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Analysis of Metals and Organics in River Water by ICP-AES and GC/MS Techniques

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This work describes the detection and identification of metals and organic compounds in Tapti river water samples collected from Bhusaval, Maharashtra, India by ICP-AES and GC/MS techniques. For detection of metal HCl-HNO_3 extract was prepared while organic compounds were detected in CH_2Cl_2 extracted mass. Also the functional groups present in organic compounds were identified by FTIR. The detection of some metals and organic compounds are found to be toxic. Beside this work, the statistical evaluations and soil and plant analysis were also carried out.

Key Words: Metals, Organics, River water, ICP-AES, GC/MS.

INTRODUCTION

Bhusawal town, situated at the bank of Tapti river lies at 75º47′ longitude and 230º3′ latitudes in Maharashtra state, India. Most of the sewage, industrial effluents and agricultural drainage containing organic, inorganic matter and hazardous metals drained into river Tapti. These organic compounds and heavy metals affect the quality of soil and ground water of the area. The organics includes the phenol, organic acids, pesticides, dyes, drugs, *etc.* and heavy metals like Cu, Zn, Cd, Pb, Fe, Ni, Cr. Some water soluble pollutants percolate into the groundwater[1]. These heavy metals enter in the human body by different pathway and causes harmful effects[2]. Complexation of metal with organic molecule has recently been the subject of much research. Numerous studies have been reported for detection and identification of organics in Western countries[3,4].

Correlation among ground water quality parameters in specific environmental conditions has been shown to be useful[5]. When such correlation exists, determination of few important parameters would sufficient to give some idea about the overall quality of ground water. Statistics in environmental science provide more attractive studies through deviation from real situation[6]. Correlation study of groundwater, soil and crop be highly advategeous.

This study was undertaken to detect and identify metals and organic compounds present in Tapti river water which are being polluted at Bhusaval, Maharashtra State, India.

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EXPERIMENTAL

The concentration of metals in HCl-HNO_3 extract was determined by ICP-AES. The CH_2Cl_2 extracted water sample was recorded for FTIR on Perkin Elmer made IR instrument and GC/MS on HP made mass spectrometer at SAIF, IIT, Mumbai, India.

The correlation coefficient (r) between various X and Y (*i.e.* metal concentration and COD in this case) was calculated using known equation:

$$(r) = \frac{\Sigma XY - X\Sigma Y}{(\Sigma X^2 - X\Sigma X)(\Sigma Y^2 - Y\Sigma Y)}$$

RESULTS AND DISCUSSION

The result obtained during the course of present study are presented in Tables 1-6 presented FTIR and GC/MS spectra in Figs. 1-2. The organic compounds identified in GC-MS analysis in sample 1 are cyclohexane, heptadecane, thiophene, hexadecanioc acid, 1,2-cyclohexamedione, octadesanoic acid, piperidine, L-tyrosine, urea and thiazole. Sample-2 contains 4,7-methanoisobenzofuran and endosulfan.

The results of heavy metals obtained are given in Table-1. These results show the concentration of heavy metals as well as the amount of COD in groundwater and soil samples. The concentration of some metals like Cu, Zn, Cd, Fe, Ni and Cr in ground water, Cd, Pb and Cr in soil samples, Zn, Cd, Pb, Ni and Cr in crop samples were found to be less than the detection limit[7,8].

The concentration of Cu in soil samples was in the range 1.46-1.54 and 0.054-8.06 μg/g in crop samples. The high concentration copper in soil samples is due to the adsorption of copper containing moieties on the soil particles[9]. Also Cu has tendency to form complexes with suitable organic species present in soil[10]. This fact is also supported by the detection of COD in soil samples. Large quantities of Cu in water irritate stomach cause neurological complaints, liver and kidney disfunction, cancer and accelerate aging[11] where as deficiency of Cu can lead to high serum cholesterol and an increased risk of cardiovascular disease[12,13]. ISI has set a limit of 0.05 mg/L of Cu.

Drinking water usually contains Zn level below 0.2 mg/L13 but ISI[14] and EEC[15] have set a maximum permissible limit of 5 mg/L. Zinc is an essential and beneficial element for human being but its produce undesirable tast to water. It is discharging into sewage and soil from pharmaceutical, paints, pigments, several insecticides and cosmetic industries[16]. The concentration of Zn was found in all soil samples and few crop samples.

