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STUDIES ON PRESENCE OF HEAVY METALS AND HALOGENATED HYDROCARBONS IN RIVER BETWA (MP), INDIA

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Studies on Presence of Heavy Metals and Halogenated Hydrocarbons in River Betwa (MP), India. – Kori R., Shrivastava P.K., Upadhyay N., Singh R. – The river Betwa receives domestic and industrial wastes of the Mandideep industrial area with various types of organic compounds and heavy metals. A study was made of the pollution of its water. Of 9 analyzed halogenated hydrocarbons 7 ones (chloroform, bromoform, 1,2-, 1,3- and 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, and chlorobenzene) were not detected in all the samples but a high value of the total halogenated hydrocarbon (AOX) content after mixing of industrial Nallah was obtained. The presence of bromodichloromethane and chlorodibromomethane indicates man-made origin of the Betwa pollution. At the same time, the river is not severely polluted with heavy metals.

Key words: heavy metals, halogenated hydrocarbons, river Betwa, India.

Количественный и качественный характер загрязнения тяжелыми металлами и галогенированными углеводородами реки Бетва (Индия). – Кори Р., Шривастава П.К., Упадий Н., Сингх Р. – Рассматривается загрязнение бытовыми и промышленными сточными водами, содержащими различные органические соединения и тяжёлые металлы, р. Бетва на территории индустриально развитой провинции Мандидип. Показано, что из 9 галогенированных углеводородов, на которые производился анализ, 7 (хлороформ, бромоформ, 1,2- 1,3- и 1,4-дихлорбензолы, 1,2,3-трихлорбензол и хлорбензол) не были обнаружены в пробах воды, но отмечено высокое общее содержание галогенированных углеводородов ниже впадения притока р. Налла, протекающего по промышленно развитому району. Наличие бромдихлорметана и хлордибромметана свидетельствует об антропогенном характере загрязнения воды р. Бетва. В то же время не отмечено сильного загрязнения тяжёлыми металлами.

Ключевые слова: тяжелые металлы, галогенированные углеводороды, р. Бетва, Индия.

INTRODUCTION

Oceans, forest fires, and fungal activity are key natural sources of organo chlorines. Living organisms produce over 2,400 organohalogens, of which more than half contain chlorine. E.g. chlorine-based compounds are synthesized by marine organisms (sponges, corals, sea slugs, jellyfish and seaweeds), plants, seeds, fungi, lichens, bacteria, freshwater algae and insects. Organic halides play an essential role in the life of these organisms.

Halogens, particularly chlorine, are used in the industry to make products which play a fundamental role in the modern society and lifestyle. These are used in a diverse range of products for disinfection (cleaning and water purification), in medicine (on the front line in hospitals and a cornerstone of modern medicine), public safety (in fire figh-

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ting and car safety measures such as seat belts), and to enhance comfort in everyday life (including leisure, electronics, cars, aviation, construction, food etc.)[1].

For centuries, small rivers and streams have been an important tool for carrying away the wastes generated by various anthropogenic activities (Barber et al., 1995). Previously, any pollution caused by waste discharge was taken care by self-purification processes in the water body. But with time the inflame of wastes has increased and the self-purification capacity of water bodies has reduced, so the pollution load on them has reached up to a danger level. Therefore, detailed information on the type of pollution of a particular water body is essential for the assessment of the pollution status of this aquatic system and ultimately to regulate the waste inflame (Fawell, Hunt, 1988).

The Betwa (also known as Betrawati or Vetrawati) is a river of great antiquity, an important river of Madhya Pradesh, one of the most sacred and prominent rivers of India. It rises from the foot of Dhondi Dant (642.2) located on the main Vindhyan range (Raisen district) and falls into the River Yamuna near Hamirpur District of Uttar Pradesh. Its tributaries are Kalisot, Anjer, Richchan, Dabar, Nion, and Bina. The river flows for about 90 km in Raisen district. The Bina and Nion rivers rise on the opposite sides of the water dividing Vindhyan spur, called the Garhi range, which cut across the western part of Gairatganj tehsil in a north-southern direction. Such rivers of the Bundhelkhand region as the Babnai, Dhasan, Dehar, and Sonar also originate in Raisen district. Note that Bhojpur and Vidisha are holy places in M.P. (Krishna, 1992).

