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Caffeine in the stream, well and sea water of Yalova, Marmara Sea, Turkey

Yalova, Marmara Denizi Dere, Kuyu ve Deniz Suyunda Kafein Tanısı

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Abstract

Caffeine is a land–based pollutant. It was detected in Taşköprü stream, a well in Yalova city and Sea of Marmara. Caffeine is existed in the thea and metabolized after taken into human body in ratio of 99%. The source of caffeine in aquatic system is the unconsumed thea discharged to the stream and sea. This is the main cause for the pollution of environment. Its identification in marine indicates anthropogenic inputs.

Keyword: Caffeine, stream, well, seawater, Yalova, Marmara Sea.

Introduction

Caffeine is an purine derivate and chemically 1,3,7 tri – methyl xanthine (7 – methyl theophylline). It was first isolated from *Caffea* spp. in 1820 by Runge (Valentin, 1950). It is found in various plants such as *Ilex paraguariensis* and other species, *Theobroma cacao*, *Paulinia cupana, Camellia* spp. (*sinensis, viridis, theifera, thea*) (black tea), *Theobroma cacao, Cola* spp and *Coffea arabica(vulgaris)* and also other spp, (Stahl, 1962, Baytop, 1963; Hoppe, 1975).

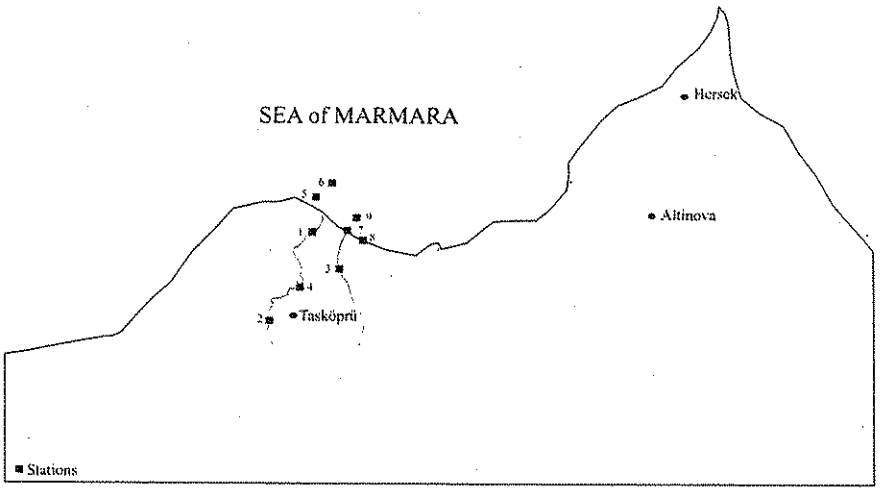

Fig 1. The Map of Sample Stations.

Thea sinensis L. (*Camellia thea* Link) (Theaceae) contains a high amount (1–5 %) of caffeine and few theophylline, theobromine, xanthine etc. It is a white crystal or crystaline powder, sparingly soluble in water, freely soluble in boiling water and also in chloroform, slightly soluble in dehydrated alcohol and in ether. Thea infusum is largely consumed in all countries. Caffeine is absorbed readily and widely distributed throughout the human body and passes readily into the central nervous system and into saliva. It stimulates the nervous system. It is biotransformed in human body 99 % in various metabolized products and only 1% unchanged form, excreted in urine (Martindale, 1996).

Caffeine was detected in river (Barber *et al.*, 1995), in well (Seiler *et al.*, 1999), in sewage (Paxeus and Schröder, 1966) and in seawater of Boston Harbour (Siegener and Chen, 2002).

This paper presents the identification of caffeine in the a stream, adjacent well and coastal seawater of Marmara Sea.

Material and Method

The location of the stations are shown in Fig 1.

The samples were collected from Taşköprü stream, a adjacent well and coastal water at the stations of Marmara Sea 21 Dec. 1999 (Station 1, 2), 26 Oct. 2000 (Station 3), in well 30 Dec. 1999 (Station 4), in Seawater 04 Feb. 2000 (Station 5, 6), 28 April 2000 (Station 7, 8), 12 July 2000 (Station 9).

Water samples were extracted within 12h of collection with dichloromethane (DCM) (HPLC Grade, LabScan) . The extract was distilled at 40°C. The residue was taken with hexane and analysed by GC/MS (HP 6890). The GC/MS analysis was made by HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD) controlled by HP ChemStation. The analytical conditions were : 30 m x 0.25 mm fused DB - WAX, glass capillary column; oven temparature programme , 40 °C at 5 min., from 40 – 260 °C at 8 °C/min., 260 °C at 10 min.; split injector temperature 250 °C; carrier gas Helium.

