

Assessment of Organic Pollutants and Their Source of Origin in Major Lake System in Pakistan

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Abstract: In Pakistan, there is an increasing apprehension regarding the pollution of drinking water resources due to the excess use of pesticides. Rawal Lake is biggest artificial water reservoir in Pakistan that provides approximately 22 million gallons/day to Rawalpindi and Islamabad, capital territory of Pakistan. Qualitative and quantitative measurement and source of origin of DDT, DDE, DCP, TCP, Cypermethrin and Endrin in the sediments and surface water samples of Rawal Lake, Islamabad, was carried out. The samples were pre-concentrated using SPE and SPME and analyzed by using HPLC and GC-MS. Simultaneous measurement of stable isotope (δ^{15} N and δ^{18} O) of nitrate in lake water were applied to identify the sources of organic pollutants in lake water systems. The overall results showed that sediments of Rawal Lake were more contaminated than the surface water and contamination level has crossed the toxic threshold level. Isotopic data revealed that nitrates in lake water were originated from agricultural and manure sources. Data advocated that the agricultural and poultry farmhouse activities in surrounding areas of lake significantly contributed towards induction of organic pollutants in lake.

Keywords: Surface Water, Sediments, Organic pollutants, $\delta^{15}N$ and $\delta^{18}O$

1. Introduction

Rawal Lake covers a surface area of 8.8 km², 31m deep lying at the foothills of Margallah range across River Korang. Rawal lake is of significant importance as it provides about 22 million gallons/day to Islamabad, capital territory of Pakistan. Total storage capacity of lakes is around 47,500 acre feet with maximum flood level of 1752 feet. The lake catchment area is about 268 km² characterized into three zones namely Korang, Shahdara and Noorpur. The sources of water include snow melt, the natural springs of Muree hills and the runoff from four major and forty three small streams. Three villages namely, Malpur, Bani Gala and Noorpur Shahan are located in the vicinity of Rawal Lake. For the residents of Islamabad and Rawalpindi, Rawal Lake is the sole source of drinking water and presence of organic pollutants in the lake may leads towards significant health impacts and environmental damages. The water quality of the reservoir is deteriorated by human settlement involved in the agricultural activities, deforestation, recreational activities and poultry [1, 2]. In addition, agricultural activities near the catchment area of Rawal Lake, causes the wash away of toxic organic pollutants (pesticides and herbicides) by excess irrigation water into the reservoir. In

addition, there is disorganized human settlement in the catchment area contributing as major source of lake contamination [3]. In 2004, the sudden death of the fishes in Rawal Lake increased; triggering authorities to take initiatives in order to analyze the water [4]. Agriculture is the basic source of income in villages where the cropping practice is done on small scale such as terrace cultivation. Even though, the agricultural activities are not carried out on larger scale in this area but to gain more productivity per unit area the use of pesticides, herbicides and fertilizers is gaining more attention. These pollutants enter the lake by drainage of excess irrigational water as well as runoff by streams hence, contributing towards the damage to the quality of wate. Furthermore there are around 170 poultry farms with 360 sheds near the catchment area where basic arrangements to manage the poultry waste are insufficient to cope with the inflow of pollutants into the Lake [5].

Organic pollutants, after being introduced into the lake water body distribute itself to the different phases of water i.e., suspending particle, aquatic biota, and sediments. Normally organic pollutants are generally 'hydrophobic' and 'lipophilic' in nature which makes them adhere strongly to the suspended solids in water and soil, preferably to the organic matter, evading from the aqueous phase [6]. They have high octanol/water partition coefficient (Kow) and being persistent in nature, move into the water bodies through runoff or atmospheric deposition where they are removed from the water column and get adsorbed onto the particulate matter, and hoard in sediments [7, 8]. These contaminants settle at the bottom and remain in equilibrium state with the water phase which, however, can be disturbed by natural and human activities and may again suspend into the water, henceforth, causes the transfer of organic pollutants too far off place via repeated sedimentation-suspending process [9, 10]. The origin of organic pollutants, being induced in lake, is very important to know for remedial techniques. The isotope tracer techniques have been useful for an assessment on the anthropogenic nitrogen pollution in lakes. The ratio of δ^{15} N and δ^{18} O NO₃ can tell us the source of pollution in the lake system. In temperate climates, nitrate is a relatively mobile form of nitrogen in soil systems because of its solubility and non-absorbability, and it is the major form of dissolved nitrogen in streams and rivers, except in heavily reduced aquatic systems. Therefore, nitrate tracing is a useful approach to understand nutrient dynamics and transport in aquatic systems in temperate climate. However, there is no remarkable difference in the $\delta^{15}N$ of nitrate between precipitation and fertilizer [11]. Using the characteristic of δ^{18} O, the nitrate supplied by precipitation can be distinguished from the nitrate produced by microbial activity in soils or added to soil as fertilizer, whereas this separation

