RESEARCH ARTICLE OPEN ACCESS

An Assessment of Water Quality of Gomati River Particular Relevant To Physicochemical Characteristics, Pesticide And Heavy Metal

Purushottam Trivedi, A Singh, A Srivastava, V P Sharma, C P Pandey, L P Srivastava & Sarika Malik*

Pesticide Toxicology Laboratory, CSIR-Indian Institute of Toxicology Research,
Department of Applied Science, Babu Banarsi Das University, Lucknow,
**Department of Chemistry, School of Sciences, Noida International University*

ABSTRACT

The study was carried out to determine physicochemical characteristics, residues of pesticide and heavy metals in water of Gomati River in Lucknow to understand its ecology. In this study the water samples were collected from 5 different locations from upstream to downstream of Lucknow from all three sites i.e, right, middle and left. Analyte including organochlorine pesticide (OCP's) and herbicides (H) α-HCH, β-HCH, γ-HCH, δ-HCH, op-DDT, pp-DDT, pp-DDE, op-DDE, op-DDD, pp-DDD, α- endosulfan, β-endosulfan, endosulfan SO_4, dicofol, heptachlor, alachlor, atrazine, butachlor, pendimethalin and heavy metals Pb, Cu, Cd, Cr, Fe, Mn, Zn, Ni were analysed. The method for pesticide residues was based on d-SPE. The quantification was done by GC-ECD and confirmation by GC-MS/MS. Heavy metals were analysed by AAS.The results revealed that river water was contaminated with HCH, DDT, alachlor, heptachlor and butachlor at hanuman sethu and gomati bairaj which may contribute to toxicity in the ecosystem of the river. The recovery ranged from 76.6 to 96.2 %, with relative standard deviations below 14%. The results revealed that river water was contaminated with ∑HCH (ND - 0.024 μg/ml), endosulfan (ND - 0.127 μg/ml), dicofol (ND - 0.041 μg/ml), alachlor (ND - 0.035 μg/ml), heptachlor (ND - 0.107 μg/ml) and butachlor (ND - 0.135 μg/ml) which may contribute to toxicity in the ecosystem of river. The heavy metals found in river water were in range: Cu (0.004 - 0.016 μg/ml); Fe (0.554 - 1.179 μg/ml); Mn (0.044 - 0.112 μg/ml); Pb (0.167 - 0.327 μg/ml) and Zn (0.046 - 0.168 μg/ml). The physicochemical parameter; pH (6.8 - 7.5), electrical conductivity (0.533 - 0.764 ms/cm), total dissolved solids (202 - 388 mg/l), chloride (17.99 - 35.98 mg/l) were recorded. The water quality has been found unsafe for civil consumption. The higher level of pollutants polluting water quality of river are disturbing the ecology of river and affecting human health directly and indirectly.

Keywords: Pesticides, heavy metal, physicochemical parameters, Gomati River

I. INTRODUCTION

No life without water is a common saying depending upon the fact that water is the one of the naturally occurring essential requirement of all life supporting activities. The quality of water is vital concern for mankind since it is directly linked with human welfare. Since it is a dynamic system, containing living as well as nonliving, organic, inorganic, soluble as well as insoluble substances. So its quality is likely to change day by day and from source to source. Any change in the natural quality may disturb the equilibrium of the system and would become unfit for designated uses. The availability of water through surface and groundwater resources has become critical day by day. Only 1% water is available on land for drinking, agriculture, domestic power generation, industrial consummation, transportation and waste disposal (Ranee et al. 2010**).** The exponential growth of Lucknow on both sides of river has led to severe pollution. The quality of water in the river is seriously affected by pollutants which enter through drains that bring domestic as well as industrial effluents and discharge into the river and also from the sewage system that pumps untreated effluent into it during its journey through the city. Upstream of Gomati river in Lucknow city receives wastes from sugar and distillery industries of Sitapur district. In Lucknow city also various industries like distillery, milk dairy, vegetable, oil, carbon etc are pouring effluents directly into the river (Singh et al. 2005; Singh et al. 2007)**.** Gomati River is a source of surface water for the nearby communities. Due to increased pollution levels, water quality of river is deteriorating continuously day-by-day at the very faster rate. The healthy aquatic ecosystem is depends on the biological diversity and physico-chemical characteristics. Cryptosporidiosis, typhoid fever, Cholera, dysentery, hepatitis are some of the common waterborne diseases that spread through contaminated water. Human faecal material is generally caused greater risk to human health because it contains human enteric pathogens (Scott et al. 2003).

Besides the other pollutants, pesticide residues are also one of the dominant contaminant of water as lot of pesticides are used to combat the insect–pest complex of agriculture and other fields related to health programme. Particularly pesticides like OCP’s and H leave residues that stay in the environment without breaking down for a long time and thus have a great detrimental effect on the environment. Monitoring of pesticide residues in water samples has been an issue of great relevance in the last decades. Many innovations have occurred in analytical methods for the extraction organic compounds from different environmental matrices that reduce the analysis time, minimize the number of analytical steps, use fewer reagents in smaller amounts and provide high recovery. Several method have been developed to accomplish this task, including: LLE (Liquid Liquid Extraction), SPE (Solid Phase Extraction), SFE (Supercritical Fluid Extraction), SPME (Solid Phase Micro extraction), MLLE (Micro Liquid Liquid Extraction) (Biziuk et al. 1996; Pihlstrbm et al. 1997; Schulein et al. 1995; Ho et al. 1995; Dugay et al. 1998; GutiCrrez et al. 1998). At present, the most effective methods of pesticides from environmental samples are QuEChERS which involves extraction with MeCN partitioned from the aqueous matrix using anhydrous MgSO4 and NaCl followed by a d- SPE cleanup with MgSO4 and PSA. This method was introduced in 2003 and, besides having several advantages; it explores the possibilities offered by modern instrumentation (Anastassiades et al. 2003). This method and several modified versions have been applied to the extraction of different types of pesticides, mainly of fruits and vegetables (Srivastava et al. 2011). Most applications in the analysis of pesticide residues are based on chromatographic determination by GC-ECD, but it is often necessary to use other techniques such as mass spectrometry for qualitative information to identify the analytes separated by the chromatographic technique. Method validation is an important requirement in the practice of chemical analysis.

