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PHYSIO-BIOLOGICAL AND HAEMATOLOGICAL PARAMETERS OF NOTOPTERUS NOTOPTERUS (PALLAS, 1769) EXPOSED TO MIXTURE OF 0.1 PPM MALATHION AND ENDRIN

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ABSTRACT
During the present experiment, Notopterus notopterus were exposed to lethal concentration (0.1 ppm) of malathion and parathion for a period of 60 min in triplicates. A marked reduction in the opercular beat frequency (90.5 to 39.0) and tail beat frequency (7.2 to 3.2) was observed at the end of 60 min. exposure time. The results on the haematological aspect of the experiment (5 replicas) revealed significant ($P < 0.05$) increase in WBC (6.06 to 7.8), and decrease in Hb, RBC, PCV, MCV, MCH, MCHC and other non-specific defence cells. The increase in the WBC count is due to the non-specific immune response of the fish.

INTRODUCTION

Indiscriminate discharge of these pesticides from agriculture runoff and in aquaculture operation may be washed into nearby water bodies and affects non-target organism such as fish and prawn which are of economics importance to humans [1].Recently the various pesticides, herbicides, weedicides, insecticides, organophosphate pesticide used in the agriculture field for prevention of the insect pest. Unfortunately, application of these synthetic derivatives of pyrethrins is highly toxic to a number of non-targets organisms such as bees, freshwater fish and other aquatic organism even at very low concentration [2-4].

Among the aquatic animals fish are highly sensitive to the pyrethroids pesticides due to their neurotoxic effects and the pesticides are lethal to fish at minimum concentration (10-1000lower) than the corresponding values for other groups of mammals and birds [5]. The use of haematological technique in fish culture is growing in importance for toxicological research, environmental monitoring and fish health conditions. Many works has been conducted on haematological changes of pesticides in the fish such as Das and Mukherjee [6]'Adebayo, et al. [7], Patnaik and Patra [8]Sampath, et al. [9]noted that there is a possibility that studies on fish blood might reveal conditions within the body of the fish long before there is any outward manifestation of disease or disorder.

Pesticides drained to the aquatic environments primarily of agriculture origin and may also stem from effluents from manufacturing plants. Since there is great concern about toxic hazards in the aquatic ecosystem due to pesticides, either from surface runoff from paddy fields or through direct application into ponds for the control of parasites, it is necessary to

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study the cellular changes in fish tissue associated with toxicity. The effect of organochlorine pesticides on fishes has been experimentally recorded by several workers [10, 11]. The toxicity of benzene hexachloride has been studied by Bhatia [12]in *Cirrhina mrigala* and *Colisa facita* distribution of benzene hexachloride on different tissues *Limanda limanda* was studied by Klick and Steinhart [13].

The environment is continuously loaded with foreign organic chemicals released by urban communities and industries. In the 20th century, many thousands of organic trace pollutants, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs) and dibenzop- dioxins (PCDDs) have been produced and, in part, released into the environment[14]. Since the early sixties mankind has become aware of the potential long-term adverse effects of these chemicals in general and their potential risks for aquatic and terrestrial ecosystems in particular. The ultimate sink for many of these contaminants is the aquatic environment, either due to direct discharges or to hydrologic and atmospheric processes [15]. Today, water quality management faces greater problems than at any time in its history. In addition to natural pollutants, varied contaminants exist in surface waters including multiple chemical compounds and different products of industrial and agricultural revolution. The insecticides constitute one group of these pollutants, both synthetic and natural, which contribute to the environmental problems. At present, it seems that the problem is more conspicuous in developing countries, where lately there has been an increase in the use of insecticides as a means of increasing agricultural productivity, without much concern to the consequences of indiscriminate application.

There are many pathways by which insecticides leave their sites of application and distribute throughout the environment and enter the aquatic ecosystem. The major route of insecticides to water ecosystems in urban areas is through rainfall runoff and atmospheric deposition [16, 17]. The uses of pesticides have negative impact on biotic factor including fisheries resources, threatened and endangered species, and their habitats. Pesticides include products, such as insect repellants, weed killers, disinfectants and swimming pool chemicals, which are designed to prevent, destroy, repel or reduce pests such as insects, mice and other animals, weeds, fungi, bacteria and viruses. Pesticides are used in nearly every home, business, farm, school, hospital and park and are found almost everywhere in our environment. In recent studies of major rivers and streams, one or more pesticides were detected more than 90% of the time in water, in more than 80% of fish sampled, and in 33% of major aquifers [18].

Haematological indices are of different sensitivity to various environmental factors and chemicals [19]. Hematology and clinical chemistry analysis, although not often used in fish medicine, can provide substantial diagnostic information. Studies have shown that when the water quality is affected by toxicants, any physiological changes will be reflected in the values of one or more of haematological parameters [20].

2. Materials and Methods

Original healthy *Notopterus notopterus* (Pallas) fish weighting 150-170 gm with a mean body length of 24-26cm were acclimatized for two weeks prior to experimentation. The fishes were fed with balanced diet/pelleted feed with 35 % crude protein diet at 2 % biomass.

Malathion ($C_{10}H_{19}O_6PS_2$) and Endrin ($C_{12}H_8Cl_6O$) both are manufactured by Shivalic Agro Chemical Industries.The lethal concentration (0.1

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ppm) of the pesticide was prepared by dissolving 1 ml of original concentration of pesticide individually in 10 liter of chlorine free water. 30 L of the diluent water was used as control. The fishes (n = 30) were kept in each aquarium in triplicates for each treatment. The stock solution of 0.1 ppm of the solution was introduced separately in each tank. The fishes were observed for 1 - 5 hours for any mortality during the exposure time.

Opercular beat frequency (OBF) was calculated by observing the opercular beats before and after the exposure to assess the impact of pesticides on the physiological requirement of oxygen.

The OBF was measured using the stopwatch, analyzed for one minute after every 20 min post exposure. Tail beat frequency (TBF) is an index of calculating the frequency (no. of times) of tail movements of the fish before and after the exposure to pesticides. TBF gives an index about the physiological imbalance/abnormal behavior a fish shows post exposure, owing to the damage to the central nervous system or other physiological processes.

The blood samples from the challenged fishes were taken after every 20, 40 and 60 min. in fishes exposed to mixed solution of the pesticides. Blood samples were collected from the caudal tail vessels with 21 or 23 gauge needles and 1 or 3 cc syringes before ventilatory response was noticeably depressed. PCV (%) was determined by centrifuging the blood for three minutes (3000 rpm). The hemoglobin content (Hb) of erythrocytes was determined by the hemoglobin cyanide method. After standardization of haemoglobin estimation with the standard cyanmethemoglobin solution of "VEB Berlin-Chemie" or Berlin Chemicals, the hemoglobin content was determined in g/100 ml. RBC value was determined by counting all the cells lying to the left and below the demarcation line of counting chamber. MCV (Mean corpuscular Volume), MCH (Mean corpuscular Hemoglobin) and MCHC (Mean corpuscular Hemoglobin Concentration) were calculated by the standard formula's [21]. For leucocyte counting, the blood was drawn in to the 0.5 mark in the erythrocyte pipette. After shaking, the counting chamber was filled in the large squares which are present at the four angular points of the Neubauer counting chamber and demarcated by triple lines (1 mm^2). Differential leucocyte count (DLC) included different cell counts. Unna-Ziehl staining was used for differentiating small and large lymphocytes. € granulation staining was used for differentiating neutrophils by the standard method, ∂-granulation staining was used for differentiating monocytes as per the standard methods and also Unna Ziehl staining was done for differentiation of thrombocytes as per the methods of Romies [22].

3. RESULTS

The RBC count expressed in ($x10^3/\mu L$) was 2.61±0.06. The lowest RBC was recorded after 60 min. of exposure, ranging from 1.75-1.95 with a mean±SD of 1.85±0.02. The effect of 0.1 ppm "M+E" on RBC of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 507.5, Y= -0.012 X + 2.52 and 0.94 respectively. The WBC (White Blood Corpuscles) expressed in ($x10^3/\mu L$) was 6.06±0.24. The WBC further showed an increase after 60 min. of exposure, ranging from 7.4-8.2 with a mean±SD of 7.8±0.98. The effect of 0.1 ppm "M+E" on WBC of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 442.46, Y= 0.035 X + 5.562 and 0.83 respectively. The mean±SD value of haemoglobin (Hb) expressed in (g/dL) was 8.3±0.23. The lowest haemoglobin was recorded after 60 min. of exposure, ranging from 5.65-5.95 with a mean±SD of 5.8±0.36. The effect of 0.1 ppm "M+E" on Hb of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 434.7, Y= -0.039 X + 8.37 and 0.96 respectively. The MCV (Mean Corpuscular Volume) expressed in (fL) was 95.8±1.25. The MCV further showed a decrease after 60 min. of exposure, ranging from 79.66-82.5 with a mean±SD of 81.08±3.55. The effect of 0.1 ppm "M+E" on MCV of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 1306.0, Y= -0.227 X + 96.15 and 0.96 respectively.

The mean±SD value of PCV (Pack Cell Volume) expressed in percent (%) was 25.0±0.83. The lowest PCV was recorded after 60 min. of exposure, ranging from 14.5-15.5 with a mean±SD of 15.0±0.88. The effect of 0.1 ppm "M+E" on PCV of *N. notopterus* showed 'variance', 'regression equation' and

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'correlation coefficient of 326.8, Y= -0.165 X + 24.2 and 0.97 respectively. The MCH (Mean Corpuscular Haemoglobin) expressed in (pg) was 31.8±0.92. The MCH further showed a decrease after 60 min. of exposure, ranging from 30.2-32.5 with a mean±SD of 31.35±4.25 pg. The effect of 0.1 ppm "M+E" on MCH of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 293.6, Y= -0.012 X + 33.41 and 0.10 respectively. The MCHC (Mean Corpuscular Haemoglobin Concentration) expressed in (g/dL) was 33.2±1.37. The MCHC further showed a decrease after 60 min. of exposure, ranging from 37.12-40.2 with a mean±SD of 38.66±5.21. The effect of 0.1 ppm "M+E" on MCHC of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 309.75, Y= 0.106 X + 34.74 and 0.72 respectively.

The large lymphocyte expressed in (x103/µL) was 1.5±0.02. The large lymphocytes further showed an increase after 60 min. of exposure, ranging from 2.0-2.4 with a mean±SD of 2.2±0.03.

The effect of 0.1 ppm "M+E" on large lymphocytes of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 514.6, Y= 0.014 X + 1.28 and 0.82 respectively. The small lymphocyte expressed in (x103/µL) was 25.3±0.02. The small lymphocytes further showed an increase after 60 min. of exposure, ranging from 34.0-38.0 with a mean±SD of 36.6±0.36. The effect of 0.1 ppm "M+E" on small lymphocytes of *N. notopterus* showed 'variance', 'regression equation' and 'correlation coefficient of 302.35, Y= 0.200 X + 22.3 and 0.85 respectively. (Table 1;) (See table 3 for statistical interpretation)

4. DISCUSSION

The observed increase in OBF and TBF during the exposure to various pesticides either solitary or in combinations had been reported earlier by Omoregie [23]. The initial increases in OBF and TBF may be associated with the sudden response to shock. In addition, the behavioral response to pesticides with marked deviation in the rate of OBF and TBF from reference sample (control) imputes an adjustment in physical fitness as a result of the stress condition [24-26] reported that organisms exhibit behavioral responses to chemical stress both at acute and sub lethal toxicity. This elicits the potency and sensitivity of the fish N. *notopterus* to the test chemical. The ecological importance of this is that the damage to non-target species in the environment and such attribute of the organism could be effectively used as toxicity biosensor of chemical stress.[27]on the other hand investigated the combined effect of aldrin dieldrin with particular reference to their production, environmental deposition and fate, bioaccumulation, toxicology, and epidemiology in the United States. The investigators concluded that the pesticides have destructive impact on the health status of the fishes irrespective of some fish species which show resistance. The resistance and susceptibility of certain fish species to pesticides is still a question to answer. The worker emphasized research onto the above mentioned aspects.

