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Trace metal surface water inflow and retention in different terms of the wetland

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ABSTRACT

Wetlands are important ecosystems that provide biodiversity and buffer aquatic ecosystems. This study monitored the quality of surface water in the Efteni wetland system in Turkey, which is intertwined with the Melen River. Basic water quality parameters and 26 different trace elements were analysed by standard methods (USEPA method 200.7 and ISO 11885) using inductively coupled plasma in water samples taken from inflows, an internal lake and the outlet of the wetland in different seasons (before, during and after the flowering) in 2011. Trace element concentrations differed between tributaries flowing to and within the wetland. Natural attenuation was observed for health risk elements such as molybdenum, copper, nickel, boron and vanadium in all seasons. Most trace elements were observed at their lowest levels during the flowering period. These results confirm that the Efteni wetland acts as a retention zone and, due to its important location in the River Melen watershed, warrants protection.

Keywords: Buffer zone; Landscape effect; Natural wetland; Trace element; Treatment

1. Introduction

Wetlands can be considered useful land as an ecologically sustainable option for water pollution control [1,2]. They have a high, long-term capacity to improve water quality and there have been many initiatives to restore them for this purpose [1]. Due to their metal retention capability, constructed and natural wetlands have been effectively used in the USA and Europe to reduce levels of copper, zinc, nickel, lead and other metals in run-off and drainage [3–6]. A number of studies have examined accumulation of heavy metals in natural riparian wetlands [7,8]. Studies on the functions of vegetation in wetlands have indicated that plant-covered wetlands may play a role in reducing heavy metals by storing them in various parts such as roots and shoots [9,10].

Wetlands are habitats for a wide variety of plant and animal life, especially water birds, and are also a nursery for several species of fish and shellfish and a variety of aquatic organisms [11,12]. Trace elements and heavy metals cause potential concerns in that they can be transferred and accumulated in the bodies of animals or humans through the food chain, with potential DNA damage and carcinogenic effects owing to their mutagenic ability [13]. Wetlands retain metals using a variety of abiotic (physical/chemical) and biotic (microbial/phytological) processes [14,15]. In addition, redox gradients influence the solubility of the metals in aquatic area, with some metals being more mobile at oxidized condition and others in reduced condition. Abiotic processes that immobilize contaminants include settling, sedimentation, sorption and chemical precipitation [11,16,17]. In biotic processes, macrophytes play the main role and can absorb pollutants in their tissue and provide a surface and environment where microorganisms can grow [18–21]. Moreover, they can carry out phytoaccumulation/phytostabilization and phytodegradation/rhizodegradation [6]. Seasonal differences of wetlands and landscape are changing very clear because of biotic activities. Yet metal retention rate in different season of wetlands is still being one of the main questions.

As a natural wetland, the Efteni wetland is important due to its location in the Melen watershed, which is located close to Istanbul and considered vital for its future water supply (Fig. 1). The wetland has not been effected by industrial, urban, or agricultural pollution and still pristine. Expectations are that the concentration of metals is mostly determined by interactions between water with biotic and abiotic (soils or sediment, precipitation and evaporation) factors.

Although the benefits of wetlands for water quality have been clearly demonstrated, to our knowledge very few wetland studies have been conducted in Turkey or at other sites with similar climate and socioeconomic development. The main purpose of this study was thus to determine transport and retention of metals along with natural treatment in the wetland, which was formed after draining of Lake Efteni. As many lakes have been dried out by water level lowering and/or intensive water use in semi-arid regions, it is important to study their current role as wetlands. Metal concentrations in the wetland and its role in buffering metal pollution were studied by monitoring water inflows and outflow. In particular, the role of vegetation density and seasonality was studied.

2. Materials and methods

2.1. Study area

The Efteni natural wetland is located in west-northern Turkey (41˚5′–40˚40′N; 30˚50′–31˚40′E). The wetland collects most of the run-off water from a 10 km^2 sub-catchment of the Melen catchment [22]. On leaving the wetland, the water flows to the river Melen and then on to the Black Sea. The former Lake Efteni had an overall surface area of 814.5 ha, but it was dried out to create a shallow lake and eventually a wetland with an area of 25 ha. Lakes were typically dried out as a precaution against malaria, in a trend which started in the 1950s. The Küçük Melen River and two tributaries (Aksu and Uğursuyu) which joined the lake in the past were redirected to the Büyük Melen River through diversion channels and thus the water volume in the lake greatly decreased (Figs. 2 and 3). The depth of the current wetland is 1–2 m and the trophic level is mezo-eutrophic [23,24].

