RESEARCH ARTICLE

Modeling relationships between catchment attributes and river water quality in southern catchments of the Caspian Sea

**Mohammad Hasani Sangani · Bahman Jabbarian Amiri ·
Afshin Alizadeh Shabani · Yousef Sakieh · Sohrab Ashrafi**

Abstract Increasing land utilization through diverse forms of human activities, such as agriculture, forestry, urban growth, and industrial development, has led to negative impacts on the water quality of rivers. To find out how catchment attributes, such as land use, hydrologic soil groups, and lithology, can affect water quality variables (Ca^{2+}, Mg^{2+}, Na^+, Cl^-, HCO_3^-, pH, TDS, EC, SAR), a spatio-statistical approach was applied to 23 catchments in southern basins of the Caspian Sea. All input data layers (digital maps of land use, soil, and lithology) were prepared using geographic information system (GIS) and spatial analysis. Relationships between water quality variables and catchment attributes were then examined by Spearman rank correlation tests and multiple linear regression. Stepwise approach-based multiple linear regressions were developed to examine the relationship between catchment attributes and water quality variables. The areas (%) of marl, tuff, or diorite, as well as those of good-quality rangeland and bare land had negative effects on all water quality variables, while those of basalt, forest land cover were found to contribute to improved river water quality. Moreover, lithological variables showed the greatest most potential for predicting the mean concentration values of water quality variables, and noting that measure of EC and TDS have inversely associated with area (%) of urban land use.

Responsible editor: Philippe Garrigues

M. Hasani Sangani · B. Jabbarian Amiri (✉) ·
A. Alizadeh Shabani · Y. Sakieh · S. Ashrafi
Department of Environmental Science, Faculty of Natural Resources,
University of Tehran, Tehran 31587-77878, Iran
e-mail: jabbarian@ut.ac.ir

Introduction

Several anthropogenic and natural factors influence river water quality. Some of them like farmland runoff spreads out over a wide scale and are known as non-point pollutants (Ahearn et al. 2005). Increasing the utilization of land resources through diverse forms of human activities, such as agriculture, forestry, urban growth, and industrial development, has led to negative impacts on river water quality (Seitz et al. 2011). Hence, shifts in land use are considered one of the most potent causes of altered river water quality (Dale et al. 2000; Zhou et al. 2012). Decreasing river water quality is mainly caused by substitution of natural land cover with specific classes of land use, such as agricultural fields and rangelands (Bruijnzeel and Sampurno 1990; McCulloch and Robinson 1993; Maillard and Pinheiro Santos 2008). There are direct relationships between particular forms of land uses, such as agriculture and urban areas with river water quality (Ahearn et al. 2005; Zampella et al. 2007).

Yang and Jin (2010) outlined the significant role of soil hydrologic properties in the movement of nitrate (NO_3^-) from farmlands into rivers. They pointed out that D hydrologic soil groups (USDA 2007) show an indirect relationship with the quantity of NO_3^- transported into surface waters. Identifying and controlling point-source pollution is more achievable in terms of measuring and monitoring pollutant sources than those of non-point origin (Baker 2003; Ahearn et al. 2005). Therefore, detecting and controlling non-point pollutants requires more complex and sophisticated methods. Much recent research into detecting and controlling non-point pollutants has involved the integrated application of geographic information system (GIS) and multivariate analysis to provide a spatio-statistical approach (e.g., Amiri and Nakane 2006, 2008; Maillard and Pinheiro Santos 2008; Atkinson et al. 2009; Yang and Jin 2010; Miller et al. 2011; Uriarte et al.

2011; Carey et al. 2011; Pratt and Chang 2012; Zhou et al. 2012).

As a valid and economical tool, applying GIS and statistical analysis has great potential in modeling river water quality (Atkinson et al. 2009). Many studies have demonstrated the importance of anthropogenic threats such as land use change and rises in human population on river water quality (Amiri and Nakane 2006, 2008; Maillard and Pinheiro Santos 2008; Miller et al. 2011; Uriarte et al. 2011; Carey et al. 2011; Zhou et al. 2012). Interestingly, few have investigated the role of soil (Haidary et al. 2013) in general and of hydrologic soil groups (Yang and Jin 2010; Pratt and Chang 2012) in particular, or indeed lithological parameters in general, on river water quality (Chen 1987). Li and Zhang (2008) indicated that spatial variations of river water quality can be related to change in both geological settings and land use types.

The present study investigates the effect of catchment attributes consisting of land use, hydrologic soil groups, and lithological features on river water quality in the southern catchments of the Caspian Sea. The primary objectives were (i) to investigate the relationship or linkage between land use, hydrologic soil group, or catchment lithological features and river water quality, and (ii) to develop models to predict river water quality based on land use, hydrologic soil groups, and lithological attributes in the catchments of interest.

Materials and methods

Study area

The study area encompasses selected southern catchments of the Caspian sea, spanning the region between 48° 48′ 20″–52° 18′ 15″ E and 36° 9′ 36″–37° 24′ 36″ N and covering a total area of 1,095 km² along the northern coastline of Iran. The area contains the administrative boundary of Mazandaran Province and comprises its western catchments. It is characterized by the Caspian Sea and the Albrorz Mountain chain as respective sink and source, the latter benefiting from abundant precipitation. This phenomenon has brought in a considerable diversity in the study area's landscape. Figure 1 shows the location of the study area and sampling sites.

Dominant land covers in the study area include dense forests, good-quality rangelands, and moderate-quality rangelands, accounting for 46.87, 26.59, and 10.33 % of the study area, respectively. The rangeland classification in terms of condition was based on the quantitative climax method (Dyksterhuis 1949) (Table 1). Although range condition is evaluated on a continuous scale from 0 to 100 %, arbitrary classes are generally reported to illustrate range condition. A value close to 100 % indicates that species composition of the existing vegetation closely reflects the composition of the climax vegetation, whereas lower values indicate a greater level of departure from perceived climax conditions. In this
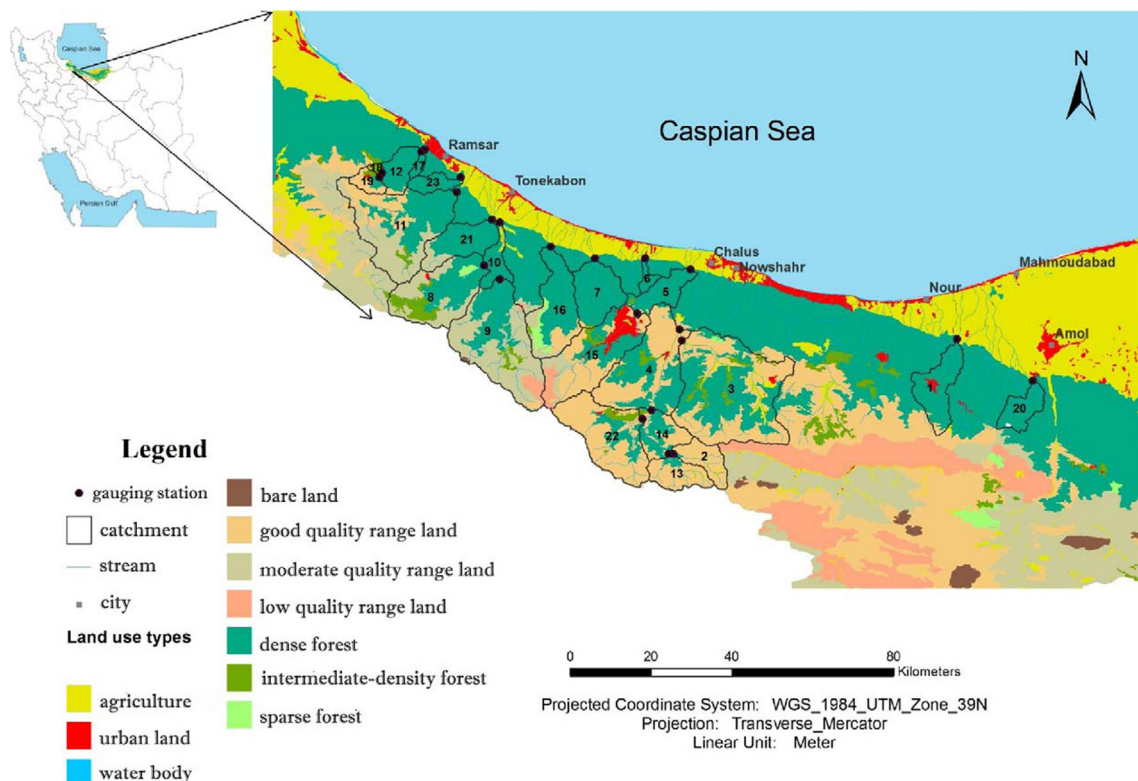

Fig. 1 Geographical location of the catchments and water sampling points in study area

