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ORIGINAL PAPER

Assessment of heavy metal pollution in Köyceğiz-Dalyan coastal lagoon watershed (Muğla) SW Turkey

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Abstract

This study is carried out to assess the water pollution in Köyceğiz-Dalyan Coastal Lagoon Watershed located near the Mediterranean Sea in Muğla province, SW Turkey, by using heavy metal pollution index (HPI). A total of 30 samples were collected from the lakes, streams, groundwaters, the subaqueous hot and cold springs, and on-land hot springs, and Cr, Fe, As, Sb, and Pb concentrations were determined. Elevated concentrations of Fe, As, and Pb were detected in most of the samples; the sources of which are either the natural or anthropogenic discharge of the geothermal springs and seawater mixing. As and Pb concentrations in some locations are found to exceed both acute and chronic exposure criteria for aquatic life, posing a threat to the species hosted by these environments. To determine the magnitude of pollution, HPI calculations were carried out. The average and maximum HPI values for the cold waters are 297.1 and 1162.9, respectively, both of which are higher than the critical pollution index value. The highest HPI values are observed in samples taken from the Dalyan Channel and Alagöl Lake. In general, pollution levels increase from north to south, reaching the maximum value at the outlet point, due to the increased contribution from thermal water discharge and mixing with seawater.

Keywords Heavy metal pollution index · Lake water · Geothermal water · Subaqueous spring · Mediterranean Sea · Turkey

Introduction

Pollution of freshwater sources is an issue that should be taken seriously, considering the fact that it threatens access to water, vital to sustaining life for almost all living things. The cause of freshwater contamination is generally human activity, such as industrial, mining, domestic, and agricultural works, leading to the generation of vast amounts of wastewater. Geothermal activities (either natural discharges or human-induced activities like electricity production) are also considered a source of contamination. The chemical content of geothermal waters with high concentrations of dissolved heavy metals like arsenic may cause the contamination of surface waters and groundwater. In fact, contamination of groundwater reserves (Gemici and Tarcan 2004; Gunduz and Simsek 2007; Aksoy et al. 2009; Jiang et al. 2016) and surface waters (Birkle and Merkel 2000; Dogdu and Bayari 2005; Gunduz et al. 2010) from geothermal activities have been widely studied throughout the world. In Turkey, although discharge of the waste waters produced as a result of geothermal activity is banned by Turkish Law governing Geothermal Resources and Natural Mineral Waters (LGRNMW 2007), there are some reported cases of uncontrolled waste geothermal fluid discharge (Gunduz et al. 2010; Baysal and Gunduz 2016).

The heavy metal pollution in surface waters and groundwaters related to geothermal activities and other sources (natural or anthropogenic) can be assessed by using the heavy metal pollution index (HPI). HPI is utilized to represent the heavy metal pollution status of freshwaters (Mohan et al. 1996; Edet and Offiong 2002; Prasad and Sangita 2008; Kumar et al. 2012; Abou Zakhem and Hafez 2015; Bhuiyan et al. 2016) since it easily identifies the combined influence of the selected pollution parameters and the total quality of a water sample with respect to heavy metals (Prasad and Jaiprakas 1999). HPI can be used by decision makers and

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environmental managers as a practical and an effective guiding tool (Prasanna et al. 2012).

The study area is situated on the Köyceğiz-Dalyan Coastal Lagoon Watershed (KDCLW) in the Western Mediterranean Region of Turkey (Fig. 1). The area was declared a Special Protection Area in 1988 by the government due to its unique and distinguishing natural features. Due to its natural importance, this area attracted many scientists and numerous studies have been carried out in the region. However, none of these studies concentrated on the causes of heavy metal pollution of the waters located in the KDCLW, although it is important to assess the degree of pollution to ensure the sustainability of the unique aquatic ecosystem of this area. Moreover, if the anthropogenic inputs of pollution can be put forward, authorities can be warned against the ecological risks of the pollution in the area and some measures can be taken. Therefore, this study aims to reveal the heavy metal pollution status of the waters in the KDCLW by using the heavy metal pollution index. To achieve this, samples from the lakes, cold and hot springs (on-land and subaqueous), channel and stream waters were collected and the concentrations of selected elements (As, Cr, Fe, Pb and Sb) were determined. These

