CHAPTER II

LITERATURE REVIEW

2.1 Mercury

2.1.1 Physical and Chemical Properties:

Mercury is the only metal that exists in liquid form at normal temperature. The chemical symbol is Hg with atomic no. = 80, atomic mass = 200.59 and mass number of stable isotope is 196 to 204. There are 2 valencies, +1 and +2, with melting point and boiling point of -38.9 °C and 356.58 °C respectively. It is one of the member of elements of group 2b. The density is 13.546 g/cu.cm. (liquid) and 14.193 g/cu.cm. (solid). It can transform and form hundreds of compounds in metallic form, inorganic salt, alkyl compounds or aryl compounds. Each of them has its own individual property (Goldwater, 1977 and Considine ed., 1976). Compounds formed with mercury always have highly strong covalent bonding (Hutchinson and Meema, eds, 1987). Mercury can be found in rocks and earthcrusts but in a very low level, about 60 ppb., except in volcanic rocks (Laws, 1981). More concentrate level of mercury can be found in sediment and living organisms but lower in water. The natural transformation cycle of mercury was shown in Fig. 2-1.

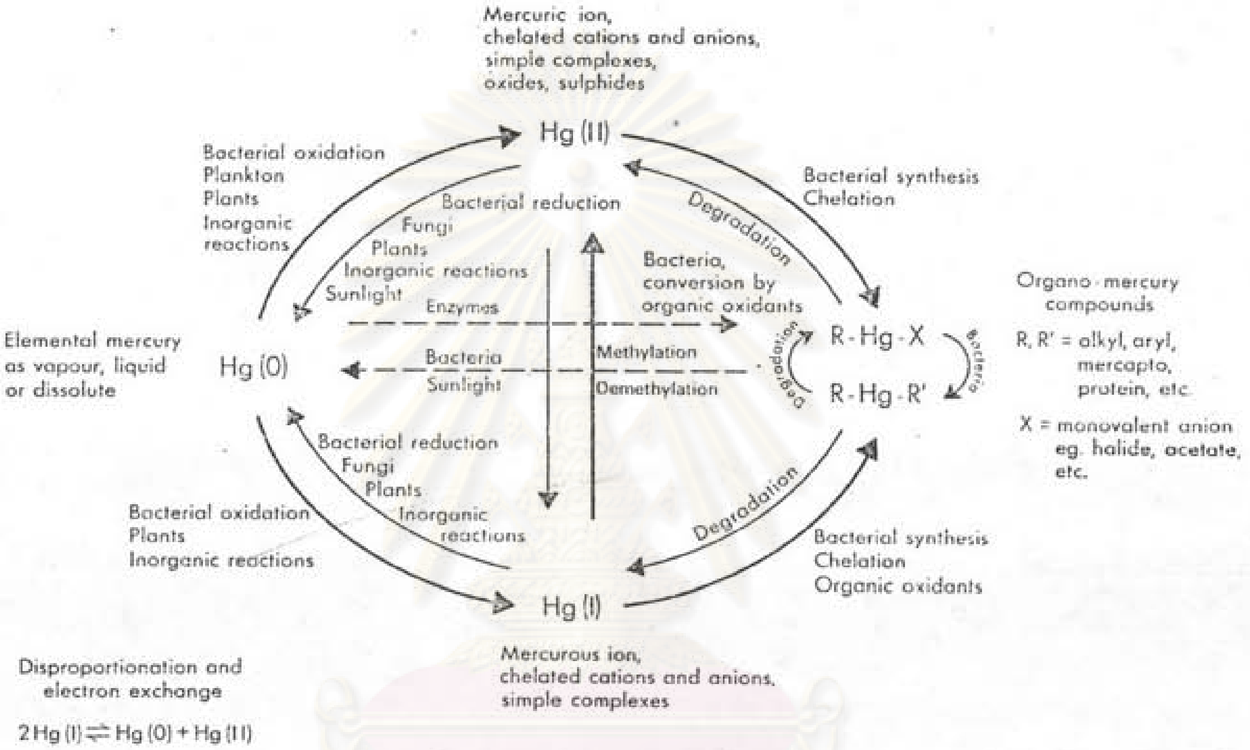

Fig. 2-1 The natural transformation cycle of mercury.
SOURCE: Lenihan and Fletcher eds. (1977).

2.1.2 Source and occurrence

The world's major source of mercury is Almaden in Spain in Europe. In north America i.e. Canada, Mexico, USA (California and Nevada) are known to be potential sources of mercury (Goldwater, 1977). The highest consumption occurred in the USA., about 30 % of total product. Cinnabar (HgS) is the only high mercury associated ore for mining or smelting for commercial uses. In natural condition, especially in water phase, low level of mercury is found which is caused by the binding and adsorption of mercury on suspended particles which settle rapidly. So, the mercury contamination in natural waterway is sharply declining downstreamly, even in the case of industries' drainage pipeline. The difference of acidity, temperature, redox potential, natural chelating agent and volume of complex ion have some influence on adsorption process. We can find mercurial compounds, especially methyl mercury, at water layer above the underwater sediment. Here, methylation occur with the help of microorganisms. Normally, methylation do not occur in deep sediment layer except from disturbance such as dredging or turbulence. (D'Itri and D'Itri, 1977)

2.1.3 Uses of mercury

Mercury is used for a great variety of purposes, including industrial and agriculture applications, as well as for scientific research and in medicine (Laws, 1981). Some uses are outlined below:

Electrical apparatus

Mercury is used in neon lights, arc rectifiers, transistor radio batteries, fluorescent lights and highway lights. Mercury is a major component in the so-called silent switches.

Production of chlorine (Cl_2) and caustic soda (NaOH)

Mercury is used as a cathode in an electrolytic process by which chlorine or sodium hydroxide are produced from a solution of sodium chloride. For each ton of chlorine or sodium hydroxide produced, about 250-500 g. of mercury are consumed. Rapid expansion of Chlor-alkali industry and the increase in demand for high quality of sodium hydroxide used in the production of rayon increase the demand of mercury in the process. Other uses of sodium hydroxide and chlorine (mercury grade) are aluminium, glass, paper, petroleum, detergent and plastics industries.

Paint

Because of its toxic properties, mercury is used as a component both of antifouling and of mildew-proofing paints. Such paints are frequently used in damp areas, such as shower rooms, laundries, basements, seashore homes, etc.

Measuring devices

Mercury is widely used in measuring devices such as thermometers and manometers. When such devices are broken or discarded, there is a good chance for mercury leaking to the environment.

Dental preparation

Mercury is combined either with silver or gold to form amalgams used in dental filling.

