Full Paper

Season- and year-wise distribution of some trace metals and anions in Gulshan Lake, Bangladesh

Shamshad B. Quraishi[1], Tasrena R. Choudhury[1], Shahidur R. Khan[1] and Mohammad A. Mottaleb [2], *

[1] Chemistry Division, Atomic Energy Centre, Dhaka-1000, Bangladesh

[2] Department of Chemistry/Physics, Center for Innovation and Entrepreneurship, Northwest Missouri State University, 800 University Drive, Maryville, MO 64468, USA

* Corresponding author, E-mail: mmottal@nwmissouri.edu or mmottaleb@yahoo.com , Tel: +1 660 562 0820, Fax: +1 660 562 1188

Abstract: A study was conducted to quantify some trace metals and anions in Gulshan Lake, Bangladesh over five years. The heavy metals, i.e. Pb, Cd, Cr, Co, Ni and Cu, were found below detection limit. The concentration ranges of other metals including anions were 170-1280 μg/L for Fe, 30-190 μg/L for Mn, 24-63 μg/L for Zn, 4-6 mg/L for phosphate, 10-15 mg/L for sulphate, 17-39 mg/L for chloride and 0.20-0.30 mg/L for fluoride. No clear trend in concentration of detected metals and anions, sampling-site-, season- or year-wise, was observed for the period of 2002 and 2004 - 2007. All measured concentrations were found to be well below drinking water standards.

Introduction

Inorganic and organic constituents are the most common environmental contaminants originating from human activities and have continuously been detected in waters and biota. The presence of some trace metals in aquatic environment causes serious problems on plants, animals and human health as well as the ecosystem [1-2]. As a result, water analysis has always attracted interest of scientists.

Organisms need trace amounts of many metals to survive. However, optimal nutritional requirements for the metals of a species generally lie in narrow concentration ranges. Severe imbalance

of metal proportions caused by exposure to elevated concentrations can induce death of an organism [3]. Metals such as Pb, Cd and As exhibit extreme toxicity even at trace levels [4]. Rivers are the dominant pathways for transport of metals [5] and trace elements may become significant pollutants of many small river banks [6]. The behaviour of a metal in natural waters is a function of the substrate sediment composition, the suspended solid composition and the water chemistry [7-8]. During their transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena [9-10], which affect their behaviour and bioavailability. A recent study revealed that the accumulation and distribution of hydrocarbons, trace metals and chlorinated compounds in soil, water and the environment are increasing at an alarming rate, causing deposition and sedimentation in water reservoirs and affecting aquatic organisms [11]. The list of sites contaminated with trace metals grows every year, presenting a serious problem for human health and a grave danger to the environment [12].

In this investigation, the water of Gulshan Lake was studied. Gulshan Lake is one of the largest lakes and a great recreational place/centre in Dhaka, the capital city of Bangladesh. Due to the discharge of sewage and untreated effluents from different factories, the quality of the water bodies around Dhaka has deteriorated [13-14]. During 1980-2006 some, major construction work had also been undertaken along the valley of Gulshan Lake, which might have adversely affected the quality of the lake water. Moreover, mass tourism around the lake is a common fashion and can also affect the water quality. The use of polluted water can lead to several problems for human health and aquatic plant lives [15]. Back in 2002, a large number of fish were found dead in Gulshan Lake. It was then a big public concern and there was a general demand to monitor the concentration levels of pollutants in the lake water to explore the possible causes of death of the aquatic organisms. In our other short-term studies [16-20], surface and drinking water quality was monitored, which revealed that levels of some ionic species were higher than Bangladesh standard. This long-term research program, initiated in 2002 and covering a period of 5 years, was designed to monitor the concentration of some trace metals and anions in water collected from various spots of Gulshan Lake. The background levels of some important trace metals (Mn, Fe, Zn, Cr, Ni, Co, Cu, Cd and Pb) and anions (phosphate, sulphate, chloride and fluoride) in the lake water were established and the season- and year-wise variation of the levels of the detected ionic species in the lake water was examined between March 2002 and September 2007.

