

**A METHODOLOGY TO STUDY THE  
BEHAVIOR OF MERCURY CHLORIDE  
IN AQUEOUS SOLUTION USING  
RADIOACTIVE TRACER**

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF  
NATURAL AND APPLIED SCIENCES  
OF  
FATIH UNIVERSITY  
BY  
**FERHAT KARACA**

97737

IN PARTIAL FULFILLMENT OF REQUIREMENTS FOR THE  
DEGREE  
OF  
MASTER OF SCIENCES  
IN THE DEPARTMENT OF ENVIRONMENTAL ENGINEERING

AUGUST, 2000

T.C. YÜKSEKÖĞRETİM BAKANLIĞI  
DOKÜMANİZASYON MERKEZİ



# Fatih Üniversitesi

Tarih: 29 / 08 / 2000

Fen Bilimleri Enstitüsü Müdürlüğü'ne

TUTANAK

Ferhat KARACA ..... 'a ait

"....."  
A methodology to study the behavior of  $HgCl_2$  in aqueous solution using radioactive tracer.  
adlı çalışma ..... 60 dk.'lık süre içinde savunulmuş ve jüri tarafından

Çevre Mühendisliği ..... Anabilim Dalında *YÜKSEK LİSANS TEZİ* olarak oy  
birliğiyle /oy çokluğuyla kabul edilmiştir / edilmemiştir.

..... yarıyıl ek süre verilmiştir.

Başkan

N.K. Aras

Üye

İlhan Ölmez

Üye

Sibel Uludağ Demirel

## ABSTRACT

### ***A METHODOLOGY TO STUDY THE BEHAVIOR OF MERCURY CHLORIDE IN AQUEOUS SOLUTION USING RADIOACTIVE TRACER***

Karaca, Ferhat

M.S., Department of Environmental Engineering

Supervisor: Prof. Dr. Namik K. Aras

Co-Supervisor: Prof. Dr. İlhan Ölmez

August 2000

Mercury contamination in remote regions can occur through long-range atmospheric transport. Because of its volatility, mercury is unique among the trace metals in its cycling in the environment, and we now understand its ability to be emitted (or re-emitted) from surfaces once deposited. Wet and dry processes to deposit atmospheric mercury environmental surfaces, however, the air/surface exchange processes in the cycling of Hg in aquatic ecosystems are not well known. This process can significantly influence its persistence in both terrestrial and aquatic systems, and Hg emissions from surface waters could influence the formation of methylmercury. Sediments in estuarine and coastal marine areas are one of the most important sinks for environmental contaminants. It is clear from a wide range of studies that a fraction of mercury ends up in bottom sediment.

In this study a simple experimental methodology was used to be used to model and measure Hg air/ water and water/sediment surface exchanges. We developed a simple box-chamber to see if we could explain the behavior of dissolved mercury. Radioactive mercury tracer was used, in order to measure direct evaded and deposited mercury amounts. Nuclear spectroscopic techniques were used for measurements.

Understanding in natural processes of actual air/water and water/sediment exchange mechanisms are out of the scope of this thesis. Further model studies are recommended for this purpose.

The relationships between evasion and temperature, solar effects, microorganisms, etc were investigated during 140 hours period. As a result of this experiment it was observed that the **28%** of mercury chloride remained in the water phase, **25%** of it emitted via the evasion process and **47%** of it deposited in sediment. The results are not conclusive.

**Keywords:** Dissolved Mercury (II), Evasion, Deposition, Sediment, and Radioactive tracer, nuclear spectroscopic techniques.

## ÖZET

### *SUDA ÇÖZÜNMÜŞ CIVA KLORÜRÜN DAVRANIŞININ RADYOAKTİF İZLEYİCİ KULLANILARAK İZLENMESİ METODU*

Karaca, Ferhat

Yüksek Lisans, Çevre Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Namık K. Aras

Ortak Tez Yöneticisi: Prof. Dr. İlhan Ölmez

Ağustos 2000

Cıva kirliliği cıvanın yayıldığı ortamlardan çok uzak bölgelerde bile gözlenebilir. Bunun nedeni cıvanın atmosferik yolla uzun mesafe taşınabilme özelliğidir. Uçucu özelliğinden dolayı cıva eser elementlerin içinde önemli bir yer işgal etmektedir. Yapılan çalışmalar göstermektedirki cıva daha önce depolandığı bir yüzeyden tekra yayılabilir. Cıvanın hava ve yüzey etkileşiminin doğadaki cıva döngüsü açısından önemli bir yeri olduğu iyi bilinmektedir. Bu durum cıvanın su fazında ve toprak fazındaki mevcudiyetinin açıklanabilmesi için ciddi bir önem arz eder.

Deniz ve göl sediman alanları kirleticiler açısından önemli bir rezarvuvar ve kaynak olabilir. Yapılan birçok çalışma açıkca göstermiştir ki çevreye yayılan cıvanın bir kısmı dip sedimanlarında depolanmaktadır.

Bu çalışmada, cıvanın hava/su yüzeyi ve suyüzeyi/sediman ilişkilerini açıklayabilmek için özel bir model dizayn edilmiş ve nükleer ölçüm teknikleri kullanılmıştır. Cıvanın doğadaki akibetini anlamak için basit bir deney odası geliştirilmiştir. Nükleer spektroskopik metodlar kullanılmıştır.

Gerçek doğal şartlar altındaki hava/su ve su/sediman ilişkilerini anlamak bu çalışmanın konusunun dışında kalmaktadır. Asıl amacımız metodun çalışabilirliğinin denenmesi ve geliştirilmesidir, ileriki ve daha gelişmiş çalışmaları bu amaç doğrultusunda tavsiye edilir.

140 saat boyunca cıvanın su fazından hava fazına kaçma (evasion) sıcaklık, mikroorganizmalar, güneş ışığı, vs. ile olan etkileşimini incelenmiştir. Sonuç olarak su fazında çözülmüş olan cıvanın ancak %28inin su fazında korunabildiği, %25inin kaçma yoluyla hava fazına yükseldiği ve geriye kalan %47lik kısmında sediman fazında depolandığı bulunmuştur. Sonuçlar sistemin çalışabilirliğini göstermesi açısından verilmiştir.

**Anahtar Kelimeler:** Çözülmüş Cıva(II), Evasion, Depolanma, Sediman, ve Nükleer spektroskopik teknikler.

## *ACKNOWLEDGMENTS*

I would like to express my sincere appreciation to my supervisor Prof. Dr. Namık K. Aras and Co-supervisor Prof. Dr. İlhan Ölmez for their encouragement guidance and kind suggestions throughout this study.

I would like to express my special thanks to Prof. Dr. Turgut Balkaş and Dr. Sibel Demirer for their valuable help and endless suggestions.

I would like to express my special thanks to ITU, Institute for Nuclear Energy for their valuable help.

My special thanks to my parents and my fiancée for their patience and moral support. They are the best.

My special thanks to my friends, graduate students of engineering faculty for their moral support and friendly help.

## **TABLE OF CONTENTS**

CHAPTER I .....	1
INTRODUCTION .....	1
1-Mercury.....	2
1.1-Historical Background .....	2
1.2-Chemical Forms of Mercury in Nature.....	3
2-Aquatic Mercury Species.....	6
2.1-Sources of Aquatic Mercury .....	6
2.2-Hg cycle and Budget.....	7
2.3 -The Role of Micro Organisms in Elemental Mercury Formation in Natural Waters .....	11
2.4-Air-Water Exchange of Mercury .....	11
2.5-Water-Sediment Interactions and Porewater .....	12
2.6-Health Effects of Mercury .....	14
3- Nuclear Spectroscopic Techniques and Analysis of Mercury Tracer	16
3.1-Activation Principles.....	17
3-2-The Purpose of This Study .....	20
CHAPTER II.....	22



EXPERIMENTAL .....	22
1-Laboratory Equipments .....	22
1-1- Sampling Site .....	22
1-2- Experimental Chamber .....	23
2-Experimental Stages .....	26
2-1- Preparation of Radioactive Mercury Tracers .....	26
2-2- Evaded Radioactive Mercury Collection Method and Evasion Measurement .....	27
2-3- Water Sampling .....	29
2-4- Sediment Collection methods .....	30
2-5- Measurements .....	32
CHAPTER III .....	33
Results and Discussions .....	33
1-1 The Air Phase Studies .....	33
1-2 The Water Phase Studies .....	47
1-3- The Sediment Phase Studies .....	49
1-4- Mass Balance .....	51
1-5- Recommendation for Future Work .....	52

References..... 54



## ***LIST OF TABLES***

Table 1-Chemical Reactions of atmospheric Mercury [Ames, (1996)].....	5
Table 2-Human health effects from breathing metallic mercury .....	15
Table 3-Physical Properties and Specifications of Commercial Calgon Carbon type PCB Activated Carbon (MSA Company).....	29
Table 4-Decay Corrected Filter Hg Activity of Sequential Experiments .....	35
Table 5- Compression of Air/water Activities.....	39
Table 6- Daytime Activity over Nighttime Activity .....	43
Table 7- Change in Activities per Hour (for First 48 hour) .....	44
Table 8- Dissolved Hg Concentration in The Water Phase .....	47
Table 9- Sediment Core Activity and Drop Point Distances .....	49
Table 10- Sediment Depth Activity Data Set.....	50

## *LIST OF FIGURES*

Figure 1- Current Mercury Budgets and Fluxes (adapted from Mason, et al. 1994)	9
Figure 2- Pre- industrial Mercury Budgets and Fluxes (adapted from Mason, et. al. 1994) .....	10
Figure 3- The location of Sampling Site .....	23
Figure 4- The Experimental Box Chamber .....	25
Figure 5- The Vapor Phase Mercury Collection System .....	28
Figure 6- Sediment Sampling Equipment 1, Piston Sediment Sampler (PSS) .....	30
Figure 7- Sediment Sampling Equipment 2, Frozen Sediment Sampler (FSS) .....	31
Figure 8- Cumulative Increase of Air Activity .....	36
Figure 9- Change in Values of Activities .....	38
Figure 10- First 48-hour Air Activity .....	40
Figure 11- Cumulative Increase of Activity per Hour (for the First 48 hour) .....	41
Figure 12- Change in Air Activities per Hour (for the First 48-hour) .....	42
Figure 13- Cumulative Increase of Activity per Hour (for after 48 hour) .....	45
Figure 14- Change in Activities per Hour (for after 48 hour) .....	46

Figure 15- Water Activity versus Elapsed Time..... 48

Figure 16- Sediment-Depth Profile..... 50



# CHAPTER I

## INTRODUCTION

Mercury is a chemical element that occurs naturally in the environment in several forms. Mercury can combine with other chemicals, such as chlorine, carbon, or oxygen to form either inorganic or organic mercury compounds.

Mercury contamination in remote regions can occur as a result of long-range atmospheric transport. Existing in the air as an atomic vapor, mercury's high vapor pressure and low solubility give it an atmospheric lifetime of up to one year [Olmez, (1993b)]. Wet and dry processes to environmental surfaces deposit atmospheric mercury, and the importance of air/surface exchange processes in the cycling of Hg in aquatic ecosystems is well known [Ames, (1995), Onal, (1996), Lindqvist, (1991), (1984), Lindberg, (1999)]. Because of its volatility, mercury is unique among the trace metals in its cycling in the environment, and we now understand its ability to be emitted (or re-emitted) from surfaces once deposited. This can significantly influence its persistence in both terrestrial and aquatic systems, and Hg emissions from surface waters could limit the formation of methylmercury.

Sediments in estuarine and coastal marine areas are one of the most important sinks for environmental contaminants. It is clear from a wide range of

studies that a part of mercury ends up in bottom sediment. Through the use of activated charcoal sorbent and direct instrumental neutron activation analysis (INAA), mercury determinations can now be routinely and simply performed at the level of about one nanogram per cubic meter of air. [Olmez, (1993, 1995)]

## **1-Mercury**

### **1.1-Historical Background**

Among the vast number of chemicals known to mankind, mercury is one of the most unique due to its long history, toxicity, and chemical and physical properties. It was known to the ancient Chinese and Hindus, and has been found in Egyptian tombs from 1500 B. C. The Phoenicians traded cinnabar (HgS, used as the pigment vermilion) from around 700 B. C. Mercury's ability to separate precious metals such as gold and silver from their ores by amalgamation was known as early as 500 B. C. and is still employed today for gold extraction in the Amazon region. Through the middle Ages, alchemists regarded the metal as the key to transforming base metals into gold.

The modern realization of mercury as a public health hazard came about because of the Mina Mata disaster of 1953-1956 in Japan. Fifty-two deaths and over seven hundred poisonings resulted in a year (and many more over the next several years) when the fish, which were the essential of the local community's diet, became contaminated with dimethyl mercury sulfide ( $\text{CH}_3\text{HgSCH}_3$ ). It was not until 1958 that the mercury was found to be the source of the poisonings and to have originated from a local chemical works where mercury salts were used inefficiently as a catalyst and discharged. The most notable case happening in rural Iraq in 1971 when 459 deaths resulted from alkyl mercury poisoning.

It is consumption of mercury-contaminated fish as in Mina Mata, which continues to keep mercury pollution a matter of scientific interest, public concern,

and government regulation. The general airborne concentration of mercury is extremely lower than any level where it might be considered a direct hazard. However, once the mercury reaches open waterways, it enters a complex web of chemical reactions and microbial activity where it may finally be transformed into methyl mercury. In this form, which is resistant to environmental degradation, mercury is ingested and retained by aquatic organisms. In fish, the mercury accumulates preferentially in the muscles with proportionately much less in neural tissues than in birds or mammals. Through the process of bioaccumulation the concentration of mercury in large fish can reach several micrograms per gram or ppm (the fish which caused acute poisonings at Mina Mata contained an average of 50 ppm mercury).

