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δ^{37}Cl OF WATERS FROM THE AKYATAN LAGOON, TURKEY

Andrzej Pelc[1], Christophe Lécuyer[2†], Anne-Marie Bodergat[2] and Stanisław Hałas[1*]

[1]Mass Spectrometry Laboratory, Institute of Physics, UMCS, 20-031 Lublin, Poland
[2]Laboratoire de Géologie de Lyon, UMR CNRS 5276, Université Lyon 1 et Ecole Normale Supérieure de Lyon, 69622 Villeurbanne, France
[*]Corresponding author, e-mail: stanislaw.halas@umcs.pl
also at Institut Universitaire de France

ABSTRACT

We report the first δ^{37}Cl data for surface waters of the Akyatan lagoon, Turkey, from 12 stations sampled over the period 2005 to 2006. The recorded variation of δ^{37}Cl values is fairly small, from -0.4 to +0.6 ‰ vs. SMOC, though the environmental conditions were highly variable seasonally. The salinity of the studied waters varied from 2.8 to 95 g/L and the δD *vs*. δ^{18}O plot significantly departures from the World Meteoric Water Line (WMWL) with a slope of 5.43±0.19. Chlorine isotopes indicate a weak positive correlation between δ^{37}Cl and δD of water and its salinity. This may be due to mixing between seawater and distinct sources of freshwater. The small spread of obtained δ^{37}Cl results demands enhanced precision of analysis and careful sample preparation.

Keywords: Akyatan lagoon, chlorine isotopes, hydrology, climate, δ^{18}O, δD

INTRODUCTION

Chlorine stable isotope ratio (^{37}Cl/^{35}Cl) variations are still poorly understood in surface waters. This ratio only shows very small variations and is therefore

difficult to determine with good precision with most analytical methods. Duane et al. (2004) studied $\delta^{37}Cl$ in waters of the Al-Khiran sabkha in Kuwait together with their δD and $\delta^{18}O$ values. In most recent studies on chlorine isotopes one of two methods to determine $^{37}Cl/^{35}Cl$ ratios is used: (1) analysis by thermal ionization mass spectrometry (TIMS), which is capable to measure small quantities, but it has rather low throughput (Xiao and Zhang 1992); (2) analysis of major beams generated by electron impact (at m/z = 50 and 52) of chloromethane gas by isotope ratio mass spectrometry (IRMS; Kaufmann et al. 1984). Both methods attain a precision that is somewhat better than ±0.1‰, but the second approach has a complicated mass spectrum (Eggenkamp 2004).

Recently a new method was developed in the Mass Spectrometry Laboratory at UMCS Lublin that is described below. The new method is also based on the ionization of chloromethane gas, but in the ionization chamber it forms negative ions that are generated on a hot metal surface. This leads to a simple mass spectrum, comprising of $^{35}Cl^-$ and $^{37}Cl^-$ peaks only, and a substantial enhancement of the precision of the $\delta^{37}Cl$ to ±0.01‰. This method was applied to study the seasonal and areal variations of chlorine isotope ratios in the Akyatan lagoon, Turkey, studied previously by Lécuyer et al. (2009, 2012) for variations of salinity and $\delta^{18}O$-δD of waters. Stable isotopes of chlorine may be useful in identifying water mixing zones if the mixing is simple in nature. For instance, a continental water with a distinctive $\delta^{37}Cl$ value mixing with a seawater having $\delta^{37}Cl$ close to zero.

STUDY AREA

The Akyatan lagoon (36°37'N – 035°16'E) is located at the south-eastern edge of the Mediterranean Sea, in the Çukurova region of Turkey about 30 km south of the city of Adana (Figs 1 and 2). The lagoon surface is 147 km^2 and its average depth is 0.75 m. It was formed 10,000 years ago as a result of the over-flowing and sediment discharge and transport from the Seyhan and Ceyhan rivers. The lagoon became separated from the sea by a thin sand barrier formed by wave action (McPherson et al. 1988). At present, the lagoon receives freshwater from rainfall and drainage–irrigation canals and probably during periods of high water levels from the Seyhan river and abandoned channels of the Ceyhan river (Davutluoglu 2010; Kuleli 2010), both of them having their springs in the Taurus Mountains (Nazik et al. 1999). The Seyhan river has a mean discharge of 180 m^3/s which varies from minimum and maximum values of 20 m^3/s (June to October) and 2,250 m^3/s (April), respectively (McPherson et al. 1988). The average river water composition is: 158 mg/L HCO_3^-, 48 mg/L Ca^{2+}, 10 mg/L Mg^{2+}, 30 mg/L SO_4^{2-}, 12 mg/L Na^+, 20 mg/L Cl^- and 1.5 mg/L K^+