Table 1 Percentage area of land uses in catchments of study area

Catchment no.	Catchment area (km²)	Mean slope (%)	Mean discharge (m³ s⁻¹)	Water sampling station elevation (m)	Agricultural land	Good-quality rangeland	Moderate-quality rangeland	Low-quality rangeland	Dense forest	Intermediate-density forest	Sparse forest	Urban land	Bare land
1	145.52	13.36	1.06	200	0.05	4.85	0.00	0.00	90.98	0.00	0.00	4.12	0.00
2	84.05	9.24	0.81	1,900	4.05	93.53	0.29	0.04	2.09	0.00	0.00	0.00	0.00
3	623.78	9.62	2.76	375	4.95	42.93	0.00	0.13	46.18	4.88	0.49	0.45	0.00
4	1,577.11	9.62	13.29	350	5.30	41.84	0.09	0.12	22.17	2.99	0.19	0.25	0.00
5	419.63	8.32	3.74	−23	0.30	31.42	8.17	6.18	20.09	2.52	0.00	10.02	0.00
6	19.09	15.83	0.49	−15	0.68	0.00	0.00	0.00	99.32	0.00	0.00	0.00	0.00
7	152.97	14.38	2.25	70	0.00	1.73	0.00	0.00	97.56	0.71	0.00	0.00	0.00
8	283.25	12.87	5.82	420	0.00	0.00	37.73	0.00	42.88	16.08	2.86	0.45	0.00
9	431.78	9.57	6.84	660	0.25	1.64	58.18	5.36	31.17	2.85	0.00	0.00	0.53
10	775.16	8.11	14.33	140	0.14	0.92	46.20	2.98	33.03	7.47	1.04	0.17	0.30
11	407.46	10.74	4.39	80	0.00	20.70	37.38	0.00	39.74	2.18	0.00	0.00	0.00
12	135.92	14.83	2.03	100	0.00	17.83	1.04	0.00	15.80	7.64	0.00	0.76	0.00
13	95.43	17.80	2.47	1,750	3.24	86.40	0.46	0.00	9.89	0.00	0.00	0.00	0.00
14	588.79	16.65	8.75	980	1.10	66.59	0.23	0.18	10.45	2.84	0.00	0.19	0.00
15	329.00	9.99	3.96	975	0.38	40.07	10.42	7.88	25.62	2.83	0.00	12.78	0.00
16	228.65	14.78	2.85	160.	0.00	12.55	12.84	0.00	64.74	0.69	9.18	0.00	0.00
17	13.14	17.83	0.27	300	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00
18	7.12	33.20	0.09	1,245	0.00	10.11	0.00	0.00	14.47	75.42	0.00	0.00	0.00
19	38.30	28.70	0.26	1,340	0.00	61.41	3.68	0.00	19.09	13.11	0.00	2.69	0.00
20	79.28	12.95	0.86	215	0.18	0.14	0.00	0.00	98.28	0.00	0.00	0.00	0.00
21	140.42	15.99	1.47	120	0.00	0.00	20.60	0.00	79.40	0.00	0.00	0.00	0.00
22	300.85	12.88	6.10	1,000	0.00	76.78	0.23	0.34	16.73	5.55	0.00	0.37	0.00
23	46.36	14.34	0.59	30	1.55	0.06	0.00	0.00	98.38	0.00	0.00	0.00	0.00

regard, good-quality, moderate-quality, and low-quality rangelands represent 50–75, 26–50, and 0–25 % of climax conditions.

Categorized according to USDA (2007) hydrologic soil groups based on a soil's runoff potential, where the A group shows the least and the D group the greatest runoff potential, the study region's soils were found to belong to three main hydrologic soil groups (B, C, D), of which the B and D predominated, covering 51.19 and 34.41 % of the area, respectively (Table 2). Group B soils are generally composed of silt loam or loam, exhibiting a moderate infiltration rate when thoroughly wetted, whereas group D soils, most often clay loam, silty clay loam, sandy clay, silty clay, or clay, show poor infiltration rates and therefore show the highest potential for runoff. Group C soils are mainly sandy clay loam with moderately fine-to-fine structure and low infiltration rates when thoroughly wetted. They are often characterized by a layer that impedes downward movement of water. Shale, sandstone, and limestone/conglomerate were the dominant subtending rock formations, covering 34.24, 28.0, and 7.97 %, respectively.

Table 2 Percentage area of hydrologic soil groups in catchments of study area

Catchment no.	B hydrologic soil group	C hydrologic soil group	D hydrologic soil group
1	67.32	26.77	5.91
2	1.75	0.00	98.24
3	68.31	13.23	18.46
4	55.80	5.78	38.42
5	59.31	1.53	39.15
6	34.73	65.22	0.00
7	79.17	20.10	0.73
8	41.81	0.00	58.19
9	33.09	0.00	66.91
10	39.81	1.66	58.54
11	52.41	2.75	44.84
12	80.73	16.67	2.60
13	2.94	0.00	97.06
14	28.41	0.00	71.59
15	50.06	0.00	49.94
16	60.24	6.45	33.30
17	73.36	26.64	0.00
18	100.00	0.00	0.00
19	56.79	33.99	9.24
20	38.80	61.20	0.00
21	56.79	17.62	25.59
22	27.11	0.00	72.89
23	68.72	31.28	0.00

Data sets

The water quality variables of Ca^{2+}, Mg^{2+}, Na^+, Cl^-, HCO_3^-, pH, total dissolved solid (TDS), electric conductivity (EC), and sodium adsorption ratio (SAR) were monitored and quantified by the Water Resources Management Company (WRMC) (http://www.wrm.ir). River water was sampled on a monthly basis. The sampling process and devices employed were based on WRMC Guidelines for Surface Water Quality Monitoring (2009). In all, 23 river water quality sampling sites were selected in the study area. Five-year means (1998–2002) of river water quality data were calculated for further statistical analysis (Table 3).

A 2002 digital land use map (Scale 1:250,000) of the study area was obtained from the Forests, Ranges and Watershed Management Organization (http://frw.org.ir). Digital elevation models (DEMs) at a 30 m × 30 m resolution were downloaded from the USGS database and used to delineate catchment boundaries in the study area. Digital geological maps (1:250,000) were obtained from the Geological Survey of Iran (www.gsi.ir) (Table 4). For mapping the hydrologic soil groups, a land suitability map (1:250,000) obtained from the Soil and Water Research Institute (www.swri.ir) was used

Spatial analysis

In a first step, all input layers, including land use, land suitability, and geological maps, were transformed into a common digital format and co-registered with the WGS84 source (zone 39n). For each river water sampling point, upper catchment boundaries were then delineated by applying the DEM. The land use map included nine classes of agriculture: good-quality rangeland, moderate-quality rangeland, low-quality rangeland, dense forest, intermediate-density forest, sparse forest, urban areas, and bare lands. The land suitability map was then reclassified according to the hydrologic soil group (A, B, C, or D). The digital geological map was classified into 19 classes: amphibolite (geological period: Tertiary), andesite (Cretaceous-Tertiary), basalt (Cretaceous-Tertiary), conglomerate (Plio-Quaternary), diorite (Tertiary), dolomite (Jurassic-Cretaceous), fan terraces (Quaternary), gabbro (Silurian), granite (Tertiary), gypsum (Tertiary), limestone (Permian-Cretaceous), limestone shale (Triassic-Jurassic), marl (Cretaceous-Tertiary), sandstone (Jurassic-Tertiary), sandstone shale (Triassic-Jurassic), sandy siltstone (Jurassic and Plio-Quaternary), schist (Tertiary), shale sandstone (Jurassic-Tertiary), and tuff (Cretaceous-Tertiary).

To determine the area (%) of each catchment attributes, land use, soil, and lithological information layers were overlaid with catchment boundary map. The spatial database was finally organized in a manner as to facilitate statistical analysis between river water quality variables and catchment attributes.

Table 3 Water quality data of rivers in the study area (±SD)

