



# **NIMD Forum 2012**

**Current topics of mercury impact  
to human and environment**

**26 January 2012**

**Conference Hall, Minamata Disease Archives**

**National Institute for Minamata Disease**

**Minamata City, Kumamoto, Japan**

# Programme

Opening Session		Pages
9:00 - 9:10	<b>Opening Remarks</b> <i>NIMD</i> <b>Director-General Juichi Abe</b>	
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9:40 - 10:10	<b>Tetsuhiro Yoshimoto</b> <i>Minamata City</i> Steps Taken by the Minamata City, "Environmental Model City"	8
10:10 - 10:30	<b>Coffee Break</b>	
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14:30 - 15:00	<b>Choong Hee Park</b> <i>National Institute of Environmental Research, Republic of Korea</i> "National Environmental Health Survey - Mercury Concentration in Blood and Urine -"	46
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15:50 - 16:20	<b>Young-Seoub Hong</b> <i>Dong-A University, School of Medicine, Republic of Korea</i> “The blood mercury concentration in a coastal area and four cases of neuropsychological abnormal findings in children with high blood methyl-mercury concentration in Korea”	53
16:20 - 16:50	<b>Pablo Higuera</b> <i>Universidad de Castilla-La Mancha, Spain</i> “Health effects of mercury in Almadén, the world's largest mercury mining district.”	57
16:50 - 17:00	<b>Closing Remarks</b> <b>Director-General Juichi Abe</b>	

## Introduction of Idrija town and Municipal Museum

**Darko Viler**

*The Idrija Municipal Museum*

Idrija is a small town in Slovenia and the site of the second largest mercury mine in the world.

It lies in a valley 300 meters above sea level, on a tectonic fault running from northern Italy to the Adriatic, which is also the border between the pre-alpine and Karst regions. The ore deposit originated due to geological activity at the fault. The town developed at the confluence of the Idrijca and Nikova rivers, amid dense forests. In the past it was precisely wood and water that contributed significantly to successful extraction of mercury. According to legend, in 1490 a bucket maker discovered an unusually heavy, glittering substance in a stream. Identified as mercury, it resulted in quick arrival of prospectors from Italian, German and Czech lands. Idrija is the seat of a municipality with population 12,000, half of them living in Idrija itself. Idrija lies an hour's drive from Ljubljana, the capital of Slovenia, 450 kilometers from Vienna, historically the capital of the Habsburg Monarchy, 200 kilometers from Venice and 100 kilometers from Trieste, the two historically important ports for mercury exports.

The Idrija Municipal Museum is a public institution with administrative seat at Gewerkenegg Castle in Idrija, which was built just decades after mine opening. The Museum has two units, the Idrija Department and the Cerklno Department. The former organizes exhibitions in the renovated Castle complex, and houses the permanent exhibition entitled »Five Centuries of the Mercury Mine and the Town of Idrija«, which the Luigi Micheletti Foundation from the European Museum Forum declared the Best European Museum of Industrial and Technical Heritage in 1997. The Idrija Department is also responsible for the many technical and cultural monuments, including the Idrija Kamšt (a large water-driven pump), a set of restored large mine machinery in the Francis Shaft, a miner's house, and the WWII Slovenia Partisan Printing Shop on the Vojsko plateau near Idrija. The Cerklno Department offers two new permanent exhibitions: »The Cerklno Region Through the Centuries« and »Pust is to Blame! – The Story of the Laufarji from Cerklno«, displaying local spring festival traditions. The Department also invites visitors to the homestead of writer France Bevk in Zakojca near Cerklno, and devotes special care and attention to a remarkable WWII monument – the Franja Partisan Hospital in Dolenji Novaki near Cerklno.

