, chemical weathering of exposed rocks also consumes oxygen. An example of surface weathering chemistry is formation of iron-oxides (rust):

$4FeO + O_2 \rightarrow 2Fe_2O_3$

Oxygen is also cycled between the biosphere and lithosphere. Marine organisms in the biosphere create calcium carbonate shell material ($CaCO_3$) that is rich in oxygen. When the organism dies its shell is deposited on the shallow sea floor and buried over time to create the limestone rock of the lithosphere. Weathering processes initiated by organisms can also free oxygen from the lithosphere. Plants and animals extract nutrient minerals from rocks and release oxygen in the process. The PHOSPHORUS CYCLE is the biogeochemical cycle that describes the movement of phosphorus through the lithosphere, hydrosphere, and biosphere. Unlike many other biogeochemical cycles, the atmosphere does not play a significant role in the movements of phosphorus, because phosphorus and phosphorus-based compounds are usually solids at the typical ranges of temperature and pressure found on Earth.

Phosphorus is an essential nutrient for plants and animals in the form of ions PO_4^{3-} and HPO_4^{2-} . It is a part of DNA-molecules and RNA-molecules, molecules that store energy (ATP and ADP) and of fats of cell membranes. When Phosphorus is in a compound (phosphate), it plays an important role in holding the DNA and RNA together.[1] Phosphorus is also a building block of certain parts of the human and animal body, such as the bones and teeth.

Phosphorus cycle is also known as a Sedimentary cycle because the cycle does not enter the atmosphere and stays in rock sediments, sand,and ocean floor. Where it is trapped until erosion occurs and the Phosphorus is released.

Phosphorus forms parts of important life sustaining molecules but is not very common in the biosphere. Phosphorous does not enter the atmosphere remaining mostly on land and in rock and soil minerals. 80 percent of the phosphorus is used to make fertilizers and a type of phosphorus such as dilute phosphoric acid is used in soft drinks. Phosphates may be effective in such ways but they also cause pollution problems in lakes and streams. Over enrichment of phosphate can lead to algal bloom, because of the excess of nutrients. This causes more algae to grow, bacteria consumes the algae and causes more bacteria to increase in numbers. They use all the oxygen in the water during cellular respiration, causing many fish to die.

Phosphorus normally occurs in nature as part of a phosphate ion, consisting of a phosphorus atom and some number of oxygen atoms, the most abundant form (called orthophosphate) having four oxygens: PO_4^{3-}. Most phosphates are found as salts in ocean sediments or in rocks. Over time, geologic processes can bring ocean sediments to land, and weathering will carry terrestrial . Plants absorb phosphates from the soil, then bind the phosphate into organic compounds. The plants may then be consumed by herbivores who in turn may be consumed by carnivores. After death, the animal or plant decays, and the phosphates are returned to the soil. Runoff may carry them back to the ocean or they may be reincorporated into rock.

The primary biological importance of phosphates is as a component of nucleotides, which serve as energy storage within cells (ATP) or when linked together, form the nucleic acids DNA and RNA. Phosphorus is also found in bones, whose strength is derived from calcium phosphate, and in phospholipids (found in all biological membranes).

Phosphates move quickly through plants and animals; however, the processes that move them through the soil or ocean are very slow, making the phosphorus cycle overall one of the slowest biogeochemical cycles.

However, recent findings suggest that phosphorus is cycled through the ocean on the timescale of 10,000 year, suggesting that the phosphorus cycle may play a role in global warming.

Plants bind the phosphate into organic compounds. (Phosphate is not very common in biospheres)Unlike other cycles of matter compounds, phosphorus cannot be found in air as a gas. This is because at normal temperature and circumstances, it is a solid in the form of red and white phosphorus. It usually cycles through water, soil and sediments. Phosphorus is typically the limiting nutrient found in streams, lakes and fresh water environments. As rocks and sediments gradually wear down, phosphate is released. In the atmosphere phosphorus is mainly small dust particles.

