ORIGINAL ARTICLE

Assessment of contamination of heavy metals and pesticides in the Kosi River in District Rampur U.P., India

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The water pollution or contamination of surface water is currently a major area of concern of researchers due to inadequately wide expansion of urban areas and industries. The rivers are severely falling into high threats of contamination, which badly affecting the water ecosystem especially in developing countries like India. The objective of the present study is to assess the quality of Kosi river water in the basin of Rampur UP, India, for drinking and irrigation purpose. The study was carried out to determine residues of pesticide and heavy metals in water of Kosi River in Rampur to comprehend its quality. The 7 different locations were identified for the sampling of water from upstream to downstream from all the sites of Kosi in district Rampur. The samples collected were tested for organochlorine pesticide (OCP's) and organo phosphates and heavy metals (Pb, and Hg). The evaluation of pesticides was done by GC-ECD and confirmation by GC-MS/MS. Heavy metals were analysed by Atomic absorption spectroscopy. The results showed that river water was contaminated with, DDT, chlorpyfos, Malathion , methyl paraoxon, Endosulfan-II etc. at S6 (NH24 Rampur kosi bridge) and S7 (Industrial drainage from kashipur). It was found that river water was contaminated with Aldrine (ND – 12.48 µg/l), endosulfan (ND – 13.95 µg/l), monocrotophos (ND to 3.06 µg/l), methyl paraoxon (0.01 to 259.67 µg/l) and chlopyrifos (ND to 3148.97), the heavy metals ranges: Hg (ND-6.7975 µg/L) and Pb (10.22-44.625 µg/L) which may contribute lethal effects in the ecosystem of Kosi river. This is the first time when attempts were made to assess the quality of river by estimating the concentration of pesticides and heavy metals in this river, such work has not been conducted as before.

Key Words: *Monocrotophos; Atomic absorption spectroscopy; Heavy metals; Pesticide; Endosulfan–II*

INTRODUCTION

The consequences of exceeding population of India are the main concern of scientists and researchers of the India and the entire world as well. Among all other adverse effects one most important aspect is the speedy industrialization and the enhancement of quantity of factories. These industries and factories are widely releasing heavy metals through their waste which causes great intimidation of water contamination. The sewage disposal along with industrial drainage also has found great source of contribution of heavy metals in the aquatic bodies. The concentration of heavy metals beyond a certain limit in the water systems results deadly effects on human beings [1]. The higher level of heavy metals was detected to be poisonous, through their tendency to be accumulated in aquatic organisms, by numerous researchers [2,3]. It has become a global area of concern during recent years that the aquatic environment gets polluted easily with heavy metals, due to their indestructible nature. Al most all of heavy metals creates toxic effects on organisms. Heavy metals have the property to be gathered in several of parts of nautical organisms, chiefly fish [4].

Anthropogenic activities have generated important transformations in aquatic environments during the last few decades. Advancement of human civilization has put serious questions to the safe use of river water for drinking and other purpose. The river water pollution due to heavy metals is one of the major concerns in most of the metropolitan cities of developing countries. These toxic heavy metals entering the environment may lead to bioaccumulation and bio magnifications.

It is studied that the contaminants present in the normal river water vary with resource of origin, properties and the amount. Through many activities as, seasoning of rocks and seepage of soil, scattering of spray molecule in the atmosphere and from many other activities like mining and the utilize of metal based supplies etc metals go into a water body [1,5,6]. These metals consequent to piercing the stream are engrossed by aquatic plants and animals thus eventually, composed in nautical organisms which are eaten by people [6]. Due to regularly growing population, industrialized and metropolitan discharge in the river basins pressure on the waterway is rising enormously. It is found that purification of water bodies is a recognized occurrence of perhaps still improved method to the quality of irrigation than to stalinize the soils. The consumption of aquatic organisms regularly may be toxic due to leading to lethal diseases by the accumulation of heavy metals. [7,8]. The Cadmium is found to be detected in agricultural and natural atmosphere due to a variety of farming, mining and manufacturing actions and also releasing through the drain gases of vehicles [9-16]. The numerous researches have been conducted on effects of heavy metals on soil and surface water [17-22].