Catalyst

Mercury is used as a catalyst for various chemical reactions. One of the most important uses is in the production of PVC.

General laboratory use

In research laboratory, various forms of mercury are used for various purposes. Waste mercury from such uses is almost always discarded rather than recycled.

Amalgamation and purification of metals

Mercury will combine with almost all other common metals (except iron and platinum) to form a fusion product called an amalgam. This tendency may also be applied to purify metals, by separating them through amalgamation from their nonmetal contaminants. This technique is used, for example, to produce high-purity zinc and aluminum.

Mercury had once been used for agricultures, pharmaceuticals and paper and pulp industries. But when its highly toxic property had been realized, the human-related applications were partially to completely inhibited.

2.1.4 Toxicity

The level or effect of mercury toxicity will be high or low, acute or chronic, depends on its chemical form. Inorganic mercury if it swallowed, 98 % of the content will be rapidly excreted. Metallic mercury will not give an acute toxicity but mercurial soluble salts will produce severe acute toxicity. Typical example is mercuric chloride, this compound will severe injure the gastrointestinal tract, liver and kidney. The inhalation of mercury vapor will also directly attack brain and nervous system.

The three common forms of toxic organic mercury are phenyl mercury, methoxy mercury and alkyl mercury, among which, alkyl mercury is the most toxic form. The most common toxic one is methyl mercury compound. The formation of this compound in nature is induced by methanogenic bacterias and molds that live in underwater sediment. Wood (1972) had done an experiment and found that any microorganisms which can self-synthesize the vitamin B-12 can also synthesize methyl mercury. This process will transform any forms of mercury to ionic mercury, Hg^{2+}, and transform to methyl or dimethyl form as well (Laws, 1981). Methylation process can occur both in freshwater and seawater. Such a process can occur in intestinal tract or fish's skin where play host to methanogenic bacterias. About 30 % of total mercury found in water and 80 % of the total found in fish body are methyl mercury. In some cases, non-biological methylation may occur in water with high concentration of iron and manganese. Slightly acidic water can enhance this non-biological methylation (Lindburg et al., 1987).

Fishes can absorb and uptake various forms of mercury into their bodies, but methyl form is the most ready-to-penetrate form. Methyl mercury can accumulate in red blood cells and fat tissues because methyl mercury can dissolve 1000 times in fat better than in water. It, also, can accumulate in muscle tissue, brain, and central nervous system. Phenyl mercury has 6 months of half-life in fish body, but methyl one has up to 2 years. Methyl mercury will degrade to inorganic mercury before excretion. The concentration of accumulated mercury depends on exposure time, age, size, species and sensitivity of individual organism to the substance. But in indifferent conditions, feeding behavior and metabolic rate are the major factors of mercury accumulation in fishes (D'Itri and D'Itri, 1977).

From the laboratory experiment, it was found that the rate of methyl mercury formation under anaerobic condition is better than in aerobic condition. So, the influence factors of methyl mercury formation, except from type and volume of bacteria, are volume and chemical form of mercury. Under the high suspended particulates condition, mercuric ion can rapidly settle. Pseudomonas K-22 can decompose organomercurials to metallic mercury where evaporation to the atmosphere can occur. Rats can transform methyl mercury to inorganic mercury in brain cell and death fishes can, sometime, transform monomethyl mercury to dimethyl form which can penetrate, in gas phase, through the fish skin to the air (D'Itri & D'Itri, 1977).

2.1.5 Standard

WHO (1985) have set the permissible level of mercury in drinking water less than 0.001 mg/L.

2.1.6 Tragedy case: Disease in Japan (Laws, 1981 and D'Itri & D'Itri, 1977)

Minamata Bay is a semienclosed coastal indentation on the eastern side of the Shiranui Sea (sometimes called Yatsushiro sea), an inland sea on the western part of Japan's southern island of Kyushu (Fig.2-2). About 100,000 persons depend in part on fish taken from the sea as a source of food. People consume on the average between 280 g. of fish in the winter and 410 g. in the summer per person per day.

In 1907 the parent company of the present Chisso Corporation built a factory in Minamata. Although the corporation was initially involved primarily in the manufacture of fertilizer and carbide products, the company soon expanded into the manufacture of petrochemicals and plastics. In 1932, the plant began using mercuric oxide (HgO) as a catalyst in the production of acetaldehyde and vinyl chloride. It is not clear how much mercury the plant dumped into Minamata Bay between 1932 and 1968, when discharges were finally terminated, but one estimate has put the total at between 200 and 600 tons. Presumably the greatest mercury

Fig. 2-2 Location of island of Kyushu, Minamata, the Chisso factory and Minamata Bay.
SOURCE: Laws (1981).

discharges occurred during the 1950's when production at the plant was apparently at a maximum.

The first reported signs of trouble involved animals rather than humans. Cats, which were fed in part on fish taken from the bay, began to go mad and die. By 1953 some dogs and pigs were dying in a similar manner. The sickness was characterized by salivating, loss of coordination and convulsion. Effects on aquatic organisms also began to appear during the early 1950's. Shellfish and seaweeds were killed off in certain parts of the bay, and dead fish were found floating on the surface of the bay and even out into the Shiranui Sea. But people still continued to fish in the bay and to eat it.

The first reported case of a human affected by the diseases occurred in April 1956, when a 5-year-old girl was brought to the pediatrics department of the Chisso Corporation's Minamata factory. The girl was suffering from symptoms of brain damage, including delirium, disturbance of gait. Her younger sister and 4 neighbour children were suffering from the same symptoms. On May 1, 1956 Dr.Hajime Hosokawa reported this symptoms to the Minamata Public Health Department as "An unclarified disease of central nervous systems has broken out."

In 1956, a research team from Kumamoto University was appointed to investigate the cause of sickness, and on October 1956 this group reported that the disease was not infectious, and in fact was caused by heavy metal poisoning associated with the eating of fish and shellfish from Minamata Bay. The government issued only a warning, instead of banning, that eating fish from the bay was dangerous.

