Assessment of Techirghiol Lake Surface Water Quality Using Statistical Analysis

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The lakes' water quality can be considered a key contributor to the human health and for the conservation of therapeutically mud properties. This study involves the statistical evaluation of water quality data for one hypersaline lake from Constanta District, Romania. Techirghiol Lake (located in South of Dobrogea Region, Romania) constitutes an ecosystem with a special morphological structure and an interesting geological past. The physico-chemical average parameters of Techirghiol Lake, registered in the period 1990 -2011) are described, analyzed and modelled. Techirghiol Lake had the highest salinity 66.14 g/L in 2009, pH values were in the interval 7.97-8.71 with low seasonal variations, indicating well buffered waters. The concentrations of some anions and cations varied as follows: Cl^- - 738.87 meq/L (in 1997) - 1019 meq/L (in 2009), HCO_3^- - 2.20 meq/L (in1 992) - 1019 meq/L (in 2009), Ca^{2+} - 8.53 meq/L (in 1993) – 20.43 meq/L (in 1992), Mg^{2+} - 171.05 meq/L (in 1993) – 230.26 meq /L (in 1995), and the dried residue - 51.50 g/L (in 2006) – 65.32 g/L (in 2004). We also report the evolution of pollution indicators: dissolved oxygen (DO), chemical oxygen demand by potassium permanganate method (COD-Mn) and biochemical oxygen demand (BOD_5). The yearly averages of the quality parameters for all sampling sites ranged as follows: DO (mg/L) - 4.04 (in 2002) - 10.17 (in 2009); COD-Mn (mgO_2/L) - 15.52 (in 1991) - 45.17 (in 1995); BOD_5 (mgO_2/L) - 2.78 (in 1993) – 20.25 (in 1995). Statistical analysis, including Kolmogorov-Smirnov [1], Levene [2], change points tests, Mann - Kendall test with Sen's slope [3, 4] calculation has been performed to evaluate the variation of statistical parameters. Hybrid linear –moving average models have been built for the series for which the hypothesis that the slope is significant has been accepted.

Key-Words: physico-chemical parameters, water quality, statistical analysis, models

Knowing the quality of the surface water is of big importance for the human life and economic activity. Therefore, a number of studies has been devoted to analyse and model the evolution of components of these waters, in Romania [5 - 7]. Techirghiol Lake, with a surface of 1.462 ha, a length of 7500 m and a maximum depth of 12 m, is situated in the district of Constanta (fig. 1). It was declared at the end of March 2006 a Ramsar site (Convention about Humid Zones) by H.G. 1586/2006, and a Special Protected Aqua-faunistic Area (SPA), at the end of 2007, being part of the European network of protected areas, Natura 2000.

Techirghiol Lake is considered to be a unique lake in Romania, due to its physico – chemical and biological characteristics, that suffered important variations of the level and salinity. The variation of the water level is due especially to the consecutive movements of abradant lacustrine cliffs. During time, the salinity of these waters varied in very large limits: 1893 – 71.6 g/L; 1931 – 110 g/L; 1970 – 78.6 g/L; 1995 – 55.05 g/L; 2011- 65.93 g/L [8]. Taking account of zone climate, considered between the most arid from Romania (about 6 month per year without precipitations), the lake's water might constantly evolve to the salinity concentration. The data comparison proves the contrary. The salinity and brackish water prevents the lake freezing during the winter, fact that is singular between the other lakes from Dobrudja [9].

The massive contribution of the waters from the irrigations, starting with the year 1970, generated the diminishing of the water salinity from 78.6 g/L to 63.6 g/L during a decade; then the decrease continued until 1997, when it reached 47.21 g/L. The determined value in 2000 was of 55.03 g/L, with a slowly increase in 2003 – 61.83 g/L, registering new significant decrease until 2005 – 53.78 g/L. One of the direct consequences of the water salinity diminishing was the modification of the lake biodiversity, generating a negative impact over the therapeutic mud quantity and quality [10]. As a response to the problems that affect the Techighiol Lake, different technical solutions have been proposed and most of them have been implemented as protection measures.

Even if Techirghiol Lake is considered as a lake with predominant feeding from precipitation, adding the contribution of underground water, these quantities don't cover processes evapotranspiration processes, that are very intense, up to 700 mm – the potential one and about of 1000 mm, that at the water surface.

