Preliminary Thermal and Mineral Water Survey of Nisyros Volcano, Aegean Sea: A Study Targeted Towards Sustainable Development.

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Abstract: - Nisyros represents the ideal candidate of a Mediterranean volcano for a pilot study on sustainable development. Nisyros was a renown Loutropolis in the past and its baths, for medicinal purposes. In this work we present a preliminary survey of the thermal and mineral waters of the island. We present chemical data revealing seawater and geothermal water mixing processes with the aim to evaluate their water character and include thermal and mineral waters of Nisyros volcano in the sustainable development plan proposed for the establishment of Nisyros to the status of a National Park and as an attraction pole for "alternative tourism". However, the use that dovetails with promotion of the volcano to a Natural Park and that most of the permanent inhabitants wish for, is their use for baths and in Spa centers, targeting the redirection of the economy towards "alternative tourism" and restoring Nisyros to its ancient status of a renown Loutropolis.

Key-Words: - Nisyros, hydrochemistry, sustainable development, Spa, thermal and mineral waters, tourism.

1 Introduction

Hellas is endowed with numerous thermal and mineral springs due to volcanism and its unstable geodynamic pattern. Nisyros is an active calcalkaline volcano in the eastern extremity of the Quaternary Aegean Volcanic Arc, formed by subduction of Africa under Eurasia. Nisyros is characterized by a volcanic stratigraphy typical of stratovolcanoes, which is shown in Fig. 1.

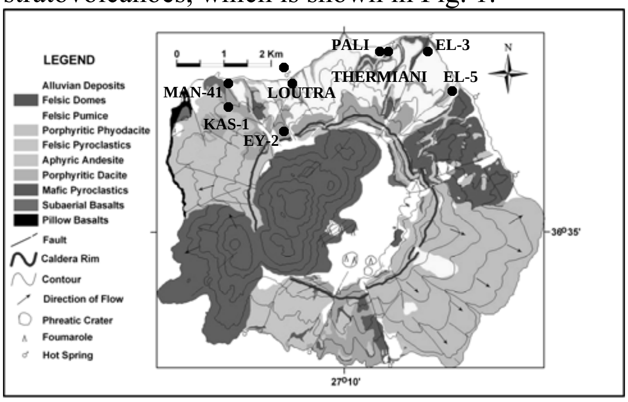

Fig 1: Simplified geological map of Nisyros volcano (black bullets indicate sampling sites).

The active geothermal system at Nisyros is of high enthalpy [1] and consists of two reservoirs at different depths of which one occurs at relatively shallow depth (250-700m and 1500-1800 respectively; [1]). Two deep exploratory drillholes have been sunk on the caldera floor by Public Power Corporation of Hellas to evaluate the geothermal potential of Nisyros; however, further development has been prevented because the local population feels that such development will result in ecological disaster.

Another expression of the active geothermal system on the island is its numerous thermal springs which are concentrated near the coastline due to intersection of steep terrain with tectonic and volcanotectonic faults. Due to its thermal springs Nisyros was a renown Loutropolis attracting visitors from all the Mediterranean cities from the times of Hippocrates till the late 1800's.

2 Present Condition

Nisyros with a permanent population of 916 inhabitants (latitude 36° 35', longitude 27° 10'), occupies one of the extremities of the "unfrequented ship line" of the Dodecanese Island Complex. The island is a rare natural monument of extreme beauty at the stage of neglect, which would have been severe in the absence of daily tourists from Kos and the international renewed scientific interest [2, 3, 4, 5, 6] in the area. We have proposed a three-pronged Sustainable Development plan (Fig. 2; [7]) targeting to the redirection of the economy towards "alternative tourism" with the development of thermal springs into Spa centers and ecotourism with the development of the volcano into a National Park. In this work we present a survey of the thermal and mineral waters of Nisyros island from the scope of their hydrogeochemistry and medicinal character with the aim to prioritize this natural resource as the first objective in the Sustainable Development plan for Nisyros volcano.

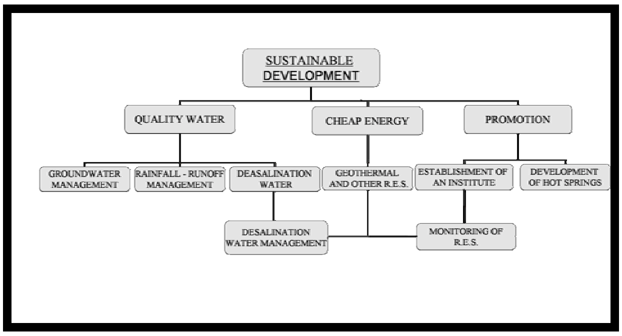

Fig 2: Proposed plan of Sustainable Development of Nisyros volcano [7].