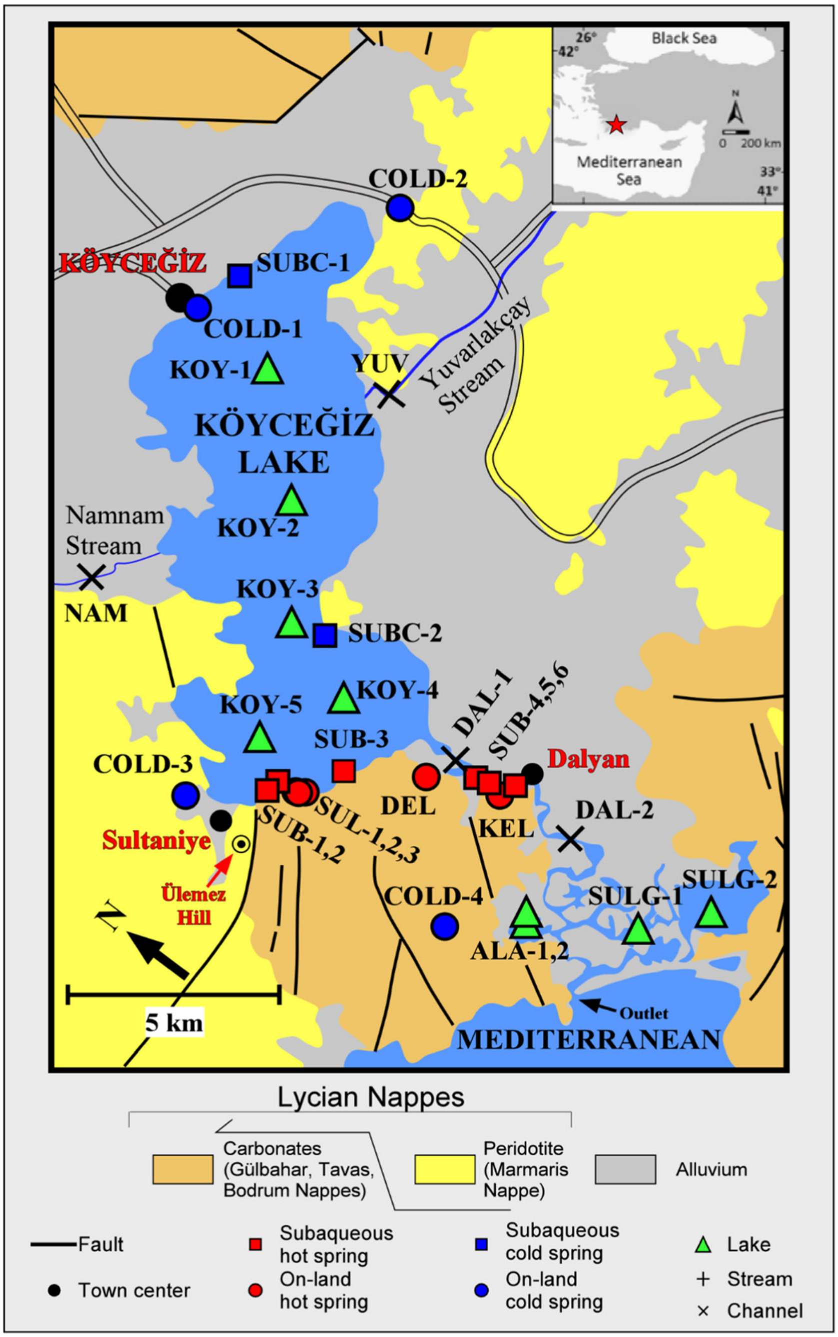


Fig. 1 Geological map of the study area. Sampling locations are marked on the map (Modified from Avşar et al. 2017)

concentrations were then used to assess the overall pollution status of different aquatic bodies together with the sources of pollution in the area.

Description of the study area

KDCLW is located in Muğla province of Turkey. There are three lakes (Köyceğiz, Sülüngür and Alagöl) and two streams (Yuvalakçay, Namnam) in the watershed (Fig. 1). Köyceğiz Lake has an area of 52 km^2 and is connected to the Mediterranean via the 10-km-long Dalyan Channel.

Köyceğiz Lake water discharges into the Mediterranean via the Dalyan channel. In the south east of Köyceğiz Lake, there are two relatively small lakes, Sülüngür (3 km^2) and Alagöl (0.55 km^2) (Fig. 1). İztuzu Beach (100–150 m wide and 4–4.5 km long) is located at the point where Dalyan Channel reaches the Mediterranean Sea. İztuzu beach, where Loggerhead Turtles (*Caretta caretta*) lay their eggs, is an important location. The climate of the study area is a typical Mediterranean climate with hot, dry summers and warm, rainy winters. The mean annual temperature and rainfall are recorded as being 18.3 °C and 1083 mm, respectively (Ertürk et al. 2017). There are several on-land and subaqueous hot and cold springs in the study area; in fact, the exact locations of the subaqueous hot springs were discovered by Avşar et al. (2014a, b) and the details of the discovery method were given in a recent contribution by Avşar et al. (2017).

One of the most comprehensive studies on the hydrogeochemistry of Köyceğiz Lake was conducted by Bayarı et al. (1995). It was found out that Köyceğiz Lake is composed of two hydrochemically different water layers, and the boundary of these two layers is located 10 m below the water surface. This indicated the existence of the subaqueous springs and stated that the bottom water was most probably fed by the subaqueous hot springs. Kazanci and Girgin (2001) studied the algae diversity and the chemistry of on-land hot springs located around Dalyan and Köyceğiz and indicated the necessity for protection of the area. Another detailed study about the thermal springs in the study area was conducted by Gökgöz and Tarcan (2006). Thirty-eight samples from the lake, sea, stream, and spring waters were evaluated and a conceptual model of the geothermal system was proposed. According to this model, meteoric water mixes with seawater, percolates down via young, normal faults, is heated at depth with geothermal gradient, and ascends to the surface forming hot springs. In addition, Gökgöz and Tarcan (2006) suggested that the thermal waters mix with seawater and the mixing ratios range between 24 and 78%. Gülşen-Rothmund et al. (2018) studied elemental contamination of Köyceğiz Lake bottom sediments. Statistical analysis of their results reveals that bottom sediments are contaminated primarily by Ni and to some extent by Cr. These two elements are highly concentrated around Namnam Stream outlet. Another recent contribution by Genc and Yilmaz (2018) investigated the environmental and health risk of heavy metal contamination in water, sediment, and fish samples from Koycegiz Lagoon system. This study revealed out that there is potential health risk for humans if the contaminated fish are consumed. In this study, only eight stations were sampled in and around Koycegiz Lake.