It is also well known that most of the pesticide chemicals used is transported and these are products of many conversions. Therefore they are not staying at their aim location but regularly penetrate water bodies by absorption through soil, air drift or surface drainage disturbing natural wealth and variety of un necessary genus creating composite result on the ecosystems and changing tropics connections. Organophosphate pesticides are employed in trade cultivation to prevent pests on crops. The accessibility of superior water is a necessary characteristic against diseases for better and healthy life [10-22].

EXPERIMENTAL PROCEDURE

Study area

The area under study is the basin of river Kosi which is passed through district Rampur, Uttar Pradesh. It is located among longitudes 78°54" to 69°28" E and latitude 28°25" to 29°10" N and on coordinate it 28.8°N" to 79.0° E. It has 2,367 Km² areas. The natives of this region work mostly in farming and industries in adjoining places. The water of Kosi River is consumed for agricultural, household use and as well as drinking purpose. It is one of the main tributaries of river Ramganga and is one of the significant tributary of northern part of Uttar Pradesh and UttraKhand. In present day, river pollution is a serious and emerging problem in the majority of developing countries. Due to rapid industrialization, there has been an increase in the amount of effluent being disposed to natural water bodies. Industrial effluents and sewage entering the water bodies are one of the prime sources of environmental toxicity, which endangers aquatic biota and deteriorates water quality. It is one of the main tributaries of river Ramganga and is one of the significant tributary of northern part of Uttar Pradesh and UttraKhand. However, due to the fast growth of local financial system in last decade, the river is under rigorous pressure from a variety of anthropogenic actions. It is originated from village Budha Peenath of Kausani region of

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district Almora (UK) and flows with higher velocity in lower Himalaya upto 100 km, it appears at Ramnagar in Indo-Gangetic Plains, after which the velocity deceases significantly then, it flows along a rice-belt region of Kashipur, where a numerous industries release their extremely contaminated runoff into it and then entered into the district Rampur (Figure 1).

Sampling

The water samples of the river were collected in sterilized plastic container. Duplicate samples for heavy metals (Pb and Hg), pesticide measurement were taken together from each sampling location. The sampling was performed every season three times in a year ie. in summer, spring and winter period for one year (2017-2018) for the period of June 2017 to February 2018. From each site five locations are selected for sampling as SB,NB,CP,29-CP and SDP location is selected only for S5 and S7 (Table 1). Standard methods were employed for the analysis of various water quality tests. 2 liter polythene bottles were used for collection of samples and water quality parameter analysis. All bottles were washed with dilute acid followed by distilled water and were dried. The containers were cautiously filled just to spilling over, without allowing air foam during sampling in sealed container. Preparation of the containers included washing with detergent rinsing with tap water and air-drying. The collected samples were sealed in an icebox and moved to laboratory as early as possible for analysis. After transportation to the laboratory, samples were stored at –20°C and extraction was normally done within 48 hours. Separately 100 ml of each water sample is collected and acidified with Conc. HNO_3 for heavy metal and pesticides analysis. Samples were collected from various sites as Dadiyal, Swar, Lalpur, Pranpur, Shahbad, Rampur Kosi Bridge and Kashipur. The Samples were analyzed for pesticides in Sophisticated Analytical Lab, New Delhi and Heavy metals were estimated at NBRI-CSIR lab Lucknow (Table 1).

MATERIALS AND METHODS

The estimation of pesticides was carried out in the water samples of each season with the help of the instrument GC MS triple quard, Bruker 436 GC/ SCION TQ MS. The detection was performed by liquid-liquid extraction process by using dichloromethane, in the Sophisticated Industrial Materials Analytical Labs Pvt. Ltd. (An ISO 9001 certified, NABL accredited, MoEF & BIS recognized Govt. approved test house.). The analyses of Lead have been done three times in a year i.e., summer, spring and winter seasons as mentioned in the table. The samples of autumn season were analyzed by titrimetric estimations using standard methods in department of chemistry, faculty of science, Mohammad Ali Jauhar University while the samples of summer, spring and winters for Pb concentration in kosi river water samples were estimated in CSIR-NBRI lab Lucknow and CPCB lab (AAS-ECIL model: 4141) Bareilly College Bly respectively by atomic absorption spectroscopy. Similarly in the samples of each season, Hg was estimated by atomic absorption spectroscopy in CSIR-NBRI and CPCB Lab (AAS-ECIL model: 4141) Bareilly respectively.