The most important factor that acts on the chemistry of saline lacustrine waters is represented by the uncontrolled irrigation from the neighbouring zones, done in the past periods. The sweetening of these waters has major repercussion on the formation of therapeutic mud. At the national level, optimal condition for the formation of sapropelic mud always existed in the case of Techirghiol Lake, where the water chemistry must be preserved, to continue the phenomena of therapeutic mud formation. This mud is the result of some complex biochemical and chemical long term processes suffered by rotting mineral and organic compounds in stagnant waters.

The general chemical characteristics of water remain generally constant, being those of chlorinate, brominates, sodium - sulphate, with magnesium derivatives. The dominant elements have constant values in all the central region of the Lake. The chlorine, as sodium and

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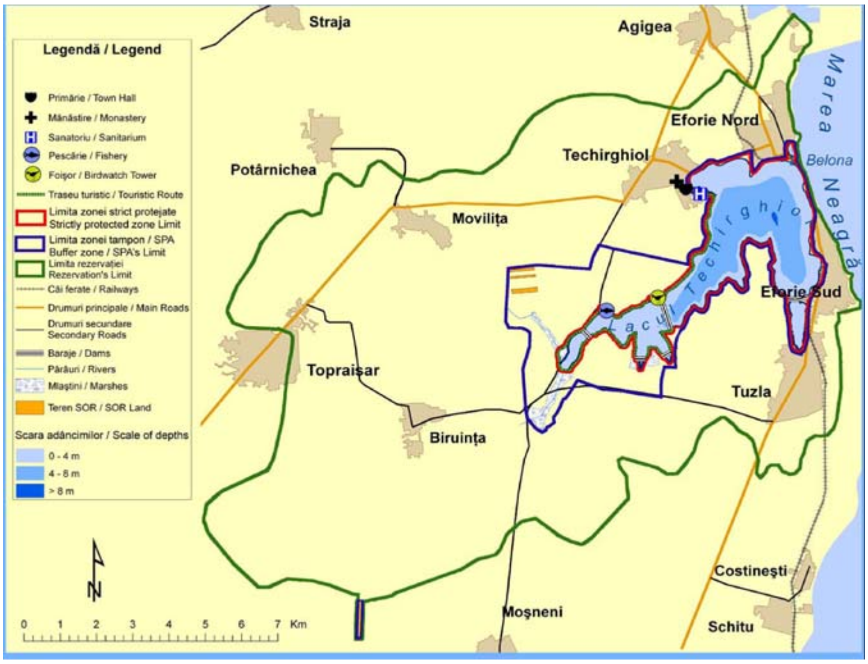

Fig. 1 The situation of Techirghiol Lake on the map of Constanta district

Table 1

PHYSICAL AND CHEMICAL MEASURED PARAMETERS

year	Salinity (g/L)	Cl^- (meq/L)	HCO_3^- (meq/L)	Dried residue (g/L)	Ca^{2+} (meq/L)	Mg2+ (meq/L)	Total hardness (^{0} G)	DO (mg/L)	COD - Mn (mg O_2/L)	BOD_5 (mg O_2/L)
1991	58.00	907.61	2.62	64.21	18.34	208.88	638.00	4.56	15.52	3.87
1992	50.89	796.34	2.20	56.72	20.43	188.32	590.80	4.87	30.73	2.94
1993	47.39	741.41	4.20	64.73	8.53	180.92	534.00	4.63	17.16	2.78
1994	48.03	751.55	5.05	56.27	10.09	205.59	624.40	5.63	27.82	9.35
1995	53.56	838.03	4.00	64.32	14.40	230.26	686.50	6.63	45.17	20.25
1996	53.96	844.51	4.46	60.63	10.22	188.32	558.80	5.33	37.24	12.53
1997	47.21	738.87	4.62	55.58	15.23	209.70	657.00	6.82	19.30	5.29
1998	52.34	818.87	4.79	56.58	13.88	171.05	589.00	5.51	31. 8	6.54
1999	52.20	816.62	4.00	55.40	12.89	173.52	557.10	6.34	27.51	9.98
2000	55.03	861.13	5.41	58.07	12.41	193.26	560.90	5.44	19.16	3.94
2001	58.86	921.13	6.23	64.25	13.52	214.64	639.58	4.86	31.79	9.51
2002	61.01	956.90	5.48	62.67	16.50	212.17	643.55	4.04	30.72	8.65
2003	61.83	965.07	7.38	63.02	14.04	211.35	632.76	6.81	29.17	7.79
2004	61.46	961.41	9.34	65.32	14.17	208.06	638.53	6.31	27.40	8.00
2005	53.78	841.41	6.89	61.49	9.20	219.57	642.28	5.90	22.30	6.80
2006	55.74	871.83	7.38	51.50	10.09	186.51	571.73	7.66	20.16	5.48
2007	61.20	957.18	7.36	55.84	10.09	221.22	594.45	6.86	39.17	7.97
2008	61.07	954.65	7.70	62.45	11.07	211.46	630.05	7.84	41.01	9.05
2009	66.14	1019.15	7.38	56.43	12.00	228.62	680.62	10.17	34.57	8.16
2010	63.91	976.62	7.87	61.22	10.36	217.11	637.08	7.62	41.88	10.01
2011	65.93	988.45	7.70	57.29	11.99	211.35	631.45	6.26	37.10	8.28

