Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.968878

56 (2015) 3368–3379
December

Taylor & Francis
Taylor & Francis Group

Seasonal variation of dissolved heavy metals in the reservoir of Shahid Rajaei dam, Sari, Iran

Seyyed Mohammad Shoaei[a,*], Seyyed Ahmad Mirbagheri[a], Abbasali Zamani[b], Jalal Bazargan[c]

[a]*Faculty of Civil Engineering, K. N. Toosi University of Technology, Tehran, Iran, Tel. +98 912 2411673; Fax: +98 24 33441688; email: sm_shoaei@yahoo.com (S.M. Shoaei), Tel. +98 912 1374357; Fax: +98 21 88779476; email: mirbagheri@kntu.ac.ir (S.A. Mirbagheri)*
[b]*Faculty of Science, Department of Environmental Science, University of Zanjan, Zanjan, Iran, Tel. +98 912 6076253; Fax: +98 24 32283203; email: zamani@znu.ac.ir (A. Zamani)*
[c]*Faculty of Technology, Department of Civil Engineering, University of Zanjan, Zanjan, Iran, Tel. +98 912 1412488; Fax: +98 24 33441688; email: jbazargan@znu.ac.ir (J. Bazargan)*

Received 18 March 2014; Accepted 17 September 2014

ABSTRACT

Water temperature (T), electrical conductivity (EC), dissolved oxygen (DO), pH and concentrations of dissolved heavy metals (Ni, Co, Zn, Cd, Pb and Cu) were measured in the reservoir of Shahid Rajaei dam, north of Iran, during a year. Consequently, seasonal variations of the studied heavy metals and influence of the mentioned physicochemical parameters on concentration variations of the heavy metals were investigated. Significant variations were observed between the warm period (May–September) and the wet period (October–April), for the studied metals. The metals exhibited the following decreasing concentration order: Zn > Pb > Cd > Cu > Co > Ni and Zn > Pb > Cu > Cd > Ni > Co in warm and wet periods, respectively. The seasonal variations could be resulted from natural or anthropogenic sources and ambient conditions such as water temperature, EC, DO, pH, etc. Significant relationships were observed between concentration of some heavy metals and physicochemical parameters during warm and wet periods.

Keywords: Dissolved heavy metals; Physicochemical parameters; Seasonal variation; Reservoir of Shahid Rajaei dam; Iran

1. Introduction

Human activities such as industry, domestic and agriculture have lead to heavy metals contamination of surface waters like rivers, lakes and reservoirs [1–7]. Generally, heavy metals in aquatic systems exist in two phases, i.e. the dissolved phase in the water column and the particulate phase adsorbed on the suspended particulate matter [8–10]. Between dissolved and particulate phases there are sorption and desorption processes which are affected by physical and chemical characteristics of the suspended particles and also ambient conditions, such as pH, temperature, salinity, etc., and hence, variations in concentration of dissolved heavy metals may occur [9–11].

Among surface water resources, dam reservoirs which are commonly built for drinking and

*Corresponding author.

agricultural water supply purposes are of utmost importance because a large amount of time and cost is spent for their construction. Therefore, assessment of the reservoir water quality including the distribution of heavy metals concentration is crucial. The velocity of water in reservoirs is relatively low, so coarse sediments entering the reservoir settle in the upper portion of the reservoir; finer sediments (e.g. clays, silts, and organic detritus) which are often most important for toxic transport remain in suspension longer and are deposited further down the reservoir, and very small particles may remain in suspension for a long time and may even be discharged with the outflow [9]. Since the resident time of water in reservoirs is long, the ambient conditions such as physicochemical parameters can highly affect the solubility of heavy metals.

Shahid Rajaei dam's reservoir (36˚,14´–36˚,15´N, 53˚,13´–53˚,19´E), one of the main reservoirs in north part of Iran, was built in 1990s for agricultural purpose in Mazandaran province (Fig. 1). Water surface area of the reservoir is 428 hectares in normal water level and total reservoir volume is 164 million m^3. It has a drainage area of about 1,248 km^2 mainly including the Sefid Rud River and the Shirin Rud River basins. The area has a typical Caspian climate with mild winters and rather warm summers. The floodplains of the Sefidrud and Shirinrud rivers are mainly under rice cultivation. So, the main source of heavy metal pollutants can be the applied various agrochemicals, fertilizers and pesticides which contain heavy metals. Despite the preliminary aim of Shahid Rajaei dam project, now this reservoir is utilized for fishery and boating purposes. Recently, the reservoir has been considered as drinking water supply of Sari, the provincial capital of Mazandaran province. So, regarding the extensive usage of this reservoir, water quality assessment such as evaluation of the dissolved heavy metals distribution is very important.

The main objectives of the current study are to (1) quantify the concentrations of dissolved heavy metals and also the value of some main physicochemical parameters (T, electrical conductivity [EC], dissolved oxygen [DO] and pH), (2) determine their distribution pattern in depth of the reservoir and explain their seasonal variations and (3) investigate the effect of physicochemical parameters on concentration variations of the dissolved heavy metals in the reservoir of Shahid Rajaei dam, Sari, Iran. Ultimately, the research is important for evaluation of the heavy metals concentration in the Shahid Rajaei dam's reservoir.

2. Materials and methods

2.1. Sampling preparation

Considering topologic and hydrologic characteristics of the reservoir, nine sampling stations were located in Shahid Rajaei dam's reservoir, Iran (Fig. 1). Three stations (S1, S2, and S3) were located in the main part of the reservoir, starting from the dam body to junction point of Sefid Rud and Shirin Rud rivers