During the present experiment the haematological parameters of *N. notopterus* were greatly disturbed on exposure to 0.1 ppm of "M+E"(Malathion and Endrin). The significant (P<0.5) Haemoglobin(g/dL) showed a decrease from 8.3±0.23 to 5.8±0.36; RBC from ($x10^6$/µL) 2.61±0.6 to 1.85±0.06; PCV from (%)25.0±0.83 to 15.0±0.88; MCV from (fL)95.8±1.25 to 81.08±3.55; MCH from (pg)31.8±0.92 to 31.35±4.25; thrombocytes from ($x10^3$/µL) 34.9±0.02 to 22±0.99. The other parameters like WBC from ($x10^3$/µL) 6.06±0.24 to 7.8±0.98; small lymphocyte from ($x10^3$/µL) 25.3±0.02to 36.0±0.36; nutrophils from ($x10^3$/µL) 1.9±0.014 to 2.8±0.05; monocyte from ($x10^3$/µL) 1.65±0.02 to 2.1±0.0 and eosinophils from ($x10^3$/µL) 0.5±0.20 to 1.9± 0.01 showed significant are increase from the normal values but thrombocyte are decrease. (Table no 2) The increase in WBC count can be correlated with an increase in antibody production which help in survival and recovery of the fish exposed to landane and malathion [28] [29]observed multiple chemical (pesticide) interactions and observed that the combined effect of the pesticides is more destructive than the individual effect of pesticides. Anita and Kumar [30]worked out the effect of water pollution on the biochemical parameters of the selected tissues in Channa striatus. Asoka and Stephen [31] in

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enumerated the toxicity of malathion to Nile tilapia, Oreochromis niloticus. The investigators potential synergistic or protective effects of common environmental pollutants on malathion toxicity, and concluded that the pesticides or more harmful, whereas the used in combinations.

Table-1. Summary of OBF and TBF values of *N. notopterus* exposed to 0.1 ppm of M+P (malathion and Endrin) pesticides.

Pesticides	**Control**	**Exposure**	**Duration**	
	00 min	20 min	40 min	60 min
OBF	90.5±2.5	65.2±2.6	45.3±0.9	39.0±1.5
	00 min	20 min	40 min	60 min
TBF	7.2±1.2	5.2±1.3	4.3±0.9	3.2±0.5

The fishes (n=30, take six fishes each group for treatment) were exposed to pesticides individually as well as in combinations. The values were enumerated by simple physical examination of the individual fish. The results are expressed as mean±SE of five replicas for each treatment.

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Table-2. Mean haematological parameters of *N. notopterus (Pallas)* exposed to five trial of mixture of 0.1 ppm Malathion and Endrin

Parameter	Control	20 minutes			40 minutes			60 minutes		
		Min.	Max	Mean±SE	Min.	Max	Mean±SE	Min.	Max	Mean±SE
RBC (X 10^6/µL)	2.61±0.06	2.15	2.25	2.2±0.02^{ab}	1.7	2.1	1.9±0.01^{ab}	1.75	1.95	1.85±0.02^{b}
WBC (X 10^3/µL)	6.06±0.24	5.3	5.5	5.4±0.65^{a}	6.8	7.6	7.2±1.2^{b}	7.4	8.2	7.8±0.98^{b}
Hemoglobin (g/dL)	8.3±0.23	7.0	8.0	7.5±0.56^{b}	6.8	7.6	7.2±0.08^{a}	5.65	5.95	5.8±0.36^{a}
MCV (fL)	95.8±1.25	89.8	92.0	90.9±3.65^{b}	88.74	90.2	89.47±5.85^{ab}	79.66	82.5	81.08±3.55^{b}
PCV (%)	25.0±0.83	18.0	22.0	20±0.29^{b}	16.2	17.8	17±0.03^{a}	14.5	15.5	15±0.88^{a}
MCH (pg)	31.8±0.92	32.98	35.2	34.09±3.21^{ab}	37.33	38.45	37.89±9.25^{b}	30.2	32.5	31.35±4.25^{ab}
MCHC (g/dL)	33.2±1.37	36.5	38.5	37.5±5.21^{a}	41.12	43.58	42.35±6.52^{ab}	37.12	40.2	38.66±5.21^{ab}
Large lymphocytes (X 10^3/µL)	1.5±0.020	1.12	1.28	1.2±0.05^{a}	1.8	2.0	1.9±0.35^{b}	2.0	2.4	2.2±0.03^{b}
Small lymphocytes (X 10^3/µL)	25.3±0.02	21.0	23.0	22±0.35^{a}	28.0	32.0	30±2.6^{ab}	34.0	38.0	36±0.36^{ab}

Note: Values are mean±SD of five replications (d.f. 5, 30). Means in the same row having different superscripts are significantly different ($P < 0.05$) and values in the same row with same superscript are not significantly different ($P > 0.05$). * The values of the MCV, MCH and MCHC are calculated by the formulae, corresponding to the appropriate values of RBC, WBC, Hb and PCV.

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Table-3. Statistical interpretation for deriving haematological parameters in Notopterus notopterus (Pallas) exposed to 0.1 ppm Malathion and Endrin

Parameters	Groups	N	Means	SD	Variance	Regression equation	'r'
RBC (X 10^6/µL)	Control	10	2.61	1.84	3.40	Y = -0.012 x+ 2.52	0.94
	Mean	20	1.98	22.5	507.5		
WBC (X 10^3/µL)	Control	10	6.06	4.28	18.36	Y = 0.035 x +5.562	0.83
	Mean	20	6.8	21.03	442.46		
Haemoglobin (g/dL)	Control	10	8.3	5.86	34.44	Y = -0.039 x + 8.37	0.96
	Mean	20	6.83	20.8	434.7		
MCV (fL)	Control	10	95.8	67.74	4588	Y = -0.227 x + 96.15	0.96
	Mean	20	87.15	36.15	1306		
PCV (%)	Control	10	25.0	17.67	312.5	Y = -0.165x + 24.2	0.97
	Mean	20	17.3	18.07	326.8		
MCH (pg)	Control	10	31.8	22.48	505.62	Y = 0.012 x + 33.41	0.10
	Mean	20	34.44	17.13	293.6		
MCHC (g/dL)	Control	10	33.2	23.47	551.12	Y = 0.106 x + 34.74	0.72
	Mean	20	39.5	17.59	309.75		
Large lymphocytes (X 10^3/µL)	Control	10	1.5	1.06	1.125	Y = 0.014 x +1.28	0.82
	Mean	20	1.76	22.6	514.6		
Small lymphocytes (X 10^3/µL)	Control	10	25.3	17.88	320.04	Y = 0.200x + 22.3	0.85
	Mean	20	29.3	17.38	302.35		

5. CONCLUSIONS

The present investigation revealed a marked reduction in the opercular beat frequency (90.5 to 39.0) and tail beat frequency (7.2 to 3.2) in N. Notopterus exposed to malathion and parathion at the end of 60 min. exposure time. The results on the haematological aspect of the experiment (5 replicas) revealed that significant ($P < 0.05$) increase in WBC (6.06 to 7.8), and decrease in Hb, RBC, PCV, MCV, MCH, MCHC and other non-specific defence cells.

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SPENT CATALYST (SOLID WASTE)OF INDUSTRY AND BIOHYDROMETALLURGY

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ABSTRACT

The industrial revolution of the 18th century in Europe had a global impact and with the advancement in science and technology there was rapid industrialization, over the world leading to mechanized forming, motorization and urbanization. It has caused blatant destruction of the natural environment. Due to rapid industrialization the demand for metals is ever increasing, but the reserves of high-grade ores are diminishing. Therefore there is a need to explore alternative sources of metals. The rapid industrialization generates a variety of spent catalysts from different industries. These spent catalyst wastes mostly contain Ni, Cu, Zn, Cr, Mo, Co and Fe like metals in it. Hence these waste (spent catalyst) materials which are causing serious environmental problems, can act as potential source for metals. In this sense these spent catalyst wastes can act as a artificial ores. The use of a biohydrometallurgical process to recover metals from such spent catalyst materials before disposal is a logical but challenging application. Biohydrometallurgy is a relatively new concept in which various microorganism (bacteria and fungi) are employed to recover metal values from spent catalyst wastes. Bioleaching is a process based on the ability of microorganism to transform solid compound into soluble and extractable elements, which can be recovered. It represents a “clean technology” given its associated lower cost and energy requirements when compared with non-biological processes.

INTRODUCTION

Catalysts are used in all sector of the chemical industry. Large quantities of solid catalyst are used in the fertilizer and petroleum refining industry. The catalyst deactivates with use and after the activity declines below the acceptable limit it must be regenerated or discarded. The environmental laws concerning spent catalyst disposal have become increasingly more severe and now classified as hazardous waste under US Environmental Protection Agency (EPA). The advancement in science and technology there is rapid industrialization, over the world leading to mechanized farming and urbanization. It has caused blatant destruction of the natural environment. So many industries generates lot of spent catalyst as sold waste byproduct which contain valuable metal such as Ni, Co, Cu, Mo, Zn, Mn and Fe. Therefore, concerted efforts are put to develop eco-friendly processes especially in the field of mineral processing and extraction of metal from spent catalyst solid waste, which have been the mainstay of world economy. Usually, metal values are recovered from the respective ores through pyro-- and hydrometallurgical processes or a combination of both. But due to gradual depletion of high-grade ores, efforts are now being directed to recover metal values from spent catalyst wastes of industrial byproduct. The reuse of such materials not only conserves the non-renewable resources but also solve the problem of environmental degradation. The important technique that has been developed so far to treat the spent catalyst solid waste materials for recovery of metals comes under the domain of hydrometallurgical processing. It involves aqueous media processing with the help of various acids alkalis, organic solvent etc. in addition to employing conventional industrial process steps. Biohydrometallurgy is a relative new concept in

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which various microorganisms are employed to recover metal values. It is also relatively free from environmental concerns unlike conventional hydrometallurgy steps. This technique exploits microbiological processes for recovery of metal from spent catalyst. In last few decades the concepts of microbiological leaching have played a great role to recover valuable metals from various sulphide minerals or low grade ores. Now the microbiological leaching process has been shifted for its application to recover valuable metals from the different spent catalyst wastes. There are many microorganisms which play important role in recovery of heavy metals from spent catalyst industrial wastes. Among the bacteria Acidithiobacillus Ferrooxidans, Acidithiobacillus thioxidans, Leptospirillum Ferrooxidans and sulfolobus sp., are well known for the bioleaching activity while penicillium, and Aspergillus niger are some fungi those help in metal leaching process. The process of recovery makes some only if the cost of recovery is much less than the the value of the metal. The main advantage in the bio-hydro technique is the ease of operation as well as limited use of process controls thus making the operation more users friendly. The technique can also be applied to different types of materials, especially lean and so for unusable resources, by which metal values can be recovered. Therefore in biohydrometallurgy, the process is carried out in close loop generating minimum effluents and thus is preferred as green technology.