## イドリヤ市とイドリヤ地方博物館の紹介

イドリヤはスロベニアの小さな町であり、世界で2番目の大きな水銀鉱山を有している。

イドリヤはイタリア北部からアドリア海に走っている断層の上の海拔 300 メートルの谷に位置し、また前アルプス山脈とカルスト地域の境を接するところでもある。地質学活動により断層部に鉱石が堆積した。町はイドリヤ川と Nikova 川の合流地点、深い森の中に発展した。昔はこの森と水が水銀の輸出に大いに役立った。

イドリヤ歴史博物館は Gewerkenegg 城内にある公共の施設で、鉱山が開かれて数十年後に建てられたものだ。博物館はイドリヤ部と、Cerkno 部という二つのユニットに分かれている。町がこの城の修復、展示物の管理にあたっており、「5 世紀にわたる水銀鉱とイドリヤの街」と題した常設展示品を収蔵している。

また Cerkno 部には“世紀を超えて、Cerkno 地方”や、“Cerkno 出身の Laufarji の話”等の新たな常設展示が加わり、また春節祭の伝統等も紹介している。

## NMD Forum 2012

### Introduction of Idrija Town and Municipal Museum

Darko Viler

The Idrija Municipal Museum

26. - 27. January

Minamata City, Kumamoto, Japan



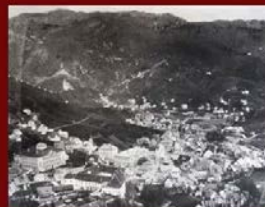
Slovenia - the heart of Europe and Idrija, the oldest  
mining town in Slovenia



work in the mine at the beginning of the 20<sup>th</sup> century



the closed mine today



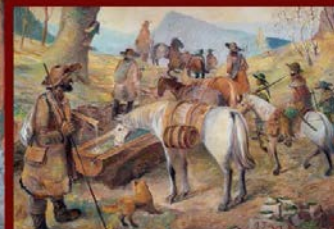
Idrija at the beginning of the 20<sup>th</sup> century and Idrija  
today



Idrija at the beginning of the 20<sup>th</sup> century and Idrija  
today - different view



the bucket maker



transport of mercury to the buyers



mercury



cinnabar – common mercury ore



the smeltery and the buildings of Kolektor Group - a worldly  
renowned company, producing electric commutators





the Joseph shaft at the beginning of the 20<sup>th</sup> century and today – the entrance to the mine, now closed



the Francizi shaft at the beginning of the 20<sup>th</sup> century and today – housing the technical department of the Idrija Municipal Museum



Gewerkenegg castle – seat of the Idrija Municipal Museum housing permanent exhibitions



„Five Centuries of the Mercury Mine and the Town of Idrija” - permanent exhibition, showing flasks for the transport of mercury and the Mercury Cube, which symbolises Idrija's underground treasure



„Milestones of the 20th Century” - permanent exhibition presenting the periods of the Italian and German occupation and the communist regime



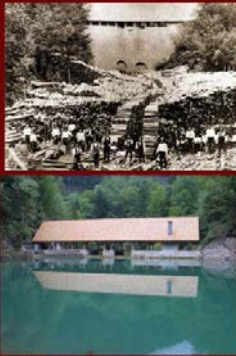
“Idrija Lace, A History Written in Thread” – permanent exhibition showing the traditional lacemaking kit and the best examples of laces



the Idrija Kamšt, the driving wheel of the water-driven pump and the Kley steam pump, Technical department of the Idrija Municipal Museum



18th century miner's house with furnishing originating from the first half of the 20th century – permanent exhibition



the "Idrija klavže" - water barriers for wood drifting



original WWII Slovenian Partisan Printing Shop in the woods near Idrija



"Laufarji" (runners) at the Cerklje department, chasing away winter - an old Slovenian custom



homestead of Slovenian writer France Bevk and Japanese translations of some of his works



original WWII the Franja Partisan Hospital before and after the reconstructive works following the flood of september 2007



the Luigi Micheletti award for the "Best European Museum of Industrial and Technical Heritage" 1997



## Steps Taken by the Minamata City, “Environmental Model City”

**Tetsuhiro Yoshimoto**

*Minamata City*

Minamata City is located in the southern part of Kumamoto Prefecture. In 1900's it is a small-scale city with abundant blessings from sea, mountains, rivers and mild climate and its population is about 27,000 and the area is 162 km<sup>2</sup>. It was a mere small farming and fishing village with the population of about 12,000 in 1900's. However, after the establishment of the Minamata Factory of Japan Nitrogenous Fertilizer Company (the forerunner of Chisso Corporation) in 1908, the city developed as an industrial city along with rapid increase of the population.

The New Japan Nitrogenous Fertilizer Company resumed production of vinyl chloride in 1949 and around 1950's serious health damage appeared on human in fishing villages. Since the director of the hospital attached to the New Japan Nitrogenous Fertilizer Company reported the occurrence of the patients to the Minamata Health Center on May 1, 1956, this day has become the day of official confirmation of Minamata disease.