Though discharging mercury directly to waterways has been prohibited for about two decades (Douglas, 1994), releases to the atmosphere continue and are now estimated to exceed direct aquatic inputs by at least an order of magnitude (Lindberg, 1986).

### **1.2-Chemical Forms of Mercury in Nature**

Mercury's atomic number is 80 and atomic weight of 200.59, with common isotopes of 198 to 202. It shares reaction and atomic characteristics with cadmium and zinc. Mercury melts at  $-39^{\circ}\text{C}$  (234 K), boils at  $357^{\circ}\text{C}$  (630 K). It is dense, 13.6 times that of water. Its "triple point," the temperature where solid, liquid and gaseous mercury coexist (at 1 atmosphere of pressure) is a mere  $-38.8344^{\circ}\text{C}$  and acts as a fixed point to measure from on the International Temperature Scale. It is the only common metal liquid at ordinary room temperatures.

Residence time of mercury in the environment is long. Mercury can change between organic and inorganic forms. For example, some or all released organic



mercury will slowly break down to become inorganic mercury and some released inorganic mercury will also slowly be changed into organic mercury (specifically, into methylmercury) in soil and water by reaction with substances produced by microorganisms and various chemical processes [Lindberg, (1999)].

Mercury is not an active element, combining with other elements only with some difficulty. It is therefore a *noble* metal, like gold, silver and the platinum group, which are all highly resistant to chemical reactions and oxidation.

Mercury forms two kinds of compounds

Hg (II), Mercurous -- uses both electrons in the bonding process.

Hg(I) Mercuric -- uses just one electron to bond with another element.

Hg (II) compounds include halides (salts) like Hg (II) Chloride ( $\text{HgCl}_2$ ) or Mercuric Fluoride. Normally a white crystalline salt soluble in water it is also called *corrosive sublimate* and is extremely poisonous. It has been used as a germicide. It can destroy kidneys in humans. If combined with the protein albumen, Hg (I) ions form an insoluble white solid that acts like what heat does to egg whites. The most important compound is  $\text{Hg}_2\text{Cl}_2$  a Mercury chloride called *calomel*, used medicinally as a liver stimulant and cathartic.

Chemical reactions of mercury in the gas phase and the liquid and Henry's constants are given in **Table1**.

<b><u>Gas-phase reactions</u></b>	<b><u>Rate (cm<sup>3</sup> / molecule second)</u></b>
1. $\text{Hg}^0(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{Hg}(\text{II})(\text{g})$	$<8 \times 10^{-19}$
2. $\text{Hg}^0(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{HgCl}_2(\text{g})$	$<4.1 \times 10^{-16}$
3. $\text{Hg}^0(\text{g}) + \text{H}_2\text{O}_2(\text{g}) \rightarrow \text{Hg}(\text{OH})_2(\text{g})$	$<4.1 \times 10^{-16}$
4. $\text{Hg}^0(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{products}$	$<6 \times 10^{-17}$
5. $\text{Hg}^0(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{products}$	$<1 \times 10^{-17}$
6. $\text{HgCl}_2(\text{g}) + \text{h}\nu \rightarrow \text{products}$	Slow
7. $\text{Hg}(\text{OH})_2(\text{g}) + \text{h}\nu \rightarrow \text{Hg}^0(\text{g})$	Not available
<b><u>Aqueous-phase reactions</u></b>	<b><u>Equilibrium or Rate</u></b>
8. $\text{Hg}^0(\text{aq}) + \text{O}_3(\text{aq}) \rightarrow \text{Hg}(\text{II})(\text{aq}) + \text{O}_2(\text{aq})$	$4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
9. $\text{Hg}^0(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{HgO}(\text{s}) + \text{Hg}^{2+} + \text{H}_2\text{O}(\text{l})$	$6.0 \text{ M}^{-1} \text{ s}^{-1}$
10. $\text{Hg}^{2+} + \text{SO}_3^{2-} \leftrightarrow \text{HgSO}_3(\text{aq})$	$5 \times 10^{12} \text{ M}^{-1}$
11. $\text{HgSO}_3(\text{aq}) \rightarrow \text{Hg}^0(\text{aq}) + \text{SO}_4^{2-}$	$0.6 \text{ s}^{-1}$
12. $\text{HgSO}_3(\text{aq}) + \text{SO}_3^{2-} \leftrightarrow \text{Hg}(\text{SO}_3)_2^{2-}$	
13. $\text{Hg}(\text{SO}_3)_2^{2-} \rightarrow \text{Hg}^0(\text{aq}) + 2\text{SO}_3^{2-}$	$1.0 \times 10^{-4} \text{ s}^{-1}$
14. $\text{HgCl}_2(\text{s}) \leftrightarrow \text{HgCl}_2(\text{aq})$	0.27 M
15. $\text{HgCl}_2(\text{aq}) \leftrightarrow \text{Hg}^{2+} + 2\text{Cl}^-$	$10^{-14} \text{ M}^2$
16. $\text{HgCl}_2(\text{aq}) + 2\text{Cl}^- \leftrightarrow \text{HgCl}_4^{2-}$	$70.8 \text{ M}^{-2}$
<b><u>Gas/liquid equilibria</u></b>	<b><u>Henry's law constant (M/atm)</u></b>
17. $\text{Hg}^0(\text{g}) \leftrightarrow \text{Hg}^0(\text{aq})$	0.11
18. $\text{Hg}(\text{OH})_2(\text{g}) \leftrightarrow \text{Hg}(\text{OH})_2(\text{aq})$	$1.2 \times 10^4$
19. $\text{HgCl}_2(\text{g}) \leftrightarrow \text{HgCl}_2(\text{aq})$	$1.4 \times 10^6$
20. $\text{CH}_3\text{HgCl}(\text{g}) \leftrightarrow \text{CH}_3\text{HgCl}(\text{aq})$	$2.2 \times 10^3$
21. $(\text{CH}_3)_2\text{Hg}(\text{g}) \leftrightarrow (\text{CH}_3)_2\text{Hg}(\text{aq})$	0.13
<b><u>Solid/liquid equilibria</u></b>	<b><u>Solubility (<math>\mu\text{g/L}</math>)</u></b>
22. $\text{Hg}_0$	$5.3 \times 10^4$
23. $\text{HgS}$	10
24. $\text{Hg}_2\text{Cl}_2$	$2 \times 10^3$
25. $\text{HgCl}_2$	$6.9 \times 10^7$

Table 1-Chemical Reactions of atmospheric Mercury [Ames, (1996)]

## **2-Aquatic Mercury Species**

Hg (II) and Hg (I) can form numerous inorganic and organic chemical compounds; however, Hg (II) is rarely stable under ordinary environmental conditions. Most of the mercury encountered in water/soil/sediments/biota (all environmental media except the atmosphere) is in the form of inorganic mercury salts and organomercurics.

### **2.1-Sources of Aquatic Mercury**

Mercury is released into the atmosphere from natural and anthropogenic sources. The source of mercury to the aquatic environment appears largely to be in the form of inorganic Hg compounds, either from direct atmospheric deposition or terrestrial runoff [Fitzgerald et. al (1991), Lindquist, (1991)]. Once in the aquatic system, biological reactions can convert inorganic mercury to methylmercury [Ramlal et. al (1985), Xun et al, (1987)], elemental mercury, or particulate bounded Hg [Hurley et. al (1991)]. The production of methylmercury is of particular importance, due to, its extreme toxicity and biomagnifications in the aquatic food chain. The reactions forming other Hg species are equally important, however, as they may serve as direct competitors to methylation, and so ultimately control the amount of methylmercury produced in an aquatic system [mason, (1998)]. In any attempt to model the ecological pathways resulting in the production of methylmercury in the environment, it is necessary to have an understanding of the chemical nature of the substrate for these reactions. Generally, it is believed that this substrate is represented by the so-called "reactive mercury" (Hg<sub>r</sub>, variously called "easily reducible", "acid labile", "ionic", "reactive", or "Hg(II) [Fitzgerald et. al (1991), Lindquist, (1991)].

## 2.2-Hg cycle and Budget

The importance of atmospheric mobilization and depositional processes in the global mercury cycle is well recognized and described in a variety of mass balance formulations for the global mercury cycle. Although the significance of the atmosphere appeared in early global calculations, environmental assessments of source strengths for natural and anthropogenic processes were subject to considerable uncertainty because of the rarity of accurate information for critical aspects of the mercury cycle [Bloom, (1988)].

The geochemical view of the global mercury cycle has improved significantly, and present estimates for mercury fluxes to the earth's surface and for the mercury content of active reservoirs are converging. The agreement among recently published budgets for the atmospheric cycling of mercury has improved considerably despite the uncertainties associated with global-scale estimates [Fitzgerald (1989), Lindqvist (1991)]. Furthermore, it has become increasingly evident that human-related (anthropogenic) emissions of mercury to the air rival or exceed natural inputs, with the principal emission sources now being coal combustion, mining and smelting, industrial use, and waste incineration. Recent estimates place the annual amounts of mercury released into the air by human activities at between 50 and 75 percent of the total yearly input to the atmosphere from all sources. Current evidence indicates that the total influence of human activities extends beyond direct mercury emissions. This is based on the conviction that emissions from terrestrial and marine systems include a "recycled" anthropogenic component.

A schematic of the most recent conceptualization of the current global mercury cycle is illustrated in **Figure 1** and **2**. Important fluxes include anthropogenic emissions, marine and terrestrial wet deposition, and evasion from the oceans. **Figure 1** and **2** provide a recent estimate of the fluxes and reservoir

burdens for such a global cycle model, as well as corresponding pre-industrial values. Comparing these models can provide insight into the extent to which anthropogenic emissions have perturbed the mercury cycle.

It appears that mercury concentrations/fluxes within terrestrial systems, oceans, and the atmosphere have been increased by human activities over the past 100 years [Lindberg,(1994)].

Complex biological and chemical interactions, such as methylation and elemental mercury production and volatilization, prolong the cycling of mercury and affect releases to the environment. Recent estimates indicate that of the approximately 200,000 tons of mercury emitted to the atmosphere since 1890, about 95 percent resides in terrestrial soils, about 3 percent in the ocean surface waters, and 2 percent in the atmosphere. Thus, contemporary anthropogenic mercury releases are adding to concentrations in active reservoirs that have already been increased by earlier human activities [Mason, (1994)].

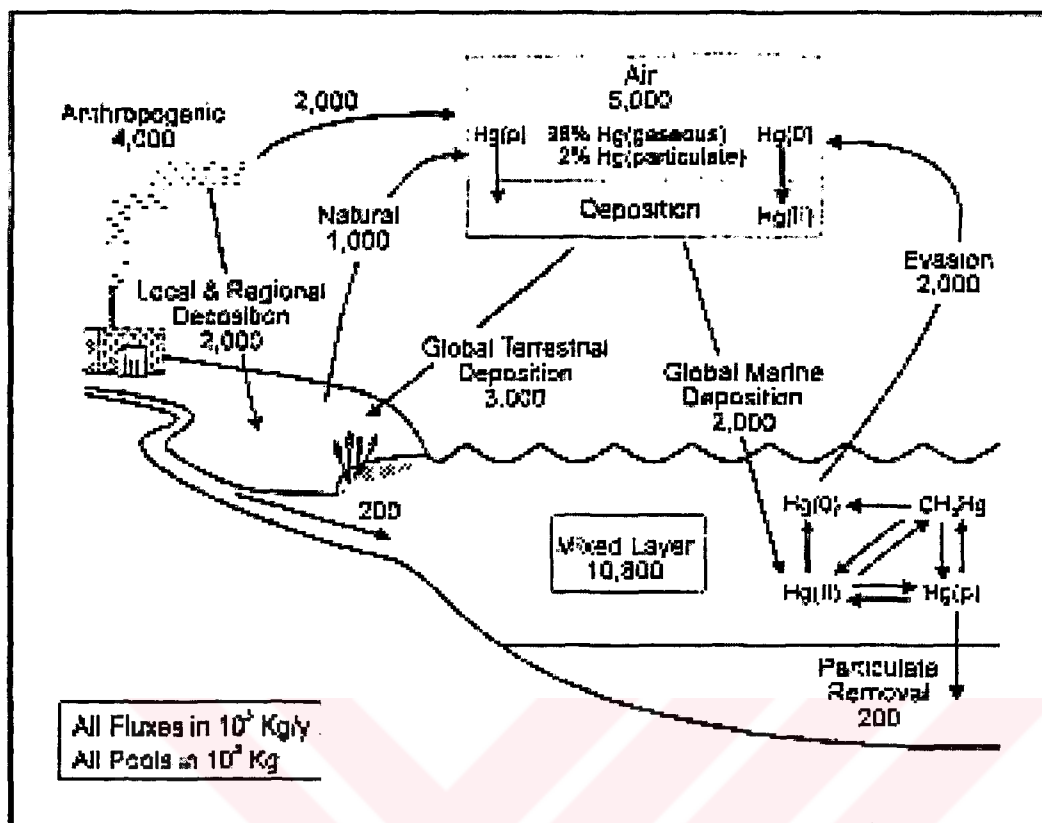


Figure 1- Current Mercury Budgets and Fluxes (adapted from Mason, et al. 1994)

Mercury accumulating in soils is released only slowly to terrestrial waters. A study [Lindqvist, (1991)] suggests that more than 80 percent on an annual basis of the atmospheric mercury deposition to a watershed is retained in the watershed. Thus, unless this mercury is permanently sequestered, the effects from the anthropogenic mercury loadings may persist and affect fish in fresh waters and estuarine/coastal regions for long periods after a cessation in mercury emissions. In contrast, the atmosphere, open ocean waters, and biota are estimated to decrease in mercury burden much more rapidly (10-20 years). The extent to which soil mercury pools are re-emitted to the atmosphere by volatilization needs to be evaluated because it has important implications for the residence time of mercury in soil.