3 Sampling and Analytical Methods

A two period sampling have been carried out during 2006, one at the end of the "wet period" (end of May) and another at the end of the "dry period" (end of October). A total of 17 samples for the two sampling period (wet-dry) have been collected from 9 sites (Fig. 1), 6 from thermal springs (Loutra, Pali, Thermiani), 6 from boreholes (Man-41, EL-5 and KAS-1), 4 from wells (EY-2 and EL-3) for comparison and a seawater sample (SEA). Field measurements included electrode measurements of temperature, pH, T.D.S., electric conductivity and redox and measurements of alkalinity with the use of alkaline kit. Samples were filtered (0.45 μm), acified with nitric acid ultrapure (acid level 0.2% or pH=2) and stored in screw top lid polythene vials. Chemical analysis was performed by the Activation Laboratories Ltd. Ontario of Canada using ICP/MS and ICP/EOS for major and trace elements with detection limits 1μg/l for Li, Mg and Sc and 0.1mg/l for recalculated Mg, 0.1μg/l for Ti, V, Mn and Mo and 10μg/l for recalculated V, 0.5μg/l for Cr and Zn, 0.005μg/l for Co, 0.01μg/l for Cd and Pb, 0.2μg/l for Cu, Se and Hg, 0.03μg/l for As, 0.04μg/l for Sr and 10μg/l for recalculated Sr, 0.3μg/l for Ni, 2μg/l for Al, 3 μg/l for Br, 5 μg/l for Na and 0.1mg/l for recalculated Na, 10 μg/l for Fe, 30 μg/l or 0.1mg/l for recalculated K, 200μg/l for Si, 700μg/l for Ca and 0.1mg/l for recalculated Ca, 0.001μg/l for Th and U. Ion chromatography has been used for the determination of ions (F, Cl, Br, NO_2, NO_3, PO_4, SO_4) with detection limits 0.01mg/l for F, NO_2 and NO_3, 0.02mg/l for PO_4 and 0.03mg/l for Cl, Br and SO_4. the determination of NH_4 was carried out in the Laboratory of Hydrogeology in the department of Geology of University of Patras using Salicylate method with detection limits 0.09mg/L NH_3–N in order to prevent further oxidation of NH_4 in our samples. Almost 90% of the samples display a mass balance below 5-7%.

4 Results

Mixing of hot geothermal waters with meteoric and sea water results in numerous thermal springs (30-60°C), which issue around the coasts of the island. The Geological Institute of Greece (I.G.M.E.) run a borehole project in the past in order to investigate Nisyros island from a hydrogeological aspect, however, no distinct fresh watertable was found due to mixing of thermal, meteoric and sea waters [8].
Our chemical data are listed in Tables 1 and 2. For a preliminary classification of the sample waters, the results have been plotted in a Langelier-Ludwig diagram for each sampling period (Fig. 3a, 3b).

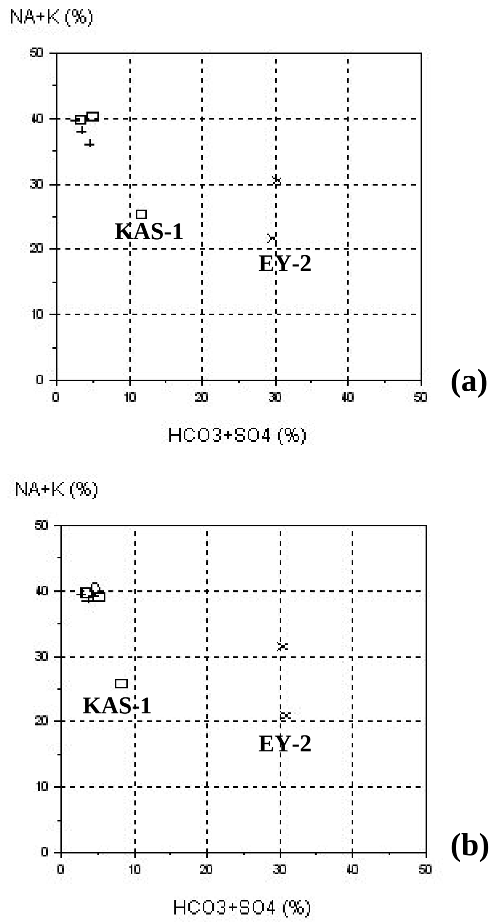

Fig 3: Langelier-Ludwig diagrams **(a)** "wet period" **(b)** "dry period" for the thermal and mineral waters of Nisyros volcano.