At that time the cause of this disease could not clarified at all. Because of the misunderstandings of this sickness as contagious disease, the families with the patients received discrimination and prejudice and many people died painful deaths.

In 1956, the population of the city exceeded 50,000 and the city had gotten flourished more and more while the outbreak of the disease continued mainly in fishing villages.

Due to the complex regional factor that sufferers and wrong doers were living in the same town, mutual distrust grew gradually among the residents. That led the local community to collapse and have a long confused period.

Some years later the cause of the Minamata disease became clear and in 1977 the Minamata Bay Pollution Prevention Project in which dredging of the sedimentary sludge containing mercury in and out of the Minamata Bay and reclamation was initiated in order to prevent diffusion of the damage. In 1990 the project was completed and the reclaimed area has become an eco-park.

And in January, 1993, the Minamata Disease Municipal Museum was opened to collect and keep materials and to disseminate the information in order to make use of the lesson of Minamata Disease in the future. Up to these days approximately 750,000 people have visited from home and abroad. Particularly all the fifth graders of Kumamoto Prefecture visit every year as a part of their environmental study.

## 「環境モデル都市」みなまたのあゆみ

水俣市は、熊本県の南に位置し、人口約 27,000 人、面積約 162 平方キロメートルで、海・山・川と自然が豊かで温暖な気候に恵まれた小規模都市です。1900 年頃は、人口 12,000 人余りの小さな農漁村に過ぎませんでしたが、1908 年にチッソ株式会社の前身である日本窒素肥料株式会社水俣工場が設立されてからは人口も急速に増加し、工業都市として発展の途を歩むこととなります。

1949 年に新日本窒素肥料株式会社が塩化ビニールの生産を再開、1950 年代頃から漁村において人に重大な健康被害が見られるようになり、1956 年 5 月 1 日に新日本窒素付属病院院長が水俣保健所へ患者発生の報告を行ったことから、この日が水俣病公式確認の日となっています。

当時は、病気の原因が全く分からず、患者が発生した家庭は伝染病など誤解され差別や偏見を受けながら、多くの人が苦しみのなか亡くなっていきました。

1956 年に本市の人口が 5 万人を超え市勢は拡大の一途をたどる傍ら、漁村地域を中心に患者の多発が続きました。

ひとつのまちに被害者と加害者が混在するという複雑な地域事情から、次第に住民間に相互不信が起こることとなり、そのことがそれまで築き上げてきた地域コミュニティを崩壊へと向かわせ、長く混迷の時代が続くこととなりました。

