J. Black Sea/ Mediterranean Environment
Vol 11: 125- 138 (2005)

Investigations on the Sediment of Lake VAN

II. Heavy metals, sulfur, hydrogen sulfide and Thiosulfuric acid S-(2-amino ethyl ester) contents

Van Gölü Sedimenti Üzerinde Araştırmalar

II. Ağır metal ve Kükürt, Hidrojen sülfit ve Tiosulfurik asit S – (2-amino etil ester) içeriği

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Abstract

Fe, Mn, Pb, Cu, Zn, Ni, Cd and Cr contents were determined by AAS in sediment of Lake Van. Cadmium and nickel levels were found high.

The sulfur forms were detected as precipitated, octa-sulfur and 1,2,3,5,6 pentathiepane by GC/MS.

Thiosulfuric acid S –(2 – amino ethyl ester) was detected first time in sediment by GC/MS analysis. This compound was also found in algae by our labroratory. The origin was probably due to marine organisms.

Hidrogen sulfide content was determined in Van Lake sediments 265.2 - 639.2 µg/g.

Key word: Lake Van, metals, sulfur forms, thiosulfuric acid S –(2 – amino ethyl ester), hydrogen sulfide

Introduction

Lake Van is the result of tectonic depression of Afro-Arabian Plate in the south meeting the Eurasian Plate from the north and east. It is the largest soda lake on earth showing an extremely high degree of carbonate saturation (Kempe *et al,* 1978a; Kempe *et al.,* 1978b). The bedrock in the lake's catchment (12522 km^2) consist of the metamorphic rocks of the Bitlis Mountain ridge, Tertiary and Quantenary conglomerates, carbonates and sandstones to the east and volcanic deposits to the north and west with the semiactive volcanoes of Nemrut and Suphan Dag in the vicinity of the Lake. It is extremely alkaline 155 meq/L^{-1}, pH 9.81 (Kempe *et al.,* 1991). Wick *et al.,* (2003) analysed sediment cores taken from Tatvan basin and determined oxygen isotope and carbonates in 294 samples. Mg/Ca ratio of the lake water was found relatively stable. The analysis of lake water showed that it contained 21 ‰ salt of which 8.3‰ was sodium carbonate / sodium bicarbonate (Degens *et al.,* 1978a; Kempe *et al.,* 1991). The other studies were made in geology (Degens *et al*., 1984), ^{18}O stable oxygen isotopes and trace elements (Lemcke and Strum, 1997), hydrography (Kempe *et al.,* 1978a; Schweiger, 1975; Öztürk and Görgün, 2004), hydrogen sulfur (Öztürk and Görgün, 2004), microbiolites (Kempe *et al.,* 1991) and mineral composition of the sediment (Khoo *et al.,* 1978; Veleton, 1978).

In our earlier study the oil content was investigated in Lake Van (Güven *et al.,* 2004)

In this work the sediments were investigated taken from Lake Van for heavy metal and sulfur compounds.

Material and Method

The sampling stations in Lake Van are shown in Fig. 1 (a b)

The samplings were made on 02 Feb 2002 at the depths as below:

Station	Depth (m)
6	320
7	200

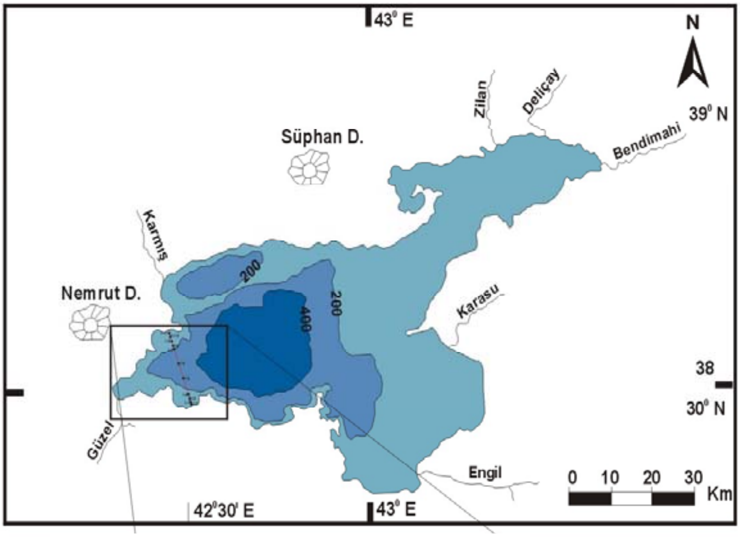

Fig. 1 The map of the Lake Van

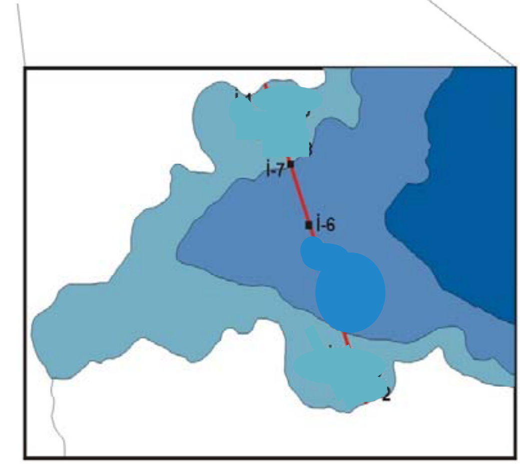

Fig 2. Sampling stations in the Lake Van

Nature of the sediments

The sediments are black colour and emit odour, include sandy and silty grain.