RECOVERY OF METAL FROM SPENT CATALYST USING BIOHYDROMETALLUGY

Leaching is the process when a solid material is dissolved into a aqueous solution. In other word, metals bound in minerals are transformed into metal ions that are released into an aqueous solution, i.e. immobilized metals become mobilized. Biohydrometallury is leaching process where the extraction of metals from solid minerals and spent catalyst wastes into a solution is facilitated by the metabolism of certain microbes-bioleaching microbes. Bioleaching is a process described as “the use of microorganism to transform elements so that the elements can be extracted from a material when water is filtered through it”. Bioleaching is a preparatory step to metal recovery from ores and spent catalyst wastes. In subsequent processes, different from bioleaching, the metal is recovered from the leachate. Bacterial oxidation such as bioleaching or bio oxidation on a commercial scale has been done on sulfide metal bearing materials such as arenopyrite, pyrite, pyrrhotite, covellite and chalcocite ores and concentrates, the one exception to this processing being the oxidation of chalcopyrite ores and concentrates.

For last several decades bioleaching getting its priority in application for metal recovery from ores and spent catalyst wastes of industry. In refinery and fertilizer industry there are so many catalyst used for manufacturing of petroleum and fertilizers product and generates lot of spent catalyst wastes which create environmental pollution. So that need to proper management and utilization of spent catalyst as recovery of valuable metal before disposal its. In the recent years, biohydrometallurgy process has shown its promising impact in treatment of infected spent catalyst wastes as the metal recovery. Among the major bacteria group those are involved in bioleaching process are autotropic acidophiles namely, Acidithiobacillus ferrooxidans, Acithiobacillus thiooxidans, and leptospirillum ferrooxidans and heterotrophs like sulfolobus. Besides, fungal species such as Penicilium and Aspergillus niger are some of bioleaching microorganism that applied in metal recovery from spent catalyst industrial wastes. Spent catalyst is the major solid waste sources for production of ammonia from fertilizer industries. The used catalysts lose their activity with time and when the activity decreased to acceptable level; it is then regenerated or reused. A number of researches have been applied Acidithiobacillus thiooxidans as well as Acidithiobacillus ferrooxidans and fungal species like Aspergillus niger to recover metals such as Ni, Co, Mo, Cu, Zn, and Fe from spent catalyst. Among the bacteria Acidithiobacillus groups are the key genuses which have been used for such process to leach out metal like Cu, Ni, Zn and Cr from spent catalyst in proper steps of biohydrometallurgy. By recovering the metal values from such sites, it has improved the

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contaminant sites the waste sludge after bioleaching can be safer for land application.

The removal of metals from various aqueous streams by biosorption and bioaccumulation has received significant attention. These processes involved typical ion-exchange process where the metal ion is exchanged for a counter-ion attached to biomass. Bioleaching is a similar process where microbes dissolve the metals present in the solid matrix of waste into soluble form. This process in general occurs in acidic medium where the metal ions an easily be mobilized in aqueous system. Most of the acidophic microorganisms play key role for bioleaching process and previously these have been used in mineral dissolution from ores/spent catalyst and concentrates for which these microbes are otherwise termed as biomining microbes. The fact that microbiological leaching is relatively inexpensive for which many environmental technologists rely on application of microorganisms for the spent catalyst industrial waste treatment. The second advantage is that the process is quite flexible and microbes can easily adapt the variations of conditions and metabolize or co-metabolize the substrates present in the concerned medium. The important aspect is that such process can be perceived as green technology. Therefore, the is continuous growing interest to adopt microbiological process over conventional technologies for the treatment of industrial spent catalyst wastes in order to recover valuable metals.

CONCLUSIONS

Worldwide assets of high grade ores are going to end as a result of rapidly increasing metals demand. Up till now, low and discarded ore/spent catalyst are secondary resource for recovery of metal but problems exist in the extraction of metals from these discarded materials, using conformist techniques, high consumption of energy and less output. Another most important crisis is environmental out lay due to the elevated level of contamination from these technologies hardens environmental standards. There is growing concern that the heavy metal contents of soil are increasing as the result of industrial, mining, agricultural and domestic activities, all through the world. Not like many other pollutants heavy metals are difficult to remove from the environment. Biohydrometallurgy encompass different disciplines on the basis of interaction between metals and microbes in industrial spent catalyst waste like bioremediation, biosorption, bioaccumulation and bioleaching. All these processes are usually slow but more environments friendly require less energy consumption then physiochemical processes which require more energy and release harmful gases and produce environmental hazards. In future, to improve the yield of metal through bioleaching of low grade ore and spent catalyst solid waste, new strains have to be identified that should be capable of sustaining higher metal concentration. For this purpose strains of genetically modified or selected by mutation can be considered. This can reduce the residence time and simultaneously enhance the economy of the process.

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Effect of Sub lethal doses of Lead Nitrate on certain Haematological parameters of Common Carp, Cyprinus carpio

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ABSTRACT

Effect of sub- lethal doses of Lead nitrate was investigated on certain Haematological parameters of Cyprinus carpio, (Common carp). It has been observed that R.B.C.s (Red Blood Corpuscles), Haemoglobin, eosinophil, basophil, neutrophil showed an overall decrease as the period of exposure increases when compared with control value.

INTRODUCTION

Lead is most widely studied occupation and environmental toxins. Lead (atomic number, 82, atomic weight, 207.19, specific gravity, 11.34) is a bluish or silver – grey soft metal. The melting point is 327.5 and the boiling point, at atmospheric pressure, is 1740°C. It is sometimes found free in nature, but is usually obtained from the ores galena (PbS), anglesite (PbSO4), cerussite (PbSO3) and minum (Pb3O4). Although lead makes up only about 0.0013% of the earth crust, it is not considered a rare element since it is easily mined and refined. It has four naturally occurring isotopes: 208, 206, 207, and 205, in order of abundance. The isotopic ratios for various mineral sources are sometimes substantially different. This property has been used to carry out non-radioactive tracer environmental and metabolic studies.

Higher concentration of Pb and other heavy metals originating from mining or by anthropogenic actions (Prasad and Freitas, 2003) such as discharges of toxic residues in rivers, lakes, maritime coast and in the air, industrial activities, farm use of fertilizers and pesticides, incineration of urban and industrial residues, among other sources, have been causing harmful effects to the environment and ecosystem (Ahluwalia and Goyal, 2007).

Depending on one location on the face of the planet, the food and water supply as well as the air we breathe expose us lead. Lead ranked second, on the 2003 comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, commonly known as Super fund) priority list of hazardous substance because it is a toxic widespread pollutants. Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders.

Long term exposure to lead or its salts (especically soluble salts or the strong oxidant PbO2 can cause nephropathy and colic - like abdominal pains.

MATERIAL AND METHODS

EXPERIMENTAL DESIGN

Experiment was setup in three groups along with control containing 20 fishes in each group and kept in plastic pools (500 litre capacity). The fishes of groups II and III were challenged with different concentrations of lead nitrate while group I was kept as control. The experiment was conducted for 90 days. The water along with metal concentration of each plastic pool was changed after 48 hrs. The fishes were fed with under mentioned food.

PREPARATION OF BASAL DIET FOR FISH

A basal diet was prepared by taking rice bran (25%), wheat flour (25%), mustard oil cake (22%), fish meal (26%) and minerals (2%) as per the method of Dutta and Kaviraj (2003) with slight modifications.

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Ingredients were mixed together and dough was prepared and passed through sieve to get appropriate sized pellets and dried in hot air oven at 60 - 70 °C temperature. Experimental fishes were fed with this feed once daily @ 10% of their body weight and the residuals were removed after 48 hours of feeding by siphonining.

COMPOSITION OF BASAL DIET

Ingredients	% dry weight
Rice Bran	25.00
Wheat Flour	25.00
Mustard Oil Cake	22.00
Fish Meal	26.00
Mineral Mix*	2.00
Total	100.00

* Mineral mixture (%) : (Agrimin; Glaxo India Ltd., Mumbai) : Copper: 3.12, Cobalt : 0.45, Magnesium : 24.14, Iron : 9.79, Iodine : 1.56, Zinc : 21.30, Calcium : 30.00, Phosphorous : 8.25.

HAEMATOLOGICAL ESTIMATION

The haematological parameters of fishes treated with lead nitrate and were compared with those of apparently healthy (control) specimens.

For this purpose, the blood samples were taken from the caudal peduncle and heart with the help of 3 ml glass syringe. collected blood samples were put in eppendrof tubes with the anticoagulant (EDTA@ 2mg/ml of blood). Red blood cells (R.B.Cs) were counted with the help of Haemocytometer. Haemoglobin concentration was measured by using haemoglobinometer. Blood smears were prepared and stained with Leishman's stain for the differential count of White Blood Corpuscles (W.B.Cs.) viz, Eosinophils, basophils, Neutrophils, Lymphocytes and monocytes(described by Anderson, 1974).

RESULTS AND DISCUSSION

Haematological Estimation:

(i) R.B.Cs. (Red Blood Corpuscles) profile

The R.B.C. count of control fish was found to be 3.70 ± 0.008. In fishes exposed to 6 mg/l lead nitrate concentration, the R.B.C. count was recorded to be 2.95 ± 0.010, 2.85 ± 0.011 and 2.80 ± 0.014, at the time period of 30, 60 and 90 days, respectively (Figure 1). In fishes exposed to 8 mg/l lead nitrate concentration, the R.B.C. count was recorded to be 2.75 ± 0.010, 2.70 ± 0.011 and 2.63 ± 0.010, at the time period of 30, 60 and 90 days, respectively (Figure 1).

In all the cases, it is observed that R.B.C. count decreased in proportion to the length of period of intoxication.

(ii) Haemoglobin profile

The haemoglobin content of control fish was found to be 9.5 ± 0.086. In fishes exposed to 6 mg/l lead nitrate concentration, the haemoglobin percentage was recorded to be 7.5 ± 0.086, 6.2 ± 0.150 and 5.2 ± 0.070, at the time period of 30, 60 and 90 days, respectively (Figure 2). In fishes exposed to 8 mg/l lead nitrate concentration, the haemoglobin content was recorded to be 6.5 ± 0.100, 5.9 ± 0.086 and 5.5 ± 0.070, at the time period of 30, 60 and 90 days, respectively (Figure 2).

In all the cases, it is observed that haemoglobin content percentage decreased in proportion to the length of period of intoxication.

(iii) Differential leucocyte count profile

The neutrophil percentage of control fish was found to be 20.2 ± 0.000. In fishes exposed to 6 mg/l lead nitrate concentration, the neutrophil percentage was recorded to be 18.8 ± 0.127, 16.5 ± 0.111 and 13.8 ± 0.100 at the time period of 30, 60 and 90 days, respectively (figure 3). In fishes exposed to 8 mg/l lead nitrate concentration, the neutrophil percentage was recorded to be 17.5 ± 0.150, 14.7 ± 0.100 and 12.2 ± 0.173 at the time period of 30, 60 and 90 days, respectively (Figure 3).