Geological background

The KDCLW is located on the Lycian Nappes (Fig. 1). The Lycian Nappes are categorized into two main groups, namely carbonate-dominated nappes (Tavas, Bodrum, Gülbahar Nappe) and peridotites (Marmaris Nappe) (Senel 1997). Carbonate rocks are mainly composed of limestone, dolomite, dolomitic limestone, radiolarite, basalt, sandstone, shale, conglomerate, claystone, and tectonically overlain by the peridotite, dominant Marmaris nappe. Lower Cretaceous Marmaris Nappe is composed of harzburgite, dunite, serpentinite, diabase, gabbro, and amphibolite (Gökgöz and Tarcan 2006). Alluvium unconformably overlies all units. N–S trending extensional tectonics formed since the Miocene resulted in an E-W trending horst and graben system bounded by young, deep seated normal faults (Graciansky 1972). Extensional tectonics are still active in the region. Thick sedimentary basins (grabens) and deep seated active faults have resulted in widespread geothermal activity in the region.

Materials and methods

In order to delineate the contamination of the waters, 30 water samples were collected from the study area in September and October 2013 (Table 1). Five of these samples were collected from the Köyceğiz Lake, two of them from the Sülüngür Lake, another two samples from Alagöl Lake, one sample from Yuvarlakçay stream, one sample from Namnam stream, two samples from Dalyan Channel, four samples from the groundwater sampling points, eight samples from either cold or hot subaqueous springs, and five samples from the on-land hot springs (Fig. 1, Table 1). On-land water samples were taken into 100-ml polyethylene bottles by using a 12 ft (3.66 m) long, Global Nasco mark water sampler. Sampling of the subaqueous springs was done by divers using syringe-type samplers, oriented directly to the outlet of the spring to avoid mixing with the lake water. These samples were then transferred immediately into the polyethylene bottles on the boat. Afterwards, the water samples were filtered with 45 μm filter paper and acidified with highly pure HNO_3, ensuring a pH value less than 2.

Table 1 pH, EC, and heavy metal concentrations in samples from Köyceğiz-Dalyan Coastal Lagoon Watershed. The World Health Organization drinking water quality guidelines (WHO 2008) and Turkish guidelines of water for human consumption (ITASHY 2005) are also presented in this table

Sample No	Type	Location	Sample ID	Sampling date	pH[a]	EC[a](mS/cm)	Cr[a] (μg/l)	Fe[a]	As[a]	Sb	Pb
1	Lake	Sülüngür	SULG-1	21.10.2013	8.26	35.7	25.34	638.1	47.06	0.86	13.69
2	Lake	Sülüngür	SULG-2	28.10.2013	8.44	35.14	55.63	1394	139.5	1.44	29
3	Lake	Alagöl	ALA-1	14.9.2013	8.18	50.57	291.4	10,280	215.4	5.61	173.4
4	Lake	Alagöl	ALA-2	10.9.2013	8.22	53.29	173.3	4713	289.8	4.35	149.5
5	Lake	Köyceğiz	KOY-1	14.9.2013	8.88	3.64	25.82	654.7	50.48	0.93	91.15
6	Lake	Köyceğiz	KOY-2	14.9.2013	8.91	3.7	26.73	735	47.56	1.43	15.47
7	Lake	Köyceğiz	KOY-3	14.9.2013	8.89	3.85	29.65	726.3	47.35	0.57	23.88
8	Lake	Köyceğiz	KOY-4	14.9.2013	8.82	3.94	38.57	1271	40.71	0.63	23.28
9	Lake	Köyceğiz	KOY-5	14.9.2013	8.82	4.06	29.83	776.4	54.71	0.68	14.82
10	Stream	Namnam	NAM	14.9.2013	8.12	0.54	4.14	< 0.001	1.01	0.25	10.36
11	Stream	Yuvarlakçay	YUV	14.9.2013	7.83	0.59	6.41	65.97	4.13	0.02	1.35
12	Stream	Dalyan Channel	DAL-1	14.9.2013	8.75	5.32	27.76	770.6	66.01	0.62	14.14
13	Stream	Dalyan Channel	DAL-2	14.9.2013	8.21	37.13	209.6	8355	281.5	3.52	169.4
14	Groundwater	Köyceğiz	COLD-1	26.10.2013	8.65	0.31	10.6	133.5	9.12	0.03	1.26
15	Groundwater	Köyceğiz	COLD-2	26.10.2013	7.92	0.63	8.97	125.2	6.12	0.05	1.33
16	Groundwater	Sultaniye village	COLD-3	21.10.2013	8.57	0.71	25.61	613.5	33.24	0.06	6.99
17	Groundwater	Çandır village	COLD-4	21.10.2013	7.02	0.47	2.79	44.97	7.77	0.03	1.26
18	Subaqueous cold spring	Köyceğiz Lake	SUBC-1	9.9.2013	8.84	2.78	32.96	1015	28.31	0.63	16.47
19	Subaqueous cold spring	Köyceğiz Lake	SUBC-2	9.9.2013	8.71	3.7	31.38	768	43.52	0.52	15.08
20	Subaqueous hot spring	Köyceğiz Lake	SUB-1	5.9.2013	N.A.	11.65	60.29	1451	103.4	0.89	32.89
21	Subaqueous hot spring	Köyceğiz Lake	SUB-2	6.9.2013	8.67	5.1	69.58	1851	97.83	1.02	30.71
22	Subaqueous hot spring	Köyceğiz Lake	SUB-3	5.9.2013	8.69	4.95	72.14	2025	113.2	1.19	30.17
23	Subaqueous hot spring	Dalyan Channel	SUB-4	10.9.2013	8.23	34.41	236.4	11,100	386.2	4.09	154.7
24	Subaqueous hot spring	Dalyan Channel	SUB-5	10.9.2013	8.26	33.95	131.2	3558	186.3	3.79	180.1
25	Subaqueous hot spring	Dalyan Channel	SUB-6	10.9.2013	8.25	30.13	182.9	4925	252.7	2.7	144.2
26	On-land hot spring	Delibey	DEL	24.9.2013	6.75	44.39	130.2	3574	290.4	3.732	154.6
27	On-land hot spring	Kelgirme	KEL	6.10.2013	6.76	24.4	117.7	3323	404.8	4.238	152.1
28	On-land hot spring	Sultaniye	SUL-1	24.9.2013	6.92	18.7	96.21	3279	257.9	4.208	144.5
29	On-land hot spring	Sultaniye	SUL-2	24.9.2013	6.74	44.25	98.82	2963	365	5.481	143.9
30	On-land hot spring	Sultaniye	SUL-3	24.9.2013	6.7	44.1	110.4	3052	234	5.026	151.8
Mean (lake samples)					8.60	21.54	77.36	2354.28	103.62	1.83	59.35
Mean (stream samples)					8.23	10.90	61.98	3063.86	88.16	1.10	48.81
Mean (groundwater samples)					8.04	0.53	11.99	229.29	14.06	0.04	2.71
Mean (on-land hot spring samples)					8.52	15.83	102.11	3336.63	151.43	1.85	75.54
WHO (2008)					6.5–8.5	-	50	-	10	20	10
ITASHY (2005)					6.5–9.5	2.5	50	200	10	5	10
Freshwater CMC (acute) US EPA (2009)							-	-	340	-	82
Freshwater CCC (chronic) US EPA (2009)					6.5–9		-	1000	150	-	3.2
Salt water CMC (acute) US EPA (2009)							-	-	69	-	140
Salt water CCC (chronic) US EPA (2009)					6.5–8.5		-	-	36	-	5.6