cannot be made using $\delta^{15}N$ only. The $\delta^{15}N$ of some nitrogen compounds reflects their source, isotopic fractionation resulting from physical and chemical reactions, and biological reactions and functions such as uptake, nitrification, denitrification, and assimilation.

The objective of present studies was to evaluate the contamination of three POPs groups viz., organochlorine (Endrin, DDT, DDE), chlorinated phenols (TCP, DCP) and pyrethroid (cypermethrin) in sediment and surface water of Rawal lake system and source of induction. The ratio of δ^{15} N and δ^{18} O were measured in Rawal Lake to determine the source of pollutants.

2. Materials and Methods

2.1. Sampling

Preliminary surveys were conducted for site selection based on recharge points from different dimensions carrying multiple pollutants like urban, municipal, sewage and agricultural waste from different areas. A total of 17 sampling points for water and sediments samples (same coordinates for both samples) were selected from upstream and downstream flow locations of the Rawal Lake during the month of November 2016. The map of an area is developed using ArcGIS (version 10.1) showing sampling points (Figure 1) and summarized in table 1.



Figure 1. Sampling locations in Rawal Lake Islamabad.

Sediment samples were collected with corer and stored in polyethylene bag while water samples were collected in 1 liter pre washed poly-propylene bottles and were stored at 4°C. Analytical grade chemicals and reagents were used. Reference pesticide standards were purchased from Dr. Ehrenstorfer Gmbh.

Tal	ble	1.	Sampl	ing	Sites	of	Rawal	Lake	2.
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Samula Cada	Sampling Locations Latitude Longitude		6	Types of Waste	
Sample Code			Sources of Pollution		
R-1	33.69464	73.11761	Boat basin	Destine estimite	
R-2	33.69683	73.1155	Near boat basin	Boating activity	
R-3	33.70136	73.11558	Near Dhokri Nala	Comoro monto	
R-4	33.70349	73.10433	Dhalmi Mala	A suisultant susta	
R-5	33.70489	73.11497	DIIOKII Ivala	Agricultural waste	

Samula Cada	Sampling Locations Latitude Longitude		- Sources of Pollution	Types of Waste		
Sample Code			- Sources of Follution			
R-6	33.73967	73.11975				
R-7	33.71002	73.12136	Bari Imam complex	Solid waste, sewage, Agricultural waste		
R-8	33.71062	73.12376				
R-9	33.70964	73.12742	Naval Sailing Club	Solid waste, sewage, petrol		
R-10	33.70954	73.13025	Lake view Park	Colid waste severe waste besting townist activities		
R-11	33.70782	73.13548	Lake view park	Sond waste sewage waste, boating, tourist activities		
R-12	33.71614	73.13961	Korang river tributary	waste from residential colonies, poultry farms		
R-13	33.70372	73.13722	Lakhwal and Bani Gala	Agricultural waste, solid waste poultry farms		
R-14	33°42'48.09	73° 8'37.49"	North Bani gala & Jillani Model village	Agricultural waste, solid waste poultry farms		
R-15	33°42'41.91	73° 8'46.65	North Bani gala & Jillani Model village	Agricultural waste, solid waste poultry farms		
R-16	33°42'3.24	73° 8'30.50	Lakhwal	Sewage and Agricultural waste		
R-17	3°41'52.64	73° 8'31.97	Lakhwal	Sewage and Agricultural waste		

2.2. Sample Preparation and Extraction

Surface water samples were filtered through Whattman filter paper No. 41 to remove the suspended solids. The fine particles were filtered through 0.45μ m filter papers by using the vacuum filtration assembly. Interstitial water of sediment sample was removed by centrifugation process. The wet sediment samples were centrifuged and supernatant water was removed by membrane syringe. Sediment sample was dried in oven at 60°C for 2-3 days and grinded to homogenize and achieve small particle size in order to have larger surface area.