The lymphocyte percentage of control fish was found to be 30.2 ± 0.000. In fishes exposed to 6 mg/l lead nitrate concentration, the lymphocyte percentage was recorded to be 31.8 ± 0.111, 34.5 ± 0.196 and 38.5 ± 0.086 at the time period of 30, 60

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and 90 days, respectively (Figure 3). In fishes exposed to 8 mg/l lead nitrate concentration, the lymphocyte percentage was recorded to be 32.9 ± 0.100, 37.2 ± 0.086 and 41.5 ± 0.100 at the time period of 30, 60 and 90 days, respectively (Figure 3).

The monocyte percentage of control fish was found to be 2.0 ± 0.000. In fishes exposed to 6 mg/l lead nitrate concentration, the monocyte percentage was recorded to be 2.0 ± 0.111, 2.0 ± 0.111 and 2.0 ± 0.200 at the time period of 30, 60 and 90 days, respectively (Figure 3). In fishes exposed to 8 mg/l lead nitrate concentration, the monocyte percentage was recorded to be 2.0 ± 0.158, 2.1 ± 0.217 and 2.1 ± 0.180 at the time period of 30, 60 and 90 days, respectively (Figure 3).

The Eosinophil percentage of control fish was found to be 15.0 ± 0.000. In fishes exposed to 6 mg/l lead nitrate concentration, the eosinophil percentage was recorded to be 14.8 ± 0.050, 14.0 ± 0.111 and 13.5 ± 0.100 at the time period of 30, 60 and 90 days, respectively (Figure 3). In fishes exposed to 8 mg/l lead nitrate concentration, the eosinophil percentage was recorded to be 14.6 ± 0.100, 13.8 ± 0.100 and 13.0 ± 0.132 at the time period of 30, 60 and 90 days, respectively (Figure 3).

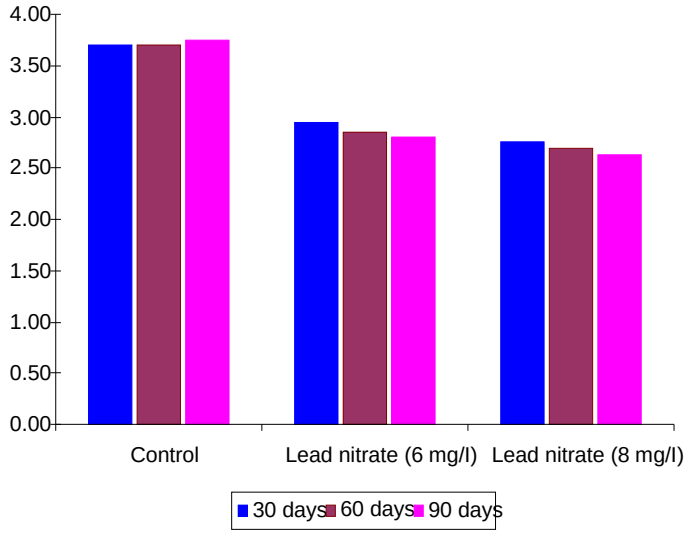
The basophil percentage of control fish was found to be 12.0 ± 0.000. In fishes exposed to 6 mg/l lead nitrate concentration, the basophil percentage was recorded to be 11.8 ± 0.122, 11.2 ± 0.132 and 10.5 ± 0.070 at the time period of 30, 60 and 90 days, respectively (Figure 3). In fishes exposed to 8 mg/l lead nitrate concentration, the basophil percentage was recorded to be 11.2 ± 0.158, 10.6 ± 0.050 and 10.0 ± 0.173 at the time period of 30, 60 and 90 days, respectively (Figure 3).

The estimation of different haematological parameters which were undertaken throughout this experimental investigation revealed the following results.

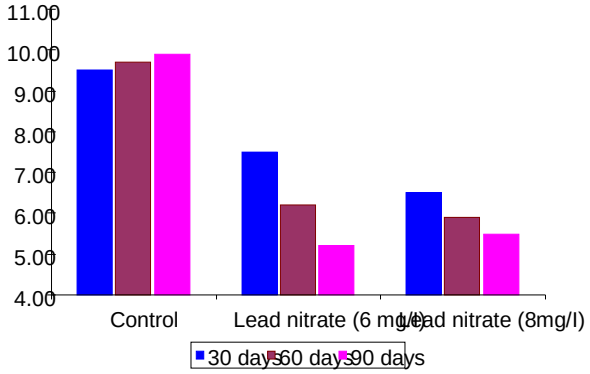
The R.B.C. values in lead nitrate treated groups of fish showed considerable decrease during the experimental investigation as compared to control.

The haemoglobin values in lead nitrate treated groups of fish exhibited a marked decrease throughout the experimental investigation in comparison to control.

The differential leucocyte counts deviated significantly when compared to control values. The increase was observed in the number of lymphocytes, while decrease was noticed in the number of neutrophils, eosinophils and basophils but monocytes did not differ significantly when compared to control values.



Graph - 1 Showing R. B. Cs. count of the fish exposed to 6 mg/l and 8 mg/l lead nitrate concentration



Graph - 2 Showing haemoglobin content of the fish exposed to 6 mg/l and 8 mg/l lead nitrate concentration

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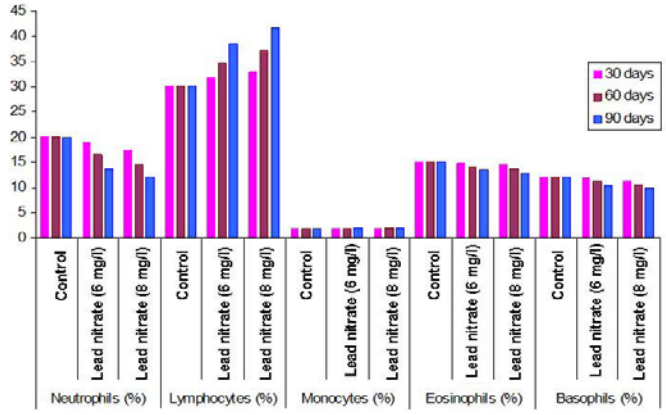

Graph -3 Showing differential leucocyte count of the fish exposed to 6 mg/l and 8 mg/l lead nitrate concentration

It has been observed that the total Red blood corpuscles (R. B. C.) count decreased significantly after 6 mg/l lead nitrate exposure for the time period of 30, 60 and 90 days as compared to the controlled one. In fishes after 8 mg/l lead nitrate exposure for the period of 30, 60 and 90 days, the total Red blood corpuscles (R. B. Cs.) count have also got decreased significantly as compared to the controlled one.

Similarly, Shah and Altindag (2004a) reported considerable decrease in the Red blood cells count of fish, *Tinca tinca* exposed to 3.2 mg/l lead nitrate for 7 days. Andrabi *et al.* (2008) reported considerable decrease in the number of Red blood cells in *Clarias batrachus* exposed to 12 mg/l and 14 mg/l of lead nitrate for 45 days. Adeymo (2005) also recorded that Red blood cells count decreased significantly in 10 mg/l lead nitrate exposed, *Clarias gariepinus* for 15 days. Decline in Red blood cells values were reported in fishes like *CommonCarp, cyprinus carpio* (Zahoor *et al*., 2014), *Rutilus frisii Kutum Fingerlings*, (Hayar *et al*., 2012), *Clarias batrachus* (Maheswaran *et al,*. 2008), *Heteroclarias, (*Kori-siakpere *et al.,* 2008), *Cirrhinus mrigala* (Kalavathi *et al*.,(2015), *Anguilla anguilla,* (Santos and Hall, 1990) and *Salmo gairdneri*, (Haux and Larsson, 1982) which were exposed to heavy metals such as mercuric chloride, copper sulphate, zinc sulphate and lead nitrate. It is stipulated that the heavy metal intoxication caused swelling in R. B. Cs. due to which their count decreased in proportion to the volume of cells.

It has been observed that the haemoglobin content decreased significantly after6 mg/l Lead nitrae exposure the time period of 30, 60 and 90 days as compared to the controlled one. In fishes 8 mg/l lead nitrateexposure for the period of 30, 60 and 90 days, the haemoglobin content have also got decreased significantly as compared to the controlled one.

Andrabi *et al.* (2008) reported considerable decrease in the haemoglobin content in *Clarias batrachus* exposed to 12 mg/l and 14 mg/l of lead nitrate for 45 days. Shah and Altindag (2004a) reported considerable decrease in haemoglobin content in the fish, *Tinca tinca* exposed to 3.2 mg/l lead nitrate for 7 days. Adeymo (2005) also recorded that haemoglobin content decreased significantly in 10 mg/l lead nitrate exposed, *Clarias gariepinus* for 15 days. Decline in haemoglobin content was reported by other workers in different fishes such as *Anguilla anguilla,* (Haux and Larson, 1982), *Barbus conchonius,* (Tewari *et al.,* 1987),*Common carp, Cyprinus carpio*, (Zahoor *et al.,* 2014), *Claris gariepinus,* Adil *et al*., (2013), *Cirrhinus mrigalia,(Kalavathi et al., (2015), Clarias gariepinus,* (Olaifa *et al.,* 2004), *Clarias batrachus,* (Maheswaan *et al.,* 2008) and *Heteroclarias,* (Kori-Siakpere *et al.,* 2008) which were exposed to different heavy metals viz., lead nitrate, Copper sulphate, mercuric chloride and zinc tetraoxosulphate.

It has been observed that the differential leucocyte count deviates significantly; the increase was observed in the number of lymphocytes, while decrease was noticed in the number of neutrophils, eosinophils and basophils but monocytes did not differ significantly after 6 mg/l lead nitrate exposure for the time period of 30, 60 and 90 days as compared to the controlled one. In fishes after 8 mg/l lead nitrate exposure for the period of 30, 60 and 90 days, the differential leucocyte counts deviate significantly, the increase was observed in the number of lymphocytes, while decrease was

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notied in the number of neutrophils, eosinophils and basophils but monocytes did not differ significantly as compared to the controlled one.

Santos and Hall (1990) observed increase in the number of lymphocytes and decrease in the number of neutrophils, eosinophils and basophils in the fish, *Anguilla anguilla* exposed to sublethal concentrations of 3.5 mg/l and 5.5 mg/l lead nitrate for 30 days. Shah and Altindag (2005) observed increase in the number of lymphocytes and decrease in the number of neutrophils, eosinophils and basophils in *Tinca tinca* exposed to sublethal concentration of 3.2 mg/l lead nitrate for 15 days. Shah and Altindag (2005) stated that the increase in lymphocyte number may be the compensatory response of lymphoid tissues to the destruction of circulating lymphocytes. Dhanekar *et al.* (1985) reported increase in large lymphocyte, reduction in small lymphocytes and decrease in, neutrophils, eosinophils and basophils and no change in monocyte cells in *Mastacebalus puncalus, Channa punctatus* and *Heteropneustes fossilis* on exposure to 0.5, 1.5 and 2.5 mg/l mercuric chloride and 4, 6 and 8 mg/l lead nitrate for 90 days. Zahoor *et al.,* (2014) observed increased in the number of lymphocytes while decrease was noticed in the number of neutrophils, eosinophils and basophil in the fish ***common carp**,cyprinus carpio* after 2mg/l and 5 mg/l Copper sulphate exposure for 90 days . Maheswaran *et al.* (2008) observed increased lymphocytes in *Clarias batrachus* after 0.02 ppm and 0.04 ppm mercuric chloride exposure for 35 days.