Materials and Methods

Standard chemicals and equipment

Nine individual standard solutions (Pb, Cd, Cr, Co, Ni, Cu, Fe, Mn and Zn) and certified reference materials used were purchased from Spex Certiprep. (NJ, USA). Concentrated sulphuric acid, concentrated hydrochloric acid, barium chloride, sodium nitrate, gum acacia, glacial acetic acid and ammonium molybdate, all of extra pure or Analar grade, were purchased from E. Merck (Germany). Standard solutions for anions and concentrated nitric acid were purchased from Sigma-Aldrich (USA). Ionic strength adjuster and total ionic strength adjustment buffer were supplied by Orion Research Inc. (USA). Atomic absorption spectrophotometers (Perkin-Elmer models 3110 and 560) were used to determine the concentrations of the metals. A UV-visible spectrophotometer

(Shimadzu, model 1201, Japan) was used to determine the concentrations of phosphate and sulphate. A digital ion-selective electrode meter (Orion ion analyser, model 470 A) was used for determination of chloride and fluoride. Electrical conductivity was measured by a conductivity meter (Jenway, model No. 4070) and pH was determined by a WTW Multiline P4 universal pH meter.

Selection of sampling spots and collection of water samples

Gulshan Lake is approximately 2.0 km long and 0.2 km wide. Three sampling stations were selected to cover the whole lake. Sampling points were at least 0.5 km distant from each other. The sampling stations are shown in Figure 1. A volume of 2 L of water sample was collected from each sampling station at a depth of 25 cm from the surface using a previously-cleaned 2L-capacity white polyethylene plastic bottles. The sampling was done on March (pre-monsoon), July (monsoon) and September (post-monsoon) starting from the year 2002 to 2007 with the exception of year 2003. On the year 2003, samples were not collected because of sample collection and analysis problems. After collection, samples were transported immediately (~ 1 hr) to the laboratory where each water sample was divided into two portions. One portion assigned for metal analysis was acidified (pH < 2.0) with concentrated nitric acid to prevent adsorption of metals onto the bottle. Measurement of anions was performed with the non-acidified portion quickly after filtration. Samples not immediately analysed were kept in the refrigerator at 4°C until further analysis.
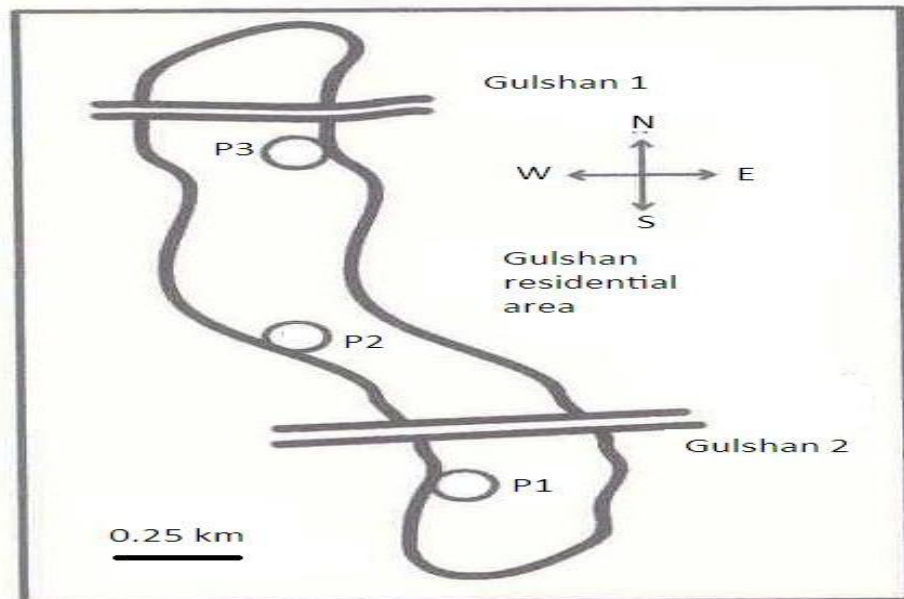
Figure 1. Location of the three sampling sites

Sample preparation and analysis

A volume of 250 mL of the acidified sample was taken into a 300-mL beaker and then heated on a hotplate with 2 mL of conc HNO_3 until the total volume was reduced to approximately 5 mL. The concentrated sample was then transferred to a 10-mL volumetric flask and made up to volume for metal analysis by AAS.