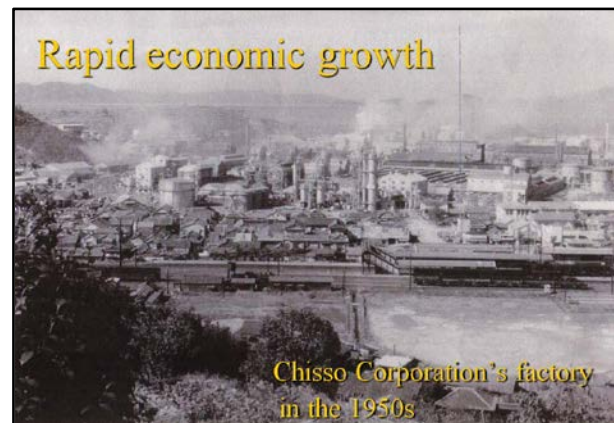
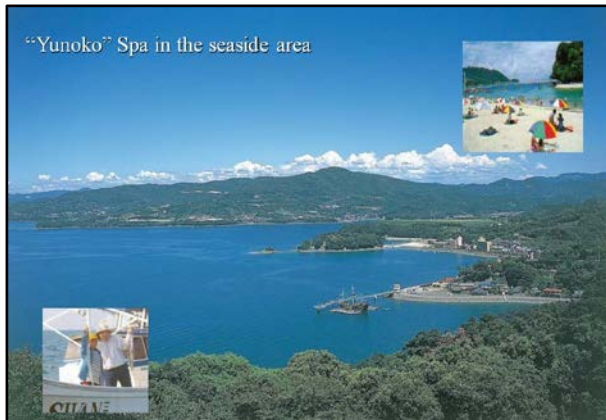
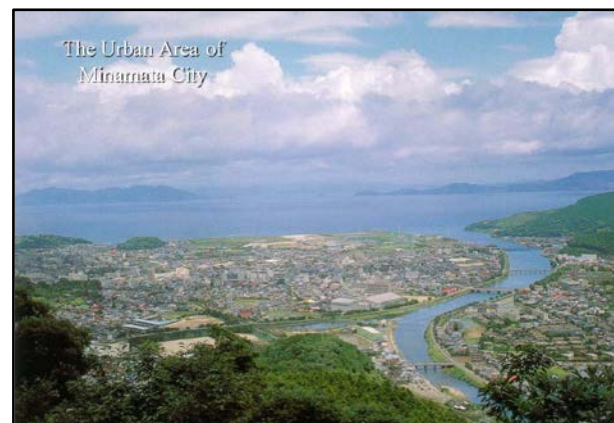
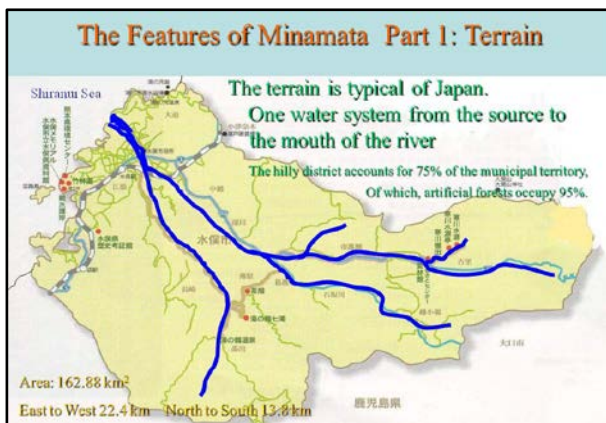
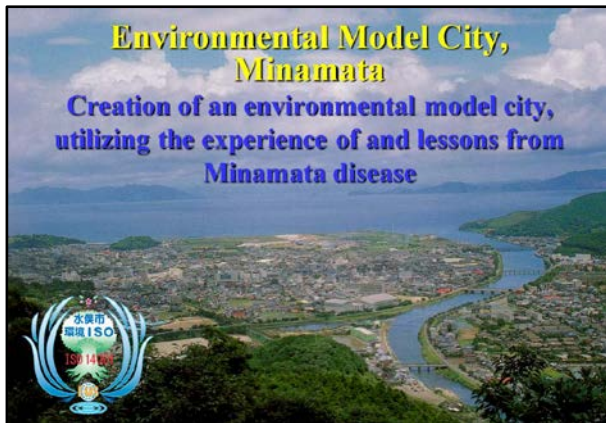
やがて水俣病の原因も判明し、被害の拡散を防止するため水俣湾内外に堆積した水銀へドロの浚渫・埋め立てを行う水俣湾等公害防止事業が 1977 年に着手され、1990 年に工事が完了、現在エコパークとして親しまれています。

また、1993 年 1 月水俣病の教訓を後世に生かすため、資料を収集・保存し、情報を発信することを目的として、水俣市立水俣病資料館が開館しました。現在まで、国内外から 75 万人の方が訪れています。特に小学校の環境学習の一環として、熊本県内全校の小学 5 年生は毎年来館しています。