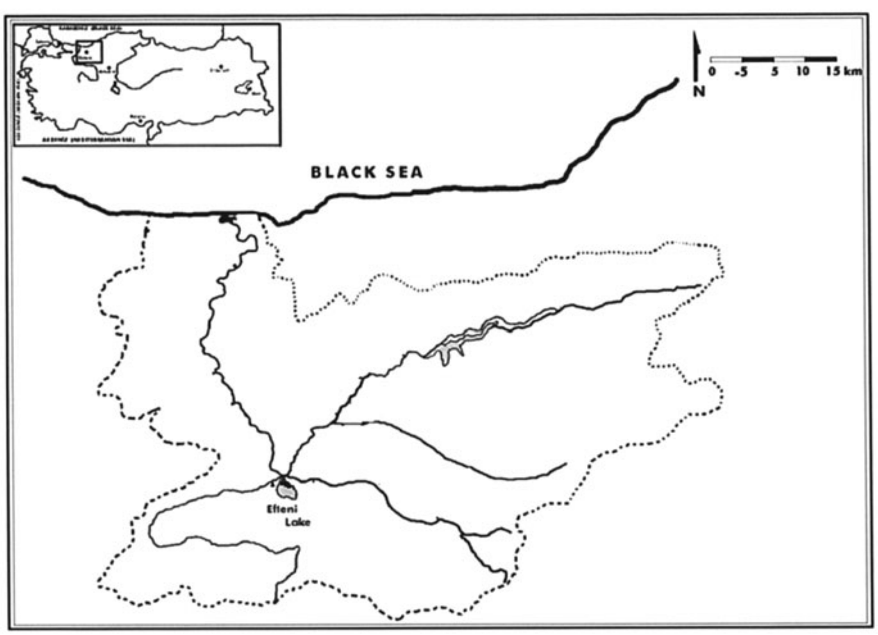

Fig. 1. Location of the Efteni natural wetland (Lake) in the Melen watershed, Turkey (Reproduced with permission from Fig. 1 in Ref. [25]).