Organic pollutants from sediments were extracted by using suitable solvents. 20gm dried sediment sample was mixed with 10 ml of each solvent i.e., acetone, hexane, dichloromethane and diethyl ether. Mixture was shaken in a tube and placed on agitator for 45 minutes then it was allowed to settle down for 30 minutes. The organic solvent layer containing the targeted compound was then collected in a separate vial with the help of the syringe. Combined organic layers were washed, dried on MgSO₄ and then were concentrated by evaporation. The extract was evaporated on rotatory evaporator under optimized condition of temperature and rotation by applying vacuum. The nitrogen stream was ensured to avoid any possible chemical deterioration of compounds. The dried compounds were dissolved in hexane with final volume of 2 mL. The organic compounds from surface water sample were removed by using the solid phase extraction techniques under vacuum by following Tanabe method [7].

3. Analysis and Measurement

Basic physiochemical parameters pH, TDS and EC were measured at the time of sampling. Organic compounds were analyzed using a gas chromatograph (HP 5890; Hawlett Packard series II) equipped with DB-5m column (30m x $0.25m \times 1\mu m$) and a quardrupole mass spectrometer (JEOL). Ionization was performed under 70eV electron impact conditions (300 μ A, 400V) where the initial temperature of the column was 35°C, raised at 15°C/min to 150°C and then at 3°C/min to 280°C. The ammonium distillation method was used to measure the nitrogen isotopes of nitrate in water sample [12]. This method involves the reduction of nitrate to ammonium, which is distilled and concentrated as an ammonium sulphate salt and then combusted to produce nitrogen gas for isotope measurement using isotope ratio mass spectrometer (IRMS). The isotopic ratios ¹⁸O/¹⁶O (δ^{18} O) of the water samples were measured on Varian MAT GD-150 mass spectrometers. For determining the oxygen isotopic composition of water samples, CO₂ equilibration method was used [13]. This method involves equilibration of CO₂ with sample water and subsequent mass spectrometric determination of "R" - the ratio of ¹²C¹⁶O¹⁸O/¹²C¹⁶O₂ obtained by suitable corrections from the masses 46 and 44 in CO₂, which have isotopically equilibrated with water sample. This is compared with R_{std} - the isotopic ratio in CO₂ equilibrated with internal laboratory standard at identical temperature. Measurement uncertainty of δ^{18} O is ±0.1‰.

$$\delta N^{15}\%_0 Vs[std] = \left[\frac{R_{sample}}{R_{std}} - \frac{R_{std}}{R_{std}}\right] (1000 \ \delta \ \%_0)$$

4. Results and Discussion

4.1. Physico-chemical Parameters

The pH values of sediments were 6.4-7.9, whereas for surface water samples it was 8.2-8.5. Surface water pH suggested a possible input of waste water from poultry and cattle feedlots, fertilizers from the agricultural lands and the marble crushing in the Margalla Hills. EC for sediment samples ranged from 166 to 174μ S/cm. High value of EC for sediments was found at site 4 and 10 where sewage and solid waste from Dhokri Nala and Lake View Park enters the lake. EC for sediments was higher at site where Bari Imam stream falls into the lake as compared to the site where Korang River tributary falls into the lake, contradicted to other studies. Whereas the EC values for the surface water was found maximum at site 1 and 13, where the input from boat basin at the foot of spillway and Lakhwal causes increase in EC values.