On these Langelier-Ludwig diagrams all samples except fresh water samples (EY-2 and EL-3) are concentrated around seawater compositions. Sample KAS-1 displays a decrease in sodium component as it is collected about 0.5 km away from the coastline at a depth of 90 m and an elevation of about 100 m hence seawater mixing seems to be minor in this sampling location. Samples EY-2 and EL-3 reveal a fresh water character and display a differentiation in sodium component since EY-2 sampling occurred at about 2 km away from the coast line. The triangular diagrams Cl-SO_4-HCO_3 (Fig. 4a, 4b) display clearly

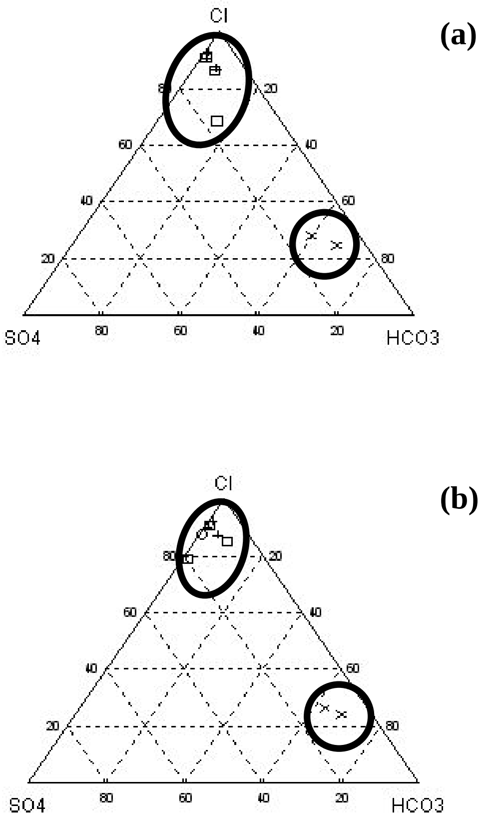

Fig 4: Triangle diagrams Cl-SO_4HCO_3 showing bicarbonate (cycle) and chloride (oval) waters for Nisyros.

the *bicarbonate* character for EY-2 and EL-3 samples and the *chloride* character of the rest samples. By plotting the CL concentration against all other analyzed chemical constituents and comparing these plots to the simple mixing lines in Figure 5 we observe a decrease in Mg and SO_4 concentrations. We attribute this to: (a) a decrease in the solubility of $CaSO_4$ with increasing temperature (b) to ionic exchange of Mg at high temperatures in several Ca – Mg – silicate in minerals and (c) to a