Conclusion:-

The effect of sublethal doses of lead nitrate exerts a profound influence on the haematological parameters of Common Carp, ***Cyprinus Carpio*** after long term exposures of lead nitrate inducing by haemodilution which could lead to anaemic condition attribute to the swelling of the red blood cells, erythroclasia, impaired haemoglobin synthesis. Result of ameliorative effects of lead nitrate divulge that there is minimum decrease in haemoblobin content, RBC count, eosinphil, basophil and neutrophil but monocyte did not differ significantly as compared to control one.The increase in the number of lymphocytes may be attributed to stimulation of the immune mechanism of the fish to eliminate the effects of the pollutants.

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DUMPSITE AND VULNERABILITY OF SHALLOW AND DEEP GROUNDWATER RESOURCES WITH SPECIAL REFERENCE TO STATUS OF POLLUTION IN BALLARPUR AREA OF CHANDRAPUR DISTRICT MAHARASHTRA, INDIA

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ABSTRACT

Nowadays there is tremendous growth in human population in urban areas. Due to increase in population the human activities like disposal of untreated municipal and industrial sewage into water bodies has increased. Also quantity of solid wastes in highly populated city like Ballarpur has increased remarkably. High level of groundwater pollution is caused due the careless management of the authorities shown in disposal of animal waste and selection of landfill sites without considering the geological and hydro geological aspects. Percolates from landfills is becoming a great threat to the aquifers of surrounding areas due to the high concentration of toxic substances. Hence, it is must to assess the leachates from landfills of the surrounding areas as it contains high concentration of toxic substances. In the present work the assessment of groundwater sources serving the selected areas situated in the vicinity of Vardha River near by Ballarpur area Sampling is done from shallow and deep aquifers of study area and were analyzed and characterized. High concentration of nitrate, chloride, TDS and hardness were detected in majority of groundwater samples. These data reflects the high level of groundwater pollution.

INTRODUCTION

The fast population growth, uncontrolled urbanization and industrialization, poor sanitation situation, uncontrolled and improper waste disposal are some of the causes for serious quality degradation of surface as well as ground water throughout the world in developed and developing countries. The urbanization rate of India has increased from 10.84% in 1901 to 28.5% in 2001. Unregulated growth of urban areas particularly over last two decades, without infrastructures services for proper collection, transportation, treatment disposal of domestic solid waste led to increased pollution and health hazards.

The municipal solid waste disposal methods followed in most of the cities and towns of India are unsystematic and non-scientific and these landfill may just be pieces of open land that have been fenced off, excavation and old mining areas. Most of the landfill sites in India are only uncontrolled dumps where a mixture of domestic, commercial, industrial and hospital wastes are dumped together. Site selection is generally based on geographical rather than geological and hydro geological considerations. That means the closer the site to the source of the waste the better in terms of logistics. It is very common to find waste disposal sites within municipal boundaries and surrounded by residential areas.

Although landfills are an indispensible part of everyday living, they may present long-term threats to surface water and also groundwater that are hydro-logically connected. Groundwater contamination is a major concern in landfill operations because of the pollutional effects of landfill leachates and its potential health risks.

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(Christensen 2001; Mor 2006; Yanful 1988). The greatest contamination treat to groundwater comes from the leachate generated from the fill material, which most often contains toxic substances especially when wastes of industrial origin are land filled (Ostman 2006). However, it has been widely reported that leachates from landfills for non-hazardous waste could as well contain complex organic compounds, chlorinated hydrocarbons and metals at concentrations, which pose a threat to both surface and ground waters. Heavy metals such as copper, iron, zinc and manganese have been reported at excessive levels in ground water due to landfills operations (Jorstad 2004; Simsek 2008; Yanful 1998). The possibility of leachates containing groundwater exists wherever wastes are disposed.

Leachate is a fluid that has passed through or emerged from the waste in a landfill, picking up a variety of suspended and dissolved materials along the way. The creation of leachates, sometimes deemed “garbage soup”, presents a major threat to the current and future quality of groundwater. Once leachate is formed and is released to the groundwater environment, it will migrate downward through the unsaturated zone until it eventually reaches the saturated zone. Leachate then will follow the hydraulic gradient of the groundwater system. The realization of the polluting effects of landfill leachates on the environment has prompted a number of studies. These include studies on domestic wastes (Mor 2006; Simsek 2008; Sridher 1985), leachate quality (Christensen 2001; Fatta 1999; Mor 2006; Ostman 2006; Sridhar 1985), as well as underground water quality (Fatta 1999; Jorstad 2004; Loizidou 1993; Mor 2006; Simsek 2008). The main objective of this study is to investigate the level of groundwater contamination in the vicinity of the landfill. And it is of particular interest as groundwater is a major source for drinking and domestic purpose. This study also aimed to provide benchmark information on the extent of pollution brought about by the open dumpsite along groundwater sources of those areas. (Agrawal 2010; Dash 2010)

Study Area

Ballarpur area generates hundreds of MT of waste per day. About 30% of this waste is organic compostable material. The remaining 70% consists of paper (11.9%), rubber, leather and synthetics (3.02%), glass (0.98%), metals (0.33%) and other inert materials (53%). Nearby Visapur villege. The landfill accepts officially, non-hazardous solid wastes of domestic, market, commercial, industrial and institutional origins but in practice all type of wastes is co disposed. The landfill is located at elevated portion of land and samples are collected along the slope direction to measure the extent of groundwater pollution. The site of Visapur villege on the way Ballarpur-Chandrapur road is being used for dumping at present, which would not meet future requirements. The climate of study area follows a typical seasonal monsoon weather pattern. The peak temperatures are usually reached in May/June and can be as high as 48^0 C. The onset of monsoon is usually from July. The season extends up to September with the monsoons peaking during July and August. After monsoons, the average temperature varies between 27^0 C and approx. 6-7^0 C right through December and January. The average annual rainfall is around 50 inches, with more rain in the east than in the west.

Methodology

In the present study, prior to data collection, a selection criterion was established to aid in the identification of appropriate sampling sites for the groundwater quality assessment in the landfill area. The site of Vardha River nearVisapur villege the samples are collected along the gradient to measure the extent of

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groundwater pollution. Those dug wells and bore wells were selected for sampling, which are active and functional and continuously in use for drinking and domestic purposes. These sampling sites are located away from toilets and have not undergone any chemical treatment. The parameters were selected based on their relative importance in landfill leachates composition, and their pollution potential on groundwater resource in particular. Cl^- was included in the groundwater quality assessment because of its measure of extent of dispersion of leachates in groundwater body.

Dug well and bore well groundwater samples were collected in plastic containers, which were previously cleaned with distilled water. As part of the quality control measures, containers were rinsed with sampled groundwater before filling. Samples were collected for major cation and anion analyses also. All samples were preserved at 25^0C and transported to the laboratory for analysis. Physico-chemical parameters of the samples are analyzed following standard analytical procedure (APHA 1995). The pH, electrical conductivity and temperature were determined in-situ, while the chloride (Cl^-), bicarbonate (HCO_3^-), total hardness (TH), alkalinity (TA), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by titrimetric method. Sodium (Na^+) and potassium (K^+) was determined using Flame photometer. Nitrate (NO_3^-) and sulphate (SO_4^{2-}) was determined using UV-visible spectrophotometer.

Result and Discussion

Hydro chemical parameters and Groundwater quality:

Groundwater quality assessment is done with 5 samples from shallow and 8 samples from deep aquifer nearby the landfill site. The result of the chemical analysis of ground water of study area is presented in Table I and their comparison with the WHO guidelines (WHO 2002) is given in Table II.

The groundwater is alkaline with pH values varying between 6.4 and 8.4. Water from well 5 at about 4 meters away from the landfill has the lowest pH of 6.4, hence the most acidic in this present study.

Electrical conductivity (EC) and total dissolved solids (TDS) signify the inorganic load of any water body. The TDS values obtained in ground water varied from 994 to 2927 mg/L. Almost all samples show TDS values higher than desirable limit suggested by WHO (WHO 2002). As the distance of sampling sites from landfill increases, TDS content decreases. To ascertain the suitability of groundwater of any purposes, it is essential to classify the groundwater depending upon their hydro-chemical properties based on their TDS values (Davis and DeWiest 1966; Freeze and Cherry 1979) which are represented in Tables III and IV respectively. The groundwater of the area is fresh water for 15.4% of the samples locations and the rest of the samples represent brackish water based on (Freeze and Cherry 1979). *The study shows that no sample is below 490 mg/L of TDS which can be used for drinking without any risk*. EC values ranges from 1422 – 3750 □S/cm. Su is attributed due to high Salinity and effect of landfill site on groundwater regime. The major inorganic ions in groundwater include Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, and Cl^-. The distribution of these constituents largely depends on the type of geological formations in contact with the groundwater flowing through. The total alkalinity (TA), as CaCO3 in water ranges from 120 to 530 mg/L in ground water. The high alkalinity imparts water with unpleasant taste, and may be deleterious to human health with high pH.

The total hardness (TH) of ground water varied from 55 to 1490 mg/L. The maximum allowable limit of TH for drinking purpose is 500 mg/L and

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the most desirable limit is 100 mg/L as per the WHO. Based on TH, groundwater exceeding the limit of 300 mg/L is considered very hard (Sawyer and McMcartly 1967). Very hard groundwater is dominant in the aquifers of study area, which may raise the risk of calcification of arteries, urinary concretions, diseases of kidney or bladder or stomach disorder (Hopps 1986). The high value of TH in supply water may cause corrosion of pipes, resulting in the presence of certain heavy metals, such as cadmium, lead and zinc in drinking water.

Ca^{2+} and Mg^{2+} are important ions for total hardness. Ca^{2+} content in the groundwater varied between 10.0 and 270.0 mg/L. In the most of the samples concentration of Ca^{2+} is within desirable limit in portable water suggested by WHO (2002). Presence of Ca^{2+} in water generally varies according to the proximity of natural sources. Sewage and industrial wastes are known to account for such anthropogenic sources of Ca^{2+} in water (Subrahmanyam 2001). The concentration of Mg^{2+} ions varied from 10.5 to 210 mg/L. A concentration of 150 mg/L is recommended for Mg^{2+} ions in drinking water WHO (2002). Except one all the studied samples are within the permissible limit in the studied area. Mg^{2+} ions are essential as an activator of many enzyme systems but its salts are cathartic and diuretic and high concentration may cause laxative effect, while deficiency may cause structural and functional changes.

The concentration of Na^{+} ions ranges from 169 to 413 mg/L in groundwater samples. Most of the samples exceeded the maximum permissible limit of Na^{+} in groundwater samples. The higher concentration of Na^{+} may pose a risk to persons suffering from cardiac, renal and circulatory diseases (Mor 2006). The high concentration of Na^{+} around landfill site indicates impact of landfill. The concentration of K^{+} ions varied from 4 to 203 mg/L. K^{+} is an essential nutrient but if ingested in excess may behave as a laxative. Except few inputs from agricultural activities, the high concentration of K^{+} has been reported to be an indication of leachate.