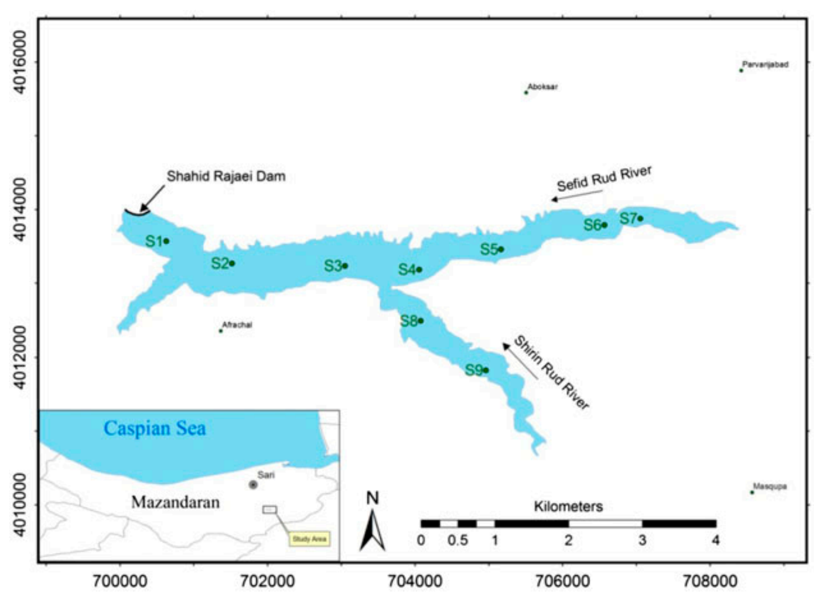

Fig. 1. Location of Shahid Rajaei dam's reservoir, Iran, and the nine sampling stations (S1, S2, and S3 in main part of the reservoir, S4, S5, S6, and S7 in Sefid Rud river zone and S8 and S9 in Shirin Rud river zone).

zones, four stations (S4, S5, S6, and S7) in Sefid Rud River zone and two stations (S8 and S9) in Shirin Rud River zone. Seasonal water samplings were performed since September 2012–August 2013. Two sampling campaigns were performed at the warm period (May–September) and the other two were carried out during the wet period (October–April). A total of 157 water samples were collected from various depths of the stations ranging from the surface to a depth of 30 m with 5 m intervals using cylindrical sampling tools with 50 m cable and 1 L volume (Table 1). Nonetheless, the samplings were not occasionally implemented in some stations or some depths because of low water level in reservoir. Water samples were collected in 1,000 mL poly ethylene bottles and immediately transported to the laboratory and kept under 4˚C till analyzing.

2.2. Sample analysis method

In the study area, the rugged luminescent/optical dissolved oxygen, gel-filled pH electrode and conductivity probes versions with 30 m cables were used to determine water temperature, EC, DO and pH at each sampling point by a portable multimeter (Hach HQ 40d) at each sampling station.

Due to low amount of dissolved heavy metals of the surface water, a pre-concentration step should be taken for the samples so that instruments such as inductive coupled plasma and atomic absorption could be applied for the measurements. This step affects the accuracy and precision of the method. The prepared standard method in DIN 38406, Part 16 describes determination of Zn, Cd, Pb, Cu, Ni and Co ions in low concentrations in drinking, ground and surface waters using polarography–voltammetry method. These metals can be determined in the detection limits of 1.0, 0.1, 0.1, 1.0, 0.1, and 0.1 μg L^{-1}, respectively [12]. The polarography parameters are given in Table 2.

The standard addition method (SAM) is the most appropriate method to compensate matrix effects. Although the water sample matrix was not as complex as biological fluid or soil samples one, but low amount of heavy metals was affected by the presence of inorganic and organic compounds in the sample. Assuming a linear change in response of the applied method due to an increased concentration of analyte, the response is measured before and after several successive additions of the analyte to a sample of unknown analyte concentration.

The water samples were analyzed for the presence of Ni, Co, Zn, Cd, Pb, and Cu using a differential pulse polarography (Metrohm 797 VA). Dissolved air was removed from the solutions by degassing with N_2 gas (99.999%) for 5–10 min, prior to each run. The digested samples were analyzed three times using SAM and the average concentrations of metal ions were reported in μg L^{-1}. Repetitious relative standard deviation of less than 5% was accepted in all determinations. A detailed description of the method is given in Metrohm application bulletin, No. 231/2e [12].

Most water samples were analyzed without pretreatment. Samples were digested where noises existed in the measurement signal or the water sample was not clear. The water samples were filtered through a microfilter (0.45 μm). Then, filtered samples were acidified using 1 mL (for 1 L of sample) of HNO_3 or HCl. The pH of the acidified filtrates should lie between 1.7 and 2.0.

2.3. Analysis of the results

Samples were classified into three groups according to the depth of sampling, namely 1 for

Table 1
Number of samples at each station

Station	Sampling date			
	September 2012	January 2013	April 2013	August 2013
S1	4	7	7	7
S2	5	7	7	7
S3	5	7	7	7
S4	5	7	7	6
S5	–	7	7	3
S6	–	–	3	–
S7	–	–	2	–
S8	5	7	7	4
S9	–	5	5	–

Table 2
Instrument operating parameters for the analysis of the investigated heavy metals

Parameters	Heavy metals	
	Ni and Co[a]	Zn, Cd, Pb, and Cu[b]
Working electrode	HMDE[c]	HMDE
Drop size	4	4
Stirrer speed	2,000 rpm	2,000 rpm
Mode	DP[d]	DP
Purge time	300 s	300 s
Deposition potential	−0.7 V	−1.15 V
Deposition time	90 s	90 s
Equilibrium time	10 s	10 s
Pulse amplitude	50 mV	50 mV
Start potential	−0.8 V	−1.15 V
End potential	−1.25 V	0.05 V
Voltage step	4 mV	6 mV
Voltage step time	0.3 s	0.1 s
Sweep rate	13 mV s^{-1}	60 mV s^{-1}
Peak potential	−1.13, −0.97 V	−0.10, −0.98, −0.56, −0.38 V

[a]10 mL sample solution + 100 μL dimethylglyoxime solution (0.1 M) + 0.5 mL NH_4Cl pH 9.5.
[b]10 mL sample solution + 1 mL ammonium acetate buffer pH 4.6.
[c]Hanging mercury dropping electrode.
[d]Differential pulse.

epilimnion, 2 for metalimnion and 3 for hypolimnion. These three layers were determined considering the chemical and physical properties of the water column provided by the portable multimeter. Statistical analyses of data were performed using PASW Statistics 18 and Excel 2007.