In fact, the effluent of the plant contained a variety of metals, including manganese, thallium, arsenic, mercury, selenium, copper and lead, so that it was far from clear which metal or combination of metals was the cause of the poisoning. Initially manganese and thallium were suspected, but the experiments on cats were fail. Until a researcher discovered that clinical and pathological finding in cases of minamata disease coincided with certain cases of methyl mercury poisoning reported in England in 1940. Then they found that feeding methyl mercury to cats did reproduce the symptoms of minamata disease. Investigation of the bay revealed that mercury levels in the sediments of Minamata Bay were on the order of 10-100 ppm. (wet weight) and concentrations in the mud of the Chisso drainage canal ranged as high as 2000 ppm. mercury levels in fish and shellfish sampled from the bay ranged from 5 to 40 ppm. wet weight (10-80 times higher than the current FDA guideline of 0.5 ppm.). At that time the Chisso maintained that their Minamata plant could not be the source of methyl mercury pollution, since the plant used only inorganic mercury in the production of acetaldehyde and vinyl chloride. However, analysis of sludge from the plant revealed that it contained methyl mercury chloride (CH_3HgCl), indicating that the inorganic mercury used by the plant had been methylated either prior to disposal from the plant, or in the sediments after disposal, presumably the result of methylation by microorganisms.

After 1959, the victims of minamata disease incredibly died down for several years. By 1962 there were 121 verified Minamata disease victims, including 46 dead. In 1965, the poisoning similar to Minamata disease broke out in the city of Niigata. The source of pollution was found to be an acetaldehyde plant operated by the Showa Denko Company about 65 km. upstream from the city on the Agano River. The numbers of Niigata victim eventually approached 500.

2.2 Cadmium

2.2.1 Physical and chemical properties:

The chemical symbol of cadmium is Cd with atomic number = 48, atomic weight = 112.40, melting point and boiling point = 320.9 ^{o}C and 766 ^{o}C respectively, density = 8.65 g/cu.cm. (at 20 ^{o}C). It is one of the member of elements of group 2b. The only oxidation state is +2 with natural occurring isotope = 106, 108, 110-114 whereas ^{113}Cd is unstable. Cadmium can dissolve slowly in hot dilute HCl or H_2SO_4 and more readily in HNO_3. It does not form stable alkyl compounds or even form toxic organic metal. The range of solubility of cadmium salts varies quite widely. Halogenated salt, sulphate and nitrate are readily soluble while oxides, hydroxides and carbonates cadmium are insoluble. Cadmium has a high vapor pressure, so cadmium oxide -in a form of high toxic vapor- can be inhaled (Doull, et al., 1980 and Considine ed. 1976).

2.2.2 Source and occurrence

Cadmium can be found in a very low level, about 200-300 ppb., in earthcrust. Normally, it can be found together with zinc, zinc sulphide ore and partly from lead ore. Wastewater from mining or smelting plant may disturb the environment and downstream agricultural zone. The smelting of zinc ores yields cadmium as a by product. The major producing countries are the USA, USSR, Japan, Canada, Belgium and France.

Cadmium can pollute the environment by the manufacture of cadmium-associated products. When those products are discarded, it can contaminate the environment in the form of cadmium waste. Generally, only 5 % of cadmium is recycled due to the difficulty found in recycling process of cadmium compound. When cadmium is disposed by burning or landfilling it will go to soil, water and air (Hutchinson & Meema, 1987). The disposal of cadmium, however, do not give much impact on water if water and environment are in a basic condition or even neutral. Because cadmium in basic condition is highly insoluble but can easily leached under acidic condition, such as in soil with high contents of humic acid (Laws, 1981).

2.2.3 Uses of cadmium

Cadmium can be used in such a variety of purposes as followed: (Hutchinson & Meema, 1987 and Laws, 1981)

1) Electroplating: a thin layer of cadmium is deposited by electrolysis on metal objects made of steel, iron, copper, brass or other alloys to prevent corrosion. It provides good electric conductivity, highly ductile and good corrosion resistance to tropical atmosphere, saltwater, and alkali substances. It should be noted, however, cadmium does dissolve readily in acid solutions, including weak acidic solutions such as fruit juices.

2) Pigments: certain cadmium compounds are used as coloring agents in a variety of products, chiefly in plas-

tics but including coated fabrics, textiles, rubbers, glass, paints, enamels, ceramic glazes, etc. Cadmium pigments are heat stable, do not bleed, resistant to degradation by light, basic substances and hydrogen sulphide.

3) Plastics stabilizers: mixtures of cadmium and barium combined with organic acid are used as heat stabilizers in plastics to retard degradation due to elevated temperatures.

4) Alloys: alloys of cadmium have found uses in a variety of applications, including the production of low melting point alloy, molds for casting plastics, safety plugs in compressed-gas cylinder and etc.

5) Nickel-cadmium batteries: Cadmium is used as the anode in nickel-cadmium batteries. These batteries are rechargeable, have a long lifetime and low self-discharge rate, operate over a wide temperature range, and can deliver maximal currents with a low voltage drop. The disadvantage of these batteries are their low energy density and high cost. They are used as a sealed cell in communications equipments, as motor starters. Larger units are used in diesel engines and in various aviation and military equipments.

6) Miscellaneous: Cadmium is used in certain pesticides both in agriculture and non-agriculture applications. Due to its effectiveness with respect to neutron absorption, cadmium has been made control rods for nuclear reactors. It is also a component of the T.V. tubes, luminescent dials and etc.

2.2.4 Toxicity

There are several similarities and dissimilarities between cadmium and mercury. Like mercury, cadmium is not required even in small amounts for the maintenance of life. Unlike mercury, only a single chemical species, Cd^{2+}, is believed to exert a toxic effect. The efficiency of cadmium absorption by the intestines is only about 5-6 %, comparable to the low efficiency (about 2 %) of inorganic mercury by the intestines. However, a dietary deficiency of calcium, protein or iron may increase intestinal absorption efficiency of cadmium. An analysis of cadmium levels in various sources has indicated that human probably ingest about 45-80 ug/d of cadmium from food they eat, 1-2.5 ug/d from water they drink and 0.02-1.0 ug/d from the air they breathe (OECD, 1975 and Friberg et al., 1974 cited by Laws, 1981).

Although almost all organs can absorb some cadmium, the highest concentrations are invariably found in liver and kidneys, and somewhat lower concentration in spleen and pancreas. Roughly one-third of the body burden of cadmium is found in the liver. Unlike mercury, cadmium apparently does not effectively penetrate the placental barrier, so that poisoning of the fetus is not of such a great concern as is the case with mercury. But in fact, ingested cadmium has an extremely long half-life in the human body, apparently about 16-33 years. As a result, cadmium can be an extremely insidious and chronically or acutely poisoning of cadmium may occur by small amount of accumulation over a period of time.

Once absorbed by the body, cadmium tends to be concentrated in the liver and kidneys on a low molecular weight protein called thionein. This protein contains large numbers of sulfhydryl groups which attract cadmium as well as other heavy metals. The metal-protein complex is referred to as metallothionein. Binding heavy metals in metallothionein may represent an intracellular defense mechanism, in the sense that the metals are prevented from interacting with crucial enzyme systems (Laws, 1981).