The HCO_3^{-} ion concentration in groundwater varies from 146.4 to 646.2 mg/L in groundwater samples. Cl^{-} is a good measure of the extent of the dispersion of leachates in groundwater. The Cl^{-} content in groundwater samples from study area ranges from 166.8 to 1562.0 mg/L. almost all the samples contained higher concentration of Cl^{-} ion than most desirable limit (200 mg/L) suggested by WHO 2002. An excess of Cl^{-} in water usually taken as an index of pollution and considered as tracer for groundwater contamination (Loizidou 1993). Cl^{-} ion concentration higher than 200 mg/L are considered to be at risk for human health and may cause unpleasant taste of water and its high consumption may be crucial for development of essential hypertension, risk for stroke, left ventricular hypertrophy, osteoporosis, renal stones and asthma (Hopps 1986). This high Cl^{-} content of groundwater is likely to originate from pollution sources such as domestic effluents, fertilizers and septic tanks and from natural sources such as rainfall. In the study area higher concentration of Cl^{-} is attributed due to anthropogenic activities associated with landfill site.

In the ground water samples of study area SO_4^{2-} concentration ranged from 0.6 to 34.8 mg/L. The concentration of SO_4^{2-} in most of the samples is lower than the desirable limit (200 mg/L) accepted for drinking water. In general the major sources of nitrate in groundwater include domestic sewage, runoff from agricultural fields, and leachates from landfill sites. (Jalali 2005; Pawar 1995). Drinking water containing more than 45 mg/L NO_3^{-} can cause blue baby or methamoglobinemia in infants and gastric carcinomas (Hopps 1986; Jalali 2005). About

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77% of samples from study area have NO_3^- content above 45 mg/L, which show high level of pollution. Nitrate concentration in groundwater samples of study area is attributed to dumping of organic waste at landfill site.

Irrigation Suitability

The irrigation water containing a high proportion of Na^+ will increase the exchange of Na^+ content of the soil, affecting the soil permeability, and the texture makes the soil hard to plough and unsuitable for seedling emergence. If the percentage of Na^+ with respect to Ca^{2+} and Mg^{2+} exchange with Na^+, thus causing deflocculation and impairment of tilt and permeability of soils. (Karanth 1987). Most of the samples from study area are highly saline having low Na^+ concentration which makes fall in good to moderate class for irrigation.

Conclusion

Solid waste landfills are a necessity in modern day society, because the collection and disposal of waste materials into centralized locations helps minimize risks to public health and safety. Solid waste landfills, which are regulated differently than hazardous waste landfills, may accept a variety of solid, semi-solid, and small quantities of liquid wastes. Landfills generally remain open for decades before undergoing closure phases, during which steps should be taken to minimize the risk of environmental contamination.

Analyses of groundwater from both deep (BW) and shallow (DW) aquifers along the gradient from The site of Vardha River nearVisapur villege show strong evidence of groundwater contamination. The aquifers located along the gradient from landfill site have higher concentration of Cl^- and NO_3^- illustrating the contribution of landfill towards groundwater pollution. There is a risk of increase in groundwater pollution around the landfill site considering the current levels of Cl^- and NO_3^- found in the groundwater. About 77% of groundwater samples have NO_3^- higher than 50 mg/L and are unsuitable for drinking. The current observed Cl^- concentration in groundwater samples is very high making water unfit for drinking. Overall analyses indicate increasing risk for sustainability of ground water resources.

The appropriate methodology for solid waste management is reduce, reuse and recycle and same is true for reducing leachate induced groundwater pollution. In order to protect the groundwater quality of leachate area, monitoring programme for groundwater quality status around the vicinity of landfill is suggested. Before setting a new landfill site, an adequate buffer zone between the landfill and the property line of the adjacent property should be maintained to minimize the effect of pollution. A buffer of 2 to 3 miles in the direction of groundwater flow is appropriate.

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Table I: Analytical data for groundwater samples in the study area

Sample No.	Distance from site (in m)	pH	EC	TDS	TH[b]	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}
1	25	7.8	2591	1426	410	345	58	64.4	388	68	420.9	415.2	8.35	213.9
2	30	7.7	2079	1243	350	530	64	46.2	356	81	645.9	334.1	11.51	25.5
3	40	7.6	2601	1688	360	455	36	63.2	379	203	554.8	404.6	12.5	311.6
4	60	7.6	1835	994	490	120	84	68.0	169	5	146.2	429.5	0.60	164.5
5	05	6.4	3260	1769	710	390	60	133.6	411	99	476.0	713.6	25.30	88.55
6	Site	7.1	3750	2927	1490	140	270	210.2	413	101	170.8	1562.0	34.80	266.7
7	20	8.4	1442	1077	55	465	10	10.5	389	89	567.0	223.6	3.95	71.74
8	40	7.6	1835	1026	255	390	78	45.0	246	78	475.8	166.8	8.4	213.1
9	85	7.5	1766	1208	330	460	20	66.8	345	75	564.2	290.9	6.78	121.2
10	105	8.0	1823	1253	270	420	60	41.3	375	81	512.4	411.9	3.20	42.8
11	45	7.6	1502	998	340	270	76	36.4	232	63	329.4	274.1	4.69	145.6
12	50	7.4	1615	1108	195	360	18	35.2	323	81	439.2	241.6	10.20	176.6
13	05	7.3	2760	1715	670	480	74	117.9	383	98	585.6	539.8	2.80	205.2
	Average	7.5	2220	1418	455.7	371	63.4	71.6	339	86.2	452.8	463.4	10.2	157.8

[a]Sample no. 1 to 5 Dug wells, 6 -13 Bore wells.

[b] All the values are in mg/L, except pH and EC. Unit for EC is □S/cm at 25 °C

Table II: Comparison of the groundwater samples of study area with WHO guidelines (WHO 2002)

Parameters	**Unit**	**Min.**	**Max.**	**WHO**
pH		6.5	8.5	7 – 9.2
EC	□S/cm	1422	3740	---
TDS	mg/L	981	2930	500 – 1500
TH	mg/L	55	1490	100 – 500
TA	mg/L	120	530	---
Na	mg/L	169	413	200
K	mg/L	4	203	---
Ca	mg/L	10	270	75 – 200
Mg	mg/L	10.5	210	50 – 150
HCO_3	mg/L	146.4	646.6	---
Cl	mg/L	156.9	1562	200 – 600
SO_4	mg/L	0.7	34.8	200 – 400
NO_3	mg/L	25.5	311.5	45

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Table III: Groundwater classification based on TDS (Davis and DeWeist 1996)

TDS (mg/L)	**Classification**	**No. of Samples**	**% of samples**
<500	Desirable for drinking	--	0.0
500 – 1000	Permissible for drinking	02	15.4
1000 – 3000	Useful for irrigation	11	84.6
> 3000	Unfit for drinking and irrigation	--	0.0
Total		13	100

Table IV: Groundwater classification based on hardness (Sawyer and Mcmcartly 1967)

Total Hardness as $CaCO_3$	Classification	No. of Samples	% of samples
<75		01	7.70
75 – 150	Moderately High	--	0.00
150 – 300	Hard	04	30.77
>300	Very Hard	08	61.54
Total		13	100

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An analytical study of Dissolved Gas Analysis for internal Faults Pre- determination in EHV Class Power Transformers

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ABSTRACT

Dissolved Gas Analysis (DGA) is used to predict the actual condition of internal health of a transformer. It is considered as one of the best methods of detecting certain problems which can lead to failure of the transformer. In DGA test of transformer oil, the gases in oil are extracted from oil and analyze the quantity of gases in a specific amount of oil. By observing percentages of different gases present in the oil, one can predict the internal condition of transformer [1]. For DGA, oil sample from the transformer has to be removed which can be done without de-energization of the transformer easily. Then by using gas chromatography technique, oil sample is analyzed in the laboratory. This paper presents complete DGA study of 12.5 MVA 132/33KV, EMCO make Transformer at 132 KV S/S Shahpura (M.P.). The data are analysed over a period of 2008 to 2015 . The DGA results by different standard methods are compared.

INTRODUCTION

Oil is used in transformers for cooling and insulation purpose. Under the influence of electrical and thermal stresses, insulating materials can decompose generating gaseous products inside transformers. From the time of World War I itself, presence of gases inside transformers have been recognized. Those gases were collected and analyzed so that information can be gained to know the cause behind its formation.

Gases are formed inside transformers under both normal conditions as well as faulty conditions. The difference is that in case of a fault, gases are generated in higher quantity.

Fault gases inside transformers can be classified into 3 groups[11]:

1. **Hydrocarbons and hydrogen.**

Methane (CH_4)
Ethane (C_2H_6)
Ethylene (C_2H_4)
Acetylene (C_2H_2)
Hydrogen (H_2)

2. **Carbon oxides**

Carbon monoxide (CO)
Carbon dioxide (CO_2)

3. **Non- Fault**

Nitrogen (N_2)
Oxygen (O_2)

Mineral oil de-gradation in oil filled transformers is a major concern. Analysis of oil sample of transformer is useful, predictive and maintenance tool for determining health of transformer. Ageing of the oil, overheat, overvoltage, environmental conditions and numerous unknown factors are responsible for the oil degradation [2]. This de-gradation can lead to pre-mature failure of the transformer. Oil used in transformer is a mixture of Hydro-carbons. Lower order of Hydro-carbons like Methane, Acetylene, Ethane, Ethylene etc. are produced with some permanent gases like Carbon Di-oxide, Carbon Mon-oxide and hydrogen during the process of degradation. Failures are inevitable in oil filled equipment such as power transformer if proper care is not taken. The mixture of hydrocarbons and permanent gases is sealed environment can cause an explosion. In the running condition, proper monitoring is needed on the concentration of these

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explosive gases[7]. Initially the generated gases will dissolve in the oil. When the generated gases increases in its volume, more of it will dissolve into the oil. Eventually a stage will come when the oil will be completely saturated with the dissolved gases and any further increase cannot be contained as dissolve gas in the oil so it will come out as free gas. By evaluating the amount of generated gas present and the rate of gas generation, abnormal condition can be detected.

II. METHEDOLOGY

DGA: It is an effective as well as practical method which helps in the detection of incipient faults along with its order of severity. After commissioning of the transformer, DGA shall be repeated once in a month whereas in case of transformer which has been repaired, DGA should be carried out in a week soon after decommissioning and then after about 3 months. DGA helps in detecting the faults at an early stage so that serious damage can be prevented.

For the improvement in reliability and power availability, DGA plays an important role. On the basis of results obtained, investigation has become easier and problems thus are resolved in less time[5]. DGA results gives us detailed information about the condition of transformers. Many industries are now aware of this tool and using it for reduced maintenance and reduced cost of repairs of power transformers. If the fault is identified at an initial stage, then remedial actions can be taken in time to prevent failure.

DGA not only detects but also gives warning of 70% of the most common failures which occurs in transformers. Undoubtly, DGA is considered the best detector for any sort of abnormalities in power transformers.

Developments in the field of DGA are still going on. Earlier only mineral oil was used for insulation purpose in transformers but now silicone oils, synthetic esters and vegetables based oils are being introduced. Specially where low fire risk is needed, there synthetic esters and silicone oils are used because both can operate at higher temperature as compared to mineral oil. But still it will take some time to completely replace mineral oil which is traditionally used[12].