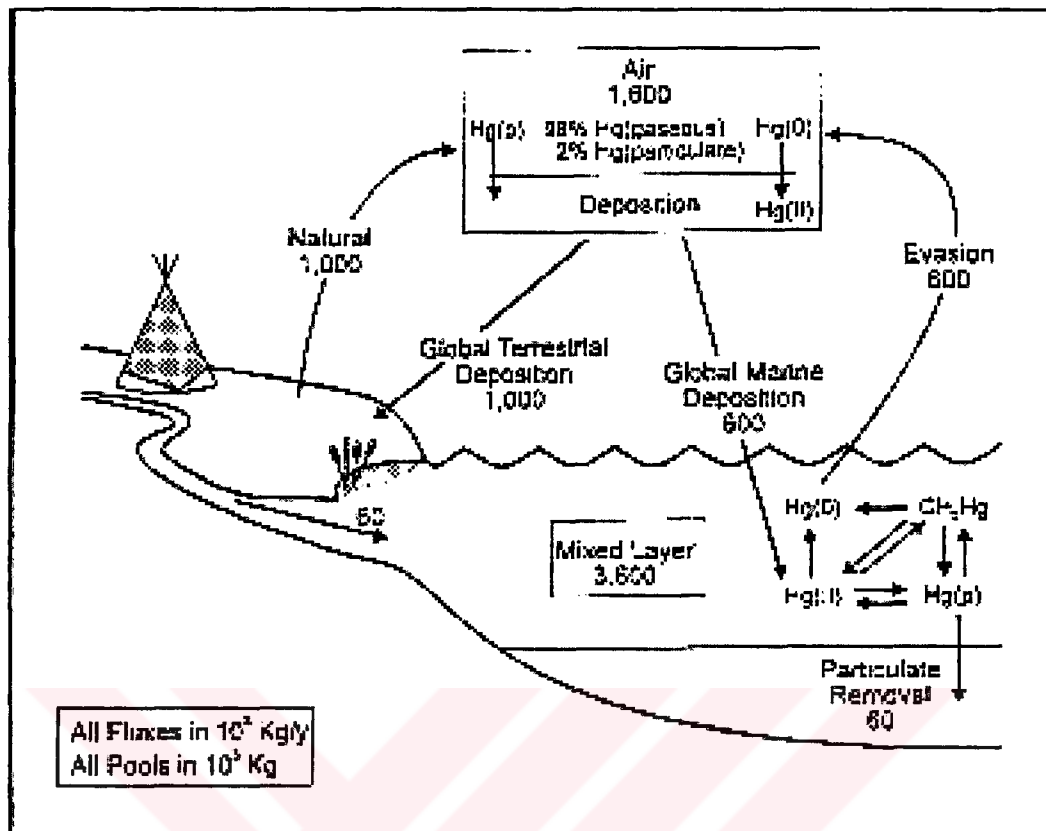


Figure 2- Pre- industrial Mercury Budgets and Fluxes (adapted from Mason, et. al. 1994)

The global model implies that about one-half of the anthropogenic mercury emissions contribute to the global cycle, and about one-half deposits on a local/regional scale. Although atmospheric mercury fluxes have increased by about a factor of five over the last century as a consequence of human activities, the net increase in the atmospheric burden is closer to a factor of three, potentially reflecting the expected near-source removal of particulate mercury and Hg (II) vapor-phase species. An annual increase of atmospheric mercury concentration has been hypothesized, at a rate of  $0.01\text{ng m}^{-3}$  (i.e., 0.6 percent per year) [Mason, (1994)].

### **2.3 -The Role of Micro Organisms in Elemental Mercury Formation in Natural Waters**

Elemental mercury ( $\text{Hg}^0$ ) plays a fundamental role in the global Hg cycle. The exchange of Hg between surface waters and the atmosphere is rapid as a result of the formation of  $\text{Hg}^0$  in natural waters, and its subsequent evasion [Mason et al, (1994)]. In the oceans, which are major source and sink for atmospheric mercury; the situation is similar for fresh waters. [Wandal et al, (1991)]. As  $\text{Hg}^0$  formation removes reactive mercury from the water column where it could be otherwise methylated, this process plays an important role in the biochemical cycling of Hg in Aquatic systems [Fitzgerald et al. (1994)].

However, the mechanisms whereby reactive Hg species are reduced to volatile  $\text{Hg}^0$  are not well known. The reduction appears to be chiefly biological. Studies of mercury reduction by procaryotic microorganisms at high  $\text{Hg}^{2+}$  concentrations have demonstrated that some bacteria can convert Hg (II) to  $\text{Hg}^0$  using plasmid-encoded enzymatic pathway. Eucaryotic microorganisms can also reduce Hg [Mason et al, (1995)].

### **2.4-Air-Water Exchange of Mercury**

Mercury air-water exchange is a critical component of Hg global cycling, as the water area on the earth's surface is far greater than the overall terrestrial surface area.

Thermodynamically, air-water exchange is governed by Henry's law, i.e.,  $[\text{Hg}^0]_{\text{air}}/[\text{Hg}^0]_{\text{water}} = H$  where  $[\text{Hg}^0]_{\text{air}}$  is the air  $\text{Hg}^0$  concentration at equilibrium,  $[\text{Hg}^0]_{\text{water}}$  is dissolved gaseous mercury concentration at equilibrium, and H is the Henry's constant. Kinetically, however, the exchange is controlled by many processes; including physical processes of  $\text{Hg}^0$  diffusion in water column and



exchange air-water interface as well as biochemical processes of dissolved gaseous mercury production and consumption.

Formation of methyl-Hg may be controlled by some processes that reduce Hg (II) in the water column to Hg<sup>0</sup> [Fitzgerald et al., (1994)]. Therefore, the fate of dissolved gaseous mercury in surface water is an important component of the Hg cycle in aquatic phase.

Mercury has an ability to be emitted (or re-emitted) from surfaces once deposited. This can significantly influence its persistence in both terrestrial and aquatic systems, and Hg emission have been widely reported from surface waters in both marine and fresh water systems [Lindberg, S.E., (1999)]. Mercury evasion from water is commonly modeled using measurements of dissolved gaseous mercury.

The mechanism of Hg emission from water (termed **evasion**) may be biologically mediated, but recent evidence suggests an important role for direct photochemical reduction of Hg<sup>2+</sup> species to dissolved elemental mercury vapor (Hg<sup>0</sup>) [Xiao, et al. (1995), Amyot, et al., (1994), Lindberg, (1999)]. Some models suggest that evasion could be a major source of mercury to the troposphere on the global scale and suggested that annual evasion rates could range from 40 to 90% of deposition rates [Mason, (1994)].

## **2.5-Water-Sediment Interactions and Porewater**

Sediments in estuarine and coastal marine areas are one of the most important reservoirs and sinks for Mercury. Coastal sediments in certain locations, where anthropogenic influence is high, may contain elevated levels of contaminants accumulated over decades. Sediment loading of Hg and other

environmental contaminants are examined severally. In the literature there are numerous studies examining the sediment-water interactions.

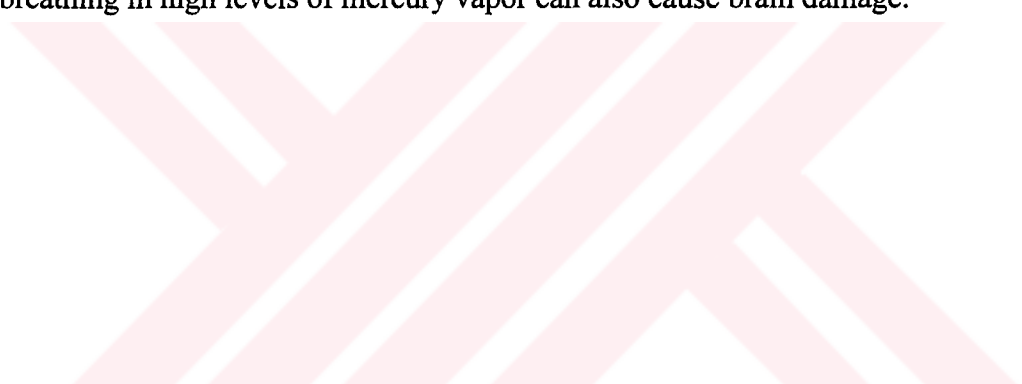
Mechanism for the transport of dissolved and particulate constituents from the sediment into the water column include diffusion and advection of pore water, sediment resuspension, and the biologically mediated processes of “bioturbation” and “bio-irrigation”. To understand the impact of these processes, detailed sediment and pore water distributions must be obtained. While techniques for collection and sectioning of bulk sediments are well developed, methods for the collections of pore waters for dissolved constituents and metals have only been recently investigated and developed.

Sediment-Water exchange, especially in shallow dynamic systems such as estuaries is an important source o water column monomethylmercury. The prevalence and bioaccumulation of mercury predominantly as monomethylmercury (MMHg), in aquatic food chains has lead to reevaluation of factors controlling methylation and monomethylmercury biochemical cycling [Mason, et. al, (1998)].

## 2.6-Health Effects of Mercury

**Table 2** shows the relationship between exposure to mercury and known health effects [<http://www.atsdr.cdc.gov>].

An exact exposure level cannot be determined for some human health effects that are known to occur. For example, we have known for a long time that eating fish or grain contaminated with high levels of organic mercury can cause brain damage, especially in developing babies (infants). However, we cannot estimate an exact level of mercury that would cause this effect because the amount of mercury in food and the amount of contaminated food eaten is not known. Also, long-term breathing in high levels of mercury vapor can also cause brain damage.



Short Term Exposure (Less than or equal to 14 days)		
Levels in air (ppm) 0,13 5,4	Length of exposure 3 hours 8 hours	Description of effects* Chest pain, cough, shortness of breath. Persistent irritability, lack of ambition, lack of sexual desire.
Long Term Exposure (Greater than 14 days)		
Levels in air (ppm) 0,0032 0,000032	Length of exposure 15 years	Description of effects Shakiness, estimated minimal risk level (based on effects seen in humans)

\*These effects are listed at the level at which they were first observed. They may also be seen at higher levels.

Table 2-Human health effects from breathing metallic mercury

### ***3- Nuclear Spectroscopic Techniques and Analysis of Mercury Tracer***

The use of nuclear spectroscopic techniques for elemental analysis relies on a few simple properties of neutrons, atomic nuclei, and gamma radiation. Nuclear spectroscopic techniques have been used in a wide range of environmental applications, especially in atmospheric studies. It can be used to measure concentrations of 40 or more elements in individual samples. As analytical technique, neutron activation has several very distinct advantages over other methods, though it also has a few very limiting disadvantages (Olmez, 1989). Among the advantages are:

- High sensitivity for a wide range of elements
- Excellent selectivity among different elements
- Virtually no matrix effects from self-absorption or enhancement
- Fairly non-destructive nature of the analysis
- Concentrations of many elements can be found from a single sample
- Analysis is generally completely instrumental.
- Very little inter-element interference

The disadvantages are however significant:

- In general a major nuclear facility such as a research reactor is required.
- The initial cost for detection equipment is high (\$50,000≈\$100,000)
- For most elements an analysis requires 2-3 weeks

- Only elemental concentrations are obtained, not chemical composition
- Elements lighter than Na (except F) as well as Si, Ni, and Pb cannot be measured well.
- It is probably the first of these limitations, which restricts the use of neutron activation analysis to the nuclear reactor research centers at a few universities and national laboratories [Ames, M. R., (1995)].

### 3.1-Activation Principles

The amount of activity of a given radioisotope produced by neutron activation is a simple function of the properties of the isotope, its parent nuclide, and the spectrum and strength of the neutron irradiation. For a given parent nuclide the activity present in its activation product immediately after its irradiation is given by:

$$A = \sigma\phi\eta\theta(1-\exp(-\lambda t_{\text{irr}}))$$

$A$  = Activity at end of irradiation ( $\text{s}^{-1}$ )

$\sigma$  = Neutron absorption cross section ( $\text{cm}^2$ )

$\phi$  = Neutron flux ( $\text{n cm}^{-2} \text{sn}^{-1}$ )

$\theta$  = isotopic abundance of given isotope

$\eta$  = Number of atoms of parent element

$\lambda$  = Decay constant of activation product ( $\text{s}^{-1}$ )

$t_{\text{irr}}$  = irradiation time (s)

Complicating matters somewhat is the fact that both the cross section and the neutron flux are functions of neutron energy, so that the proper expression for their product is:

$$\int_{E=0}^{\infty} \sigma(E)\theta(E)dE$$

Usually the number of atoms of parent element is more conveniently expressed as its weight  $w$ , in which case  $n$  should be replaced by  $N_A/m$  where  $N_A$  is Avagadro's number,  $6.02 \times 10^{23}$  and  $m$  is the element's atomic weight. The isotopic abundance of the activable parent nuclide is included explicitly to show that not all isotopes of an element may activate, and because the isotope's abundance will influence the eventual activity produced. Because the gamma rays produced by the activation products are not typically counted immediately after irradiation, an additional factor of  $\exp(-\lambda t_{\text{cool}})$  is needed to account for the cooling time between the production and the detection of the products.

