XXXVIII
IAH Congress

Groundwater Quality Sustainability
Krakow, 12–17 September 2010

Extended Abstracts

Editors:
Andrzej Zuber
Jarosław Kania
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University
of Silesia
Press 2010

abstract id: **430**

topic: **2**
Groundwater and dependent ecosystems

2.3
Interactions of surface and ground waters

title: **Threats to a coastal aquifer in northern Albania**

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keywords: coastal, intrusion, heavy metals, recharge, isotopes

ABSTRACT

The Mati plain aquifers in Northern Albania serves as water source for two larger towns and the local habitation. An inventory of threats to the sustainability of the aquifers has been done. Brackish water in the outer portion of the aquifers turns out to be old and the salinity seems to come from diffusion from intercalated clay. Artesian conditions indicate that the current pumping rate is safe. Heavy metals from upstream mines and smelters is adsorbed onto sediments under a stable pH, mirroring the carbonate bedrock in the catchment. What is a serious threat is the sand and gravel extraction in an alluvial cone where the Mati river enters into the plain. This is an important recharge area and the digging lowers the head versus the sea level, may clog the sediments and cause spills of hydrocarbons from machinery used.

BACKGROUND

Coastal aquifers are globally under threat due to several facts. A large fraction of the global population lives in coastal areas leading to a high demand for water supply. The coastal plains, often situated on river deltas, offer good agricultural lands with irrigated agriculture. This is especially the case in S and SE Asia (Ericson et al., 2006). Sea water intrusion has been experienced in many coastal aquifers (Ballykrya & Ravi, 1998; Shammas & Jacks, 2007). The threat of sea water intrusion is often difficult to foresee as recharge rates are not known and recharge mechanisms are complex (Shammas, 2008). Countermeasures in addition to decreased water extraction have been tested and found useful in several cases (Ballykrya & Ravi, 1998; Shammas, 2008). Other threats are land subsidence (Phien-wej et al., 2006) and climate change with a rising sea level (Ericson et al., 2006). The coastal aquifers are often large and have a complex past history with sea water transgression and regression mirrored in the groundwater chemistry (Jacks et al., 2009). Thus any brackish water occurrence does not necessarily mean sea water intrusion. The redox conditions in delta plains globally has caused widespread mobilisation of arsenic even from sediments having background contents of arsenic (Bhattacharya et al., 1997).

Albania is not poor in water resources. The southern part of the country is blessed with many large karstic springs. Several of the rivers are polluted which may indirectly pollute the groundwater (Cullaj et al., 2005). This investigation deals with a major aquifer in Quaternary sediments in the northwestern part of Albania. The aquifer serves as water supply to two towns, Durres to the south and Lezha to the north. The current water extraction rate is about 1.5 m^3/s in two major well fields. The investigation was initiated due to concern about the future water quality of these well fields. The groundwater in the outer portion of the Mati river aquifer is brackish with chloride levels up to 2 000 mg/l. In the catchment there are many sites polluted by copper and chromium mining and smelting. About 10 M tons of copper containing waste is present in the catchment. A source for chromium and nickel is the large Burrel chromium smelter (Shiza et al., 2005). Another obvious threat is gravel extraction in the alluvial cone in the river Mati at its entry into the plain.

The aim of this investigation has been to elucidate and assess the threats to the Mati river plain aquifer, including the origin of brackish groundwater, possible pollution risk from upstream sites and other threats.

SITE AND METHODS

The Mati river has a catchment area of 2441 km^2 and the mean annual discharge is 103 m^3/s. The rainfall in the catchment is between 1000 and 1500 mm. The river forms a plain in northern Albania which is about 20 km broad from the foothills to the sea side and about 30 km long in north-south direction. It consists of three main aquifers of Quaternary age sandwiched between clay layers. Topmost there is a clay layer with about 20 m thickness. Where the river Mati enters into the plain, there is an extensive alluvial cone of sand and gravel contacting all the three aquifers (Fig. 1). In the plain there are two large well fields supplying Durres and Lezha towns.

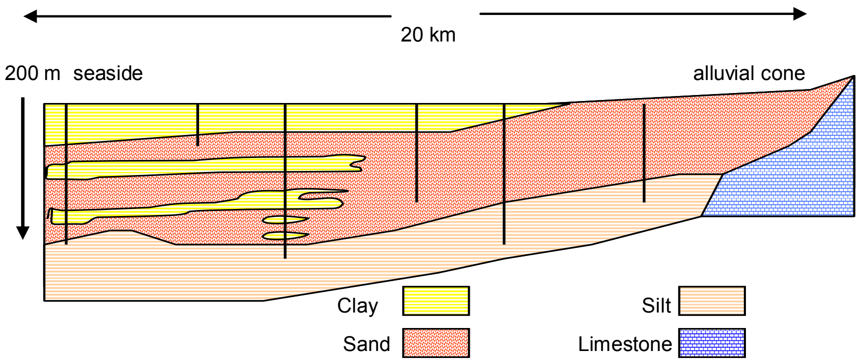

Figure 1. Cross section through the Mati Plain aquifers.