The river Betwa plays a significant role in the human life of the villages located in Mandideep, Bhojpur and Raisen areas. It has become polluted at some places of Mandideep due to industrial activities and the confluence of sewage, domestic wastes and industrial effluents of many big and small enterprises with various types of organic compounds and heavy metals detrimental to human health and aquatic organisms. Urban areas, farms, factories and individual households – all contribute to the contamination of this river. The pollution affects the ecology of the river and carries undesirable vegetation and organisms. Moreover, the river has religious importance and its water is widely used for drinking, agricultural and power generation purposes.

The water quality in the stretch of the river Betwa extending from its origin near Mandideep industrial area up to Bhojpur remains poor because of the regular inflow of domestic waste of the Bhopal city through the Kaliyasot river and industrial/domestic waters from Mandideep. However, this scenario exists during pre monsoon period, which gradually improves during monsoon and post monsoon. Owing to the above facts and public complaints from local agencies the overall quality of the river water in this area has been marked as poor. The quality of the Betwa river water improves after Bhojpur due to the confluence of some smaller rivers like Ricahan, Dawar etc. flowing from the forest area located in the central part of the district. The average quality in the northwestern part of the district, i.e. towards Vidisha District falls under a medium category with some patches of low quality attributed to the industrial/domestic contamination from isolated large Industries and scattered settlements (Leser, 1978).

Many villages, towns of M.P. and U.P. rely on the water of the Betwa river. Little data are available of the persistence of halogenated hydrocarbons in it. Therefore, this

[1] www. epa. gov /OGWDW/mdbp/chapter3.html; www .ubavie .gv. at

study was undertaken to assess the persistence of metals and organic compounds in a particular stretch of the river Betwa at Raisen district.

MATERIALS AND METHODS

Sampling stations and sampling

Proper selection of sampling stations plays an important role. Of course, the choice basically depends on the situation and objectives of the work. Selection of the sampling points was done so as to cover the entire study area and to give a representative picture.

On the basis of the survey conducted and literature available, nine monitoring stations were selected to sample water. The stations were selected mostly on the basis of various activities occurring on surrounding area of the river. The river course was kept under observation for one year on a bimonthly basis from April, 2003 to March, 2004. The samples for physicochemical parameters, heavy metals, halogenated hydrocarbons and AOX were collected separately as per a standard procedure. Samples were taken at the following points:

1) River Betwa at Road Bridge, Nayapura, Mandideep
2) Industrial Nalla before confluence with River Betwa, Mandideep
3) River Betwa at Road Bridge, Bhojpur
4) River Kaliyasot, Mandideep
5) River Betwa at Road Bridge, Raisen
6) River Betwa at Road Bridge Pugneshwar, Raisen

a. Samples were collected from the river for physicochemical analysis in 2 L. jeri cans (polyethylene bottles).

b. One portion of each sample was collected in a 100-mL polyethylene bottle and preserved in extra pure HNO_3 for heavy metal determination.

c. Water samples were collected in one litre glass bottles for determination of volatile halogenated hydrocarbons.

d. Water sample were collected in clean, dry 300 mL B.O.D. glass stoppared bottles for AOX analysis – while sampling caution was taken to eliminate the air bubbles in the sampling bottle.

Analysis

Physicochemical analysis. Analysis of pH, conductivity, and turbidity was performed by instrumental methods. Volumetric methods were used for the analysis of dissolved oxygen, chloride hardness, alkalinity and COD.

Nitrate, nitrite, amm. N, and phosphate were analysed by spectrophotometer methods whereas total solids were estimated using a gravimetric technique. Water analysis was performed as per the standard procedure for the examination of water and waste water (APHA, 18th edition, 1991).

Heavy Metals. Heavy metals were analyzed using a Perkin Elmer Spectrophotometer Model-2380. Prior to instrumental analysis, water samples were treated with acid to bring the metals into their dissolved forms.