Phosphorus is one of the longest cycles, and takes a long time to move from sediments to living organisms and back to sediments.

Initially, phosphate weathers from rocks. The small losses in a terrestrial system caused by leaching through the action of rain are balanced in the gains from weathering rocks. In soil, phosphate is absorbed on clay surfaces and organic matter particles and becomes incorporated (immobilized). Plants dissolve ionized forms of phosphate. Herbivores obtain phosphorus by eating plants, and carnivores by eating herbivores. Herbivores and carnivores excrete phosphorus as a waste product in urine and feces. Phosphorus is released back to the soil when plants or animal matter decomposes and the cycle repeats.

SULFUR CYCLE

Sulfur is one of the constituents of many proteins, vitamins and hormones. It recycles as in other biogeochemical cycles.

The essential steps of the sulfur cycle are:

- Mineralization of organic sulfur to the inorganic form, hydrogen sulfide: (H_2S).
- Oxidation of sulfide and elemental sulfur (S) and related compounds to sulfate (SO_4^{2-}).
- Reduction of sulfate to sulfide.
- Microbial immobilization of the sulfur compounds and subsequent incorporation into the organic form of sulfur.

These are often termed as follows:

Assimilative sulfate reduction in which sulfate (SO_4^{2-}) is reduced to organic sulfhydryl (otherwise known as thiol) groups (R–SH) by plants, fungi and various prokaryotes. The oxidation states of sulfur are +6 in sulfate and –2 in R–SH.

Desulfuration in which organic molecules containing sulfur can be desulfurated, producing hydrogen sulfide gas (H_2S), oxidation state = –2. Note the similarity to deamination.

Oxidation of hydrogen sulfide produces elemental sulfur (S^o), oxidation state = 0. This reaction is done by the photosynthetic green and purple sulfur bacteria and some chemolithotrophs.

Further *oxidation of elemental sulfur* by sulfur oxidizers produces sulfate.

Dissimilative sulfur reduction in which elemental sulfur can be reduced to

hydrogen sulfide.
Dissimilative sulfate reduction in which sulfate reducers generate hydrogen sulfide from sulfate.

Human impact on the sulfur cycle is primarily in the production of sulfur dioxide (SO_2) from industry (e.g. burning coal) and the internal combustion engine. Sulfur dioxide can precipitate onto surfaces where it can be oxidized to sulfate in the soil (it is also toxic to some plants), reduced to sulfide in the atmosphere, or oxidized to sulfate in the atmosphere as sulfuric acid, a principal component of acid rain.

WATER CYCLE

The different processes are as follows:

· Precipitation is condensed water vapor that falls to the Earth's surface. Most precipitation occurs as rain, but also includes snow, hail, fog drip, graupel, and sleet. Approximately 505,000 km³ of water fall as precipitation each year, 398,000 km³ of it over the oceans.

· Canopy interception is the precipitation that is intercepted by plant foliage and eventually evaporates back to the atmosphere rather than falling to the ground.

· Snowmelt refers to the runoff produced by melting snow.

· Runoff includes the variety of ways by which water moves across the land. This includes both surface runoff and channel runoff. As it flows, the water may infiltrate into the ground, evaporate into the air, become stored in lakes or reservoirs, or be extracted for agricultural or other human uses.

· Infiltration is the flow of water from the ground surface into the ground. Once infiltrated, the water becomes soil moisture or groundwater.

· Subsurface Flow is the flow of water underground, in the vadose zone and aquifers. Subsurface water may return to the surface (eg. as a spring or by being pumped) or eventually seep into the oceans. Water returns to the land surface at lower elevation than where it infiltrated, under the force of gravity or gravity induced pressures. Groundwater tends to move slowly, and is replenished slowly, so it can remain in aquifers for thousands of years.