The release of heavy metals into the environment has alarmingly increased because of emissions from automobiles, coal burning, mining, industrial activities and trash incineration. Most heavy metals are released into the environment, then find their way into the aquatic phase as a result of direct input, atmospheric deposition, and erosion caused by rains. Aquatic life in the Gomati River was destroyed in June, 2003, when untreated sewage was dumped into the river water, causing a drastic drop in oxygen level. Sugar mills and distilleries located upstream from Lucknow together with more than 20 sewage outlets in Lucknow were thought to be responsible for this pollution load leading to the critical situation. Such episodes occur from time to time in this river as reported in the newspapers. Both natural process and anthropogenic activities are responsible for introducing metals into the aquatic system. Some of the metals are important for the growth, development and health of living organisms. But the same metal may be considered toxic one as its concentration exceeds to the normal permissible limit. There have been indiscriminate discharges of factory effluents into river. The quality of water was monitored based on its organic and inorganic constituents, biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO) and some factors like Hardness, Alkalinity, Dissolved oxygen etc which plays an important role for the good water ecology.

In view of above the present study was aimed to present QuEChERS approach intended for pesticide residues analysis and also monitor the pollution level of pesticide residues and heavy metal which affecting the water quality of river and emphasizing probable effect on ecology. The study is to reveal out the pollution status of whole stretch of river Gomati in terms of pesticide residues and heavy metal analysis and physicochemical characteristics in Uttar Pradesh.

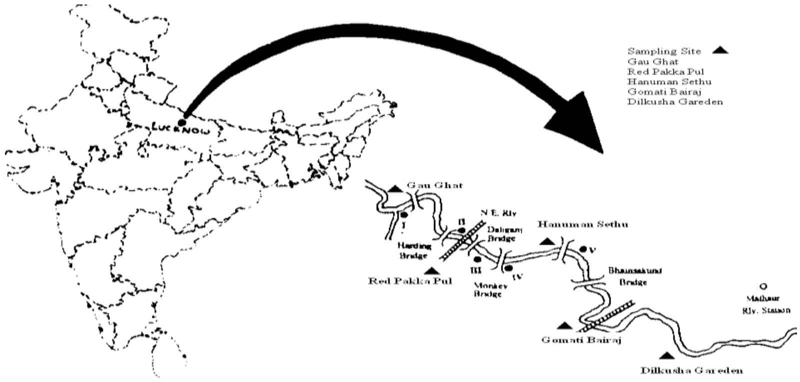

Fig 1. Map showing the River Gomati and the sample site, India

II. MATERIAL AND METHODS

Chemicals

OCP's and H pesticide standards of α-HCH, β-HCH, γ-HCH, δ-HCH, op-DDT, pp-DDT, pp-DDE, op-DDE, op-DDD, pp-DDD, α-endosulfan, β-endosulfan, endosulfan SO_4, dicofol, heptachlor, alachlor, atrazine, butachlor and pendimethalin were procured from Supelco Sigma-Aldrich USA, Fluka Sigma- Aldrich Schweis and Rankem Pvt. Ltd. New Delhi, India. All solvents like n-hexane, acetone, and ethyl acetate (HPLC grade) were purchased from Sigma-Aldrich. Co. USA, Spectrochem Pvt. Ltd. India. Sodium chloride (NaCl) and anhydrous magnesium sulphate ($MgSO_4$) were purchased from Himedia Pvt. Ltd. India. Primary secondary amine (PSA) bondasil 40 μm part 12213024 of agilent was used for sample preparation. Metal standard of Pb, Ni, Cd, Cr, Cu, Fe Zn and Mn were procured from Qualigens fine chemicals. The remaining chemicals used in this study were purchased from Merck Pvt Ltd Mumbai.

III. SAMPLING

Five sampling sites was selected which cover the residential Lucknow region namely Gaughat (I), Red pakka Pul (II), Hanuman Sethu (III), Gomati Bairaj (IV), Dilkusha Garden (V) (Fig. 1). Gaughat is the upstream of the river. The river water at this place is used as raw water supply for civil consumption to the city. Dilkusha garden is the last site, where the river leaves the city and other three sites in between these two sites were chosen where river receives effluents coming from urban homes and industries through various drains. The samples of water were collected from both the banks and middle stream of the river on each site. For collection of water sample, sampling bottles were soaked overnight in 10% HNO_3, washed twice with double distilled water rinsed three times with stream water, leaving the last rinse for five minute to equilibrate. Water samples were collected in acidified PVC bottles. Preservation and transportation of the samples to the laboratory were as per standard methods (APHA 1998). These samples were transported to laboratory in an ice box to avoid unpredictable changes in physicochemical characteristics.

Water samples were pre-filtered for remove suspended materials and preserved by adding 5 ml of concentrated H_2SO_4 to prevent biological activity. The containers were carefully filled just to overflowing, without passing air bubbles through sample or trapping air bubbles in sealed containers. Preparation of the containers included washing with detergent, rinsing with tap water, ultrapure water (Millipore) and air-dried. Preservation and transportation of the water samples to the laboratory were as per standard methods. Each sample was identified clearly and indelibly by allocating a unique identification number. All analyses were undertaken within the shortest time possible (within 2 days) to minimize potential analyte losses.

