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Speciation of Zinc Heavy Metal in Ground Water of Middle Palar River Basin by DPASV Technique

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ABSTRACT

The determination of various forms of zinc heavy metal in the ground water was carried out by differential pulse anodic stripping voltammetry (DPASV) technique. Twenty samples of ground water were collected during three different seasons from January-2014 to November-2014 from bore wells. The sampling stations were located in middle palar river basin near areas influenced by tanneries and textiles dying industries. The samples were analyzed for labile, non-labile and total dissolved forms of zinc content. It was found that non-labile form dominated the speciation of zinc in Ranipettai and Kancheepuram stations. The concentrations of Zn labile fractions were found to be the highest during monsoon and summer seasons in and around Kancheepuram stations. It was found that the percentages of labile and non-labile forms varied widely with respect to the stations in different seasons.

Keywords : Trace metals, Speciation, chemical form, ground waters

I. INTRODUCTION

Pollution has resulted in destruction of our safe drinking water resources and heavy metal contamination has risen to alarming levels in areas adjoining industrial belts. Knowledge of the different forms of metal in the ground water is thus essential to understand the role of nutrient and polluting elements. Investigations of heavy metals such as Pb, Cd, Cu, Zn and Cr place special importance on environmental samples (Selehattin Yilmaz et al.2009, Novotry et al.2000 and Abollino et al.2000). A study on the distribution of metal speciation in middle palar river basin ground waters will give an insight in to understanding the various physico chemical processes taking place and also throw some light on the trace metal pollution. In the present study we aim at discriminating the zinc heavy metals present in ground water samples as labile, non-labile and total dissolved forms. Although there are a few studies (Swaminathan et al.2011 and Balakrishnan et al.2008) dealing with determination of heavy metals pollution in Indian ground water, very little work has been carried out using metal speciation studies (Kuppusamy. M. R and Giridhar.V.V,2004,2006,Nithila et al.1991).The advantages for using DPASV technique include its ability to detect extremely low concentrations, ability to detect even in the presence of high salt content, it further aids in the determination of metal speciation where it can differentiate between free and complexed metal ions. Non-metals such as anions or organics can also be estimated (Raj.j et al.2013).The destruction of organic matter using prolonged UV irradiation with addition of H2O2 to the samples have been reported to be an efficient method to remove organic matter from ground water samples (Bately.G.E and Y.J.Farrar.1978 and Zannaty R.Komy.1993). In this work, extensive chemical analysis of different chemical forms present in the ground water of middle palar river basin have been carried. The concentration of Zn heavy metal was estimated by speciation studies along with the evaluation of their toxicity in respect to bioavailability of Zn, was performed.

II. METHODS AND MATERIAL

2.1. Instrumentation and operating conditions

Voltammetric determination of Zinc was performed with Metrohm 757 Computrace (Herisau,Switerland) using a three electrode system. Hanging mercury drop electrode (HMDE) was used as a working electrode, Platinum (Pt) as auxiliary electrode and Ag/AgCl/KCl (3mol/L) as reference electrode. The operating parameters are given in Table-1.

2.2. Reagents

The standard zinc solutions for the voltammetric measurements were prepared from the stock solution of 1000 mg/L^{-1}(MERK). A 0.2Mol L-1 acetate buffer (pH 3.5) prepared by mixing of appropriate amounts of Suprapure acetic acid, Liquid ammonia (MERK) and NaOH was used to prepare solutions of the supporting electrolyte. Ultra pure water was obtained from milli Q water systems and was used to prepare to all solutions.

2.3. Sample collection

A total of 20 bore wells sampling locations have been selected for ground water sample collection based on their location and representative nature and five bore wells sampling stations are located in and around Ranipettai town. This town comprises anthropogenic inputs from tannery industries. 10 Bore wells sampling stations are located in Kancheepuram town were the sources of contamination include agricultural runoff, dying industries effluents and rice mill wastes. 6 borewells sampling stations are located along middle palar river basin in and around chengalpattu town. The bore wells sampling points was designed to cover wide range of determinants at key sampling sites, which reasonably represent the water quality of middle palar river basin accounting for tributary and inputs from waste water drains that have impact on downstream.

Sampling survey was carried out during three seasons for a period of one year. They are January 2014 (Post monsoon), June-2014 (summer) and November-2014 (Monsoon). Ground water samples were collected using a pre-cleaned and acid washed Zinc free polypropylene one liter container. Samples from bore wells were collected from the outlets after flushing water for 10 to 15 minutes in order to remove the stagnant water. Ground water samples were stored in iceboxes (0-2°C) and brought to the laboratory for further analysis.