· Evaporation is the transformation of water from liquid to gas phases as it moves from the ground or bodies of water into the overlying atmosphere. The source of energy for evaporation is primarily solar radiation. Evaporation often implicitly includes transpiration from plants, though together they are specifically referred to as evapotranspiration. Total annual evapotranspiration amounts to approximately 505,000 km³ of water, 434,000 km³ of which evaporates from the oceans.

· Sublimation is the state change directly from solid water (snow or ice) to water vapor.

· Advection is the movement of water — in solid, liquid, or vapour states — through the atmosphere. Without advection, water that evaporated over the oceans could not precipitate over land.

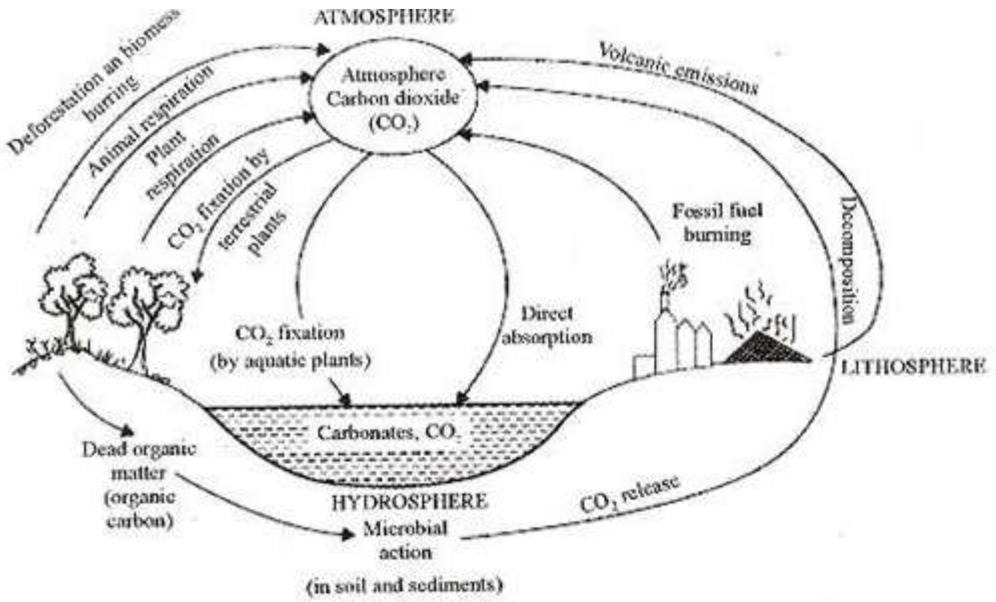
· Condensation is the transformation of water vapour to liquid water droplets in the air, producing clouds and fog.

Effects on climate:The water cycle is powered from solar energy. 86% of the global evaporation occurs from the oceans, reducing their temperature by evaporative cooling. Without the cooling effect of evaporation the greenhouse effect would lead to a much higher surface temperature of 67 °C, and a warmer planet.

Effects on biogeochemical cycling

While the water cycle is itself a biogeochemical cycle, flow of water over and beneath the Earth is a key component of the cycling of other biogeochemicals. Runoff is responsible for almost all of the transport of eroded sediment and phosphorus from land to waterbodies. The salinity of the oceans is derived from erosion and transport of dissolved salts from the land. Cultural eutrophication of lakes is primarily due to phosphorus, applied in excess to agricultural fields in fertilizers, and then transported overland and down rivers. Both runoff and groundwater flow play significant roles in transporting nitrogen from the land to waterbodies. The dead zone at the outlet of the Mississippi River is a consequence of nitrates from fertilizer being carried off agricultural fields and funnelled down the river system to the Gulf of Mexico. Runoff also plays a part in the carbon cycle, again through the transport of eroded rock and soil. Human activities that alter the water cycle include:

- agriculture
- alteration of the chemical composition of the atmosphere
- construction of dams
- deforestation and afforestation
- removal of groundwater from wells
- water abstraction from rivers
- urbanization



A Carbon Cycle

Carbon Cycle:

The carbon cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the Earth. It is one of the most important cycles of the earth and allows for carbon to be recycled and reused throughout the biosphere and all of its organisms.

