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Developing water quality maps of a hyper-saline lake using spatial interpolation methods

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Anions.

Abstract. Urmia Lake, the second largest hyper-saline lake in the world, has experienced a significant drop in water level during the last decade. This study was designed to examine the water quality of Urmia Lake and to characterize the spatial heterogeneity and temporal changes of the physiochemical parameters between October 2009 and July 2010. Two spatial interpolation methods, Inverse Distance Weighting (IDW) and Ordinary Kriging (OK), were used and compared with each other to derive the spatial distribution of ionic constituents as well as TDS and density along the lake. Results showed that the main dominant cations and anions in Urmia Lake were Na^+, Mg^{++}, K^+, Ca^{++}, Cl^-, SO_4^{--}, and HCO_3^-, respectively. Although water quality of the lake is homogeneous with depth, it differs between the northern and southern parts. Water quality also varies seasonally, determined by river inflows and the lake bathymetry. Moreover, with the present salinity level, salt precipitation is likely in Urmia Lake and is becoming one of the principal factors determining the distribution of solutes within the lake. This study shows that the combined use of temporal and spatial water quality data improves our understanding of complex, large aquatic systems like Urmia Lake.

1. Introduction

Lakes are valuable water resources supporting a various range of human activities including agriculture, commerce, transportation, recreation, tourism, and the production of food and energy. They also provide unique habitats for a diverse array of organisms and play a key role in the meteorological conditions of their surrounding environments. Monitoring water quality is crucial to the proper management and restoration of many lakes particularly in large lakes.

Urmia Lake is located in north-west Iran and is the second most saline lake in the world [1]. It is a shallow terminal lake which lies between 37°04′N to 38°17′N latitude and 45°E and 46°E longitude. Its surface area has been estimated to be 6059 km^2 in 1995 [2], but since then it has been declining [3] and was estimated to be only 2366 km^2 in August of 2011 [4]. Urmia Lake has been divided by a 15.4 km dike-type causeway which provides road access between the western and eastern provinces (Figure 1). A 1.25 km long opening was left in the causeway to hydraulically connect the northern and southern parts of the lake. Because of its high salinity, Urmia Lake has a low diversity of flora and fauna, and except *Artimia Urmiana Salina* and some algae species, no other living organisms exist [5]. Urmia Lake has been designated as a Ramsar Convention Site of international importance (since 1971), Biosphere Reserve (since 1976), and a national park and is one of the largest natural biotopes of *Artemia* in the world [6]. The locations of the four major islands, Kabudan, Arezu, Ashk, and Espir, which are considered as protected areas by the

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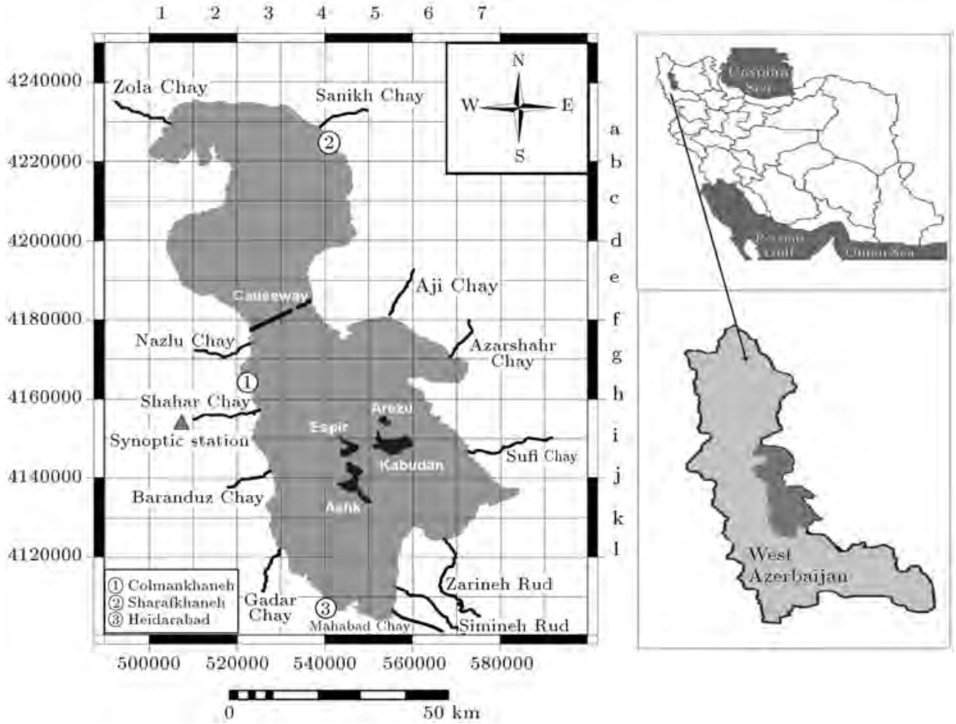

Figure 1. West Azerbaijan province and Urmia Lake map.

Environmental Protection Organization, are shown in Figure 1.

Upstream river discharges as well as seasonal precipitation are the main sources of the water to this terminal lake, while evaporation is the main water loss. The average surface and ground water inflows to the lake have been estimated to be 5.3 km^3/year. The semi-arid local climate of the region leads to the high evaporation and low precipitation rates. The average volume of evaporation from the lake is estimated to vary between 900 and 1170 mm/year while the average precipitation over the lake is 350 mm/year [2].

In recent years, due to drought and increased demands for agricultural water in the lake's basin, its water level has dropped by more than 7.5 meters below its maximum level (see Figure 2), and large areas of the lake bed have desiccated. Concurrently, the salinity of the lake has risen to more than 300 g/L which has caused the severe disturbances to the lake ecosystem [7]. Several factors including climate changes and anthropogenic changes such as dam construction and over exploitation of water in the Urmia basin have influenced the water quality of Urmia Lake during the past two decades. However, due to the lack of continuous measurements from the physiochemical parameters of the lake, little is known about the spatial and temporal variation of its water quality.

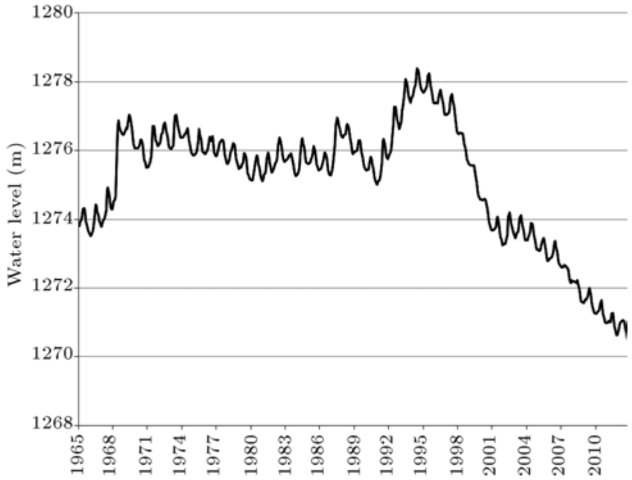

Figure 2. Mean annual water level fluctuation of Urmia Lake measured in Golmankhaneh station (depicted by No.1 on Figure 1) from 1967 to 2010.

During the past decades, several studies have been performed by different organizations on the water quality of Urmia Lake. However, in the majority of these studies either the spatial coverage or the temporal frequency of samplings was not adequate enough to achieve a clear understanding of the water quality in Urmia Lake. For instance, West Azerbaijan Regional Water Company regularly gathers samples from the lake shores and interprets the lake chemistry based on them. As other examples, Aazami-Oscoie [8] and Daneshgar and Ashasi [9] studied the water composition of Urmia Lake at the Heidarabd area (Station 3 in Figure 1) and Sharafkhaneh (Station 2 in Figure 1). However, due to the low water depth and very high salt concentration at the lake shores, the shoreline samples

Table 1. Summary of water quality monitoring studies in Urmia Lake.

Reference	Total number of samples	Number of surface samples	Number of deep samples	Sampling dates		
Kelts & Shahrabi,1986	1	1	0	June-77		
Daneshvar & Ashasi,1995	182	182		May-87	Oct-87	
Ghaheri et al., 1999	6	2	4	Oct-93	Jun-94	
Alipour, 2006	10	3	7	Oct-02	Feb-03	Mar-03
Esmaeili Dahesht et al., 2010	4	4	0		June-05 to Feb-06	
Karbassi et al., 2010	48	48	0	Jun-08		

are not suitable representatives of whole-lake water quality.