Physicochemical analysis

The samples were analyzed for physicochemical parameters. pH was measured using a pH analyzer (WTW model Multi 340),while conductance and salinity were analyzed by MohrKundsen AgNO3 titration method (APHA 1998). Temperature was measured on the site using mercury thermometer. Dissolved oxygen was fixed immediately after collection and then determined by Winkler's method. Samples for BOD were incubated in laboratory for five days at 20^0C. Total hardness was estimated by the complex metric titration with standard EDTA solution using Eriochrome Black T as indicator. Whatman 541 filter papers were used for the determination of TSS and TDS.

Sample extraction for pesticide residues analysis

10 ml water sample was extracted with 10 ml ethyl acetate, 4 gm of anhy. $MgSO_4$, 1.0 gm NaCl, and shaken for 5 min @ 50 rpm on rotospin test tube mixture. The extract was centrifuged for 5 min @ 3,000 rpm. 5 ml aliquot of sample extract was cleaned with the mixture of 300 mg PSA, 300 mg C_{18} and 650 mg $MgSO_4$. The extract was again shaken for 5 min @ 50 rpm on rotospin and centrifuged for 5 min @ 3,000 rpm. The supernatant was collected in 2 ml auto sampler-vial and mixed with 5 μl acidified ethyl acetate (ethyl acetate acidified with 5% formic acid). 1 μl of clean sample injected in GC-ECD.

GC-ECD analysis

An Shimadzu GC-2010/ECD (Shimadzu Technologies) equipped with fused silica capillary column, DB-1 (30 m. × 0.25mm. id) coated with 1% phenyl-methylpolysiloxane (0.25 μm film thickness) was employed for the separation and determination of OCP'S and H using Electron capture detector (ECD). General operating conditions were as follows; Injector temperature: 280^0C; detector temperature 300^0C; ultra pure Nitrogen was used as carrier gas at a constant flow rate of 0.75 ml/min, Column temperature program: initially 160^0C for 1 min, increase at 2.4 C/min to 235^0C hold for 2 min, injection volume: 1 μl split ratio 1:5.

GC-MS/MS confirmation

Trace GC Ultra coupled with TSQ Quantum XLS mass spectrometer system (Thermo Fisher Scientific, Austin, USA) was used for confirmation. The column used was a TR-Pesticide, 30 m X 0.25 mm i. d., 0.25 μm film thickness (Thermo Fisher Scientific, Runcorn, UK). Carrier gas: helium (purity 99.999%) with a flow rate of 1.0 ml/min. 2.0 µl aliquot of the final extract was injected using the split-less mode. The initial oven temperature program is 70^{o}C for 1 min and then at 15^{o}C min^{-1} to 210^{o}C and then at 2^{o}C min^{-1} to 230^{o}C and at 15^{o}C min^{-1} to 280^{o}C hold for 5 min. The injector temperature was set at 280^{o}C.

Estimation of heavy metals in water

For Determination of Pb, Ni, Cd, Cr, Cu, Fe Zn and Mn in water 100 ml of water sample with blank which was digested in a K'jeldhal flask with concentrated nitric acid (10 ml), in hot plate in fume hood and cooled and filtered through whatman no. 42 filter paper. The volume was made upto 10 ml with 0.1N nitric acid.

AAS analysis

Analysis was performed using AAS (atomic absorption spectrophotometer) in flame mode. The digested samples were analyzed by the AAS equipped with a vapour generation assembly (Alalytik jena ZEEnit 700)

IV. RESULTS AND DISCUSSION

Variations were observed in measured parameters at all sites. The temperature was ranging from 31-34^{o}C during the study period. pH values varied between 7.8 to 8.6. EC (electrical conductivity) is a measure of water capacity to convey electric current and it signifies the amount of total dissolved salts (Dahiya et al. 1999). Conductivity of surface water varied in the range of 0.533 to 0.764 ms/cm. High EC values were observed at dilkusha garden because presence of high amount of dissolved inorganic substances in ionized form. Salinity and restivity was recorded 0.3 ppt and 1.332 to 1.953 respectively. Dissolved oxygen (DO) is important parameter in water quality assessment and reflects the physical and biological processes prevailing in the water. DO values varied from 4.0 to 5.8 mg/l which is correlated to temperature and salinity of surface water. The maximum value of DO was at red pakka pul and hanuman sethu and the lowest value was at gaughat. During the study period biological oxygen demand (BOD) was observed to be in the range 2.4 to 4.4 mg/l. Chemical oxygen demand (COD) value indicates the presence of high concentration of both bio-degradable and non bio-degradable pollutants in there. COD value was in range between 10.4 to 26.62 mg/l and remarkably high in gomati bairaj and dilkusha garden. Total dissolved solids (TDS) indicate the salinity behavior of groundwater. TDS of surface water varied from 202 to 388 mg/l which are within the permissible limit. TDS value was maximum recorded at dilkusha garden and minimum at gau ghat. Total suspended solids (TSS) and total solids (TS) value varies from 26.0 to 292 mg/l, 328 to 566 mg/l respectively. Hardness is the property of water which prevents the lather formation with soap and increases the boiling points of water. The hardness values shown range from 172 l to 196 mg/l. Hardness of water mainly depends upon the amount of calcium or magnesium salts or both. Calcium (Ca2+) and magnesium (Mg2+) are directly related to hardness. Calcium concentration ranged between 25.65 to 36.87 mg/l which was below permissible limit. Magnesium content in the investigated water samples was ranging from 136.73 to 166.35 mg/l. The chloride concentration serves as an indicator of pollution by sewage. People accustomed to higher chloride in water are subjected to laxative effects (Dahiya et al. 1999). In the present analysis, chloride concentration was found in the range of 17.9 to 35.9 mg/l (Table 1).