following measurements compiled by Meybeck and Ragu (1996). The lagoon is connected to the sea through a 2 km narrow canal on its southeastern side and exchanges water and sediments in response to tidal activity. Maximum tide height is about 40 cm to 60 cm, except in periods of strong winds that can generate a 150 cm increase in sea level (McPherson et al. 1988). Around the Akyatan lagoon, air temperatures range from 9°C (January) to 28°C (August) with a mean annual value of 19°C. Precipitation is up to 120 mm mostly occurring during the cold season from November to February, at which period access to the lagoon is difficult.

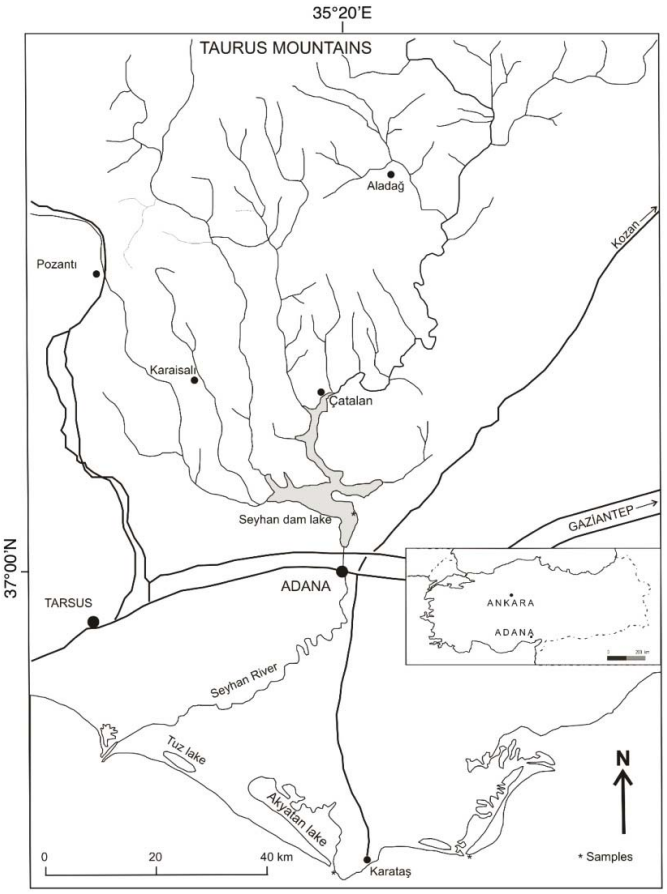

FIG. 1. Geographic map of southeast Turkey with the location of the Akyatan lagoon, Seyhan dam lake, and its catchment basin (the Taurus Mountains).