Literature data on Urmia lake water chemistry are summarized in Table 1. In all studies performed before 2000, water quality of the lake was described based on only a few samples and hardly any deep water samples. Many attempts have been made over the past decade to examine the lake water quality using more comprehensive sampling schemes. For example, Alipour [10] studied the hydro-geochemistry of the lake and determined seasonal variation of the major anions and cations based on 10 samples collected at three depths in the western half of the lake. He concluded that Urmia Lake was geochemically uniform in the south and north side of the causeway. Later, Esmaeili Dahesht et al. [11] reported results of the measurements of some main water quality parameters of the lake including TDS, chloride, sulfate, magnesium and bicarbonate concentrations based on the two samples from the north, and two samples from the south part of the lake. Subsequently, Karbassi et al. [7] performed a complete water quality analysis based on 48 samples gathered from the lake surface in order to investigate the impacts of desalination on the ecology of Urmia Lake. Besides these studies, few studies was carried out to examine the spatio-temporal variation of Urmia Lake surface temperature (e.g. [12]), which in turn can affect the water chemistry of the lake.

All of these studies are based on datasets collected at different sites or along track lines occupied during cruises. However, environmental managers often require spatially continuous data over the region of interest to make effective and confident decisions. Spatial interpolation methods can be used to overcome such shortcomings by estimating spatially continuous data from discrete data points [13].

A number of methods have been developed for spatial interpolation in various disciplines including mining engineering [14], meteorology [15-17] and environmental sciences [14,18,19]. A bibliographic research carried out by Zhou et al. [20] ranked environmental sciences as the third highest field to use spatial interpolation methods. Nevertheless, there are few studies which have compared different interpolation methods used to determine water quality maps within lakes. For example, Bellehumeur et al. [21] described a geostatistical technique based on conditional simulations to assess pH values on the Canadian Shield. Nas et al. [22] applied Ordinary Kriging to develop spatial distribution maps of total nitrogen and phosphorus, turbidity, Secchi disk depth and chlorophyll-a over Beysehir Lake. Alcântara [23] studied turbidity in an Amazon floodplain lake through OK and wavelet analysis. In another study, Murphy et al. [24] compared three interpolation methods comprising inverse distance weighting, Ordinary Kriging, and a Universal Kriging method to evaluate spatial and vertical distribution of water quality parameters (salinity, water temperature, and dissolved oxygen) in the Chesapeake Bay. They concluded that the Kriging methods generally outperform inverse distance weighting for all parameters and depths. Recently, a study has been performed on the pollution control of three Forks Lake using cluster analysis and inverse distance-weighted interpolation, to determine the spatial distribution of water quality parameters such as pH, NH_3-N, total phosphorus, total nitrogen, permanganate index, transparency, Total Dissolved Solids (TDS), Dissolved Oxygen (DO), and conductivity [25]. Spatio-temporal changes in the total phosphorus concentrations of the Everglades wetland (Robertson) were assessed using an ordinary Kriging spatial interpolator with an acceptable error [26].

At least 42 different spatial interpolation methods have been recognized in various disciplines [27]. Although some methods have been shown to perform better than others, the results appear to be study and site specific, and thus no definite conclusion has been made on which method is the best or most appropriate [24]. Nonetheless, in the field of environmental sciences, ordinary Kriging and Inverse Distance Weighting (IDW) methods are recognized as the most widely used stochastic and deterministic techniques [27,28].

The objective of this study was to develop seasonal maps of Urmia Lake water chemistry using spatial interpolation methods. To accomplish this task, water quality data collected during three sampling periods from 2009-2010 were applied. Next, two conventional interpolation techniques, IDW and OK, were employed and compared using cross-validation to find the most appropriate interpolation scheme for each parameter. Subsequently, applying the proper interpolation technique for each ion, maps of major anions and cations as well as density were developed. Finally, spatial and temporal variations of ion concentrations in Urmia Lake were examined using the retrieved maps and compared with previous water quality studies.

This is the first comprehensive limnological investigation to present spatial distribution of water quality parameters in Urmia Lake and contains several unique aspects, such as its application to a large hyper-saline lake, its reasonably adequate ability to compare parameters on an inter-annual scale, and its comparison of techniques currently being considered for management applications. This study provides insights into the development of water quality data of adequate spatial and temporal resolution to be used for validation purpose in hydrodynamic models. Furthermore, determining water quality distribution along Lake Urmia and its potential effects on the lake fauna can help managers to make informed decisions on suitable restoration plans.

2. Methodology

2.1. Sampling

Selection of sampling points on the lake surface was made using a topographic map with a scale of 1:250,000 on which a 10×10 km rectangular network was designed to cover the entire lake (Figure 1). However, as a result of significant water level decline, vast parts of the lake shores have desiccated and been altered into muddy surfaces covered by saline sediments. It is awkward to take samples from these inshore regions (areas of about 1 m water depth) either by motorboat or hiking. Moreover, water level drop and resultant salt precipitation has caused the formation of salt mounds in some parts of the lake bed which halts navigation of boats. Therefore, it was not feasible to exactly track the designed, regular network. Instead, through cruising along the accessible parts of the lake, samples were collected approximately at 10 km intervals and the locations were recorded using a GPS recorder. The spatial distribution of sampling locations and the depth of samples are shown in Figure 3.

We considered seasonal frequency for sampling between October 2009 and to July 2010. Nonetheless, during the cold season, December to March, harsh climate conditions trigger wind-driven currents along the lake which prohibits the safe use of motor boats. Therefore, excluding the winter, samplings were carried out during the three periods from October 2009 to July 2010 (Table 2).

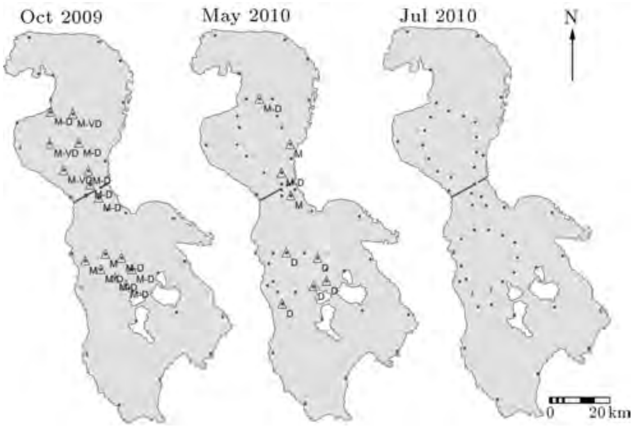

Figure 3. Sampling locations along Urmia Lake, where S, M, D and VD represent surface (0.5 m), middle (1 m), deep (1.5 m) and very deep samples (> 2.5 m).

Table 2. Number and location of sampling points.

Date of sampling	Total number of samples	Number of surface samples	Number of deep samples
2009/10/5-2009/10/7	74	44	30
2010/5/3-2010/5/5	61	50	11
2010/7/18-2010/7/20	52	52	0

Most of the samples were taken from the lake surface (0.5 m depth) with the objective of determining the spatial distribution of water quality parameters within the entire lake. In addition, during the two first sampling periods, several samples were collected from different depths of the lake to examine the vertical distribution of water quality parameters. Information about the number and depth of samples in each period can be found in Table 2.

2.2. Chemical analyses

All collected samples were transferred to the laboratory and analyzed for various physiochemical parameters according to Standard Method protocols [29]. Temperature, pH, and density of the water samples were measured at the sampling sites using a thermometer, a digital pH meter (Hach pH meter) and a density meter (Anton Paar: DMA 35N), respectively. Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) were gravimetrically determined at $105-110^\circ$C. Chloride concentration was determined by silver nitrate ($AgNO_3$) titration, using potassium chromate (K_2CrO_4) solution as the indicator. Sodium and potassium were measured by flame photometry, while the concentration of Ca^{++} and Mg^{++} were obtained

Table 3. Dilution rate of Urmia Lake water samples in physico-chemical tests.