TABLE 1

Description of sampling sites and their geographical locations

Site of each sample for collection		Geographical location
S1	Dadiyal Tanda	28.974°N 78.942°E.
S2	Swar	29.027°N 79.057°E
S3	Lalpur barrage	27.406^{0}N 77.611^{0}E
S4	Pranpur Said Nagar	28.84^0 N 79.005^0 E
S5	Shahbad	28.34°N 79.10°E
S6	NH24 Rampur kosi bridge	29.027°N 79.057°E
S7	Industrial drainage from kashipur	29.22^{0}N 78.95^{0}E

RESULTS AND DISCUSSION

The sampling of summer season was carried out from 5th June 2017 to 12th June 2017, all sample sites were found in extremely dry condition. In spring season the samples were collected from 25th Aug 2017 to 6th Sept 2017, all sites were found in over flooded condition. The sampling of winter season was performed from 10th Jan.2018 to 21st Jauary 2018. The study showed that all the sites were contaminated by organo phosphorus as well as chlorine pesticides residue. Amongst all the pesticides the organo chlorine detected were Aldrine 2, 4 DDT Malathion, Alpha HCH, Beta HCH, Gama HCH while in organophosphorus pesticides the Endosulfan-II, Monocrotophos, Methyl paraoxon, Chlorpyrifos were observed in the samples. The highest concentration of 3148.97 µg/L was observed for Chlorpyrifos at S7 and 259.67 µg/L for methyl paaoxon at S6. Variations were observed in measured parameters at all sites. The organo phosphates like Methyl-parathion, Endosulfan, Chlorpyrifos were found in significant concentration. While organo chlorines detected were atrazine, 2,4 DDT, Malathion, Gama HCH, Lindane. Alpha HCH were detected only at S6 in winter season and Beta HCH was detected at S6 and S7 in winter season, it may be due to their low solubility in water. The Concentration of organochlorine and organophosphate pesticides in water of river, during different season of study period are summarized in Table 2. Some physicochemical parameters as pH has straight effect on the solubility of these pesticides in river water of Kosi. The discharge of agro-chemicals from flood plains, farming fields through agricultural overflow may have elevated the pesticide concentration at S7.

The OCP atrazine was detected at S1, S2, S3 and S4 in winters only ranging from 6.72, 6.67, 11.86 and 12.48 µg/L concentration respectively. The 2, 4 DDT were also detected only in Winters at S1, S2, S3, S5, S6 and S7 in 3.39, 0.809, 1.67, 1.31 and 2.3 µg/L concentration respectively. Malathion was found at S3 in 2.7 in winters, at S4 in 2.13 and 1.93 in summers and spring season respectively (Table 2).

While in S5, S6 and S7 it was detected only in winters in 0.84, 2.19 and 29.92 respectively. Lindane was observed only at S6 and S7 in winters 7.03 and 6.86 respectively.