Catchment no,	n	SAR Mean	Na^+ (meq l^{-1}) Mean	Mg^{2+} (meq l^{-1}) Mean	Ca^{2+} (meq l^{-1}) Mean	Cl^- (meq l^{-1}) Mean	HCO_3^- (meq l^{-1}) Mean	pH Mean	EC (µS cm^{-1}) Mean	TDS (mg l^{-1}) Mean
1	42	0.57±0.43	0.86±0.80	2±0.35	2.24±0.38	0.46±0.33	3.8±0.44	7.94±0.15	531.47±137.75	348.52±89.80
2	56	0.39±0.24	0.49±0.32	1.42±0.44	1.67±0.47	0.42±1.13	2.55±0.62	8.16±0.21	373.87±101.83	245.25±66.35
3	60	0.45±0.22	0.62±0.30	1.73±0.33	2±0.35	0.33±0.09	3.18±0.54	8.17±0.14	450.98±71.29	296.15±46.16
4	58	0.45±0.23	0.66±0.38	1.95±0.48	2.25±0.55	0.37±0.14	3.06±0.77	8.13±0.17	503.36±117.05	330.42±77.91
5	57	0.43±0.24	0.52±0.32	1.3±0.48	1.57±0.49	0.27±0.10	2.44±0.89	8.17±0.15	351.49±119.76	231.42±77.34
6	12	0.18±0.09	0.2±0.10	1.23±0.28	1.45±0.26	0.2±0.00	2.35±0.47	8.1±0.13	303.58±54.07	198.41±37.28
7	13	0.18±0.06	0.19±0.08	0.97±0.25	1.26±0.38	0.18±0.07	2±0.55	8.06±0.19	252.61±65.25	166.76±42.94
8	8	0.21±0.12	0.26±0.16	1.27±0.30	1.55±0.41	0.21±0.06	2.57±0.73	8.15±0.20	324.87±80.08	214.25±53.12
9	9	0.23±0.12	0.32±0.19	1.57±0.33	1.95±0.44	0.32±0.11	3.03±0.52	8.02±0.15	399.55±82.78	262.88±55.64
s10	34	0.37±0.18	0.48±0.25	1.48±0.41	1.79±0.50	0.31±0.10	2.94±0.80	8.08±0.10	391.2±100.63	256.14±65.60
11	30	0.42±0.20	0.48±0.21	1.28±0.42	1.62±0.59	0.28±0.10	2.67±0.69	8.11±0.14	354.26±89.00	231.9±58.42
12	34	0.33±0.16	0.41±0.21	1.36±0.35	1.66±0.42	0.27±0.10	2.75±0.63	8.08±0.11	356.58±77.36	234.55±50.84
13	60	0.6±0.35	0.93±0.62	1.99±0.66	2.54±0.83	0.5±0.26	2.95±0.95	8.11±0.16	565.91±178.30	370.46±116.00
14	60	0.48±0.26	0.73±0.46	2.05±0.61	2.47±0.75	0.41±0.19	2.77±0.80	8.13±0.15	543.45±157.78	354.73±102.62
15	58	0.37±0.18	0.38±0.19	1.08±0.44	1.31±0.57	0.22±0.08	2.02±0.82	8.17±0.17	290.94±108.89	190.63±71.22
16	32	0.31±0.15	0.35±0.18	1.17±0.34	1.39±0.38	0.22±0.08	2.25±0.63	8.1±0.16	298.65±77.66	199.18±52.62
17	23	0.33±0.19	0.41±0.24	1.48±0.39	1.6±0.31	0.27±0.07	2.81±0.56	8.05±0.11	360.95±70.54	236.13±46.40
18	3	0.11±0.02	0.1±0.00	0.73±0.31	0.93±0.31	0.13±0.06	1.46±0.55	8.13±0.12	185±65.96	121.66±42.85
19	22	0.38±0.17	0.46±0.22	1.39±0.37	1.57±0.42	0.28±0.10	2.72±0.68	7.75±1.54	353.9±82.97	232.04±55.45
20	38	0.45±0.24	0.62±0.34	1.8±0.29	2.02±0.35	0.35±0.06	3.45±0.47	7.94±0.15	460.44±70.92	300±47.68
21	23	0.35±0.18	0.41±0.23	1.29±0.33	1.48±0.35	0.26±0.08	2.5±0.61	8.1±0.12	332±78.37	217.6±50.90
22	59	0.44±0.28	0.68±0.45	2.09±0.56	2.56±0.71	0.37±0.14	2.74±0.80	8.11±0.11	551.88±142.30	361.57±93.34
23	4	0.25±0.07	0.3±0.08	1.35±0.40	1.52±0.43	0.25±0.06	2.52±0.91	8.25±0.37	328.5±85.14	214.5±56.39

Table 4 Percentage area of lithological variables in catchments of study area

Catchment code	Amphibolite	Andesite	Basalt	Conglomerate	Diorite	Dolomite	Fan terraces	Gabbro	Granite	Gypsum
1	0.00	0.00	0.00	4.71	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	12.04	0.00	0.00	0.00	2.84	0.00	0.00	0.00
3	0.00	0.00	2.31	0.89	0.00	4.26	6.00	0.00	0.00	0.00
4	0.13	2.65	6.87	1.02	1.25	4.91	6.00	0.00	0.00	1.44
5	1.53	0.08	6.83	0.00	0.00	0.00	8.70	0.00	12.65	0.00
6	0.00	0.00	9.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	35.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	4.61	0.00	0.06	0.12	0.00	1.16	10.20	0.58
9	0.00	0.00	11.38	0.00	0.03	5.11	0.00	0.00	8.80	0.32
10	0.00	0.00	8.03	0.00	0.00	2.89	1.43	0.42	8.63	0.00
11	0.00	0.00	6.98	10.15	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	42.89	0.00	0.00	0.00	0.00	0.00	0.56
13	4.20	4.20	1.57	0.00	2.58	0.00	0.91	0.00	0.00	3.87
14	6.37	6.37	2.62	0.00	3.34	8.63	2.38	0.00	0.00	0.00
15	1.95	0.10	1.68	0.00	0.00	0.00	10.99	0.00	16.14	0.00
16	0.00	0.00	12.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	5.02	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	27.67	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	69.66	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	3.59	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	5.21	0.00	0.00	0.00
22	11.13	11.13	0.00	0.00	2.42	11.98	3.57	0.00	0.00	7.40
23	0.00	0.00	0.00	17.71	0.00	0.00	0.00	0.00	0.00	0.00

Catchment code	Limestone	Limestone shale	Marl	Sandstone	Sandstone shale	Sandy siltstone	Schist	Shale/sandstone	Tuff
1	46.77	0.00	8.79	0.00	0.00	0.00	0.00	39.73	0.00
2	24.32	0.19	0.00	0.00	3.07	0.00	0.00	57.53	0.00
3	32.50	27.90	4.19	2.51	6.02	3.33	0.00	10.08	0.00
4	18.58	14.27	2.52	1.92	6.22	2.80	1.12	25.73	1.52
5	27.15	14.57	0.00	0.87	5.32	0.00	3.04	18.11	1.16
6	90.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	24.83	0.14	0.00	0.00	0.00	0.00	0.00	39.69	0.00
8	53.79	13.04	0.00	0.00	0.00	0.00	0.00	17.08	0.00
9	15.95	29.97	0.00	0.00	0.58	0.00	0.00	14.67	12.89
10	34.80	21.46	0.00	0.00	0.32	0.00	0.00	14.48	7.18
11	45.99	0.00	0.00	0.00	0.00	0.00	0.00	36.87	0.00
12	5.28	0.00	0.00	0.00	0.00	0.00	0.00	51.84	0.00

Table 4 (continued)

Catchment code	Limestone	Limestone shale	Marl	Sandstone	Sandstone shale	Sandy siltstone	Schist	Shale/sandstone	Tuff
13	7.13	0.00	0.00	0.00	8.22	0.00	0.00	49.69	25.16
14	4.68	7.19	2.30	2.49	8.26	3.96	1.54	35.53	4.08
15	15.66	18.58	0.00	1.10	6.79	0.00	3.88	21.65	1.48
16	22.27	9.53	0.00	0.00	22.39	0.00	0.00	33.58	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	94.98	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	72.33	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	30.34	0.00
20	68.05	0.00	3.46	0.00	0.00	0.00	0.00	24.90	0.00
21	70.39	0.00	0.00	0.00	0.00	0.00	0.00	24.41	0.00
22	0.00	7.05	4.51	3.40	6.74	3.66	3.01	29.73	0.00
23	37.66	0.00	0.00	0.00	0.00	0.00	0.00	44.63	0.00

Table 5 Results of normality test for all the catchment attributes and river water quality based on Shapiro-Wilk test ($p < 0.05$, $df = 22$)

Catchment attributes	Symbol	Shapiro-Wilk	
		Statistic	Significance
Agriculture land	A_g	0.64	<0.01
Good quality rangeland	R_g	0.80	<0.01
Moderate quality rangeland	R_m	0.67	<0.01
Low quality rangeland	R_l	0.52	<0.01
Dense forest	F_d	0.86	<0.01
Intermediate-density forest	F_i	0.39	<0.01
Sparse forest	F_s	0.36	<0.01
Urban land	U	0.45	<0.01
Bare land	B_r	0.34	<0.01
B hydrologic soil group	S_b	0.98	0.86
C hydrologic soil group	S_c	0.74	<0.01
D hydrologic soil group	S_d	0.89	0.02
Amphibolite	A_m	0.36	<0.01
Andesite	A_n	0.48	<0.01
Basalt	B	0.69	<0.01
Conglomerate	C_g	0.56	<0.01
Diorite	D_i	0.50	<0.01
Dolomite	D	0.60	<0.01
Fan terraces	F_t	0.73	<0.01
Gabbro	G	0.32	<0.01
Granite	G_r	0.57	<0.01
Gypsum	G_s	0.44	<0.01
Limestone	L	0.92	0.09
Limestone shale	L_{sh}	0.77	<0.01
Marl	M	0.60	<0.01
Sandstone	S	0.61	<0.01
Sandstone shale	S_{sh}	0.67	<0.01
Sandy siltstone	S_s	0.50	<0.01
Schist	SH_t	0.55	<0.01
Shale /sandstone	Sh_s	0.94	0.17
Tuff	T	0.48	<0.01
Ca^{2+}	Ca^{2+}	0.95	0.30
Mg^{2+}	Mg^{2+}	0.95	0.29
Na^+	Na^+	0.98	0.86
Cl^-	Cl^-	0.98	0.87
HCO_3^-	HCO_3^-	0.98	0.94
pH	pH	0.93	0.11
TDS	TDS	0.95	0.27
EC	EC	0.95	0.28
SAR	SAR	0.97	0.77

Statistical analysis

Prior to modeling, all data were tested for normality using the Shapiro-Wilk test. Independent variables consisted of

catchment attributes were evaluated in terms of multi-collinearity. In regression models, t tests were applied to identify significant differences in independent variables' multipliers. Moreover, model residuals were then examined for normality through the Shapiro-Wilk test. Multiple linear regression based on stepwise algorithms was finally employed to explore and model relationships between land use, hydrologic soil groups, and lithology with river water quality. The models' goodness-of-fit was evaluated using scatter plots and simple linear regression of the observed versus predicted values of the river water quality variables. SPSS17 software package was employed for all statistical analyses.