Gas chromatography: One of the most widely used methods is Gas Chromatography (GC) .Gas Chromatography apparatus of Chemito Company is used in MPPTCL. For the separation of different complex mixtures, GC is used. M .S. Tsvet, a Russian botanist coined the term “chromatography”. Earlier chromatography was used for separation of mixture of liquids. From 1950 onwards, this method was improved to separate mixture of gases[10]. From the operating transformers, oil samples are collected and taken to the laboratory for the gas extraction and analysis. Oil sample is taken from the transformers and transported to the laboratory using syringes, flexible metal cans, special glass bottles or in the calibrated stainless steel cylinders. From the bottom of the tank, oil samples are usually taken.

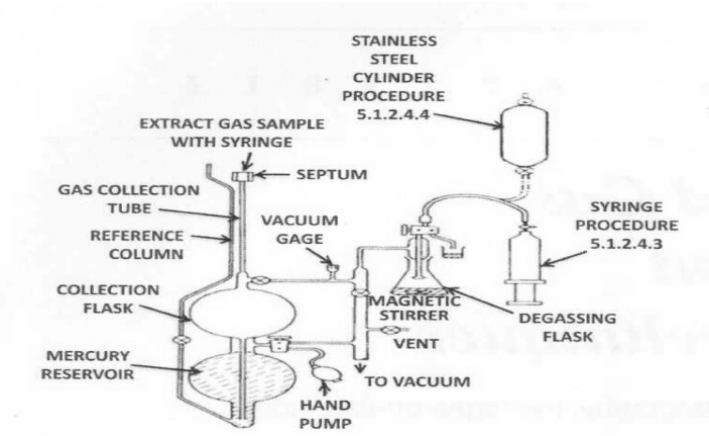

FIG.1 Extraction of dissolved gases from transformer oil using vacuum extraction method

This method for DGA is used once in a year only as it is a costly process. For extraction of gases from the oil, stripper extraction, headspace sampling and vacuum extraction can be used. Disadvantages of this method are it is very expensive and also time taking.

Due to limitations of GC, two new techniques namely hydrogen on-line monitoring and photo acoustic spectroscopy have been developed. Both of these methods requires less time as compared to GC. For analyzing dissolved gases in insulating oil, GC has been used for the last 60 years. After IEC, IEEE and ASTM published relevant guidelines, this method became more popular. Among the three methods, GC is accepted as the best method for measuring the

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concentration of gases dissolved in transformer oil. In the laboratory environment, GC analysis is successfully conducted [7].

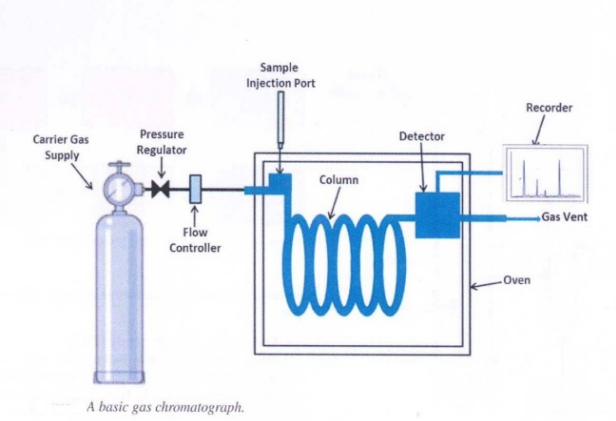

Fig. 2 A Gas Chromatograph

III. ANALYSIS METHODS

3.1 Rogers Ratio Method: In this method a 4 digit ratio code is generated from the five fault gases namely hydrogen, methane, ethane, ethylene and acetylene for determining 15 diagnosis rules for transformer conditions.

Roger's ratio gas

Ratio	Code
CH_4/H_2	1
C_2H_6/CH_4	2
C_2H_4/C_2H_6	3
C_2H_2/C_2H_4	4

1. If all the four ratios are equal to zero then it indicates no fault.
2. If code 2=5, in other words when the ratio of ethane to methane is equal to 5 and remaining three codes are zero then it indicates partial discharge of low energy density or hydrolysis.
3. If code 1=1 and code 2=5, in other words when the ratio of methane to hydrogen is equal to one and that of ethane to methane is equal to 5 respectively with remaining two ratios equal to zero, it indicates partial discharge of high density which is possible with tracking.
4. If code 2=5 and code 3=1, in other words when the ratio of ethane to methane is equal to 5 and ratio of ethylene to ethane is equal to 1 with remaining two ratios zero, then it indicates coincidental partial discharges and conductor overheating.
5. If code 2=5 and code 4=1, in other words when the ratio of ethane to methane is equal to 5 and that of acetylene to ethylene is equal to 1 with remaining two ratios equal to zero, it then indicates partial discharges of increasing energy density.
6. If code 1 is greater than 1 but less than 2, in other words when the ratio of methane to hydrogen is greater than 1 but less than 2 and remaining ratios are zero, it then indicates low energy discharge (flashover without power flow through).
7. If code 1 is greater than 1 but less than 2 and code 3 is equal to 1, in other words when the ratio of methane to hydrogen is greater than 1 but less than 2 and ratio of ethylene to ethane is equal to 1 with remaining ratios equal to zero, it indicates low energy discharge (continuous sparking to floating potential).
8. If code 1 is greater than 1 but less than 2 and code 3 is equal to 2, in other words when the ratio of methane to hydrogen is greater than 1 but less than 2 and ratio of ethylene to ethane is equal to 2 with remaining ratios equal to zero, it indicates high energy discharge (arc with power flow through).
9. If code 3 is equal to zero, in other words when the ratio of ethylene to ethane is equal to 1 with remaining ratios equal to zero, it indicates insulated conductor overheating.
10. If code 3 is equal to one and code 4 also equal to 1, in other words when the ratio of ethylene to ethane is 1 and ratio of acetylene to ethylene is also equal to 1 with remaining two ratios equal to zero, it indicates complex thermal hotspot and conductor overheating.
11. If code 1 is equal to one and code 4 is equal to one, in other words when the ratio of methane to hydrogen is 1 and ratio of acetylene to ethylene is also 1 with remaining two ratios equal to zero, it indicates coincidental thermal hotspot and low energy discharge.
12. If code 2 is equal to one, in other words when the ratio of ethane to methane is equal to 1 with the remaining three ratios equal to zero, it indicates

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thermal fault of low temperature range less than 150 degree Celsius.

13. If code 2 is greater than zero but less than 2 and code 4 is equal to 1,in other words when the ratio of ethane to methane is greater than zero but less than 2 and ratio of acetylene to ethylene is 1 with remaining two ratios equal to zero, it indicates thermal fault of temperature range from 100 degree Celsius to 200 degree Celsius.

14. If code 2 is equal to one and code 3 is also equal to one, in other words when the ratio of ethane to methane is equal to 1 and ratio of ethylene to ethane is 1 with remaining two ratios equal to zero, it indicates thermal fault of temperature range from 150 degree Celsius to 300 degree Celsius. It occurs due to overheating of copper due to eddy currents.

15. If code 2 is greater than 1 but less than 2 and code 3 is equal to 2, in other words when the ratio of ethane to methane is greater than 1 but less than 2 and ratio of ethylene to ethane is equal to 2 with remaining two ratios equal to zero, it indicates thermal fault of temperature range from 300 degree Celsius to 700 degree Celsius. It occurs due to bad contacts/joints.[3]

3.2 IEC Basic Ratio Method: This method has originated from the Rogers Ratio Method, except that the ratio of ethane to methane is not included in this method as it only indicated a limited temperature range of decomposition.

Ratio	Code
C_2H_2/C_2H_4	1
CH_4/H_2	2
C_2H_4/C_2H_6	3

1. When the ratio of acetylene to ethylene is not significant (code 1=not significant), ratio of methane to hydrogen is less than 0.1 (code 2<0.1) and ratio of ethylene to ethane is less than 0.2 (code 3 <0.3) it indicates partial discharges.
2. When the ratio of acetylene to ethylene is greater than 1(code 1>1), ratio of methane to hydrogen is in the range of 0.1 to 0.5 (0.1<code 2<0.5) and ratio of ethylene to ethane is greater than 1 (code 3 <1) it indicates discharges of low energy.
3. When the ratio of acetylene to ethylene is in the range of 0.6 to 2.5 (0.6<code 1>2.5), ratio of methane to hydrogen is in the range of 0.1 to 1 (0.1<code 2<1) and ratio of ethylene to ethane is greater than 2 (code 3 <2) it indicates discharges of high energy.
4. When the ratio of acetylene to ethylene is not significant (code 1=not significant), ratio of methane to hydrogen is greater than 1 (code 2 >1) and ratio of ethylene to ethane is less than 1 (code 3 <1) it indicates thermal fault of temperature less than 300 degree Celsius.
5. When the ratio of acetylene to ethylene is less than 0.1 (code 1<0.1), ratio of methane to hydrogen is greater than 1 (code 2>1) and ratio of ethylene to ethane is in the range of 1 to 4 (1<code 3 <4) it indicates thermal fault of temperature between 300 degree Celsius to 700 degree Celsius.
6. When the ratio of acetylene to ethylene is less than 0.22 (code 1<0.22), ratio of methane to hydrogen is greater than 1 (code 2>1) and ratio of ethylene to ethane is greater than 4 (code 3>4) it indicates thermal fault for temperature greater than 700 degree Celsius.
7. Increasing value of acetylene may indicate that the hot spot temperature is higher than 1000 degree Celsius.[4]

3.3 Key Gas Method:

Gas	Normal	Abnormal	Interpretation
H_2	<150 ppm	>1000 ppm	Arcing, Corona
CH_4	<25 ppm	>80 ppm	Sparking
C_2H_6	<10 ppm	>35 ppm	Local Overheating
C_2H_4	<20 ppm	>100 ppm	Severe Overheating
CO	<500 ppm	>1000 ppm	Severe Overheating
CO_2	<1000	>15000 ppm	Severe

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	ppm		Overheating
N_2	1-10%	N.A	
O_2	0.2-3.5%	N.A>0.5%	Combustibles

IV. DATA OBTAINED FROM MPPTCL

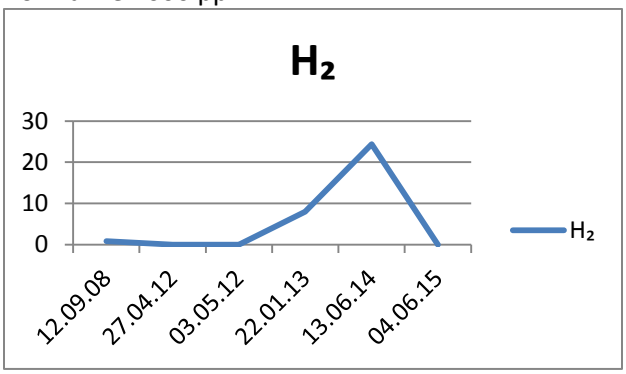
This is presented in Table 1 given in annexure

V. TEST RESULTS and ANALYSIS

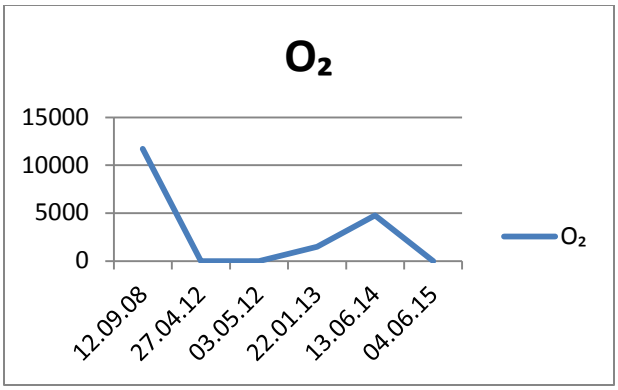
5.1 RESULT OBTAINED ACCORDING TO ROGER'S RATIO METHOD: collected data of transformer is checked according to roger's ratio method. It is not possible to find fault according to this method. The results are presented in TABLE 2 given in Annexure.