The organo phosphorus pesticides like Endosulfan–II were detected at S2, S3 and S7 (winters) in 7.98, 7.55 and 13.95 µg/L respectively. Monocrotophos was found at S2 (spring and winters) in 2.83 and 2.93 µg/L respectively, at S3 (Summer and spring) in 2.45and 2.95 µg/L respectively, at S4 (Summer and spring) in 3.16 and 3.06 µg/L respectively, at S6 (Summer) in 14.80 µg/L respectively, at S7 (Summer and spring) in 2.82 µg/L. The Methyl paraoxon was detected at S1 (summer and spring) in 72.53 and 82.53 µg/L respectively, at S2 (spring and winter) in 5.98 and 6.98 µg/L respectively, at S3 (Summer and spring) in 126.28 and 146.28 µg/L respectively, at S4 (Summer and spring) in 4.12 and 6.12 µg/L respectively, at S5 (Summer and spring) in 91.51and 101.51 µg/L respectively, at S6 (Summer and spring) in 229.67 and 259.67 µg/L respectively, at S7 (Summer and spring) in 114.2 and 124.2 µg/L respectively. The Chlorpyrifos detected at S1 (winter) in 459.53 µg/L, at S2 (winter) in 966.83 µg/L at S2 (winter) in 946.83 µg/L, at S4 (winter)

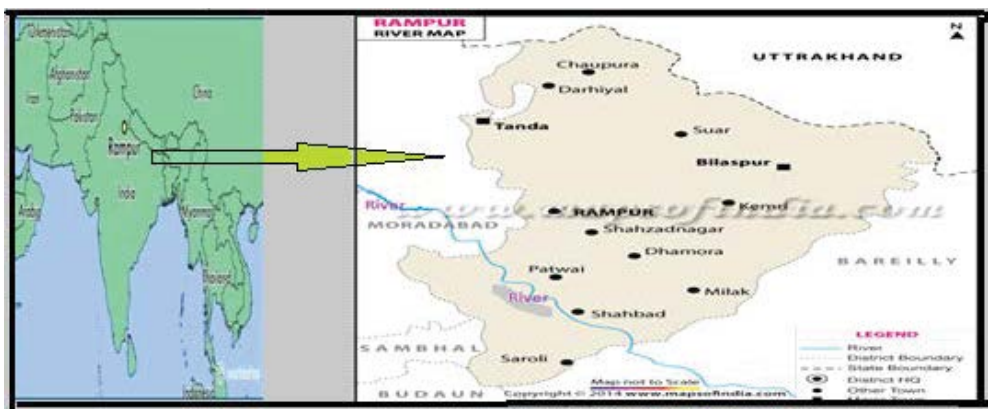

Figure 1) *Diagrammatic image of District Rampur showing the flow of Kosi River*

TABLE 2

Concentration of pesticides at different sites of Kosi River in District Rampur

Sites	Seasons	Organo chlorine pesticides in µg/L						Organophosphates pesticides in µg/L			
		Aldrine	2,4 DDT	Malathion	Alpha HCH	Beta HCH	Gama HCH Lindane	Endosulfan-II	Monocrotophos	Methyl paraoxon	Chlorpyrifos
S1	Summer	BDL	ND	ND	ND	ND	ND	BDL	BDL	72.53	BDL
	Spring	BDL	ND	ND	ND	ND	ND	BDL	BDL	82.53	BDL
	Winter	6.72	3.39	ND	ND	ND	ND	BDL	BDL	- BDL	459.53
S2	Summer	BDL	ND	ND	ND	ND	ND	BDL	2.83	5.98	BDL
	Spring	BDL	ND	ND	ND	ND	ND	BDL	2.93	6.98	BDL
	Winter	6.67	0.809	ND	ND	ND	ND	7.98	BDL	BDL	966.83
S3	Summer	BDL	ND	ND	ND	ND	ND	BDL	2.45	126.28	BDL
	Spring	BDL	ND	ND	ND	ND	ND	BDL	2.95	146.28	BDL
	Winter	11.86	1.67	2.7	ND	ND	ND	7.55	BDL	BDL	946.83
S4	Summer	BDL	ND	2.13	ND	ND	ND	BDL	3.16	4.12	1.12
	Spring	BDL	ND	1.93	ND	ND	ND	BDL	3.06	6.12	1.02
	Winter	BDL	ND	ND	ND	ND	ND	BDL	BDL	BDL	784.58
S5	Summer	BDL	ND	ND	ND	ND	ND	BDL	BDL	91.51	BDL
	Spring	BDL	ND	ND	ND	ND	ND	BDL	BDL	101.51	BDL
	Winter	BDL	1.31	0.84	ND	ND	ND	BDL	BDL	BDL	100.81
S6	Summer	BDL	ND	ND	ND	ND	ND	BDL	14.80	229.67	3.96
	Spring	BDL	ND	ND	ND	ND	ND	BDL	BDL	259.67	3.96
	Winter	BDL	ND	2.19	9.85	6.29	7.03	BDL	BDL	BDL	2344.8
S7	Summer	BDL	ND	ND	ND	ND	ND	BDL	2.82	114.2	3.96
	Spring	BDL	ND	ND	ND	ND	ND	BDL	2.92	124.2	1.03
	Winter	12.48	2.3	29.92	ND	7.03	6.86	13.95	BDL	BDL	3148.97
Detection limit		**NA**	**NA**	**NA**	**0.1**	**7.03**	**NA**	**NA**	**0.01**	**0.01**	**NA**