Determination of phosphate [13,16,19] was performed by taking a known volume of water sample (depending on phosphate concentration on trial basis) in a 100-mL volumetric flask. 2N H_2SO_4

(20 mL), 2% ammonium molybdate (2.5 mL) and 0.35% $BaCl_2$ (1 mL) were added successively into the flask, which was then heated for 15-20 min in a water bath. After cooling down to ambient temperature, the final volume was made up to 100 mL with distilled deionised water. Four standard solutions (0.1, 0.2, 0.4 and 0.8 ppm) were prepared in the similar way and the absorbance of the solutions were measured at 578 nm. A calibration curve was made and the concentration of phosphate in water sample was determined using the calibration curve.

For sulphate determination [13,16,19], 50 mL of water sample was taken in a 100-mL volumetric flask. Then 1% gum acacia (1 mL) prepared in 1:1 glacial acetic acid: deionised water, 6N HCl (1 mL) and 10% $BaCl_2$ (5 mL) were added successively into the flask and the final volume of 100 mL was made up with distilled deionised water. Standard solutions (1.0, 2.0, 4.0, 6.0, 8.0 and 10 ppm) were prepared in a similar fashion and their absorbance measured at 420 nm. Concentration of sulphate in water sample was measured using the calibration curve.

The concentrations of chloride and fluoride in water samples were measured using ion selective electrodes based on direct calibration [21]. A volume of each of the calibration standard solutions (0.01, 0.10, 1.0, 10.0 and 100 ppm) was added with the required amount of an ionic strength adjuster. For chloride, this was 2% of 5M $NaNO_3$. For fluoride, an equal volume of a total ionic strength adjustment buffer was used. The electrode potential (mV) of the standards was measured using the target electrode connected the ion-selective electrode meter. A calibration curve was prepared by plotting the electrode potential versus concentration. The concentration of the anions in the real sample was determined directly from the slope and the measured electrode potential value of the sample.

Calibration curve and quality assurance/quality control

A series of calibration levels were prepared from known concentrations of each reference standard solution.   Calibration curves were prepared for all target elements using at least four different concentration levels of each standard solution. A regression analysis was carried out and a coefficient of determination (R^2 value) of 0.9995 was obtained for all elements. Individual calibration curve was used to determine the concentrations of each element/metal. Quality assurance includes measurement of detection limits (Table 1), recovery and analysis of standard certified reference materials. Procedural blanks were used throughout sample preparations to evaluate contamination from reagent, container, etc. No contamination was detected in the blanks. Procedures for sample preparations and analyses were validated by carrying out all operations in triplicate.

Results and Discussion

General

In this investigation, heavy metal concentrations and other physicochemical properties of the water of Gulshan Lake are presented for the period from 2002 to 2007 (excepting year 2003). In general, the levels of the different ionic species including toxic metals were much lower than the Bangladesh drinking-water standards [22]. Table 2 reports the concentrations of metals and anions observed in the lake water above the detection limit. The annual average values of phosphate were at borderline or only slightly lower than the standard value of 6 mg/L. The annual average chloride concentrations were 17-39 mg/L and were much lower than drinking water standard of 150-600 mg/L.

Table 1. Limit of detection (LOD) for metals and anions
analysed by AAS and other techniques

Metals/ anions	LOD (μg/L)	Technique used
Pb	20	AAS
Cd	3	
Cr	4	
Co	4	
Ni	10	
Cu	4	
Fe	5	
Mn	3	
Zn	3	
Cl^-	1000	ISE[*]
F	20	
SO_4^{2-}	1000	UV/VIS
PO_4^{3-}	60	