magnesium chlorine, is the most important indicator of the mineralization, being almost constant. The increasing content in chloride (maximum of 1019.15 meq/L) corresponds to a moderate degree of mineralization and an increasing salinity. The content of chloride in water presented significant seasonal variations. The maximum values were registered in summer due to the mixing of the influx of water from the autumn and spring period; the minimum values were registered in winter, when the lakes are in the calming period. The magnesium quantity is between the 171.05 meq/L (in 1993) and 230.26 meq/L (in 1995). Examining the elements less characteristics for the water, we remark that the bicarbonates and the carbonates values present some variations, due to the lability of the system $CO_3^{2-} \leftrightarrow HCO_3^-$. The calcium values register variations in the sense of its values increasing from the surface of the water to its bottom, probably due to the reversibility of the equilibrium of soluble bicarbonate into the insoluble carbonate. The dissolved oxygen varies in different zones of the lake [11].

The aim of this study is the presentation of the hydrochemical characteristics of the Techirghiol ecosystem, unique in Romania by its hypersaline character and the important quantities of sapropelic mud with therapeutic properties. The analyzed parameters are: salinity, chloride, bicarbonates, magnesium, calcium concentrations, the dried residue, total hardness, the dissolved oxygen (DO), chemical oxygen demand by potassium permanganate method (COD-Mn) and biochemical oxygen demand (BOD_5). The statistical analysis has been performed, followed by the trend detection (by Sen's method), and the residual modelling for those series for which a significant trend has been detected.

The data analyzed in the present article are presented in table 1 and they are taken from the reports of national

Agency of Environment, Constana. The volumes of the data samples is 22, that is at the limit of the statistic tests for the confidence level of 90%, in conformity to [12].

Methodology

In the first part of our study we perform the statistical analysis of the data series, as follows:

- the normality test (Kolmogorov – Smirnov [1]), in which, the null hypothesis is: *The series is normally distributed,* and its alternative is: *The series is not normally distributed*;

- the outliers detection, using the boxplot: cases with values between 1.5 and 3 box lengths (inter-quartile range) from the upper or lower edge of the box are identified as outliers [13];

- the series autocorrelation, using the autocorrelation function [14].

The autocorrelation function at lag *h* ($h \in N^*$), associated to a time series (X_t) is the defined by:

$$\rho(h) = \frac{M(X_t X_{t+h}) - M(X_t)M(X_{t+h})}{D(X_t)D(X_{t+h})}, h \in \mathrm{N}^*$$

where $D^2(X_t)$ is the variance of X_t and $D(X_t)=\sqrt{D^2(X_t)}$.

For a sample data $\{x_1, x_2, ..., x_n\}$ and a given confidence level, the empirical autocorrelation function (ACF) is calculated together with the deterministic confidence interval. If the values of ACF are inside this interval, then the hypothesis that the series is autocorrelated can be rejected [17].

- the homoscedasticity (by the Levene test [2]), where the null hypothesis is H_0: *The data have the same variance,* and the alternative is H_1: *The data have not the same variance* [15];

- the change point (break point) tests that allow the detection of a change in a time series mean. The tests of Pettitt, Buishand, Lee & Heghinian find only a single break point in the series and the segmentation procedure of Hubert detects multiple change points. In all of them the null hypothesis is: *There is no break in the series*, and its alternative is *There is a break in the time series*. The tests are described in [16]. We notice only that normality is required for using the Buishand and Lee & Heghinian tests;

- the existence of a linear trend in data series (by Mann – Kendall test) and the slope determination (by Sen's method) [3].