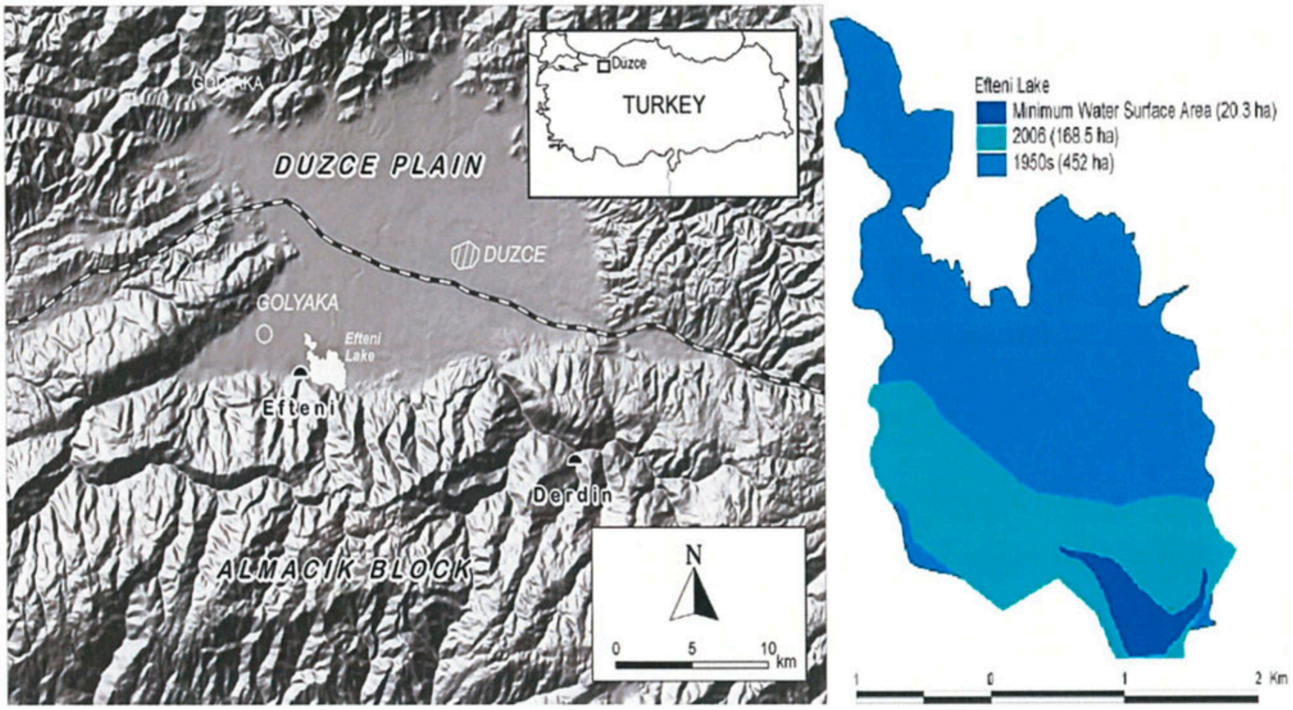

Fig. 2. Location of the Efteni wetland and its catchment in north-western Turkey [26] with its widest boundaries (before drainage), existing boundaries and minimum surface area (in 2006) of Lake Efteni [24] (Partly reproduced with permission from Fig. 1 in Ref. [26]).

The wetland catchment forms two distinct morphological units. In the southern part, the Almacik Block has peaks with elevations of 1,500–1800 m above sea level (masl), while towards the north, the Duzce plain is at 120–150 masl. Mean annual temperature is 13.1˚C and mean annual precipitation is about 840 mm on the plain and exceeds 1,100 mm in the Almacik Block [26]. The wetland area comprises 27.5% open water, 38.1% meadow and the remaining 34.4% is agricultural land. The Efteni wetland outflow is one of the water sources for the Melen River (Fig. 2). The Küçük Melen River (10.53 m^3/s), tributaries (1.88, 5.08 and 6.25 m^3/s) and the Efteni wetland outflow together form the Greater Melen River, which has a watershed average long-term flow rate of 51.23 m^3/s [27].

The Efteni wetland is of ecological and ornithological importance because of its location on the migratory routes of birds. The region has been established as a "Water Bird Protection and Breeding Area," Aquatic plants in the wetland are *Nuphar lutea* (L.) Sm, *Nymphaea alba* L. and *Trapa natans* L. in the lake area, marshy plants (*Carex vesicaria* L., *Eleocharis quinqueflora* (Hartmann) O. Schwarz, *Schoenoplectus litoralis* (Schrader) Palla, *Juncus effusus* L., *Typha latifolia* L., *Phragmites australis* (Cav.) Trin. ex Steudel) at the edge of the lake, meadows near the lake maquis, shrubs (*Arbutus andrachne* L., *Phillyrea latifolia* L., *Pistacia terebinthus* L. ssp. *Palaestina* (Boiss.) Engler, *Erica arborea* L., *Cistus creticus* L., beyond the maquis and forest on the northern slope of the Elmacik Mountain [28].

2.2. Sampling and analytical methods

Surface water in the Efteni wetland was monitored at 7 locations; 4 inlets, 1 outlet and 2 locations inside Lake Efteni (Fig. 3). Monitoring of surface water trace elements was carried out in 2011 over three different vegetation transition periods from spring, summer and winter. Samples were taken before flowering (November–April), during flowering (May) and in the full plant coverage period after flowering (June–October). These occasions were chosen to examine how the wetland reacts to surface water trace element concentrations when under different vegetation covers. A groundwater sampling point was established (40,816N; 31,107E) in an area of the wetland dominated by agriculture. Sampling was carried out at the same period.

HACH pH, dissolved oxygen concentration (DO), electrical conductivity (EC), resistivity, total dissolved solids (TDS), salinity and temperature (*T*) were analysed at the sampling site. The samples were filtered through 0.45 μm Millipore paper, acidified with supra-pure nitric acid to pH <2 and stored in