TDS values for the sediment samples remained 365 to 376 mg/l as shown in table 2. Highest TDS value in sediment was found at site 6 and 10. At site 6 high disturbances at Lake View Park where input in form of drinks foods and other related stuff from people visiting the lake causes the increase in TDS. For water samples TDS value ranged from 772 to 781 mg/l which is beyond the WHO recommended limit (500 mg/l), as stated by others [1]. Maximum TDS value in surface water was found at site 1 and 13 where discharge from agricultural lands falls in the lake. Higher concentration of TDS in water samples at recharge points were might be due to higher turbulence in sediment of lake.

Sediments/Surface Water Samples							
Sample code	рН	TDS (mg/l)	EC (µS/cm)				
RP 1	6.9	375	170				
RP 2	7.96	365	171				
RP 3	7.4	367	169				
RP 4	7.45	375	167				
RP 5	7.4	373	174				
RP 6	7.8	376	172				
RP 7	7.29	371	170				
RP 8	7.1	371	170				
RP 9	7.25	372	168				
RP 10	6.84	376	166				
Surface Water Sample	es						
R1	8.35	781	349				
R2	8.3	777	344				
R3	8.28	775	339				
R4	8.25	774	347				
R5	8.2	778	354				

Table 2. Physiochemical parameters.

Sediments/Surface Water Samples								
Sample code	рН	TDS (mg/l)	EC (µS/cm)					
R6	8.37	776	344					
R7	8.32	774	345					
R8	8.42	773	338					
R9	8.35	775	345					
R10	8.43	772	339					
R11	8.41	779	349					
R12	8.29	780	352					
R13	8.3	781	348					

4.2. Distribution and Occurrence of Organic Pollutants

4.2.1. Concentration of Organic Pollutants in Surface Water

Concentration of organic pollutants in surface water is shown in Figure 2 whereas mean concentration and range values of these compounds are shown in table 3.

Table 3. Organic Pollutant Concentration in Water Samples Of Rawal Lak	: (n=17)).
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Class	Compounds	Concentration				
Class	Compounds	Mean	Minimum	Maximum		
	Endrin (ppb)	0.53	0	1.5		
Organochlorine Insecticides	DDT (ppm)	0.73	0.01	1.9		
	DDE (ppm)	0.28	0.01	1.2		
Chloringted Dhonols	2,4,6 TCP (ppm)	0.04	0.001	0.12		
Chiormated Filehols	2,4, DCP (ppm)	0.28	0.01	0.9		
Pyrethroid	Cypermethrin (ppb)	0.50	0	1.9		

Maximum concentration of cypermethrin in surface water was found at points R-12, R-15, R-16 and R-17. R-12 is a point where streams from agricultural and farms houses from Bani Gala and Bara Kohe areas fall into the lake. Points R-15, 16 and 17 are the sites where drains from the agricultural of Lakhwal areas recharge the lakes. High concentration of DDT was found in R-7 to R-15. It is the part of lake where streams passing through agricultural and residential areas fall into the lake. Higher concentration of DCP and TCP were found at R-14 and 15, where runoff from agricultural areas discharged into lake. Endrin was found higher at points where runoff from agricultural areas discharged into lake. Higher concentration of organic pollutants at points R-14, 15 and 16. Higher concentrations of pollutants at these points as compare to the rest of lake suggested that water current relaxed in these areas allowing the pollutants to settle at these points.



Figure 2. Concentration of organic pollutants in surface water samples.

In general distribution of organic pollutant in surface water sample was found higher at points next to the lake recharge

points in clockwise direction. It suggested that the water current in the lake is in clock wise direction that drifts the pollutants from discharge points to the adjacent areas. Concentrations of pollution in Rawal Lake found in present study are compared with the other water bodies around the world as shown in table 4.

Studu and	POPs (mg/l)	Deference						
Study area	Endrin	Endrin DDT DDE 2,4,6 TCP		2,4,6 TCP	2,4 DCP	Cypermethrin	- Kelerence	
Rawal lake	0.00053	0.73	0.28	0.04	0.28	0.0005	Present study, 2014	
Dailo River, China		0.646					Li et al., 2009	
El-Rahawy, Egypt	0.00064						Bouraie. Et al., 2011	
Selenga River, Russia				0.16			Batoev et al., 2005	
Tyemnik River, Russia				0.28	0.58		Batoev et al., 2005	
Mehkong delta						0.00335	Pham, 2013	
Isipingo river, South Africa				0.0016			Roger et al., 2002	
Nowshera, KPK, Pakistan		0.07					Jan et al. 2013	
	0.0006	0.001		0.005		0.0001	WHO, 2004, WHO, 2005	
	0.0002	0.02	0.02	0.0014	0.077		USEPA	

Table 4. Worldwide POPs assessment in surface water.