* Ion-selective electrodes

The annual average concentrations of fluoride were 0.20-0.30 mg/L, which were much lower than the standard at 1.0 mg/L. Annual mean sulphate concentrations ranged from 9.6 to 15 mg/L and were much lower than the drinking water standard (400 mg/L). The concentrations of toxic metals (Pb, Cd, Cr, Co, Ni and Cu) were below the limits of detection and the drinking water standard levels. The average concentration ranges of the essential elements were 170-1280 μg/L for Fe, 30-190 μg/L for Mn and 24-63 μg/L for Zn. Although the majority of samples provided Fe levels that meet Bangladesh drinking water standard (300-1000 μg/L), those collected on 2002 and 2007 showed Fe concentrations below the standard (Table 2). The Mn concentrations were higher than the drinking water standard of 100 μg/L with the exception of the 2007 value (Table 2). The Zn concentrations were much lower than the Bangladesh drinking water standard (5000 μg/L).

Location- and season-wise variation

         The distribution of trace metals and anions in surface water of Gulshan Lake was not uniform. Figure 2 shows concentrations of Fe, Mn, Zn, phosphate, sulphate, chloride and fluoride, and water electrical conductivity measured at three sampling stations (Figure 1) throughout the study period. Attempt was made to correlate the concentrations of the metals and anions observed in the sampling stations. However, due to their irregular trends of highest or lowest concentrations in a particular season, correlation efforts were not fruitful for Fe, Mn, Zn and phosphate. This shows that the origins of contamination that caused these differences were not uniform and could be related to tourist activities.   In the case of sulphate, chloride, fluoride and electrical conductivity, no significant variation was observed among the sampling stations. Season-wise variation of concentrations of water quality characteristics are also shown in Figure 2. Inconsistency of observed results in season-wise

Table 2. Concentrations of metals and anions in Gulshan Lake water over a period of five years

Sample grabbing year	Sampling time	Concentration of anions (mg/L)								Concentration of metals						Electrical Conductivity	
		PO_4		SO_4		Cl		F		Fe (mg/L)		Mn (mg/L)		Zn (μg/L)		(μS/cm)	
		Avg ± S.D.	Yr avg	Avg ± S.D.	Yr avg	Avg ± S.D.	Yr avg	Avg ± S.D.	Yr avg	Avg ± S.D.	Yr avg	Avg ± S.D.	Yr avg	Avg ± S.D.	Yr avg	Avg± S.D.	Yr avg
2002	Mar	4.00± 0.19		19.6± 2.62		19.2± 3.37		0.25± 0.10		0.21± 0.10		0.09± 0.00		9.03± 2.98		391± 5.03	
	Jul	1.86± 0.25	3.7	6.27± 1.16	12	1.85± 0.09	17	0.13± 0.05	0.2	0.10± 0.02	0.2	0.04± 0.02	0.1	7.30± 1.68	26	400± 22.3	397
	Sep	5.12± 1.42		8.67± 0.58		29.2± 2.43		0.24± 0.02		0.29± 0.21		0.25± 0.08		60.2± 32.1		396± 9.71	
2004	Mar	5.40± 1.15		12.5± 1.01		12.8± 1.36		0.27± 0.00		0.65± 0.26		0.17± 0.01		51.9± 12.7		494± 11.1	
	Jul	4.03± 0.94	3.7	12.8 ± 0.19	12	29.0± 5.59	22	0.21± 0.02	0.2	0.95± 0.70	0.8	0.19± 0.04	0.2	31.9± 15.6	41	376± 48.5	372
	Sep	1.57± 0.43		9.48± 1.15		23.7± 0.55		0.09± 0.01		0.83± 0.72		0.08± 0.02		38.1± 2.15		247± 21.0	
2005	Mar	9.90± 1.96		23.2± 7.04		46.2± 4.81		0.33± 0.00		1.69± 1.03		0.24± 0.06		128± 56.1		543± 37.6	
	Jul	1.95± 0.57	4.1	9.65± 1.43	11	31.9± 2.75	30	0.26± 0.02	0.2	1.10± 0.85	1.3	0.17± 0.08	0.2	30.7± 8.02	63	413± 32.2	367
	Sep	0.42± 0.10		1.44± 0.19		11.4± 0.67		0.13± 0.03		1.05± 0.40		0.16± 0.04		30.7± 18.9		145± 3.06	
2006	Mar	9.35± 4.27		11.3± 1.31		46.0± 6.30		0.27± 0.01		0.52± 0.16		0.16± 0.05		72.6± 10.3		370± 26.8	
	Jul	6.20± 1.16	6.1	9.53± 1.16	9.6	40.9± 17.9	39	0.25± 0.04	0.3	0.62± 0.05	0.6	0.17± 0.05	0.2	50.3± 37.3	51	369± 31.6	368
	Sep	2.67± 0.85		7.94± 0.62		29.1± 3.59		0.24± 0.00		0.71± 0.05		0.19± 0.05		28.6± 2.87		365± 17.4	
2007	Mar	5.31± 0.76		21.8± 1.27		49.9± 4.89		0.27± 0.01		0.26± 0.04		0.06± 0.04		27.1± 11.6		510± 39.3	
	Jul	3.60± 0.88	3.6	15.5± 2.86	15	35.8± 14.2	36	0.23± 0.03	0.2	0.16± 0.05	0.2	0.04± 0.01	.04	24.3± 8.70	24	373± 13.2	373
	Sep	2.02± 0.07		8.84± 0.47		21.9± 2.98		0.14± 0.01		0.09± 0.06		0.02± 0.00		20.5± 0.88		235± 21.8	