Parameter	Measurement method	Instrument	Dilution rate
[Cl^-]	Silver nitrate titration	–	1:2000
[SO_4^{--}]	Spectrophotometery	Hach, DR 2800 Spectrophotometer	1:1000
[HCO_3^-]	HCl titration	–	–
[Ca^{++}]	EDTA titration	–	1:25
Total hardness	EDTA titration	–	1:100
[K^+]	Flame photometry	Sherwood, model 420 flame photometer	1:2000
[Na^+]	Flame photometry	Sherwood, model 420 flame photometer	1:200

through EDTA titration and HCO_3^- by acid titration. Concentration of SO_4^{--} was also determined using a Hach DR2000 spectrophotometer. As the concentration of the lake anions and cations was high, it was necessary to dilute samples with super pure water. The applied dilution rates for each test are presented in Table 3.

2.3. Developing water quality maps

2.3.1. Interpolation methods

To visualize the spatial patterns of the water quality data within Urmia Lake, two spatial interpolation methods, IDW and OK, were applied. Estimations of nearly all spatial interpolation methods can be represented as weighted averages of sampled data as:

$$\hat{z}(x_0) = \sum_{i=1}^{n} w_i . z(x_i), \tag{1}$$

where $\hat{z}$ is the estimated value of an attribute at the point of interest x_0, z is the observed value at the sampled point x_i, w_i is the weight assigned to the sampled point, and n represents the number of sampled points used for the estimation [19].

Inverse Distance Weighting (IDW) is a deterministic and exact interpolation method which requires few decision parameters. IDW is a robust method that estimates the values of an attribute at unsampled points using a linear combination of values at sampled points weighted by an inverse function of the distance from the point of interest to the sampled points. The assumption is that sampled points closer to the unsampled point are more similar to it than those further away in their values [30]. In IDW, weights can be expressed as:

$$w_i = \frac{1/d_i^P}{\sum_{i=1}^{n} 1/d_i^P}, \tag{2}$$

where:

$$\sum_{i=1}^{n} w_i = 1,$$

in which d_i is the distance between sampled point, x_i, and the estimated point, x_0; p is a power parameter, and n represents the number of sampled points used for the estimation. The accuracy of IDW is mainly determined by the value of the power parameter and search radius [31]. Weights diminish as the distance increases, especially when the value of the power parameter increases. The Inverse Distance Weighting method (IDW) works best with a limited sample size and random data points. Further details on the IDW method can be found in Ashraf et al. [32]. Although the choice of power parameter and neighborhood size is arbitrary [19], they significantly affect the accuracy of the resulting estimations. They can also be determined on the basis of error measurement [33]. The smoothness of the estimated surface increases as the power parameter increases. The most popular choice of power is 2 [34]. In our case, we tested IDW with powers of 1 and 2, and various neighboring radius to optimize the variables of the inverse distance function for various water quality constituents during each sampling period. Selection of optimum variables was performed based on the results of the Leave-One-Out Cross Validation (LOOCV).

Kriging is considered the best linear unbiased interpolation method to estimate the value of regionalized variables at an unsampled location. Kriging assigns weights according to a stochastic function which is calculated based upon the spatial correlation structure of the observations [31]. Kriging makes use of Regionalized Variable Theory (RVT), which postulates that variation is best described by a stochastic surface and defines the value of the random variable Z at x as:

$$Z(x) = m(x) + \varepsilon' + \varepsilon'', \tag{3}$$

with x representing a generic spatial location assumed to vary continuously over some domain of interest, m structural (deterministic) component, ε' the spatially correlated random component, and ε'' spatially uncorrelated random (noise) component.

In Kriging, weights are optimized based on the true spatial structure of the parameter throughout the region of interest, which is unknown. Semivariogram function is used to estimate the actual spatial structure of the parameter within the study area from the spatial structure of the observations. Weights are then obtained by solving the system of equations:

$$\sum_{i=1}^{n} w(i).\gamma(x_i, x_j) + \varphi = \gamma(x_j, x_0) \quad \text{for all } j, \tag{4}$$

$$\sum_{i=1}^{n} w_i = 1, \tag{5}$$

where $\gamma(x_i, x_j)$ represents the value of the semivariogram function for the distance between the points x_i and x_j, $\gamma(x_j, x_0)$ is the value for the distance between x_j and the estimated location x_0, and φ is the Lagrange parameter. The semivariogram function is derived by fitting a semivariogram model to the empirical semivariogram, which can be calculated for all distances h by solving:

$$\hat{\gamma}(h) = \frac{1}{2n} \sum_{i=1}^{n} \left(z(x_i) - z(x_i + h)\right)^2. \tag{6}$$

Several semivariogram models are available and commonly used to estimate semivariograms based on sampled data (e.g. spherical, exponential, linear, Gaussian, power, circular) [35,36].

Kriging can be classified into three types of Simple Kriging (SK), Ordinary Kriging [37], and Universal Kriging (UK). SK assumes a known constant trend, OK assumes an unknown constant trend, and UK assumes a general polynomial trend model. Amongst the different types of Krigings, OK has been most commonly applied in environmental studies [38], and as in Poon et al. [28,37]. OK can be represented with Eq. (3), but with no covariates $m(x)$. The OK approach thus contains just the spatially correlated random component, ε', and the noise term, ε'', accounting for all of the spatial variation in the observations. For more detailed explanation of the Kriging method see [39].

Creutin and Obled [40] discussed that, for low- to medium-density networks, Kriging performed better results than simple weighting methods. However, when the sampling network is dense enough, most interpolation techniques produce similar results [14]. In such high density networks, Kriging is not considerably superior to simpler methods, such as IDW [41]. Consequently, improvements in prediction cannot be obtained by applying more sophisticated methods, but rather by gathering more useful and high quality data [42].

In this study, IDW and OK were applied to derive the spatial distribution of ionic constituents, TDS, and density within Urmia Lake. For IDW, two powers (1 and 2) and five neighborhood radii (20, 25, 30, 35 and 40 km) were tested and compared through cross-validation to find the optimum scheme. Similarly for OK, different types of semivariogram models including spherical, exponential, linear and Gaussian were examined. Then, proper IDW scheme was compared to the OK scheme with appropriate semivariogram using the performance criteria calculated in the cross-validation process.

2.3.2. Evaluation of interpolation techniques

The performance of each of the applied interpolation techniques was evaluated using the cross-validation method, originally proposed by Seaman [43]. In implementing cross-validation, the sample value of a given location is temporarily discarded from the sample dataset, and the interpolation was performed using the remaining samples to generate an estimate at the location of the removed value. This procedure was then repeated for each sample in a data set and the error between the true value and the estimated value was assessed in each run [44].

In this study, cross-validation (LOOCV) was implemented using GS$^+$ Geostatistics for the Environmental sciences version 5.1.1. Several performance measures were calculated during the cross-validation procedure in GS$^+$ in order to evaluate the accuracy of the estimations. Regression coefficient between estimated and actual values, Standard Error (SE) of the regression coefficient which is equal to Root Mean Squared Error (RMSE), the coefficient of determination (R^2), and Standard Error of Prediction (SEP) were used. As the values of the regression coefficient and R^2 approach one and values of SE and SEP become smaller, the accuracy of estimation improves [45]. The RMSE and SEP measures are defined as:

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\hat{z}_i - z_i)^2}, \tag{7}$$

$$\text{SEP} = \text{SD}\sqrt{(1 - R^2)}, \tag{8}$$

where $\hat{z}_i$ and z_i are the predicted and observed sample values, respectively, and n is the total number of samples, and SD is the standard deviation of the actual data.

Among calculated accuracy criteria, RMSE was primarily used to assess the results of cross-validation, while the regression coefficient and R^2 were used as supplementary measures. RMSE is thought to be amongst the best overall measures of model performance, as it summarizes the mean difference between the units of observed and predicted values [46].

In this study, the described performance measures were applied to: (1) compare different IDW schemes, 2) select the optimum semivariogram model for OK,

Table 4. Results of water quality analysis for outstanding surface samples during the three samplings in Urmia Lake.