Analysis of the experimental data was carried out using Mann Whitney U and Kolmogorov–Smirnov (K–S). All significance statements reported in this study are at $p < 0.05$ level of significance. *T*-test and the Mann Whitney method, as parametric and non-parametric tests, respectively, allow testing the significant difference of the means between the two groups. Parametric methods are those for which it is known that the population is approximately normal. In contrast to the parametric methods, non-parametric methods are defined that are statistical techniques for which no assumption of normality is needed for the population being studied. Normal distribution assumptions were checked by using K–S test.

Regression analysis, as a statistical process, is used for estimating the relationships among variables. It helps us understand how the typical value of the dependent variable changes when any one of the independent variables is varied, while the other independent variables are held fixed. In this study, this method was used for investigating the relationships among the studied metals concentrations and the physicochemical parameters in the Shahid Rajaei dam's reservoir in the three layer depths.

3. Results and discussion

3.1. Physicochemical parameters

The statistical values of physicochemical parameters in Shahid Rajaei dam's reservoir during two different sampling periods are given in Table 3 and the distribution patterns of these values in depth of the reservoir are shown in Fig. 2. The water temperatures were higher in the warm period from May to

Table 3
Physicochemical parameters in warm and wet periods in Shahid Rajaei dam's reservoir

Period	Parameter	Min	Max	Average
Warm	Temperature (°C)	19.80	26.20	23.30
	EC (μS cm^{-1})	457.00	599.00	501.00
	DO (mg L^{-1})	0.06	11.02	5.55
	pH	7.50	8.60	8.08
Wet	Temperature (°C)	10.00	16.30	12.80
	EC (μS cm^{-1})	466.00	661.00	515.00
	DO (mg L^{-1})	7.31	11.62	8.96
	pH	7.21	8.55	8.24

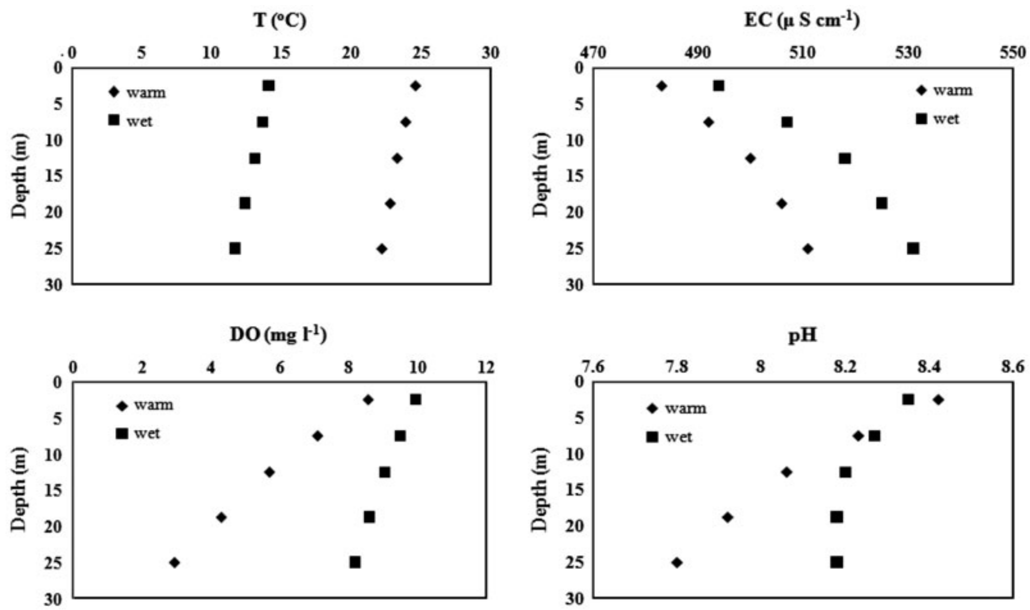

Fig. 2. Variation of physicochemical parameters with depth of Shahid Rajaei dam's reservoir.

September because of meteorological conditions. Decreasing pattern of the temperature with depth of the reservoir was relatively uniform. Unlike the temperature, the values of EC in the warm period were lower. It may be due to lower total dissolved elements in water induced by a lower entrance of sediment loads from the upstream rivers. Also, EC values had a relatively uniform and ascending distribution pattern with depth of the reservoir. It can be attributed to the increasing sediment concentration at deeper points due to sedimentation process.

The values of DO were lower in the warm period and decreasing rate of DO values with depth of reservoir was higher in this period. Since in warm period the reservoir is commonly stratified, the upper water layers are warmer and lighter and do not mix with the cool, deep layers. Therefore, DO levels typically remain high in the upper layers because of reaeration and photosynthesis process of algae. However, entrapped DO in the bottom layers can be decreased and even depleted due to bacterial consumption, oxidation of organic carbon and nitrification [9]. The minimum measured value of DO was 0.06 corresponding to the depth of 30 m. It is noteworthy that, large reduction in the amount of water DO will put aquatic life under stress. The lower the concentration, the greater the stress will become. Oxygen levels lower than 1–2 mg L^{-1} for a few hours can result in a large number of fish deaths. Ultimately, the values of pH were often lower in the warm period. That could be attributed to an increase in the amount of released carbon dioxide due to increased consumption of oxygen at greater depths of the reservoir in warm period [9]. However, the pH value in the surface layer of the reservoir was higher during warm period. It might due to higher algal photosynthesis and a decrease in the amount of carbon dioxide which will lead to a decrease in hydrogen ions and an increase in pH value [9].

Normal data distribution assumptions were checked by using K–S test. It was confirmed that the data distribution was not normal. Hence, Mann Whitney test, as a non-parametric test, was used for the comparison of the average values of the parameters in two sampling periods. It showed a statistically significant difference between the temperature, DO and EC depending on the sampling period. However, the average pH values in the two sampling periods did not show a statistically significant difference.