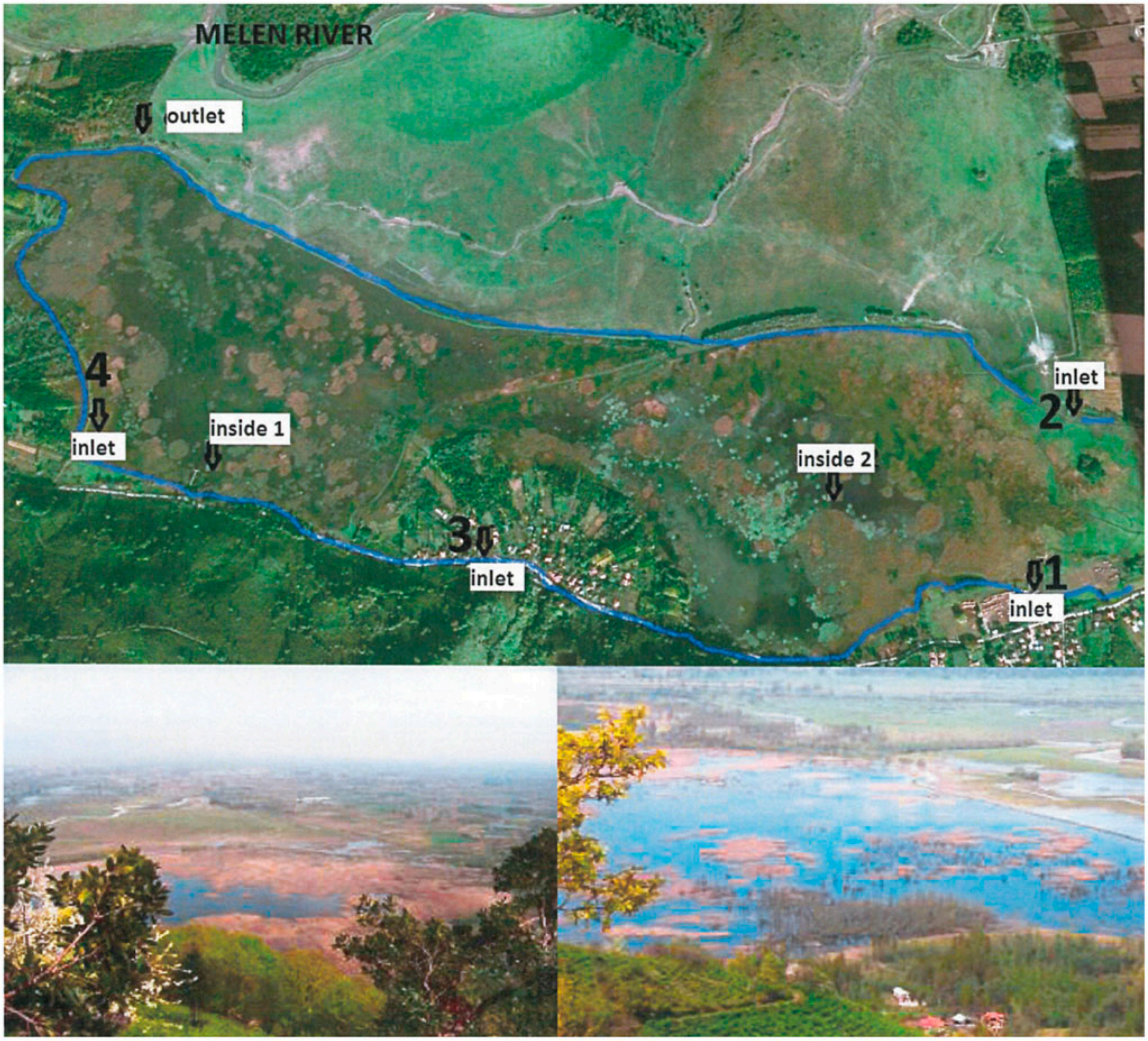

Fig. 3. Sample points in the wetland area and the appearance of the wetland after flowering (below left) and before flowering (below right) (modified from [24]).

polyethylene bottles in +4˚C until their analysis in the laboratory. Trace elements were selected for analysis based primarily on their human health risk and international drinking water standards. Aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), phosphorus (P), potassium (K), selenium (Se), silver (Ag), sodium (Na), thallium (Tl), vanadium (V) and zinc (Zn) concentrations were determined according to USEPA method 200.7 and ISO 11885. The dissolved trace elements were determined by ICP.

The ICP system was initially calibrated with a carrier blank and 1, 2, 3, 4 and 5 ppm aqueous solutions of the selected trace metals of interest. All the calibration standards were prepared from 1,000 ppm of stock solutions of each metal using further dilution. Certified standards were run periodically in between the samples to ensure the accuracy. In all cases, accuracy was acceptable (statistically the same). Each sample was analysed with three replicates and multi-element standards were used.

2.3. Statistical analyses

Basic descriptive parameters were obtained using the SPSS 20.0 programme (Armonk, NY, USA). After viewing the data distribution, correlation analyses were performed to determine the correlation level among parameters. Sampling occasions were grouped as: just before the start of the change in vegetation, the middle of the flowering period (May) and after flowering. Analysis of variance (ANOVA) test was applied to determine whether there were significant differences of seasonal and spatial values for water quality in terms of basic parameters and detected metals.

3. Results

3.1. Metal variation

The water samples had concentrations above the detection limit for 14 of the 26 trace elements analysed, while no traces were found of 12 metals (Ag, As, Be, Cd, Cr, Co, Li, Pb, Sb, Se, Tl and Zn). The concentrations were lowest during maximum flowering, when Al, B, Ca, Fe, Mn, Mo, K and V were present in their lowest concentrations and Mn, B, Mo and Al were below the detection limit in all samples. However, Ba, Ca, B, Fe, Mg, P, K and V reached their highest levels at the end of the flowering period. The concentrations of Mn and Mo were highest before flowering (Figs. 4–6).