The QuEChERS method resulted in extracts that contained the target analyte, with high recovery and free from interferences in the region of the chromatogram near the retention time of the pesticides. Validation is an essential requirement to ensure quality and reliability of the results for all analytical approaches. The recoveries obtained for all pesticides in water ranged from 76.6 % - 96.2 %, with relative standard deviations below 14% (Table 2). The spiked samples as well as the unspiked control were analyzed in five replicates. Repeatability of the method was evaluated through the relative standard deviations (%RSD) associated to measurements of the pesticides taken during recovery. The LOD were calculated from the standard deviation of these determinations (Table 2). The specificity of the method was determined by analyzing blank water samples. The absence of background peaks, above a signal-to-noise ratio of 3, at the retention times of the target pesticides, showed that no interferences occurred (Fig. 2). Chromatographic methods are widely used for analytical separation, identification and quantification of as many pesticides as possible in single run. The residues of OCP's and H at different sites in river water during the study period are summarized in Table 2. Among the various pesticides analyzed only HCH, DDT and α-endosulfan residues were found. ΣHCH 0.024 µg/ml, dicofol 0.041 µg/ml, endosulfan 0.128

µg/ml, butachlor 0.135 µg/ml, alachlor 0.035 µg/ml and heptachlor 0.107 µg/ml were detected. Among the targeted pesticides endosulfan sulphate, op-DDD, pp-DDD, pp-DDT and op-DDT, pendimethylin and atrazine were not detected in any samples. The highest concentration of 0.134*µ*g/ml was observed for butachlor and 0.128 *µ*g/ml for α-endosulfan. The concentration ranged values of heavy metals in Gomati river surface water are presented in Table 3. All the samples were analyzed in triplicate, and the mean of each value was taken. During the analysis, blank determinations in triplicates also were run in the same manner. In water the concentration of Cd, Ni and Cr were not detected during study period. The average and ranged value of Mn 0.078 (0.044-0.112 µg/ml), Zn 0.112(0.046-0.168 µg/ml), Fe 0.718(0.554-1.179 µg/ml), Pb 0.227 (0.046-0.168 µg/ml), Cu 0.007(0.004-0.016 µg/ml) respectively.

The QuEChERS method was applied to sample preparation in this study, because it has several advantages over most of the traditional extraction techniques, high recoveries; very accurate results; low solvent usage and waste; and high sample throughput (Lehotay 2006). Besides these advantages, a single analyst can perform the method without much training or technical skill, the method is quite rugged, relatively inexpensive and few materials and glassware are needed. QuEChERS is nowadays the most applied extraction method for the determination of pesticide residues in food samples, providing acceptable recoveries for acidic, neutral and basic pesticides, such as fruits and vegetables, rice, milk, eggs and avocados, olives and olive oil and soil (Srivastava et al. 2011; Aysal et al. 2007; Koesukwiwat et al. 2008; Lehotay et al. 2005; Cunha et al. 2007; Lesueur et al. 2008). It was observed that in QuEChERS method the recovery was 76.66-96.24% at 0.1 µg/ml spiking level with relative standard deviation less than 14%. The used chromatographic condition resulted to maximize the resolution among the peaks and minimize the total run time (about 34.85min.) The representative chromatograms obtained from extracts of pesticide-fortified in water (0.1 µg/ml) after the QuEChERS method are shown in Fig. 2. In practice, GC using capillary columns with selective and sensitive detectors ECD was one of the most often employed analytical techniques. Relative retention times are the criteria applied for identification of chromatographic peaks, but an additional confirmatory technique is also necessary. To this end GCMS was extensively used, as it increases the selectivity and certainty of identification, avoiding false positives in pesticide multiresidue determinations in water (Fig. 3). Among the HCH isomers α-HCH was dominated, followed by β-HCH, γ-HCH and δ-HCH. This may be attributed to the high percent of *α*-HCH present in the commercial formulation of HCH. The levels of ΣHCH 0.024 µg/ml and α-endosulfan 0.127 *µ*g/ml were in river water. Several studies have indicated that the environmental concentrations of HCH isomers are a world-wide problem (Doong et al. 2002; Zhang et al. 2003). β-endosulfan and endosulfan sulfate were not detected in any of samples. Though endosulfan is less soluble in water, the concentrations of endosulfan and its derivatives were high in water samples, accidental spills, spray drift, soil texture and run-in plays a vital role in endosulfan contamination. Among the DDT metabolites, op-DDT, pp-DDT, pp-DDD and op-DDD were not detected. The use of heptachlor has been banned in India for many years while heptachlor was detected in samples. Pendimethylin and atrazine were not detected in any of the samples. It is worth mentioning here that the river receives high inputs of mixed domestic and industrial wastewater (about 150 million litres per day) between the red pakka pul, hanuman sethu and gomati bairaj. These results may be mainly due to the continuing use of OCP’s and other environmental factors such as soil types, pH, and temperature in the study area. In the summers the river system was under the stabilized conditions except some man-made disturbances or recreational activities like bathing, swimming, boating and commercial, industrial activities; therefore, the effect of anthropogenic inputs on these sampling sites is expected to be high (Singh et al. 2005). 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 (Singh et al. 2007). It is well known that most of the applied pesticides are subject to many transport and conversion products. Thus, they do not remain at their target site but often enter aquatic environment via soil percolation, air drift or surface runoff affecting abundance and diversity of non-target species producing complex effects on the ecosystems and altering tropic interactions (Singh et al. 2005; Singh et al. 2007). In addition, many pesticides eventually end up in water and their transformation products may remain for years.