When one considers the order of magnitude of some of the parameters in the equation, the need for a nuclear reactor to perform NAA becomes evident. Foremost among these is the neutron absorption cross section, which is routinely expressed in barns or  $10^{-24} \text{ cm}^2$ . In general the actual value for the cross section is on the order of a few or tens of barns, but even when it is a few thousand barns, a very small number of activations actually take place. To make up for the low probability of activation taking place the neutron flux needs to be as high as possible. However because the cross section is a function of neutron energy (with a typically inverse proportionality to the neutron velocity), it is not enough to simply have a lot of neutrons, they should also be low energy neutrons. Specifically for mercury (in its natural isotopic composition), the total cross section for thermal energy neutrons (those in thermal equilibrium at room

temperature, 0.025 eV) is 380 barns, while above 10 eV it is on the order of 10 barns.[Parry, J.S. (1991), Onal (1996), Ames (1995) ].

Following irradiation, a gamma ray spectroscopic detector is needed to measure the induced activity of the sample. When gamma rays interact with matter there are three main processes, which occur, and these are used to detect the radiation. At low energies (up to about 150 keV in a germanium crystal) photoelectric absorption is the primary type of interaction. This results in all of the gamma's energy being transferred to an electron, which then comes to rest within the detector. The signal derived from this event has a narrow peak, the photo peak, at the full energy of the gamma ray, and at the energy of the X-rays, which arise from the filling of the space left by the photoelectron.

Currently NAA spectroscopy relies on the use of semi-conductor detectors, primarily made of high purity germanium (HPGe). Electron-hole pairs are produced in these crystals in a number proportional to the absorbed gamma ray energy, with the pairs requiring about 3 electron volts to be formed. By applying a bias of a few thousand volts across the crystal the pairs can be collected and subsequently amplified to produce a measurable electronic pulse. The height of the pulse is proportional to the number of electron-hole pairs and thus to the original gamma ray energy. An energy spectrum is derived from these pulses by using an analog to digital converter (ADC), and a multi-channel analyzer (MCA) which totals all the gamma ray events which occur in specific energy bands over a period of time.



### 3-2-The Purpose of This Study

There is an increased interest in the problem of determining mercury evasion from water surface to air and deposition through the sediment basin.

As discussed in previous parts determination of mercury evasion and mercury depositions in sediments are not easy tasks. Understanding of the fate of discharged mercury into water has a high scientific importance. The fate of dissolved mercury (II) in surface water is an important component of global Hg cycle. The use of radioactive dissolved mercury for determination of evasion and deposition processes will be a very useful technique for understanding the processes. Therefore, we decided to use radioactive dissolved mercury,  $^{197}\text{Hg}$ , 64 h half-life, for modeling of the processes in this study.

Experiments performed on water and sediment samples obtained from Büyükçekmece Lake (BCL), which is one of the most important water sources of the regions.

This study is a new methodology first application in Turkey to understand and have a model about the evasion of mercury from water surface to air and uptake of mercury through the sediment.

For air/water:

To design a system to study water/air exchange and measurement methods and approaches were developed and modified in our laboratory, which provides evasion rates of mercury under specific experimental conditions.

Determine the effects of temperature, sunlight, and some other factors, which are important in the control of Hg evasion from surface waters.

Develop a water/air exchange mass balance for dissolved mercury in the natural waters on a short time scale using the obtained data.

For Water/Sediment:

Determine the water/sediment exchange rate.

To understand the reduction rates of mercury (II) to mercury (0) as a function of temperature and diurnal cycle.

To determine the importance of sediment as a sink for mercury.

To develop proper undisturbed sediment sampling methods, and study sediment depth profile

To obtain distribution of mercury as a function of depth.

## CHAPTER II

### ***EXPERIMENTAL***

#### ***1-Laboratory Equipments***

##### **1-1- Sampling Site**

Water and sediment samples used in this study were collected at the station in the region of Istanbul called Büyükçekmece lake at approximately 5 km north from the town of Büyükçekmece. The location of the sampling station is shown in **Figure 3**.

Büyükçekmece Lake is a natural lake and one of the main water sources of the city.

Sediment sampling location was approximately 10 m from the coast, and at about 1 m depth.

Water sample was collected manually in the field using clean handling methods in 20L polyethylene container dipped directly into the water column above the sediment sampling point. All materials used for sampling and storage

were cleaned with deionized water in the laboratory prior to use in the field and rinsed again with lake water.

Ten cm deep sediment samples were collected manually by using a plastic paddle and carried to laboratory in a plastic bucket.

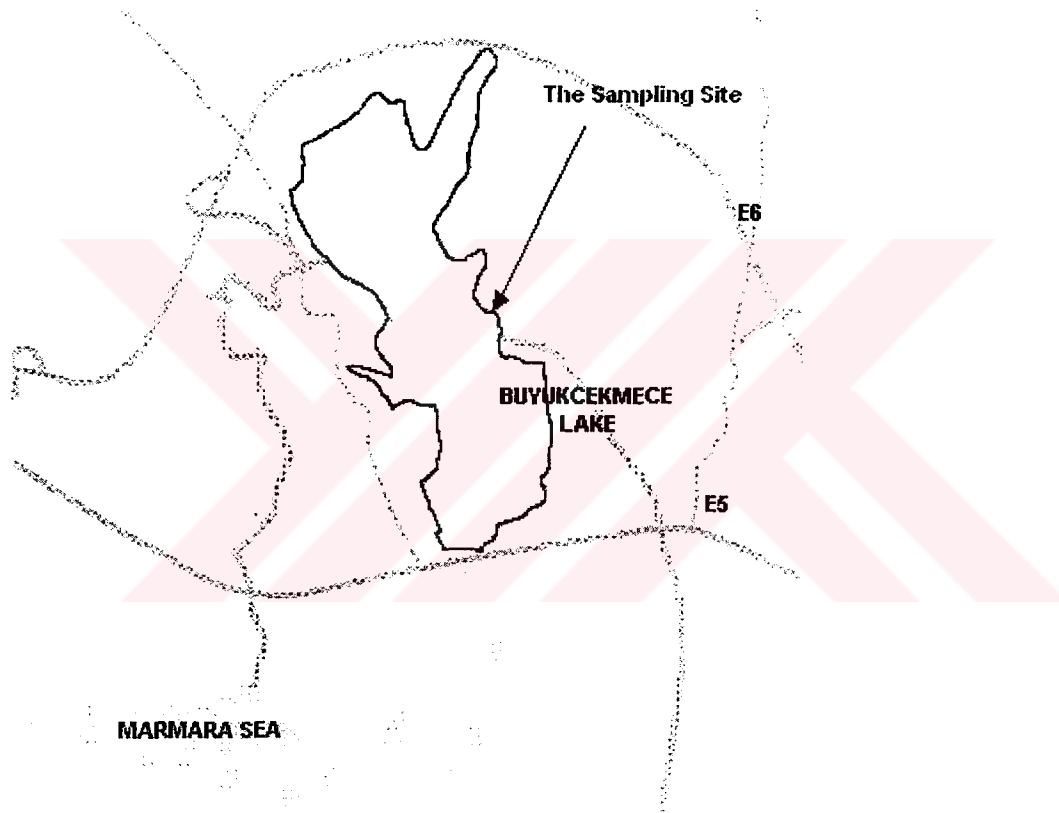


Figure 3- The location of Sampling Site

## 1-2- Experimental Chamber

The fate of dissolved mercury (II) in surface water is an important component of global Hg cycle. We developed a simple interactive laboratory

chamber model of dissolved mercury (II) to see if we could explain the behavior of dissolved mercury (II) in natural lake waters. It is based on measuring the change in mercury concentration in air (head-space) and water column through the use of radioactive mercury tracer.

A schematic diagram of the experiment set up is shown in **Figure 4**. The chamber was a closed system which consists of three regions, A, B, C. The A region is the air region with depth of 11.5cm with a 17.5 L volume where evaded mercury vapor from water phase are collected. Second region B is the water phase with the depth of 12.5 cm. The last region C is the sediment region with the depth of 6cm. The entire chamber was made from glass with the dimension of 30×30×50 (cm<sup>3</sup>) and exposed to direct sunlight examine the photochemical reactions.

Using this system amount of mercury evaded is captured with activated charcoal filter and counted.

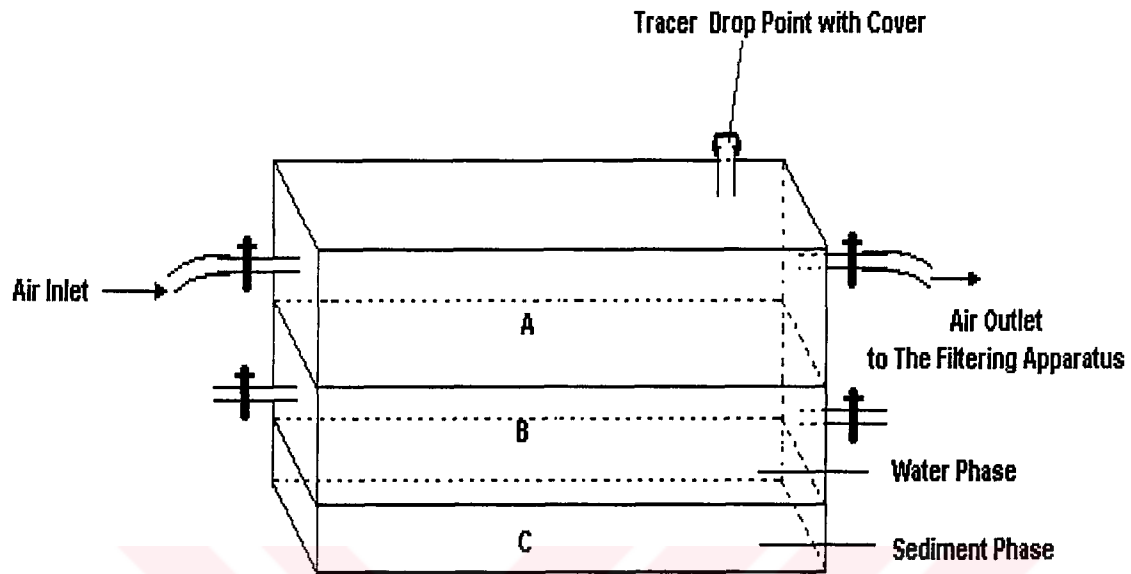


Figure 4- The Experimental Box Chamber

## 2-Experimental Stages

### 2-1- Preparation of Radioactive Mercury Tracers

Five separate sample of  $\text{HgCl}_2$  were weighed placed into pre-cleaned polyethylene vials and heat-sealed along with Buffalo River Sediment, 2704, as a reference were put into irradiation container, and bombarded with neutrons. Irradiation was performed for 1 hour at a neutron flux of  $\approx 10^{12}$  n/cm<sup>2</sup>.sec. using the Triga Research Reactor of Istanbul Technical University.

Following the irradiation they are cooled for 3 days to allow the short half-lived radioisotopes to decay, and than transferred to the laboratory.

The sample weights and numbers are given below.

Label	Weight of $\text{HgCl}_2$
Tracer 1	4.9 mg
Tracer 2	1.4 mg
Tracer 3	2.5 mg
Tracer 4	1.1 mg
Tracer 5	2.7 mg
Standard	149.3 mg

## 2-2- Evaded Radioactive Mercury Collection Method and Evasion Measurement

One of two radioactive Hg, in the form of  $\text{HgCl}_2$ , tracer was counted to obtain the total Hg-197 and Hg-203 activity and introduced into the chamber. After 2.5 hours evaded gas phase mercury was collected by filtering headspace air through the activated charcoal sorbent. Related figure is given in **Figure 5**.

Air was sucked from the inlet at a flow rate of 2 L/min. The air was directly filtered with the apparatus, which contained 100 m activated charcoal. This filter was connected to the vacuum pump by short silicone tubing. Two sorbent tubes run in series were used, so that the charcoal's collection efficiency or break-through can be detected. The airflow was calibrated prior to the experiment, and was run between 1 to 2 liters per minute. The sections were separated by glass wool plugs. A cotton plug with 1.5cm length was placed to the entrance of the filter, to prevent any water particulate to enter the system.

In this study commercial type PCB Activated Carbon (CALGON) used for vapor phase collection. It is made from selected grades of coconut shell to impart the superior hardness that is necessary for the long life expected in such applications. PCB Carbon provides high surface area and ease of regeneration. Some of physical properties and specifications of commercial (CALGON) Carbon Type PCB Activated Carbon are given in the **Table 3**.