Result and Discussion

The results are summarized in Table 1.

Caffeine was found on different dates at the stations :

in the stream Nr:1, 2 , 3,

in well at Nr: 4,

in coastal water (Sea of Marmara) Nr: 5, 6, 7, 8, 9, near the stream exit.

The GC/MS chromatograms and mass spectra of caffeine in the samples and standard caffeine obtained from the thea are shown in Fig. 2 and 3 respectively.

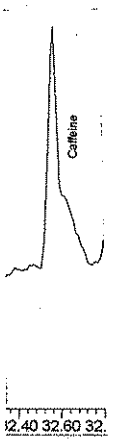

Fig.2a. Stream Station 1
21/12/1999

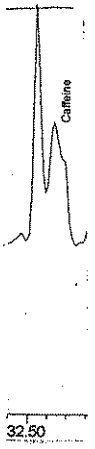

Fig.2b. Stream Station 2
21/12/1999

Fig.2c. Stream Station3
26/10/2000

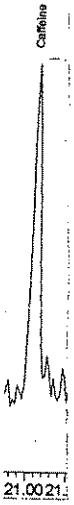

Fig.2d. Well Station 4
30/12/1999

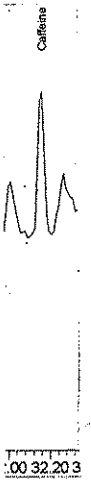

Fig.2e. Seawater Station 5
04/02/2000

Fig.2f. Seawater Station 6
04/02/2000

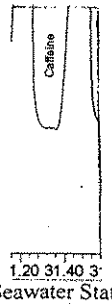

Fig.2g. Seawater Station 7
28/04/2000

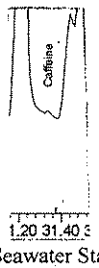

Fig.2h. Seawater Station 8
28/04/2000

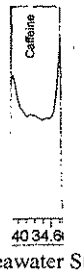

Fig.2i. Seawater Station 9
12/07/2000

Fig 2. The chromatograms of the samples in examined stations.