The Mann-Kendall test is a nonparametric trend test applicable in cases when the data values Y_i of a time series can be assumed to obey the model $Y_i = f(t_i) + \varepsilon_i$ where $Y_i = f(t_i)$ is a continuous monotonic increasing or decreasing function of time and the residuals can be assumed to be from the same distribution with zero mean. It is therefore assumed that the variance of the distribution is constant in time.

The null hypothesis in this test is: H_0: *There is no monotonic trend of the series.*

When only one datum per time period is taken, as in our case, the following notations are done:

n - the number of data,

P - the number of pairs of observed values Y_i, Y_j (i>j) for which $Y_i > Y_j$,

Q - the number of pairs of observed values Y_i, Y_j (i>j) for which , $Y_i > Y_j$

S = P - Q

$$Var(S) = \frac{n(n-1)(2n+5)}{18} \text{ - the variance of } S,$$

$$Z = \begin{cases} \frac{S-1}{\sqrt{Var(S)}}, & S > 0 \\ 0, & S = 0 \\ \frac{S+1}{\sqrt{Var(S)}}, & S < 0 \end{cases}$$

The standardized test statistic Z is approximately normally distributed. A positive (negative) value of Z indicates an upward (downward) trend. To test for the either upward or downward trend (a two-tailed test), at the level of significance α, H_0 is rejected if $|Z| > Z_{1-\alpha}$. If the alternative hypothesis is for an upward trend (a one-tailed test), H_0 rejected if $Z > Z_{1-\alpha}$. H_0 is rejected in favour of the alternative hypothesis of a downward trend if Z is negative and $|Z| > Z_{1-\alpha}$. Using P- value calculated for Z, H_0 is rejected if $P < \alpha$.

To estimate the magnitude of an existing trend (as change per unit time) the Sen's nonparametric method may be used. This approach involves computing slopes for all the pairs of time points, Q_i, and then using the median of these slopes as an estimate of the overall slope Q. This method is very useful in cases where the trend can be assumed to be linear: $f(t_i) = Qt_i + B$, where *Q* is the slope and *B* is a constant [4].

- for the series for which the trends have been detected by Sen's methods, the model resulted after the previous stage is:

$$Y_i = Qt_i + B + \varepsilon_i, \quad (1)$$

where t_i is the time and ε_i the error.

For a good statistical model, (ε_t) must be a white noise (that is a sequence (ε_t) of uncorrelated random variables, each with zero mean and a constant variance σ^2).

A linear process (ε_t) is called a moving average process of first order, MA(1) if:

$$\varepsilon_t = \xi_t - \theta_1 \xi_{t-1}, \theta_1 \neq 0, \quad (2)$$

where(ξ_t) is a white noise with the variance σ^2 [14].

For the series for which the error (ε_i) did not satisfy the white noise hypothesis, a model with autocorrelated errors has been detected:

$$Y_i = Qt_i + B + \xi_t - \theta_1 \xi_{t-1}, \quad (3)$$

where (ε_i) is a MA(1) process.

Results and discussions

The results of the statistical analysis are presented in the following. The tests are performed at the significance level of 0.05, if it is not otherwise specified.

The results of the Kolmogorov-Smirnov are presented in table 2, where, mean represents the data average, stdev is the standard deviation of the data, KS is the test statistic and p-val represents the p-value, i.e. the minimum probability for which the null hypothesis can not be rejected. Since the p-values of salinity, Cl^-, HCO_3^-, dried residue, Ca^{2+}, DO, COD – Mn series are greater than 0.05, we don't find enough evidence to reject the null hypothesis for these series. For Mg^{2+}, total hardness, BOD_5 the normality hypothesis are rejected.

Analyzing the boxplots from figure 2 we remark that two series presents outliers; they are DO and BOD_5. The outliers are represented by stars on the boxplots.

The study of the autocorrelation function (ACF) reveals the first order autocorrelation for only for the salinity, Cl^-, HCO_3^-, DO series. We remark this from the chart presented in figure 3, where the bars represent the values of ACF, Lag is the lag between the data, and the dashed lines represent the limits of the confidence intervals at the confidence level of 95%. Since the first values of ACF are outside the confidence intervals, the null hypothesis that the data are not correlated is rejected for these series.