The trace elements varied spatially between the four wetland inflows. Nickel was observed only in inlet 2 and Cu only in inlet 3 and only in one period. In inlet 3, Al levels were at their highest and Ba, Ca, Mg, Fe and Na were at their lowest. Vanadium was at its highest level in inlet 1, while P and K were at their lowest. The highest level of K occurred in inlet 3 and the lowest value of Fe in inlet 4. The concentrations of B, Mg and Na were highest within the lake and those of Ba and Ca were highest at the lake outlet. Vanadium was present in all tributaries entering the wetland, with the highest concentration at inlet 1. Aluminium was observed only in inlets 2 and 3. Although Fe was observed at all tributaries, it was observed most frequently in inlet 2. Manganese was observed in inlets 2 and 4 and Mo in inlets 1 and 4. Nickel was observed only in inlet 2, Cu only in inlet 3 and boron only in inlet 4 and phosphorus was observed in inlets 1, 3 and 4. All these elements were below the detection limit at the lake outlet (Figs. 4–6).

3.2. Variation of non-metal parameters

Clear variations were observed in pH, EC, TDS and DO along with trace element concentrations in the wetland. Changes in the vegetation cover also affected these parameters. The pH showed a seasonal variation, with increased values in the flowering period. The values of DO, salinity, TDS and EC varied before, during and after flowering, with EC, TDS and DO decreasing in the flowering period. Salinity, EC and TDS reached their highest values at the end of the flowering period, while DO regressed to its lowest values at that time.

TDS, EC, pH and DO values varied spatially in the wetland. The highest TDS, EC and salinity values and the lowest pH, resistivity and DO values were observed within the lake. The TDS, EC and salinity decreased from highest to lowest in wetland inlets in the order 1, 2, 4 and 3. The situation was completely the reverse for DO. TDS, EC and salinity were always higher at the outlet of the wetland than at the inlets, but lower than inside the lake.

3.3. Degree of retention and comparison with groundwater

The highest variation was observed for microelements used by plants, such as Ca, Mg, K and Na. Other elements showed limited variation. The highest value recorded (mg/L) was 0.029 (mean 0.017) for Al, 0.023 (mean 0.01) for Fe, 0.184 for Ba, 0.330 for B and P, 0.043 for V, 0.0029 for Mo, 0.0023 for Mn, 1.5 for K, 10.4 for Mg and 13.7 mg/L for Na. The mean value for Mg and Na was around 5 mg/L and for Ca around 30 mg/L and the rest of analysed metals were not detected. TDS and EC showed the highest variation among basic parameters. The highest TDS was 130.1 mg/L, the highest salinity was 0.00013, and EC was in the range 75–272 μS/cm (mean 163 μS/cm). Mean DO was 9 mg/L and the lowest value was 4.1 mg/L (Table 1).

There was a strong positive correlation between trace elements. Phosphorus was positively correlated with B and Fe. There was also a powerful positive relationship between Mg and Na, and a strong correlation with T, EC and TDS. Calcium had a strong positive correlation with all metals except Fe and P. In addition, EC had a positive correlation with metals and DO had a strong negative correlation with other basic parameters. There was no strong correlation between pH and metals, but DO had a strong negative correlation with B, Mg, K, Na, TDS, T and EC (Table 2). Correlation levels of the parameters were calculated according to less than 5 and 1% sensitivity. Most of the parameters showed strong correlation which they have probability of the correlation is more than 99% (strong correlation). Besides ANOVA test results showed that there was significant difference