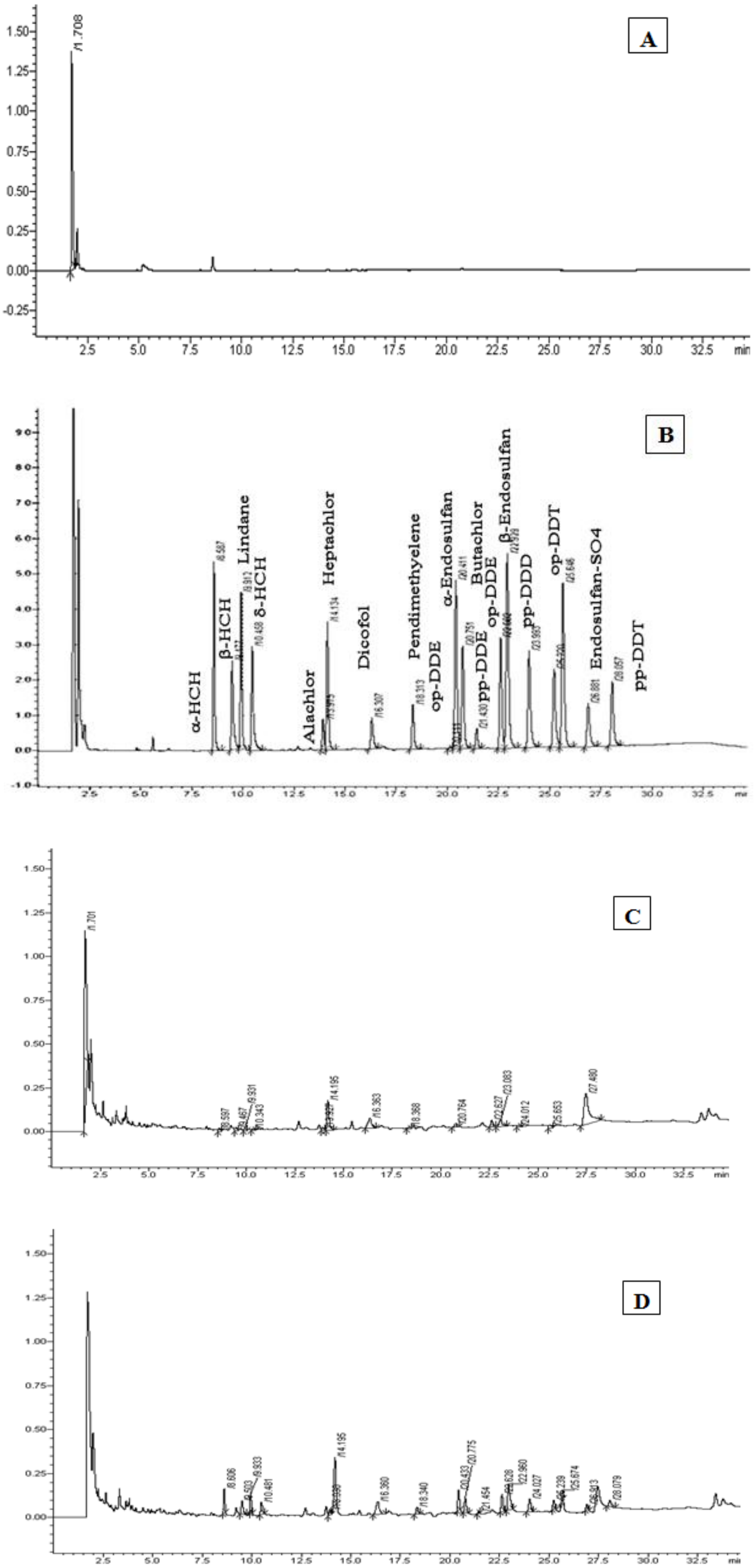

Fig 2.GC-ECD Chromatograms of OCP's and H following QuEChERS extraction: separation was performed using a DB-1 column: A)-blank sample, B)-Chromatograms of Standard of mixture of OCP's and H. C)- control water sample D)- Spiked water sample