Halogenated Hydrocarbons. The analysis was performed on a gas chromatograph Sigma-2000, Perkin Elmer, equipped with a Ni 63 electron capture detector (ECD). Gas

Chromatographic, high-purity *n*-hexane was used as an extractant. Reference samples were prepared in *n*-hexane for standardization.

Adsorbable organic halides (AOX). AOX is a group of halogenated organic compounds (Yamamoto et al., 1992). Toxic forms of AOX are formed when elemental chlorine is used in the pulp bleaching process (Frederick et al., 1998).

AOX is a quantity to estimate the total content of activated carbon-adsorbable halogenated organic material in water samples. In the present study a IDC Multi × 2000 AOX Analyzer was used for the summary determination of organically bound halogens in aqueous samples. AOX were analyzed according to DIN 38409/14 and EN 1485.

RESULTS AND DISCUSSION

All the results are presented in Tables 1 – 5 and Figs 1 – 3. Of the 9 analyzed volatile halogenated hydrocarbons, 7 ones (chloroform, bromoform, 1,2,3-trichiorobenzene, 1,2-, 1,3- and 1,4-dichlorobenzenes, and chlorobenzene) were not detected in all the samples. Bromodichloromethane ranges from ND to 0.85 μg/l. The concentration of chlorodibromomethane was found in a range from ND to 0.65 μg/l in the stretch of the river Betwa, which might be due to industrial wastes of various industries in the Mandideep industrial area.

Table 1

Concentration of total AOX in River Betwa at Different Locations

Sampling Stations	Ist Sampling	IInd Sampling	IIIrd Sampling	IVth Sampling	Vth Sampling	VIth Sampling
R.Betwa US M'deep	76	89	78	234	110	100
R.Betwa RdBr Npura	1987	5658	3232	4567	5454	5300
Ind.Nala Mandideep	879	2345	1567	2345	6545	6400
R Betwa RdBr Bhojp	1189	3456	2345	2312	3232	3200
Kalyasot Mandideep	230	1234	898	1212	897	800
R Betwa Rd/BrRaisen	567	2230	1780	2111	2543	2500
R Betwa Ping.Raisen	233	1245	879	1222	878	880

(Results in μg/l).

Table 2

Concentration of individual AOX in River Betwa at Different Locations

Sampling Stations	Chloroform	Bromodi-chloromethane	Chlorodi-bromomethane	Bromoform	Trichloro-benzene (1,2,3-)	Dichloro-benzene (1,2-1,3-1,4)	Toluene
	Min – Max	Min – Max	Min – Max	Min – Max	Min – Max	Min – Max	Min – Max
R. Betwa US M'deep	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND
R. Betwa RdBr Npura	ND – ND	0.25 – 0.50	0.02 – 0.65	ND – ND	ND – ND	ND – ND	32 – 45
Ind. Nala Mandideep	ND – ND	0.40 – 0.85	0.20 – 0.55	ND – ND	ND – ND	ND – ND	38 – 55
R Betwa RdBr Bhojp	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND	29 – 31
Kalyasot Mandideep	ND – ND	0.25 – 0.50	0.04 – 0.25	ND – ND	ND – ND	ND – ND	ND – ND
R Betwa Rd/BrRaisen	ND – ND	0.02 – 0.35	0.02 – 0.05	ND – ND	ND – ND	ND – ND	ND – ND
R Betwa Ping.Raisen	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND	ND – ND

(Results in μg/l).

Heavy metals (Ni, Fe, Mn, Cu, Cr, Cd, Pb, Zn, and Co) were analyzed in all the samples. Except Zn, Cu, Fe and Mn, the other metals were not detected throughout the year in the stretch selected. Iron ranges between ND and 0.87 mg/l, manganese ranges

from ND to 0.27 mg/l, zinc ranges from ND to 0.57 mg/l, and copper fluctuates from ND to 0.30 mg/l during the study period. In the Mandideep industrial area the river Betwa receives an immense amount of domestic and industrial wastes, which may be the source of heavy metals.