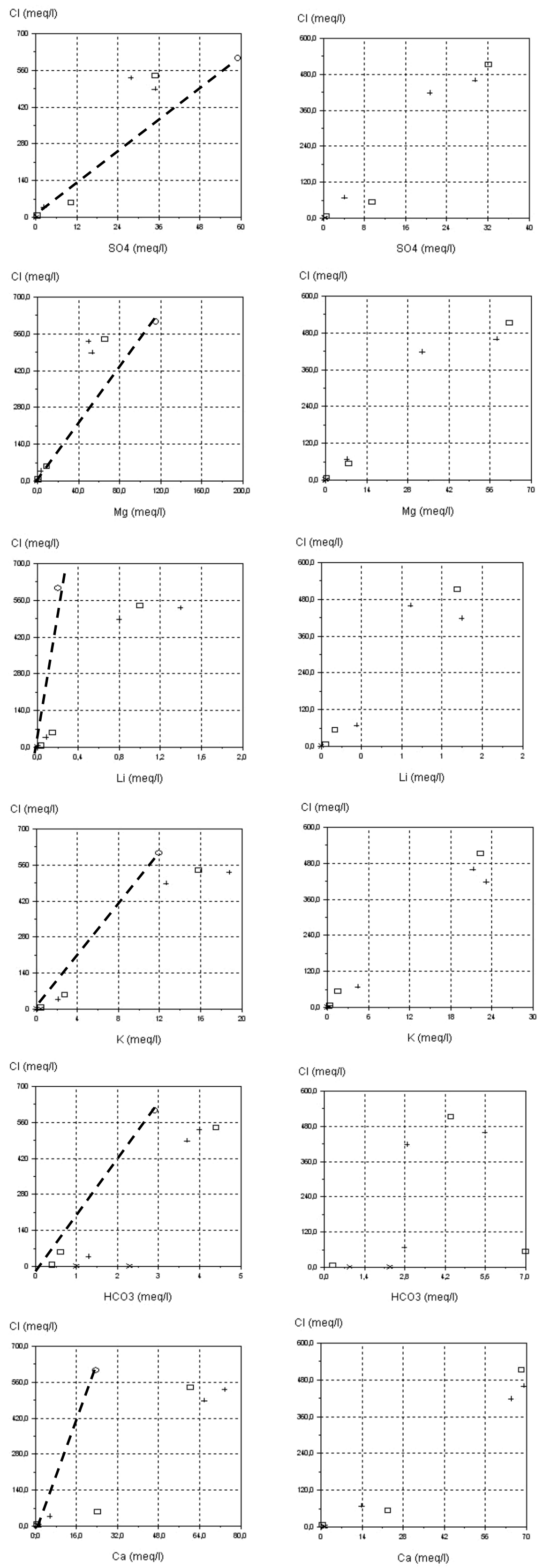

Fig 5: Plots of Cl against the other analyzed components (left column: “dry period”; right column: “wet period”; x represents fresh water samples, cross represents thermal springs, open square represents boreholes and open cycle represent seawater)

general increase in Ca, K, Li, HCO_3 and Na than in seawater possibly related to simple rock dissolution processes [9].
The seawater sample was collected in the vicinity of Loutra near the pumping station of the desalination installations. This sample displays very high values in V, Fe, Ni, Se, Mn and Co (Table 2) compared to their respected values in seawater. This could be explained by the presence of thermal submarine springs near the pumping point with waters enriched in these elements due to leaching from basaltic andesite bedrock.

5 Discussion

Medicinal waters are ground and/or spring waters that issue naturally or are extracted artificially, which have medicinal qualities due to their physical, chemical or radiological properties. *Thermal* and *mineral springs* qualify as medicinal waters. *Medicinal tourism* is a special type of tourism which is targeted towards the preservation, amelioration or healing of the psychosomatic health of a person without the use of medications or other type of therapeutic procedures. *Thermalism*, is a special type of tourism which encompasses a host of activities targeted towards the preservation or amelioration of the human well-being with the use of medicinal and/or sea waters, medicinal gases, mudbaths etc. These activities take place in especially built facilities which serve these purposes i.e. in *Spas*.
Thermal and mineral springs are characterized by temperatures over 19^{o}C, high values of total dissolved solids in the form of ions and gases. Mineral springs are considered to have values of Total Dissolved Solids (T.D.S.) over 1000mg/L. Thermal and mineral springs are characterized as *cold* (up to 20^{o}C), *hypothermal* (20^o-35^{o}C), *mesothermal* (35^o-50^{o}C) and *hyperthermal* (over 50^{o}C) [10]. According to their radioactivity thermal springs are classified as *weak* (3.5-20 Mache), *moderate* (20-100 Mache) and *strong* (over 100 Mache). The T.D.S. in the thermal and mineral springs can be in the form of ions (Ce^{+3}, Br^-, SO_4^{-2}, HCO_3^-, J^-, F^-, Na^+, K^+, Li^+, Mg^{+2}, Fe^{+2}, Ba^+, Sr^+, Al^+, NH_4^+) or gases (N_2, CO_3, SO_4, CH_4, O_2, H_2S, He, Ne, Ar, Kr, Xe). The water type classification/profile of thermal and mineral springs is depended on the geology and particularly on the lithologies of an area. Higher temperatures increase the ability of leaching elements from the country rocks and solubility potential of the thermal waters. According to their chemical profile they can be classified as *sulfide*, *sulfurous*, *bicarboniferrous*, *chlorine-sodium* and *ferric*.
As we have mentioned in the "*Results*" section, in Nisyros mixing of hot geothermal waters with meteoric and sea waters results in numerous thermal springs with *mesothermal-hyperthermal* waters (30^o-60^{o}C), which issue around the coasts of the island. For this reason Nisyros was selected by the Father of Medicine, Hippocrates, for its baths and was a renown Loutropolis during Roman times and even more recently during the late 1800's A.D. Presently an effort has been made to re-establish the baths in the vicinity of Loutra. The *Loutra Baths* are supplied by a natural spring that provides mesothermal-hyperthermal waters of about 50^{o}C that is collected in a cistern to cool to a desirable temperature for bathing. The facilities at Loutra offer a capacity of 65 beds and they are open to the public from May to October. Our chemical analyses indicate Na-Cl-(K-Br) mineral water with a profile similar to the Salin Baths in France, the Weisbaden in Germany and the Monte Cantini in Italy [11]. We are now in the process of collecting radioactivity data for thermal springs of Nisyros. However, medicinal waters with chemical profiles similar to these of Loutra Baths are known to be used for treating affections such as rheumatisms, arthritis and healing gynaecological and skin problems, as well as problems of the circulative and lymphatic system. Two other very well known bath sites in Nisyros are *Thermiani* and *Pali Baths* (Fig. 6).