4.2.2. Concentration of Organic Pollutants in Sediments

The residual concentration and range values are given in table 5.

Table 5. Organic pollutant concentration in sediment samples of Rawal Lake.

Class	Compounds	Concentration				
Class	Compounds	Mean	Minimum	Maximum		
	Endrin (ppb)	1.03	0.0012	0.0052		
Organochlorine Insecticides	DDT (ppm)	2.29	1.2	7		
	DDE (ppm)	1.03	0.6	6.5		
Chloringtod Dhonols	2,4,6 TCP (ppm)	0.57	0.01	1.2		
Chiofinated Filehois	2,4, DCP (ppm)	2.26	1.2	5.8		
Pyrethroid	Cypermethrin (ppb)	0.50	0.1	4		

In sediments, the organic pollutants were present in higher concentration than in surface water. Higher concentration of DDT and DDE were found at R-1 to R-12. The OPs at site 1, 2 and 3 are linked with the Dhokri Nala from where the pollutants spread out at into the lake with water flow. Sites 3, 4 and 5 are associated with the large input of waste from Bari Imam, agricultural runoff, waste from diplomatic enclave and farm houses. Here, the inflow of water doesn't cause much of the turbulence and allows the settling of the organic pollutant into the lake sediments. High concentration of DDT was found in R-7 to R-15. DDE, a metabolic of DDT, did not show high concentration in this area. It might be due to flux of DDE from sediment to water or due to higher mixing of sediments. At site 6, 7 and 8 highest concentrations of the pollutants were subjected to recreational activities carried out at Naval sailing club and Lake View Park where the anthropogenic activities and boating increases the pollution levels in the sediments. At site 9 the concentration of organic pollutants was high, but less as compared to the sites of Bari Imam Complex tributary because here the inflow of water into the lake occurs from Korang tributary that contain high pollutant contents but at the same time the flow rate is higher that cause disturbances in the inner water pressure providing less contact time to the organic pollutants to settle down in sediments. At site 10 least concentration of OPs was found in the sediments. Here no major tributary enters the Rawal Lake plus at this point the depth of the lake is less that allows the movement of the organic pollutants towards the other side of the lake along with the water currents.

Chlorinated phenols were present in higher concentration at site 4, 5, 6 and 9. Sites linked with Bari Imam Complex (3, 4 and 5) showed maximum concentration of phenolic compounds. At these sites the waste from agricultural areas of Nurpur Shahan adds to the chlorinated phenols in the lake. At site 6 where the petrochemicals from the boating activities from naval sailing club cause an increase in the concentration of chlorinated phenols. Least concentration was found at site 1 and 2 associated with Dhokri Nala where less inflow of water occurs and the pollutants moves away from these sites towards the other through water currents.

At site 1 and 2 very low concnetration of cypermthrin was found in sediments. At site 4 and 5 the input from the Bari Imam tributry loaded with the waste from agricultural and residential waste from Nurpur Shahan causes the increase concentation of cypermethrin at these sites. Highest conenctration was found at site 9 where the water from korang tributary carrying the waste from residential areas and industries from Muree enter the lake. In general high concentrations of pollutants were found at east and east southern part of lake (R-14, 15 and 6). It is part of lake where the water currents relax due to sudden expansion of area. This phenomenon provided time for maximum settling of sediment and suspended particles. At extreme south of the lake, next to discharge point of lake, concentrations of organic pollutants were low. Concentrations of studied pollutants have shown in Figure 3.



Figure 3. Concentration (mg/l) of organic pollutants in sediment samples.