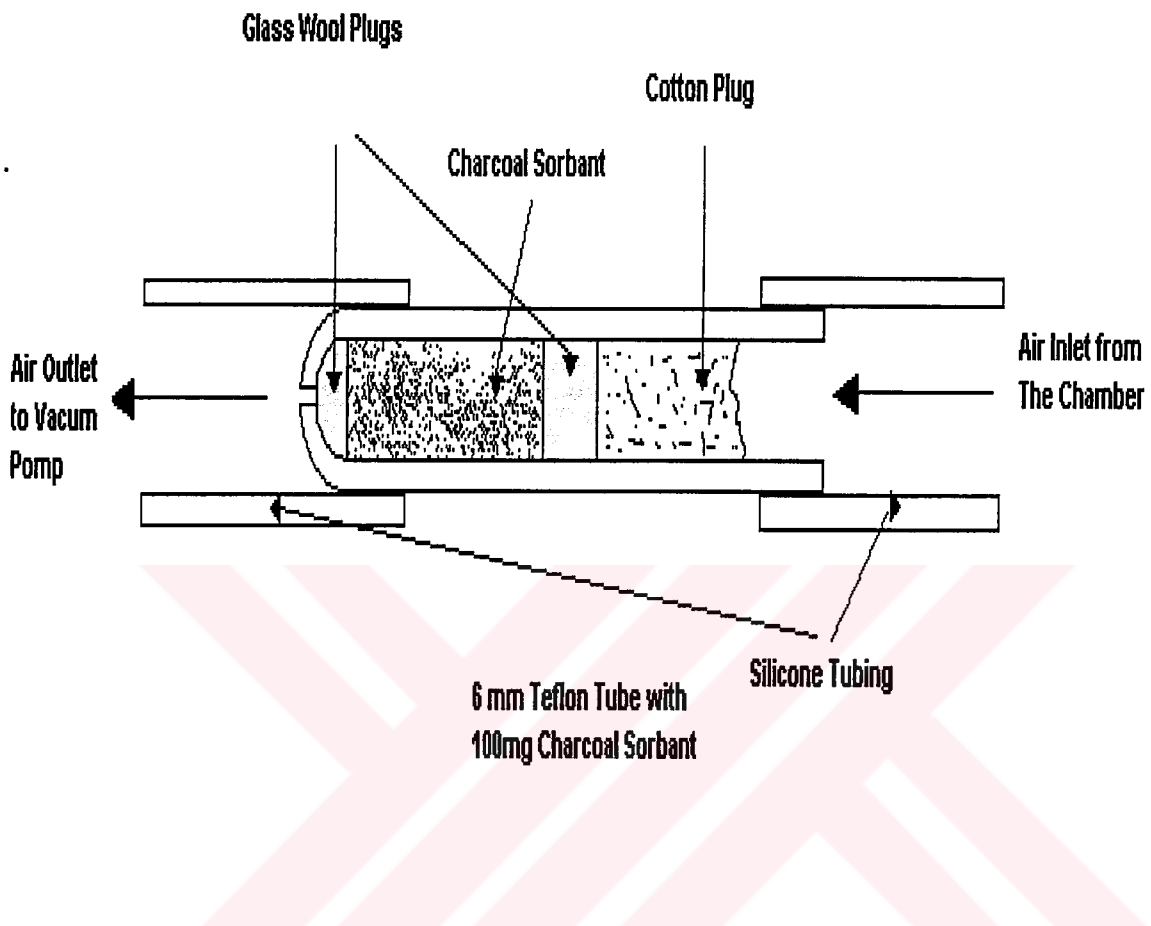


Figure 5- The Vapor Phase Mercury Collection System

The filtering processes were cumulative with several hours interval, thus we have used only two filters during the experiments filter and back-up filter. After each filtering processes Teflon filters were placed into plastic bags and radioactive mercury measured.

<b><i>Physical Properties</i></b>	
Total surface area	1150-1250[m <sup>2</sup> /gr]
Apparent density (Bulk density dense packing)	0,44[g/cm <sup>3</sup> ]
Particle density (Hg displacement)	0,850 [g/cm <sup>3</sup> ]
Real density	2,2 [g/cm <sup>3</sup> ]
Pore volume (within particle)	0,72 [cm <sup>3</sup> /g]
Specific heat at 100 <sup>0</sup> C	0,25
<b><i>Specifications</i></b>	
Iodine number, mg/g minimum	1200
Ash, maximum %	6,0
Moisture, maximum, % as packet	3,0
Hardness number, Minimum	92
<b><i>Commercial Information</i></b>	
Standard mesh size	12×30

Table 3-Physical Properties and Specifications of Commercial Calgon Carbon type PCB Activated Carbon (MSA Company)

### 2-3- Water Sampling

During the experiment, water samples were taken during certain intervals and measured. About 3 cm<sup>3</sup> of water samples were dripped directly into polyethylene tubes from the sampling port of the chamber and tube's covers were tightly closed. After taking the samples they were placed in plastic bags and counted.

TC. YEMERİ-ADANLI KURULU  
Bölüm Başkanı Dr. M. K. KAZAN

## 2-4- Sediment Collection methods

Some methods were tested for sampling undisturbed sediment with pore water.

Two kinds of methods were used. Specific sediment sampling equipments designed and constructed in our laboratory. They are illustrated below in **Figure 6** and 7.

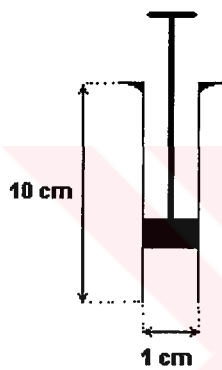


Figure 6- Sediment Sampling Equipment 1, Piston Sediment Sampler (PSS).

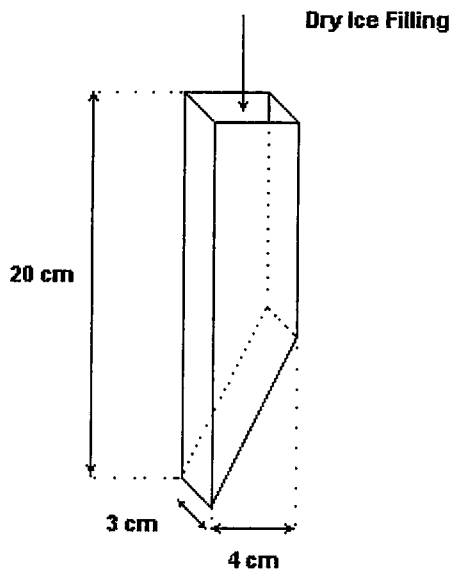


Figure 7- Sediment Sampling Equipment 2, Frozen Sediment Sampler (FSS)

Whole sediment core samples were taken with PSS. The equipment (PSS) is pushed into sediment by hand and vacuum created above the sediment section by pulling the piston so that sediment would not be dislocated.

Immediately, the sediment cores and samples were all capped in a separate pre-cleaned polyethylene tubes, which were same size and geometry with water sampling tubes, and put into plastic bags with the vials for counting.

Distribution of mercury with respect to depth is critical information. Equipment, FSS, was designed for obtaining sediment sections without destroying pore water and sediment characteristics, which would be used to get Hg depth-profile.

First, FSS pushed into sediment by hand and stabilized. Immediately following, dry ice ( $\text{CO}_2$  (Solid)) particles were filled into WST. Freezing process was

complete after 10 minutes and sediment portion that is in contact with the sampler was frozen on the surface. WST was taken back from the sediment with sediment loading, and cut into sections. Each section of frozen sediment samples were weighted, capped in the polyethylene vials and then put into plastic bags for counting.

### **2-5- Measurements**

All of the samples produced during the experiment were measured by using a high purity germanium detector, which is connected to Canberra, multi channel analyzer, (MCA). Before and throughout the experiment, calibration was made using  $\text{Co}^{60}$  and  $\text{Cs}^{137}$  standards.

Counting geometry is another parameter that should be under consideration during counting. Position of all the samples should have the same geometry and distance. Throughout the counting period all samples were placed at a distance of 3 cm to the detector.

## CHAPTER III

### Results and Discussions

#### 1-1 The Air Phase Studies

The fate of dissolved mercury in surface water is an important component of the Hg cycle in natural waters. Dissolved mercury levels are regulated by several factors: available reactive Hg, photo-reduction rates or rates of other production processes, temperature, and loss rates of Hg concentration including oxidation and evasion [Lindberg (1999)].

We developed a simple box-chamber to see if we could examine the behavior of dissolved mercury. This study is a methodology to understand of behavior of dissolved mercury in aquatic phase. The experimental results showed that the radioactive tracer methodology is very useful technique and very simple to

modify and develop depending upon the purpose of study under consideration. Understanding the natural process of actual air/water and water /sediment exchange mechanisms are out of the scope of this study. Further advanced studies are necessary to understand of actual mechanisms. The experimental results are given below and discussed.

Data obtained following individual headspace air collection processes are given below in **Table 4**. All the data are decay corrected counts per second, cps, to the end of irradiation. In the table obtained cumulative activities are given in the first row and the second row is change in values of sequential measurements.

We had filtered headspace of chamber during certain intervals, so concentration of captured mercury increased continuously. **Figure 8** is illustrates the cumulative amount of Hg captured. As expected, the amount of mercury activity decreased by time due to the decrease in water concentrations. The plot is used to understand a general idea about the trend of data set. By using this plot, it is easy to understand the evasion process's characteristics. In order to understand the characteristics and behavior of evasion process more specific examination should be done.

	Corrected Cumulative Value	Change in value	Elapsed Time	Date and Time
	(cps)	(cps)	(hour)	(Hour)
Total Activity	3040±4			7/15/00 15:30
Filter 1	6.57±0.07	6.57±0.07	2.5	7/15/00 18:00
Filter 2	58±1	51±1	5.0	7/15/00 20:30
Filter 3	119±1	61±1	8.0	7/15/00 23:30
Filter 4	165±1	46±2	10.5	7/16/00 2:00
Filter 5	230±1	65±2	16.0	7/16/00 7:30
Filter 6	301±1	71±2	22.0	7/16/00 13:30
Filter 7	407±1	106±2	25.5	7/16/00 17:30
Filter 8	527±2	120±2	44.5	7/17/00 12:00
Filter 9	592±2	65±2	48.5	7/17/00 16:00
Filter 10	671±2	79±3	65.5	7/18/00 10:00
Filter 11	718±2	47±3	90.5	7/19/00 10:00
Filter 12	729±2	11±3	115.0	7/20/00 11:30
Filter 13	767±3	37±3	140.0	7/21/00 11:00

Table 4-Decay Corrected Filter Hg Activity of Sequential Experiments



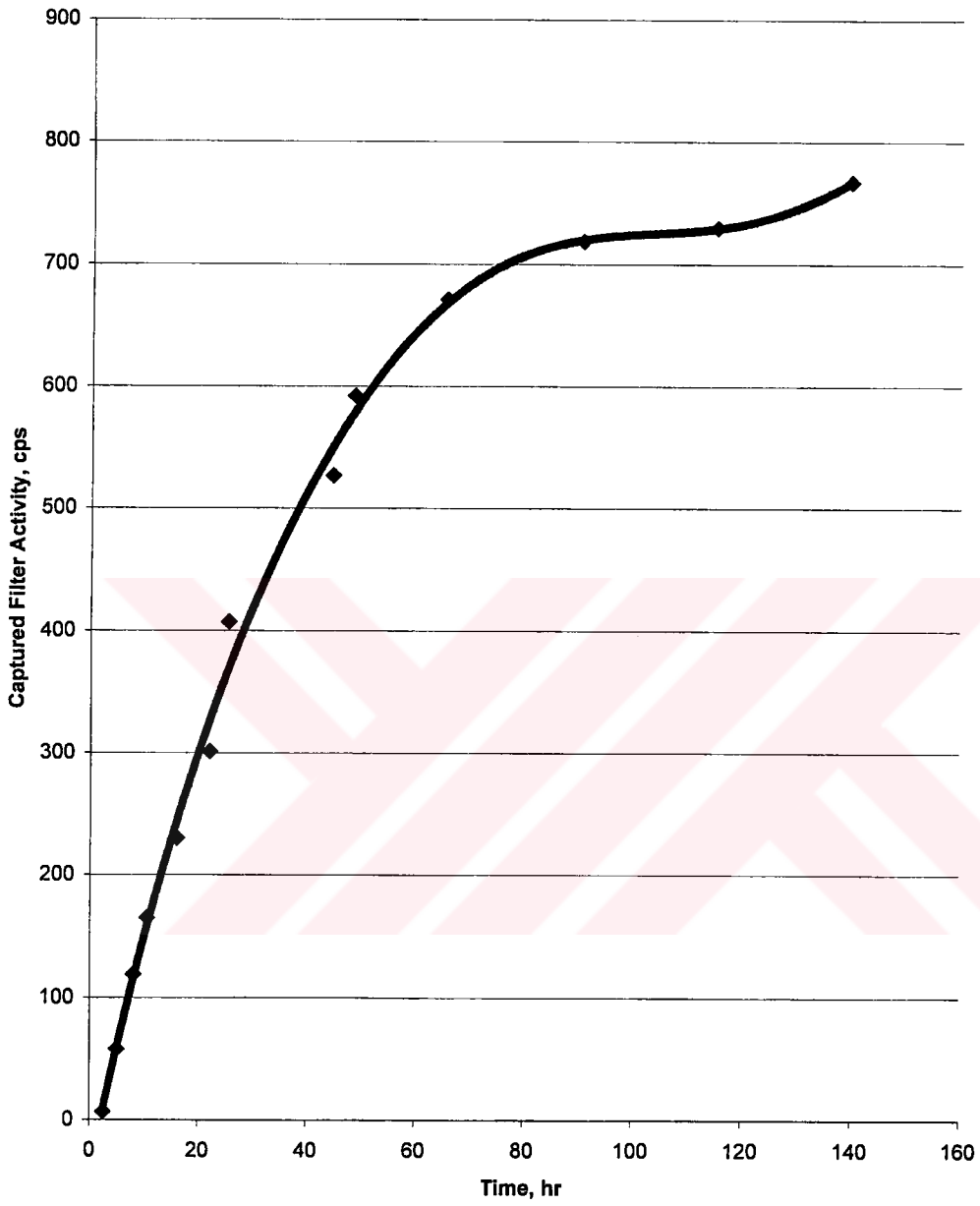


Figure 8- Cumulative Increase of Air Activity

Using this methodology daily and hourly evasion and reduction rates, effects of some parameters such as temperature, solar density, etc., can be found and measured as shown in our experiments.