The Carbon Cycle is a complex series of processes through which all of the carbon atoms in existence rotate. The wood burned just a few decades ago could have produced carbon dioxide which through photosynthesis became part of a plant. When you eat that plant, the same carbon from the wood which was burnt can become part of you. The carbon cycle is the great natural recycler of carbon atoms.

Without the proper functioning of the carbon cycle, every aspect of life could be changed dramatically. Plants, animals, and soil interact to make up the basic cycles of nature. In the carbon cycle, plants absorb carbon dioxide from the atmosphere and use it, combined with water they get from the soil, to make the substances they need for growth. The process of photosynthesis incorporates the carbon atoms from carbon dioxide into sugars.

Animals, such as the rabbit eat the plants and use the carbon to build their own tissues. Other animals, such as the fox, eat the rabbit and then use the carbon for their own needs. These animals return carbon dioxide into the air when they breathe, and when they die, since the carbon is returned to the soil during decomposition. The carbon atoms in soil may then be used in a new plant or small microorganisms. The following major reservoirs of carbon interconnected by pathways of exchange:

i. The atmosphere.

ii. The terrestrial biosphere, which is usually defined to include fresh water systems and non-living organic material, such as soil carbon.

iii. The oceans, including dissolved inorganic carbon and living and non-living marine biota.

iv. The sediments including fossil fuels

v. The Earth’s interior, carbon from the Earth’s mantle and crust is released to the atmosphere and hydrosphere by volcanoes and geothermal systems.he annual movements of carbon, the carbon exchanges between reservoirs, occur because of various chemical, physical, geological, and biological processes. The ocean contains the largest active pool of carbon near the surface of the Earth, but the deep ocean part of this pool does not rapidly exchange with the atmosphere in the absence of an external influence, such as an uncontrolled deep-water oil well leak.

The global carbon budget is the balance of the exchanges (incomes and losses) of carbon between the carbon reservoirs or between one specific loop the carbon cycle.

Carbon is released into the atmosphere in several ways:

i. Through the respiration performed by plants and animals. This is an exothermic reaction and it involves the breaking down of glucose (or other organic molecules) into carbon dioxide and water.

ii. Through the decay of animal and plant matter. Fungi and bacteria break down the carbon compounds in dead animals and plants and convert the carbon to carbon dioxide if oxygen is present, or methane if not.

iii. Through combustion of organic material which oxidizes the carbon it contains, producing carbon dioxide (and other things, like water vapour). Burning fossil fuels such as coal, petroleum products releases carbon dioxide. Burning agro fuels also releases carbon dioxide

iv. Volcanic eruptions and metamorphism release gases into the atmosphere. Volcanic gases are primarily water vapour, carbon dioxide and sulphur dioxide.

v. Carbon is transferred within the biosphere as heterotrophs feed on other organisms or their parts (e.g., fruits). This includes the uptake of dead organic material (detritus) by fungi and bacteria for fermentation or decay.

vi. Most carbon leaves the biosphere through respiration. When oxygen is present, aerobic respiration occurs, which releases carbon dioxide into the surrounding air or water, following the reaction C6H12O6 + 602 —> 6CO2 + 6H2O. Otherwise, anaerobic respiration occurs and releases methane into the surrounding environment, which eventually makes its way into the atmosphere or hydrosphere (e.g., as marsh gas or flatulence).