Note: S.D. represents standard deviation calculated from the measurements at three sampling sites (P1, P2 and P3) for each sampling time. Avg and Yr represent average and year respectively. Year average was calculated from averages of three sampling times for each year.
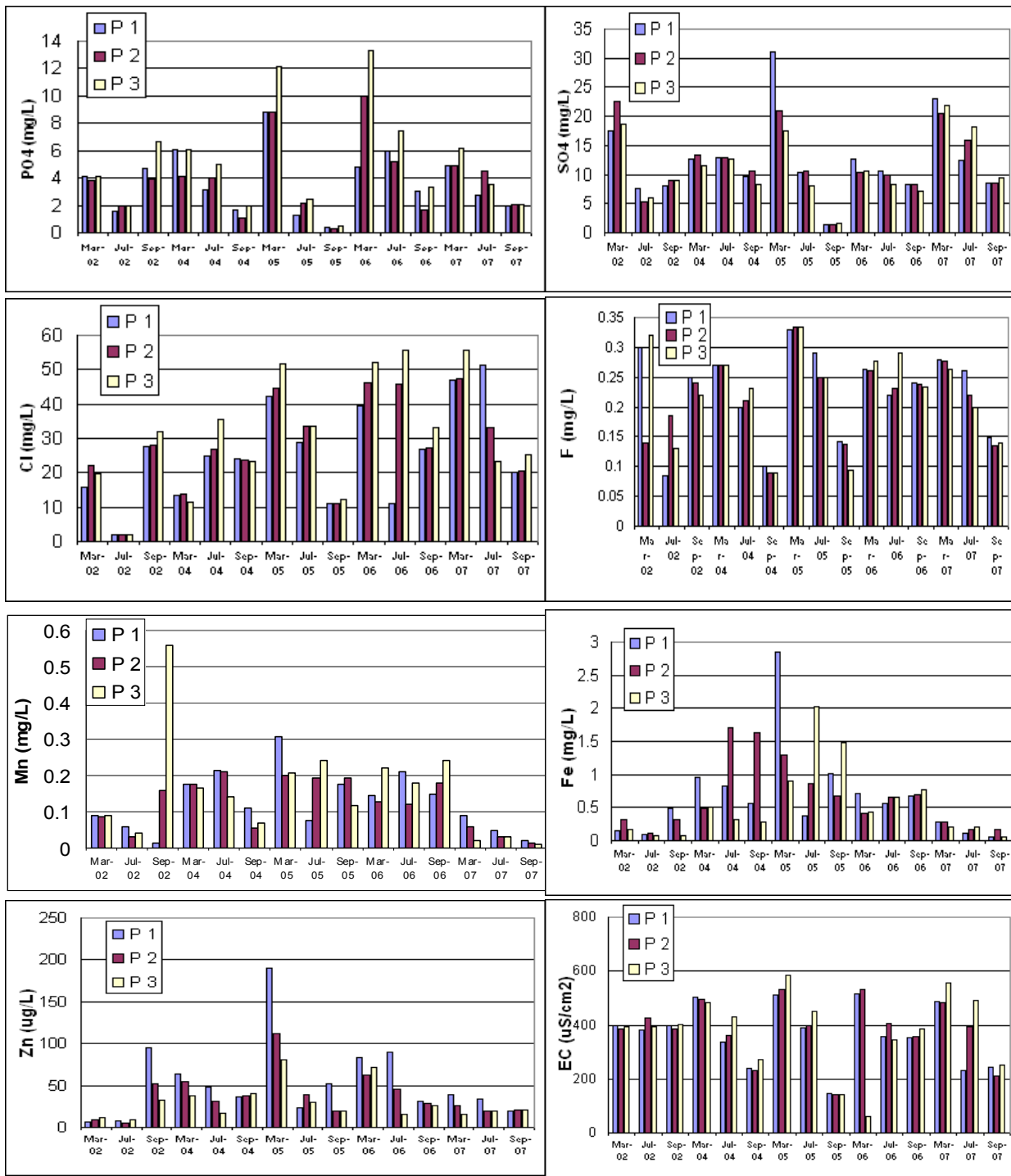
Figure 2. Variation of water quality of Gulshan Lake at three sampling points over five years (2002, 2004-2007)