The sampling was done on five occasions in March and August 2008 and in January and in December 2009, covering all the seasons. Water was sampled from pumps and from the overflow of artesian wells. pH and temperature were measured on the sites and the water was passed through 0.20 μm filters. On the last two occassions sulphate was sampled for sulphur isotope analysis along a section from the alluvial cone of Mati river to the seashore in direction ENE to WSW to distinguish between sulphate of sea water origin and that of sulphide oxidation origin from the mine polluted sites in the catchment.

Six samples were taken for ^{14}C and ^{13}C analysis. The carbonate was precipitated from about 5 litres of water and the pH was raised by the addition of a sodium hydroxide pellet. The clear supernatant was decanted after the precipitate had settled.

A number of samples were taken for stable isotope analysis of ^{18}O and D in dense polyethylene bottles. The anions were analysed by ion chromatography and cations and trace metals by ICP-OES.

RESULTS

There exist two types of groundwater in the aquifers, a Ca-Mg-HCO_3 type in the eastern and central part of the aquifers and a Na-Ca-Cl type in the near shore areas. The majority of the brackish groundwater wells in the clay covered western portion of the plain were artesian with a pressure head of up to about 1 m.

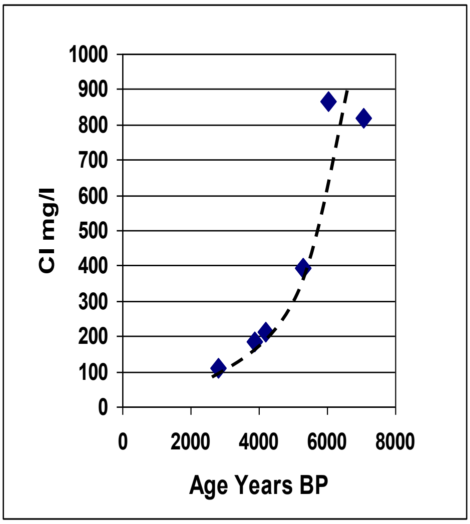

Figure 2. Chloride versus ^{14}C ages.

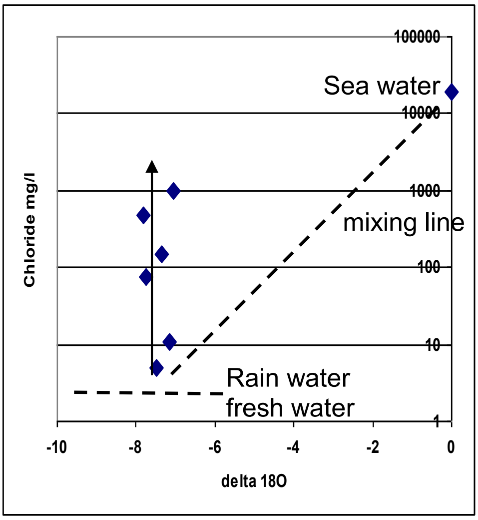

Figure 3. Chloride versus $\delta\ ^{18}O$.

The dating of six samples with elevated chloride content gave a range of 2 800 to 7 000 years of age BP. The ages were related to the chloride content (Fig. 2).

The ^{18}O analyses revealed a narrow range of values between -7 to -8‰ (Fig. 3) and no relation to the chloride concentrations. The river water is an isotopic blend of rainwater from low altitudes to levels around 2000 m. Rainwater $\delta^{18}O$ in the region (Vreca et al., 2006) show values for that range of altitudes of 5 to 10‰. The seasonal variations of $\delta^{18}O$ and range in values depending on altitude is in the river narrowed down by the mixing of groundwater of different flowpaths and the Ulez and Lake Shkopet reservoirs upstream.

Copper, chromium and nickel concentrations are elevated in sediment samples taken from the alluvial cone (Table 1). The concentration of arsenic is lower than found in other investigations in Albania (Lazo et al., 200). In groundwater, no case of excess concentrations of heavy metals has been found. Two samples showed slightly above permissible levels of arsenic with 11 respectively 16 µg/l as compared to the WHO limit of 10 µg/l.

Table 1. Cu, Ni, Zn and As contents in sediments in river Mati and reference values (Taylor, 1964; Plant et al., 2004).