After performing the Levene test (table 3), it was concluded that the homoscedasticity hypothesis could be rejected only for the series of BOD_5, because the corresponding p-value (p – val) is less than 0.05. So, this is the only series for which the data variance is not homogenous.

The results of the change point tests are presented in table 4, where *yes* means that the null hypothesis can not be rejected, so there is no change point in the data series. *No*, followed by a number in brackets, means that the year mentioned in the brackets is a change point. We remark different results given for the same series by different tests, for salinity, BOD_5 and DO series. For total hardness series two tests were not because the data did not satisfy the normality hypothesis.

After the analysis of the tests results it can be concluded that not all the series have the same properties: two series have outliers, the normality hypothesis has been rejected

Table 2
RESULTS OF KOLMOGOROV-SMIRNOV TEST

	mean	stdev	KS	p - val
salinity	55.29	5.89	0.152	> 0.150
Cl^-	865.04	86.43	0.180	0.077
HCO_3^-	5.89	1.90	0.173	0.098
dried residue	59.88	4.00	0.152	> 0.150
Ca^{2+}	12.27	3.05	0.124	> 0.150
Mg^{2+}	202.35	17.15	0.204	0.031
Total hardness	610.04	42.04	0.201	0.034
DO	6.04	1.41	0.128	> 0.150
COD - Mn	29.01	8.84	0.107	> 0.150
BOD_5	8.37	3.79	0.199	0.037

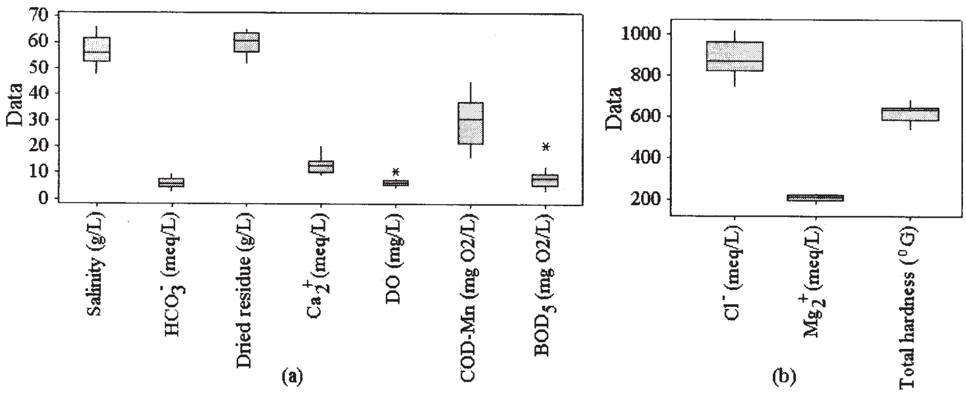

Fig. 2. Boxplots of: a. salinity, HCO_3, dried residue, Ca^{2+}, DO, COD-Mn, BOD_5, b. Cl^-, Mg^{2+}, total hardness

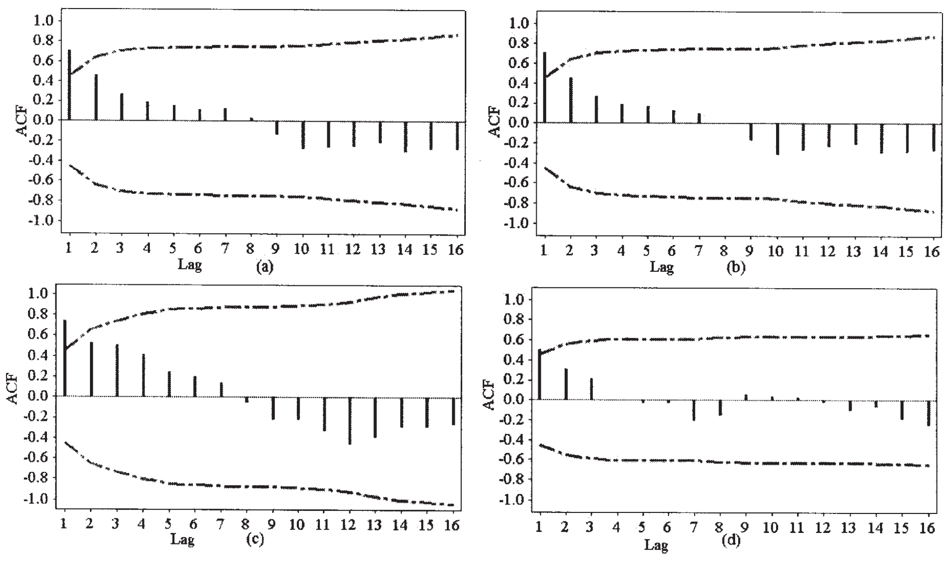

Fig. 3. ACF of: a. salinity, b. Cl^-, c.HCO_3^-, d. DO

Table 3
RESULTS OF LEVENE TEST
(α=0.05)