variation leads to a similar explanation with regard to sampling stations, indicating no particular sources of contaminants from local pollution events or other local anthropogenic origins other than tourism influence.
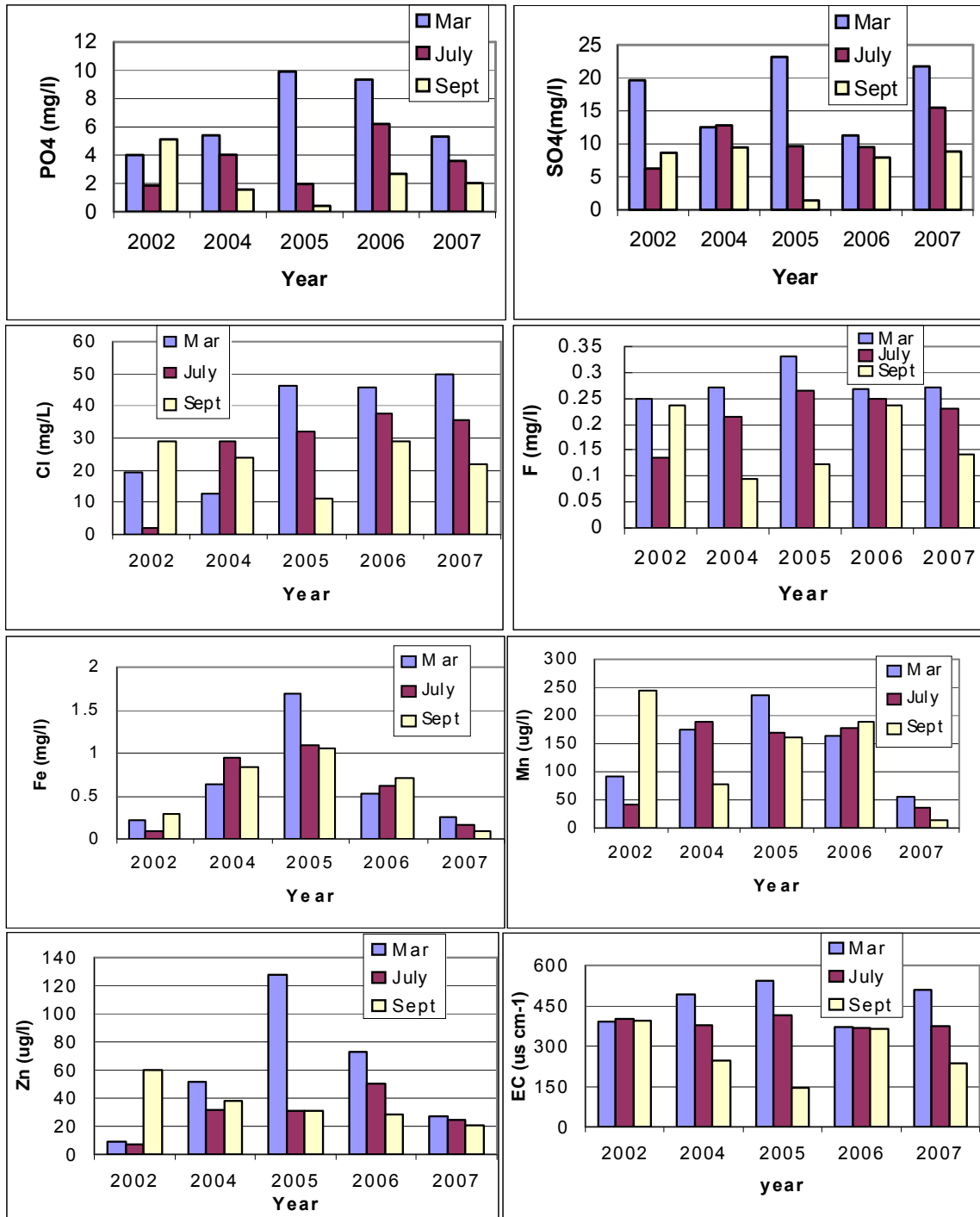