Sample	Cu mg/kg	Cr mg/kg	Ni mg/kg	Zn mg/kg	As mg/kg
Sand < 2 mm	372	328	369	209	11
Organic matter	289	235	364	193	10
Crustal average	55	100	75	70	1-10

The $\delta^{34}S$ samples taken gave values for the fresh water samples in the range of 4-6‰ and values of 21-23‰ for the brackish groundwaters (Table 2).

Table 2. Sulphur isotope data for samples with different chloride concentration.

Sample	$\delta^{34}S$‰	Cl- mg/l	Note
A3:1	+11.6	4.3	Municipal well N:o 1 at river side
A3:2	++4.5	12	Private well 1 km from eiver
A3:3	+7.3	23.7	Village well
A3:4	+4.8	3.4	Durrres pumping station
A3:5	+5.3	15.8	Well 3 km from sea side
A3:6	+23.1	418.9	Close to sea side
A3:7	+21.8	186.3	1 km from sea side
A4:1	+3.6	6.5	Municipal well N:o 2 at river side
A4:2	+24.4	700	Artesian well 2 km from sea
A4:3	+23.0	550	Artesian well 1 km from sea
A4:5	+3.6	12	Well in eastern part of plain
A4:M	+1.6		Copper ore from mining site

DISCUSSION AND CONCLUSIONS

The plain is covered by a 20 m thick clay layer making the aquifers below confined. The clay must have been deposited below water. The sea water level in the Mediterranean has not been appreciably higher than present for the last 120 ky BP (kilo-year before present) (Lambeck & Parcell, 2005). However, while most of the eastern coast of the Adriatic sea has been subject to subsidence, north in Slovenia and Croatia (Antonioli et al., 2007) and in south in Greece (Palyvos et al., 2008) the Albanian coast has with some exceptions (Aliaj et al., 2001) been subject to uplift (Mathers et al., 1999). Mathers et al. (1999) have observed beach ridges on Landsat images close to the foothills in the Mati river plain which is verified by Foache (2006). The age of these beach ridges should be of late Holocene age or from the last 10 ky BP and of the same age as the Flandrian transgression in western Europe. Thus the brackish groundwater dated at 2 to 7 ky BP could be a remnant from the period when the plain was under sea level. The presence of the Na-HCO_3 type of groundwater indicates the aquifers are under a late stage of fresh water flushing. Possibly the age interval of the groundwater may be related to a period of wetter climate that appeared after 7 ky BP (Rolph et al., 2004).

A crucial issue is the hydraulic connection between the alluvial cone and the two pumping stations in the plain where 0,8 m^3/s respectively 0,4 m^3/s are extracted. The sulphate concentrations are elevated in the river or about 20 mg/l and most of it originating from sulphide oxidation from copper mines and smelters upstream. As the $\delta^{34}S$ ($^{34}S/^{32}S$ ratio) is close to 0‰ in sulphides and clearly differs from that in sea water ($\delta^{34}S$ = 21‰) or in sea spray ($\delta^{34}S \sim$ 15-17‰) it was considered possible the assess the fraction of water in the pumping stations coming from the river and the alluvial cone and from the seaside to the west by stable sulphur isotopes. The values for the fresh groundwater samples indicate a mixture of rainwater sulphate and sulphate from sulphide oxidation. The pumping stations thus appear to be completely fed by river water as per the sulphate isotope results.

The heavy metals leached from the copper mines and the smelters upstream have made an imprint in the sediments leaving elevated copper, chromium and nickel concentrations but due to the stable and high pH, mirroring the limestone-dolomite in the catchment this does not comprise a problem for the groundwater quality. In addition to carbonate rocks the copper ores are hosted in ophiolitic structures built up by mafic and ultramafic rocks (Economou-Eliopoulos et al., 2008) also providing good buffering towards acidification by sulphide oxidation. However, the most polluted sites should be identified and remediated.

The most immediate threat to the recharge is the gravel extraction in the alluvial cone at the entrance of the river Mati into the plain. This will decrease the head of the groundwater at the recharge area which today is situated about 10 to 20 m above the sea level. The risk for clogging of the sediments exists as well and finally the risk of oils spills from the bulldozers and digging machines. The soil erosion in Albania is considerably high (Grazhdani & Shrunka, 2007). This is another threat to the recharge as the suspended load is very high in October and November. However, the soil erosion is lesser in Mati river catchment then elsewhere in Albania and the reservoirs mentioned above act as sinks for the suspended sediments. As is evident from the sulphur isotope results the groundwater extracted in the well fields is more or less completely derived from the river recharge.

ACKNOWLEDGEMENTS

We are thankful to colleagues at the Albanian Geological Survey, notably the Director Prof. Dr Adil Neziraj and Dr Arben Pambuku. We are also thankful for the support from Swedish Environmental Agency.

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2-vol. set + CD
ISSN 0208-6336
ISBN 978-83-226-1979-0