To specify relationships between land use, hydrologic soil groups, and lithology with water quality variables, stepwise multiple linear regression algorithm was applied. Accordingly, all the determination coefficients were >0.85, except for pH and SAR accounting for 0.61 and 0.76, respectively. Using ANOVA ($p > 0.01$), significance of the regression equation between each water quality variable and catchment attributes (land use, hydrologic soil groups, and lithology classes) was evaluated, as well.

Results and discussion

Catchments attributes and river water quality variables (Table 5) were assessed in terms of normal distribution of the datasets. Since the datasets did not conform to the assumption of normal distribution, a Spearman rank correlation test was applied. All the water quality variables, area (%) of B hydrologic soil group and those of shale and limestone were normally distributed. Other catchment attributes (e.g., agriculture land, C soil hydrologic group, and dolomite) did not conform to a normal distribution (Table 5).

Land use and river water quality relationships

Spearman rank correlation coefficients between different land uses in the targeted area and river water quality variables showed only percentages of good-quality rangelands and agricultural fields to be significantly correlated with water quality variables (Table 6). Specifically, the percentage of good-quality rangeland had a direct correlation with the water quality variables of Ca^{2+}, Cl^-, EC, SAR, Na^+, and TDS. Similarly, the percentage of farmland showed significant positive correlations with Cl^-, SAR, and pH. Thus, as the percentages of good-quality rangelands and agricultural land increase in the catchments, so did concentrations/levels of these water quality parameters. It should be noted that increase in measure of water quality parameters has positively been associated with area (%) of urban land use.

Table 6 Spearman correlation analysis of water quality variables and land use/land cover variables ($n = 23$)

Water quality variables	Agriculture land	Good-quality rangeland	Moderate-quality rangeland	Low-quality rangeland	Dense forest	Intermediate-density forest	Sparse forest	Urban land	Bare land
Ca^{2+}	0.39	0.47*	−0.04	0.30	−0.33	−0.01	0.01	0.17	0.16
Mg^{2+}	0.39	0.39	−0.15	0.28	−0.23	−0.08	−0.05	0.18	0.15
Na^+	0.40	0.60**	−0.06	0.29	−0.36	−0.15	−0.04	0.32	−0.11
Cl^-	0.47*	0.58**	−0.02	0.29	−0.39	−0.17	−0.08	0.14	0.12
HCO_3^-	0.32	0.13	−0.09	0.12	0.00	−0.03	0.13	0.16	0.28
pH	0.46*	0.42	0.03	0.34	−0.38	0.22	0.15	0.30	−0.34
TDS	0.38	0.45*	−0.06	0.27	−0.31	−0.08	−0.02	0.15	0.16
EC	0.39	0.44*	−0.07	0.27	−0.29	−0.09	−0.04	0.13	0.16
SAR	0.44*	0.61**	−0.08	0.27	−0.32	−0.17	−0.05	0.35	−0.18

*$p < 0.05$; **$p < 0.01$

Table 7 Spearman correlation analysis of water quality variables and hydrologic soil group variables ($n = 23$)

Water quality variables	B hydrologic soil group	C hydrologic soil group	D hydrologic soil group
Ca^{2+}	−0.52*	−0.20	0.48*
Mg^{2+}	−0.44*	−0.07	0.36
Na^+	−0.41*	−0.13	0.45*
Cl^-	−0.54**	−0.19	0.52*
HCO_3^-	−0.24	0.11	0.15
pH	−0.05	−0.41	0.25
TDS	−0.49*	−0.15	0.44*
EC	−0.50*	−0.15	0.44*
SAR	−0.38	−0.10	0.40

*$p < 0.05$; **$p < 0.01$

Hydrologic soil groups and water quality relationships

While the extent of the B hydrologic soil group showed a significant negative Spearman rank correlation with river water Mg^{2+}, Cl^-, EC, Ca^{2+}, Na^+, and TDS, the D hydrologic soil group showed a significant positive correlation with 5-year mean concentrations of Na^+, Ca^{2+}, Cl^-, EC, and TDS (Table 7). The fact that a rise in percentage area of the B hydrologic soil group led to lowered river water Mg^{2+}, Cl^-, EC, Ca^{2+}, Na^+, and TDS levels can likely be attributed to B group soils having the lowest runoff potential in the study area. Likewise, the rise in Na^+, Ca^{2+}, Cl^-, EC, and TDS associated with a greater expanse of D group soils is likely tied to D group soils' high runoff potential. This concurs with the study of Yang and Jin (2010), who reported that D hydrologic soil group showed an inverse relationship with river water NO_3^- concentration in river water. According to their work, the D hydrologic soil group was associated with the lowest runoff and leaching potentials. They also noted that subsurface movement is the main route of NO_3^- displacement alongside Iowa's Cedar River.

Lithology and water quality variables

The Spearman rank correlation analysis showed that a direct association was found between the lithological properties of catchments and their river water quality variables (Table 8). To be more specific, percentage areas of marl and diorite were directly correlated with study area river water concentrations of Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, EC, SAR, Na^+, and TDS.

River water levels of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, EC, and TDS were positively correlated with the percent catchment area covered by gypsum, while SAR, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, EC, and TDS were similarly correlated with the percent catchment area of sandy silt soils. The percent catchment area covered by andesite was positively correlated with SAR, Na^+, Ca^{2+}, Mg^{2+}, EC, and TDS levels in river water, the percent catchment area covered by dolomite was positively correlated with river water Ca^{2+}, Mg^{2+}, HCO_3^-, EC, and TDS levels, while the percent catchment area covered by sandstone correlated with river water levels of Na^+, pH, and SAR. Furthermore, positive correlations were also found between the percent catchment area with fan terraces and river water levels of Na^+, pH, and SAR. While a direct correlation was observed between the percent catchment area with sand-shale and river water Na^+ and SAR, for schist and amphibolite area, only river water pH showed a significant positive correlation.

Catchment attributes and river water quality linkages

Based on the ANOVA, associations between water quality variables and predictive variables were significant ($p \leq 0.01$; Table 9). Variance inflation factors calculated in order to identify multi-collinearity between independent variables were all less than 1.0, implying no multi-collinearity existed between independent variables in any regression models (Table 9). Using t tests, the significance of independent variable multipliers in regression models was assessed. Given that in all cases $p < 0.01$, the independent variable coefficients in the regression models were deemed to be non-zero (Table 9). Evaluating model validity by testing model residuals for their normality of distribution (Shapiro-Wilk test) showed all model residuals not to differ significantly from normality ($p \leq 0.05$; Table 9). Model goodness-of-fit was evaluated using scatter plots and simple linear regressions (Fig. 2a–i). Equations are as follows:

$$Ca^{2+} = 1.56 + 0.21\ D_i + 0.10\ M + 0.02\ T - 0.01\ F_i \quad (1)$$

$$Mg^{2+} = 1.41 + 0.17\ D_i + 0.07\ M - 0.01\ F_i - 0.01\ B \\ + 0.64\ B_r + 0.05\ A_g - 0.02\ F_t \quad (2)$$

$$Na^+ = 0.38 + 0.05\ M + 0.01\ T \\ + 0.01\ R_g - 0.01\ F_i - 0.01\ B \quad (3)$$

$$Cl^- = 0.33 - 0.02\ S_B + 0.03\ M + 0.01\ T + 0.01\ SH_s \quad (4)$$

$$HCO_3^- = 2.94 + 0.13\ M - 0.02\ F_i - 0.17\ Sh_t - 0.02\ B \\ + 0.98\ B_r - 0.01\ F_d \quad (5)$$

$$pH = 8.11 - 0.02\ M + 0.08\ S - 0.01\ D \quad (6)$$

Table 8 Spearman correlation analysis of water quality variables and lithology variables ($n=23$)

Water quality variables	Amphibolite	Andesite	Basalt	Conglomerate	Diorite	Dolomite	Fan terraces	Gabbro	Granite	Gypsum
Ca^{2+}	-0.10	0.47*	-0.16	-0.03	0.70**	0.57**	0.26	-0.03	-0.18	0.69**
Mg^{2+}	-0.12	0.44*	-0.28	0.01	0.66**	0.55**	0.24	-0.09	-0.22	0.66**
Na^+	0.12	0.56**	-0.21	-0.04	0.51*	0.30	0.47*	-0.16	-0.20	0.48*
Cl^-	-0.06	0.40	-0.11	-0.03	0.58**	0.37	0.31	-0.15	-0.21	0.56**
HCO_3^-	-0.16	0.09	-0.24	0.20	0.43*	0.44*	0.03	0.06	-0.13	0.42*
pH	0.44*	0.36	0.03	-0.09	-0.04	0.10	0.55**	0.02	0.22	-0.05
TDS	-0.12	0.45*	-0.21	-0.03	0.68**	0.52*	0.26	-0.08	-0.22	0.67**
EC	-0.12	0.45*	-0.20	-0.03	0.68**	0.52*	0.26	-0.08	-0.22	0.67**
SAR	0.19	0.55**	-0.22	0.00	0.43*	0.23	0.49*	-0.21	-0.17	0.38