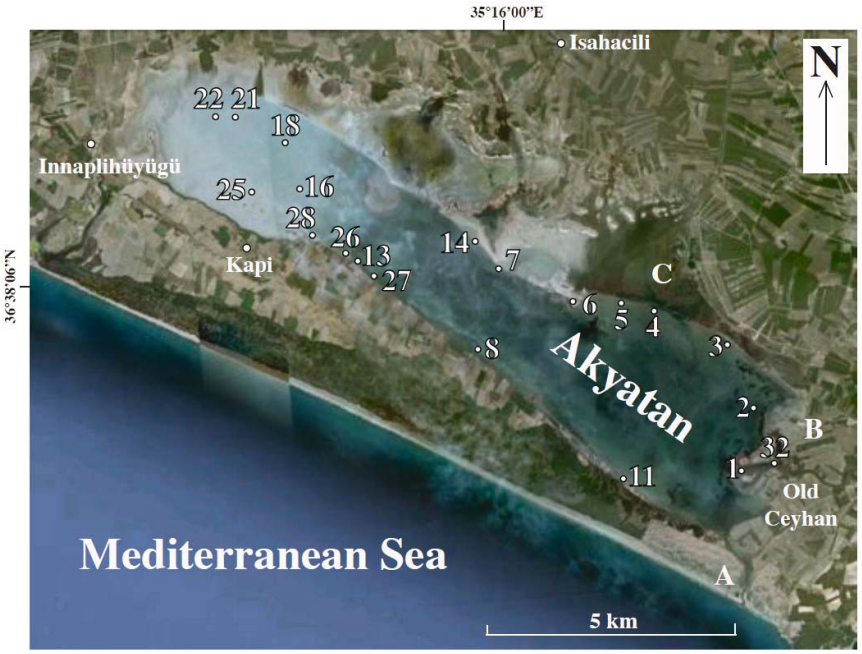

FIG. 2. Satellite view of the Akyatan lagoon, Turkey, and the location of water sampling sites indicated by outlined numbers.

ANALYTICAL METHODS

CHLORINE ISOTOPE ANALYSIS IN WATERS FROM THE AKYATAN LAGOON

Water samples were delivered in hermetically closed plastic bottles to the laboratory, where after filtration AgCl was precipitated. The precipitate was washed with distilled water and dried in an oven and then reacted with iodomethane (CH_3I) to form chloromethane (CH_3Cl), which is the most common gas used in chlorine isotope ratio analysis (Eggenkamp 2004). Chloromethane is very convenient for mass spectrometry as it has no memory effect in vacuum systems and can be easily obtained from a chlorine sample and transferred from the preparation line to the inlet system of mass spectrometer since its melting point is −97.7 °C. For CH_3Cl preparation the exchange reaction between the iodomethane (CH_3I) and silver chloride (AgCl) was applied (Kaufmann et al. 1984, Eggenkamp 2004). The reaction requires at least a 10-fold molar excess of CH_3I over AgCl, which results in a difficult purification procedure of CH_3Cl from CH_3I due to their similarity in physical properties. So far two purification

methods of chloromethane are used: (i) gas chromatography and (ii) cryogenic separation.

In both methods CH_3I is introduced to a preparation line by injection through a septum and because of this procedure also some impurities (air, water vapor) are admitted to the sample. Additionally in the above mentioned methods sealing and subsequently cracking of a sample tube is needed. To eliminate these drawbacks a new triple-stage cryogenic procedure with two different cryogenic substances was developed, similar to the one described by Wu and Satake (2006). The most important novelty in our preparation line is a new and simple pipette system, comprising of two glass containers separated by two stopcocks with a Teflon plug, for CH_3I introduction to the cryogenic separation line. Additionally we considerably simplified the separation procedure of both chloro- and iodo-methanes because we replaced the break-seal tubes with ampoules having stopcocks with Teflon plugs. This modification of the chloromethane purification method allowed shortening of the time needed for completion of the CH_3Cl separation.

The improvements of the chloromethane preparation technique in combination with the recently developed method of chlorine isotope ratio analysis based on negative ion mass spectrometry (Hałas and Pelc 2009) leads to enhanced precision of the measurements. The improved uncertainty of single δ^{37}Cl determinations was reduced to about ±0.05‰, which is important in studies of small natural variations of chlorine isotope ratios.

OXYGEN AND HYDROGEN ISOTOPE ANALYSIS OF WATERS FROM AKYATAN LAGOON

Aliquots of 200 μL from 37 water samples were automatically reacted at 40°C with CO_2 and H_2 in the presence of a platinum catalyst and analyzed using a MultiPrep™ system on-line with a GVI IsoPrime™ dual-inlet isotope ratio mass spectrometer. Reproducibility of δD and $\delta^{18}O$ values was estimated to be ±1‰ and ±0.1‰, respectively, by normalizing raw data to the isotopic ratios of SMOW, SLAP and GISP international standards that were measured along with the samples. Corrections of the hydrogen and oxygen isotope ratios caused by changes in the salinity-dependent fractionation factors $\alpha CO_2–H_2O$ and $\alpha H_2O–H_2$ were taken into account using the equations determined by Lécuyer et al. (2009) and Martineau et al. (2012).