	salinity	Cl^-	HCO_3^-	dried residue	Ca^{2+}
Stat	0.14	0.79	0.68	0.02	0.85
p-val	0.713	0.386	0.420	0.901	0.369
series	Mg^{2+}	total hardness	DO	COD-Mn	BOD_5
Stat	3.99	4.11	1.70	0.12	6.97
p-val	0.06	0.057	0.207	0.733	0.016

	Test			
Series	Buishand	Pettitt	Lee & Heghinian	Hubert
salinity	no	no (2000)	no (2000)	no (2000)
Cl^-	no	no (2000)	no (2000)	no (2000)
HCO_3^-	no	no (2000)	no (2002)	no (1992, 1999, 2003)
dried residue	-	yes	-	yes
Ca^{2+}	yes	yes	no (1992)	no (1992)
Mg^{2+}	yes	yes	no (2000)	yes
Total hardness	-	yes	-	yes
DO	no	no (2002)	no (2005)	no (2005)
COD - Mn	yes	yes	no (2006)	no (2006)
BOD_5	yes	yes	no (2003)	yes

Note: *yes* means that the null hypothesis can not be rejected

Table 4
CHANGE POINTS (95% CONFIDENCE LEVEL)

	Mann-Kendall		Sen's slope estimation (at the confidence level of 0.95)					
series	Z	p-val	Q	Qmin	Qmax	B	Bmin	Bmax
salinity	3.84	***	0.87	0.48	1.05	47.38	45.3	51.6
Cl^-	3.77	***	11.56	6.09	15.3	758.09	712	814
HCO_3^-	4.72	***	0.26	0.20	0.31	3.05	2.62	3.80
dried residue	-0.69		-0.09	-0.39	0.25	61.10	56.46	64.21
Ca^{2+}	-1.30		-0.18	-0.51	-0.15	15.12	11.77	17.72
Mg^{2+}	2.03	*	1.20	0.01	2.38	194.17	182.73	209.63
Total hardness	0.88		1.35	-1.35	5.19	601.37	569.53	648.98
DO	2.93	**	0.13	0.06	0.21	4.71	4.19	5.43
COD-Mn	1.66	+	0.55	-0.04	1.26	24.60	16.77	30.77
BOD_5	1.18		0.14	-0.13	0.33	5.72	3.70	9.76

+ Significant at 0.1; * Significant at 0.05; ** Significant at 0.01; *** Significant at 0.001