Sampling period	Sampling points	Density (g/L)	TDS (g/L)	Cations (g/L)				Anions (g/L)			Sum of cations $\times 10^3$ (meq/L)	Sum of anions $\times 10^3$ (meq/L)	Diff%	Measured TDS/ calculated TDS
				Na^+	K^+	Mg^{++}	Ca^{++}	Cl^-	SO_4^{--}	HCO_3^-				
Oct-09	c2	1.225	375	90.16	4.97	21.76	0.18	145.79	37	1.15	5.87	4.90	9.0	1.2
	d2	1.225	371	87.40	5.53	24.79	0.17	166.62	38	1.15	6.02	5.50	4.5	1.1
	e2	1.225	390	86.02	6.06	20.54	0.17	166.62	38	1.15	5.62	5.50	1.0	1.2
	d3	1.225	393	90.62	5.70	25.39	0.18	156.20	45	1.44	6.21	5.36	7.3	1.2
	e3	1.223	393	88.78	5.40	22.37	0.16	166.62	44	1.32	5.87	5.63	2.1	1.2
	f3	1.225	404	94.30	5.93	28.43	0.17	169.95	44	1.29	6.63	5.73	7.3	1.2
	h3	1.237	399	81.88	6.69	27.23	0.14	166.62	53	1.59	6. 01	5.82	1.6	1.2
	i4	1.237	400	74.06	6.75	33.90	0.16	145.79	58	1.99	6.23	5.35	7.6	1.2
May-10	c2	1.215	368	97.98	3.08	24.25	0.09	173.86	34	0.95	6.36	5.62	6.2	1.1
	d2	1.218	392	95.68	3.08	24.25	0.08	173.86	34	0.98	6.26	5.62	5.4	1.2
	e2	1.216	376	105.80	3.08	24.25	0.09	195.59	34	0.96	6.70	6.23	3.6	1.0
	d3	1.210	391	99.82	3.08	20.61	0.08	184.73	34	0.93	6.14	5.93	1.8	1.1
	e3	1.210	368	103.96	3.08	20.60	0.09	173.86	32	0.90	6.32	5.58	6.2	1.1
	f3	1.200	360	111.78	3.08	23.65	0.07	173.86	38	0.88	6.91	5.70	9.6	1.0
	h3	1.175	358	80.04	2.31	19.39	0.08	152.13	32	0.75	5.16	4.96	1.9	1.2
	i4	1.191	356	91.54	2.56	19.37	0.11	173.86	28	0.85	5.67	5.49	1.5	1.1
Jul-10	c2	1.237	409	105.34	4.10	26.07	0.08	190.21	38	0.84	6.86	6.16	5.4	1.1
	d2	1.237	407	109.02	3.08	26.67	0.10	190.21	40	0.84	7.05	6.21	6.4	1.1
	e2	1.236	413	104.88	3.59	25.47	0.08	190.21	38	0.84	6.78	6.16	4.8	1.1
	d3	1.235	401	93.84	3.59	26.08	0.07	190.21	38	0.84	6.35	6.16	1.5	1.1
	e3	1.235	408	97.52	4.10	29.12	0.06	190.21	42	0.88	6.78	6.25	4.1	1.1
	f3	1.235	413	96.60	4.10	25.46	0.09	190.21	36	0.84	6.43	6.12	2.5	1.2
	h3	1.22	395	103.50	2.82	22.41	0.11	182.02	32	0.74	6.45	5.81	5.2	1.1
	i4	1.229	403	112.24	3.08	21.77	0.16	182.02	30	0.76	6.78	5.76	8.1	1.2

and (3) compare between the most appropriate IDW and OK schemes.

3. Results and discussion

3.1. *Results of water quality analysis*

3.1.1. *Water quality data*

Results of the water quality analysis for eight surface samples from different parts of the lake are tabulated in Table 4. As there were a large number of samples, data for nominated samples from different regions of the lake (samples c_2, d_2, e_2, c_3, and d_3 in the north; f_3 in the middle, near the causeway's opening; h_4 and i_4 in the south of the lake) are presented (see sampling grid in Figure 1). Moreover, results of the lake water temperature and density analyses at various depths during May 2010 are presented in Table 5.

3.1.2. *Checking for correctness of analysis*

To control the correctness of chemical analyses, ion balance of each sample as well as its TDS ratio was checked according to the Standard Methods [29]. As described in the following sections, the Standard Methods correctness criteria were met in all of the chemical analyses. The anion and cation sums, when expressed as milli-equivalents per liter (meq/L), must approximately balance. The balance is checked based upon the percentage difference (Diff) which is defined as follows:

$$\text{Diff} = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} \times 100. \qquad (9)$$

Regarding the concentration of total anions, Diff should meet the typical criteria for acceptance of the ion balance check (Table 6). Owing to the high concentration of ionic constituents in Urmia Lake (anion sum=5000-6000 meq/L), the calculated differences fall beyond the criteria advised by [29]. Consequently, the maximum acceptable difference was considered to be 10%. The percent difference between anions and cations was calculated for all the samples, and acceptable balances amongst anions and cations were observed (Table 4).

To perform TDS check, the ratio of measured TDS to the calculated TDS, which is the sum of concentrations of major anionic and cationic constituents (in milligrams per liter), should fall between 1 and 1.2. If the measured value is less than the calculated one, the higher ion sum and measured values were considered suspicious and the sample should be reanalyzed. If the measured TDS concentration is more than 20% higher than the calculated one, the low ion sum is doubtful and selected constituents should be reanalyzed. TDS control was done for all 185 samples and the over range samples were reanalyzed.

3.2. *Validation of the spatial interpolation methods*

For those water quality parameters of the lake which OK outperforms IDW methods, the optimum fitted variogram is illustrated in Figure 4. Table 7 also summarizes the comparison results for the major anions and cations, TDS, and density during the three

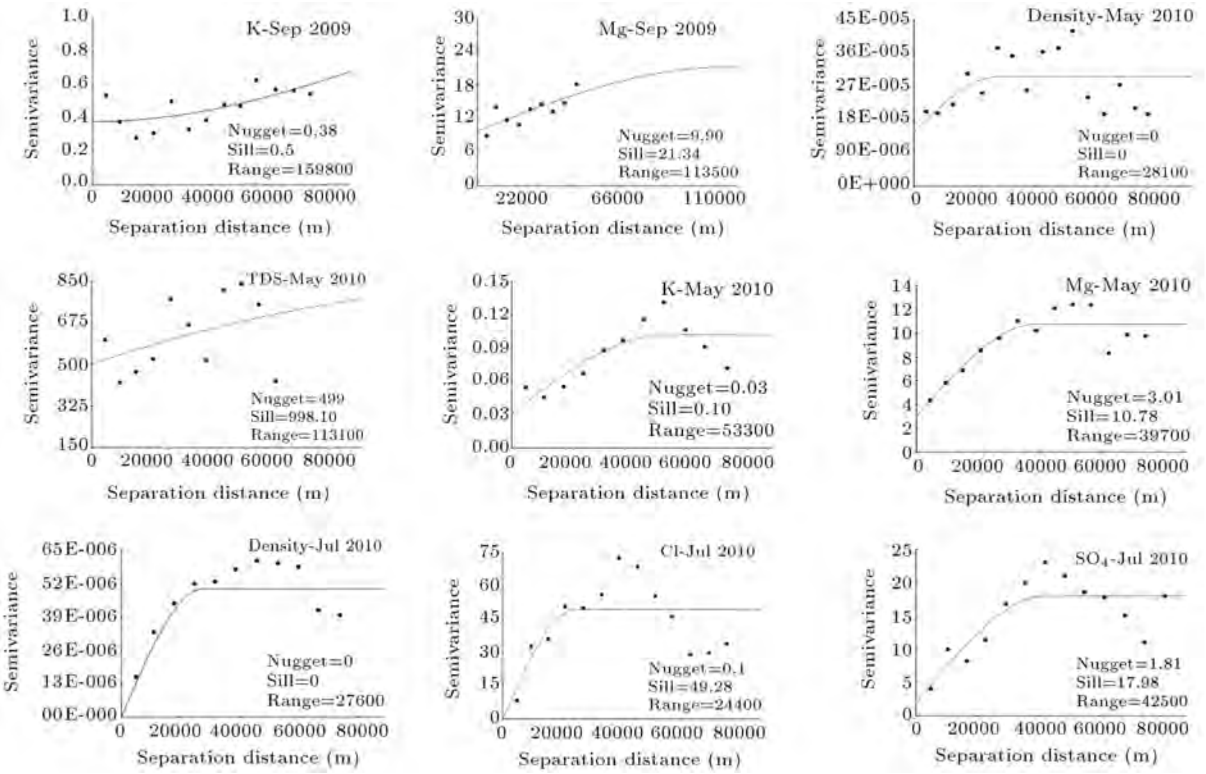

Figure 4. Experimental and fitted variograms for some water quality parameters of Urmia Lake.