RESULTS AND DISCUSSION

SALINITY/δ^{18}O-δD RELATIONSHIPS IN AKYATAN LAGOON WATERS

Hydrogen and oxygen isotope compositions of the brackish waters and brines from the Akyatan lagoon range from –48.2‰ to +35.8‰ and from –6.62‰ to +6.95‰, respectively (Lécuyer et al. 2012). Hydrogen and oxygen isotope compositions of the lagoon waters plot either between the two fresh and marine water end-members or on the right of the World Meteoric Water Line (WMWL). Models of source-water mixing and evaporation were developed by Lécuyer et al. (2012). In this study, it is clear from salinity and stable isotope compositions of Akyatan lagoon waters that brackish waters result from mixing of fresh water from the Seyhan River with Mediterranean seawater (Fig. 1). Such mixing, however, is complicated by evaporation processes, as suggested by the slope (5.43±0.19) of the regression line in the δD–δ^{18}O diagram which is much lower than the slope of the WMWL which is close to 8 (Craig 1961; Dansgaard 1964). According to Lécuyer et al. (2012), during winter and spring the water in the lagoon is dominated by mixing processes between fresh waters and Mediterranean seawater. Most samples taken during the spring are the result of evapoconcentration of brackish water at moderate temperatures of 22±2°C. During the summer, hypersaline waters result from evaporation of seawater and brackish waters formed during spring. Evaporation over the Akyatan lagoon reaches up to 76 wt% based on salinity measurements and operated with a dry (relative humidity of 0.15 to 0.20) and hot (44±6°C) air. These residual waters are characterized by the highest seasonal isotope enrichment in both deuterium and ^{18}O relative to VSMOW. During the autumn, most lagoonal waters become hypersaline and are formed by evaporation of water that had isotope compositions and salinities close to that of seawater. These autumnal hypersaline waters result from an air humidity close to 0.45 and an atmospheric temperature of evaporation of 35±5°C, which are responsible for up to 71 wt% of evaporation, with restricted isotopic enrichment relative to VSMOW.

VARIABILITY OF δ^{37}Cl IN WATERS FROM THE AKYATAN LAGOON

The variability of the δ^{37}Cl values is very difficult to discuss. The main problem concerns the end-member values. The fresh water samples had chlorine concentrations that were too low to be analyzed, whereas a sample of marine water (indicated at the bottom of Table 1) is affected by an enhanced standard deviation of δ^{37}Cl. Waters from the Akyatan lagoon show a rough positive correlation between δ^{37}Cl and δD as shown in Fig. 3. Winter sample #2006-2010 has both low δ^{37}Cl and δD of -0.55 and -34.8‰, respectively, while summer

sample #0607-11 exhibits the highest values of 0.38 and 35.4‰, respectively. At first sight, both δ^{37}Cl and δD of waters increase when water temperatures are high during the warm seasons (summer and autumn), corresponding to the highest rates of evaporation. Moreover, during the warm seasons, inputs of freshwater are lowest and water mixing is therefore dominated by the seawater end-member. This relation is, however, disturbed by two samples (0607-5 and 0604-19) that suggest that mixing took place between seawater and a few different sources of freshwater with distinct δ^{37}Cl signatures.

This hypothesis is supported by the complex relations observed between δ^{37}Cl and salinity S in Fig. 4. Low salinity waters have distinct δ^{37}Cl values and the highest δ^{37}Cl value which is found in a sample with a high salinity does not correspond with samples with even higher salinities which have δ^{37}Cl values close to 0‰. Two processes are responsible for δ^{37}Cl variability in waters from the Akyatan lagoon. The first is mixing between seawater, different sources of freshwater (local rain and the Seyhan River) and brackish waters inherited from earlier seasons. As seawater contains about a thousand times more chlorine than the Seyhan River, δ^{37}Cl variability can only be observed if reservoirs have highly contrasted chlorine isotope compositions. The second process is water evaporation that concentrates the heaviest chlorine isotope in the residual water.

TABLE 1. Analytical data from Lécuyer et al. (2012) along with measured δ^{37}Cl.