TABLE-1
METAL CONCENTRATION IN RIVER WATER, SOIL AND PLANT SAMPLES (ppm)

Sites of samples collection	Cu	Zn	Cd	Pb	Fe	Ni	Cr	COD
Tapti river water samples								
Sample 1	< 0.1	< 0.1	< 0.1	< 1.0	< 0.1	< 0.1	< 0.1	408
Sample 2	< 0.1	< 0.1	< 0.1	< 1.0	< 0.1	< 0.1	< 0.1	252
Sample 3	< 0.1	< 0.1	< 0.1	< 1.0	< 0.1	< 0.1	< 0.1	36
Sample 4	< 0.1	< 0.1	< 0.1	< 1.0	< 0.1	< 0.1	< 0.1	92
Sample 5	< 0.1	< 0.1	< 0.1	< 1.0	< 0.1	< 0.1	< 0.1	172
Soil samples								
Sample 1	1.50	1.00	< 0.1	< 0.1	541.97	1.83	< 0.1	136.7
Sample 2	1.51	1.10	< 0.1	< 0.1	488.84	1.95	< 0.1	125.9
Sample 3	1.46	0.98	< 0.1	< 0.1	478.94	1.83	< 0.1	101.4
Sample 4	1.51	1.12	< 0.1	< 0.1	554.87	2.06	< 0.1	128.3
Sample 5	1.54	1.00	< 0.1	< 0.1	495.14	1.95	< 0.1	160.5
Crop samples								
Sample 1	0.05	< 0.1	< 0.1	< 0.1	3.00	< 0.1	< 0.1	ND
Sample 2	0.28	< 0.1	< 0.1	< 0.1	2.87	< 0.1	< 0.1	ND
Sample 3	0.12	0.5	< 0.1	< 0.1	7.19	< 0.1	< 0.1	ND
Sample 4	1.30	0.4	< 0.1	< 0.1	5.28	< 0.1	< 0.1	ND
Sample 5	8.06	0.5	< 0.1	< 0.1	16.14	< 0.1	< 0.1	ND
Sample 6	0.11	0.5	< 0.1	< 1.0	3.60	< 0.1	< 0.1	ND

TABLE-2
IR SPECTRA OF CH_2Cl_2 EXTRACTED MASS

Samples	Wavelength (λ_{max})	Characteristics bands
Sample 1	3434	O–H str.
	2930	C–H str.
	1744	C=O str.
	1632	C=O or C=N str.
	1499	C=N str.
	1459	C=H band methyl/methylene
	1387	C–N str. (amide)
	1270	C–O str.
	1026	C–O str.
	756	C–H band, N–H det
Sample 2	3455	–OH (alcoholic)
	2930	C–H str.
	1642	C=C str.
	1214	C–O str.
	1056	C–O str.
	598	C–Cl str.

TABLE-3
CORRELATION (r) BETWEEN VARIOUS METALS OF SOIL SAMPLE

Parameters	Cu	Zn	Fe	Ni
Cu	1.0000	–	–	–
Zn	0.2945	1.0000	–	–
Fe	0.2153	0.3959	1.0000	–
Ni	0.5752	0.8285	0.3846	1.0000
COD	0.9358	-0.0279	0.2255	0.3049

TABLE-4
REGRESSION COEFFICIENT (a AND b) BETWEEN VARIOUS PARAMETERS OF SOIL SAMPLE

Parameter pair	a	b
Cu and Zn	0.0434	0.6626
Cu and Fe	128.6766	254.8370
Cu and Ni	-0.9843	1.9337
Cu and COD	-909.0100	691.2000
Zn and Fe	295.3348	208.2857
Zn and Ni	0.6364	1.2381
Zn and COD	140.0930	-9.1660
Fe and Ni	1.3646	0.0011
Fe and COD	58.5180	0.1407
Ni and COD	1.6540	66.9980

TABLE-5
CORRELATION (r) BETWEEN VARIOUS METALS OF CROP SAMPLES

Parameter	Cu	Zn	Fe
Cu	1.0000	–	–
Zn	0.3864	1.0000	–
Fe	0.9469	0.5587	1.00

TABLE-6
REGRESSION COEFFICIENT (a AND b) BETWEEN VARIOUS PARAMETERS OF CROP SAMPLE

Parameter pair	a	b
Cu and Zn	0.2666	0.0302
Cu and Fe	3.8436	1.5133
Zn and Fe	2.7332	11.4108

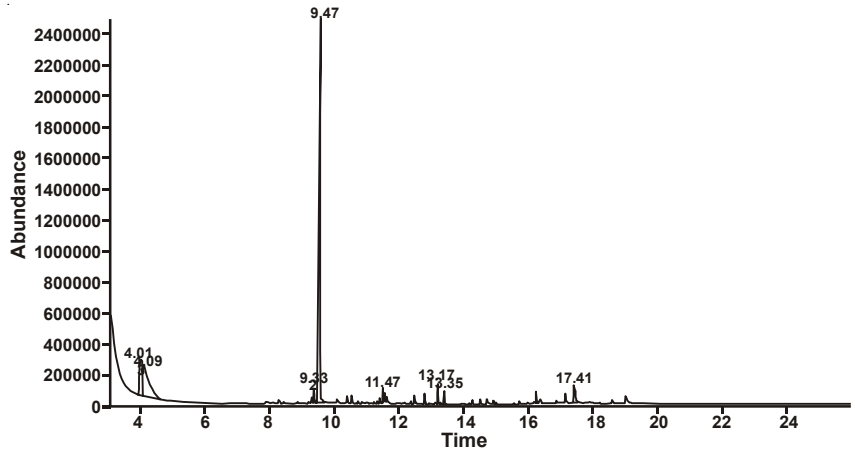

Fig. 1. GC/MS spectra of CH_2Cl_2 extracted mass (Sample no. 1).