Table 5. Temperature and density of Urmia Lake water at various depths during May 2010.

Location	Sampling depth (m)	Date	Time	T_{air} (C)	T_w (C)	ρ (g/cm^3)	pH
North of the causeway	0.5	3-May-10	12:53	16.4	17.8	1.20	7.4
	1.5				17.8	1.21	7.3
	3				17.7	1.21	7.3
Northeast	0.5	3-May-10	13:10	1 6.1	17.6	1.20	7.3
	2				17.6	1.21	7.4
North-deep water	0.5	3-May-10	14:00	1 9.1	16.9	1.22	7.3
	4				16.9	1.22	7.3
	6				16.9	1.22	7.3
South of the causeway	0.5	3-May-10	15:50	1 5.8	18.0	1.20	7.5
	2				18.8	1.21	7.4
South	0.5	5-May-10	11:00	1 7.7	18.7	1.22	7.4
	2				18.5	1.22	7.4
South-near the islands	0.5	5-May-10	11:20	1 8.3	19.9	1.21	7.4
	1.5				19.4	1.21	7.4
South west	2	5-May-10	12:00	1 9.5	19.2	1.18	7.6
	2.5				19.4	1.21	7.4

Table 6. Acceptable difference between anions and cations in common water and wastewater samples (APHA, 1998).

Anion sum (meq/L)	Acceptable difference
0-3	±0.2 meq/L
3-10	±2%
10-800	5%

sampling periods. The optimum semi-variogram models show that for all elements, the ranges are higher than 20 km. This means that a 20 km sampling design is suitable to capture the spatial variation in the lake water chemistry. Moreover, comparing the semi-variogram models of K^+ and Mg^{++} between September 2009 and May 2010, the apparent shorter ranges for spring are because of the freshwater inflows to the

Table 7. Comparison of the proper IDW and OK interpolation scheme for the seven water quality parameters of Urmia Lake during the three sampling periods.

Sampling period	Water quality parameter	Slope of the regression line		RMSE / Standard Error (SE)		R^2		SEP		Selected method	
		IDW	OK	IDW	OK	IDW	OK	IDW	OK	Method	Description
9-Sep	Density	0.89	0.94	0.15	0.21	0.60	0.32	0.00	0.56	IDW	P2,[a] r30k
	TDS	0.92	1.08	0.23	0.27	0.28	0.27	12.83	12.86	IDW	P2, r20k
	Na	0.62	0.62	0.23	0.44	0.15	0.05	4.34	4.58	IDW	P1, r20k
	K	0.81	1.05	0.20	0.24	0.27	0.29	0.57	0.57	OK	Gauss
	Mg	0.75	0.92	0.22	0.25	0.22	0.24	3.31	3.23	OK	Spherical
	Cl	0.82	0.79	0.23	0.33	0.23	0.12	11.58	12.39	IDW	P2, r20k
	SO_4	0.97	1.04	0.18	0.19	0.42	0.41	4.72	4.75	IDW	P2, r25k
10-May	Density	1.12	1.09	0.19	0.17	0.43	0.48	0.01	0.01	OK	Spherical
	TDS	0.84	1.09	0.20	0.26	0.26	0.26	20.97	20.94	OK	Exponential
	Na	0.98	0.94	0.18	0.20	0.39	0.32	6.95	7.32	IDW	P2, r20k
	K	0.89	1.01	0.13	0.14	0.50	0.51	0.20	0.20	OK	Spherical
	Mg	0.94	0.97	0.18	0.17	0.36	0.42	2.44	2.32	OK	Spherical
	Cl	1.01	0.94	0.20	0.19	0.35	0.33	12.22	12.41	IDW	P1,r20k
	SO_4	0.8	1 0.84	0.23	0.25	0.21	0.19	3.74	3.76	IDW	P2, r20k
10-Jul	Density	0.98	0.93	0.13	0.11	0.55	0.59	0.00	0.00	OK	Spherical
	TDS	0.93	0.88	0.15	0.15	0.43	0.42	4.58	4.63	IDW	P2, r40k
	Na	0.91	0.98	0.19	0.25	0.32	0.24	5.02	5.33	IDW	P2, r25k
	K	0.94	0.98	0.22	0.23	0.28	0.27	0.50	0.50	IDW	P1,r20k
	Mg	0.96	0.80	0.12	0.11	0.55	0.51	1.28	1.33	IDW	P1,r35k
	Cl	1.02	0.98	0.12	0.09	0.60	0.73	4.30	3.56	OK	Spherical
	SO_4	0.94	0.95	0.13	0.11	0.53	0.60	2.65	2.42	OK	Spherical

[a] P and R represent the optimum power and neighborhood radius (in terms of km) for IDW method, respectively.
For OK the superior semi-variogram models and their parameters are mentioned.

lake. Therefore, if a coarser sampling network is chosen for each constituent, the sampling distance should be reduced for the spring samples.

The last two columns of the Table 7 show the superior interpolation method and related parameters applied to derive water quality maps. The cross-validation graphs for all ionic constituents, TDS and density are also displayed in Figure 5. Although it is important to have independent measurements to validate the prediction results [47], the limited number of water quality samples along the large areal extent of the lake inhibited us from dividing samples to the calibration and validation sets. Instead, the LOOCV approach was used to compare the interpolation models. Hence, adding to the number of samples can help to improve the validation procedure of the models based on independent data.

3.3. *Ionic composition of the lake*

According to the water quality analysis, Na^+, Mg^{++}, K^+, and Ca^{++} are the main cations while Cl^-, SO_4^{--}, and HCO_3^- are the dominant anions. Stumm and Morgan [48] noted that, in freshwater and marine systems, predominant cations and anions appear in the following order of dominance: $Ca^{++} > Mg^{++} > Na^+ > K^+$, $HCO_3^- > SO_4^{--} > Cl^-$, $Na^+ > Mg^{++} > Ca^{++} > K^+$, and $Cl^- > SO_4^{--} > HCO_3^-$, respectively. Consequently, the dominant ions of Urmia Lake match with that of typical sea waters, except for the potassium ion concentration which exceeds the calcium concentration in the lake.

Ionic compositions of Urmia Lake during the three sampling periods were calculated based on the average values of the anions and cations along the lake surface (Figure 6). The lake water comprises of 72-84% sodium and chloride, 15-23% magnesium and sulfate ions, 2-5% potassium, and less than 1% calcium and bicarbonate ions. Moreover, the ionic composition of the lake does not change noticeably between the northern and southern parts. Furthermore, no significant temporal variation in the ionic composition was recognized.

3.4. *Spatio-temporal variation of water quality parameters*

After selection of the proper interpolation methods for each individual parameter, final maps were created