Fig 6: View of the front of the Pali Baths in Nisyros.

The natural spring of Thermiani was the ancient baths of Hippocrates. Thermiani nowadays is occupied by the church Panagia Thermiani but no further development was obtained. The Pali Baths is hosted in an exquisite stone building which is extremely well organized for bath function and as a Spa center. However, its development has been arrested due to litigation procedures.

Analyte Symbol	T	pH	E.C.	eh	Alkaline	TDS	Na	Mg	K	Ca	Si	NH_4	NO_2	NO_3	HCO_3	SO_4	PO_4	Water Type
Unit Symbol	ºC		μS/cm	mV	mg/L $CaCO_3$	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
EL-3	22	7.59	393	9	115	294	52.8	3.63	14.1	27.8	9.4	0	0.03	17.51	140.3	15.6	0.88	Na-Ca-HCO_3-Cl
EL-5	26.5	6.11	928	93	150	629	131	4.42	12.9	9	7	0.05	0.05	0.44	18.3	25.2	1.8	Na-Cl
EY-2	19.5	7.27	165.8	28	45	130	17.2	1.44	2.13	18.5	2	0	0.23	0.73	54.9	11.3	0.03	Na-Ca-HCO_3-Cl
KAS-1	29.2	6.84	6720	52	350	Over	706	95.6	60.1	457	65	3.35	0.5	3.21	427	450	0.92	Na-Ca-Cl
MAN-41	31.5	5.72	58100	95	220	Over	11300	762	873	1370	82	1.85	0.5	2.2	268.4	1540	3.06	Na-Cl
PALI	19.2	7.86	15600	-4	140	Over	1200	90	175	280	41	0.01	0.66	13.2	170.8	198	1.22	Na-Cl
THEMIANI	19.2	7.85	40500	-4	280	Over	8890	709	833	1390	70	0.08	1.65	61.6	341.6	1420	3.06	Na-Cl
LOUTRA	27.4	7.26	41400	28	145	Over	8170	402	910	1300	95	0.05	1.65	30.8	176.9	998	4.59	Na-Cl

Analyte Symbol	Li	Sc	Ti	V	Mn	Fe	Co	Ni	As	Se	Cd	Pb	Th	U	F	Zn	Sr	Br	Cl
Unit Symbol	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	ug/L	mg/L	mg/L	mg/L
EL-3	2	2	2.2	4.9	0.9	-	0.053	0.7	1.83	0.6	0.03	0.1	-	0.337	0.01	0.02	0.05	0.1	50.4
EL-5	40	5	2	0.5	452	5800	1.68	7	0.15	1	0.5	0.05	0.89	0.005	0.54	12.7	0.06	0.77	268
EY-2	1	-	0.2	2.8	0.9	-	0.04	0.5	0.62	-	0.06	0.08	-	0.041	-	-	-	-	25.5
KAS-1	130	10	9	17	47	50	0.5	14	6.5	1	2.4	1.8	1.02	0.03	0.15	4.89	1.79	13	1900
MAN-41	1350	20	15	0.5	1080	11300	3.07	134	87.8	26	0.3	0.2	0.97	0.2	0.5	-	17.6	63	18200
PALI	350	5	7	24	3	50	0.1	9	38.8	29	0.2	0.2	0.86	1.51	0.2	0.05	4.69	7.8	2430
THERMIANI	890	20	12	0.5	1	50	0.12	124	42.2	1	0.9	0.05	0.86	0.52	0.5	-	13.8	56	16300
LOUTRA	1400	20	14	0.5	749	50	0.4	294	269	1	0.3	0.05	0.87	0.33	0.5	0.06	14.3	49	14800

Table 1: Physical characteristics and chemical composition of major and trace elements of thermal, mineral and fresh waters from Nisyros volcano for the "wet period" of 2006.