CMC criterion maximum concentration, *CCC* criterion constant concentration

[a] Avşar et al., 2017

The physico-chemical parameters such as pH, temperature, and EC were measured in situ by a YSI 6600 Multiparameter water quality sonde. The coordinates of the sampling locations were recorded with the help of a Garmin Etrex 10 mark hand GPS. The heavy metal analyses were conducted in Hacettepe University Water Chemistry and Environmental Tritium Laboratory (Ankara, Turkey), in accordance with the standards given in Clesceri et al. (1989). Thermo Electron X7 model ICP-MS (Inductively Coupled Plasma–Mass Spectrometer) was used to measure trace element concentrations. In the ICP technique, firstly the heavy metals to be measured are ionized by argon plasma within the ICP. This plasma is heated to 10,000 K by electromagnetic induction.

Secondly, the ionized elements are separated by mass spectrometry followed by the measurement of element concentrations by an electron-multiplying detector (http://www.icp.hacettepe.edu.tr). The detection limit is reported as 0.1 μg/l for the trace element analyses and the average errors are 5.89, 5.27, 10.74, 14.32, 2.49% for Cr, Fe, As, Sb, Pb, respectively. The average error has been reported as 10% for all ICP-MS analyses by the laboratory. The laboratory is reporting the average of the results of three repetitive analyses as the final concentration of an element. Regular measurements of the standards (internal and calibration) and laboratory reagent blanks were carried out by the laboratory for quality control and quality assurance purposes. The measurements of standard included at least three consecutive series. The device memory effects between sample readings are eliminated by bringing all the samples to a similar concentration range. This is achieved by diluting the samples with ultra-pure water. To avoid mixing of samples between consecutive measurements, the flow system is automatically flushed by a 3% ultra pure acid solution (http://www.icp.hacettepe.edu.tr).

To investigate the relationship between two metric variables, correlation can be used. The Pearson's correlation coefficient is widely used in statistics which is actually a number between − 1 and − 1 (Pearson's Correlation Coefficient (2008)). The positive values of the coefficient indicate that the values of two selected variables would both increase or decrease together. On the other hand, negative values indicate that the decrease of values of one variable will be accompanied by an increase in the values of the other variable and vice versa. The closer the coefficient value to 1 means that there is strong linear association between these two variables. The correlation matrix table (Table 2) is prepared by using IBM SPSS Statistics program. Two-tailed test of significance is used that is a method used to test whether a sample is less than or greater than a particular range of values (Hayes 2019). In this testing for statistical significance, the critical area of a distribution is two-sided.

Table 2 Correlation matrix table including Pearson correlation coefficients

	EC	Cr	Fe	As	Sb	Pb
EC	1	0.830**	0.759**	0.826**	0.886**	0.806**
Cr		1	0.971**	0.919**	0.955**	0.915**
Fe			1	0.904**	0.904**	0.860**
As				1	0.891**	0.884**
Sb					1	0.936**
Pb						1

**Correlation is significant at the 0.01 level (two-tailed)

Equation 1 given by Mohan et al. (1996) was used to calculate the HPI. This equation was made up of W_{i} and Q_{i}, which are the unit weight and the sub-index parameter belonging to the *i*th parameter, respectively. W_{i} depends on the relative importance of a parameter in quality considerations and mostly defined as inversely proportional to the recommended standard (S_{i}) for each parameter (Horton 1965; Mohan et al. 1996; Prasad and Sangita 2008). The value assigned to W_{i} is between zero and one. On the other hand, the sub-index, Q_{i}, is calculated by using Eq. 2. In this equation, S_{i}, I_{i}, and M_{i} the standard permissible, highest desirable, and the monitored values of the i^{th} parameter, respectively. The critical pollution index value is 100 (Prasad and Sangita 2008).