The most serious effects of cadmium poisoning usually involve damage to the kidneys, particularly the renal tubules. The symptoms include elevated urinary levels of protein (proteinuria) and cadmium. In more severe cases there may also be an increase of glucose in the urine (glucosuria) and of alkaline phosphatase in the blood. Extreme cases of cadmium poisoning are associated with a softening of the bones, apparently caused by disruption of calcium-phosphorus balance in the renal tubules (OECD, 1975 cited by Laws, 1981).

In 1972, FAO/WHO established guidelines for acceptable levels of cadmium intake by humans. The guidelines were based on the assumption that an accumulated cadmium concentration of 200 ppm (wet weight) in renal cortex represents a critical or threshold level of cadmium in the kidney. Assuming that about 4.5 % of ingested cadmium is initially retained in the body and that about 0.005 % of the cadmium stored in the body is excreted each day (corresponding to a half-life of 38 years), they concluded that a cadmium intake of 400-500 ug/wk. should lead to a renal cortex cadmium level of no more than 50 ppm by age 50. (FAO/WHO, 1972 and OECD, 1975 cited by Laws, 1981).

2.2.5 Standard

The maximum tolerable limit of cadmium from foodstuffs, for European have been set at 1 ug/kg. of body weight/day. FAO has ruled at 70 ug/person/day (Hutchinson & Meema, 1987).

The EPA's drinking water standard for cadmium is less than 10 ppb. But WHO (1973) has recommended its level in drinking water must not exceed 5 ppb (Laws, 1981).

2.2.6 Tragedy and case study: Itai-itai disease in Japan (Laws, 1981).

In 1955, the two Japanese physicians reported the occurrence of a mysterious disease in the Jintsu River Basin of Japan near the city of Toyama (Fig. 2-3). The disease was characterized by severe pain in the back, joints and lower abdomen, development of a waddling or ducklike gait, kidney lesions, proteinuria, glycouria and lose of calcium from the bones leading in some cases to multiple bone fractures (Yamagata & Shigematsu, 1970 and Emmerson, 1970 cited by Laws, 1981). Discussion with local doctors revealed that symptoms of the disease had been noted in the region as early as 1935. The disease was seemed to be confined to post menopausal women who had experienced multiple pregnancies in

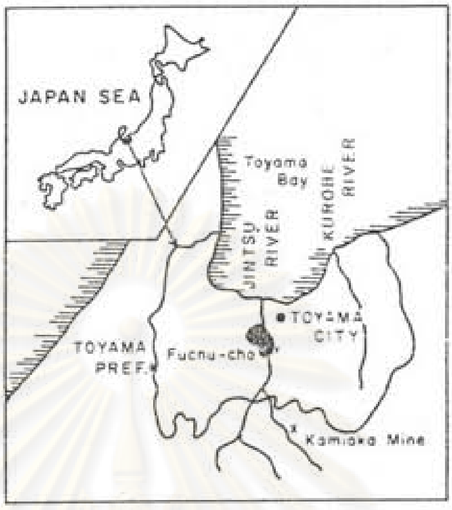

Fig. 2-3 Location of Toyama City and Jintsu River Basin.
SOURCE: Laws (1981).

their earlier lives and who had lived in the region for all or most of their lives (Emmerson, 1970 cited by Laws, 1981).

Initially, some doctors suspected the disease was caused by a local malnutritions as the victims were largely confined to a poor farmers. However, observations were made also that there might be other causes and the fact that the Mitsui Mining Company at Kamioka, upstream of the affected region on the Jintsu River, had been operated since 1924 were noted. The mining produced zinc, lead and cadmium and until 1955 had routinely discharged its wastewater into the Jintsu River. Occasional accidents or flooding resulted in sludge's being washed into the river.

Initially zinc was suspected as being the cause of the disease, but zinc feeding experiments with animals failed to produce the Itai-itai symptoms. Analyses of metal concentrations in the victims' bones and affected rice revealed that cadmium concentration were 10-100 times higher than in control samples. Zinc were little different in affected rice samples but like cadmium in bones, about two orders of magnitude were elevated. The cadmium and zinc or a combination of cadmium, zinc, copper and lead feeding on rats could produce bone degeneration similar to Itai-itai disease.

The studies of cadmium concentraion in the Jintsu River system found that most of the drainage water from the mine was weakly basic and in such water cadmium is highly insoluble. So, the cadmium runoff was transported in a particulate form. Filtered water samples from the river were found to contain less than 10 ppb of cadmium, lower than WHO guidelines for drinking water. However, analyses of suspended materials in the river above and below the mine revealed roughly as high as eightyfold increase in cadmium concentration (Yamagata & Shigematsu, 1970 cited by Laws, 1981).

In 1955 the Kamioka mine built a dam to retain its wastewater in a lagoon. Since that time the incidence of Itai-itai disease has dropped sharply, and evidence of damage to crops has similarly declined (Anonymous, 1971 cited by Laws, 1981). Based on the analysis, it has been estimated that inhabitants of the area was probably ingesting at least 4200 ug of cadmium/week prior to 1955 (Yamagata & Shigematsu, 1970 cited by Laws, 1981). During the period of 1939-1954, approximately 200 persons were afflicted with this disease, and of these nearly 100 died (Anonymous, 1970 cited by Laws, 1981).

2.3 Manganese

2.3.1 Physical and chemical properties

The chemical symbol of manganese is Mn. Its atomic number is 25, atomic mass is 54.9380. It is one of the member of 7b group of element in periodic table (transition metal). Its melting point and boiling point is 1224 ^{o}C and 1962 ^{o}C respectively. The density is 7.3 g/cu.cm. (as solid) and 7.21 g/cu.cm. as single crystal at 20 ^{o}C. The common oxidation state are +2, +3 and +7. There are 8 isotopes, Mn^{50} - Mn^{57}, all of them, except Mn^{55}, are radio-isotope (Considine ed. 1976 and Chaitiamwong, 1988). Manganese is one of the important elements for living organism but only low level is needed. It helps to develop connective tissues, bones, carbohydrate and lipid metabolism and reproductive system. Human need 2-3 mg of manganese per day for adults and only 1.25 mg/d for children. It has been estimated that we can intake manganese up to 2-9 mg/d from our foodstuff and 10-50 ug/d from drinking water (WHO, 1981). Manganese can develop colors and particulates in water, especially in iron-containing water (Sawyer and McCarty, 1985).

2.3.2 Source and occurrence

Manganese can be found in earthcrust in forms of oxide, sulphide, carbonate and silicate compound. The highest proportion of manganese can be found together with iron ores at 50-350 g/kg. The present of manganese in earthcrust is about 1000 mg/kg.

