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ENVIRONMENTAL – HYDROGEOLOGICAL INVESTIGATIONS ON THE CLAY DEPOSITS IN THE BROAD AREA OF MESOLOGGI – AITOLIKO LAGOONS

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Abstract

A hydrogeological study took place in the broader area of Mesologgi – Aitoliko lagoons (West Greece) aiming at the investigation of a) the hydrogeological conditions of the area as well as the surface and groundwater influences on the quality of the clay deposits found in the lagoons and b) the properties of the clay in order to be identified as "therapeutic peloids". Due to their location, the clay deposits could be influenced and possibly polluted from the surface waters. The aquifer of the unconsolidated formations presents low hydraulic conductivity, while the carbonate aquifer is bounded from the foregoing aquifer and therefore the possibility of clay pollution from the groundwater is very limited. pH of the sediments showing neutral and alkaline values, limits the mobility of some pollutants. Seawater affects some of the clay samples, which present high electrical conductivity. Iron and manganese show also high concentrations, while some of trace elements such as Cd, Hg, Hf, Be, Ag present concentrations under the detection limit. Most of the organic material of the clay consists of humus and therefore they could be suitable for fangotherapy.

Key words: *clay sediments, trace elements, fangotherapy, Mesologgi – Aitoliko lagoons, West Greece.*

1. Introduction

The properties that a natural resource (water, gas, clay) should present in order to be identified as "natural therapeutic resource" were not clearly described in Greek legislation. Especially for the clays, the references are quite limited. The first legislation 2188/1920 which concerns "About Therapeutic Springs" in Greece has determined the "therapeutic springs" as well as the process of their recognition and the ownership condition. According to the last law 3498/2006, which concerns "The Development of Therapeutic Tourism" in Greece, "the therapeutic natural resources comprise a commodity, as part of our natural inheritance and therefore belong to the Greek state which manages and protects them. The therapeutic natural resources are the natural cold, thermal, mineral, thermal mineral waters and gases as well as the peloids (clay, mud, peat), of specific geographical location, which present curative properties according to both the experience of the past and modern scientific validation". In the same law, it is referred that for the recognition of the therapeutic natural sources, their certification is needed. More specifically, their hydrochemical character is defined in relation to the contained dissolved salts and gases, the trace elements and the total radioactivity. Other categories are distinguished according to their minerality, their temperature and osmotic pressure. According to the same law, the conduction of hydrogeological, radiological and medical studies is required for the certification of a therapeutic natural resource. Studies for the current situation and the existing facilities, as well as microbiological, physical and chemical analyses that are carried out in laboratories that function according to the applying arrangements are also necessary. Since this study took place before 2006, it is based on the legislation plan of 8th November 2005.

Generally, the rudiments of Balneology appeared as early as the 5th century BC when Herodotus called attention to the methods of prescription and application of mineral waters (Albu et al, 1997). Therapeutic Tourism was developed even in the ancient time in the area of Mesologgi – Aitoliko, since the clay deposits found in the broader area have been always considered as therapeutic. During summer, many people visit the area and especially the sites of interest of the current study (Agia Triada, Panagia and Rebakia). However, Therapeutic Tourism needs to be further organized in the area for, a) the safety of the bathers, b) the development of the area, c) the protection and sustainability of the environment, d) the improvement of services provided to the visitors by public and private sector. The hydrogeochemical study conducted by the Hydrogeological Laboratory, Department of Geology of the University of Patras, is conformed with the effort of the local Authorities, to further organize Therapeutic Tourism in the broad area of Mesologgi – Aitoliko. The study was dictated by the District of West Greece and was conducted on the sites of therapeutic clays suggested by the local authorities of Mesologgi-Aitoliko. This paper presents the methodology of the hydrogeological - hydrogeochemical study as well as the first results.

2. Study area

The lagoons of Mesologgi – Aitoliko are located in Western Greece, in the south-western part of prefecture of Aitoloakarnania. The lagoon system of Mesologgi – Aitoliko is the biggest in Greece and one from the biggest and more important, ecologically and economically, in Europe. The importance of lagoons has been recognized internationally and has been included in the beneficial and protective provisions of convention RAMSAR (Mpali et al, 1986).