The samples were kept in deep – freeze until the analysis.

1. Heavy metal analysis (AAS)

Sediment samples were dried at 105 ºC and ground in an agate mortar. All metals were determined by flame atomic absorption spectrophotometer (AAS) (Shimadzu 6701 –F) after a total digestion. 1g of sample material was preoxidized with 10 ml HNO_3 in an open teflon beaker and then heated with 5 ml HF and 5 ml $HClO_4$ in closed teflon beaker for 30 min. After a formation of dense white fumes, the cover was removed to allow the $HClO_4$ to evaporate. To further digest the resistant particles, 5 ml of HF was added and the mixture allowed to reflux for a further 30 min. The remaining solutions were evaporated on a hot plate at 180 ˚C to obtain dry residues, which were redissolved with 10 ml of 1 M HCl, and then diluted to 50 ml with 1 M HCl and analysed by AAS (Loring and Rantala, 1972; Tessier *et al.,* 1979).

2. Sulfur compounds

- 2.1. Hydrogen sulfide
- 2.2. Sulfur forms
    - 2.2.1. Precipitated (colloidal, flowers)
    - 2.2.2. Octa-sulfur (S_8)
    - 2.2.3. 1,2,3,5,6 Pentathiepane (Lenthionin)
- *2.3. Thiosulfuric acid S-(2 –amino ethyl ester)*

Sulfur compounds analysis

2.1. Hydrogen sulfide analysis

Hydrogen sulfide was determined after the steam distilation of 5 g sediments. The hydrogen sulfide content was determined iodometrically in the distillate. It was added 0.02 N KI and 6 N HCl to 100 ml distillate and then titrated by 0.02 N sodium thiosulfate.

2.2. Sulfur forms

Sulfur forms were determined in sediment by GC/MS.

The sediment sample was extracted with dichloromethan (DCM) in Soxhlet at 40 ˚C for 4h. DCM phase was separated and distilled, the residue taken with hexane and applied to GC/MS.

2.3. Thiosulfuric acid S-(2 –amino ethyl ester)

This compound was determined after extraction of sediment with DCM as described above.

2.4. GC/MS (HP 6890) Analysis

The GC column was an HP 5 MS 30 mx 0.25 mm i.d. (film thickness 0.25 µm) fused-methyl siloxane (Hewlett-Packard). Injections (2 µl) were conducted in the splitless mode with the column held at 50˚C for 1 min, from 50-320˚C for 10˚C/min, 320˚C at 5 min; the carrier gas helium (0.8 ml/min). The injector temperature was held at 300˚C. Mass spectral data acquired in Selected Ion Monitoring (SIM) mode.

Results

1. The heavy metal contents of Lake Van are shown in Table 1.

Table 1. The heavy metal contents of the sediment of Lake Van (µg/g).

Metals / Station	Mn	Pb	Cu	Zn	Ni	Cd	Cr	Fe(%)
6	663	9	13	33	90	7	48	0.42
7	415	15	6	29	54	4	29	3.19

The results were compared with the values given by Krauskopf (1979) for shelf (µg/g); Mn 850, Pb 20, Cu 50, Zn 90, Ni 80, Cd 0.2, Cr 100, Fe % 4.7).

As can be seen from the table the values of cadminum and nickel are high at Nr: 6 station. The high content of Ni is probably a result of volcanic source (Veleton, 1978).

Khoo *et al., (1978)* were determined mineral contents of Lake Van sediments at various stations and depths as (µg/g): Mn (MnO 0.22-0.88 %), Pb 12-44, Cu 32-106, Zn 48-98, Ni 80-294, Cd 1-13, Cr 82-222, Fe (Fe_2O_3 %) 2.15-6.36.

Veleton, 1978 analysed the laminated lacustrine sediments in the terraces and the traventine of Lake Van and found that:

Fe^{3+} (Fe_2O_3 %), 0.08-5.98 and (ppm): Mn 15-1080, Cu 12-50, Zn 9-94, Ni 29-256, Cr 18-200.

The comparison of Khoo *et al.,* (1978) and Veleton, (1978) findings with our results showed that their levels of all metals were higher than ours since, their stations were quite different.

The amorphous Fe^{3+} complex is responsible for the reddish or yellow colour of the sediments (Veleton, 1978).

Through the finding of Kempe *et al.,* (1978) the amount of metals and anions in water of Lake Van are (mg/L); as pbb; Pb 15, Cu 1.7, Ni 0.88, Cd 0.45, Co 0.06, (Fe, Zn and Cr not detectable).

2. Sulfur compounds

There is no information in the literature on the sulfur compounds and hydrogen sulfide content of sediments of Lake Van.

2.1 Hydrogen sulfide

The amount of hydrogen sulfide of Lake Van sediments are shown in Table 2.