Both soluble and suspended manganese can be found in natural water. The analytical of manganese is mostly express in term of total manganese. Manganese in surface water in the lake of the USA. was around 0.02-87.5 ug/L (mean = 3.8 ug/L) and the determination of manganese level in 37 rivers in the UK was found 1-530 ug/L. Seasonal change can be affect to the level of manganese, it will decline in winter. The high level of manganese, in order of mg/L, can be detected in discharged water from manganese mines or manganese-related industries. Manganese composition in ground water in the USSR was found to be 1-250 ug/L and 0.55 ppb by average in Japan's ground water. In treated water for drinking in the USA, manganese was found from nil to 1.1 mg/L with the median at 5 ug/L and more than 97 % of samples have manganese composition less than 100 ppb. Manganese composition in German's drinking water is 1-63 ug/L (WHO, 1981).

2.3.3 Uses of manganese

Manganese is widely used for various of purposes. Manganese is used in the production of alloys, iron and steels. Manganese is also used in the production of pesticides, as depolarizer in Leclanche dry cell batteries (Kemmitt, 1975), pigments medicines, fertilizers, dyes and as a catalyst in various chemical industries. Over 90% of manganese produced in the world is used in the making of steel, either as ferromanganese, silicomanganese or spiegeleisen. Manganese is also used in the production of non-ferrous alloys, such as manganese bronze, for machinery requiring high strength and resistance to sea water, and in alloys with copper, nickel, or both in the electrical industry. Many manganese chemicals are used in animals feeds, pharmaceuticals, dyes, paint dryers, catalysts and wood preservatives. Some of these uses contribute to environmental pollution (WHO, 1981).

2.3.4 Accumulation in living organism

In aquatic ecology, manganese cycle is more familiar than iron cycle. Manganese is a trace element in water which plays role as cofactor for some enzymes in plants and animals. The experiment indicated that the blooming of blue green algae and freshwater algae sometimes have been controlled by the natural increase of manganese-level. In general, manganese plays a minor role for supporting the algal blooming in freshwater and lake (Goldman and Horne, 1983).

Manganese is found in soil mostly in a form of pyrolusite or manganese dioxide (MnO_2) which is insoluble in CO_2-contained water. Insoluble manganese (Mn^{4+}) can transform to soluble form (Mn^{2+}) under the strong anaerobic reducing condition. Reduced manganese can maintain for a period of time in aerated water under the pH less than 9 condition (Sawyer and McCarty, 1985).

The distribution of manganese in various organs of human is shown in table 2-1.

Table 2-1 Manganese in human tissues.

Tissue	Kehoe et al. (1940) (emission spectroscopy)	Tipton & Cook (1963) [a] (emission spectroscopy)	Kitamura (1974) (atomic absorption)
aorta	—	0.11	—
brain	0.30	0.27	0.25
fat	—	—	0.07
heart	0.32	0.22	0.19
intestine	0.35	—	—
kidney	0.60	0.90	0.58
liver	2.05	1.30	1.20
lung	0.22	0.19	0.21
muscle	—	0.06	0.08
ovary	—	0.16	0.19
pancreas	—	1.18	0.74
spleen	—	0.13	0.08
testis	—	0.13	0.20
trachea	—	0.19	0.22
rib	—	—	0.06

[a] Values calculated using the given ash percentage wet weight and the median value of manganese in tissue ash.

SOURCE: WHO, 1981.

Table 2-2 The acute toxicity of various forms of manganese.

Compound	Animal	Administration route	LD_{50} (mg/kg)	Reference
manganese dioxide	mouse	subcutaneous	550 [b]	Date (1960)
manganese chloride	mouse	oral	275—450	Sigan & Vitvickaja (1971)
	rat	oral	250—275	Hazaradze (1961)
	guineapig	oral	400—810	Hazaradze (1961)
manganese sulfate	mouse	intraperitoneal	64	Yamamoto & Suzuki, (1969)
	mouse	subcutaneous	146 [b]	Date (1960)
	mouse	oral	305 [b]	Date (1960)
manganese nitrate	mouse	intraperitoneal	56	Yamamoto & Suzuki (1969)
potassium permanganate	mouse	subcutaneous	500 [b]	Date (1960)
	mouse	oral	750	Sigan & Vitvickaja (1971)
	rat	oral	750	Sigan & Vitvickaja (1971)
	guineapig	oral	810	Sigan & Vitvickaja (1971)
DAP-Mn cake [a]	mouse	oral	> 8000	Suzuki et al. (1972)
	mouse	intraperitoneal	> 1200	Suzuki et al. (1972)
DAP-Mn dust [a]	mouse, male	oral	2790	Suzuki et al. (1972)
	mouse, female	oral	2570	Suzuki et al. (1972)
	mouse, male	intraperitoneal	378	Suzuki et al. (1972)
	mouse, female	intraperitoneal	352	Suzuki et al. (1972)

[a] DAP refers to a process for the removal of sulfur dioxide from flue gas. DAP-Mn cake: manganese oxides used in the desulfurization process. DAP-Mn dust: exhaust gas and dust from the desulfurization process in a plant.

[b] Lethal dose (LD_{100}).

SOURCE: WHO (1981)

For an average man with 70 kg. body weight will have 10-20 mg. of manganese in their body. Manganese can be found in liver, pancrease, renal and intestine. Manganese can also be absorbed to nervous system. Its half-life in human body is 37 days but longer in brain. The major excretion of manganese is the role of bile fluid, so that most of inorganic manganese can be excreted through the feces together with bile fluid.

2.3.5 Toxicity

The manganese toxicity can be found only in contaminated water from mining (Goldman and Horne, 1983). The acute toxicity of various forms of manganese are shown in table 2-2.

Divalent manganese is the toxic form with its toxicity is higher about 2.5-3 times than trivalent form. Manganese particulate is the major form and the easiest way uptaken to human.

The manganese toxicity to human is chronically where brain (central nervous system) is the major target of attacking. Workers in manganese mines and manganese-related industries, who breath manganese dust for a period of time, supposed to be affected by the toxic of manganese.

The toxic organic manganese can be divided into 2 groups. "Maneb" (Manganese ethylene-bis-dithiocarbamate) is the fungicide in plant. Manganese tricarbonyl is another group of toxic organic manganese. This compound is used as anti-knock in unleaded gasoline, instead of lead. Low amount of it was released after being combusted in the engine. This compound can rapidly denature, by the stimulation of sunlight. Only closely related workers may be affected.