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} W_{\mathrm{i}} Q_{\mathrm{i}}}{\sum_{i=1}^{n} W_{\mathrm{i}}} \tag{1}$$

$$Q_{\mathrm{i}} = \sum_{i=1}^{n} \frac{|M_{\mathrm{i}} - I_{\mathrm{i}}|}{S_{\mathrm{i}} - I_{\mathrm{i}}} \times 100 \tag{2}$$

Results and discussion

In Table 1, electrical conductivity (EC), pH, and the concentrations of As, Cr, Fe, Pb, and Sb detected in the samples collected from the KDCLW are presented along with the World Health Organization (WHO), Turkish drinking water standards (WHO 2008; ITASHY 2005), National Recommended Water Quality Criteria-Aquatic Life Criteria (US EPA 2009). The samples are near neutral to basic in character since pH values range from 6.70 to 8.91. To be more specific, pH values of the cold water samples ranged from 7.02 to 8.91, subaqueous hot spring samples range from 8.24 to 8.69, and the on-land hot springs display lower values varying between 6.70 and 6.92. EC values of all the samples vary between 0.31 and 53.29 mS/cm, exhibiting a wide range. The samples collected from Alagöl Lake have the highest EC values, similar to the ones of typical seawater. Some of the on-land hot springs also have high EC values (DEL, SUL-2, SUL-3). The lowest EC values belong to the groundwater samples collected from different parts of the study area.

When compared to cold waters, relatively elevated concentrations of heavy metals were detected in the subaqueous and on-land hot springs. Likewise the EC values, Alagöl lake samples showed high concentrations of dissolved heavy metals owing to the fact that Alagöl lake is located downstream of the area where most surface waters gather. As, Cr, Pb, and Sb are found in all of the samples in concentrations ranging from 1 to 404.8 μg/l, 2.8 to 291.4 μg/l, from 1.3 to 180.1 μg/l, and from ~0 to 5.6 μg/l, respectively (Table 1, Fig. 2). Dissolved Fe is also present in all of the samples, with the exception of one, collected from Namnam stream, in concentrations up to 11,100 μg/l (Table 1, Fig. 2). The safety limits of heavy metals in freshwater and seawater are designed to protect both freshwater and salt water organisms from short-term and long-term exposure to chemicals (US EPA 2009). Accordingly, the recommended aquatic life criteria is presented in Table 1 and both acute (e.g., growth and survival effects) and chronic (e.g., reproduction) levels of risk concentrations are given for Cr(VI), As and Pb, and Fe (US EPA 2009). For Fe, only freshwater chronic concentration set at 1000 μg/l is given and all the freshwater samples collected from the study area has dissolved Fe concentrations below this value. For Cr, data presented in Table 1 is for total Cr, no criterion is presented in Table 1 since US EPA (2009) has given criteria for Cr (VI) and Cr (III) separately. US EPA (2009) criteria suggest that salt water chronic and acute allowable concentrations for As are much lower than those reported for freshwater. For freshwater samples, As poses no threat to aquatic life. However, for As concentrations in salt water samples from the study area, both short-term and long-term exposure criteria are exceeded. In the same manner, Pb concentrations also exceed both acute and chronic exposure criteria for Alagöl lake samples and one sample collected from Dalyan Channel. On the other hand, for freshwater samples collected from Köyceğiz Lake and and groundwater sampling locations, the short-term exposure criterion for aquatic life is exceeded in only one lake sample. For the long-term exposure criterion, most of the samples exceed the maximum desired concentration suggesting that Köyceğiz Lake environment pose a risk to some species. High concentrations of Fe, As, and Pb in cold waters are attributed to either the anthropogenic or natural discharge of the geothermal system at the site. Pearson correlation coefficients for EC, Cr, Fe, As, Sb, and Pb are presented in Table 2, and not surprisingly, the positive correlation between them is highly significant. The highest correlations are observed between Cr and the remaining elements (Fe, As, Sb, and Pb) where Pearson correlation coefficients are > 0.9.

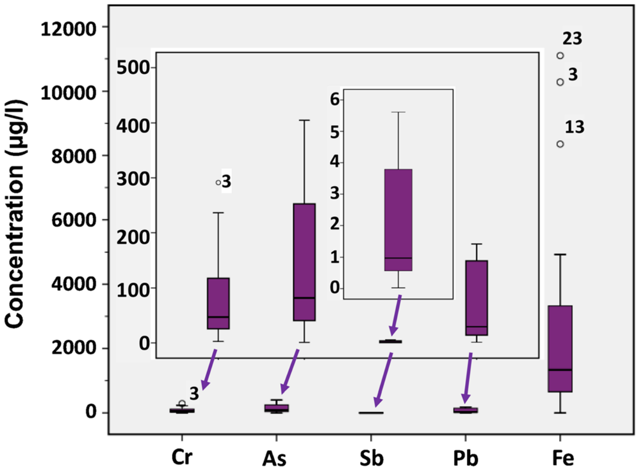


Fig. 2 Boxplot of the heavy metal contents of the water samples. In this figure, sample numbers given in Table 1 are used instead of sample ID's

To examine the distribution of heavy metal concentrations in KDCLW, a boxplot is used. Boxplot visualization shows the spread and centers of a dataset by using the minimum, first quartile (the middle number between the smallest value and the median within a dataset), median, third quartile (is the middle number between the median and the highest value of a dataset), and maximum (Tukey 1977). A dataset can contain outliers which are defined as anomalously high or low values falling outside the other values of the data set. Outliers can represent erroneous data points or can simply show anomalies. According to the boxplot presented in Fig. 2, Cr concentration in the Alagöl lake sample (ALA-1) and Fe concentrations in samples ALA-1 and DAL-1 (stream water collected from Dalyan Channel) and SUB-4 (subaqueous hot spring sample from the Dalyan Channel) are labeled as the outliers.