Circulation of carbon dioxide:

i. Plants absorbs the carbon dioxide from the atmosphere.

ii. During the process of photosynthesis, plants incorporates the carbon atoms from carbon dioxide into sugars.

iii. Animals, such as the rabbit eat the plants and use the carbon to build their own tissues, chain the carbon content

iv. Through the food chain, carbon is transferred into foxes, lions etc.

v. The animals return carbon dioxide into the air when they breathe, and when they die, since the carbon is returned to the soil during decomposition

In Case of Ocean:

In regions of oceanic upwelling, carbon is released to the atmosphere. Conversely, regions of down welling transfer carbon (CO_2) from the atmosphere to the ocean. When CO_2 enters the ocean, it participates in a series of reactions which are locally in equilibrium:

i. Conversion of CO_2 (atmospheric) to CO_2 (dissolved).

ii. Conversion of CO_2 (dissolved) to carbonic acid (H_2CO_3).

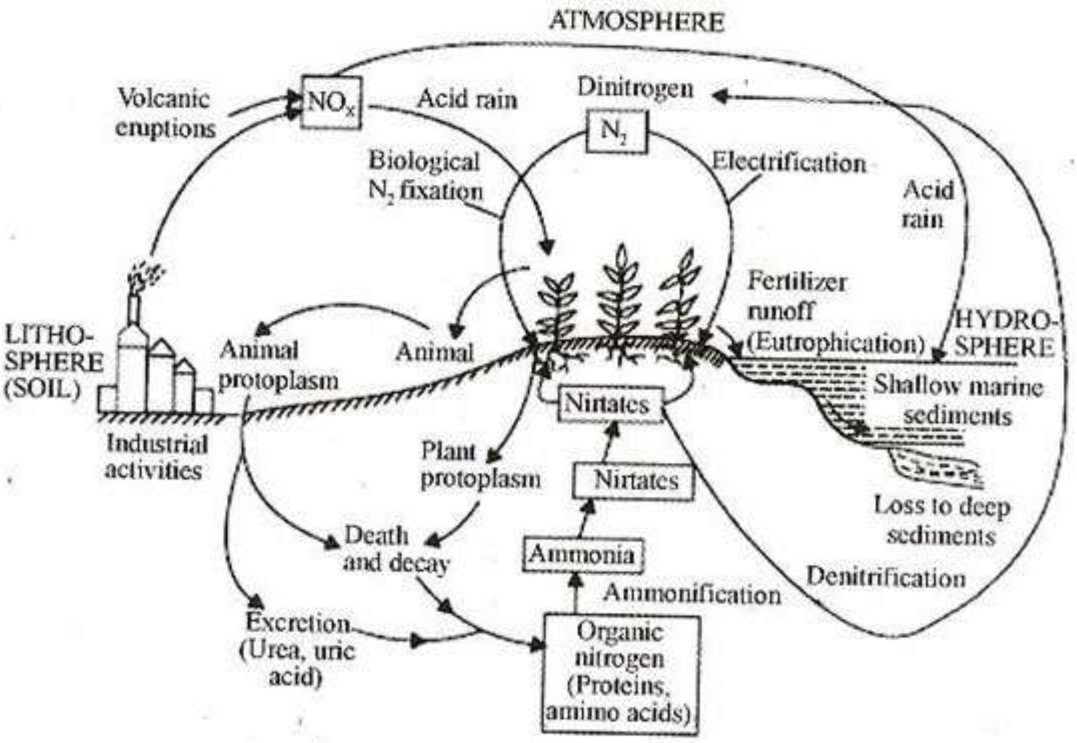
iii. Conversion of carbonic acid (H_2CO_3) to bicarbonate ion.

iv. Conversion of bicarbonate ion to carbonate ion.

In the oceans, dissolved carbonate can combine with dissolved calcium to precipitate solid calcium carbonate, $CaCO_3$, mostly as the shells of microscopic organisms. When these organisms die, their shells sink and accumulate on the ocean floor. Over time these carbonate sediments form limestone which is the largest reservoir of carbon in the carbon cycle.

The dissolved calcium in the oceans comes from the chemical weathering of calcium-silicate rocks, during which carbonic and other acids in groundwater react with calcium-bearing minerals liberating calcium ions to solution and leaving behind a residue of newly formed aluminium-rich clay minerals and insoluble minerals such as quartz.