Water quality variables	Limestone	Limestone shale	Marl	Sandstone	Sandstone shale	Sand siltstone	Schist	Shale sandstone	Tuff
Ca^{2+}	-0.15	0.14	0.68**	0.39	0.38	0.57**	0.20	-0.01	0.38
Mg^{2+}	-0.19	0.09	0.71**	0.38	0.34	0.58**	0.19	0.01	0.34
Na^+	-0.10	0.06	0.67**	0.47*	0.46*	0.51*	0.34	0.04	0.33
Cl^-	-0.13	0.08	0.60**	0.29	0.41	0.44*	0.15	0.10	0.37
HCO_3^-	0.02	0.09	0.63**	0.14	0.09	0.34	-0.11	-0.09	0.27
pH	-0.09	0.30	-0.11	0.50	0.36	0.29	0.44*	-0.08	0.07
TDS	-0.18	0.10	0.66**	0.35	0.38	0.54**	0.16	0.03	0.38
EC	-0.15	0.08	0.66**	0.35	0.36	0.54**	0.16	0.02	0.38
SAR	-0.05	0.06	0.66**	0.48*	0.46*	0.49*	0.36	0.01	0.32

*$p<0.05$; **$p<0.01$

Table 9 Results of multiple linear regression analysis based on stepwise approach

Variable		Coefficient	Statistics							Shapiro-Wilk test	
Dependent	Independent		SE	r^2	F	Significance	t	Significance	VIF	Statistics	Significance
Ca^{2+}	Constant	1.558	0.043	0.899	40.165	<0.001	36.444	<0.001		0.914	0.049
	Diorite	0.209	0.040				5.288	<0.001	0.687		
	Marl	0.097	0.016				6.137	<0.001	0.837		
	Muff	0.021	0.007				3.173	<0.005	0.695		
	Intermediate-density forest	−0.007	0.002				−3.460	<0.003	0.962		
Mg^{2+}	Constant	1.410	0.037	0.958	48.732	<0.001	38.167	<0.001		0.973	0.750
	Diorite	0.175	0.021				8.259	<0.001	0.875		
	Marl	0.073	0.009				7.732	<0.001	0.848		
	Intermediate-density forest	−0.009	0.001				−6.472	<0.001	0.880		
	Basalt	−0.013	0.003				−4.628	<0.001	0.821		
	Bare land	0.637	0.162				3.931	<0.001	0.927		
	Agriculture land	0.048	0.013				3.766	<0.002	0.811		
	Fan terraces	−0.017	0.007				−2.528	0.023	0.846		
Na^+	Constant	0.380	0.032	0.887	26.813	<0.001	11.764	<0.001		0.956	0.393
	Marl	0.052	0.008				6.294	<0.001	0.847		
	Tuff	0.013	0.003				4.014	<0.001	0.857		
	Good-quality rangeland	0.002	0.001				3.902	<0.001	0.872		
	Intermediate-density forest	−0.004	0.001				−3.521	<0.003	0.899		
	Basalt	−0.006	0.002				−2.509	<0.023	0.856		
Cl^-	Constant	0.328	0.027	0.848	25.104	<0.001	12.100	<0.001		0.962	0.502
	Hydrological soil group B	−0.002	0.000				−4.794	<0.001	0.650		
	Marl	0.026	0.004				6.770	<0.001	0.957		
	Tuff	0.005	0.002				2.804	0.012	0.687		
	Shale sandstone	0.001	0.000				2.670	0.016	0.890		
HCO_3^-	Constant	2.938	0.095	0.906	25.819	<0.001	30.862	<0.001		0.969	0.663
	Marl	0.135	0.018				7.337	<0.001	0.847		
	Intermediate-density forest	−0.018	0.003				−6.889	<0.001	0.813		
	Schist	−0.167	0.037				−4.508	<0.001	0.756		
HCO_3^-	Basalt	−0.020	0.005				−3.779	0.002	0.824		
	Bare land	0.976	0.322				3.034	0.008	0.890		
	Dense forest	−0.003	0.001				−2.163	0.046	0.670		
pH	Constant	8.109	0.012	0.610	9.399	<0.001	658.704	0.001		0.897	0.026
	Marl	−0.023	0.005				−4.339	<0.001	0.804		
	Sandstone	0.079	0.020				4.019	<0.001	0.269		

Table 9 (continued)

Variable		Coefficient	Statistics							Shapiro-Wilk test	
Dependent	Independent		SE	r^2	F	Significance	t	Significance	VIF	Statistics	Significance
TDS	Dolomite	−0.014	0.006				−2.335	0.031	0.286		
	Constant	268.189	8.831	0.970	69.168	<0.001	30.368	<0.001		0.911	0.042
	Diorite	16.762	4.225				3.967	<0.001	0.509		
	Marl	16.840	1.552				10.853	<0.001	0.726		
	Intermediate-density forest	−1.822	0.221				−8.257	<0.001	0.733		
	Tuff	2.707	0.615				4.404	<0.001	0.679		
	Basalt	−1.527	0.412				−3.702	0.002	0.829		
	Dense forest	−0.483	0.114				−4.240	<0.001	0.539		
	Urban land	−3.632	0.994				−3.655	0.002	0.798		
EC	Constant	408.336	13.820	0.969	66.455	<0.001	29.546	<0.001		0.925	0.086
	Diorite	26.284	6.612				3.975	<0.001	0.509		
	Marl	25.630	2.428				10.555	<0.001	0.726		
	Intermediate-density forest	−2.783	0.345				−8.059	<0.001	0.733		
	Tuff	4.133	0.962				4.297	0.001	0.679		
	Basalt	−2.421	0.645				−3.751	0.002	0.829		
	Dense forest	−0.720	0.178				−4.037	0.001	0.539		
	Urban land	−5.536	1.555				−3.559	0.003	0.798		
SAR	Constant	0.336	0.082	0.759	14.148	<0.001	12.605	<0.001		0.975	0.810
	Marl	0.021					3.088	0.006			
	Good-quality rangeland	0.002	0.001				3.718	0.002	0.937		
	Basalt	−0.005	0.002				−3.507	0.003	0.964		
	Intermediate-density forest	−0.003	0.001				−2.310	0.033	0.905		
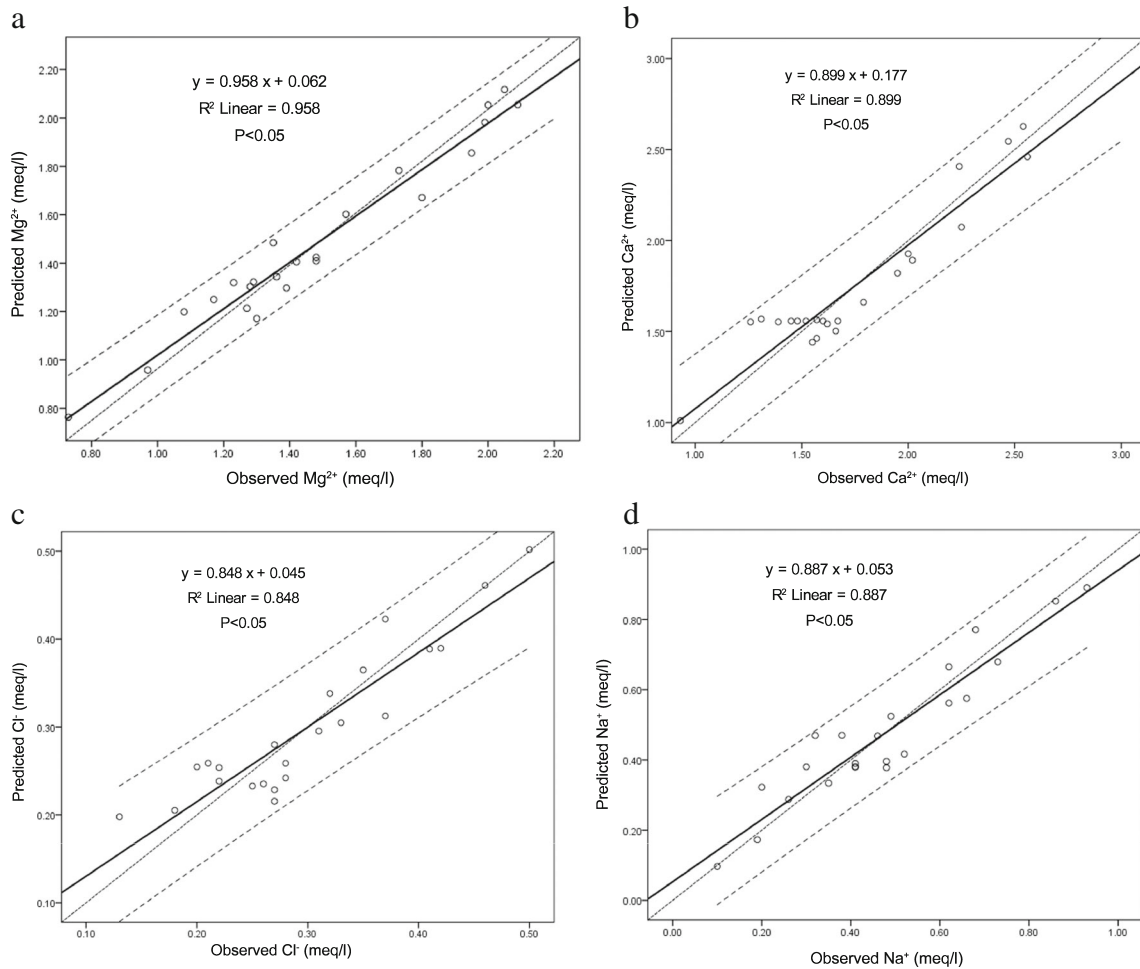
Fig. 2 The observed versus predicted values for Mg^{2+} (**a**), Ca^{2+} (**b**), Cl^- (**c**), Na^+ (**d**), pH (**e**), HCO_3^- (**f**), EC (**g**), TDS (**h**), and SAR (**i**)