3.2. Concentration of dissolved heavy metals

Table 4 shows briefly the concentrations of the studied dissolved heavy metals in the reservoir of Shahid Rajaei dam during warm and wet periods and the variation patterns are shown in Fig. 3. On the mean scale, the metals exhibited the following decreasing concentration orders of Zn > Pb > Cd > Cu > Co > Ni and Zn > Pb > Cu > Cd > Ni > Co in warm and wet periods, respectively. The concentrations of dissolved heavy metals were higher in the wet period, except for

Table 4
Dissolved heavy metals concentrations (μg L^{-1}) in the Shahid Rajaei dam's reservoir

Period	Metal	Min	Max	Average
Warm	Ni	0.16	3.44	1.56
	Co	0.28	9.49	3.08
	Zn	9.62	123.52	60.44
	Cd	0.25	13.87	6.86
	Pb	4.03	37.49	24.23
	Cu	0.96	9.22	3.60
Wet	Ni	0.67	5.82	2.33
	Co	0.50	3.73	1.07
	Zn	13.04	152.49	71.78
	Cd	0.67	17.96	8.49
	Pb	6.49	45.16	22.57
	Cu	2.74	53.86	8.95

Co and partly Pb. Since many agricultural lands and mainly paddies are located in flood plain of the Sefid Rud and Shirin Rud Rivers, fertilizers can be the main source of heavy metal pollutants in wet period (especially in March and April) which contain heavy metals. For example, Cd is found predominantly in phosphatic fertilizers because Cd is commonly present as an impurity in phosphatic rocks [13–16]. Also, superphosphate fertilizer contains Cd, Cu, and Zn as impurities and copper sulphate and iron sulphate are fertilizers containing Ni [13]. Another source of the mentioned heavy metals in wet period can be rock weathering and transportation of sediments containing heavy metals that is caused by higher values of rainfall in the reservoir basin [17]. Higher values of Co and Pb in the warm period can be induced by the pesticides [13,18] that are used in upstream farm lands.

Heavy metals concentration often showed a decreasing pattern with depth during the wet period. However, Co along the whole depth and Ni in the upper layers of the reservoir showed increasing patterns. Also, the distribution patterns of Co along the

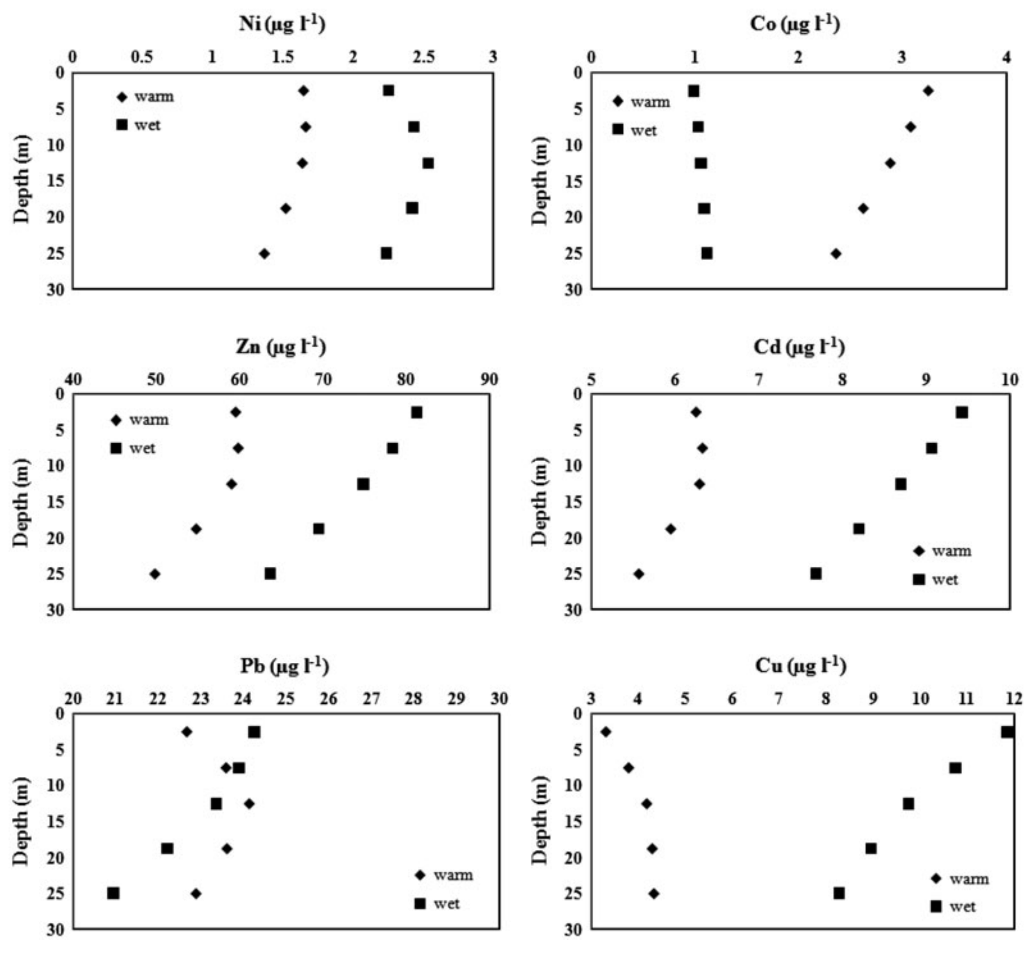

Fig. 3. Variation of dissolved heavy metals concentrations with depth of Shahid Rajaei dam's reservoir.