in 784.58 µg/L at S5 (winter) in 100.81 µg/L, at S6 (summer, spring and winter) in 3.96, 3.96 and 2344.8 µg/L respectively, at S7 (summer, spring) in 114.2 and 124.2 µg/L respectively. In kosi river it was found that except alpha HCH all the OCP pesticides were present mostly in winters and OP were found in summer and spring (Monocrotophos and Methyl paraoxon) while Chlorpyrifos was detected in all the three seasons (Figures 2 and 3).

In the present study the samples were also analysed for the concentration of lead and mercury (Tables 3 and 4). The outcome obtained from the present study revealed that higher lead concentration found at S2 and S7 in spring season as compared to other sites. Minimum concentration was recorded during winter at S6 season while it was observed that the Pb concentration was high in spring season as compared to other seasons in all waste water samples like S1, S2, S3, S4, S5, S6 and S7. It was also observed that in wide-ranging, the metal concentrations were minimum in S6 in winter season but still exceed the stabilized quality standards for CPCB (1992). The minimum concentration of Pb found at S1 (Dadiyal Tanda was from (0.0197-0.0131), at S2 (0.0222-0.0125) at S3 (0.0275-0.0183) at S4 (0.0252-0.0148), at S5 (0.027-0.0147), at S6 (0.0217-0.0102), at S7 (0.02075-0.0138). It was studied that the raise of heavy metals in the surface waters depends on the anthropogenic

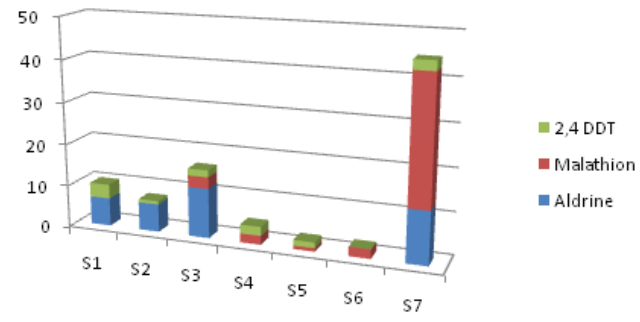

Figure 2) *Concentration of OCP at different sites of Kosi River in µg/L*

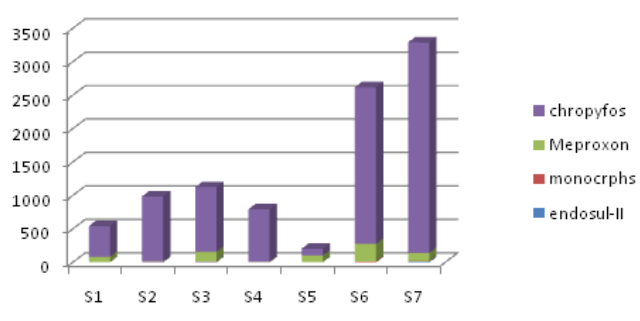

Figure 3) *Concentration of OCP at different sites of Kosi River in µg/L*

TABLE 3

Acceptable limits of Lead and Mercury in drinking water in mg/l [12]