$$TDS = 268.19 + 16.76 \ D_i + 16.84 \ M - 1.82 \ F_i$$
$$+ \ 2.71 \ T - 1.53 \ B - 0.48 \ F_d - 3.63 \ U \qquad (7)$$

$$EC = 408.34 + 26.28 \ D_i + 25.63 \ M$$
$$+ \ 4.13 \ T - 2.78 \ F_i - 2.42 \ B - 0.72 \ F_d - 5.54 \ U \qquad (8)$$

$$SAR = 0.34 + 0.02 \ M + 0.01 \ R_g - 0.01 \ B - 0.01 \ F_i \qquad (9)$$

where

Ca^{2+}, Cl^-, HCO_3^-, Mg^{2+}, Na^+	The mean river water concentrations of calcium, chloride, bicarbonate, magnesium, and sodium, respectively (meq l^{-1})
EC, pH, SAR, and TDS	The mean river water concentrations/ levels of electrical conductivity (μS cm^{-1}), pH, sodium adsorption ratio,

and total dissolved solids (mg l^{-1}).

A_g, B_r, F_d, F_i, R_g, S_B, U	The areas of agriculture, bare land, dense forest, intermediate-density forest, good-quality rangeland, hydrologic soil group B, and urban, respectively (% of catchment).
B, D, D_i, F_t, M, S, Sh_t, SH_s, T	The areas of basalt, dolomite, diorite, fan terrace, marl, sandstone, schist, shale sandstone, and tuff, respectively (% of catchment).

Of 31 independent variables (9 land use classes, 3 hydrologic soil groups, and 19 lithological variables), 16 variables consisting of 6 land use variables, 1 variable of soil hydrologic groups, and 9 lithological variables were identified as significant ($\alpha \leq 0.05$) attributes in the finalized models. Area (%) of marl was significant and had a positive coefficient in all developed models (Eqs. 1–9), namely those for mean river water levels of HCO_3^-, TDS, Mg^{2+}, EC, Cl^-, Ca^{2+}, and Na^+. This implies that as marl increases in catchments, these water
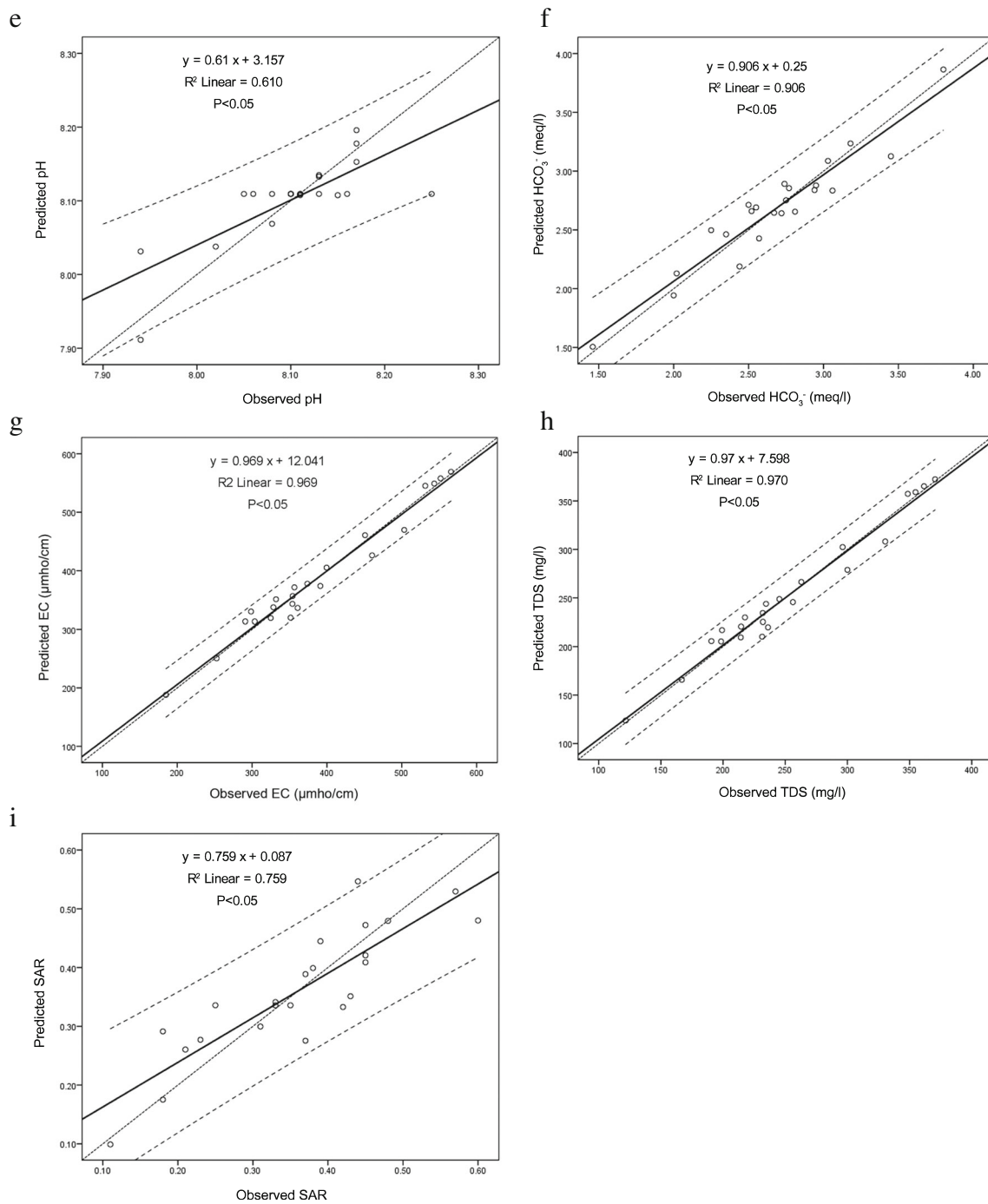
Fig. 2 (continued)

quality parameters tend to increase in river water. The percentage area of marl showed an inverse relationship with river water pH. Marl is a sedimentary rock consisting of clay and carbonate minerals. Inherent parent materials could have different effects on concentrations of cations and anions in river water. For example, water Ca^{2+} and Mg^{2+} concentrations might be under the influence of weathering of carbonate, silicate, and

evaporative minerals in the catchments. Moreover, HCO_3^- concentrations could be influenced by carbonate and silicate minerals (Chen 1987; Li and Zhang 2008). Marl's hardness coefficient of 2.0, placing it as a relatively soft material (Rzhevsky and Novick 1971) and its classification as an erodible stone with a high potential of sedimentation (PSIAC 1968) are likely strong contributing factors to its positive correlation
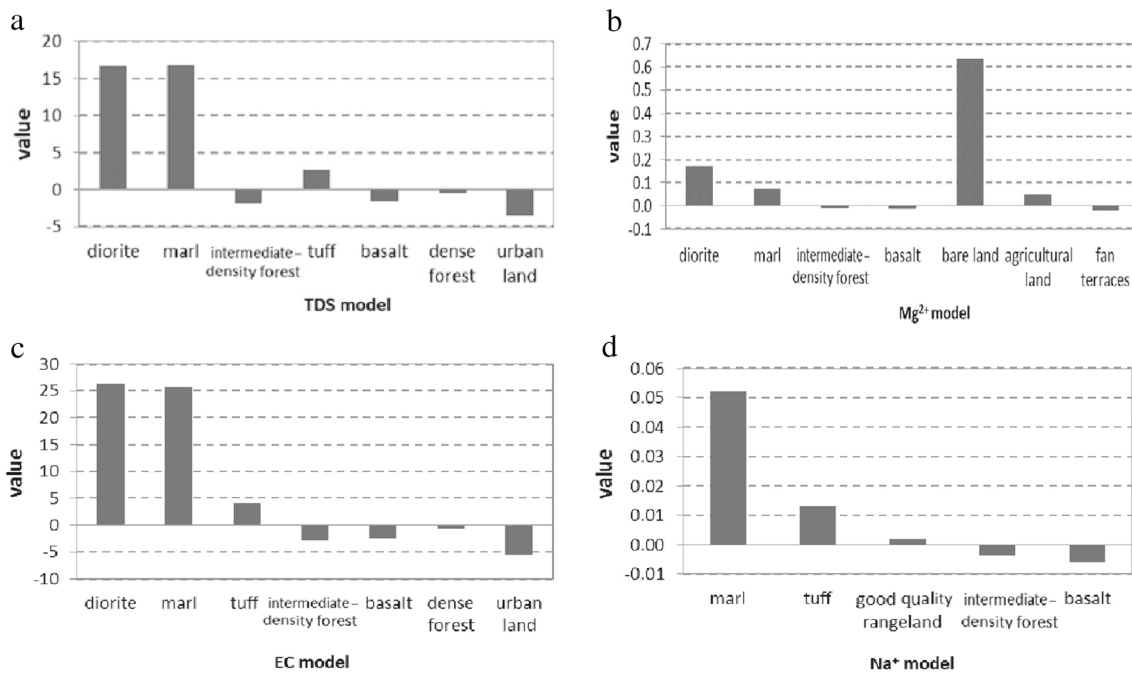
Fig. 3 Parametric analysis of the explaining variables of the regression models: TDS (**a**), Mg^{2+} (**b**), EC (**c**), Na^+ (**d**), SAR (**e**), pH (**f**), Cl^- (**g**), Ca^{2+} (**h**), and HCO_3^- (**i**)