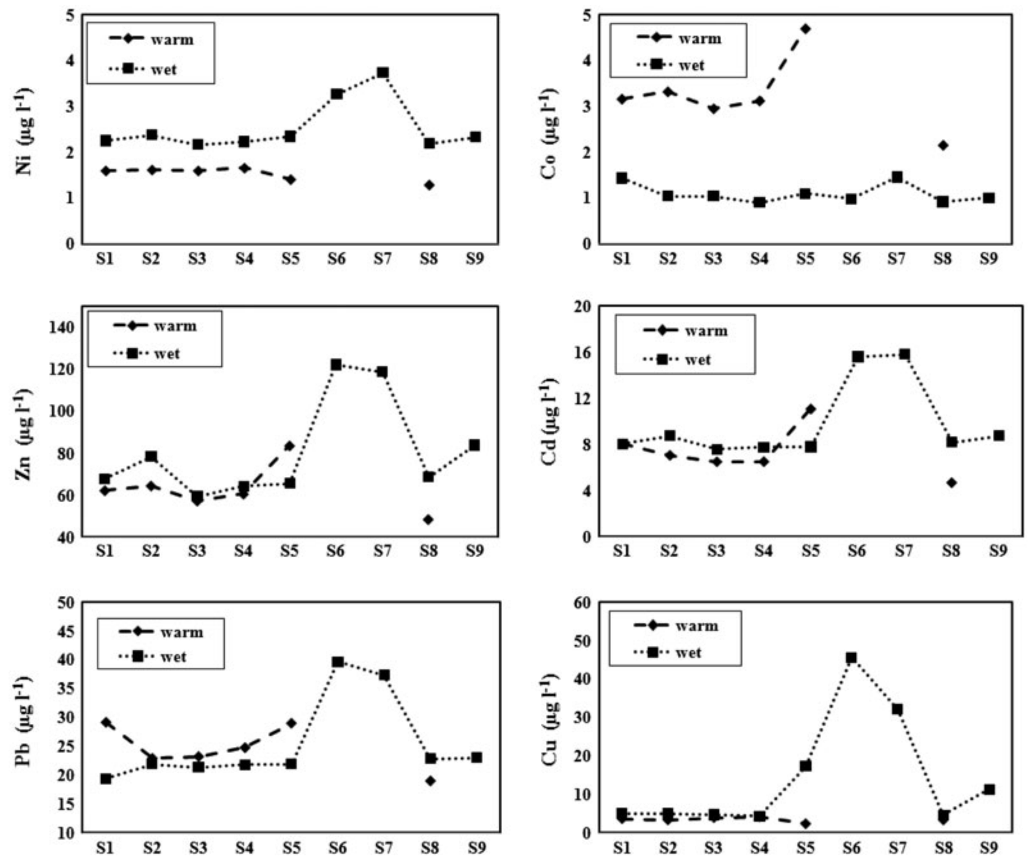

Fig. 4. Spatial pattern of the dissolved heavy metals concentrations (mean values) in the Shahid Rajaei dam's reservoir, Iran.

Table 5
Average concentration of the entered heavy metals from the Sefid Rud and Shirin Rud rivers to the Shahid Rajaei dam reservoir during each season (in µg L^{-1})

River	Sampling date	Ni	Co	Zn	Cd	Pb	Cu
Sefid Rud	September 2012	6.814	7.463	20.01	0.515	11.375	6.547
	January 2013	0.859	0.823	32.869	2.818	7.407	4.203
	April 2013	4.179	1.164	119.924	15.433	38.378	51.115
	August 2013	7.22	5.838	91.673	13.9	34.903	2.5
Shirin Rud	September 2012	3.76	7.076	19.303	0.549	10.73	7.418
	January 2013	1.263	0.892	23.922	1.883	8.014	3.816
	April 2013	1.87	2.059	131.183	16.2	40.295	47.8
	August 2013	1.471	3.619	78.139	11.78	30.661	1.435

whole depth and Ni, Zn, Cd and Pb in the lower layers of the reservoir were decreasing in warm period. The concentrations of Ni, Zn and Cd in the upper layers and Cu in the lower layers of the reservoir did not change significantly. Ultimately, the concentrations of Cu and specially Pb showed increasing patterns in the upper layers of the reservoir. Mann Whitney test was used for comparing the heavy metals average concentrations in two sampling periods. A statistically significant difference was shown considering Ni, Co, Zn and Cu concentrations between the warm and wet seasons. However, Pb showed similar average concentrations in the two periods.

The spatial distributions of the dissolved heavy metals concentrations are shown in Fig. 4. In wet period, all heavy metals have rather uniform

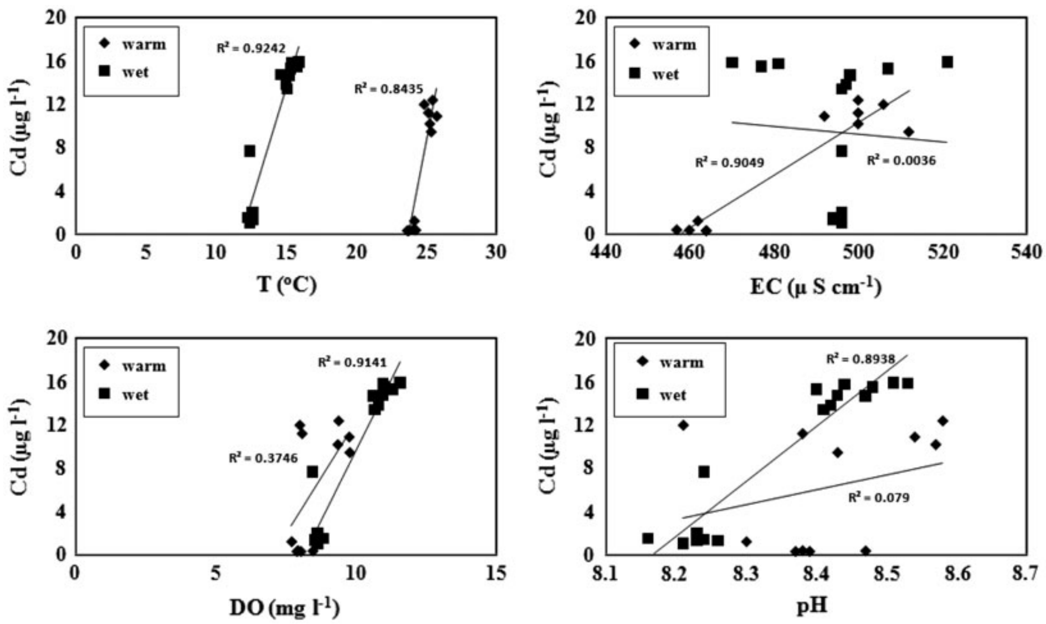

Fig. 5. Linear relationship between dissolved Cd and physicochemical parameters in Shahid Rajaei dam's reservoir in epilimnion.