Table 5
RESULTS OF MANN KENDALL TREND TEST AND SEN'S SLOPE ESTIMATION

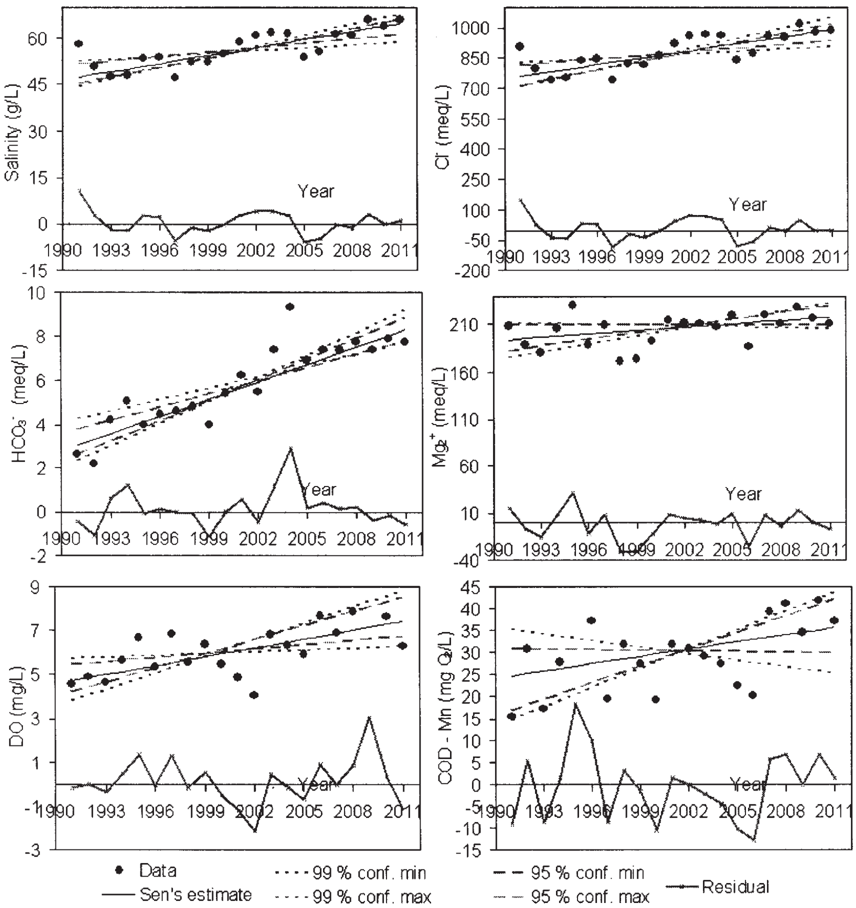

Fig. 4. Results of Sen's metod for the series of: salinity, Cl^-, HCO_3, Mg^{2+}, DO, COD-Mn

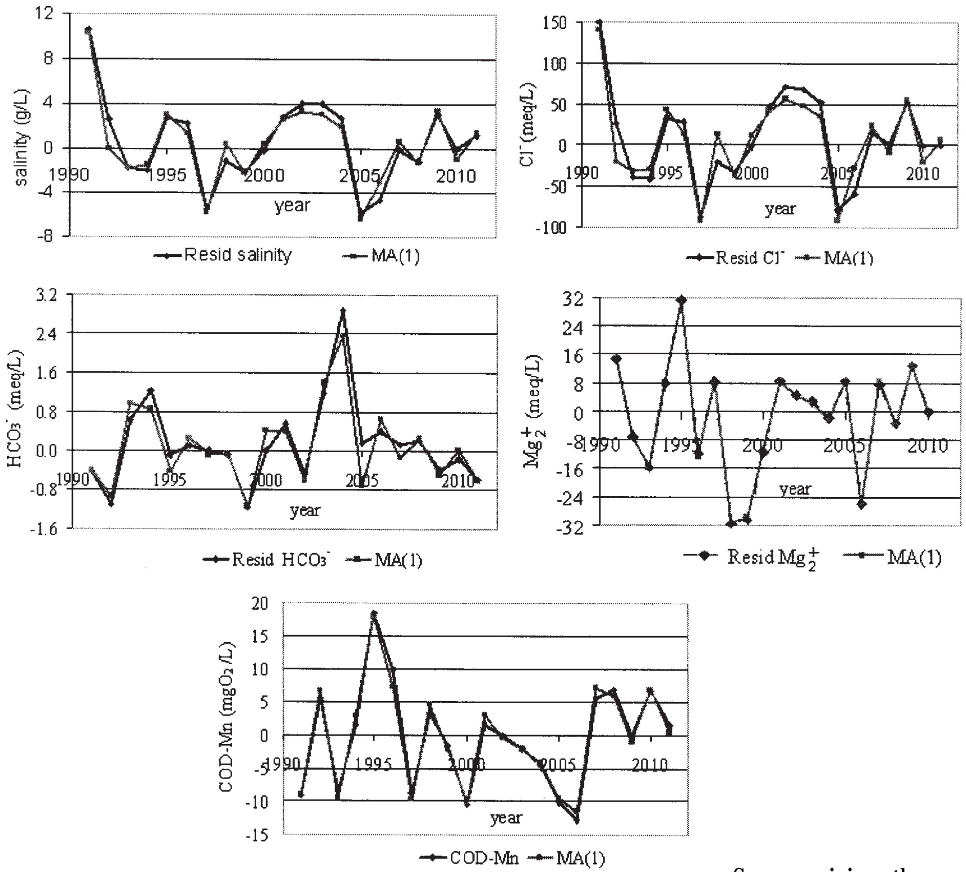

Fig. 5. MA(1) models of residual series: Resid salinity, Resid Cl^-, Resid HCO_3,, Resid Mg^{2+}, Resid COD – Mn (in conformity with (2))

for three series, four series have the autocorrelation property, the homoscedasticity hypothesis has been rejected for one series and some series presents change points. Therefore, to complete the analysis, it is important to study the existence of a significant increasing or decreasing trend. It has been done performing the Mann Kendall trend test with Sen's slope estimation. The results are presented in table 5 and figure 4.