with changes water quality variables levels. The existence of clay minerals in marl stones could also explain the negative association between the area of marl and river water pH.

The negative correlations between percent area of basalt in the catchment and river levels of SAR, Na^+, Mg^{2+}, HCO_3^-, EC, and TDS imply that an increase in the relative contribution of basalt in a catchment resulted in lower levels of these water quality parameters in a given catchment. Harrington and Humphreys (2004) noted that phosphorus availability in soils originating from basalt was lower than that in soils originating from sandstone. Accordingly, the release of anions and cations and their transport into rivers could be influenced by the soils originating from basalt in the catchments under study. Moreover, basalt, with a hardness coefficient of 20, could be accounted as one of the hardest stones (Rzhevsky and Novick 1971), which substantiates the logic of a negative correlation between the area of basalt and the water quality parameters mentioned above. The decrease in river water concentration of anions and cations might equally be due to basalt's high resistance to erosional processes in the catchment.

Negative correlations were also found to exist between the area (%) of intermediate-density and dense forest land covers in the catchment and levels of TDS, EC, Mg^{2+}, Na^+, Ca^{2+}, HCO_3^-, and SAR in catchment river water. This implies that if the area of the forest cover in the catchments is increased, concentration of certain river water contaminants goes down. This concurs with the findings of Li and Xang (2008). Similarly, Versace et al. (2008), Li et al. (2009), and Pratt and Chang (2012) documented that increased forest

cover can lead to decreased water EC. This might be due to the lower erosion rate of forested land, which prevents transportation of soil nutrients into rivers (Kaste et al. 1997; Amiri and Nakane 2006).

Change in the area (%) of urban land use of the catchments is negatively correlated with EC and TDS loads in river water, i.e., if urban areas increase, EC and TDS values decrease downstream. Zampella et al. (2007) reported a direct association between percentage area of urban land use and levels of Ca^{2+}, Cl^-, EC, pH, and Mg^{2+} in a New Jersey watercourse. The fact that our findings do not concur with those of Pratt and Chang (2012) and Zhou et al. (2012) might be attributable to the different environmental settings (climate, soil, and lithological features) of the study areas. Accordingly, the effects of urban areas on river water quality in semi-arid climates could be a subject for further research.

Percentage area of good-quality rangeland in the catchments was significant in the predictive model of Na^+ (Eq. 3) and SAR (Eq. 9), indicating a direct association between the extent of good-quality rangeland and the concentrations of Na^+ and SAR. Similarly, a direct association existed between the area (%) of bare land and Mg^{2+} and HCO_3^- concentrations, suggesting that the greater the area of bare lands, the greater the Mg^{2+} and HCO_3^- concentrations downstream. The positive association between area (%) of bare land and NO_3^- concentrations in river water found by Li et al. (2008) might be attributable to the weathering of bare rocks (Sliva and Williams 2001; Holloway et al. 1998). Considerable caution is required in interpreting the findings on bare lands since it
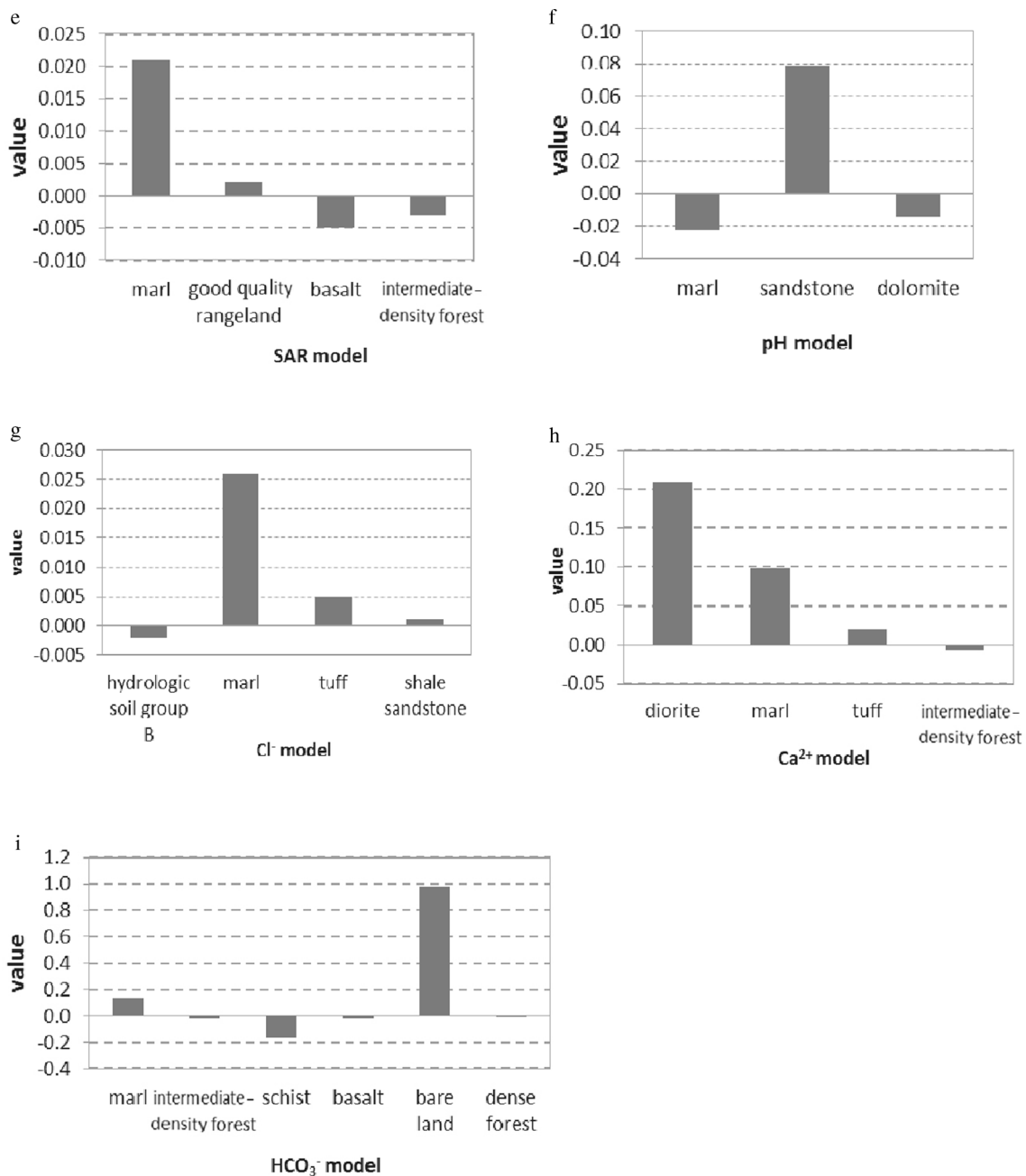
Fig. 3 (continued)

was observed in two out of the 23 catchments in the study area. Based on Eqs. 7 and 8, it should be noted that negative relationships have been observed between area (%) of urban land use and measure of EC and TDS. Accordingly, if area (%) of urban land use increases in the catchment, measure of EC and TDS will decrease downstream.

While the equation for the mean concentration of river Mg^{2+} (Eq. 2) shows an inverse association with the areal extent of fan terraces, it shows a direct association with the area (%) of agricultural land. Zampella et al. (2007) found that the area (%) of agricultural land was directly tied to Ca^{2+}, Cl^-,

EC, pH, and Mg^{2+} concentrations in Mullica Catchment, NJ, USA. In their study, agricultural land use was identified as the most important predictive variable in anticipating Ca^{2+} and Mg^{2+} concentrations in rivers. The present study concurs with Zampella et al. (2007). Direct relationships between area (%) of shale sandstone and the Cl^- concentrations can be attributed to shale sandstone's permeability and its high potential to erodibility (PSIAC 1968), as shale can be easily eroded once saturated by water. Moreover, the negative association between area (%) of B hydrologic soil group and concentration of Cl^- is attributable to the

B hydrologic soil group's low runoff potential resulting in lesser runoff moving Cl^- into water bodies. Atkinson et al. (2009) noted that soil organic matter (SOM) has a negative association with Cl^-.