Analyte Symbol	T	pH	E.C.	eh	Alkaline	TDS	Na	Mg	K	Ca	Si	NH_4	NO_3	NO_2	HCO_3	SO_4	PO_4	Water Type
Unit Symbol	ºC		μS/cm	mV	mg/L CaCO3	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
EL-3	23.7	8.07	433	-17	115	309	55.9	3.39	15.4	27.4	9.3	0	17.91	-	140.3	15.6	0.52	Ca-Na HCO_3-Cl
EL-5	35.2	6.32	1064	85	20	611	101	4.46	16.1	9.9	8	0.27	0.22	0.03	24.4	19	0.05	Na-Cl
EY-2	20.9	7.68	190.9	8	50	145	15.2	1.12	2.37	18.1	1.8	0	1.8	0.03	61	10.4	0.06	Ca-Na HCO_3-Cl
KAS-1	32.9	6.9	7560	52	30	Over	743	105	106	483	70	0	7.04	0.16	268.4	494	0.46	Na-Cl
MAN-41	34.7	5.76	61100	117	220	Over	10900	795	617	1210	70	1.6	2.2	1.65	268.4	1680	3.06	Na-Cl
PALI	21.4	7.56	4190	14	65	Over	740	45.4	82.9	113	16	0.01	7.04	0.16	79.3	118	0.3	Na-Cl
THERMIANI	23.8	7.73	45800	5	185	Over	9030	684	495	1320	60	0	88	3.3	225.7	1680	6	Na-Cl
LOUTRA	39.2	7.13	85800	38	200	Over	10500	611	736	1480	80	1.35	17.6	3.3	244	1340	4.59	Na-Cl
SEA	22.5	7.88	56500	-3	145	Over	13100	1400	465	470	-	0	4.4	3.3	176.9	2840	12.24	Na-Cl

Analyte Symbol	Li	Sc	Ti	V	Mn	Fe	Co	Ni	As	Se	Cd	Pb	Th	U	F	Zn	Sr	Br	Cl
Unit Symbol	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	mg/L	mg/L	mg/L	mg/L
EL-3	3	2	2.4	7	0.4	-	0.057	0.8	2.19	0.5	0.02	0.15	-	0.35	0.04	0.007	0.06	0.13	49.4
EL-5	34	2	0.9	-	498	2580	1.81	3.8	-	3.6	0.44	0.16	0.006	-	0.59	9.96	0.06	0.75	246
EY-2	2	-	0.3	3.7	2.9	-	0.042	1	1.46	0.5	0.02	0.07	-	0.07	-	0.017	0.04	0.08	25.5
KAS-1	143	15	7.8	23	18.1	-	0.31	19.6	12.6	26	1.69	0.72	0.001	0.006	0.3	2.82	2.24	6.7	1960
MAN-41	1000	50	20	5	1240	7000	4.4	60	99	160	-	0.5	0.05	0.2	0.5	0.025	15	64	19200
PALI	84	3	2	11	1.1	-	0.034	7.3	10.9	15.1	0.09	0.08	-	0.059	0.05	0.01	0.88	4.5	1340
THERMIANI	800	50	5	60	5	500	0.25	40	77	160	-	0.5	0.05	0.4	1	0.025	13.3	54	17300
LOUTRA	1400	50	20	5	4920	500	4.2	40	339	170	0.5	0.5	0.05	0.2	1	0.025	17.7	64	18800
SEA	200	50	5	5	5	500	0.25	220	34	210	0.5	0.5	0.05	3.6	1	0.025	8.62	74	21500

Table 2: Physical characteristics and chemical composition of major and trace elements of thermal, mineral, fresh and seawater from Nisyros volcano for the "dry period" of 2006.

Other uses of thermal waters on Nisyros can include activities such as fish farming, mushroom farming and marginally, due to the mild climate, for heating of greenhouse. However, the targeted use of the Nisyros hot springs, the use that dovetails with promotion of the volcano to a Natural Park and that most of the permanent inhabitants wish for is their use for baths and in Spa centers, targeting the redirection of the economy towards "alternative tourism" and restoring Nisyros to its ancient status of a renown Loutropolis.

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