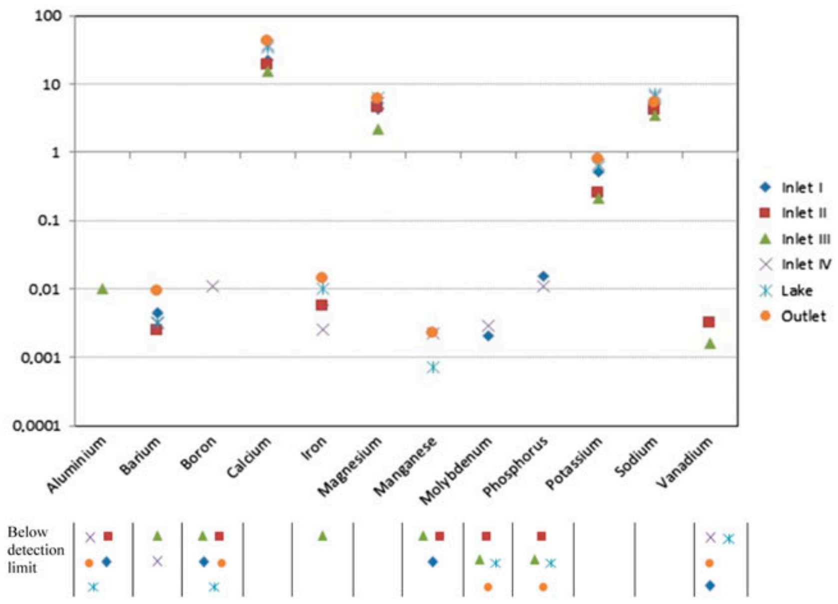

Fig. 4. Spatial dissolved trace element concentrations (mg/L) at different locations in the Efteni natural wetland (before flowering term).

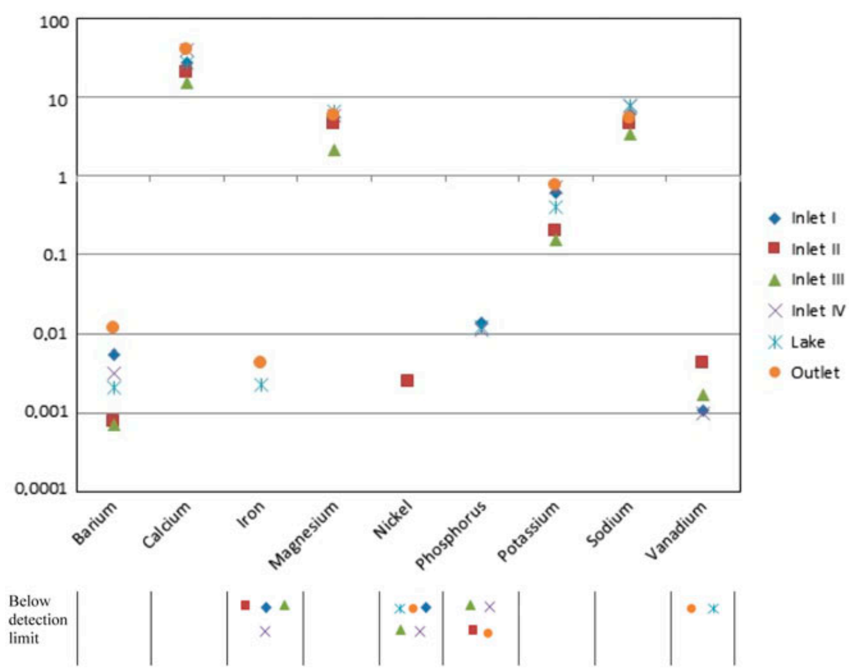

Fig. 5. Spatial dissolved trace element concentrations (mg/L) at different locations in the Efteni natural wetland (during flowering).

between the metal and basic parameters values in terms of seasonal and spatial in the wetland. Especially DO and temperature (seasonal); Ca, Ba, Mg, pH and EC (spatial) were showed statistically strong (<5% sensitivity) differences according to ANOVA.

Although groundwater trace element concentrations were significantly different from those in all surface waters in the wetland area, the wetland ecosystem may depend on groundwater directly or indirectly, and the reliance may be continuous,