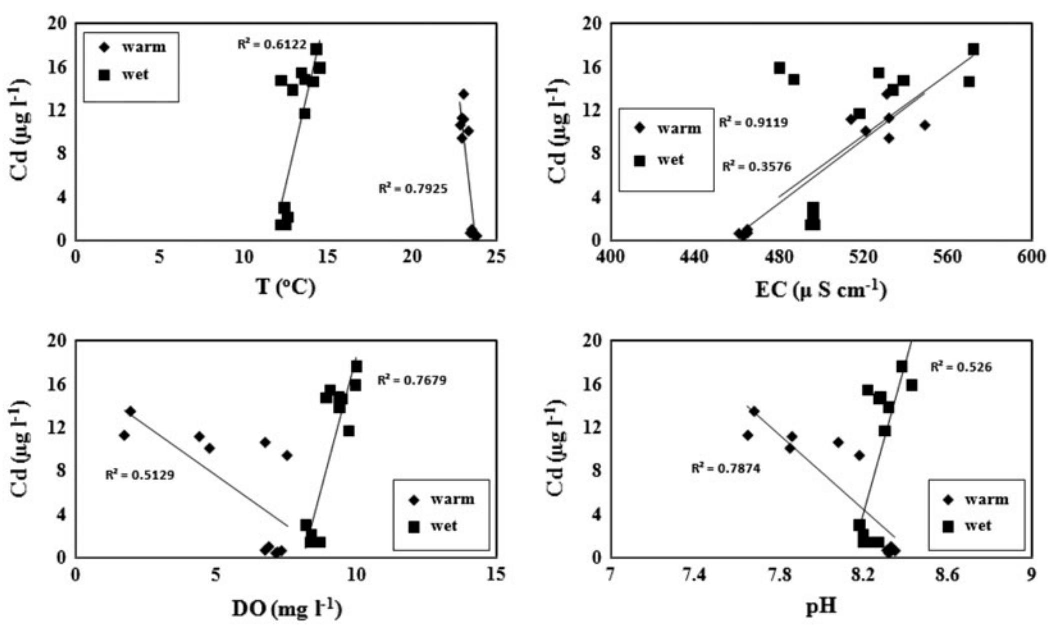

Fig. 6. Linear relationship between dissolved Cd and physicochemical parameters in Shahid Rajaei dam's reservoir in metalimnion.

distributions in all stations except in S6 and S7 where the concentrations are significantly higher. This is because the sampling in these stations was performed only in April 2013 during which the concentration of the entered heavy metals was high (Tables 1 and 5). During other sampling times, water surface level was lower than bed elevation at these stations. This phenomenon was also partly seen in S9 station located near the Shirin Rud River entrance. However, a uniform distribution of Co concentration was observed in

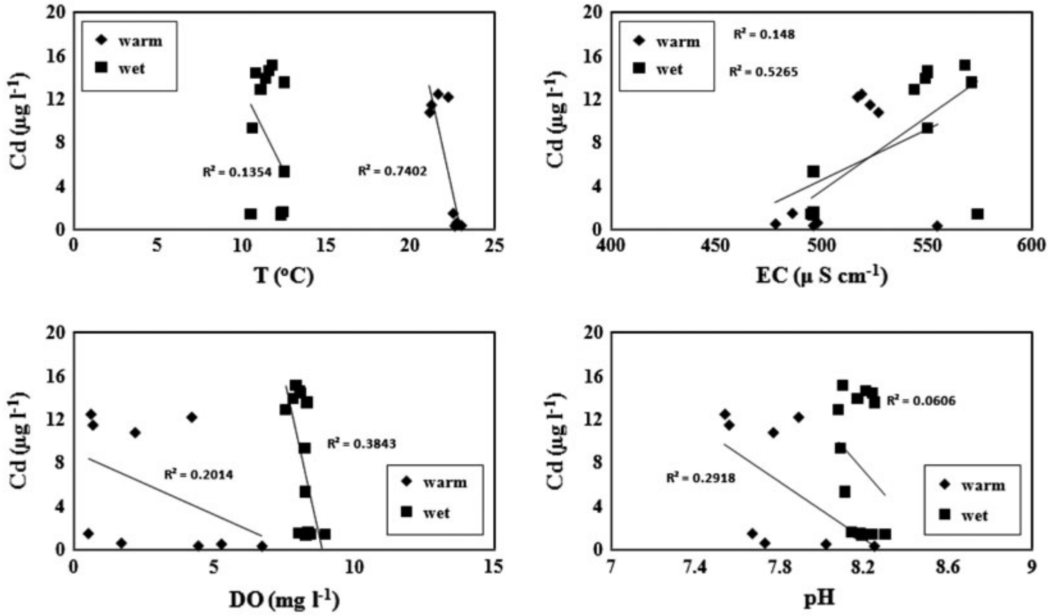

Fig. 7. Linear relationship between dissolved Cd and physicochemical parameters in Shahid Rajaei dam's reservoir in hypolimnion.

Table 6
Existing R^2 values between dissolved heavy metal concentrations and physicochemical parameters in Shahid Rajaei dam's reservoir-warm period

Parameter	Layer	Ni	Co	Zn	Cd	Pb	Cu
Temperature (℃)	Epilimnion	0.388	0.679	0.794	0.844	0.684	0.490
	Metalimnion	0.009	0.502	0.705	0.793	0.690	0.490
	Hypolimnion	0.717	0.789	0.713	0.740	0.439	0.779
EC (µS cm^{-1})	Epilimnion	0.237	0.808	0.717	0.905	0.492	0.668
	Metalimnion	0.046	0.647	0.724	0.912	0.598	0.653
	Hypolimnion	0.230	0.088	0.102	0.148	0.000	0.260
DO (mg L^{-1})	Epilimnion	0.194	0.295	0.269	0.375	0.202	0.453
	Metalimnion	0.112	0.170	0.545	0.513	0.522	0.273
	Hypolimnion	0.097	0.229	0.275	0.201	0.477	0.038
pH	Epilimnion	0.342	0.123	0.036	0.079	0.042	0.157
	Metalimnion	0.100	0.406	0.717	0.787	0.632	0.469
	Hypolimnion	0.130	0.338	0.381	0.292	0.502	0.071

Note: Significant correlation coefficients are underlined.

all the stations. Comparison of the average concentrations of the heavy metals obtained in the Sefid Rud (S4 and S5) and Shirin Rud (S8 and S9) Rivers related zones of the reservoir showed relatively equal values of the heavy metals. In the warm period, the distribution pattern of the heavy metals was rather uniform except in S5 for Co, Zn, Cd, and Pb. High values of heavy metal concentration were achieved in S5 because the sampling in this station was performed only during August 2013 during which the concentration of the entered heavy metals was high (Tables 1 and 5). Decreased concentration of the heavy metals downstream of the Sefid Rud (S5–S4) and Shirin Rud (S9–S8). Rivers zones in both warm and wet periods can be attributed to the dilution and sedimentation of particulate phase of the heavy metals and a decrease in water disturbance. This phenomenon was observed for all the investigated heavy metals.