The change in activity rates versus elapsed time is given in give **Figure 9**. Evasion rates show some differences depending on the some other factors for instance temperature, microorganisms, distributions of water, etc. Further advanced model studies are recommended for understanding of these effects of the parameters. Since we did not performed studies, short duration air measurements without disturbing the equilibrium, our results can not be conclusive to obtain too much information about the real life evasion processes.

During first 24 hour, there is a continuous increase in the amount of filtered mercury. It shows that evasion is a rapid and continuous process and start with the introduction of mercury into the water phase.

After first 24 hour, the amount of evasion rate started to decrease. This could be explained with loss of mercury in water phase due to uptake into sediment and loss to the air. Reduction of mercury (II) to mercury (0) is a very complicate process and may be related to many functions. Water activities over air activities are given in **Table 5**. Results suggest that there could be a relatively constant water/air value. However to establish this fact several more experiment with lower mercury concentration should be performed.

In order to understand, the effects of temperature and sunlight on the mercury evasion process, we examined more detailed the first 48 hour of experiment. Related **Figures 10, 11, 12** are given below. The general trend, although not scientifically proven, indicates the possibility of high evasion rates during daytime and/or higher ambient temperatures.

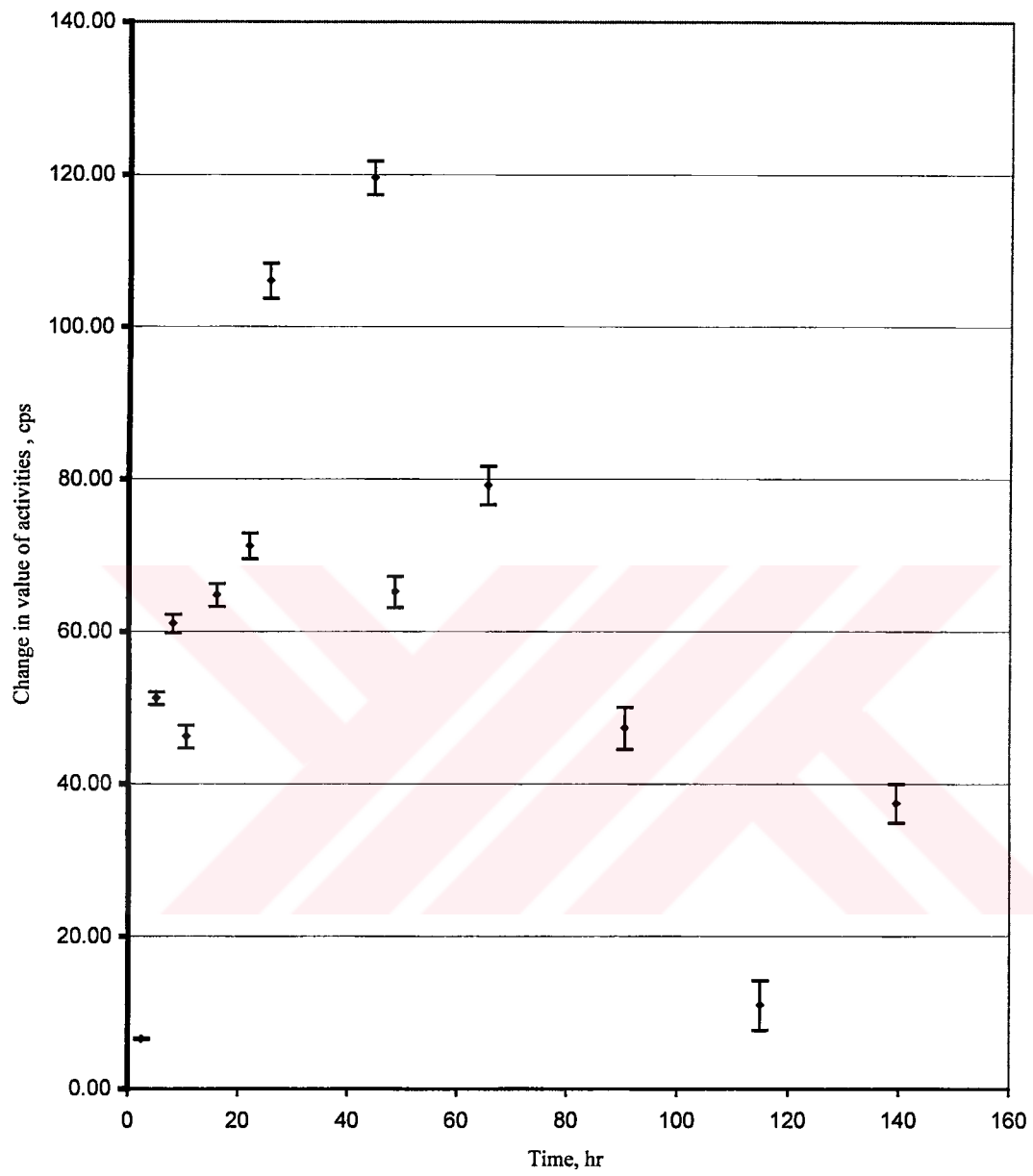


Figure 9- Change in Values of Activities

Air Sample	Change in Value of Air Activity (cps)	Water Sample	Water Activity (cps)	Water/air
Filter 8	120±3	Water 8	1790±270	15.0
Filter 9	65±2	Water9	1680±72	25.7
Filter 11	47±3	Water 11	1110±58	23.5
Filter 12	11±4	Water 12	815±136	74.2
Filter 13	37±3	Water 13	853±101	22.8
Average				32.2
Standard deviation				23.8
Max				74.2
Min				15.0

Table 5- Compression of Air/water Activities

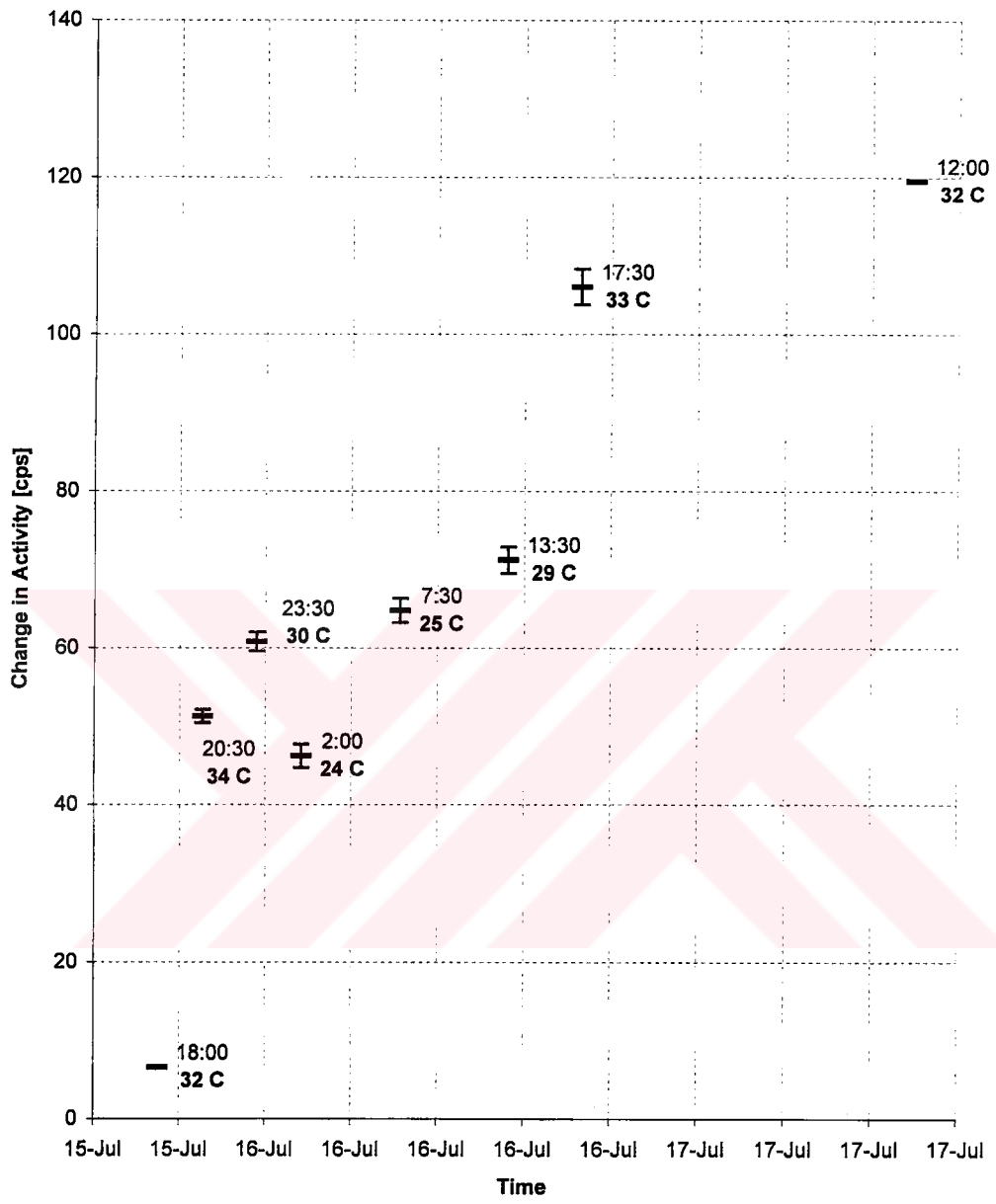


Figure 10- First 48-hour Air Activity

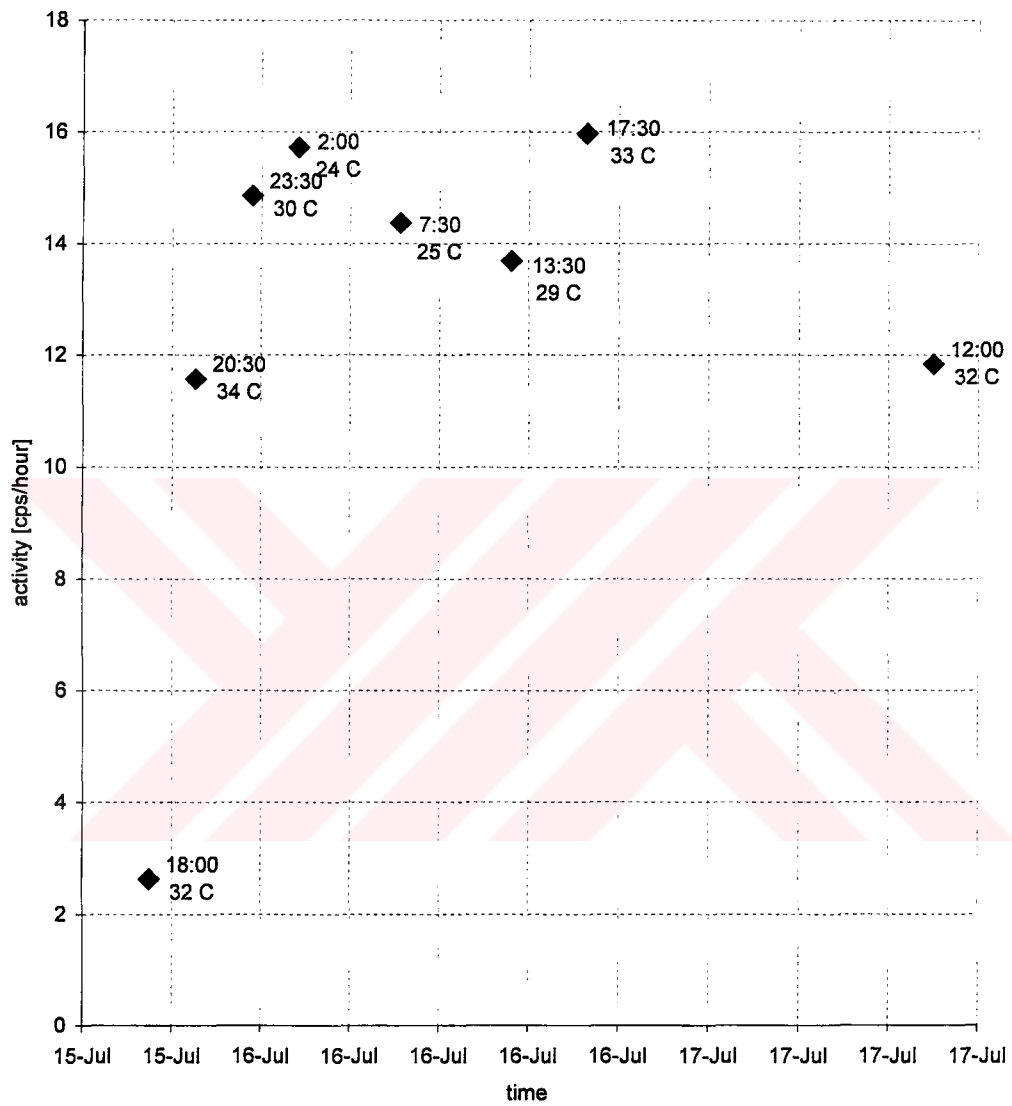


Figure 11- Cumulative Increase of Activity per Hour (for the First 48 hour)