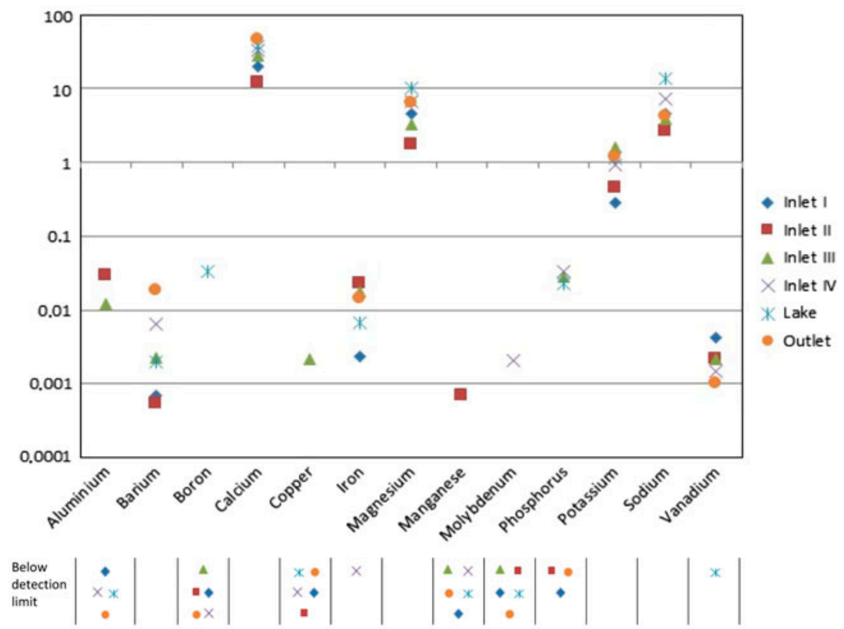

Fig. 6. Spatial dissolved trace element concentrations (mg/L) at different locations in the Efteni natural wetland (after flowering term).

Table 1
Descriptive statistics for surface water analyses

	n	Minimum	Maximum	Mean	Std. dev.
Aluminium (mg/L)	4	0.0100	0.0290	0.017000	0.0104403
Barium (mg/L)	20	0.0006	0.0184	0.004519	0.0047318
Boron (mg/L)	3	0.0110	0.0330	0.022000	0.0155563
Calcium (mg/L)	21	11.9000	47.1000	28.8167	10.64796
Iron (mg/L)	14	0.0023	0.0230	0.009083	0.0068195
Magnesium (mg/L)	21	1.7200	10.3000	5.082778	2.0244267
Manganese (mg/L)	5	0.0007	0.0023	0.001478	0.0008979
Molybdenum (mg/L)	4	0.0021	0.0029	0.002367	0.0004619
Vanadium (mg/L)	13	0.0010	0.0043	0.002182	0.0012082
Phosphorus (mg/L)	11	0.0110	0.0330	0.018375	0.0085178
Potassium (mg/L)	21	0.1520	1.5700	0.632833	0.3858793
Sodium (mg/L)	21	2.62	13.70	5.6833	2.53334
TDS (mg/L)	21	35.000	130.100	77.8166	27.06546
Salinity (%0)	21	0.03	0.13	0.0761	0.02789
DO (mg/L)	21	4.1500	10.2000	8.987778	1.4627032
EC (μS/cm)	21	75.4000	272.0000	163.833333	55.9978781
pH	21	7.3400	8.4900	8.063889	0.3508836
T (°C)	21	10.4000	25.9000	15.888889	4.0576564

seasonal, or occasional [29,30]. Arsenic and Zn were only observed in groundwater, in mean concentrations of 0.019 and 0.0659 mg/L, respectively, while Al, Ni, Cu, V and Fe were only detected in surface waters. Groundwater trace element concentrations were very high for the other elements detected (B, Mn, Ca, Ba, Mg, K and Na) besides EC and TDS were also very high. The pH values were usually neutral and close to surface water levels (7–8), but DO was very low in groundwater (Table 3).

Table 2
Correlations between metals and some of basic parameters

	Ba	Ca	Fe	Mg	P	K	Na	TDS	Salinity	T (°C)	DO	EC
Ba	1											
Ca	.716[b]	1										
Fe	ns	ns	1									
Mg	ns	.727[b]	ns	1								
P	ns	ns	.906[a]	ns	1							
K	ns	.665[b]	ns	ns	.747[a]	1						
Na	ns	.515[a]	ns	.895[b]	ns	ns	1					
TDS	ns	.738[b]	ns	.778[b]	ns	ns	.656[b]	1				
Salinity	ns	.711[b]	ns	.769[b]	ns	ns	.639[b]	.996[b]	1			
T (°C)	ns	ns	ns	.589[a]	ns	ns	.542[a]	.590[b]	.593[b]	1		
DO	ns	ns	ns	−.708[b]	ns	−.510[a]	−.708[b]	−.624[b]	−.617[b]	−.871[b]	1	
EC	ns	.738[b]	ns	.777[b]	ns	ns	.654[b]	1.000[b]	.995[b]	.592[b]	−.625[b]	1

Note: ns: not significant.
[a]Correlation significant at the 0.05 level.
[b]Correlation significant at the 0.01 level.

4. Discussion

Landscape and vegetation cover effects were important for heavy metal concentrations in surface water. In this study, seasonal and spatial differences were revealed in terms of surface water purification. Similarly, a study in Ontario, Canada, reported a slight seasonal difference in the interaction between landscape factors and water quality, with water quality being better explained by landscape factors in spring and autumn than in summer [31]. The main source of trace elements in this study was natural catchment characteristics, as there are no intense urban or industrial activities with impacts on the wetland. The weathering effect in the Melen watershed around the Efteni wetland is moderate [32] and it constitutes the main source of trace elements. Plant flowering and wetland structure significantly affected trace element concentrations in the wetland and watershed system.