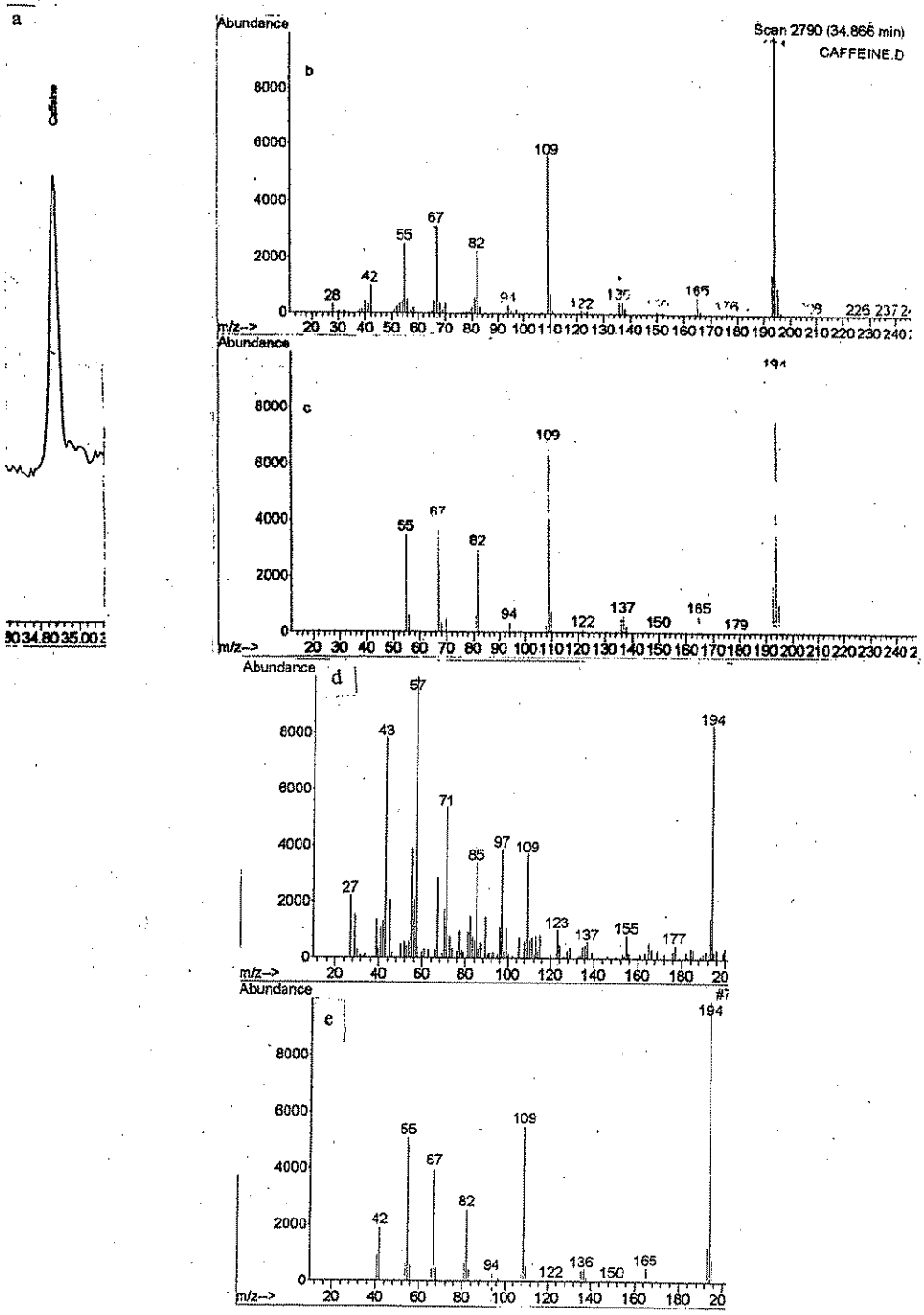

Fig. 3. The chromatogram of caffeine standard (a) and its mass spectrum (b)
The mass spectrum taken from HP memory (c) ; The spectrum of Station 1 (d),
the mass spectrum taken from HP memory (e)

Table 1. Caffeine detected in samples.

Source	Stations (Nr.)	Date
Stream	1 (Fig.2a)	21 Dec. 1999
	2 (Fig.2b)	21 Dec. 1999
	3 (Fig.2c)	26 Oct. 2000
Well	4 (Fig.2d)	30 Dec. 1999
Sea water (Sea of Marmara)	5 (Fig.2e)	04 Feb. 2000
	6 (Fig.2f)	04 Feb. 2000
	7 (Fig.2g)	28 April 2000
	8 (Fig.2h)	28 April 2000
	9 (Fig.2i)	12 July 2000

The biotranformation of caffeine in human body occured almost completely (99%) in the liver via oxidation, demethylation and acetylation and excreted products in the urine are :

1 – methyluric acid,
1 – methyl xanthine,
7 – methyl xanthine,
1,7 – dimethyl xanthine (paraxanthine),
5 acetyl – amino- 6 – formylamino – 3 methyl uracil,
and other metabolities.

Its half–life was approximately 3 to 6 h. (Martindale, 1996). Thus the percentage of the biotransformation of caffeine in human body is very high. Only 1 % caffeine is eliminated in unchanged form. The daily thea consumption per person is approx. 6x100 ml and caffeine amount taken 42 mg and unmetabolized amount is 0.042 mg considered negligible for pollution of aquatic systems. Thea infusum unconsumed is discharged to seawage and then into sea. It contained high amount of caffeine unchanged form which had a role in the detection of caffeine in aquatic systems.

Conclusion

The source of caffeine in this area was the discharge of unconsumed thea from village of Yalova. It was entered the stream, then distributed into adjacent well near the stream and finally coastal sea (Sea of Marmara).

Thus caffeine can be used as an indicator of anthropogenic inputs to marine systems.

Özet

Kafein kara kaynaklı bir kirleticidir. Yalova, Taşköprü deresindeki, bir kuyuda ve Marmara Denizinde tespit edilmiştir. Kafein çaydan bulunur ve içimini takiben %99 oranında insan vücudunda metabolize olur, %1' inin değişiminden ve büyük kısmı ise değişik metabolitleri itrah olur. İncelenen istasyonlarda kafein kaynağı, tüketilmemiş çayın dereye ve oradan kuyu ve denize ulaşması sonucudur. Bu şekilde kafeinin su – deniz sisteminde bulunması, çevre kirliliği saptanmasında bir indikatör olarak kullanılabilir.

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