The manganese toxicity experiment on rats, by epidermal injection of manganese dioxide, showed that the lethal dose 100 (LD_{100}) of manganese was 550 mg/kg of body weight. The effect of manganese toxicity is the disturbance of breathing, liver and cardio-systems. The prior studies did not find the significance of manganese toxicity by ingestion, but found in inhalation.

Although, WHO (1981) indicated that manganese toxicity on human was insignificant. But Rojarayanont (1982) and Doull, et al.,eds. (1980) said that the manganese toxicity on human, in case of extremely exposed to both ingestion and inhalation, showed the chronic effect on two major systems:-

1) Central nervous system: can be divided into 3 stages.

- Initial stage: by first 6-24 months. The distinc symptom is to catch a cold, headache, mascular weaken, deny of foods.
- Middle stage: The symptoms are mucles pain, speech disturbance, speak without different tone, convulsion, masklike face.
- Last stage: The symptoms aare psychiatric disorder, difficult in walking speech disturbance, retropulsion or propulsion and Parkinson-like syndrome.

2) Respiratory system: This symptom was the effect

of manganese-inhalation. The obvious symptoms are catch a cold, coughing, improper respiration, manganese pneumonitis, epithelial necrosis. Avoidance of exposure for a period of time may reduce these symptoms.

2.3.6 Standard

The allowable level of manganese in water sources for treating as drinking water should less than 0.05 mg/L.

2.4 Related works.

There are several related works being done by Thai and foreign experts and researchers some of which will be mentioned here, leachate characteristics, heavy metals contamination in some waterways and basins etc. But there is no any similar work done at the same parameters and locations. So, it is very difficult to compare our results with others for determining the changing trend at these locations over a different period of time. But these following works can give some points of view on heavy metals contamination in environment caused by solid waste disposal, both drastic and not. The related works are concluded below:

2.4.1 Related work on leachate characteristics.

Khaodhian et al. (1989) had done their research on solid waste leachate charactistics at Nong Kham disposal site. The results are:

		Range	Typical value
Total BOD	(mg/L)	310-400	635
Total COD	(mg/L)	6313-10060	8140
pH		8.4-8.7	8.5
SS	(mg/L)	490-855	630
TDS	(mg/L)	18700-25100	22300
TS	(mg/L)	19200-25800	22900

Pattamapirat (1989) had done the research on leachate characteristics at On-nuch disposal site. The related results are:

		Range
BOD-5 days	(mg/L)	178.2-1881.1
COD	(mg/L)	980.7-9214.6
pH		7.0-8.6
SS	(mg/L)	81.9-2732.0
TS	(mg/L)	3275-21541.6
Mercury	(mg/L)	3.8-4.7

It has been noted that the measured mercury of this case is very high when compared with other works. This exceptional case may occur occasionally and cannot be predicted.

Sheu Jenn-Hung (1988) had studied the leachate characteristics from On-nuch disposal site. The results are:

		Range	Typical value
BOD-5 days	(mg/L)	105-140	120
COD	(mg/L)	1442-1866	1640
pH		7.6-8.2	8.2
DO	(mg/L)	0.1-0.2	0.10
Alkalinity	(mg/L)	2110-3370	2540

Chang Tung Nien (1988) had studied the leachate characteristics from On-nuch disposal site. The results are:

		Range
BOD-5 days	(mg/L)	150-210
COD	(mg/L)	1560-2075

pH		7.6-8.2
DO	(mg/L)	0.3-0.8
SS	(mg/L)	79-250
TS	(mg/L)	4046-6600
Alkalinity	(mg/L)	2100-3250
Cadmium	(mg/L)	0.007-0.01
Mercury	(mg/L)	0.006-0.025

The study team of JICA (1982) had studied the physical composition of Bangkok's refuse at disposal site during 1979-1981. The study results are as follows:-

Component	% on dry weight basis
Paper	18.0
Textile	4.4
Garbage	16.5
Grass and Wood	19.6
Plastics	10.3
Synthetic glue	-
Rubber and Leather	2.7
Ferrous metal	4.5
Non-ferrous metal	0.3
Glass	5.5
Bones, Stones & Ceramics	10.3
Dry cells	0.4
Sand paper	-
Miscellaneous	7.5

Karnchanawong, Ikeguchi and Koottatep (1990) had studied the shallow well water quality nearby Mae-Hia solid waste disposal site of Chiangmai municipality. The observed data during June 1989 to May 1990 are as follows:

Parameter		Range
Temperature		23.0-27.0
pH		6.3-7.8
Conductivity	(umhos/cm)	80-9100
TS	(mg/L)	140-5700
Alkalinity	(mg/L)	35-1500
COD	(mg/L)	10-610
Manganese	(mg/L)	0.082-18

Van Coillie et al.(1983) (cited by Nriagu and Lakshminarayana, eds. (1989)) had studied and evaluated the effluent characteristics from unrevealed dumpsites in Canada. The results are as follows:

Parameters		Site B domestic source	Site D mixed source
pH		7.1	6.9
Alkalinity	(mg/L)	515	1820
Conductivity	(uS/cm)	2133	4100
COD	(mg/L)	404	1680
BOD	(mg/L)	283	1503
DO		ND	ND
SS	(mg/L)	51	61

TS	(mg/L)	1420	3353
Mercury	(ug/L)	0.3	0.3
Cadmium	(mg/L)	14	26
Manganese	(mg/L)	2-7	3.3

Tchobanoglous et al. (1977) have evaluated the composition of leachate from proper landfill sites as followed:

		Range	Typical value
BOD	(mg/L)	2000-30000	10000
COD	(mg/L)	3000-45000	18000
TSS	(mg/L)	200-1000	500
Alkalinity	(mg/L)	1000-10000	3000
pH		5.3-8.5	6.0

Borden and Yanoschak (1990) has reported the ground and surface water quality impacts of N.Carolina sanitary landfills. Some aspects of water quality are summarized in table 2-3.

2.4.2 Related works on river water quality in central region of Thailand. Nearly all of them were carried out by NEB and can be served as a reference for the work reported here as far as the water quality is concerned. They are summarized below:

NEB (September 1988:a) had reported the water quality of Bang Pakong, Nakorn Nayok and Prachinburi river during 1986-1987 as shown in table 2-4.