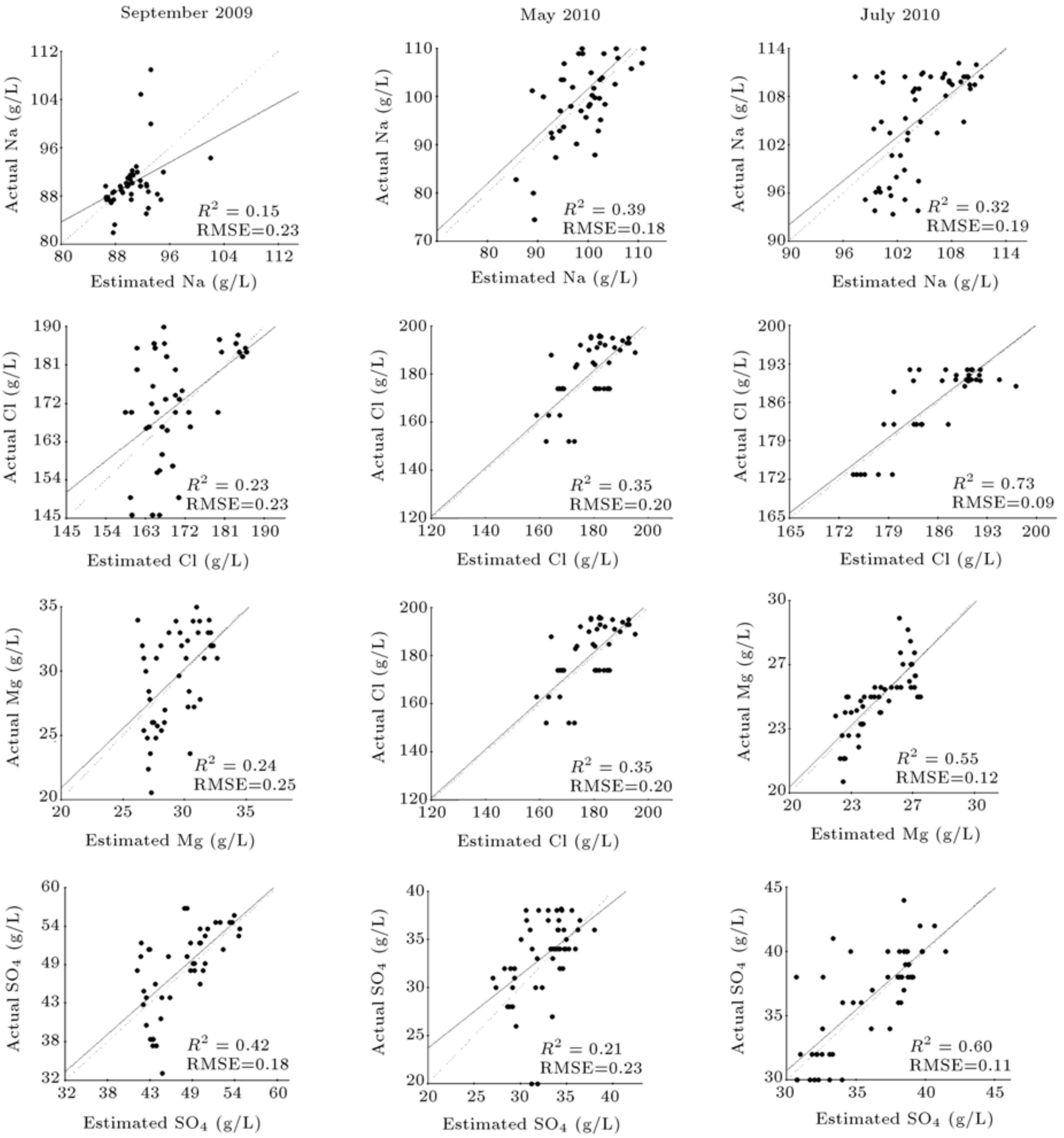

Figure 5. Validation of the predicted ionic concentrations; TDS and density of Urmia Lake water during the three samplings between October 2009 and July 2010.

using the software ILWIS 3.3 [49]. Distribution of major cations (Na^+, Mg^{++} and K^+) and anions (Cl^-, SO_4^{--}) as well as density and TDS in Urmia Lake during October 2009, May, and July 2010 are displayed in Figures 7 and 8. The minimum, maximum, average, and standard deviation of each parameter are also presented.

In terms of spatial variation, three different zones can be distinguished: (1) lake shores, (2) the northern part, and (3) the southern part. The spatial distribution of anions and cations along the lake is principally affected by the volume and direction of rivers inflow to lake as well as the bathymetry. Other possible factors such as wind and internal currents can also play a minor role [50].

Generally, the lake shores can be distinguished by having higher concentrations for nearly all ionic constituents during the three sampling periods. In October 2009, for all water quality parameters, the northern part of the lake had lower concentrations than the southern part. Since the rivers inflow during this time of the year is minimal, the spatial distribution of anions and cations is most likely determined by the lake bathymetry. Therefore, deeper parts of the lake in the center of the northern and southern section seem to have lower solute concentrations. Moreover,

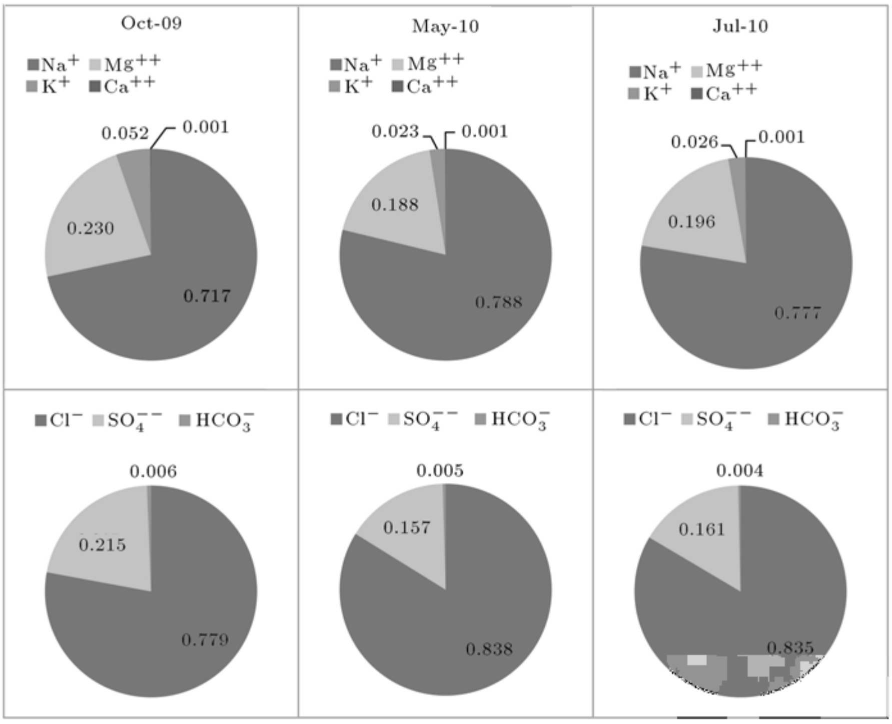

Figure 6. Ionic composition of Urmia Lake during three samplings.

since the southern section of the lake is shallower, deepening towards the north [10], concentrations of all ions decrease spatially from the south to the north. The same spatial pattern was also observed for density and TDS.

In May 2010, when the lake level was at its maximum (Figure 9), rivers discharge had a more profound effect than topography in determining the spatial pattern of Urmia Lake water chemistry. As most of the freshwater inputs to the lake are from the Shahar Chay River in the west, the anion and cation concentrations in the south decline significantly, so that the northern section becomes denser (see Figure 7). Furthermore, standard deviation (Std. dev.) of the sodium and chloride ions as well as the density is highest in May, indicating a wide range of values resulting from the difference between the fresh water and saline water chemistry.

In July 2010, both the rivers discharge and topography played roles in the distribution of ionic constituents along the lake. However, the role of rivers inflow was moderate. For all ions except sodium, the southern section remains slightly more dilute compared to the north. Density and TDS are nearly evenly distributed along the lake surface.

Additionally, analysis of the deep samples (from the depths of 1.5, 2, and 3 meters) collected in May 2010 (Table 5) revealed that the lake was not stratified thermally and differences in the concentrations of ionic constituents with depth are negligible. Since the lake is not stratified during the spring, when the maximum density difference is expected because of the freshwater inflows to the lake, homogeneous distribution of anions and cations with depth can be taken for granted during all seasons.

Temporally, sodium and chloride concentrations constantly increased from October 2009 to July 2010. In contrast, maximum concentrations of sulfate and magnesium ions were observed in October 2009. In May 2010, concurrent with the rise in water level, concentrations of Mg^{++} and SO_4^{--} decreased. Then, following the water level drop in July 2010, their concentrations increased slightly. Similar temporal variations were evident for potassium. Maximum values of TDS and density were observed in October 2009. In May 2010, as a result of increased rivers inflow (Figure 5), the lake becomes diluted in terms of TDS and density. From May to July 2010, the average concentrations of all ionic constituents increased, leading to an increase in the density and TDS of Urmia Lake. This can be inferred by the water level drop of about 25 cm, which is probably due to the limited river inflows and increased evaporation.