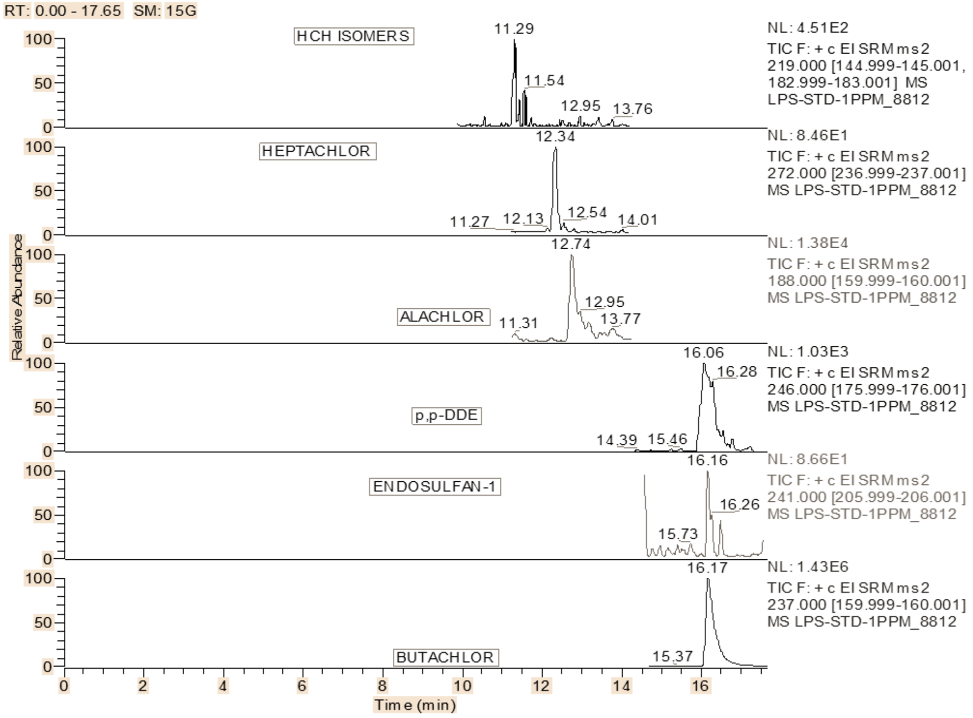

Fig 3.GC-MS Chromatograms of confirmed OCP's and H in water sample

The surface water T showed an increasing trend was influenced by the intensity of solar radiation evaporation fresh water influx and cooling and mix up with ebb and flow from adjoining nritic water (Saravanakumar et al. 2008). The highly alkaline nature of river water was revealed by the elevation of pH from 7.8-8.6. The increase in pH could be due to either increased of carbonates and or increased photosynthetic activities of producers. Results gives wide variation due to diverse chemical and technical procedures used in different industries and variations in the quantity of waste discharged at time. It is well known that the temperature and salinity effect the distribution of O_2. BOD ranges varied from 2.4-4.4 which indicating heavy load of bio-degradable matter in the effluents, high oxygen consumption by heterotrophic organisms, and a high rate of organic matter remineralization. COD value indicates the presence of high concentration of both bio-degradable and non bio-degradable pollutants in there.COD value is remarkably high in dilkusha garden. The DO values indicate the degree of pollution in water bodies. Due to the addition of high organic content in the fishing jetting leading to O_2 depletion. BOD depends on temperature, extent of biochemical activities, concentration of organic matter and such other related factors. BOD remains less than 4.4 in all cases showing normal microbial activity. In waters contaminated with fertilizers, suspended material, or petroleum waste, microorganisms such as bacteria will break down the contaminants. The oxygen will be consumed and the water will become anaerobic. Typically DO levels less than 2 mg/l will kill fish. The maximum value of TSS was observed at gomati bairaj due to floating materials like fine silt and detritus carried by agriculture water & drainage in and around the city. The salinity was found to be lower during study period at all sites. EC in natural water is the normalized measure of the water's ability to conduct electric current influenced by dissolved salts such as sodium chloride and potassium chloride. The higher value of EC were observed in the present study at dilkusha garden, this was due to the high level of dissolved salts in the agricultural water which comes from agriculture land. Chloride was in the range of 17.99 -35.98 mg/l. Generally the natural sources of heavy metals in coastal waters are through land and river runoff and the mechanical and chemical weathering of rocks. The component also were washed from the atmosphere through rain fall, wind, blown dust, forest fire and volacanic particles, adding to the distribution of heavy metals in water. It is therefore concluded that the gomati river water is getting polluted with these metals the substantiating. Zn and Cu are generally good indicator are anthropogenic inputs. In study period these metals might slightly elevated in content because the low salinity and high pH water might have cause the absorbance of these metals leading to their removal from the water column. In addition phytoplankton activity can also cause seasonal variation in copper as this metal is an essential one for phytoplankton. Soil dust input in water increases the heavy metal concentration in river system. Higher concentration of these metals in study period could be due to high amount of untreated effluent / sewage coming from in and around city.

Table 1: Different water physicochemical parameters of different site (*G-Gaughat, R-Red Pakkpul, H-Hanuman sethu, B-Gomati Bairaj, D-Dilkusha Garden) of Gomati River

Site Station	T°c	Cl	pH	TDS	TS	BOD	COD	DO	TSS	Salinity	Restivity	Condu -ctivity	TH	CaH	MgH
G1*	34	17.99	8.46	268	366	2.4	11.20	4.0	98	0.3	1.806	0.590	172	28.85	143.14
G2	31	19.99	8.54	230	402	4.2	13.91	4.8	172	0.3	1.953	0.533	172	30.46	141.53
G3	33	19.99	8.65	202	478	4.4	19.02	5.0	276	0.3	1.931	0.533	172	28.85	143.14
R1	34	25.99	8.29	292	476	3.6	10.40	4.2	184	0.3	1.655	0.636	188	33.66	154.33
R2	34	29.99	8.18	324	512	3.4	23.71	5.4	188	0.3	1.659	0.640	176	28.85	147.14
R3	33	23.99	8.20	288	328	4.2	14.97	5.8	40	0.3	1.655	0.641	180	35.27	144.72
H1	32	31.99	7.90	324	402	4.0	18.30	4.8	78	0.3	1.582	0.661	188	33.66	154.33
H2	32	29.99	7.99	308	430	3.0	19.93	4.4	122	0.3	1.608	0.659	172	35.27	136.72
H3	34	27.99	7.87	306	332	3.4	19.60	5.6	26	0.3	1.513	0.677	176	36.87	139.12
B1	31	35.98	7.98	274	566	4.0	15.39	4.4	292	0.3	1.539	0.700	188	36.87	151.12
B2	31	29.99	8.12	344	400	3.6	26.62	4.4	56	0.3	1.56	0.692	192	25.65	166.34
B3	33	33.98	7.92	268	412	4.2	22.04	4.2	144	0.3	1.534	0.698	188	33.66	154.33
D1	33	31.99	7.92	278	422	3.8	20.80	4.2	144	0.3	1.422	0.763	188	36.87	151.12
D2	32	29.99	7.86	388	414	3.8	24.54	4.4	146	0.4	1.332	0.764	196	32.06	163.93
D3	34	31.99	7.89	302	418	3.4	25.37	4.4	116	0.3	1.422	0.757	192	35.27	156.72