Figure 3. Seasonal variation of water quality of Gulshan Lake over five years (2002, 2004-2007)

Year-wise variation

Figure 3 represents time-course-dependent average concentrations of phosphate, sulphate, chloride, fluoride. Fe, Mn and Zn in Gulshan Lake water including its electrical conductivity. Year-wise phosphate and sulphate concentrations were almost constant excepting year 2006 and 2007. For chloride, approximately 1.4 times year-wise increment was observed starting from 17.0 mg/L in year 2002 (but excluding year 2007 in which there was a decrease). In the case of fluoride, there was virtually no year-wise variation throughout the study duration. For Fe, Mn and Zn, the year-wise highest and lowest average concentrations were all found in 2005 and 2007 respectively. Specifically, Mn concentration had dropped dramatically about 3 to 5 times in 2007 compared to other years' results. Year-wise distributions of Fe and Zn can be observed in the plots (Figure 3), which depict an initial increase and subsequent decrease of concentrations of both Fe and Zn. The unplanned discharges of untreated effluents from different factories such as tanneries, pharmaceutical industries, textile plants, sulfuric acid production and metal-working industries, apart from sewage, could be contributing to the variation of the above monitored items.

Conclusions

A five-year water quality monitoring program was conducted for Gulshan Lake water, which indicates that the lake water was still not polluted by of different metals and anions that might have caused the death of aquatic organisms such as fish in 2002. Neither sampling-site-wise, season-wise nor year-wise concentrations of all the studied variables showed any clear pattern of change. Thus, a possible explanation might be that the lake has been an acceptor of both regular and non-regular pollution pulses. Investigation of organic pollutants may be worthy.

References

1. M. A. Sheikh, N. M. Noah, K. Tsuha and T. Oomori, "Occurrence of tributyltin compounds and characteristics of heavy metals", *Int. J. Env. Sci. Technol.*, **2007**, *4*, 49-60.
2. C. M. Zvinowanda, J. O. Okonkwo, P. N. Shabalala and N. M. Agyei, "A novel adsorbent for heavy metal remediation in aqueous environments", *Int. J. Env. Sci. Technol.*, **2009**, *6*, 425-434.
3. I. E. Agbozu, I. K. E. Ekweozor and K. Opuene, "Survey of heavy metals in the catfish synodontis clarias", *Int. J. Env. Sci. Technol.*, **2007**, *4*, 93-98.
4. R. Nicolau, A. Galera-Cunha and Y. Lucas, "Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river", *Chemosphere*, **2006**, *63*, 469-476.
5. C. V. Miller, G. D. Foster and B. F. Majedi, "Baseflow and stormflow metal fluxes from two small agricultural catchments in the coastal plain of Chesapeake Bay Basin, United States", *Appl. Geochem.*, **2003**, *18*, 483-501.
6. M. Dassenakis, M. Scoullos, E. Foufa, E. Krasakopoulou, A. Pavlidou and M. Kloukiniotou, "Effects of multiple source pollution on a small Mediterranean River", *Appl. Geochem.*, **1988**, *13*, 197-211.
7. R. Shrestha, R. Fischer and M. Sillanpaa, "Investigations on different positions of electrodes and their effects on the distribution of Cr at the water sediment interface", *Int. J. Env. Sci. Technol.*, **2007**, *4,* 413-420.