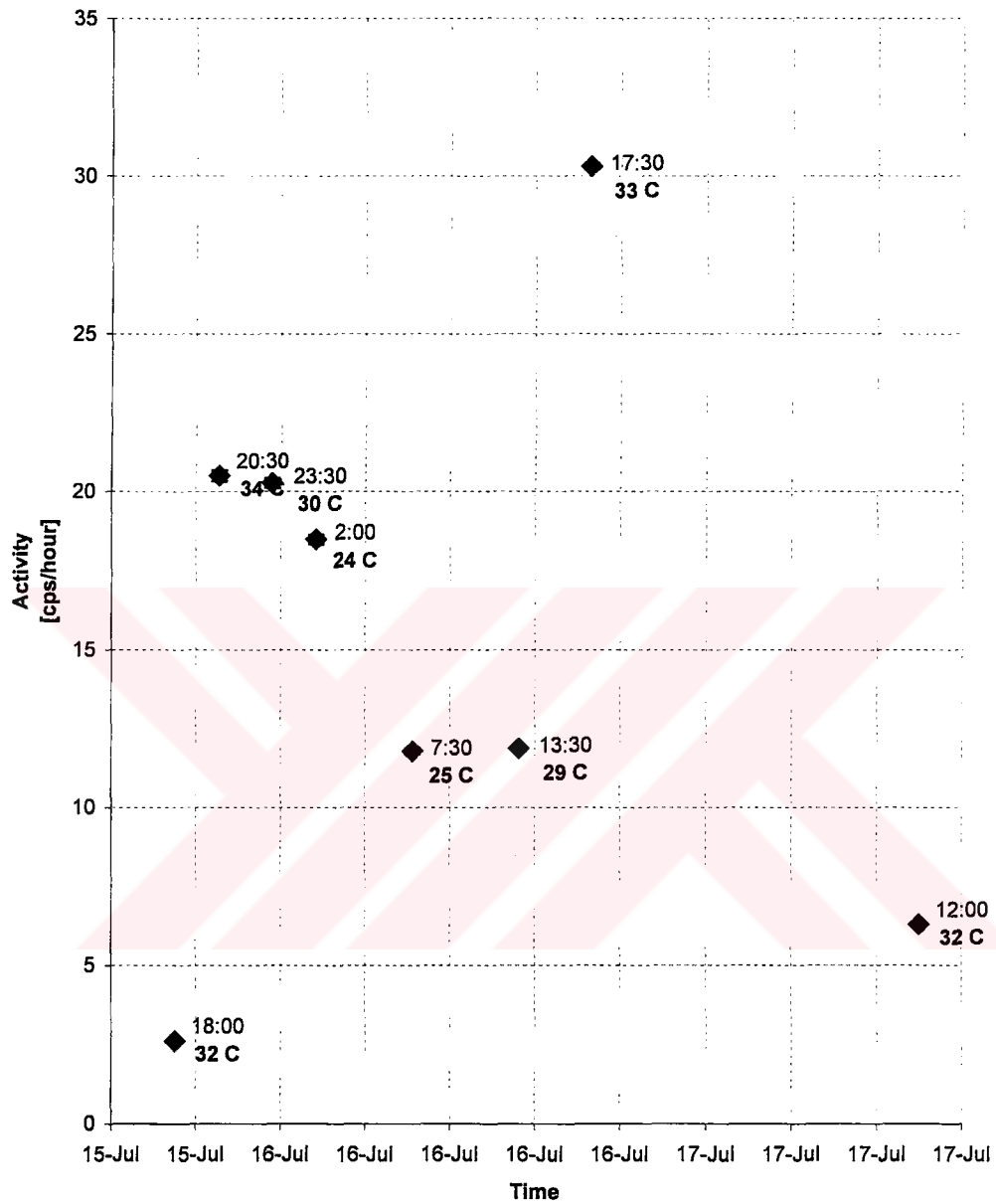


Figure 12- Change in Air Activities per Hour (for the First 48-hour)

	Order	Change in Value	Date and Time
Daytime activities for first 48-hour	Filter 5	65±2	7/16/00 7:30
	Filter 6	71±2	7/16/00 13:30
	Filter 7	106±3	7/16/00 17:30
	Average	81±2	
Nighttime activities for first 48-hour	Filter 2	51±1	7/15/00 20:30
	Filter 3	61±2	7/15/00 23:30
	Filter 4	46±2	7/16/00 2:00
	Average	53±1	
Average value of DT/NT		1.53	

Table 6- Daytime Activity over Nighttime Activity

Average value of daytime activities over nighttime activities is 1.53.

During the day, between 13:30 and 17:30, sunlight was directly available and the solar density was the highest, because of the location of experimental chamber. The increase in activity found in filter 7 can be due to this effect (Table 7).

In this study the counting processes were continued during 140 hour. In **Figure 13 and 14** show that there is a steady decrease of evasion amount, most probably because of the decrease of the Hg concentration in the water phase.



	Activity (cps/hour)
Filter 2	20.5±0.3
Filter 3	20.3±0.4
Filter 4	18.5±0.6
Filter 5	11.8±0.3
Filter 6	11.9±0.3
Filter 7	30.3±0.7

Table 7- Change in Activities per Hour (for First 48 hour)



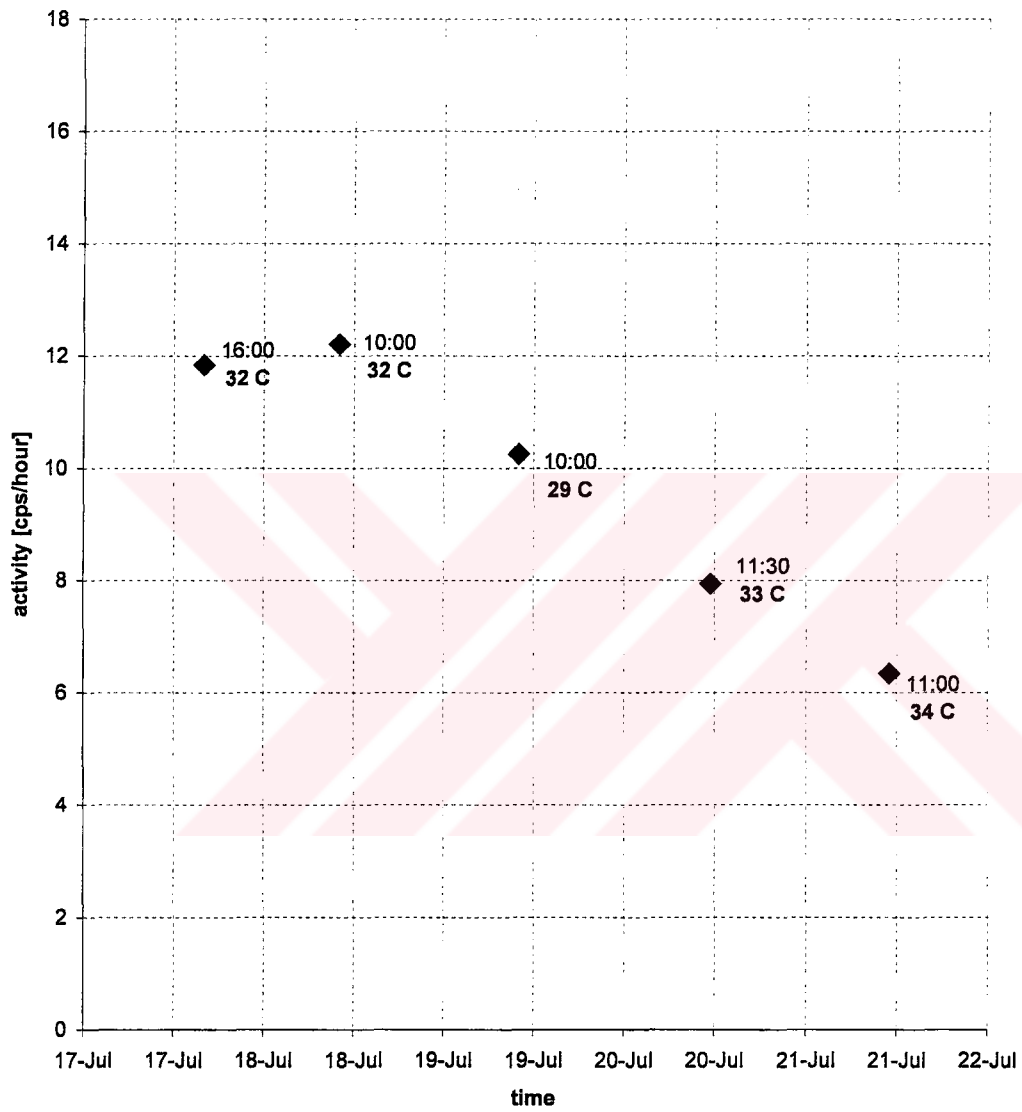


Figure 13- Cumulative Increase of Activity per Hour (for after 48 hour)

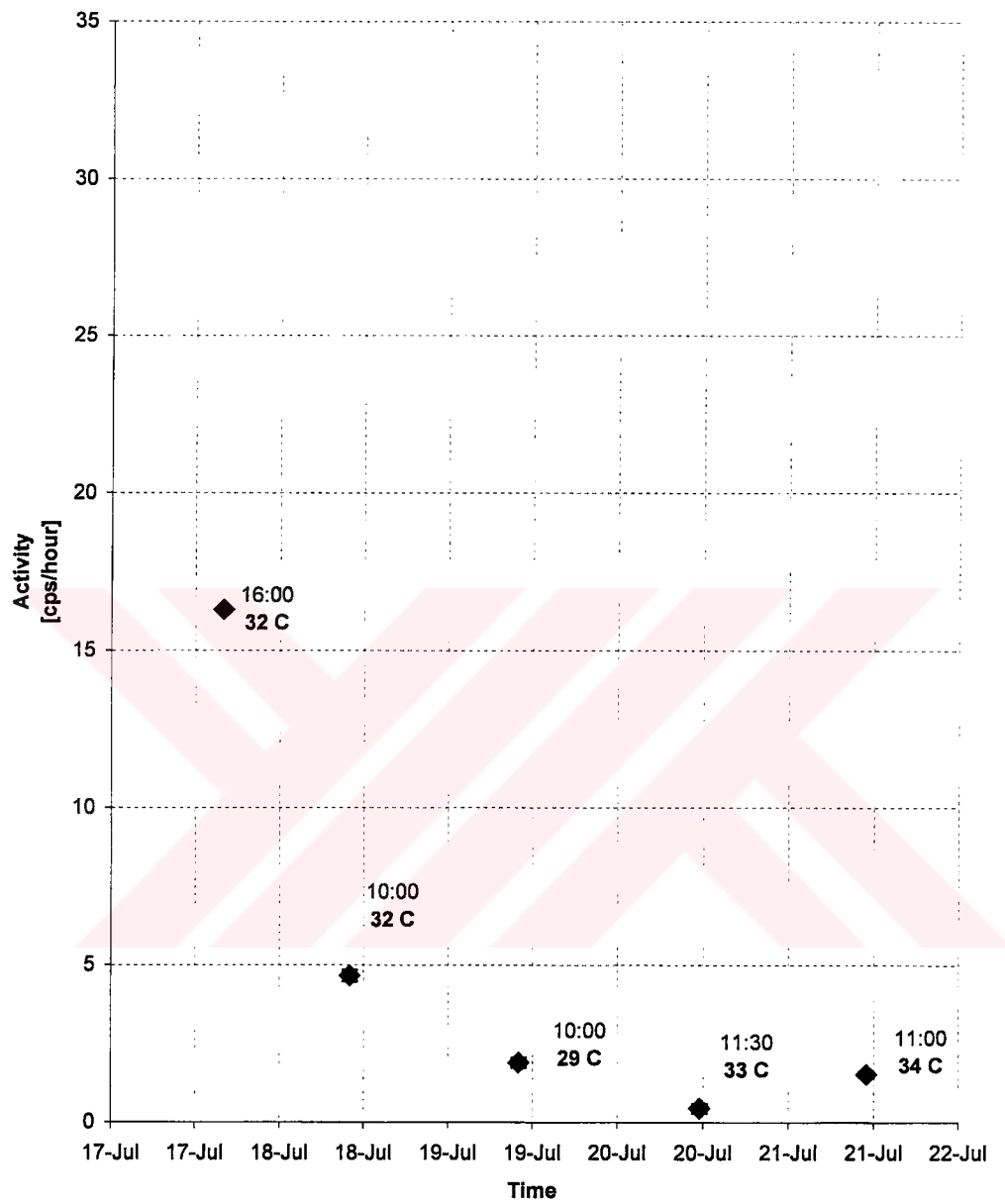


Figure 14- Change in Activities per Hour (for after 48 hour)

## 1-2 The Water Phase Studies

Since the evasion process and an uptaking of mercury by sediment, the plot of Mercury concentration in the water phase should have a decreasing curve. As estimated, our data shows mercury concentration in the water phase decreases, which was illustrated in the **Figure15**.

Concentration of dissolved mercury had decreased from 0.16cps/g to 0.046cps/ g. After 140 hour merely 28% of dissolved mercury is remaining in the water phase. To measure of periodical value of water concentration was very easy and effective. In **Table 8** data set of dissolved mercury in the water phase is given.