Heavy metals	WHO	USEPA	ISI	CPCB	ICMR
Mercury	0.001	0.002	0.001	No relaxation	0.001
Lead	5.0	-	0.10	No relaxation	0.05

TABLE 4

The concentration of Pb (µg/L) in different rivers of Uttar Pradesh, India

S. No	River	Site	Mean	References
1.	Ganga River (Allahabad)	Mawaiya drain and Bairagiya drain	0.038	[13]
2.	Ganga & Yumna (Allahabad)	Arail Ghat	0.284	[14]
3.	Ganga River, (Gonda)	Colonelganj	22.75	[15]
4.	Ganga River (Varanasi)	Nishadraj	0.86	[16]
5.	Kali River (Meerut)	-	0.01	[16]

actions and weathering deposition. The municipal, farming overflow and manure runoff stations are directly or indirectly affecting the water quality by the deposition of heavy metals. A considerable relation between site differences and in the concentrations of heavy metals has been observed in the present study. Table 5 and Figure 4 shows the spatial and temporal variations in the temperature (°C) of river Kosi at Rampur city. Figure 5 shows the seasonal variations in the concentration of Pb in water of river Kosi at Rampur city. It was observed that the Pb concentrations were higher in spring season with the highest value 0.0446 µg/L at S2 and lowest value 0.0102 µg/L in January at S6 (Figures 6 and 7). The data obtained from the present study indicated that higher Hg concentration occurs at S1 in summer season as compared to other sites. While the minimum concentration was recorded during summer at S6 season but still exceed the stabilized quality standards for USEPA, ISI, CPCB (1992) and WHO (2007). The maximum concentration of Hg was recorded at S1 0.00675 µg/L in summer season, while the concentration at other sites were S2 0.001 µg/L (Summer), S3 0.0009 µg/L (Summer), S4 0.0002 µg/L (Summer), S5 0.001 µg/L (Summer) and 0.00012 µg/L in winters, S6 0.0009 µg/L (Summer) and 0.019 µg/L in winters and at S7 0.00006 µg/L in winters. It was observed that in spring season the Mercury concentration was not detected at any site it may be due to the dilution effect of the rivers due to rain fall. At all the sample sites the Hg value was not detected in spring and season.

CONCLUSION

Since Rampur city comes under Himalayan tarai region, where the soil of agricultural fields is rich in chlorine and phosphorus compounds therefore the further use of fertilizers of chlorine and phosphorus content in agricultural fields of this region leads to the excessive accumulation of these elements in the soil which reach to the Kosi River through surface runoff and leachates. In the summers the river system was under the stabilized conditions except some anthropogenic activities; therefore, the effect of these disturbing activities on these sampling sites gave rise to such results. In spring season only organo phosphorus pesticides are obtained in the results while organo chlorine pesticides are not detected during analyses due to the increased dilution level of all the sites of river. This year in winters the temperature was close to concerning at freezing point in district Rampur. In this season the results showing higher concentration of all the pesticides are obtained.

Our results revealed considerable variations in residue levels of the OCP's insecticides according to the sampling sites. So then residue levels of the studied OCP's in the river may affect aquatic life and lead to their accumulation into the food chain. Similarly the present study revealed that the concentration of Pb and Hg was exceeding their standard value at many sites therefore to maintain and preserve the aquatic food chain and water quality of Kosi river it is recommended that some significant actions must be taken by the government of Uttar Pradesh India through the public awareness programmes and some appropriate protection & conservation of river schemes should be implemented as early as possible.