Table 2: Selected pesticides with chemical formula, class, retention time (RT), recovery (%), limit of detection (LOD), limit of quantification (LOQ), RSD (%), residue level of OCP's and H in different site of Gomati river *ND- Not Detected

Pesticides	**Chemical Formula**	**RT (min)**	**Recovery %**	**RSD %**	**LOD** (µg/ml)	**LOQ** (µg/ml)	**Residue Level** (µg/ml)
α-HCH	$C_6H_6Cl_6$	8.59	90.95	6.7	0.001	0.019	ND* - 0.024
Atrazine	$C_8H_{14}ClN_5$	9.48	79.81	4.9	0.001	0.012	ND
β-HCH	$C_6H_6Cl_6$	9.91	76.66	12.7	0.003	0.035	ND
γ-HCH	$C_6H_6Cl_6$	10.45	87.78	8.8	0.002	0.023	ND
δ-HCH	$C_6H_6Cl_6$	13.92	85.63	12.2	0.003	0.031	ND
Alachlor	$C_{14}H_{20}ClNO_2$	14.13	83.05	3.3	0.001	0.009	ND - 0.035
Heptachlor	$C_{10}H_5Cl_{17}$	16.30	85.50	4.0	0.001	0.011	ND - 0.107
Dicofol	$C_{14}H_9Cl_5O$	18.31	86.81	2.4	0.001	0.007	ND - 0.041
Pendimethylene	$C_{13}H_{19}N_3O_4$	20.10	89.34	3.0	0.001	0.009	ND
Op-DDE	$C_{14}H_8Cl_4$	20.41	96.24	12.9	0.003	0.034	ND
α-Endosulfan	$C_9H_6Cl_6O_3S$	20.75	84.81	9.0	0.002	0.022	ND - 0.127
Butachlor	$_{17}H_{26}ClNO_2$	21.43	79.58	1.2	0.001	0.003	ND - 0.135
pp-DDE	$(C_3H_6)_n$	22.61	89.75	4.1	0.001	0.012	ND -0.129
Op-DDD	$C_{14}H_{10}Cl_4$	22.92	91.63	6.4	0.002	0.018	ND
β-Endosulfan	$C_9H_6Cl_6O_3S$	23.99	91.17	5.2	0.001	0.014	ND
pp-DDD	$C_{14}H_{10}Cl_4$	25.21	88.49	1.9	0.001	0.005	ND
Op-DDT	$C_{14}H_9Cl_5$	25.64	94.44	8.5	0.002	0.022	ND
Endosulphan- SO_4	$C_9H_6Cl_6O_4S$	26.88	84.13	14.0	0.003	0.038	ND
pp-DDT	$C_{14}H_9Cl_5$	28.05	86.66	6.7	0.002	0.019	ND

Table 3: Concentration of heavy metal in different sites of Gomati River water

METAL	Gaughat		Red Pakka Pul		Hanuman Sethu		Gomati Bairaj		Dilkusha Garden	
	mean	range(µg/ml)	mean	range(µg/ml)	mean	range(µg/ml)	mean	range(µg/ml)	mean	range(µg/ml)
Pb	0.182	(0.167-0.191)	0.199	(0.190-0.215)	0.231	(0.211-0.262)	0.264	(0.221-0.327)	0.260	(0.254-0.266)
Cu	0.006	(0.004-0.010)	0.006	(0.005-0.008)	0.005	(0.004-0.006)	0.008	(0.004-0.016)	0.008	(0.007-0.008)
Fe	0.798	(0.595-1.180)	0.672	(0.654-0.704)	0.587	(0.554-0.612)	0.908	(0.841-1.017)	0.626	(0.502-0.695)
Mn	0.054	(0.044-0.072)	0.065	(0.062-0.068)	0.088	(0.075-0.109)	0.103	(0.098-0.112)	0.078	(0.074-0.084)
Zn	0.110	(0.07-0.168)	0.118	(0.117-0.119)	0.130	(0.081-0.168)	0.104	(0.046-0.18)	0.100	(0.077-0.115)

V. CONCLUSION

The new modified QuEChERS method proved to be simple and very efficient for the determination of OCP's and H in Gomati River water. This analytical methodology enables the determination of selected pesticide residues at trace levels with good analytical performance. This method was successfully applied to the analysis of water samples, thus showing that it is suitable for the determination of the selected pesticides in real samples. The present baseline information of physicochemical parameters, heavy metals, pesticide residues in water would form a useful tool for further ecological assessment and monitoring of Gomati river ecosystem. The study reveals that there is a considerable variation in the concentration of residues of pesticides and heavy metal in surface water samples of Gomati River. The observation of heavy metal and pesticide residues pollution in river water may be used to identify major pollution sources entering into Gomati River. These baseline data important in designing the management and conservation policies of Gomati River Water. On the basis of the study it may be inferred that apart form contaminated water this also responsible in ecological decline of Indian River.

ACKNOWLEDGEMENT

The authors are grateful to Director of the Indian Institute of Toxicology Research Lucknow, for his interest. Authors are also grateful to Council of Scientific Industrial Research, New Delhi for financial support as fellowship to Purushottam Trivedi.

REFERENCE

[1]. Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in produce. Journal of Association of Official Analytical Chemists International 86(2), 412-431.

[2]. APHA (1998) Standard Methods for the Examination of Water and Waste Water

[3]. Aysal P, Ambrus A, Lehotay SJ, Cannavan A (2007) Validation of an efficient method for the determination of pesticide residues in fruits and vegetables using ethyl acetate for extraction. Journal of Environment Science Health, Part B 42, 481–490.