Table 2. Hydrogen sulfide contents of sediment of Lake Van (µg/g).

Station	H_2S (µg/g)
6	639.2
7	265.2

Hydrogen sulfide produced by reduction of sulfate in sediment. It has been a major problem in marine life. It is the result of bacterial community at the oxic-anoxic interface. Anoxia is favoured in estuaries where high loads of organic matter and/or nutrients are supplied, and semi-enclosed water bodies where water mixing and tidal exchanges are strongly restricted. Dissolved hydrogen sulfide (DHS) appears since 1800 years ago in the Black Sea. The hydrogen sulfide contents of the sediments are compared with the findings from western Black Sea (31.7 – 249 µg/g) and Danube eustary (3.4. – 20.4 µg/g) (Güven *et al.*, unpublished data) and found that it is appreciably higher.

Hydrogen sulphide content in sediment of Lake Van was found 2µg/g (Öztürk and Görgün, 2004). The difference from our finding can be related to analysis of different parts of the sediment core.

2.2. Sulfur forms

Sulfur is known in three allotropic forms as rhombic, monoclinic and plastic. Powdered sulfur (flowers) of sulfur are a combination of the allotropic forms 1 and 3.

These compound were detected by GC/MS analysis.

Sulfur precipitated (flowers) and octa sulfur were detected by GC/MS analysis. Their chromatograms are shown in Fig. 2a and 2b.

1.2,3.5,6 Pentathiepane was also detected by the GC/MS. Its chromatogram of spectrum are shown in Fig 3a and 3b.

Sulfur found in the sediment is originated from the oxydation of hydrogen sulfide.

2.3. Thiosulfuric acid S- (2- amino ethyl ester)

GC/MS chromatogram and spectrum of this compound is shown in Fig 4a and b.

This compound was found recently in algae (Erakın and Güven unpublished data). The origin of this compound in Lake Van sediment is probably due to marine organisms.

There has been no information in the literature on sulfur compounds and especially thiosulfuric acid S- (2 amino ethyl ester) of sediment in the Lake Van.

These are the first record in this field.

Fig 2a. The chromatogram of precipiated sulfur

Fig 2b 1. The spectrum of precipitated sulfur of the extract of the sediment Fig 2b 2. The spectrum taken from the HP memory

Fig 3a. The chromatogram of 1,2,3,5,6,- Pentathiepane

Fig 3b 1. The spectrum of 1,2,3,5,6,- Pentathiepane from the extract the of the sediment, Fig. 3b 2.The spectrum taken from the HP memory

Fig 4a. The chromatogram of thiosulfuric acid S-(2- aminoethyl ester)

Fig 4b 1. The chromatogram of thiosulfuric acid from the extract of the sediment, Fig. 4b 2. The spectrum of taken HP memory

Özet

Bu çalışmada Van Gölü sedimentinde ağır metal ve hidrojen sülfür, presipite kükürt ve thiosulfurik asit S-(2-amino etil ester) bileşiği tayin edilmiştir.

Ağır metaller AAS metodu ile sedimentte tayin edilmiştir.

Bulunan metal bileşik içeriği ele alınan 6 ve 7 numaralı istasyonlar arasında farklılık göstermiştir. Krauskopf'un (1979) verdiği limitlere göre 6 numaralı istasyonda Cd ve Ni miktarı, 7 numaralı istasyonda ise sadece Cd içeriği yüksektir.Ayrıca Khoo *et al.,* (1978) ve Veleton (1978)'in Van Gölü sedimenti üzerinde yaptığı çalışmada bütün sahil şeridi taranmış ve bulunan metal miktarları bizim bulgularımızdan yüksektir. Biz 2 istasyonda ve 200-320 m derinlikte çalıştık. Yapılan bu çalışmalar arasındaki farklılık incelenen bölge ve derinlikten kaynaklanmıştır.

Hidrojen sülfür sedimentin distilasyonu sonunda ele geçen distilada iodometrik olarak tayin edilmiştir. Hidrojen sülfür miktarı (μg/g) 6 numaralı istasyonda 639, 7 numaralı istasyonda ise 265 bulunmuştur. Bu rakamlar Batı Karadeniz Türkiye sahillerindeki sedimente nazaran yüksektir.

Kükürtün allotropik şekillerinden presipite kükürt ve ayrıca octa-sulfur GC/MS analizinde tesbit edilmiştir. Bunlardan başka 1,2,3,5,6 pentathiepan mevcudiyeti sedimentte saptanmıştır.

Bunlara ek olarak bir diğer kükürt bileşiği tiosulfurik asit S-(2-amino etil ester) yine GC/MS analizi sonunda sedimentte bulunmuştur. Bu madde yeni olarak alglerde tesbit edilmiştir (Erakın and Güven, yayınlanmamış çalışma) Bu maddenin sedimentte bulunuş kaynağının deniz canlıları olduğu düşünülmüştür.

Acknowledgment

The authors would like to thanks TUDAV (Turkish Marine Research Foundation) for providing the sediment materials.

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Received: 08.12.2003
Accepted: 05.02.2004