In fact, dissolved Fe concentrations in these samples are twice as much higher than the maximum concentration detected in the rest of the samples. Fe has a key role in aquatic ecosystems because it has an influence upon the biochemical cycles of some elements (by acting as a C and P sink; Lalonde et al. 2012) and it is an essential micronutrient for organisms (Herzog et al. 2020). Iron precipitates as Fe hydroxides at near neutral pH values and oxic conditions (Herzog et al. 2020). These conditions usually prevail in surface water systems; therefore, elevated Fe concentrations are not expected in such systems. However, the control of Fe stability is complex. Fe can be mobilized from the sediments and/or from suspended particulate matter and can precipitate back with a change in pH or Eh; thus, temporal variations can be observed (Hölemann et al. 2005).

The heavy metal load and the pH of the samples were used in Fig. 3 and a scatter diagram was prepared. In this diagram, the groundwater samples and two of the stream samples (NAM and YUV) are plotted in the near neutral-low metal (NN-LM) region. On the other hand, the on-land hot springs gathered in a near neutral-high metal (NN-HM) region together with the subaqueous springs. One sample from Sülüngür Lake is plotted in the NN-LM region, and the other one plotted in the NN-HM region.

To determine the extent of pollution, HPIs were calculated for all of the samples and the results are reported in Tables 3 and 4. Although individual HPI values for the geothermal

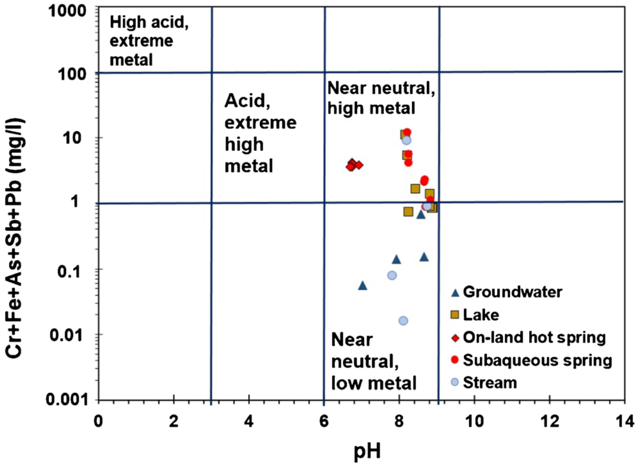


Fig. 3 Scatter diagram of the concentration of the heavy metals Cr + Fe + As+Sb + Pb vs. pH (modified from Gray et al. 2000)

water samples are reported herein, they are not used in the overall HPI calculation for the area; only the cold water samples are included. Moreover, herein, S_i values are assigned by using the drinking water quality guidelines for Turkey (ITASHY 2005) and I_i values are assumed to be zero for all of the metals (Arslan et al. 2017).

Accordingly, the HPI calculated for the study area is 297.1 and this value is higher than 100, which is the critical pollution index level reported by Prasad and Sangita (2008). In fact, there are only five samples exhibiting HPI values below the critical level.

These samples were collected from the groundwaters (except for COLD-4 which has an HPI value of 101.3, slightly above the critical level) and the streams (NAM and YUV). The subaqueous hot springs have higher HPI values up to 1398.7 (SUB-4) compared to the subaqueous cold springs. Actually, this value is the highest HPI value in the region. On the other hand, the highest HPI values are observed in a sample from the Dalyan Channel and in two other samples from Alagöl Lake (Table 4; Fig. 4). These sampling points are situated at the outlet for the area, and there is most probably an accumulation of contamination at these points. The situation is different in the Sülüngür Lake since it exhibits relatively lower HPI values close to the average ones. The relatively lower HPI values observed in Sülüngür Lake is due to its location. This lake is located on the east side of the outlet to the Mediterranean Sea receiving recharge from a relatively less contaminated drainage area.

Table 4 HPI values of the samples in KDCLW

Sample ID	HPI	Deviation	% Deviation
SULG-1	157.19	− 139.89	− 47.09
SULG-1	423.43	126.35	42.53
ALA-1	1055.52	758.44	255.30
ALA-2	1118.59	821.51	276.53
KOY-1	348.25	51.17	17.23
KOY-2	168.57	− 128.51	− 43.26
KOY-3	180.02	− 117.06	− 39.40
KOY-4	167.56	− 129.52	− 43.60
KOY-5	177.35	− 119.73	− 40.30
NAM	29.50	− 267.58	− 90.07
YUV	14.10	− 282.98	− 95.25
DAL-1	201.54	− 95.54	− 32.16
DAL-2	1162.90	865.82	291.44
COLD-1	26.44	− 270.64	− 91.10
COLD-2	19.59	− 277.49	− 93.41
COLD-3	101.28	− 195.80	− 65.91
COLD-4	22.04	− 275.04	− 92.58
SUBC-1	120.38	− 176.70	− 59.48
SUBC-2	150.26	− 146.82	− 49.42
SUB-1	122.95	NI[a]	
SUB-2	329.47		
SUB-3	367.27		
SUB-4	1398.72		
SUB-5	931.04		
SUB-6	1005.52		
DEL	1115.46		
KEL	1380.86		
SUL-1	1014.77		
SUL-2	1275.73		
SUL-3	983.41		

[a] NI: stands for not included in the calculation. Please refer to text for details

Table 3 HPI calculation for the study area based on Turkish guidelines for drinking water quality (ITASHY 2005)

Metals	Mean value (M_i) (μg/l)	Standard permissible value (S_i) (μg/l)	Highest desirable value (I_i) (μg/l)	Unit weightage (Wi)	Subindex (Q_i)	$W_i \times Q_i$
Cr	55.60	50	-	0.020	111.21	2.22
Fe	1837.79	200	-	0.005	870.53	4.59
As	74.38	10	-	0.100	743.84	74.38
Sb	1.17	5	-	0.200	23.40	4.68
Pb	40.62	10	-	0.100	406.23	40.62