Table 3

Concentration of Heavy Metals in River Betwa at Different Locations

Station► Metals▼	R. Betwa US M'deep	R. Betwa RdBr Npura	Ind. Nala Mandideep	R Betwa RdBr Bhojp	Kalyasot M'deep	R Betwa Rd/BrRaisen	R Betwa Ping.Raisen
	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max
Zn	ND – 0.32	ND – 0.02	ND – 0.01	ND – 0.29	ND – 0.16	ND – 0.57	ND – 0.04
Fe	0.15 – 0.4	0.18 – 0.43	ND – 0.13	0.12 – 0.18	ND – 0.87	0.14 – 0.72	0.12 – 0.25
Mn	0.03 – 0.07	0.04 – 0.16	0.04 – 0.23	ND – 0.27	0.05-0.12	0.03 – 0.06	0.03 – 0.19
Cr	ND	ND	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND-0.02	ND-0.03	ND	ND
Cd	ND	ND	ND	ND	ND	ND	ND
Pb	ND	ND	ND	ND	ND	ND	ND
Ni	ND	ND	ND	ND	ND	ND	ND
Co	ND	ND	ND	ND	ND	ND	ND

(Results in mg/l).

Table 4

Physicochemical Characteristics of River Betwa water at Different Locations

Parameter	Unit	B_1			B_2			B_3			B_4		
		min	max	Avg	min	max	Avg	min	max	Avg	min	max	Avg
pH	pH	7.37	8.65	8.09	7.54	8.8	8.09	7.51	8.81	8.11	7.12	8.83	7.75
Turb	NTU	15	260	65.2	16	368	103	17	388	104	13	390	136
Cond	m.mhos	150	920	452	150	10300	2508	170	7600	2049	1100	3700	2263
T.S.	mg/l	268	815	418	232	7109	1657	266	5940	1449	975	3549	2030
D.S.	mg/l	176	529	324	75	6698	1430	69	5672	1236	673	3360	1822
S.S.	mg/l	25	286	94.3	20	411	227	60	400	212	25	422	204
T.Hard	mg/l	152	570	274	126	4210	1123	108	3440	977	308	2430	880
Ca.Hard	mg/l	82	228	147	74	3870	983	84	3210	897	248	1570	661
Mg.Hard	mg/l	44	370	127	12	390	140	24	230	79.7	12	860	219
T.Alk.	mg/l	150	420	315	130	320	222	140	330	223	160	530	357
Flouride	mg/l	0.13	0.73	0.43	0.14	0.49	0.27	0.12	0.51	0.27	0.15	0.89	0.42
Chloride	mg/l	19.9	93.9	40	26.9	3998	889	29.9	1485	440	291	1659	833
Phosphat	mg/l	0.34	1.24	0.69	0.34	0.94	0.54	0.22	1.33	0.63	0.7	6.6	3.37
Amm.Nit.	mg/l	0.5	5.99	2.13	0.74	7.61	2.8	0.66	5.11	2.38	0.78	20	10.2
Nitrite	mg/l	0.25	5.72	3.01	0.5	7.93	4.03	0.97	9.53	4.45	3.21	28.5	17.8
Nitrate. N	mg/l	0.26	10.5	4.34	0.8	17.8	6.97	0.75	20.2	6.86	2.08	41.3	15.8
B.O.D.	mg/l	4.3	8.0	6.54	3.3	47.0	13.8	4.0	18.4	8.96	10.3	52.0	20.8
COD	mg/l	8.4	120	38.1	16.0	1880	333	24	560	125	101	352	204
DO	mg/l	1.2	7.9	5.57	0.8	8.9	5.27	3.2	8.5	5.53	nil	4.9	2.4
TKN	mg/l	5.6	5.6	5.6	2.8	11.20	6.54	2.8	14	9.34	22.4	61.6	48.6

A remarkable concentration of AOX (76 to 6545 μg/l) in the stretch of the river Betwa in the Mandideep industrial area during 2003 – 2004 was detected at all the sampling stations. The presence of AOX at the river Betwa upstream, Village Khamkheda