5.2 RESULT OBTAINED ACCORDING TO IEC BASIC RATIO METHOD:
Collected data of transformer is checked according to IEC basic ratio method : It is found that on date 22.01.13, it indicates high energy discharge which was the cause of abnormality in the transformer. The results are presented in TABLE 3 given in Annexure.

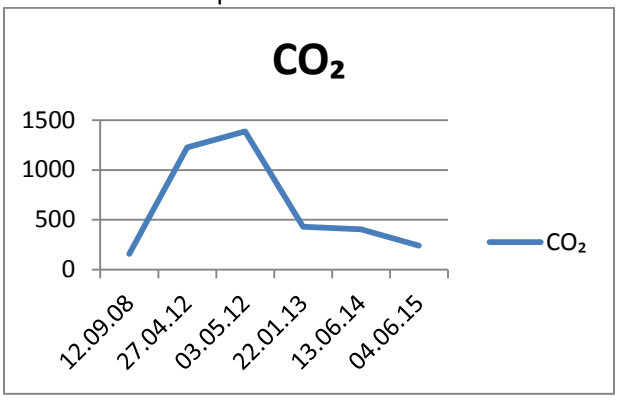
5.3 RESULT OBTAINED ACCORDING TO KEY GAS METHOD: According to key gas method , on 03.05.12 concentration of CO_2 was found slightly more than normal i.e 1000 ppm.



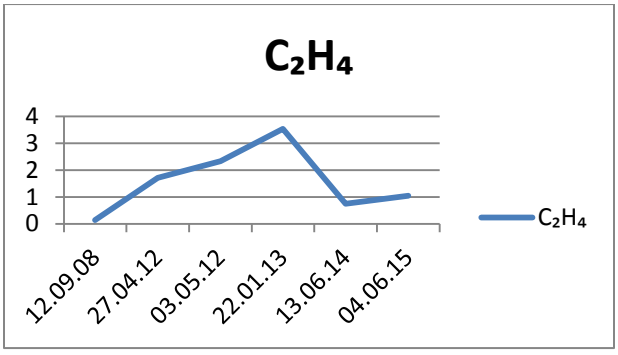
The above graph indicates that H2 is almost constant from September 2008 to May 2012, it then increases due to internal arcing and corona discharge. During overhauling of transformer some loose connection were found and the same were rectified by soldering and tightning of bushing to internal winding connection.



The graph shows the content of oxygen decreases due to combustion and ingress of particle impurity. The oil flirtation was done in May 2012 and the oxygen increase, it further continuously decreases over a period from 2014 to 2015 . The oil filtration is recommended at present.



The above graph indicates that CO_2 has increased from September 2008 to May 2012 due to severe overheating. After that its concentration reduced due to oil filtration.



This graph shows that C_2H_4 increased from September 2008 to January 2013 due to severe overheating. Remedial actions were then taken to decrease its concentration.

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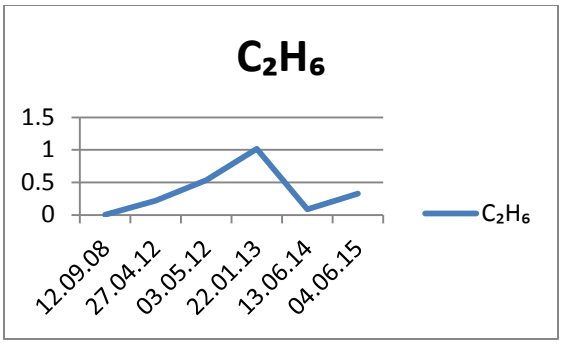
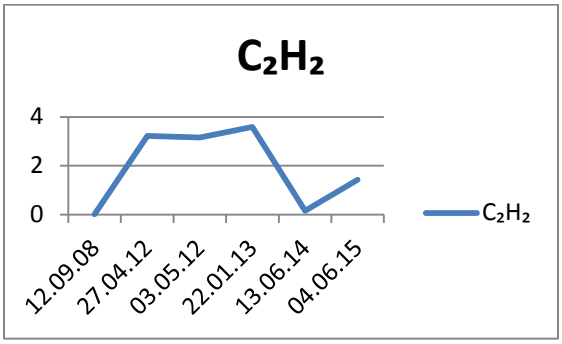
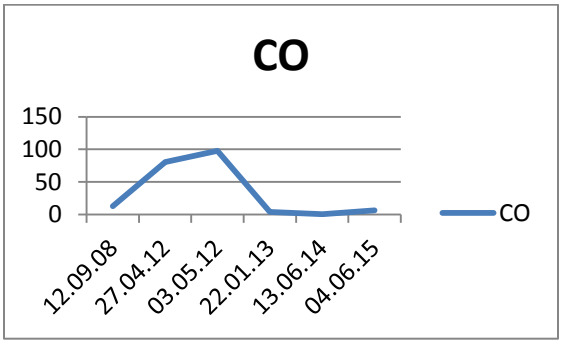


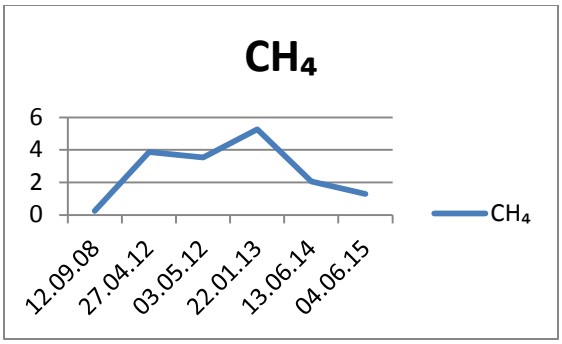
This graph indicates that C_2H_6 increased from September 2008 to January 2013 due to local overheating. Due to remedial actions taken in time its concentration decreased in June 2014. It further increased but is under normal limits.



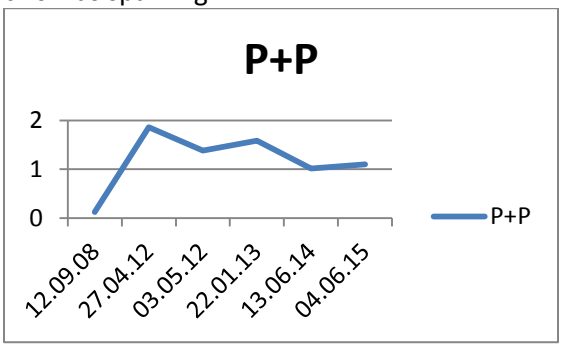
This graph shows that concentation of C_2H_2 increased from September 2008 to January 2013 due to overloading. Then it reduced to normal limits as transformer was not overloaded.



This graph indicates that concentration of CO has increased from September 2008 to May 2012 as a result of overloading.Due to some remedial actions it decreased to some extent.



This graph indicates that CH_4 increased from September 2008 to January 2013.The cause behind this was sparking.



This graph shows that concentration of P+P i.e propylene and propane initially increased and then decreased over the years.

VI. CONCLUSION

The rate of decomposition and the type of gases change during defective operation, which could be a result of thermal overloading and/or electrical faults has been analysed for 12. 5 MVA 132 /33 kv Transformer . It is shown that using DGA , based on the quantity or type of fault gases, the gas increase rates and the proportions between the gases, the type of failure can be pre -deduced. Partial discharges with lower energy mainly lead to the formation of hydrogen and methane, as well as small quantities of ethane. Electrical discharges (arcs and spark discharges) cause separation of hydrogen and acetylene, as well as methane and ethylene. By thermal-oxidative cellulose degradation, larger quantities of CO and CO2 are formed. By contionusly conducting the DGA Test and monitoring the results , the internal Faults can be Pre- determined in EHV

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Class Power Transformers, hence to prevent transformer failure which further causes major power interruption. Effective steps can be taken when internal arcing and corona discharge , severe overheating etc are predicted by DGA. During ovehauling of transformer, loose connections should be rectified by soldering and tightning of bushing to internal winding connection, addition of DBPC Powder, oil reclaimation and other remedial actions should be taken to decrease the concentration of gases in oil. It will increase the active life span of the transformer.

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ANNEXURE :

TABLE 1

Date	Methane(in parts per million ppm)	Ethane (in parts per million ppm)	Ethylene (in parts per million ppm)	Acetylene (in parts per million ppm)	Hydrogen (in parts per million ppm)	Carbon monoxide(in parts per million ppm)	Carbon dioxide (in parts per million ppm)	Oxygen (in parts per million ppm)	p+p (in parts per million ppm)	Total (in parts per million ppm)
12.09.08	0.2605	0.003239	0.1428	0.008311	0.8255	12.8368	159.0378	11718.923	0.1202	11892.16
27.04.12	3.8728	0.2183	1.7159	3.217	0	80.4972	1226.5643	0	1.857	1317.943
27.04.12	3.8728	0.2183	1.7159	3.217	0	80.4972	1226.5643	0	1.857	1317.943
03.05.12	3.5288	0.5341	2.3305	3.1579	0	97.7727	1387.2407	0	1.3822	1495.947
22.01.13	5.2715	1.0146	3.5303	3.5846	7.9832	3.8179	430.2994	1481.2629	1.5878	1938.352
04.06.15	1.3	0.33	1.05	1.43	0	6.5	239.95	0	1.1	251.66

TABLE 2

Dates	Code 1	Code 2	Code 3	Code 4
12.09.08	0.2605/0.8255=0.3155	0.003239/0.2605=0.01243	0.1428/0.003239=44.08768	0.008311/0.1428=0.05820
27.04.12	3.8728/0	0.2183/3.8728=0.0563	1.7159/0.2183=7.8602	3.217/1.7159=1.8748
03.05.12	3.5288/0	0.5341/3.5288=0.1513	2.3305/0.5341=4.3634	3.1579/2.3305=1.35503
22.01.13	5.2715/7.9832=0.66032	1.0146/5.2715=0.192468	3.5303/1.0146=3.47949	3.5846/3.5303=1.01532
13.06.14	2.0595/24.3465=0.084591	0.08875/2.0595=0.04309	0.7478/0.08875=8.4259	0.1502/0.7478=0.2008
04.06.15	1.3/0	0.33/1.3=0.253	1.05/0.33=3.18	1.43/1.05=1.3619

TABLE 3

Dates	Code 1	Code 2	Code 3
12.09.08	0.008311/0.1428=0.05820	0.2605/0.8255=0.3155	0.1428/0.003239=44.08768
27.04.12	3.217/1.7159=1.8748	3.8728/0	1.7159/0.2183=7.8602
03.05.12	3.1579/2.3305=1.35503	3.5288/0	2.3305/0.5341=4.3634
22.01.13	3.5846/3.5303=1.01532	5.2715/7.9832=0.66032	3.5303/1.0146=3.47949
13.06.14	0.1502/0.7478=0.2008	2.0595/24.3465=0.084591	0.7478/0.08875=8.4259
04.06.15	1.43/1.05=1.3619	1.3/0	1.05/0.33=3.18

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