The flux or absorption of carbon dioxide into the world's oceans is influenced by the presence of widespread viruses within ocean water that infect many species of bacteria. The resulting bacterial deaths spawn a sequence of events that lead to greatly enlarged respiration of carbon dioxide, enhancing the role of the oceans as a carbon sink.



A Nitrogen Cycle

Nitrogen Cycle:

The nitrogen cycle is the set of biogeochemical processes by which nitrogen undergoes chemical reactions, changes form, and moves through difference reservoirs on earth, including living organisms.

Nitrogen is required for all organisms to live and grow because it is the essential component of DNA, RNA, and protein. However, most organisms cannot use atmospheric nitrogen, the largest reservoir. The five processes in the nitrogen cycle

i. Nitrogen fixation

ii. Nitrogen uptake

iii. Nitrogen mineralization

iv. Nitrification

v. De-nitrification

Humans influence the global nitrogen cycle primarily through the use of nitrogen-based fertilizers.

I. Nitrogen fixation: N2 -> NH4+

Nitrogen fixation is the process wherein N2 is converted to ammonium, essential because it is the only way that organisms can attain nitrogen directly from the atmosphere. Certain bacteria, for example those among the genus Rhizobium, are the only organisms that fix nitrogen through metabolic processes.

Nitrogen fixing bacteria often form symbiotic relationships with host plants. This symbiosis is well-known to occur in the legume family of plants (e.g. beans, peas, and clover). In this relationship, nitrogen fixing bacteria inhabit legume root nodules and receive carbohydrates and a favourable environment from their host plant in exchange for some of the nitrogen they fix. There are also nitrogen fixing bacteria that exist without plant hosts, known as free-living nitrogen fixers. In aquatic environments, blue-green algae (really a bacteria called cyanobacteria) is an important free-living nitrogen fixer.