Random distribution of pollutants in sediments suggests a higher mixing of sediment in the lake. Concentrations of organic pollutants in sediment are compared with other studies in table 6.

Table 6. Worldwide POPs Assessment in Sediments.

Study ana	POPs (mg/l)	Deference					
Study area	Endrin	DDT	DDE	2,4,6 TCP	2,4 DCP	Cypermethrin	Kelerence
Rawal lake	0.0004	0.73	0.27	0.13	0.24	0.0004	Present study, 2014
Jukskei River, South Africa	0.002						Sibali et al., 2009
Lake Manyas, Turkey	0.000	0.0001					Erkmen et al., 2010
Tamiraparani River	0.0038						Kumarasamy, 2012
St. Maurice River, Canada							Yin et al., 2003
Creeks Of King County						0.0028	Anderson, 2011
						0.0089	Kuivila et al., 2012
River Chenab, Pakistan		0.000					Eqani et al., 2011

4.2.3. Distribution of Organic Pollutant in Water and Sediments

Distribution of organic compounds in water and sediment was determined in order to understand the transport behavior of these compounds between aqueous and solid phase in Rawal Lake.

High concentration of DDE in sediment samples as compare to water refer to its hydrophobic nature and aerobic degradation of DDE in Rawal Lake. Higher concentration of DDT in both water and sediments as compared to DDE suggested a recent input of DDT into the lake. DDT and it's metabolites in sediments, tends to bond to large-molecule organic matters and remained sorbed onto the solids, thus transported to the water body through runoff of particulate matter. Different studies suggested that surface sediments of Rawal Lake have high clay contents [15]. High concentration of DDT and DDE in sediments was ascribed to high contents of clay.

A comparative low concentration of Endrin found in sediment and water sample recommend the least input of this insecticide into the lake. Low concentration of Endrin in sediment was might be due to its structural hindrance that made it difficult to bind with the sediments. Furthermore its high molecular weight enhances its hydrophobicity. Whereas, the solubility in water might be due to the hydrogen bonding with water as result of competition of molecules of water [16].

Higher concentrations of 2, 4, 6 TCP in sediment samples

ascribed to chloro groups on phenol ring that increases the sorption on sediments rather than in water phase [17, 18]. In addition 2,4,6 TCP contains three chlorine molecules which results in the increase of octanol/water partition coefficient (K) that in turn increases the affinity for organic content of the sediments. However, the lone pair on hydroxyl group and three chlorine atom creates a strong hydrogen bonding making it soluble in water. Less concentration of TCP in surface water than sediments suggests high hydrophobicity making the compound to strongly associate with organic colloids.

Equal distribution of 2,4 DCP in sediments and water sample was attributed to its pKa value which affects the reactivity and transport between water and sediment phase. It exists as anion in environment that causes low sorption of 2,4 DCP on the clayey sediments than other chlorophenols and it might lead reason of its availability in water phase.

Low concentration of cypermethrin in water refers to the rapid sorption of this organic pollutant on the sediments being highly hydrophobic. [19]. Secondly, it refers to the ability of cypermethrin to hydrolyze at pH of 7 and this rate increases at pH 9. It has higher partition coefficient thus binds to the soil organic contents strongly [20, 21]. Direct relationship has been found between the increasing organic content of the sediment and the concentration of cypermethrin. The detection of small values in surface water may be due the dissolved organic content as suggested by Manud et al [16]. In general, high hydrophobicity of organic pollutants caused high concentration in sediments than in water phase [22, 23]. High contents of organic carbon (TOC) in sediments of Rawal Lake enhanced its sorption capacity for organic pollutants, resulting unavailability of organic pollutants in water phase [24].

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5. Source of Contamination in Rawal Lake

The source of pollution in the lake was assessed by using the stable isotope tools. Ratio of δ^{18} O and δ^{15} N were applied to determine the source of pollutants as shown in Figure 4.



Figure 4. Schematic diagrams of typical ranges of $\delta^{15}N$ and $\delta^{18}O$ values of nitrate from various sources [11].