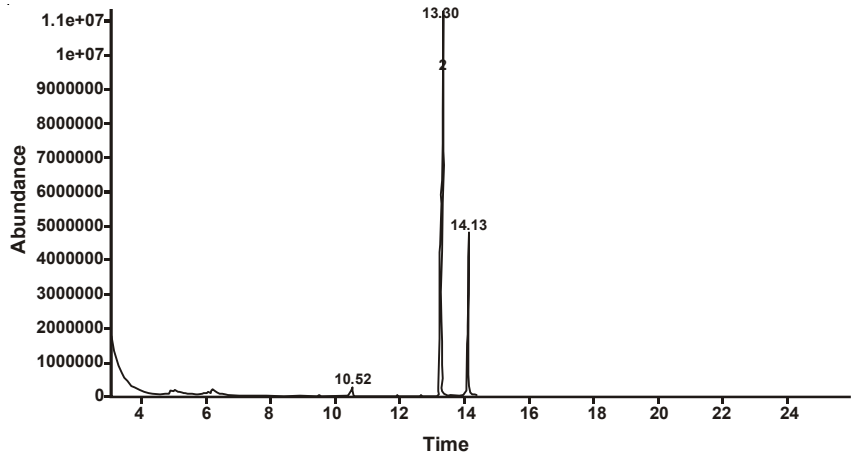

Fig. 2. GC/MS spectra of CH_2Cl_2 extracted mass (Sample no. 2).

The concentration of Zn ranges from 0.98-1.12 μg/g in soil samples and 0.40-0.50 μg/g in crop samples.

Cadmium, lead and chromium are not detected in groundwater, soil and crop samples.

The concentration of iron was found to be higher in soil 478.94-554.87 and 2.87-16.14 μg/g in crop samples indicated adsorption of iron containing species from the sewage and finally get absorbed on soil particles. Iron is an essential micronutrient required in trace quantities for the normal metabolism of plant and animals. The concentration of Ni was found to be 1.83-2.06 μg/g in soil samples. The soil containing Ni in trace amount could have better plant growth.

When organic compounds enter in the water streams, they undergo degradation and put refraction by bacterial activity. They consume dissolve oxygen which is an essential requirement for aquatic plants and animals life in water.

Phenolic compounds[17,18] impart taste and odour to water and are toxic to fish and aquatic life. Aromatic compounds including phthalic acid are crystalline compounds. These type of organics are toxic to environment, use as reactants to synthesize many pesticides and pesticide formulations. Biphenyl compounds are structurally similar to DDT and DDE and are persistent in the environment because of their chemicals stability. Their acute effects are not a serious problem but their chronic effects are so similar to those of DOT and DOE that it is likely that they act synergistically.

Pesticides[19] gradually seep into the ground water. Endosulfan is an contact and stomach poison, which induces acute nurotoxicity. It acutely affect man, animal, plant, soil as well as the aquatic biota. Pesticides are considered to affect the vital organs, heart, brain, kidney and liver producing chronic disturbances.

The excess of fertilizers like urea not consumed by crops are washed away from land by rain water and pollute water bodies. It can cause eutrophication and the whole stretch of water may become chocked.

The organics compounds[20] affect the quality of soil and ground water of the area. Out of these detected organic compounds some are carcinogenic. Therefore, the industrial wastages and sewage should be treated before ponding to open place or to the river.

Correlation among the metal ions concentration and COD

Any correlation will be statistically significant[21] only if its r value is very close to 1 or -1. In the present investigation Table-4 shows the correlation coefficient of soil samples. High positive correlation were observed between Zn and Ni (0.82), Cu and Ni (0.57). Some parameters were independent on each other, such as Cu and Zn, Cu and Fe, Zn and Fe, Fe and Ni. Some high positive correlation were found in Cu and Fe (0.94), Zn and Fe (0.55) where as Cu and Zn were not correlated with each other.

Pairs having high positive correlation between them show the dependency of one metal on the other. The values of regression coefficient (a and b) greatly help in finding out the regression equation between the two parameters, observed values and 95 % confidence limit. However in this purpose we have carried out correlation coefficient and regression analysis of all possible parameters pairs.

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