TABLE 5

Mean and standard deviation value of Pb and Hg at different sites of Kosi River in µg/L

Sites	Season	Pb		Hg	
		Mean	SD	Mean	SD
	Summer	0.0197	0.03423	**0.00675**	0.0068
S1	Spring	0.0365	0.6321	ND	-
	Winter	0.0131	0.02281	0.001	0.0125
	Summer	0.0222	0.03856	0.001	0.0014
S2	Spring	**0.0446**	0.037750	ND	-
	Winter	0.0125	0.02170	ND	-
	Summer	0.0275	0.047631	0.0009	-0.00066
S3	Spring	0.0255	0.047631	ND	-
	Winter	0.0183	0.04416	ND	-
	Summer	0.0252	0.031835	0.0002	-0.000236
S4	Spring	0.0387	0.04376	ND	-
	Winter	0.0148	0.02567	ND	-
	Summer	0.027	0.04676	0.001	-0.000514
S5	Spring	0.03575	0.061920	ND	-
	Winter	0.0147	0.02576	0.00012	0.0006.788
	Summer	0.0217	0.07320	0.019	-0.000180
S6	Spring	0.0422	0.01732	ND	-
	Winter	**0.0102**	0.03594	0.0009	0.0008.8
	Summer	0.02075	0.07591	ND	-
S7	Spring	**0.0432**	0.01498	ND	-
	Winter	0.0138	0.02391	0.00006	-0.000588

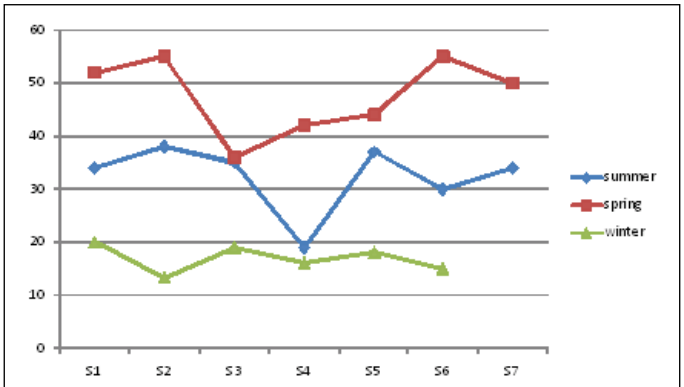

Figure 4) *Spatial and temporal variation of Pb at different sites*

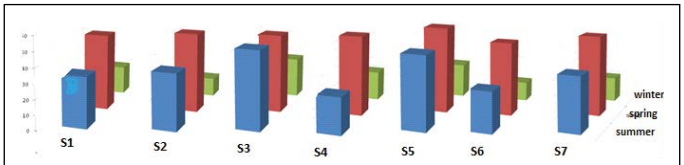

Figure 5) *Seasonal variation of Pb at different sites*

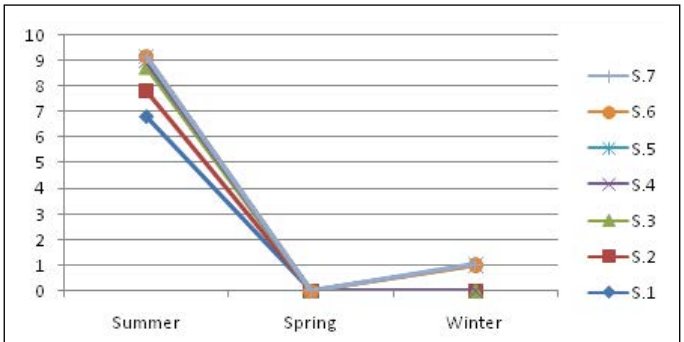

Figure 6) *Spatial and temporal variation of Hg at different sites*

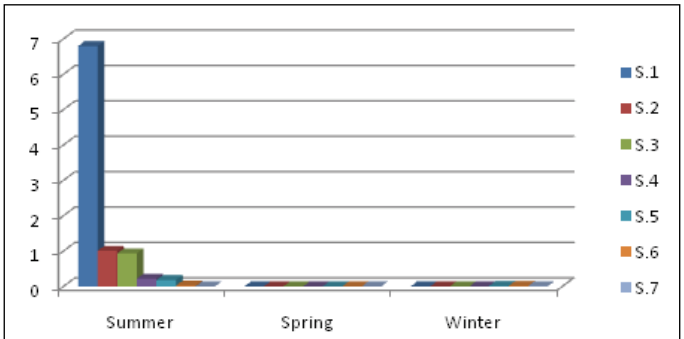

Figure 7) *Seasonal variation of Hg at different sites*

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