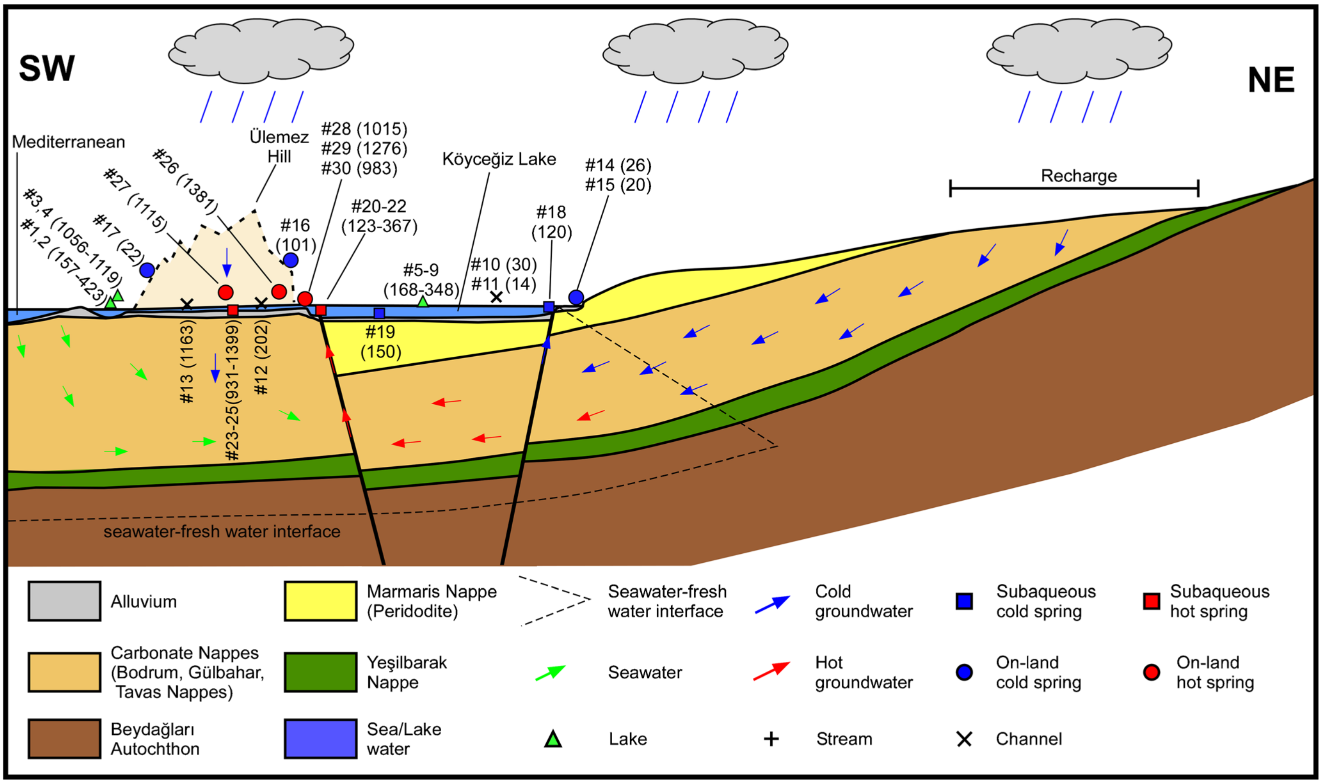


Fig. 4 Sketch of a conceptual hydrogeochemical model for the study area (Modified from Avşar et al. 2017). The calculated HPI values are given in parenthesis. The location of Ülemez Hill is shown in Fig. 1. Please refer to Table 1 for sample ID's

Not surprisingly, there is positive correlation between the HPI and EC values (Fig. 5). As can be seen in Fig. 5, the samples are gathered in four different groups. In group I, there are six samples including four groundwater samples and two surface water samples (YUV and NAM). This group represents freshwater samples having the lowest EC values and HPI values. HPI values of the samples in this group are below the critical pollution level (HPI = 100). Eleven samples are included in group II, which are Köyceğiz Lake water samples, all of the subaqueous cold and hot springs located in Köyceğiz Lake and one stream sample collected from Dalyan Channel. It is worth mentioning that Dalyan Channel sample is located close to the outlet of Köyceğiz Lake therefore has HPI and EC values similar to Köyceğiz Lake samples. This group stands for samples having EC values higher than group I samples but lower than group III samples.