Sample no.	Station	Sampling date	Water temp. (°C)	Air temp. (°C)	pH NBS scale	Salinity (g/L)	$\delta^{18}O$ (H_2O) (‰) SMOW	δD (H_2O) (‰) SMOW	δ^{37}Cl (‰) SMOC
2006-13	1	03-11-2006	18.0	15.5	8.00	32.0	-0.64	1.2	0.06
0604-5	1	04-27-2006	28.0	30.0	9.10	14.0	-3.28	-24.9	0.06
0607-2	2	07-07-2006	27.7	34.6	8.13	12.1	-4.15	-14.5	-0.12
2006-10	4	03-11-2006	15.0	17.0	8.00	15.0	-4.70	-34.8	-0.55
0604-21	5	05-03-2006	29.7	25.2	9.03	25.0	1.26	3.5	0.08
0607-5	5	07-07-2006	32.3	28.0	8.03	2.8	-6.23	-47.3	-0.20
AMB-6	6	10-08-2005	25.7	28.8	8.24	64.0	2.59	17.3	0.16
0607-6	6	07-07-2006	32.2	30.2	8.32	17.4	-1.52	4.3	-0.17
2006-6	7	03-04-2006	23.0	18.0	8.58	25.0	-1.93	-11.8	-0.14
0604-19	7	05-03-2006	30.0	21.4	8.78	34.0	2.80	15.7	-0.38
0607-7	8	07-07-2006	34.8	25.2	9.03	50.3	6.67	35.4	0.38
AMB-11	11	10-08-2005	25.5	29.1	8.32	44.0	2.09	10.8	-0.15

0604-17	13	04-29-2006	26.0	30.0	8.40	24.0	1.70	9.1	-0.13
AMB-18	18	10-09-2005	24.5	26.6	8.43	90.0	4.23	25.5	-0.06
0607-11	18	07-08-2006	32.6	26.6	7.98	40.8	4.47	29.7	0.00
AMB-22	22	10-13-2006	26.0	31.0	8.40	95.0	4.21	20.0	0.07
MSW-2	A	10-11-2006	n.a.	n.a.	n.a.	38.0	1.54	11.3	0.0*

*Standard deviation = 0.1‰, n.a. = not available

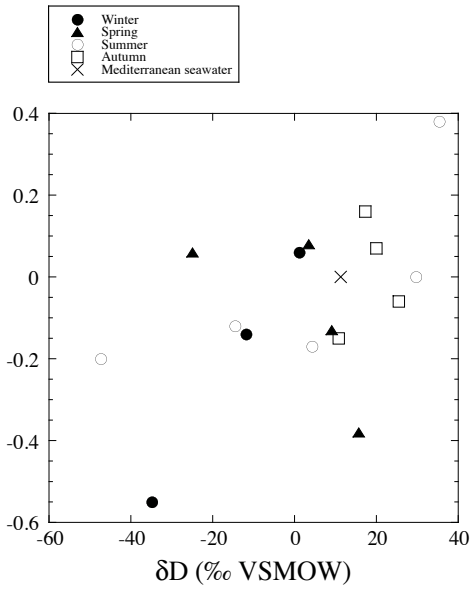

FIG. 3. A plot of δ^{37}Cl in ‰ SMOC with respect to δD (‰ VSMOW) of analyzed water sample.

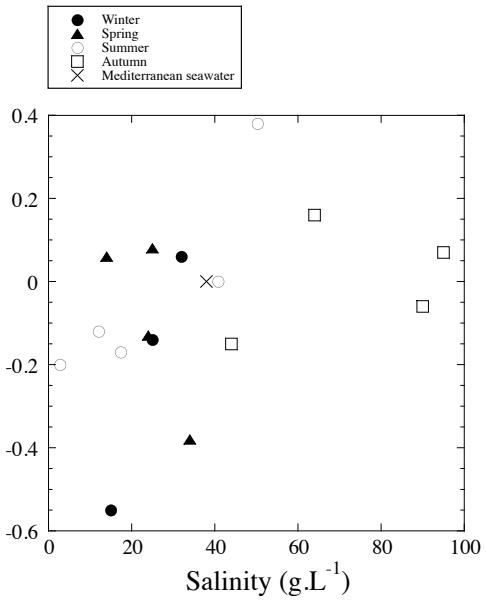

FIG. 4. A plot of δ^{37}Cl in ‰ SMOC versus salinity in g/L.