2.4. Sample Preparation for DPASV Measurements

The analysis of labile zinc metal in ground water samples were carried out using 10ml of the sample after filtering using 0.45µ membrane filter and 1ml of acetate buffer were added to the voltammetric cell. Oxygen free Nitrogen gas purged 300s so as to remove the dissolved oxygen. The presence of Zn was analyzed at the operating conditions that are applied to the deposition potential of -1.5V. The solution was stirred at the deposition time of 300s. After a period of 10s for equilibration time, the potential scan was scanned in the anodic direction using differential pulse mode. After the addition of series of different concentrations of zinc standard solution, the procedure was repeated three times. Typical standard addition voltammogram and calibration plot for zinc metal are shown in Figure.1. The stripping peak for zinc was observed at -1.1V.

For the determination of total dissolved zinc in ground water 50ml of the samples were irradiated with UV light from a 300W mercury lamp (UV photo oxidation unit) in MilliQ water in a beaker in the presence of H_2O_2 for 5 hrs to remove dissolved organic matter (Batley and Florence,and Bately.G.E (1980) ,Eaton,et al.,1995). 10 ml of the water sample after UV irradiation and 1ml of acetate buffer were put in to a voltammetric cell. The metal of interest zinc was deposited at a reduction potential of -1.5V on the medium size drop of HMDE electrode under stirred conditions. After removing oxygen from the solution by purging high purity nitrogen for 300s the deposited metal was oxidized by scanning the potential of the electrode from -1.5 to -0.8 volt in the differential pulse mode. Standard addition method and DPASV were used to determine the concentration of total dissolved metal. The typical voltammograms of middle palar river basin ground water samples before and after UV-irradiation are shown figure.2. The stripping peak for Zinc occurred around -1.1V. The chemical speciation in this study is restricted to the labile and non-labile discrimination in the total dissolved form. The difference in concentration between the total dissolved and labile zinc corresponded to the non-labile zinc metal.

III. RESULTS AND DISCUSSION

The results of different forms and concentration of Zn metal in summer season (JUNE-2014) ground water samples of middle palar river basin are given in Table 2. The results of speciation analysis of zinc metal estimated from ground water samples collected from middle palar river basin during monsoon (November-2014) season are given. In the Table 3. The results obtained from different forms and concentration of Zn metal present in ground water samples of middle palar river basin

collected during post monsoon season (January-2014) are given in Table 4.

The labile and non-labile form of Zn varied from 0.001mg/l to 0.088mg/l and 0.004mg/l to 0.305mg/l during the study period. The percentage form of Zn varied from 1.24% to 80.0% during the entire period of study. On the whole, the average % of labile from of Zn was < 50% at most of the stations. A similar percentage of labile form of Zn was noticed by Florence et al(1980) in their study in natural waters. The non-labile form of Zinc on the other hand, varied from 20.0% to 98.76%. However, the average % of non-labile Zn was mostly > 50%. The dominance of % of non-labile form indicated that organic effluents containing ligands were brought to the runoff.

Results show that concentration of Zn in ground water does not overcome acceptable limits. The highest concentration of total dissolved Zn was observed during post monsoon season at Emerald nagar and Kaveripakkam in Ranipettai town ground water samples. On the other hand the lowest concentration was found during the monsoon and summer seasons at Chengalpattu town ground water samples (Thimmarajakulam). The results also showed that after five-hour irradiation of ground samples (300W), concentration of Zn metal ions had increased. The highest rate of Zn ions after irradiation was found in stations that where very close to palar river during study period. This phenomena was not observed as we move away from palar river banks on both sides by 5 kms and above. These ranges were to similar to that noticed at down palar river and ground water (Balakrishnan et al.2008). Average increase was around five to ten times which indicates that the most of Zn was bound to stable complex with organic matter in ground water. In general there was a decreasing trend of zinc metal concentration as one moved from Ranipettai stations to Chengalpattu stations during the study period.

IV. CONCLUSION

A seasonal variation of different forms of zinc metal speciation was noticed from this study in middle palar river basin ground water. It was found that non-labile form dominated the speciation of zinc at Ranipettai and Kancheepuram stations. The concentration of Zn labile fractions is highest in monsoon and summer seasons on near Kancheepuram stations. The degradation of organic substance present results in rapid changes of physical-chemical parameters. The source of these organic substances arises from the influences by dye and tannery effluents seeping into these ground water stations. In general, middle palar river ground water the total dissolved concentration of zinc is with the maximum permissible concentration at these sampling stations as recommended by WHO.

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