8. P. S. Harikumar, U. P. Nasir and M. P. M. Rahman, "Distribution of heavy metals in the core sediments of a tropical wetland system", *Int. J. Env. Sci. Technol.*, **2009**, *6*, 225-232.

9. T. N. Abdel-Ghani and G. A. F. Elchaghaby, "Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption", *Int. J. Env. Sci. Technol.*, **2007**, *4*, 451-456.

10. H. Akcay, A. Oguz and C. Karapire, "Study of heavy metal pollution and speciation in Buyak Menderes and Gediz River sediments", *Water Res.*, **2003**, *37*, 813-822.

11. P. H. F. Hobbelen, J. E. Koolhaas and C. A. M. van Gestel, "Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, the Netherlands, taking bioavailability into account*", Env. Pollut.*, **2009**, *129*, 409-419.

12. A. Marin, A. Lopez-Gonzalvez and C. Barbas, "Development and validation of extraction methods for determination of zinc and arsenic speciation in soils using focused ultrasound: Application to heavy metal study in mud and soils", *Anal. Chim. Acta*, **2001**, *442*, 305-318.

13. M. A. Azim, S. B. Quraishi and R. Islam, "Impact of dumping waste water on water quality of the river Buriganga, Bangladesh", *Dhaka Univ. J. Sci.*, **2009**, *57*, 101-106.

14. H. M. Zakir, S. Sharmin and N. Shikazono, "Heavy metal pollution in water and sediments of Turag River at Tongi area of Bangladesh", *Int. J. Lake River*, **2006**, *1*, 85-96.

15. A. H. Khan, M. Ali, S. K. Biswas and D.A. Hadi, "Trace elements in marine fish from the Bay of Bengal", *Sci. Total Env.*, **1987**, *61*, 121-130.

16. S. B. Quraishi, M. N. Chowdhury, M. M. K. Khan and S. Akhter, "Impact of flood of some water quality parameters of lake waters in Dhaka City area", *Nucl. Sci. Appl.*, **2006**, *15*, 82-85.

17. Z. Hossain, "Study on quality of lake water in Dhaka City: Monitoring of seasonal variation of water quality parameters for evaluation of water pollution", *MSc. Thesis*, **2005**, Gogonath College, Dhaka, Bangladesh.

18. S. B. Quraishi, "Aluminum and silicon concentrations in some lake waters of Bangladesh", *Bangladesh J. Acad. Sci.*, **2008**, *32*, 33-39.

19. L. Sarower, "Study of water quality of five lakes in Dhaka City: A seasonal monitoring of micro and macro parameters", *MSc. Thesis*, **1999**, Gogonath College, Dhaka, Bangladesh.

20. S. A. Tarafder, D. A. Hadi and Y. Mia, "The study of nitrate, nitrite and phosphate in some river water around Dhaka City", *Nucl. Sci. Appl.*, **1991**, *3*, 69-75.

21. Orion Research Inc., "Instruction Manual for Chloride and Fluoride Electrodes**",** Orion Research Laboratory Products Group, Boston, **1990**.

22. MEF, "Drinking water quality criteria", in "A Compilation of Environmental Laws (Bangladesh Gazette Additional 28)" (Ed. M. E. Huq), Department of Environment, Ministry of Environment and Forests (MEF), Dhaka, Bangladesh, **1997**, pp. 52-54.