The relief of the broad area of Mesologgi – Aitoliko lagoon is very gentle and is formed from Koutsiliaris Mt. (434m) in the West and Arakynthos Mt. (410m) in the East (fig. 1). The lagoon area is limited between Acheloos River in the West and Evinos River in the East and has been formed by tectonic activities and sedimentation processes. The tectonic activities of Upper Miocene constructed the tectonic trench of Patras Gulf, part of which is the study area. During Holocene, Acheloos River has transported and deposited enormous quantities of sediments resulting to the extension of the land (Marinos, 1993; Psilovikos, 1975). The current shape of the lagoon is due to engineering works of the last 70 years. According to Blachos (2005), the first intervention that changed the lagoon's shape, took place in 1930, with the construction of the Mesologgi port canal and the separation of the eastern part of the lagoon (Kleisova) from the main lagoon, and the construction with dredges of the Tourlida islet. From 1960 onwards, extended irrigation works in the broad area, large-scale exsiccations, as well as interventions for the construction of salt works in particular places of the lagoon, took place.

The geology of the broad area is structured from a) Ionian Zone sediments, which are the conglomerates located in the Aitoliko area, limestones and the flysch of Arakynthos Mt., b) Olocene deltaic, lacustrine-marine deposits and c) recent fluvial deposits (Marinos, 1993).

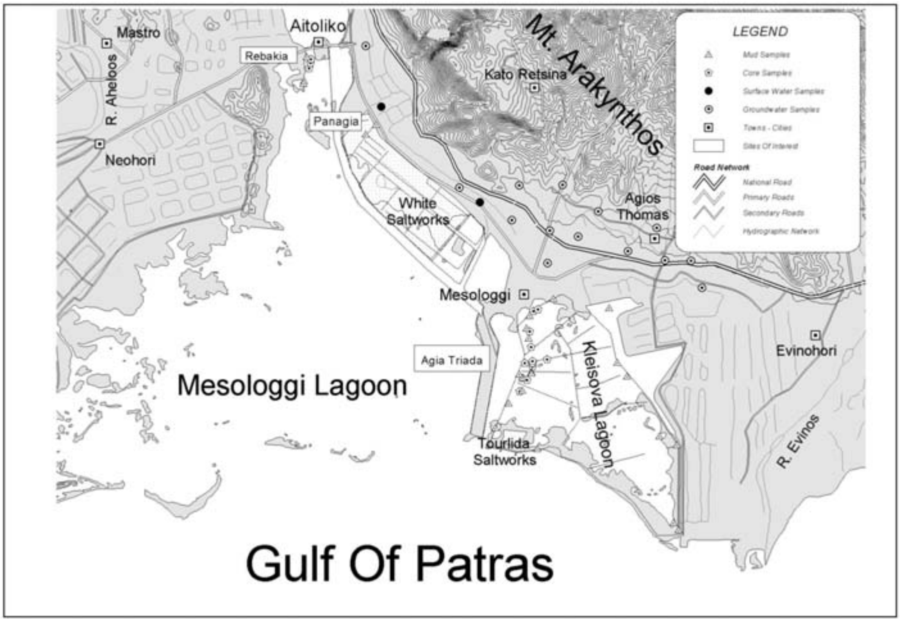

Fig. 1: Study area and sampling sites**.**

3. Methods

3.1 General

The investigation of the hydrogeological conditions of the broad area of Mesologgi and the quality of the surface and groundwater as well as the clays was based on the German reference «DEUTSCHER TOURISMUSVERBAND E.V & DEUTSCHER HEILBAEDERVERBAND E.V» (Deutscher Tourismusverband E.V, 2005) as well as the proposed law of 8th November 2004 for the therapeutic natural resources.

The framework of the research project was planned to include all the tasks needed for the better examination of the hydrogeological status and the quality of water and sediment of the study area, so that this project could act as a key report for the development and utilization of therapeutic resources on both administrative and organization level.

Specifically, for the hydrogeological study that was anticipated in the proposed law of 8th November 2004, record of water occurrences in the area, study of the aquifers, measurements of the water level and collection of water samples were included among the field activities. Clay samples were also collected in order to measure the physicochemical parameters of the clays.

Thirteen (13) surface and groundwater samples were collected and analyzed in total. Fifteen (15) sediment samples from both the bath locations and the lagoon bed were also collected. Field tasks for the clay sampling took place with a local boat. For the sampling of the bed sediment cores, a van veen type core-sampler of 6 cm diameter was used. All sample sites are shown in figure 1.