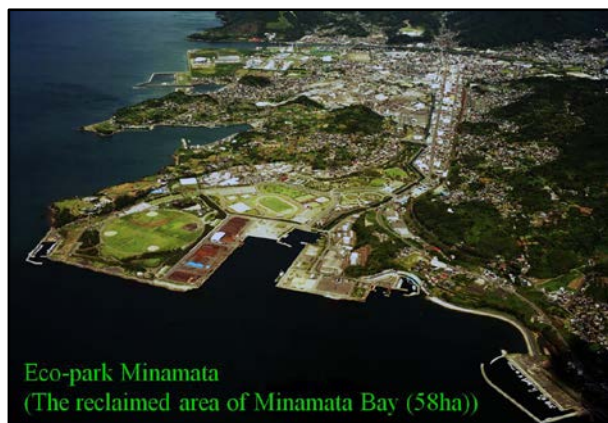
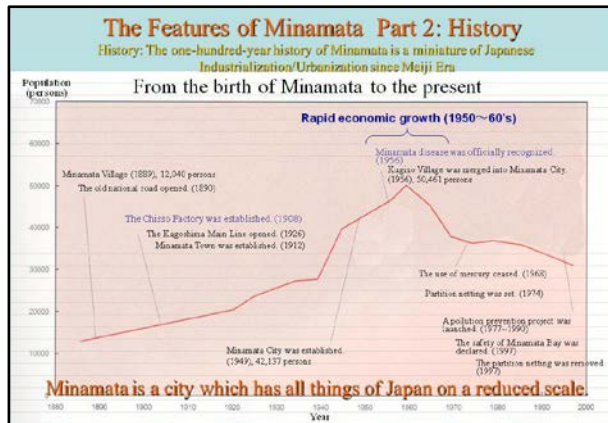
本市は、これまでの長い混迷と苦しみを教訓に、二度と人の健康や環境に悪影響を及ぼすことがないように、1992 年に全国に先駆け「環境モデル都市づくり」宣言を行い、水俣再生の目標としました。家庭などから出るゴミの高度分別への取り組みを初め、学校などにおける環境 ISO の取り組み、食など安全にこだわったものづくりを实践する環境マイスターの認定、国によるエコタウンの承認、みなまた環境大学事業の実施など、市民協働の取り組みを行い、住民同士の絆を取り戻す「もやい直し」へと進んできました。

このような実践行動が高く評価され、2001 年から 10 年間実施された NGO による「日本の環境首都コンテスト」において 2011 年 3 月に「日本の環境首都」の称号を獲得しました。

本市は、これからも持続可能な地域社会のさらなる構築を目指すとともに、「真の豊かさ」を感じることができ、多くの人が交流する活力あるまちを、市民協働で築いていきます。











### Minamata's ISO throughout the city

- Get rid of waste (No garbage)
- Efforts to save energy/resources

#### "A school version of ISO"



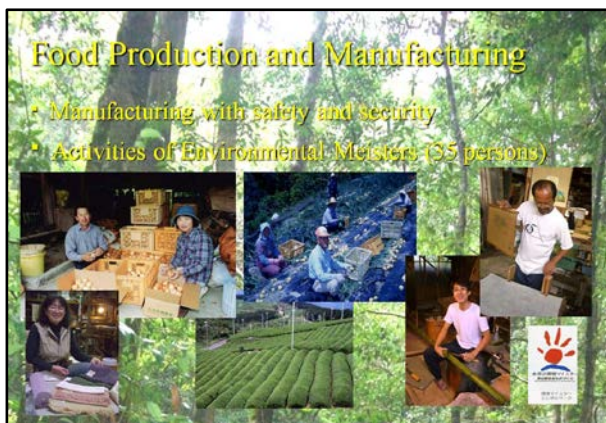
Experimenting waste collection



Recording activities



Restoring and maintaining the environment



### Moyai-naoshi

Like a rope combining ships with each other,  
Retie the rope to connect the hearts of people with one another.

#### "Minamata Disease Municipal Museum"



#### "Prayer Dedication with Fire"



### Moyai-naoshi

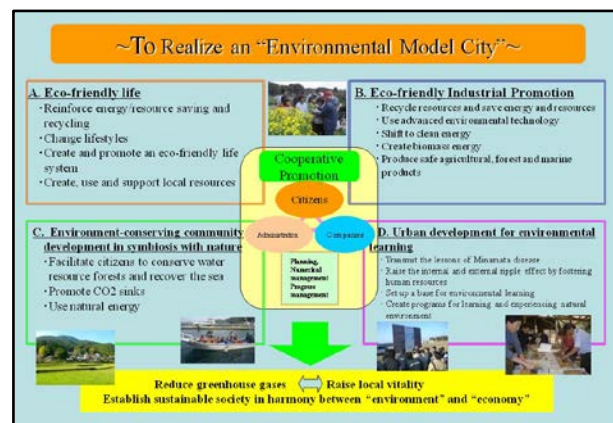
Reviewing the reality of the local community for hope for the future  
- Dialogue and Cooperation -