With a negative association with HCO_3^- in river water, the area (%) of schist in catchments is, however, only significant in predicting this water quality parameter (Eq. 5). According to the rocks' hardness classification of Rzhevsky and Novick (1971), schist has hardness coefficient of 15 and can therefore be categorized as a very hard stone. This might explain its negative relationship with the river water HCO_3^- concentrations.

Independent variables were evaluated, aiming to explore their predictive ability in anticipating water quality variables. The model parameters are illustrated in Fig. 3a–i in conjunction with their type and effectiveness level. For example, in the Mg^{2+} predictive model, some variables such as the area (%) of bare land, those of agricultural land, diorite, and marl show direct association, and other variables such as the area (%) of forest land cover and those of basalt and fan terrace show a negative association with Mg^{2+} concentrations. Area (%) of bare land and forest land cover were, respectively, scored as the most and the least effective factors in explaining concentrations of Mg^{2+} in river water. Accordingly, the variable of bare land area has a significant contribution, some 70-fold greater than that of forest land cover in predicting Mg^{2+} concentrations (Fig. 3b). Parameters of the models indicate that lithological attributes' multipliers, such as those for marl and diorite, could be designated as degrading factors of water quality due to their higher values compared to those of forest land cover (intermediate-density and dense) and basalt (improving factor of water quality). Finally, it can be concluded that in our study area, lithology variables may have a significant role in predicting water quality variables, rather than simply land use variables.

Conclusions

In this study, the effects on water quality variables of catchment attributes, including land use, hydrologic soil groups, and lithology-based parameters, were assessed through a spatio-statistical approach. To conduct the present study, mean values of the water quality variables derived from a 5-year (1998–2003) sampling period at 23 sampling sites were analyzed.

All input data layers including digital maps of land use, soil, and lithology parameters were prepared through application of GIS and spatial analysis. Applying correlation analysis and multiple linear regressions, the associations between water quality variables and catchment attributes were quantified.

According to Spearman rank correlation tests, the whole set of independent variables showed direct correlations with water quality attributes, except for the B hydrologic soil group (S_B), which showed an inverse relationship. Multiple linear regression analysis showed most of the predictive variables of water quality attributes to demonstrate positive associations. Conversely, B hydrologic soil group (S_B), area (%) of basalt in the catchments (B), area (%) of intermediate-density and dense forest in catchments (F_m and F_d) and urban area (%) in catchments (U) showed inverse associations with water quality properties. Moreover, increase in area (%) of urban land use has shown to decrease in measure of EC and TDS downstream. For our study site, lithology-related variables represented greater predictive ability than land use and soil-related variables for water quality. Hence, the effects of urban areas and lithology-related variables at a finer spatial resolution on river water quality in semi-arid climates merit further investigation.

References

Ahearn DS, Sheibley RW, Dahlgren RA, Anderson M, Johnson J, Tate KW (2005) Land use and land cover influence on water quality in the last free-flowing river draining the western Sierra Nevada, California. J Hydrol 313(3–4):234–247

Amiri BJ, Nakane K (2006) Modeling the relationship between land cover and river water quality in the Yamaguchi Prefecture of Japan. J Ecol Field Biol 29(4):343–352

Amiri BJ, Nakane K (2008) Entire catchment and buffer zone approaches to modeling linkage between river water quality and land cover—a case study of Yamaguchi Prefecture, Japan. Chinese Geogr Sci 18(1):85–92

Atkinson S, Johnson D, Venables B, Slye J, Kennedy J, Dyer S, Price B, Ciarlo M, Stanton K, Sanderson H (2009) Use of watershed factors to predict consumer surfactant risk, water quality, and habitat quality in the upper Trinity River, Texas. Sci Total Environ 407(13):4028–4037

Baker A (2003) Land use and water quality. Hydrol Process 17(12):2499–2501

Bruijnzeel LA, Sampurno SP (1990) Hydrology of moist tropical forests and effects of conversion: a state of knowledge review. The Netherlands: Faculty of Earth Sciences, Free University, Amsterdam, p 224

Carey RO, Migliaccio KW, Li Y, Schaffer B, Kiker GA, Brown MT (2011) Land use disturbance indicators and water quality variability in the Biscayne Bay Watershed, Florida. Ecol Indic 11(5):1093–1104

Chen J (1987) Water environment chemistry. Higher Education Press, Beijing

Dale VH, Brown S, Haeuber RA, Hobbs NT, Huntly N, Naiman RJ, Riebsame WE, Turner MG, Valone TJ (2000) Ecological principles and guidelines for managing the use of land. Ecol Appl 10(3):639–670

Dyksterhuis EJ (1949) Condition and management of rangeland based on quantitative ecology. J Range Manag 2(3):104–115

Haidary A, Amiri BJ, Adamowski J, Fohrer N, Nakane K (2013) Assessing the impacts of four land use types on the water quality of wetlands in Japan. Water Resour Manag 27(7):2217–2229

Harrington BA, Humphreys G (2004) Plant accessible phosphorus as a discriminator of native vegetation in the upper Blue Mountains. Supersoil: 3rd Australian New Zealand Soils Conference, 5–9 December 2004

Holloway J, Dahlgren R, Hansen B, Casey W (1998) Contribution of bedrock nitrogen to high nitrate concentrations in stream water. Nature 395(6704):785–788

Kaste O, Henriksen A, Hindar A (1997) Retention of atmospherically-derived nitrogen in subcatchments of the Bjerkreim River in south-western Norway. Ambio 26(5):296–303

Li S, Zhang Q (2008) Geochemistry of the upper Han River Basin, China, 1: spatial distribution of major ion compositions and their controlling factors. Appl Geochem 23(12): 3535–3544

Li S, Gu S, Liu W, Han H, Zhang Q (2008) Water quality in relation to land use and land cover in the upper Han River Basin, China. Catena 75(2):216–222

Li S, Gu S, Tan X, Zhang Q (2009) Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone. J Hazard Mater 165(1–3):317–324

Maillard P, Pinheiro Santos NA (2008) A spatial-statistical approach for modeling the effect of non-point source pollution on different water quality parameters in the Velhas River watershed—Brazil. J Environ Manag 86(1):158–170

McCulloch JS, Robinson M (1993) History of forest hydrology. J Hydrol 150(2–4):189–216

Miller JD, Schoonover JE, Williard KW, Hwang CR (2011) Whole catchment land cover effects on water quality in the Lower Kaskaskia River watershed. Water Air Soil Pollut 221(1–4):337–350

Pacific Southwest Interagency Committee (PSIAC) (1968) Report of the Water Management Subcommittee on Factors Affecting Sediment Yield in the Pacific Southwest Area and Selection and Evaluation of Measures for Reduction of Erosion and Sediment Yield. ASCE 98, Report No. HY12

Pratt B, Chang H (2012) Effects of land cover, topography, and built structure on seasonal water quality at multiple spatial scales. J Hazard Mater 209–210:48–58

Rzhevsky V, Novick G (1971) The physics of rocks. MIR, Moscow, 320pp

Seitz NE, Westbrook CJ, Noble BF (2011) Bringing science into river systems cumulative effects assessment practice. Environ Impact Assess 31(3):172–179

Sliva L, Williams D (2001) Buffer zone versus whole catchment approaches to studying land use impact on river water quality. Water Res 35(14):3462–3472

Uriarte M, Yackulic CB, Lim Y, Arce-Nazario JA (2011) Influence of land use on water quality in a tropical landscape: a multi-scale analysis. Landsc Ecol 26(8):1151–1164

USDA, Natural Resources Conservation Service (2007) Hydrologic soil groups. National Engineering Handbook. http://directives.sc.egov. usda.gov/viewerFS.aspx?hid=21422. Accessed 23 Nov 2013

Versace V, Ierodiaconou D, Stagnitti F, Hamilton A, Walter M, Mitchell B, Boland A-M (2008) Regional-scale models for relating land cover to basin surface-water quality using remotely sensed data in a GIS. Environ Monit Assess 142(1–3):171–184

Water Resources Management Company (WRMC) of Iran (2009) Guidelines for monitoring surface water quality variables. WRMC of Iran, Tehran

Yang X, Jin W (2010) GIS-based spatial regression and prediction of water quality in river networks: a case study in Iowa. J Environ Manag 91(10):1943–1951

Zampella RA, Procopio NA, Lathrop RG, Dow CL (2007) Relationship of land-use/land-cover patterns and surface-water quality in the Mullica river basin. J Am Water Resour Assoc 43(3):594–604

Zhou T, Wu J, Peng S (2012) Assessing the effects of landscape pattern on river water quality at multiple scales: a case study of the Dongjiang River watershed, China. Ecol Indic 23:166–175