3.2 Water samples analyses

The physicochemical parameters were measured in situ during sampling. A portable CONSORT®

conductivity-temperature device was used for the determination of temperature, electrical conductivity and pH, whereas the chromato-metric method of MERCK was used for the measurement of dissolved oxygen. Dissolved CO_2 and alkalinity were determined with titration method. The rest of elements were determined in the Hydrogeology laboratory of the Department of Geology, University of Patras, immediately after the collection. Cl^- ions were calculated with titration, while for SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} a HACH® DR/4000 spectrophotometer was used. Ca^{2+}, Mg^{2+}, Na^+ and K^+ were estimated by atomic absorption spectroscopy (GBC Avanta). Finally, for the trace-metals Ag, As, B, Ba, Be, Cd, Cr, Co, Cu, Ga, Li, Fe, Mn, Mo, Ni, Hg, Pb, Sr, Zn, U, V the ICP-MS (inductively coupled plasma mass spectrometer) technique was used in a PERKIN-ELMER® ELAN 6100 device.

3.3 Clay samples analyses

The physicochemical parameters like grain–size, electrical conductivity, total moisture, organic material content, total organic carbon and humus content were determined in the Department of Geology, University of Patras. Trace elements were also determined with the use of both total resolution method and BCR-SEP (sequential extraction method) method. The use of sequential extraction schemes gives the opportunity to study metal distribution in different sediment phases and helps to predict metal mobility and their possible transfer from sediment to aquatic media (Larner et al., 2006; Thomas et al, 1994). The total resolution method was carried out for the surface sediment of every sediment core.

4. Results

4.1 Hydrogeology

In the broad area aquifers are hosted in carbonate rocks and fluvial deposits. The carbonate rocks aquifer located north from Mesologgi city presents remarkable yield capacity and it possibly feeds lateral the aquifer developed in fluvial deposits. The last one is very extended and feeds a large number of shallow wells and boreholes. The aquifer is developed in coarse – grained material mixed with clay and silt. Therefore it presents low hydraulic conductivity. The well discharge ranges between 5 and 15 m^3/h. The potentiometric-surface map, which has been constructed from water level measurements, shows a north to southwest groundwater flow direction. That means, some quantities of groundwater flows into lagoons. According to estimated water balance of the area, 40% of the precipitation reaches as surface water the lagoons (Lemesios, 2008). Surface waters from the draining channel – system of Acheloos River reach also the lagoons. As it is shown in figure 1, Kleisova lagoon is protected from surface runoff, therefore the clay deposits at the bath locations in this lagoon could only be influenced from the seawater and the physicochemical conditions of the lagoon.

4.2 Water Quality

Groundwater from fluvial deposits presents elevated electrical conductivity, due to the dissolution of the salts contained in the sediments. Ca^{2+}, Na^+, Mg^{2+} and HCO^{3-} dominate. Nitrate concentrations show low levels. All samples of surface water present very high electrical conductivity (up to 94,3 mS/cm). This is due to seawater influences. The extreme values of electrical conductivity could be attributed to evaporation. Nitrate concentrations show low levels. Table 1 presents the results of the chemical analyses of surface and groundwaters. The concentration of the most trace elements show low levels in ground waters, while in surface waters they present elevated concentrations. This is also

Table 1. Chemical analyses (mg/l) of groundwater (W4-W14) and surface water (REM1-L2).

Sampling sites	W4	W5	W8	W12	W13	W14	REM1	REM2	PAN1	SK2	SK4	L2	MIN	MAX	MEAN
T° C	17.4	18.6	16.8	17	18.1	16.4	21.2	20.3	21.3	18.7	17.2	21.5	16.4	21.5	18.7
EC	1365 µS/cm	980 µS/cm	2.53 mS/cm	2.51 mS/cm	1752 µS/cm	829 µS/cm	1535 µS/cm	1007 µS/cm	73.5 mS/cm	12.8 mS/cm	53.8 mS/cm	94.3 mS/cm	829 µS/cm	94.3 mS/cm	
pH	7.6	7.7	7.2	6.9	7.2	7.6	7.9	8.3	8.1	8.2	8.0	8.2	6.9	8.3	7.7
Redox (mV)	130.0	151.0	134.0	21.0	147.0	123.0	135.0	133.0	158.0	209.0	241.0	115.0	21	241	141
DO	259.0	160.0	325.0	349.0	265.0	122.0	211.0	104.0	257.0	127.0	268.0	216.0	104	349	222
Ca^{2+}	98.0	77.0	139.0	185.0	116.0	482.0	142.0	59.0	1256.0	115.0	265.0	405.0	59	1256	278
Mg^{2+}	10.4	4.8	42.3	15.0	11.3	10.6	14.7	18.0	165.0	165.0	689.5	797.0	5	797	162
Na^{+}	43.0	25.1	62.6	68.6	29.2	123.8	34.5	39.9	7700.0	1104.0	5200.0	10320.0	25	10320	2063
K^{+}	1.4	7.0	1.9	1.0	2.2	4.7	1.4	2.8	407.0	65.6	302.0	554.0	1	554	113
NO_3^-	1.0	14.0	1.0	9.0	0.0	0.0	0.0	14.0	1.0	14.0	24.0	3.0	0	24	7
NH_4^+	0.0	0.0	0.1	0.1	0.1	0.2	0.0	0.2	0.5	0.1	0.1	0.0	0	0	0
NO_2^-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0	0
HCO_3^-	322.1	290.4	480.7	403.8	363.6	250.1	395.3	163.5	135.4	278.2	219.6	174.5	135	481	290
SO_4^{2-}	31.5	43.5	198.5	91.3	63.8	22.7	68.3	42.0	5475.0	262.5	2562.0	4100.0	23	5475	1080
Cl^-	58	26	119	220	38	205	300	400	12520	2620	18500	19500	26	19500	4542