Variations of the dissolved heavy metals concentration are predominately affected by the water temperature

Table 7
Existing R^2 values between dissolved heavy metal concentrations and physicochemical parameters in Shahid Rajaei dam's reservoir-wet period

Parameter	Depth	Ni	Co	Zn	Cd	Pb	Cu
Temperature (°C)	Epilimnion	0.855	0.160	0.866	0.924	0.976	0.410
	Metalimnion	0.545	0.150	0.646	0.612	0.574	0.312
	Hypolimnion	0.351	0.375	0.127	0.135	0.156	0.012
EC (μS cm^{-1})	Epilimnion	0.011	0.126	0.007	0.004	0.004	0.310
	Metalimnion	0.352	0.166	0.311	0.358	0.320	0.146
	Hypolimnion	0.426	0.070	0.561	0.527	0.550	0.157
DO (mg L^{-1})	Epilimnion	0.894	0.172	0.892	0.914	0.969	0.311
	Metalimnion	0.692	0.254	0.772	0.768	0.754	0.238
	Hypolimnion	0.263	0.009	0.330	0.384	0.375	0.060
pH	Epilimnion	0.807	0.251	0.830	0.894	0.909	0.406
	Metalimnion	0.420	0.409	0.610	0.526	0.517	0.388
	Hypolimnion	0.028	0.116	0.036	0.061	0.032	0.000

Note: Significant correlation coefficients are underlined.

[2,19], salinity [8,20–22], redox condition [23–25] and pH [25–28]. Temperature influences on the metabolism and growth rates of the aquatic organisms, plant photosynthesis, oxygen solubility in water, and sensitivity of the organisms to disease, parasites and toxic materials. At higher temperature, plants grow and die faster, leaving behind matter that requires oxygen for decomposition. Trace elements that accumulate in phytoplankton may become soluble during the decay of plants [25]. Seasonal variations of the water temperature in an aquatic system may influence the variability of the studied metals indirectly via biological activities (decay of phytoplankton) or due to possible decrease of the DO which is related to redox potential decrease [25]. Increasing salinity leads to an increased competition between cations and metal ions and a decreased concentration of the adsorbed heavy metals [29]. This phenomenon can increase the dissolved phase of heavy metal concentrations in water system. Generation of the hydrogen sulphide in the sediments and in the anoxic parts of the water column is consequently followed by a precipitation of heavy metals as sulphides and a decrease in the dissolved heavy metals in water column [30].

In this research, linear relationships between the studied physicochemical parameters and the dissolved heavy metals in the sampling site of the Shahid Rajaei dam's reservoir in the warm and wet periods were investigated. An example of the estimated linear relationships for Cd is given in Figs. 5–7. Tables 6 and 7 show the linear correlation coefficients (R^2) between the studied metals concentrations and the physicochemical parameters in the Shahid Rajaei dam's reservoir in three depth layers. Significant correlation coefficients between temperature and dissolved heavy metals concentrations were shown in warm period except for Ni in metalimnion. However, in wet period the correlations between temperature and Co in epilimnion and metalimnion and between temperature and Zn, Cd, Pb and Cu concentrations in hypolimnion were not remarkable. The correlations between EC and dissolved heavy metals concentrations in warm period in epilimnion and metalimnion were considerable except for Ni. However, in wet period remarkable correlations were shown in metalimnion and hypolimnion except for Co and Cu. No remarkable correlation was observed between DO and heavy metals concentrations in warm period except for Cd and Cu in epilimnion, Zn, Cd and Pb in metalimnion and finally Pb in hypolimnion. In contrast to warm period, these correlations were significant in epilimnion and metalimnion except for Co and Cu. Ultimately, the correlations between pH and heavy metals concentrations in warm period only in metalimnion were considerable except for Ni. However, in wet period the correlations were considerable in epilimnion and metalimnion.

4. Conclusions

The results of this research showed that although in warm period the water temperatures were higher in depth of the reservoir than wet period due to meteorological conditions, the EC, DO, and pH values were lower than wet period except pH in surface layer that it might be due to higher algal photosynthesis and a decrease in carbon dioxide content which leads to a decrease in hydrogen ions and an increase in pH values. Also, concentrations of Ni, Zn, Cd, and Cu in wet period are higher than warm period. The increased concentration of these heavy metals in wet period could be mainly attributed to the used fertilizers which contain heavy metals as impurities and also rock weathering in the reservoir basin. Also, concentration of Co through the whole depth and Pb in lower depths of the reservoir in warm period was higher than wet period. The increased concentration of these heavy metals in warm period could be mainly attributed to the used pesticides in upstream farm lands. Significant relationships were observed between the heavy metals concentration and both temperature and EC in warm period. Also, the correlations between heavy metals concentration and both DO and pH were considerable in wet period. The relationships between the heavy metals concentration and ambient physicochemical parameters showed that besides the external sinks and sources, sorption and desorption processes between dissolved and particulate phases of heavy metals could be another sink and source of the concentration variations of dissolved heavy metals which are affected by various ambient conditions, such as temperature, EC, DO, and pH.

Acknowledgements

The authors express their sincere gratitude to the Environmental Science Laboratory in University of Zanjan, Iran, and they gratefully acknowledge Dr. Seyyed Aliasghar Arjmandi and Hossein Soltani for their contribution to this work.