The Mann –Kendall test, for testing the hypothesis of trend existence, rejected H_0 in the cases of dried residue, Ca^{2+}, total hardness, BOD_5, at all the significance levels, and accepted it at the significance level of 0.1 for COD – Mn, 0.05 for Mg^{2+}, 0.01 for DO and 0.001 for salinity, Cl^- and HCO_3^-. So, the hypothesis that these series have an increasing trend has been accepted. The slopes values (Q) are, respectively, 0.87, 11.56, 0.26 for salinity, Cl^-, HCO_3^-; 0.13 for DO, 1.20 for Mg^{2+}, 0.55 for COD-Mn; they are inside the deterministic confidence intervals, whose limits are given in the columns Qmin and Qmax (table 5) and drawn in figure 4 by dashed lines.

For the series for which the trend have been determined, the errors' series (ε_t) have been analyzed. For DO series, the in the following model is a white noise, so the equation:

$$Y_t = 0.13t + 4.71 + \varepsilon_t$$

satisfy the statistical conditions of a correct model for the trend evolution.

For the others five series (salinity, Cl^-, HCO_3, Mg^{2+}, COD-Mn), the error series (ε_t) were not white noises, so the idea was to improve the models. It has been done by detecting models for (ε_t) of the salinity, Cl^-, HCO_3, Mg^{2+}, COD-Mn) series. They are of moving average of first order type - MA(1), and fit well the residual series $((\varepsilon_t)$ from model (1)), as it can be seen in figure 5.

Summarizing, the models of the series (in conformity to (3)) are respectively:

- for salinity:

$$Y_t = 0.87t + 47.38 + \xi_t + 0.2703\xi_{t-1},$$

- for Cl^-:

$$Y_t = 11.56t + 758.09 + \xi_t + 0.3534\xi_{t-1},$$

- for HCO_3^-:

$$Y_t = 0.26t + 3.05 + \xi_t + 0.3781\xi_{t-1},$$

- for Mg^{2+}:

$$Y_t = 1.20t + 194.17 + \xi_t + 0.0309\xi_{t-1},$$

- for COD – Mn:

$$Y_t = 0.55t + 24.60 + \xi_t + 0.266\xi_{t-1},$$

where: t is the time, (Y_t) is the data series and (ξ_t) is a white noise.

Conclusions

In this article is presented a statistical analysis of the main physico - chemical parameters of Techirghiol Lake, whose evolutions are important for the conservation of the quality of the therapeutic mud, with unique properties, produced here.

The existing of change points in the series evolutions has been proved. The same change points have been determined for salinity, Cl^-, HCO_3^- series, in conformity to the Buishand and Pettitt tests, proving an analogous evolution of these series. No change point has been detected for the total hardness and dried residue series. For six series the trend equations have been determined. For DO series a linear equation of the trend has been determined. For five series (salinity, Cl^-, HCO_3, Mg^{2+}, COD-Mn) , after the determination of a linear model, by Sen's method, the residual has been modeled by moving average models. So, the evolution of these five series was described by hybrid models, linear – moving average of first order. For testing the quality of the models, two coefficients have been used: the determination coefficient (R^2), that measures the accuracy of the linear models and the correlation between the registered data and those calculated by the models, which can be used for all the types of models. For the model of DO series, $R^2 = 95\%$ and the correlation coefficients in all the models were over 96%, proving their high accuracy.

For the studied series the standard deviation registered values between 1.41 and 42.04 (5.89 – for salinity, 86.43 for CL^-, 1.90 for HCO_3, 4.00 for dried residue, 3.05 for Ca^{2+}, 17.15 for Mg^2, 42.04 for total hardness, 1.41 for DO, 8.63 for COD - Mn, 3.79 for BOD). Taking into account the existence of the increasing trend detected for a part of the studied series (salinity, Cl^-, HCO_3, Mg^{2+}, COD-Mn), it results that the water properties of Techirghiol Lake varied the last years due to the climate change (especially to the high temperatures registered in summers).

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Manuscript received: 11.02.2013