Using characteristic of δ^{18} O and δ^{15} N, the nitrate supplied by precipitation can be distinguished from the nitrate produced by microbial activity in soils or added to soil as fertilizer. Nitrification of ammonium and/or organic-N in fertilizer, precipitation, and organic waste can produce a large range of d values. The values of δ^{18} O and δ^{15} N were plotted and source of origin of pollutants were determined as shown in Figure 5.



Figure 5. Plot of $\delta^{18}O$ and $\delta^{15}N$ values to assess the origin of pollutants.

The ratios of δ^{18} O and δ^{15} N of nitrates in water samples were placed in the assigned plot values of Kendall and source of organic pollutants induced in Rawal Lake were assessed. The sources of pollutants assessed at sample points based on isotopic data are given as:

Sampling points R-3, R-5, R-6, R-12, R-16, R-17 R-8, R-9, R-10, R-14, R-15 R-1, R-2, R-11, R-13 R-4, R-7

6. Conclusion

Manure and septic NO₃⁻ fertilizers NH₄⁺ in fertilizer and precipitates Mixed

Origin of pollutants

Concentration of organic pollutants in surface water and sediments collected from potential polluted sites of Rawal Lake were found to be following order.

Surface water = DDT> Endrin> Cypermethrin >DDE = DCP P>TCP

Sediments = DDT >DCP >DDE = Endrin> TCP > Cypermethrin

Concentration of studied organic pollutants in lake water is attributed to the point sources. The areas where the agricultural runoff discharged in lake have high concentration of pollutants in general. The areas present next to recharge points have shown high concentration of organic pollutants as compared to points where runoff and streams carrying organic pollutants fall into lake. It suggested a significant of sediment drift in clockwise direction along with the water currents. The random concentration of organic pollutants in sediments advocated a higher mixing of sediments in lake system. The stable isotopic ratio suggests that nitrates present in sediment of lake have the origin of fertilizer and manure used for agricultural purposes. As the nitrates induced in system are from agricultural activities and manure, it means that organic pollutants in lake are mainly coming from agricultural areas and farm houses situated in east, east west and north east vicinities of lake. The mixed origin of nitrates suggested a significant mixing of sediment in lake system.

Relatively higher concentration of organic pollutants in Rawal Lake as compared to the lake systems in other part of the world is attributed to the absence of proper rules and regulation and lack of knowledge among the farmers for proper management of agricultural and farmhouse activities.

References

- [1] Ghumman, A. R. 2010 Assessment of water quality of Rawal Lake by long-time monitoring. *Environmental Monitoring and Assessment* 180 (1-4), 115-26.
- [2] Troyanskaya, A. F., Velyamidova, A. V. 2017 Persistent organic pollutants in subarctic lakes in the extreme North of European Russia *Water Resources*, 44 (4), 465–474.
- [3] Butt, A. 2013 Change analysis of watersheds in Islamabad using remote sensing and gis applications: a comparative case study of rawal and simly watershed. BS Dissertation, Unpublished.
- [4] Ahad, K., Mohammad, A., Mehboob, F., Sattar, A., & Ahmad, I. 2006 Pesticide residues in Rawal Lake, Islamabad, Pakistan. *Bulletin of environmental contamination and toxicology* 76 (3), 463-470.