	Corrected activity (cps)	Weight (g)	Activity (cps/g)	Elapsed Time (Hour)
Total Activity	3040	18750	0.16±0.02	0
Water 8	0.27	2.81	0.10±0.01	45
Water 9	0.29	3.28	0.09±0.00	49
Water 11	0.17	2.94	0.06±0.00	97
Water 12	0.13	2.97	0.04±0.01	116
Water 13	0.14	3.08	0.05±0.00	140

Table 8- Dissolved Hg Concentration in The Water Phase

The experimental data were obtained both under daytime conditions (characterized by bright sunlight, clear skies and temperature in the 25 °C to 35 °C range) as well as under nighttime conditions. This data set may be too small to draw definitive and wide-ranging conclusions about the existence of day/night Hg concentration variations from natural freshwater systems. Solar radiation-induced photochemical conversion (involving reduction of Hg species to the elemental form of Hg), biotic or abiotic production of volatile Hg, loss to container walls, water evaporation accompanied by “co-distillation” of volatile Hg species, or

meteorological/micrometeorological (distributions in the water phase) processes are specific environmental processes which might contribute to its explanation and should be investigated in future research activities.

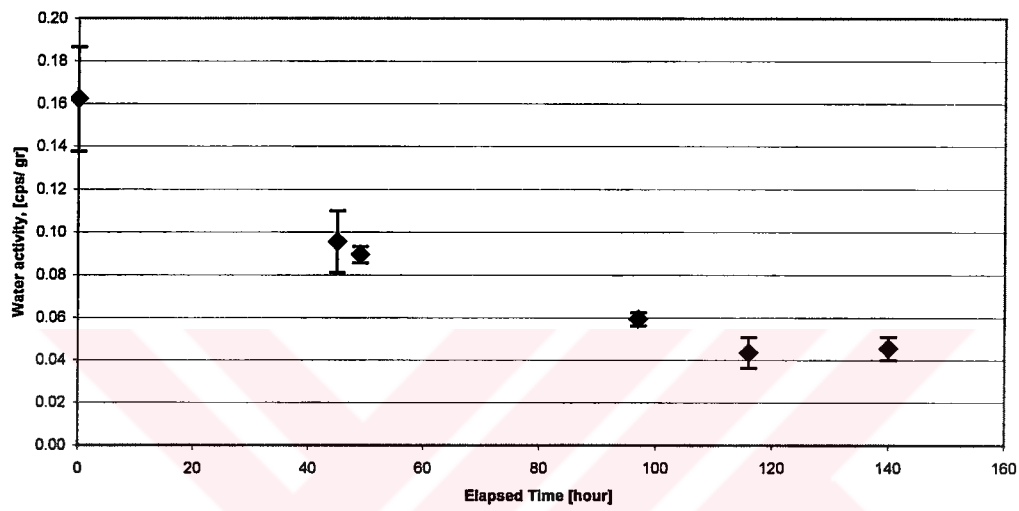


Figure 15- Water Activity versus Elapsed Time

### 1-3- The Sediment Phase Studies

The samples were obtained using the corer PSS and FSS, which were designed in our laboratory. After the samples pushed out from PSS, they were counted and assigned as total sample. Data set was given below in **Table9**.

Sample	Activity/g	Distance form drop point (cm)
Sediment total1	0.84±0.07	3
Sediment total2	0.64±0.27	12
Sediment total3	0.32±0.06	30
Sediment total4	0.37±0.09	38
<b>Average</b>	<b>0.54±0.30</b>	

Table 9- Sediment Core Activity and Drop Point Distances

**Table 9** shows that sediment mercury concentrations in the surfaces of sediment phase show variations, because we dropped  $\text{HgCl}_2$  sample in the solid form. It could not be dissolved totally before reaching the surface of sediment. This is a weakness of this experiment, for further studies it can be used in liquid form.

The concentrations of mercury in sediment profiles were examined using FSS. The results showed that only 1,5 cm depth of sediment is loaded with the mercury in such a short time (140 hour). It was assumed that the other counted activities in the depth over 1.5 cm came from contamination during sediment taking process. We suggested that the mercury ions most probably attached themselves into organic particles and deposited to the surface of sediment. We did not observe any penetration into the sediment layer under these experimental conditions.

Sediment depth profile data was given below in **Table 10** and depth profile versus activity diagram was illustrated in the **Figure 16**.

	Activity/g	Depth
Surface only	$1.48 \pm 0.06$	0
Sediment 0-1.5	$1.20 \pm 0.04$	-1.5
Sediment 1.5-2.5	$0.08 \pm 0.02$	-2.5
Sediment 2.5-3.5	$0.02 \pm 0.00$	-3.5
Sediment 3.5-4.5	$0.01 \pm 0.00$	-4.5
Sediment 4.5-5.5	$0.01 \pm 0.00$	-5.5
	$0.37 \pm 0.09$	

Table 10- Sediment Depth Activity Data Set

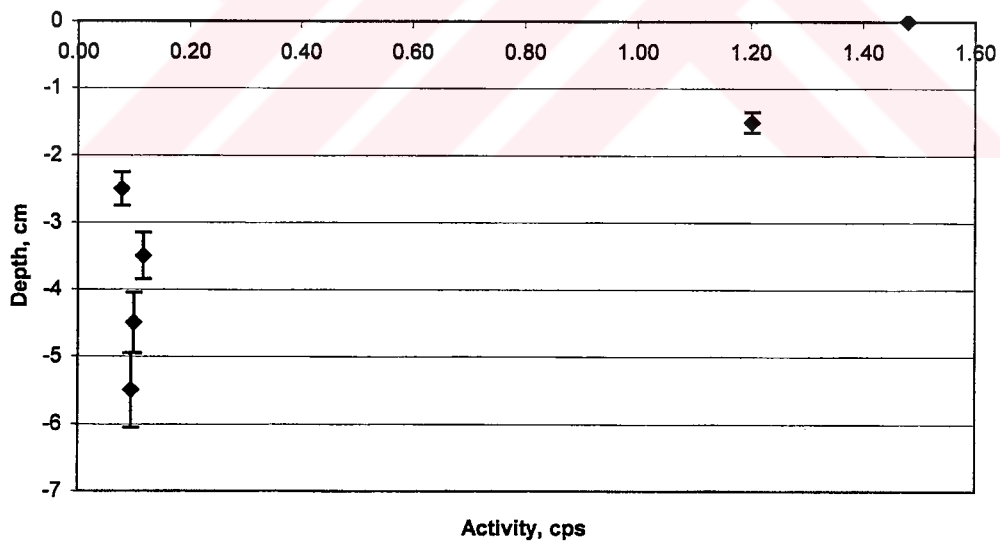


Figure 16- Sediment-Depth Profile

#### 1-4- Mass Balance

The chamber is a closed system, and there is no mercury loss. Basic mass balance equation can be given as:

Total dissolved Hg (II) = Evasion amount of mercury (0) + remaining amount of total mercury in the water phase + deposited amount of mercury in the sediment phase

Total amount of mercury = input value

= 3040 cps

Remaining amount of mercury in the water phase = activity/g \* volume of the water phase

= 0,045 \* 18750

= 845 cps

Evasion amount = the last filtered cumulative activity

= 767 cps

Deposited amount of mercury in the sediment phase = activity [ $1/\text{cm}^3$ ] \* volume of sediment it was assumed that there was deposition only in 1.5cm depth

Area of sediment sample = width of sample \* length of sample

= 0,4 \* 3,5

= 1,4  $\text{cm}^2$



Sediment total activity=sediment sample area\*sediment surface area

$$=1,11^*/1,4*30*50$$

$$=1188 \text{ cps}$$

\*In this equation activity of sediment cross-section calculated as a mean value of entire 1 cm depth profile.

$$\text{Total counted activity}= 1188+767+845$$

$$=2799 \text{ cps}$$

$$\text{Start value}= 3040 \text{ cps}$$

Total counted activity is nearly equal start value. There is only 8% of change in between the values.

As a result of this calculations it can be said for the fate of dissolved mercury chloride (II) that 28% of it remained in the water phase, 25% of it emitted via the evasion process and 47% of it deposited in the sediment under these very restrictive experimental conditions.

### **1-5- Recommendation for Future Work**

This is a preliminary work for the determination of the fate of dissolved mercury (II) in the fresh water systems. This data set may be too small to draw definitive and wide-ranging conclusions about the existence of day/night change, in Hg re-emission (evasion) rates from natural freshwater systems. Solar radiation-induced photochemical conversion (involving reduction of oxidized Hg species to the elemental form of Hg), biotic or abiotic production of volatile Hg, water evaporation accompanied by "co-distillation" of volatile Hg species, or

meteorological/micrometeorological processes are specific environmental processes should be investigated in future research efforts.

In order to have a complete picture of behaviors of Hg in the aquatic systems following points must be considered.

Firstly the number and time period of measurements should be increased without disturbing the equilibrium and sampling should be spread throughout the year in order to see seasonal variations and have complete set of data for sophisticated statistical analysis.

Secondly, environmental conditions, such as characteristics of sediment and should be changed and investigated in more detail.

Shorter sampling time is recommended in order to see daily and hourly variations of mercury evasion. By this way it will be easy to understand the trend of Hg concentration during day and hours. By using different tracers, Hg(0), Hg(II), in different phases one can ever calculate the Henry's constant for mercury species and produce experimental data for semi-empirical models.

## References

Ames, M. R., Development and application of a methodology for measuring atmospheric mercury by instrumental neutron activation analysis, Ph. thesis in nuclear engineering at the Massachusetts institute of tech., 1995.

Fitzgerald, W.F., Mason, R.P., and Vandal, G.M., *Atmospheric cycling and air-water exchange of mercury over mid-continental Lacustrine regions*, Water Air Soil Pollut, 56:745. 1991.

Fitzgerald, WE, *Atmospheric and Oceanic Cycling of Mercury*. Chapter 57. In: vol. 10 of the Chemical Oceanography Series. (eds. Riley, J.P and Chester, R.). Academic Press, 151-186, 1989.

Hurley. J.P., Watras, C.J., and Bloom, N.S., Mercury cycling in a northern Wisconsin seepage lake: the role of particulate matter in vertical transport, Water Air Soil Pollut., 56:543, 1991.

Lindberg, S. E., Vette, A. F., Miles, C., and Schaedlich, "mercury speciation in natural waters: measurement of dissolved gaseous mercury with a field analyzer", biochemistry, 1999.

Lindberg, S. E., Zhang, H. "Air-Water exchange of mercury in everglades I. Measurement and modeling evasion of mercury from surface waters", manuscript for submission to STOTEN, (1999)

Lindberg, S. E., Zhang, H. "Air-Water exchange of mercury in everglades II .Measurement and modeling evasion of mercury from surface waters", manuscript for submission to STOTEN, (1999)

Lindqvist, O., and Rodhe, H., *Regional and Global Atmospheric Budgets. Mercury in the Swedish Environment; Water, Air, and Soil Pollution*, vol. 55, 65-71, 1991.

Lindqvist, O., Jernelov, A., Johansson, K., and Rhode, H., *Mercury in the Swedish Environment, Global and Local Sources*, SNV PM 1816, Swedish Environment Protection Agency, S-171-85 Solna, Sweden, 1984.

Mason, R., Bloom, N., Cappelino, S., Gill, G., Benoit, J., and Dobbs, C., "Investigation of porewater sampling methods for mercury and methylmercury", American Chemical society Published on Web, 1998.

Mason, R.P., Morel, F.M.M., and Hemond, H. F., "The role of microorganisms in elemental mercury formation in natural waters", *Water, Air, and Soil pollution* 80: 775-785, 1995.

Olmez, I., and N. K. Aras, Determination of mercury in selected fishes living in Turkish coast by neutron activation analysis, *Radiochemical and Radioanalytical Letters*. 22, 19-23, 1975.

Olmez, I., Instrumental neutron activation analysis of atmospheric particulate matter, in *Methods of Air Sampling and Analysis*, 3rd edition, Lewis Publishers, Inc., 143-150, 1989.

Olmez, I., M. Ames, J. Che, S. Meier, and P. Galvin, *Elemental composition of charcoal sorbants, Proceedings: Second International Conference of Managing Hazardous Air Pollutants*, 1993, Electric Power Research Institute, VII-145-162, 1993a.

Olmez, I., M. Ames, and N. K. Aras, *Mercury determination in environmental materials: methodology for instrumental neutron activation*

*analysis*, Proceedings of the 1993 U.S. EPA/AFjWMA International Symposium: Measurements of Toxic and Related Air Pollutants, Air & Waste Management Association, 1993b.

Olmez, I., X. Huang, and M. R. Ames, The role of instrumental neutron activation in environmental mercury analysis, to appear in: Proceedings: AWMA 88th Annual Meeting F~ Exhibition, San Antonio, TX, 1995.

Onal, M. *Determination of vapor phase mercury in Mediterranean atmosphere*, Ms. Thesis, The Middle East Technical University, 1996.

Parry. J.S., *Activation spectrometry in Chemical analysis*, A willey-interscience publications volume: 119, 1991.

Ramlal, P. S., Rudd , I.W.M., Furutani, A., and Xun, L., *The effect of pH on methyl mercury production and decomposition in lake sediments*, Can. J. Fish. Aquatic. Sci., 42:685, 1985.

Xun, L., Campbell, N.E.R., and Rudd, J.W.M., Measurements of specific rates of methylmercury production in the water column and surface sediments of acidified and circum neutral lakes, Can. J. Fish Aquat. Sci., 44:750, 1987.

W.H. Sschoreder, J. Munthe, Q. Lindquist, "Cycling of mercury between water, air and soil compartments of the environment", 1989

<http://www.hermograph.com/science/mercury3.htm>

<http://www.atsdr.cdc.gov/ToxProfiles/phs8916.html>