CONCLUSIONS

We have found both temporal and spatial variability of δ^{37}Cl in the analyzed waters. A weak positive correlation was found between δ^{37}Cl and δD of water and its salinity. This may indicate a mixing between seawater and distinct sources of freshwater (local rain and the Seyhan River and mixing with brackish waters inherited from the former seasons). The overall spread of obtained δ^{37}Cl results is relatively narrow, from +0.38 to -0.55 ‰, which demands enhanced precision of analysis and careful sample preparation.

REFERENCES

1. Craig, H. (1961) *Isotopic variations in meteoric waters*. Science **133**, 1702-1708.
2. Dansgaard, W. (1964) *Stable isotopes in precipitation*. Tellus **16**, 436-468.
3. Davutluoglu O.I., Seckin G., Kalat D.G., Yilmaz T., Ersu C.B. (2010) *Speciation and implications of heavy metal content in surface sediments of Akyatan lagoon – Turkey*. Desalination **260**, 189-210.
4. Duane M.J., Al-Zamel A., Eastoe C.J. (2004) *Stable isotope (chlorine, hydrogen and oxygen), geochemical and field evidence for continental fluid flow vectors in the Al-Khiran Sabkha (Kuwait)*, Journal of African Earth Sciences **40**, 49-60.

5. Eggenkamp H. (2004) Chapter 28, in: P. de Groot (ed.) *Handbook of Stable Isotopes*, Elsevier.
6. Hałas S, Pelc A (2009) *New isotope ratio mass spectrometric method of precise $\delta^{37}Cl$ determinations*. Rapid Comm. in Mass Spectrom. **23**, 1061-1064.
7. Kuleli T (2010) *Quantitiative analysis of shoreline changes at the Mediterranean Coast in Turkey*. Envir. Monitor. Assess **167**, 387-397.
8. Lécuyer C., Bodergat A.-M., Martineau F., Fourel F., Gürbüz K. and Nazik A. (2012) *Water sources, mixing and evaporation in the Akyatan lagoon, Turkey*. Estuarine, Coastal and Shelf Science **115**, 200-209.
9. Lécuyer, C., Gardien, V., Rigaudier, T., Fourel, F., Martineau, F., Cros, A. (2009) *Oxygen isotope fractionation and equilibration kinetics between CO_2 and H_2O as a function of salinity of aqueous solutions*. Chemical Geology **264**, 122-126.
10. MacPherson N, Cittolin G, Cook H, Besiktepe S. (1998) *The farming of sea bass, sea bream, and shrimp in Iskenderun Bay, Turkey. Food and Agriculture Organization of the United Nations (FAO) report*. Available as a PDF file at the following URL : http://www.fao.org/docrep/field/003/S8479E/S8479E00.htm
11. Martineau, F., Fourel, F., Bodergat, A.-M., Lécuyer, C. (2012) *D/H equilibrium fractionation between H_2O and H_2 as a function of the salinity of aqueous solutions*. Chemical Geology **291**, 236-240.
12. Meybeck M., Ragu A. (1996) *River discharges to the oceans: an assessment of suspended, major ions and nutrients*. GEMS/EAP, 245 pp.
13. Nazik A., Evans G., Gürbüz K. (1999) *Sedimentology and palaeontology with special reference to the ostracoda fauna of Akyatan lagoon (Adana – SE Turkey)*. Geosound **35**, 127-147.
14. Pelc A., Hałas S. (2008) *Negative ion source for chlorine isotope ratio measurements*. Rapid Communications in Mass Spectrometry **22**, 3977-3982.
15. Wu J., Satake H. (2006) *Purification of CH_3Cl from CH_3I using cold trap with sealed 2,2,4-trimethylpentane for $\delta^{37}Cl$ measurements*, Analytica Chim. Acta **555**, 41-46.
16. Xiao Y.K., Zhang C.G. (1992) *High precision of isotopic measurement of chlorine by thermal ionization mass spectrometry of theCs_2Cl^+ ion*. Int. J. Mass Spectrom. Ion Proc. **116**, 183-192.