In October 2009, Na^+ and Cl^- were the dominant cation and anion, respectively (Figure 4). Na^+ and Cl^- were lower in the next two sampling periods, while Mg^{++} and SO_4^{--} were at their maximum concentrations. This is likely due to the salt dissolution/precipitation mechanism in Urmia Lake. However, in order to confidently discuss the roots of such variation, information about the mineralogy of the lake sediment is required. However, such information could

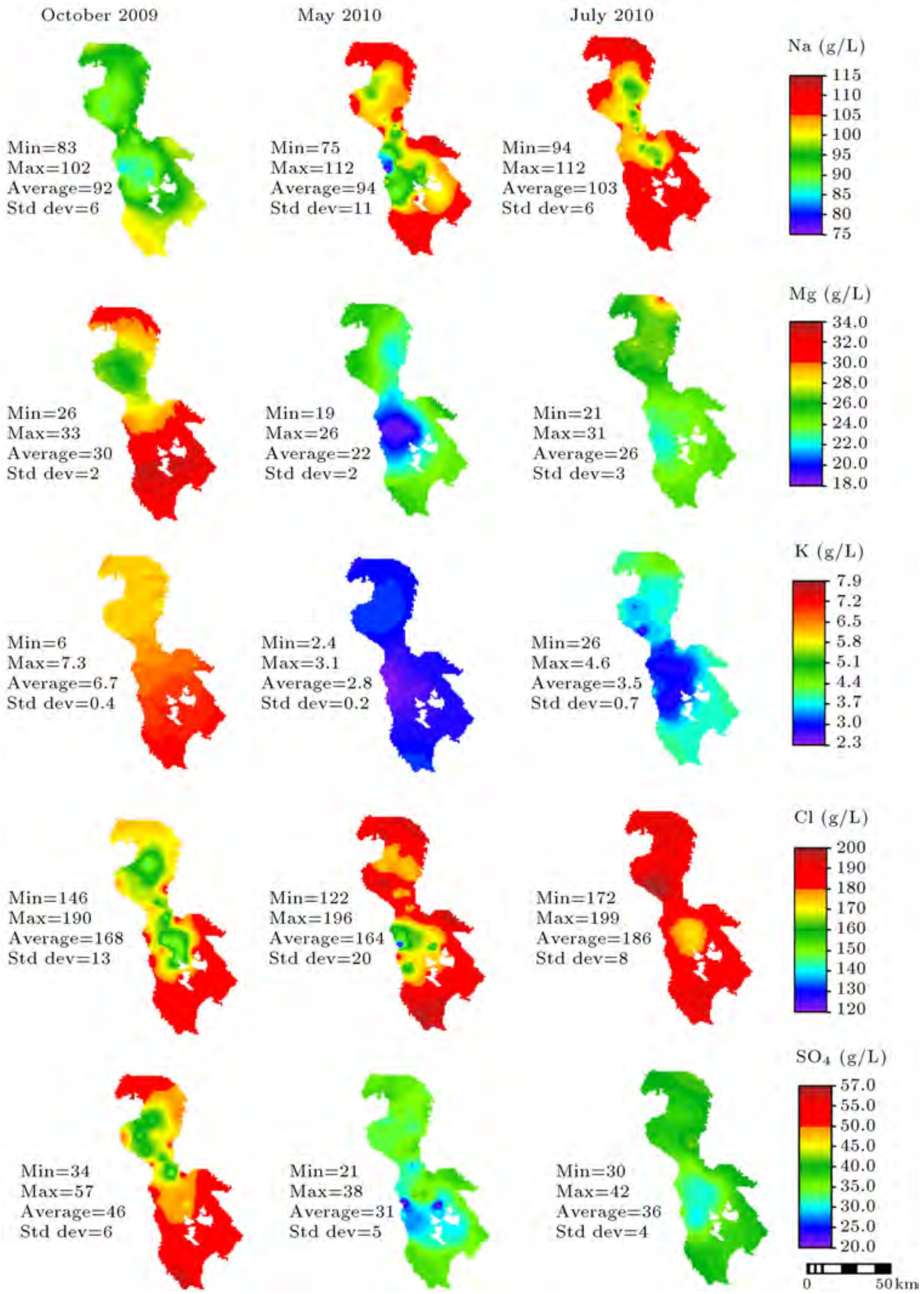

Figure 7. Map of major ions concentration in Lake Urmia during October 2009, May and July 2010.

not be found for Urmia Lake, and investigation of lake sedimentation and dissolution mechanisms is beyond the scope of this study. Nevertheless, this represents a gap in knowledge that should be further addressed in order to improve our current understanding about the chemistry of Urmia Lake.

3.4.1. Comparison to previous studies

To compare the results of the current work with the previous water quality studies, two aspects were considered: the spatial distribution of parameters, and the average salinity variation. For comparison of the spatial patterns of ionic constituents along the lake, the studies of Alipour [10] and Karbassi et al. [7] were used (Table 1). Although both studies relied on discontinuous data of the lake ionic constituents, there is spatially sufficient data of the lake chemistry to be compared with the extracted water quality maps from this work.

Alipour [10] presented distributions of K^+ and Na^+ concentrations in the western half of the lake in October 2002. For both cations, the southern part of

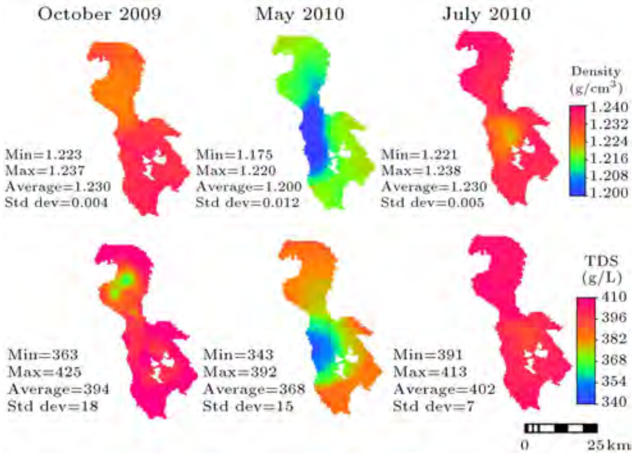

Figure 8. Spatial distribution of density and TDS within Urmia Lake.

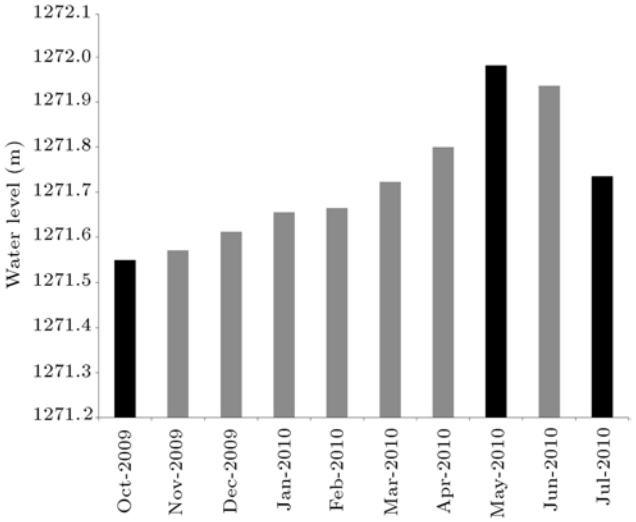

Figure 9. Water level fluctuation in Urmia Lake between October 2009 and July 2010.

the lake was reported to be more concentrated than the northern part. The potassium and sodium maps derived from our study in October 2009 show the same pattern.

Based on the study of Karbassi et al. [7], samples collected in June 2008 show that the average concentration of Mg^{++}, K^{+}, Cl^{-}, and SO_4^{--} ions in north are higher than in the south. Na^{+} concentrations in the interior part of the lake, in both the southern and northern sections, had the lowest concentrations. Their results are consistent with our findings from July 2010.

To examine the long term water quality variation of Urmia Lake, TDS was used as a water quality indicator. TDS has been measured in nearly all water quality studies, and most samplings have been performed between the summer and autumn. Therefore, the summer and autumn samples from various studies were used for comparison.

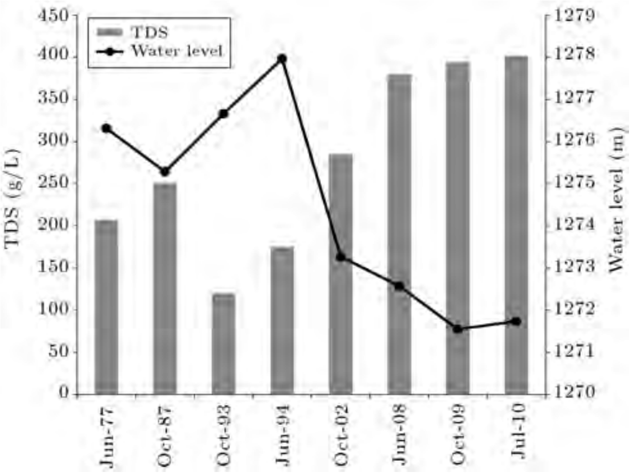

Figure 10. TDS and water level variations in Urmia Lake between 1977 and 2010 from several water quality studies.