due to seawater influences. Strontium shows in both ground and surface waters higher levels. This is due to the dilution of the limestones of the broader area as well to the seawater influences. In table 2 the trace elements of ground and surface waters are shown. Surface runoff from streets due to dissolution of solid, liquid and gas pollutants however, will presumably be particularly invidious.

4.3 Clay Quality

The concentrations of all pollutants and specifically of trace elements in sediments are related with the physical properties of the sediments, such as their grain-size, mineral composition, pH, temperature, redox potential and the biological activity (Salomons and Forstner, 1984). Grain size distribution of sediments used the method of burette showed that sediments belong to clay and silt-clay classes. An increase in sand material along with a depth increase was also observed (Lemesios, 2008). In general pH of sediments is a parameter, which presents the general chemical character of the sediment. pH values of most sediment samples present neutral to alkaline character (Table 3). Therefore it could constrain the movement of some trace elements. The highest pH value measured in some samples reaches 9.4. Electrical conductivity is very high in samples that have been influenced from seawater. The organic material content is very important and reaches up to 10%. The concentration of TOC in sediments is low compared to the organic material. This, in combination with

Table 2. Trace elements (μg/l) of groundwater (W4-W14) and surface water (REM1-L2).

	W4	W5	W8	W12	W13	W14	REM1	REM2	PAN1	SK2	SK4	L2	MIN	MAX	MEAN
Ag	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3			
As	<3	<3	<3	<3	<3	<3	<3	<3	60	10	39	75	10	75	46
B	40	81	133	56	54	75	101	117	4083	647	2186	4678	40	4678	1021
Ba	22	31	64	59	37	18	32	26	97	43	52	17	17	97	41
Be	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5			
Cd	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3			
Co	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3			
Cr	13	8	9	9	9	6	18	127	354	45	170	390	6	390	97
Cu	3	7	<3	<3	<3	6	<3	5	116	16	77	152	3	152	48
Ga	<3	<3	<3	<3	<3	<3	<3	<3	4	2	2	1	1	4	2
Li	9	6	13	17	11	3	10	14	213	43	165	319	3	319	69
Fe	<10	<10	<10	17	<10	<10	35	227	289	40	50	288	17	289	135
Mn	3	9	15	4	<4	129	4	72	29	9	60	27	3	129	33
Mo	<3	<3	<3	<3	<3	<3	<3	<3	10	6	7	13	6	13	9
Ni	5	5	<5	<5	<5	<5	8	15	48	38	<5	23	5	48	20
Pb	<3	<3	<3	<3	<3	<3	<3	<3	<5	<3	<3	<5			
Sr	235	226	1743	466	432	310	839	325	25321	1284	4593	8471	226	25321	3687
U	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	4	4	4	4
V	4	4	3	3	2	2	6	40	105	17	50	116	2	116	29
Zn	9	11	28	116	20	46	28	30	112	46	94	103	9	116	54
Hg	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5			
Hf	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2			

the relatively low concentrations of organic nitrogen suggests the dominance of compounds rich in hydrogen. Humus comprises the bigger part of the organic material in sediments as it is derived from the determination of their concentration. This fact encourages the use of clays for curative purposes (Komatina, M. 2004). In the international literature does not exist trace elements concentrations standards for therapeutic peloids. Table 4 shows the concentrations of trace elements determined with the total resolution method of the clay samples of the study area. Generally the concentrations of trace elements have been considered as low, with exception the iron and manganese concentrations, which are relatively high. Papatheodorou et al. , 2002 have also shown that Fe chemistry is an important factor in Klisova lagoons sediment.