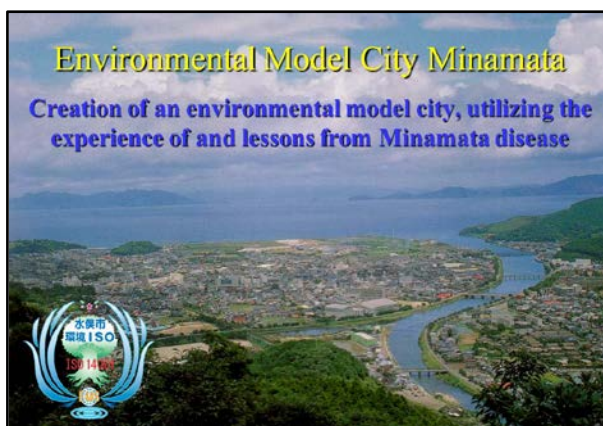
水俣病と水俣の明日を語り合う青年の夕べ  
Evening Talks among the Youth on Minamata disease and the future of Minamata



水俣の再生を語る市民の集い  
Citizens' meeting on the regeneration of Minamata







## Closure of the Mercury Mine and the Quality of Life in Idrija

**Tatjana Dizdarevič<sup>1</sup>, Urška Repinc<sup>2</sup>**

<sup>1</sup>: *Idrija Mercury Mine, Ltd. – in liquidation*

<sup>2</sup>: *Municipality of Idrija; Slovenia*

The town of Idrija is known worldwide mostly for its mercury mine, one of the oldest mines in Europe. It has been estimated that from 1490 till 1995 over 12 million tons of mercury ore were excavated and a total of 153,309 tons of commercial mercury (Hg) were extracted, which represents over 13% of the entire world Hg production to date. All activities in the Idrija Mercury Mine Company relating to the shutdown of the mine were completed by the end of the year 2009.

In view of man's growing ecological awareness in the 70's, when Hg production reached its final peak, first systematic measurements of total mercury in water, soil, air, plants, animals and humans were introduced. Mining and reprocessing of ore has severely enhanced the mobilisation of Hg - it has been estimated that during the mine operation about 44,616 tons of Hg have been released to the environment uncontrolled. Unfortunate outcome of the mining activities has been the constant exposure of the inhabitants of Idrija and miners to Hg. Considerable decrease of Hg content in air in Idrija was observed in the last decades after the processing of mercury ore in the smelting plant was discontinued. The concentrations of Hg in air were reduced from about 2,000 ng/m<sup>3</sup> in 1970's to about 10 ng/m<sup>3</sup>. Airborne Hg caused elevated Hg levels in surficial soil layers. On specific locations naturally increased levels of mercury are found in soil where the ore deposit reaches the surface in the immediate area of the town (Pront area), or due to many abandoned improvised smelting/tailing sites from the earlier periods of Hg production. Despite drastic reduction and final ceasing of mining and smelting activities in Idrija in the 90's, the mercury concentration in soils and vegetation remain high. Though Hg levels in vegetation are several orders of magnitude lower than those in soils, the results show high persistence of Hg, despite drastically diminished airborne Hg emissions. Concentrations of Hg in surface waters upstream are below 10 ng/L and downstream of the mining district increase to about 200 ng/L, and remain elevated until the confluence with the Soča River. Significant decrease of Hg concentrations in surface water with the increasing distance from the town of Idrija is observed today. The fact is that Hg concentrations in river sediments are still relatively high and there are no signs of the expected decrease. Concentrations of Hg in mine waste water, which is periodically released to Idrijca River, are within the permitted values set by Slovenian legislation. The tailings and contaminated soils in the

Idrija region are continuously eroded and serve as a continuous source for the river and the flood plains. Therefore Idrija area continues to supply Hg into the Idrijca River and Soča river systems, which empties into the Gulf of Trieste some hundred km downstream. At the current level of exposure to Hg in the town of Idrija, no directly perceivable toxic effects are expected. Nutritional habits of inhabitants have changed in the past decades; therefore the intake of Hg through inhalation is considered the most significant. The latest study on mercury exposure revealed that children living in the area of the former mercury mine are not under any significantly elevated risk of mercury exposure.