From Figure 7 it can be seen that TDS levels of the lake have steadily increased between 1977 and 2010, doubling from 1977 to 2010. This constant increase in the lake salinity is due to the negative water balance since 1977 (Figure 10). However, in the coming years, this growing trend will be ceased since the lake is already supersaturated with respect to some salts, mainly halite [7].

We also compared results with results of the hydrodynamic models developed for Urmia Lake. Historically, several attempts have been made to quantify Urmia Lake hydrodynamics using 2D models [51-55]). Most recently, Zeinoddini et al. [50] investigated flow patterns and salinity distribution along the lake surface in the period from 1994 to 2002 using a 3D hydrodynamic model. They stated that their 3D model is superior to 2D models since it considers vertical variations in velocity and flow. Based on their results, wind was recognized as the dominant climatic factor affecting water flow regime in the lake. However, it has a relatively minor effect on the salinity condition of the lake (less than 4%). On the other hand, river discharge, evaporation, and rainfall were found to be the prevailing hydrological parameters affecting salinity distribution in the lake [50]. They found that in the spring, due to rivers inflow to the southern sections, the north part had a higher density and salinity. Whereas, in summer and autumn, interior parts of the lake have higher salinity compared to the shores, which are affected by the rivers inflow. During winter months, the lake is almost homogeneous in terms of salinity [50,53].

However, apart from similarities in the temporal variation of the lake salinity, our findings contradict the results of the hydrodynamic models in several aspects. First, in summer and autumn, the northern part is slightly less saline than the south. Second, the salinity concentration is generally lower in interior parts of the lake than along the shores. The differences arise from the variations in the lake condition during the recent

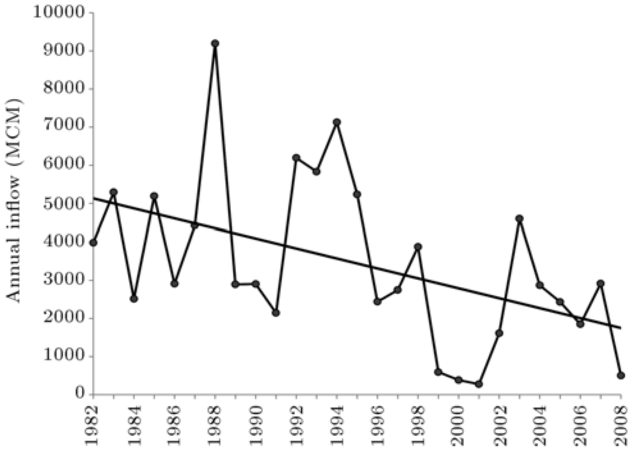

Figure 11. Variations of upstream rivers inflow to Urmia Lake during 1982-2008.

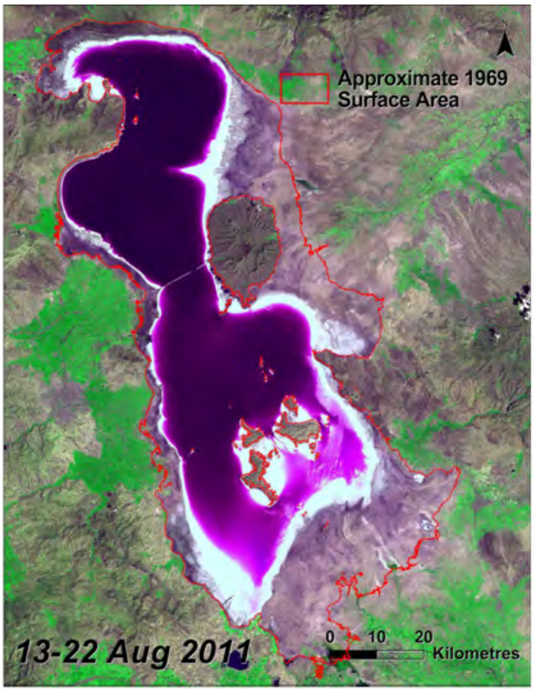

Figure 12. Landsat satellite images of Urmia Lake [4]. The lake boundary change between 1969 and 2011 is demonstrated.

decade, including a remarkable decline in freshwater inflows (Figure 11), as well as the substantial drop in water level (more than 2 meters). There has been significant retreat from the lake shores, so that vast areas of the shore have converted to salt-covered, muddy wastelands which absorb freshwater inflows and prohibit them from entering the lake (see Figure 12). Therefore, except some parts where the river mouth has not yet been dried (e.g. Shahar Chay mouth in the west), river discharges cannot considerably alter the salinity pattern within the lake. Taking into account the present situation of the lake, salinity is mainly determined by the lake bathymetry rather than the river inflows, particularly in dry seasons. Thus, interior, deep parts of the lake have lower salinity concentrations compared to the shores. Likewise, since the northern part is deeper than the south, when river inflows from the south are restricted, the southern section remains denser.

4. Conclusions

Urmia Lake, which is of national and international importance, has experienced a dramatic water level decline in recent years. This negative water balance has strongly influenced the salt content within the lake. The objective of this study was to characterize the spatial heterogeneity and temporal change of physiochemical parameters within Urmia Lake by means of two spatial interpolation methods, IDW and OK. The ionic constituents of Urmia Lake were measured in 185 samples during three sampling periods from October 2009 to July 2010. Then, based on the appropriate spatial interpolation scheme, water quality maps were developed and used to examine the spatial and temporal variations. The main conclusions of this study are:

- The dominant ionic composition of Urmia Lake is as follows; Cl$^-$, Na$^+$, SO$_4^{--}$, Mg^{++}, K$^+$, HCO$_3^-$ and Ca^{++}, respectively. No significant spatial and temporal variations in the ionic composition of the lake were recognized.
- Comparison of ionic constituents using the IDW and OK interpolation techniques indicates that the superior method differs between parameters and season. Thus, no general method can be applied to individual water quality parameters.
- Monitoring temporal fluctuations of the major ions showed that the lowest concentrations of sodium and chloride occurred in October 2009 while the maximum values were observed in July 2010. In contrast, maximum and minimum concentrations of sulfate and magnesium occurred in October 2009 and May 2010, respectively.
- Rivers discharge, bathymetry, and salt precipitation/dissolution mechanism were recognized as the three fundamental factors controlling the spatial pattern of Urmia Lake chemistry. During the spring, the chemical distribution patterns along the lake are dominated by inflows from the surrounding rivers, while in dry seasons, the role of the other two factors becomes stronger.
- It was found that the lake density varies between 1.18 and 1.24 g/cm^3 depending on the region and season, which is much higher than the density of open ocean water. Although freshwater inflows during spring may dilute the lake water in the short

term, they are not significant enough to stabilize the lake in this condition.

- The salinity level of the lake has been consistently increasing since 1977, so that TDS concentration has been doubled from 1977 to 2010. Historically, the salinity concentration of the lake is highly dependent upon the lake water level, and currently the lake is nearly saturated with several minerals.

Results of the previous hydrodynamic models cannot be applied to investigate the flow and salinity patterns of the lake since they relied on the water quality data with inadequate spatial and temporal distribution. To have a clear and sufficient understanding of the lake dynamics, models should be updated and validated based on currently available water quality data.

To improve predictions of the spatial distribution of the lake chemistry, we suggest considering the lake bathymetry as a covariate through using hybrid interpolation methods such as regression-Kriging [56] or Linear mixed models [57]. Moreover, investigation of the effect of considering the temporal correlation between water quality parameters through the spatial interpolation on the quality of predictions is recommended. It is also crucial to investigate salt precipitation/dissolution mechanism in Urmia Lake as one of the foremost factors influencing its chemistry. Inclusion of such mechanisms in the spatio-temporal variations of ionic constituents requires information about the mineralogy of the lake sediments. However, long term monitoring of the lake sediment is currently lacking but highly recommended.

This study demonstrates the successful application of interpolation techniques to analyze spatio-temporal variation of lakes water chemistry. This shows a great potential to increase the understanding of water quality variation in complex aquatic systems. Results of such research can assist in the implementation of adaptive management and restoration projects in large lakes by providing new insights and information to managers.

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