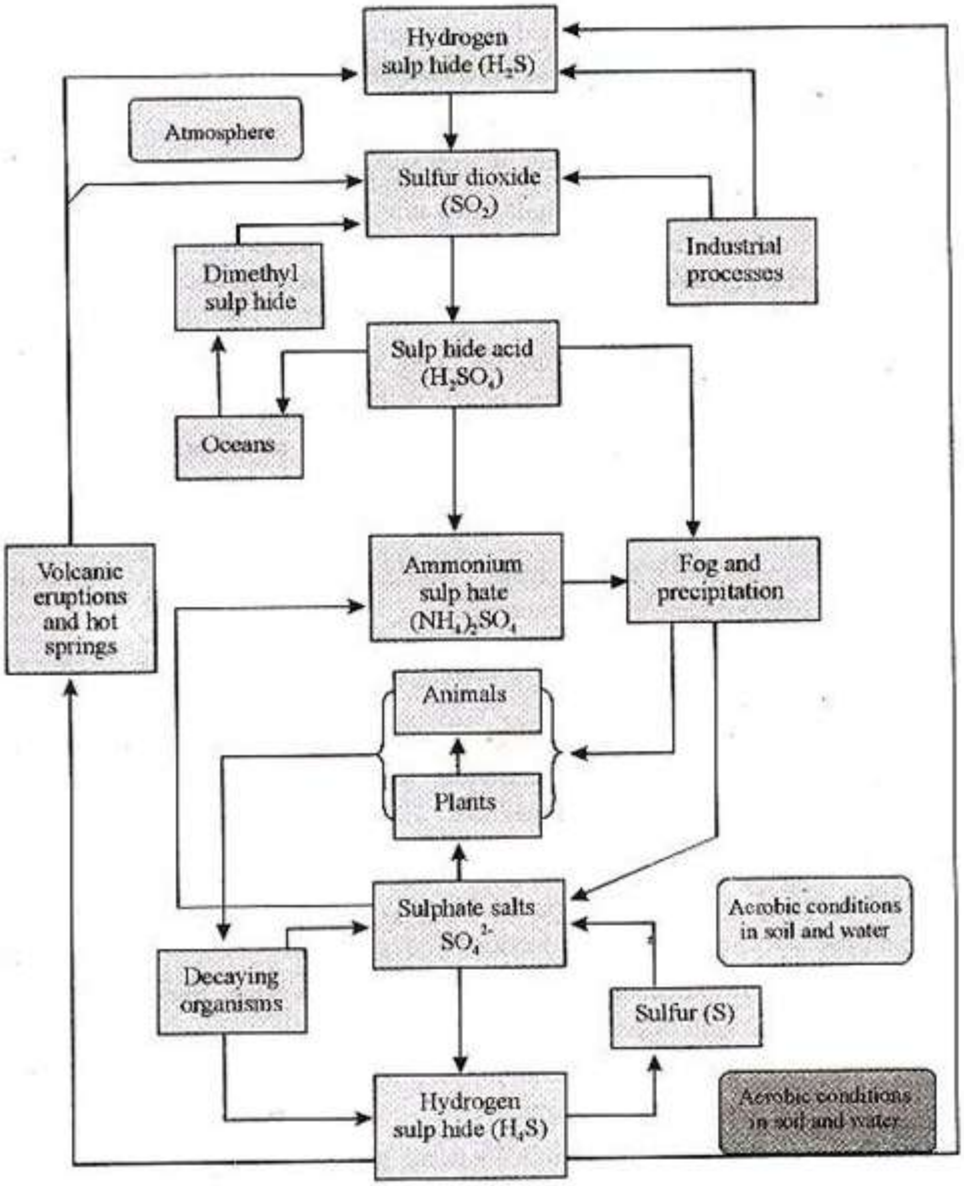
II. Nitrogen uptake: NH4+ -> Organic N

The ammonia produced by nitrogen fixing bacteria is usually quickly incorporated into protein and other organic nitrogen compounds, either by a host plant, the bacteria itself, or another soil organism.

III. Nitrogen mineralization: Organic N ->NH4+

After nitrogen is incorporated into organic matter, it is often converted back into inorganic nitrogen by a process called nitrogen mineralization, otherwise known as decay. When organisms die, decomposers (such as bacteria and fungi) consume the organic matter and lead to the process of decomposition.

During this process, a significant amount of the nitrogen contained within the dead organism is converted to ammonium. Once in the form of ammonium, nitrogen is available for use by plants or for further transformation into nitrate (NO3–) through the process called nitrification



A Sulphur Cycle

Sulphur Cycle:

Sulphur is one of the components that make up proteins and vitamins. Proteins consist of amino acids that contain sulphur atoms. Sulphur is important for the functioning of proteins and enzymes in plants, and in animals that depend upon plants for sulphur.

It enters the atmosphere through both natural and human sources. Natural recourses can be for instance volcanic eruptions, bacterial processes, evaporation from water, or decaying organisms. When sulphur enters the atmosphere through human activity, this is mainly a consequence of industrial processes where sulphur dioxide (SO2) and hydrogen sulphide (H2S) gases are emitted on a wide scale.

When sulphur dioxide enters the atmosphere it will react with oxygen to produce sulphur trioxide gas (SO3), or with other chemicals in the atmosphere, to produce sulphur salts. Sulphur dioxide may also react with water to produce sulphuric acid (H2SO4). Sulphuric acid may also be produced from demethyl-sulphide, which is emitted to the atmosphere by plankton species.

All these particles will settle back onto earth, or react with rain and fall back onto earth as acid deposition. The particles will then be absorbed by plants again and are released back into the atmosphere, so that the sulphur cycle will start over again.

i. Fossil fuels like coal and petroleum are extremely important energy resources which are getting exhausted.

ii. Hydrocarbon fuel based resources create pollution levels and green house gases. Their management is related to improved technology and finding alternative energy sources taking this into account.

iii. An overall prudent and sustainable uses of resources both at an individual and collective level can benefit a wide cross section of society as well meet the future generations.

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