- [5] Aftab, N. 2010 Haphazard colonies polluting Rawal Lake. Retrieved: 7th December, 2014. From: Daily Times. http://www.dailytimes.com.pk/default.asp...009_pg11_1.
- [6] Jones, K. C., & De Voogt, P. 1999 Persistent organic pollutants (POPs): state of the science, *Environmental Pollution* 100 (1), 209-221.
- [7] Tanabe, A., Mitobe, H., Kawata, K. And Sakai, M., 2000 New monitoring system for ninety pesticides and related compounds in river water by solid phase extraction with determination by gas chromatography/ mass spectrometry. J. AOAC. 83, 61-71.
- [8] Liu, M., Cheng, S., Ou, D., Yang, Y., Liu, H., Hou, L., &Xu, S. 2008 Organochlorine pesticides in surface sediments and suspended particulate matters from the Yangtze estuary, China. *Environmental Pollution* 156 (1), 168-173.
- [9] Liu, Y., Wu, G., & Zhao, X. 2013 Recent declines in China's largest freshwater lake: trend or regime shift? *Environmental Research Letters* 8 (1), 014010.
- [10] Iwata, H., Tanabe, S., Aramoto, M., Sakai, N., & Tatsukawa, R. 1994 Persistent organochlorine residues in sediments from the Chukchi Sea, Bering Sea and Gulf of Alaska. *Marine Pollution Bulletin* 28 (12), 746-753.
- [11] Kendall C. 1998 Tracing nitrogen sources and cycling in catchments. In: Isotope tracers in catchment hydrology (eds. C. Kendall and J. J. McDonnell) Elsevier, New York, pp. 519-576.
- [12] Sigman D. M., Altabet M. A., Michener R., McCorkle D. C., Fry B. and Holmes R. M. 1997 Natural abundance-level measurement of the nitrogen isotopic compositionof oceanic nitrate: an adaptation of the ammonia diffusion method. *Marine Chemistry* 57, 227-242.
- [13] Silva S. R., Kendall C., Wilkison D. H., Ziegler A. C., Chang C. C. Y. & Avanzino, R. J. 2000 A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios, Journal of Hydrology 228, 22–36.
- [14] Tanabe, S. & Tatsukawa, R., 1992 Chemical modernization and vulnerability of Cetaceans: increasing toxic threat of organochlorine contaminants. In: Walker, C. H., and Livingstone, D. R. (eds.), *Persistent Pollutants in Marine Ecosystems*. Oxford: Pergamon Press, pp. 161-177.
- [15] Idowu, E. O; Ugwumba A. A. A; Edward J. B and Oso J. A 2013 Study of the Seasonal Variation in the Physico-Chemical Parameters of a Tropical Reservoir. *Greener Journal of Physical Sciences* 3 (4): 142-148.

- [16] Maund, S. J., Hamer, M. J., Lane, M. C., Farrelly, E., Rapley, J. H., Goggin, U. M., & Gentle, W. E. 2002 Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments. *Environmental Toxicology and Chemistry* 21 (1), 9-15.
- [17] Delle Site, A. 2001 Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. Journal of Physical and Chemical Reference Data 30 (1), 187-439.
- [18] Zhang, H. B., Y. M. Luo, Q. G. Zhao, M. H. Wong and G. L. Zhang. 2006. Residues of organochlorine pesticides in Hong Kong soils. *Chemosphere*, 63: 633-641.
- [19] Munir, D. C. G., Rawn, G. P., Townsend, B. E., Lockhart, W. L., & Greenhalgh, R. 1985 Bioconcentration of cypermethrin, deltamethrin, fenvalerate and permethrin by Chironomustentans larvae in sediment and water. *Environmental Toxicology and Chemistry* 4 (1), 51-61.
- [20] Crossland, N. O. 1982 Aquatic toxicology of cypermethrin. II. Fate and biological effects in pond experiments. *Aquatic Toxicology* 2 (4), 205-222.

- [21] Kutty, P. C., Nomani, A. A., & Thankachan, T. S. 1994 Carry over of some high molecular weight organics from seawater to MSF distillates. *Desalination* 97 (1), 401-413.
- [22] Arinaitwe, K., Rose N. L, Muir D. C, Kiremire B. T., Balirwa J. S., Teixeira C. 2015 Historical deposition of persistent organic pollutants in Lake Victoria and two alpine equatorial lakes from East Africa: Insights into atmospheric deposition from sedimentation profiles *Chemosphere* 144, 1815-1822.
- [23] Włodzimierz, J., Włodzimierz, M., & Wojciech, T. 2015 Differentiation of the concentration of heavy metals and persistent organic pollutants in lake sediments depending on the catchment management (Lake Gopło case study) *Bulletin* of Geography. Physical Geography Series. 8 (1), 71-80.
- [24] Jiao R., XiaopingW., ChuanfeiW., Ping G., & Tandong, Y. 2017 Atmospheric processes of organic pollutants over a remote lake on the central Tibetan Plateau: *implications for regional cycling Atmos. Chem. Phys.* 17, 1401-1415.