References

[1] S.K. Bozbas, U. Ay, A. Kayan, Novel inorganic–organic hybrid polymers to remove heavy metals from aqueous solution, Desalin. Water Treat. 51(37–39) (2013) 7208–7215.
[2] M. Iwashita, T. Shimamura, Long-term variations in dissolved trace elements in the Sagami River and its tributaries (upstream area), Japan, Sci. Total Environ. 312 (2003) 167–179.
[3] M. Olías, J.M. Nieto, A.M. Sarmiento, J.C. Cerón, C.R. Cánovas, Seasonal water quality variations in a river affected by acid mine drainage: The Odiel River (South West Spain), Sci. Total Environ. 333 (2004) 267–281.
[4] S. Li, Z. Xu, X. Cheng, Q. Zhang, Dissolved trace elements and heavy metals in the Danjiangkou Reservoir, China, Environ. Geol. 55 (2008) 977–983.
[5] G. Nabulo, H. Oryem Origa, G.W. Nasinyama, D. Cole, Assessment of Zn, Cu, Pb and Ni contamination in wetland soils and plants in the Lake Victoria basin, Int. J. Environ. Sci. Technol. 5 (2008) 65–74.
[6] K.M. Mohiuddin, K. Otomo, Y. Ogawa, N. Shikazono, Seasonal and spatial distribution of trace elements in the water and sediments of the Tsurumi River in Japan, Environ. Monit. Assess. 184 (2012) 265–279.
[7] M.T. Sikder, Y. Kihara, M. Yasuda, S. Yustiawati, Y. Mihara, S. Tanaka, D. Odgerel, B. Mijiddorj, S.M. Syawal, T. Hosokawa, T. Saito, M. Kurasaki, River water pollution in developed and developing countries: Judge and assessment of physicochemical characteristics and selected dissolved metal concentration, Clean Soil Air Water 41 (2013) 60–68
[8] M. Hartnett, B. Lin, P.D. Jones, A. Berry, Modelling the fate and transport of nickel in the Mersey Estuary, J. Environ. Sci. Health., Part A 41 (2006) 825–847.
[9] Z.-G. Ji, Hydrodynamics and Water Quality: Modeling Rivers, Lakes, and Estuaries, John Wiley & Sons, Hoboken, NJ, 2008.
[10] A. Roshanfekr, S.M. Kashefipour, N. Jafarzadeh, Numerical modelling of heavy metals for riverine systems using a new approach to the source term in the ADE, J. Hydroinform. 10 (2008) 245–255.
[11] Y. Wu, R. Falconer, B. Lin, Modelling trace metal concentration distributions in estuarine waters, Estuarine Coastal Shelf Sci. 64 (2005) 699–709.
[12] Metrohm, Application Bulletin No. 230/2e, Voltammetric determination of zinc, cadmium, lead, copper, thallium, nickel and cobalt in water samples according to DIN 38406 Part 16, Metrohm, Herisau, 2009.
[13] E. Gimeno-García, V. Andreu, R. Boluda, Heavy metals incidence in the application of inorganic fertilizers and pesticides to rice farming soils, Environ. Pollut. 92 (1996) 19–25.
[14] S.S. Mann, A.W. Rate, R.J. Gilkes, Cadmium accumulation in agricultural soils in western Australia, Water Air Soil Pollut. 141 (2002) 281–297.
[15] N. Otero, L. Vitòria, A. Soler, A. Canals, Fertiliser characterisation: Major, trace and rare earth elements, Appl. Geochem. 20 (2005) 1473–1488.
[16] S.S. Huang, Q.L. Liao, M. Hua, X.M. Wu, K.S. Bi, C.Y. Yan, B. Chen, X.Y. Zhang, Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China, Chemosphere 67 (2007) 2148–2155.
[17] M.B. McBride, Environmental Chemistry of Soils, Oxford University Press, New York, NY, 1994.
[18] M. Marković, S. Cupać, R. Đurović, J. Milinović, P. Kljajić, Assessment of heavy metal and pesticide levels in soil and plant products from agricultural area of Belgrade, Serbia, Arch. Environ. Contam. Toxicol. 58 (2010) 341–351.
[19] S.M. Kashefipour, A. Roshanfekr, Numerical modelling of heavy metals transport processes in riverine basins, in: Peep Miidla (Ed.), Numerical Modeling, Intech, Rijeka, 2012, pp. 91–114.
[20] A.R. Valikhani Samani, A.R. Karbassi, M. Fakhraee, M. Heidari, A.R. Vaezi, Z. Valikhani, Effect of dissolved organic carbon and salinity on flocculation process of heavy metals during mixing of the Navrud River water with Caspian Seawater, Desalin. Water Treat. Forthcoming, (2014) 1–9.
[21] A. Turner, Trace-metal partitioning in estuaries: Importance of salinity and particle concentration, Mar. Chem. 54 (1996) 27–39.
[22] A. Turner, S.M. Le Roux, G.E. Millward, Speciation and partitioning of cadmium and zinc in two contrasting estuaries: The role of hydrophobic organic matter, Limnol. Oceanogr. 49 (2004) 11–19.

[23] E. Szarek-Gwiazda, G. Mazurkiewicz-Boroń, Deposition of copper in the eutrophic, Submontane Dobczyce dam reservoir (Southern Poland)–Role of speciation, Water Air Soil Pollut. 140 (2002) 203–218.
[24] A. Turner, G.E. Millward, Suspended particles: Their role in estuarine biogeochemical cycles, Estuarine Coastal Shelf Sci. 55 (2002) 857–883.
[25] A.K. Papafilippaki, M.E. Kotti, G.G. Stavroulakis, Seasonal variations in dissolved heavy metals in the Keritis river, Chania, Greece, Global Nest J. 10 (2008) 320–325.
[26] M.R. Lasheena, I.Y. El-Sherifa, D.Y. Sabryb, S.T. El-Wakeela, M.F. El-Shahatb, Removal of heavy metals from aqueous solution by multiwalled carbon nanotubes: Equilibrium, isotherms, and kinetics, Desalin. Water Treat. Forthcoming, (2013) 1–10.
[27] A. Turner, G.E. Millward, S.M. Le Roux, Sediment-water partitioning of inorganic mercury in estuaries, Environ. Sci. Technol. 35 (2001) 4648–4654.
[28] R. Nicolau, A. Galera-Cunha, Y. Lucas, Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river, Chemosphere 63 (2006) 469–476.
[29] G. Du Laing, J. Rinklebe, B. Vandecasteele, E. Meers, F.M.G. Tack, Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review, Sci. Total Environ. 407 (2009) 3972–3985.
[30] H. Paucot, R. Wollast, Transport and transformation of trace metals in the Scheldt estuary, Mar. Chem. 58 (1997) 229–244.