Table 2-3 Ground and surface water quality impacts of N.Carolina sanitary landfill

PARAMETER	UPSTREAM SURFACE WATER			DOWNSTREAM SURFACE WATER			GROUND WATER		
	MEAN	SD	MAX	MEAN	SD	MAX	MEAN	SD	MAX
pH	6.63	1.08	7.6	6.88	0.53	7.8	6.37	0.58	7.47
ALK.	38.9	53.4	182	96.7	113.2	400.6	42.2	45.4	130.2
CON.	141.3	6.7	146	414.1	519.4	2237.5	294.6	350.3	1579.2
TDS	120*	11.3	128	284.6	381	1812	203.6	220.6	924.1
Cd	0.0050	0.0000	0.0050	0.0050	0.0001	0.0060	0.0056	0.0023	0.0205
Mn	0.335	0.831	3.200	1.994	4.555	28.200	0.816	1.532	7.071
Hg	0.00021*	0.00003	0.00025	0.00020	0.00001	0.00028	0.00022	0.00005	0.00045

* These statistics based on data from less than ten landfills.
All units in mg/L except pH (pH units) and CON. (mmhos/cm).
SD = standard deviation
MAX = Maximum value observed at any sampling location.

Table 2-4 Water quality of Bangpakong, Nakorn Nayok and Prachinburi river during 1986-1987.

PARAMETER	BANGPAPAKONG		NAKORN NAYOK		PRACHINBURI	
	1986	1987	1986	1987	1986	1987
TEMP	25.0-34.0	24.5-34.5	-- SIMILAR TO BANGPAKONG --			
pH	6.0-8.0	5.8-8.2	-- SIMILAR TO BANGPAKONG --			
SAL.	0-25.7	0-25.5	0-0.7	0	0-0.5	0
CON.	62-41800	50-38500	33-1120	50-399	50-850	28-640
DO	3.1-6.1	2.6-7.4	1.1-5.7	0.8-6.3	4.8-6.6	3.9-7.2
BOD	0.3-4.6	0.1-3.4	0.6-4.5	0.2-1.9	0.1-1.8	0.1-2.1
COD	4.4-94.6	6.2-46.0	2.0-32.0	9.0-22.0	0.9-20.4	9.3-20.0
ALK.		5.8-8.0 IN 1986 AND 4.5-101.6 IN 1987				
Mn	max.1.82					
Hg	max.2.25		max.2.62			
Cd						

NOTE: All parameter are express in mg/L except pH (pH units), CON. (umhos/cm) and SAL. (ppt.)
Measured heavy metals (except from max.measured values as stated) are not exceed the standard of surface water.

SOURCE: NEB (September 1988)

The samples of Bang Pakong river were obtained 120 km. from river's mouth and the rest were 50 km. from their river's mouths.

NEB (September 1988:b) had reported the Ta Chin River's water quality during 1984-1987. Results of which are highlighted below:

pH	7.8 with high fluctuation near the river's mouth
DO	5-6 (mg/L) at 320-250 km. from river's mouth
	1-2 (mg/L) at 118 km. from river's mouth (Banglane, Nakorn Pathom)
	2.0-3.5 (mg/L) at 80 km. from river's mouth (Nakorn Chaisri, Nakorn Pathom)
	0.5-1.0 (mg/L) at 60 km. from river's mouth (Sampran, Nakorn Pathom)
Temp	30 °C mean value throughout the river.
Salinity	17 ppt. at km. 0
	0 ppt. from 60 km. from river's mouth
Hardness	73-2939 (mg/L) in lower part
	58-404 (mg/L) in middle and upper parts
SS	has less than 50 mg/L differentiation (except near the river's mouth)
TS	1-10 mg/L from km.30 to upper part (high fluctuation at river's mouth)

NEB (September, 1989:c) had reported the water quality of Mae Klong river within 140 km. from river's mouth. Typical qualities are as follows:

		1986	1987	1988
Temp.	(mg/L)	23.1-29.6	27.7-31.5	25.5-30.5
pH		7.5-7.7	7.7-8.0	7.6-7.9
Conductivity	(umhos/cm)	170-19000	190-21000	195-21500
Salinity	(g/L)	14.5	12.3	18.0
Alkalinity	(mg/L)	124-132	124.137	
DO	(mg/L)	3.8-9.2	3.7-8.9	4.5-8.1
BOD	(mg/L)	1.2-4.5	1.2-2.5	0.9-1.7
COD	(mg/L)	3.3-60.0	2.9-37.5	1.5-23.0
SS	(mg/L)	19-37	23-48	44-79
Cadmium	(ug/L)	nd-1.74	0.5-1.0	nd-0.5
Mercury	(ug/L)	nd-1.61	nd-0.78	nd-0.44

The fluctuation of some parameters from what shown above may occurred when the examination obtained from river's mouth area.

NEB (March 1991:e) had studied the water quality of Mae Klong River during the year 1989-1990. The results are:

		1989	1990
Temp	(^{o}C)	28.6-29.3	30.1-31.1
pH		7.6-7.8	7.5-7.8
Salinity	ppt.	0-7.4	0-10
Conductivity	(umhos/cm)	204-11820	200-17000
DO	(mg/L)	5.3-7.7	4.2-7.3
BOD	(mg/L)	0.2-3.4	0.8-3.2
COD	(mg/L)	5.8-23.1	7.3-19.0
SS	(mg/L)	11.5-75.0	14.5-141

Cadmium	(ug/L)	<0.10-1.40
Total mercury	(ug/L)	<0.2-4.1

Onodera (January 1985), on behalf of NEB, had evaluated the water quality of the lower Chao Phraya River and Klongs, especially focusing on the contamination of heavy metals. The results can be concluded like this:

			Sept. 1984	Oct.1984
Manganese	(ug/L)	mean	124	315
		range	10-330	97-1187
Cadmium	(ug/L)	mean	2.52	0.65
		range	nd-4.29	0.24-1.46
Mercury	(ug/L)	mean	< 0.2	< 0.2
		range	nd-0.43	nd-0.43

The water quality had been obtained in 1984 (summer and rainy season) at river's mouth stretch to km. 82 from it.

		Summer	Rain
pH		neutral	neutral
DO	(mg/L)	< 1	> 3
BOD	(mg/L)	> 3	< 2
COD	(mg/L)	> 20	

The researcher claimed that the fluctuation of data occurred due to the influence of the water level, flow rate and volume of wastewater discharged onto the river.

NEB (1991:f) had reported the water quality of the Chao Phraya River (7-62 km. from river's mouth). This report was the results of the examination during 1981-1988. The concluded results in term of mean values are as follows:

	DO	BOD-5 days	Cd	Hg	Sal.
1981	1.1	2.2	-	-	-
1982	1.5	2.2	-	-	2.9
1983	1.2	2.2	< 5 ppb	0.005	2.8
1984	1.3	1.9	0.009	0.0003	2.6
1985	0.8	2.6	0.0003	0.0002	4.2
1986	1.0	2.8	0.0008	0.0003	-
1987	1.3	3.4	0.0007	0.0002	4.3
1988	1.3	3.2	0.0008	nd	1.5

Note:
- All parameters were reported in term of mg/L except Sal. in term of ppt.
- Sal. = Salinity

Medej (1985) had studied the water quality emphasizing on total and organic mercury of the lower Chao Phraya River. Some interesting information are:

<u>Total</u> <u>mercury</u>:

Max mean = 2.10 ug/L SD = 0.962 ppb in April

Min range = 0-0.137 and 0-0.268 ug/L in August and December respectively.