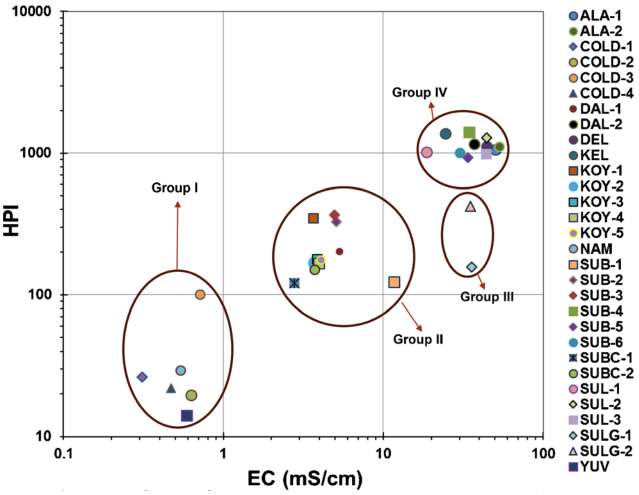
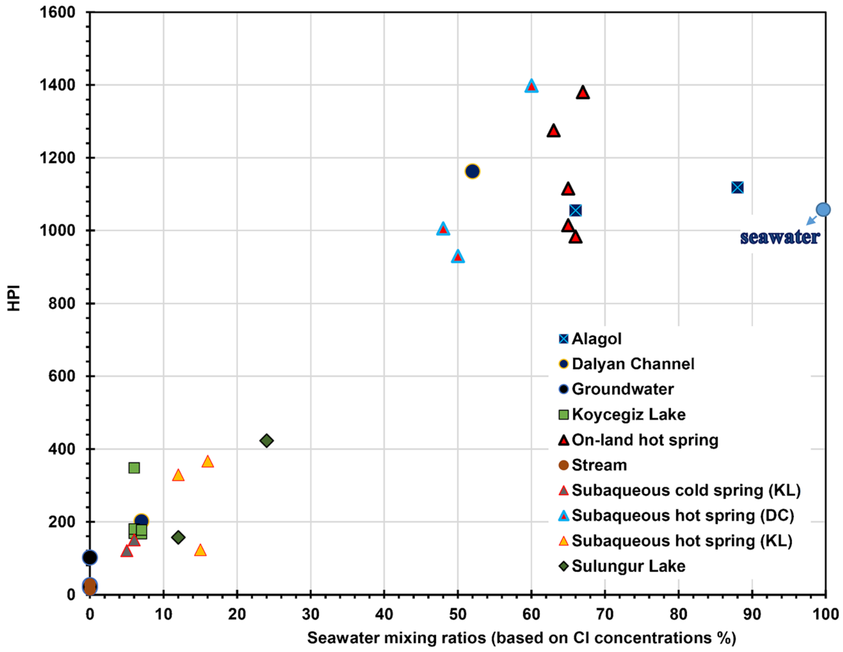


Fig. 5 Heavy metal pollution index vs electrical conductivities (EC) for all samples

The pollution levels in both group II and group III samples are in the same range. Group III includes samples collected from Sülüngür Lake. This group exhibits high EC values analogical to the samples in group IV but lower HPI values than that of the samples in group IV.

Sulungur Lake samples are recharged by a different drainage area; therefore, the pollution is relatively diluted giving way to lower HPIs. Group IV includes Alagöl samples, subaqueous hot spring samples collected from Dalyan Channel, and all of the on-land hot spring samples. Group IV samples have both the highest HPI and EC values. Seawater samples collected and analyzed by Avşar et al. (2015) also plot in this group, very close to ALA-2 sample, although not shown in Fig. 5. Seawater contribution to the lake water and geothermal waters in this region has already been reported several times (Bayarı et al. 1995; Gökgöz and Tarcan 2006; Avşar et al. 2015; Avşar et al. 2016; Avşar et al. 2017); in fact, Avşar et al. (2015) considered Cl

Fig. 6 HPI vs seawater mixing ratios calculated by Avşar et al. (2015) based on chloride concentrations



content of the waters as seawater contribution and calculated seawater mixing percentages. These percentages are used to make a comparison with the HPI values of all samples. Figures 5 and 6 are similar to each other since seawater mixing causes an increase in the EC values. In Fig. 6, the samples are gathered in two different regions, the ones with seawater contribution percentages less than 30% that have HPI values up to 500 and the others gathered in the region where there is considerable seawater mixing and extremely high HPI values. The on-land hot spring samples in this region have HPI values higher than seawater together with two samples (one subaqueous hot spring and one stream sample) collected from Dalyan Channel.

The extremely high HPI values of the on-land hot springs can be attributed to the heavy metals that incorporate during these springs' journey underground (water-rock interaction) and the heavy metals embodied as a result of seawater mixing. Therefore, it can be stated that the increase in the pollution state of the Dalyan Channel can be attributed to both uncontrolled geothermal discharge and seawater mixing. The difference between two stream samples collected from Dalyan Channel is eye-catching (Figs. 1 and 6). DAL-1 is located close to the outlet of Köyceğiz Lake and receives little or no geothermal discharge; on the other hand, DAL-2 sample receives both geothermal discharge and is exposed to seawater mixing, leading to an incredible increase in HPI levels in this sample.

Conclusion

In light of the results, it can be concluded that there is an increase in the level of pollution from north to south in the study area (Fig. 4). This phenomenon can be explained by the location of the contaminated hot springs (on-land and subaqueous) and the freshwater resources, namely, cold springs and Namnam and Yuvarlakçay. In the north, the lake water is fed by the relatively less-contaminated fresh stream and cold spring waters. However, on-land and subaqueous hot springs are concentrated in the south of the study area and there has been continuous natural and anthropogenic discharge of the pollution load into Köyceğiz Lake and the Dalyan Channel in the south for many years, leading to an increase in contamination towards the south. Although Sülüngür Lake is located downstream (in the south), it owes its low level of contamination to its location. Being located on the opposite side (east) of the outlet to the Mediterranean, Sülüngür Lake is away from the main stream running from north to south, and Sülüngür lake waters are most probably diluted by the recharge from its own catchment area.

This study puts forward the current contamination status of the freshwaters located in Köyceğiz-Dalyan Coastal Watershed which a Special Protection Area hosting a unique ecosystem. The increase in the pollution load in Dalyan Channel is incredibly high and this situation should further be investigated by collecting additional samples with systematically fine sampling intervals. Previous studies carried out in the study area found out that there is bioaccumulation of the metals in some of the fish species in Köyceğiz Lake. This is an expected finding because concentrations of toxic metals in some parts of the area are high and they exceed the short-term and long-term exposure criteria suggested by US EPA (2009) and these metals pose a risk to the species habitats. The water resources sampled herein are not used as drinking water supplies; however, they host marine animals consumed by the locals. Therefore, necessary precautions should be undertaken by the authorities and the uncontrolled discharge of geothermal wastes should be prevented. Strong casing materials should be used in geothermal wells to hinder blowouts. Besides, treatment of these geothermal wastes can be performed under the strict inspection of authorities.

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