5. Conclusions

For the identification of natural resources (clays, waters and gases) as therapeutic, hydrogeological – hydrogeochemical studies have to be conducted. The following observations were derived from

Table 3. Physicochemical parameters of the clay samples.

Sampling sites	pH	EC (µS/cm)	Moisture Content (%)	Organic Content (%)	TOC (%)	TON (%)	Humus Content (%)
T1	9.4	3470	70.2	6.6			
T2	7.9	1975	26.2	3.4			3.2
T3	7.9	2850	55.3	8.3	2	0.2	7.9
T4	7.6	5870	35.1	6.5		0.2	6.9
T5	8.2	2250	62.1	9.8	2.4	0.1	9.6
T6	9.4	3480	57	9	2.3	0.3	8.2
T5A	9	4350	56.9	8	2.2	0.1	7.8
T10	7.7	2460	51.7	8.5	2	0.1	8.2
T11	7.7	3000	37.7	7.2		0.1	6.8
T12	8	2370	38.9	5.4		0.1	5.1
T13	7.7	3750	68.4	13.1	3.3	0.3	11.2
T14	9.1	4050	53.4	8.2	2.1	0.1	7.6
T15	8	2560	33.5	5.3		0.1	5

Table 4: Trace elements (mg/l) in clay samples.

	T1	T2	T3	T4	T6	T5A	T10	T11	T13	T14	MIN	MAX	MEAN
As	8.1	3.5	8.5	10.6	9.6	9.7	11.7	12.6	8.8	7.0	3.5	12.6	9.0
Ag	0.6	0.4	0.7	0.2	0.7	0.3	0.6	0.7	0.5	0.3	0.2	0.7	0.5
Ba	166.9	290.0	177.6	76.5	208.3	155.1	202.0	197.2	170.7	155.8	76.5	290.0	180.0
Cd	0.2	0.0	0.2	0.1	0.1	0.2	0.2	0.1	0.2	0.2	0.0	0.2	0.2
Co	17.3	12.8	17.2	6.5	16.1	17.2	18.0	16.7	23.3	16.7	6.5	23.3	16.2
Cr	116.9	191.2	154.9	88.1	163.9	143.6	168.2	156.8	143.7	137.8	88.1	191.2	146.5
Cu	38.6	20.8	41.8	12.9	29.4	36.8	36.1	33.4	42.8	43.3	12.9	43.3	33.6
Ga	17.6	18.9	19.5	8.0	20.5	17.7	20.5	19.2	18.4	18.1	8.0	20.5	17.9
Li	80.8	52.5	84.2	28.9	71.8	77.5	74.2	73.2	80.2	80.1	28.9	84.2	70.3
Fe	43217	29346	45693	12687	39470	44172	42755	38165	42645	45578	12687	45693	38373
Mn	723	399	965	353	718	825	626	795	917	641	353	965	696
Mo	9.9	0.2	3.4	1.3	4.0	5.7	13.1	3.9	11.4	7.4	0.2	13.1	6.0
Pb	22.5	14.1	23.7	8.8	15.5	20.3	17.0	30.3	27.1	22.9	8.8	30.3	20.2
Sr	237	93	176	372	208	206	211	581	175	140	93	581	240
U	3.9	1.4	2.4	1.4	2.4	2.9	4.5	2.9	3.7	2.9	1.4	4.5	2.8
V	82	56	98	35	89	96	101	95	103	100	35	103	85
Zn	36	8	41	18	24	38	33	19	25	42	8	42	28
Hg	0.3	0.0	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.3	0.1
Hf	2.2	2.2	2.7	0.2	3.0	1.3	2.8	3.0	2.0	1.2	0.2	3.0	2.1

the hydrogeological - hydrogeochemical study in the broader Mesologgi – Aitoliko area: Aquifers are hosted in carbonated rocks and alluvial deposits. The carbonate rocks aquifer presents remarkable yield capacity; the aquifer hosted in fluvial deposits show low hydraulic conductivity. Surface water, which comprises at least 40% of the rainfall, flows into lagoons. Pollution from trace elements in both ground and surface waters is insignificant and therefore the chemical composition of lagoon clays is not risk to be degraded by ground and surface waters of the broader area, which flow into lagoon. Sediments pH presents neutral to alkaline values and it constrains the movement of some trace-metals. The impact of seawater is quite obvious in most of the samples, which present relatively high values of electrical conductivity. The concentration of TOC in sediments is low compared to the organic material. Most of the organic material of the clay consists of humus and therefore they could be suitable for fangotherapy. The concentrations of trace elements calculated with the total resolution method present low values.

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