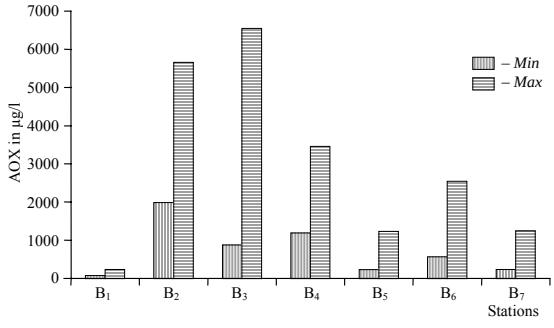

Fig. 1. AOX in river Betwa water (2003 – 2004)

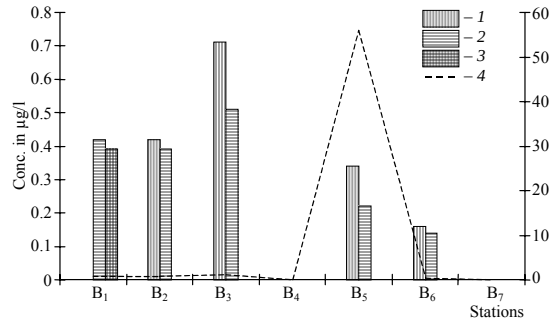

Fig. 2. Average concentration of halogenated hydrocarbons in river Betwa water (2003 – 2004): *1* – $CHCl_2Br$, *2* – $CHClBr_2$, *3* – $CHBr_3$, *4* – TTHMs

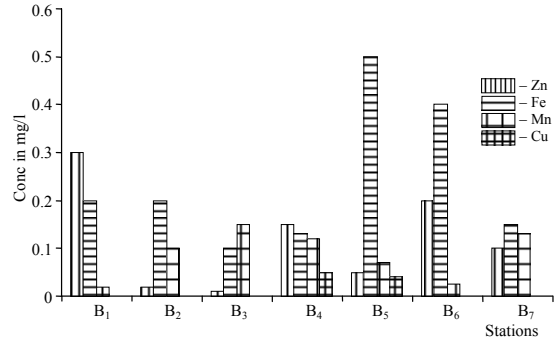

Fig. 3. Average concentration of heavy metals in river Betwa water (2003 – 2004)

(76 – 234 µg/l), River Betwa road bridge, Nayapura (1987 – 5658 µg/l), River Betwa at Bhojpur (1189 – 3456 µg/l), River Betwa at Raisen (567 – 2543 µg/l), River Betwa at Pugneshwar (232 – 1245 µg/l), River Kaliyasot, Mandideep (230 – 1245 µg/l) and Industrial Nalla, Mandideep (879 – 6548 µg/l) indicates man-made origin of these AOX.

AOX formation in the river is initiated at Mandideep Industrial Area immediately after the confluence of industrial wastes, and further enhanced after mixing of domestic wastes. It reaches a maximum value of 6545 µg/l at Nayapura. The presence of bromodichloromethane, chlorodibromomethane, and toluene indicates that man-made pollution containing halogenated hydrocarbons is received by the aquatic system.

Residual chlorine is reported to be within a range of 0 to 2 ppm. Physicochemical analysis of water samples reveals that the river water quality is rather good at upstream but the river Betwa gets polluted at Nayapura, Mandideep due to the influence of Industrial Nallah which carries domestic wastes as well as industrial effluents because of occasionally discharge of treated industrial sewage from various industries and probably due to run-off during rains.

CONCLUSION

On the basis of the foregoing discussion, it is suggested that the industrial effluent discharged from the industrial area should be treated to a maximum possible extent to maintain the proper quality of river water. Heavy metals are injurious to health; intense

care should be taken to monitor their concentrations. There is no doubt that chlorinated solvents should be withdrawn due to large-scale deleterious environmental changes. Proscription would also be treated in a precautionary way.

Therefore, detailed investigation is required for identification of individual toxic compounds present in AOX which are hazardous in the nature and adversely affect living organisms. Individual specific and advanced analytical procedures are also proposed to be developed for identification of individual halogenated hydrocarbons.

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