The thorough maximum detectable was 1.98 ppb (mean) at 25 km. from the river's mouth.

The year-through minimum detectable was 0.526 ug/L (mean) at 4 km. from the river's mouth.

The highest detectable was 3.820 ug/L at 8 km. from the river's mouth in April 1984.

The correlation determination between total and organic mercury or DO, pH or temperature showed no statistical correlation.

2.4.3 Related law and standards involved to this research. They are summarized in table 2-5.

Table 2-5 Standard for various uses of water.

USES	PARAMETER	UNIT	VALUE	BY	REMARK
DRINKING WATER	pH		6.5-8.5	NEB	
	TS	mg/L	500 (600)	NEB	
	Mn	mg/L	0.3 (0.1)	NEB	
	Hg	mg/L	0.001	NEB	
		mg/L	< 0.001	WHO	1985
	Cd	mg/L	0.01 (0.005)	NEB	
		mg/L	< 10 ppb.	FDA	
		mg/L	< 5 ppb.	WHO	1973
BOTTLING WATER	pH		6.5-8.5	NEB	
	TS	mg/L	500	NEB	
	Cd	mg/L	0.01	NEB	
	Mn	mg/L	0.05	NEB	
	Hg	mg/L	0.002	NEB	
INDUSTRIAL EFF.	BOD-5	mg/L	20-60	NEB	max.100
	SS	mg/L	up to dilutio	NEB	
	DS	mg/L	2000	NEB	max.5000
	pH		5-9	NEB	
	PERMANGANATE	mg/L	max.60	NEB	
	Hg	mg/L	max.0.005	NEB	Zn industry 0.002
	Cd	mg/L	max.0.03	NEB	Zn industry 0.1
	Mn	mg/L	max.5.0	NEB	
SURFACE WATER QUALITY CLASS 4	pH		5-9	NEB	
	DO	mg/L	2	NEB	
	BOD	mg/L	4.0	NEB	
	Mn	mg/L	1.0	NEB	
	Cd	mg/L	0.005	NEB	Hardness < 100 mg/L
		mg/L	0.05	NEB	Hardness > 100 mg/L
WELL WATER NEAR SAN. LANDFILL	Cd	mg/L	0.01	NEB	
	Hg	mg/L	0.001	NEB	
	Mn	mg/L	0.30	NEB	

NOTE: All are expressed in acceptable value.
The value in parenthesis are proposed values

SOURCE: NEB (1989)

2.5 Definition of some related terms used in this work.

CONDUCTIVITY: Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of irons, their total concentration, mobility, valence, relative concentrations and on the temperature of measurement. Solution of most inorganic acids, bases and salts are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all. The term "conductivity" is preferred and customarily is reported in micromhos per centimetre (umhos/cm). In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as millisiemens per metre (mS/m), 1 mS/m is equivalent to 10 umhos/cm.

TOTAL SOLIDS: Total solids is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at the defined temperature. Total solids includes "total suspended solids", the portion of total solids retained a filter, and "total dissolved solids", the portion that passes through the filter.

SALINITY: Salinity is an important measurement in the analysis of certain industrial wastes and seawater. It is defined as the total solids in water after all carbonates have been converted to oxides, all bromide and iodide have been replaced by chloride, and all organic matter has been oxidized. It is numerically smaller than the total dissolved solids and usually is reported as grams per kilogram or parts per thousand.

ALKALINITY: Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is of particular significant in the treatment of natural waters and wastewaters. Because the alkalinity of many surface water is primarily a function of carbonate, bicarbonate and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digestors typically have supernatant alkalinities in the range of 2000 to 4000 mg. calcium carbonate ($CaCO_3$)/L.

DISSOLVED OXYGEN: Dissolved oxygen (DO) levels in natural and wastewaters depend on the physical, chemical and biochemical activities in the water body. The analysis for DO is a key test in water pollution and waste treatment process control.

BIOCHEMICAL OXYGEN DEMAND: The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents and polluted waters. The test measures the oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulphides and ferrous iron. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor.

CHEMICAL OXYGEN DEMAND: The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established.

CONFIDENCE LEVEL: This term (usually expressed as a percentage; e.g., 95 % confidence level), is commonly used in establishing the probability of precision statements and means that there are (for example) 95 in 100 chances of being correct, and 5 in 100 chances of being wrong, in predicting that the expected precision (or expected value) will fall within the specified limits or range.

CORRELATION COEFFICIENT: A measure of the degree of correlation between two variables. Values of r may range from -1 to +1. A value of +1 denotes perfect functional relationship between the two variables, an increasing value of one being associated with an increasing value of the second. A value of -1 also denotes a perfect relationship, but in this case an increasing value of one variable is associated with a decreasing value of the second. When r=0, there is no effect of one variable upon the other variable.

DEGREE OF FREEDOM: Generally equal to the number of observations minus the number of constants calculated from it. For example: Variance is the average squared deviation about the mean of n observations. The variance can be calculated only after the mean has been calculated and this uses up one degree of freedom. No other constants are necessary to estimate the variance. Hence, the estimate of the variance has n-1 degrees of freedom.

F-test: A variance ratio test used to decide whether two independent estimates of variance can reasonably be accepted as being two estimates of the variance of a single normally distributed universe.

HYPOTHESIS: An assumption made concerning a parameter to provide a basis for a statistical test; usually expressed as a null hypothesis or as an alternative hypothesis.

MEAN: The arithmetic average of a series of measurements.

MEDIAN: For samples with an odd number of items, the median is the middle item when the items are arranged in order of magnitude. For samples with an even number of items, the median is the arithmetic average of the two middle items when they are arranged in order of magnitude. The median is an estimate of the mean for symmetrical distributions.

RANGE: The absolute value of the algebraic difference between the highest and lowest values in a set of data.

SCHEFFE'S TEST: The most widely applicable of all the method of post hoc comparison is Scheffe's test. It permit comparisons of pairs of means and of complex combinations of means. Furthermore, it is the most widely accepted test for making post hoc comparison.

STANDARD DEVIATION: A measure of the dispersion of a series of results around their average, expressed as the square root of the variance.