[4]. Biziuk M, Przjazny A, Czerwinski J, Wiergowski M (1996) Occurrence and determination of pesticides in natural and treated waters. Journal of Chromatography A 754, 103-123.

[5]. Cunha SC, Lehotay SJ, Katerina M, Fernandes JO, Oliveira MBPP (2007) Sample preparation approach for the analysis of pesticide residues in olives. Journal of Separation Science 30: 620–632.

[6]. Dahiya S, Kaur A (1999) Physico chemical characteristics of underground water in rural areas of Tosham subdivisions, Bhiwani district, Haryana. Journal of Environment Pollution 6 (4), 281.

[7]. Doong RA, Sun YC, Liao PL, Peng CK, Wu SC (2002) Distribution and fate of organochlorine pesticide residues in sediments from the selected river in Taiwan. Chemosphere 48,237–246.

[8]. Dugay J, Miege C, Hennion MC (1998) Effect of the various parameters governing solid-phase microextraction for the trace-determination of pesticides in water. Journal of Chromatography A 795(1), 27-42.

[9]. GutiCrrez AF, Martinez-Vidal JL, Arrebola- Liebanas FJ, Gonzilez-Casado A, Vilchez JL (1998) Determination of endosulfan and some pyrethroids in waters by micro liquid-liquid extraction and GC-MS Fresenius. Journal of Analytical Chemistry 360(5), 568-572.

[10]. Ho JS, Tang PH, Eichelberger JW, Budde WL (1995) Liquid-Solid Disk Extraction Followed by SFE and GC-Ion-Trap MS for the Determination of Trace Organic Pollutants in Water. Journal of Chromatography Science 33(1), 1-8.

[11]. Koesukwiwat U, Sanguankaew K, Leepipatpiboon N (2008) Rapid determination of phenoxy acid residues in rice by modified QuEChERS extraction and liquid chromatography-tandem mass spectrometry. Analytica Chimica Acta 626(1), 10–20.

[12]. Lehotay SJ (2006). Quick, easy, cheap, effective, rugged and safe (QuEChERS) approach for determining pesticide residues. *In: Vidal JLM, Frenich AG (ed) Pesticides Protocol, Methods in biotechnology*, 19, 239-261

[13]. Lehotay SJ, Katerina M, Jong YS, (2005). Evaluation of two fast and easy methods for pesticide residue analysis in fatty food matrixes. Journal of Association of Official Analytical Chemists International 88(2), 630–638.

[14]. Lesueur C, Gartner M, Mentler A, Fuerhacker M (2008). Comparison of four extraction methods for the analysis of 24 pesticides in soil samples with gas chromatography–mass spectrometry and liquid chromatography–ion trap–mass spectrometry. Talanta 75, 284–293.

[15]. Malik A, Singh KP, Ojha P (2007). Residues of Organochlorine Pesticides in Fish from the Gomti River, India Bulletin of Environment Contamination Toxicology 78(5), 335–340.

[16]. Pihlstrbm T, Hellstrorn A, Axelsson V (1997). Gas chromatographic analysis of pesticides in water with off-line solid phase extraction Analytica Chimica Acta 356, 155-163.

[17]. Ranee SJ, Vasantha S (2010). Physicochemical analysis of bore well

water samples of anaiyur area in Madurai district, Tamilnadu, India. Journal of Current Science 15(2), 403–408.

[18]. Saravanakumar A, Rajkumar M, Serebiah JS, Thivakaran GA (2008). Seasonal variations in physico-chemical characteristics of water, sediment and soil texture in arid zone mangroves of Kachchh-Gujarat. Journal of Environment Biology 29, 725-732.

[19]. Schulein J, Martens D, Spitzauer P, Kettrup A (1995). Comparison of different solid phase extraction materials and techniques by application of multiresidue methods for the determination of pesticides in water by high-performance liquid chromatography *(*HPLC*)*, Fresenius. Journal of Analytical Chemistry 352(6), 565-571.

[20]. Scott TM, Parveen S, Portier KM, Rose JB, Tamplin ML, Farrah SR, Koo A, Lukasik J (2003). Geographical variation in ribotype profiles of Escherichia coli isolates from human, swim, poultry, beef and dairy cattle in Florida. Applied Environment Microbiology 69(2), 1089-1092.

[21]. Singh KP, Mohan D, Singh VK, Malik A (2005). Studies on distribution and fractionation of heavy metals in Gomati river sediments-a tributary of the Ganges, India. Journal of Hydrology 312, 14-27.

[22]. Singh KP, Malik A, Mohan D, Takroo R (2005). Distribution of persistent organo-chlorine pesticide residues in Gomati River, India. Bulletin of Environment Contamination Toxicology 74(1), 146–154.

[23]. Singh KP, Malik A, Mohan D, Sinha S (2005). Persistent organochlorine pesticide residues in alluvial groundwater aquifers of Gangetic plains, India. Bulletin of Environment Contamination Toxicology 74, 162–169.

[24]. Singh KP, Malik A, Sinha S (2007). Persistent organochlorine pesticide residues in soil and surface water of northern Indo-Gangetic alluvial plains. Environment Monitoring Assessment 125, 147-155.

[25]. Srivastava A, Trivedi P, Srivastava M, Lohani M, Srivastava LP (2011). Monitoring of pesticide residues in market basket samples of vegetable from Lucknow City, India: QuEChERS method. Environment Monitoring Assessment 176, 465–472.

[26]. Zhang ZL, Hong HS, Zhou JL, Huang J, Yu G (2003). Fate and assessment of persistent organic pollutants in water and sediment from Minjiang river estuary, Southeast China. Chemosphere 52, 1423–1430.