Difference between inflow and outflow concentrations was most distinct for Mo, Ni, B and V. In particular, Mo, Ni and B were at their lowest values in wetland outlet water, always below the detection limit. Vanadium was observed only at the end of the flowering period and at low concentrations in this study. In a similar study in a city in North Holland, the Netherlands [33], the average concentrations of the metals studied were generally higher in the wetland inflow (after passage through the road drainage system) and lowest in the wetland outflow. The concentrations of Pd, Zn and Cr were consistently highest in road run-off, with a strong decline towards the wetland inflow and a further reduction towards the wetland outflow, while the Cu concentration was consistently lowest in wetland outflow. In a study in South Carolina, USA [6], copper removal efficiency was high, in excess of 80% removal from inflow to outflow of the wetland system studied. In addition, the system removed 83% of Pb and 60% of Zn, but Ni was generally unaffected. In a constructed wetland study, the wetland showed high Fe, Cr and Ni retention. The overall mean throughout the study period was 95, 86 and 67% retention for Fe, Cr and Ni, respectively [34]. Surface water of the Efteni wetland was not contaminated with trace elements, as no trace element with a high risk value was present in concentrations above international threshold values [35]. However, the Efteni wetland provided considerable purifying of metals that can have impacts on human health.

According to non-metal variation of the wetland, similar findings of higher values of EC in summer months have been reported by Mishra et al. [36]. Regular changes in parameters between seasons showed that no acute contamination had occurred in the wetland. Among the basic parameters, there was least fluctuation in pH (7.3–8.5). According to George and Heaney [37], high pH values promote the growth of phytoplankton and result in blooms and eutrophication [38]. Similarly, in the study by Tromp et al. [33] in the Netherlands, changes in vegetation had a limited effect on pH level, which remained mostly in the range 7.0–8.2 in the three water types studies. The pH value in the Efteni wetland area reached its lowest value at the end of the flowering period, at which time DO amount reached its minimum level in the lake. As the

Table 3
Comparison of average values of parameters in surface water and groundwater in the wetland area

	Al[a]	B[a]	Mn[a]	Ni[a]	Cu[a]	V[a]	Mo[a]	Fe[a]	Ca[a]	Ba[a]	Mg[a]	K[a]	Na[a]	pH	DO[a]	EC[b]	TDS[a]
Inlet (I–IV)	0.017	0.011	0.00146	0.0025	0.0022	0.002	0.0023	0.009	24.09	0.0027	4.21	0.54	4.91	8.16	9.43	138.7	65.7
Lake (I–II)	nd	0.033	0.00071	nd	nd	nd	nd	0.006	33.3	0.0024	7.67	0.71	9.46	7.65	7.38	208.7	99.4
Outlet	nd	nd	0.00227	nd	nd	0.001	nd	0.011	43.23	0.0131	5.97	0.904	4.97	8.05	8.79	219.2	104.4
Groundwater	nd	0.0695	0.851	nd	nd	nd	nd	nd	117.5	0.0721	15.12	2.377	14.07	7.47	3.25	577.5	282.5

Note: nd: not detected.
[a]mg/L.
[b]μS/cm.

flowering period approached, DO decreased regularly (from 10 to 4 mg/L), probably due to consumption of DO by the metabolism of aquatic plants and algae. The minimum and maximum concentrations of DO are reported to be directly related to the maximum and minimum amount of phytoplankton, respectively [38]. In an idealized lake, the oxygen concentration in spring circulation is between 12 and 13 mg per litre [39,40], but DO in the Efteni wetland was occasionally lower, indicating pressure from eutrophication. EC is a key parameter related to ecosystem metabolism [41]. EC and TDS were not generally high, but increased inside the wetland and at the outlet. This was the natural result of biological activities and increasing ion or solute concentration.

5. Conclusion

There was a clear effect of vegetation cover in the landscape on surface water quality in the Efteni wetland. Different stages of plant development (before, during and after flowering) provoked different responses in trace elements, with a positive effect of wetland passage on elements likely to pose a risk to human health. The biological richness of the wetland was very important, as it is in many other buffer zones. Most trace elements were at their lowest values during flowering and at their highest values after flowering. With its connection to the Melen River, an important water resource for the region, and its topographical structure, the Efteni wetland occupies a very important hydrological location. Inlet tributaries to the wetland were distinctly different from each other in terms of trace element concentrations. In water at the wetland outlet, there was no serious pollution in terms of trace elements, with no concentration exceeding international standards (USEPA, EU) in any period.

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