Although Hg is present in Idrija region mostly in inorganic forms, numerous research studies were performed to address Hg, transport and transformation processes of different Hg species in Idrija region. The results have served as a basis in preparing long term rehabilitation measures for reducing the effects of the past mining activities. On the basis of the provisions of the EU Strategy for Mercury (2005) as well as the applicable laws and implementing regulations of the Republic of Slovenia (1999-2004) stipulating the final rehabilitation of the environment and elimination of the consequences of mining works, the *Mining project of monitoring* in the period after the termination of mining activities in the Idrija Mercury Mine was prepared. Also Municipality of Idrija has become aware of the importance to address environmental issues in order to continuously improve the quality of life of its inhabitants. The strategic goals of the *Idrija Municipal Environmental Protection Program* prepared in 2009 include the setup of an effective environmental management system (ISO 14001), reduction of environmental pollution, regulation of public utility infrastructure, waste management, sustainable use of energy, protection of natural resources and biotic diversity, as well as awareness raising and information transfer.

The decision that Slovenia can also contribute to the full implementation of the EU Strategy concerning mercury led to the establishment of the *Information and Research Centre for Mercury* (IRC Hg) in Idrija in June 2008. The opening of this Centre has brought new dimensions to the existing activities of the Idrija Mercury Mine. Unfortunately IRC Hg could not reach its potential due to the liquidation process of the Idrija Mercury Mine, which started in 2010. The Slovenian Government is currently working on establishment of a new public institute named *Idrija Mercury Heritage Management Centre*, whose operation will also be harmonised with the management plan according to the application for inscription on *UNESCO's World Heritage List*. The international project "*Heritage of Mercury. Almadén and Idrija*" nominated by Slovenia and Spain for inscription on *UNESCO's World Heritage List*, is by all means one way of directing and planning activities in the future. Emphasis is laid on the conservation, development and presentation of heritage of exceptional universal value to contribute to a broader awareness of its significance and respect, as

well as to the sustainable development of the region and the local community. In addition to technical and cultural attractions, we are also aware of the natural features in the environment of Idrija. With its exceptional geological heritage, botanical diversity, unique forests and rich mining heritage, Idrija holds an important place in the European environment. The emerging *Geopark Idrija*, which represents a form of informal protection, interpretation, promotion and marketing of natural heritage in a geographical area, connects natural and cultural heritage in a unique and original way.

For almost 500 years the Idrija Mercury mine was the only driving force for development in Idrija region. The crisis in the mercury market in the 1970's and consequently the stagnation of the Idrija Mercury Mine favoured and led to the development of more environmentally friendly technologies and industry, that changed the appearance of the town in many aspects. Rich scientific, technical and cultural heritage that gave unique and recognizable shape to Idrija town during half a century of mercury mining, is a legacy of immeasurable value, therefore we shall have to find ways to preserve it for the generations to come.

### イドリヤの水銀鉱山の閉鎖と生活の質

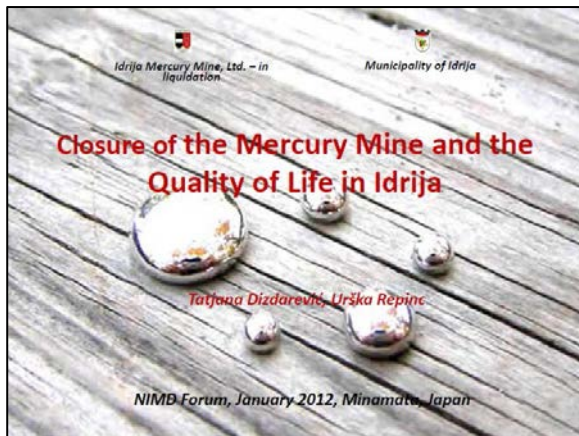
イドリヤの町はヨーロッパで一番古い水銀鉱山として世界的に知られている。1490 年から 1995 年まで 1,200 万トン以上の水銀鉱石が掘り出され、合計で 153,309 トンの商業水銀が掘り出された。これは現在までで全世界の水銀生産の 13%以上になる。鉱山閉鎖に関連した活動は 2009 年末に完了した。

大気中の水銀の大幅な減少は、精錬工場での水銀鉱石の加工が止まった後の過去 10 年に観測された。大気中の水銀濃度は約 2,000 ng/m<sup>3</sup> から 1970 年代には約 10 ng/m<sup>3</sup> にまで減少した。大気中の水銀が、地層表面の水銀レベルの増加を引き起こした。90 年代におけるイドリヤの採鉱や溶錬活動の徹底した現象にもかかわらず、土壌と植生中の水銀濃度は依然として高いままである。川の堆積物中の水銀濃度はいまだに高く、イドリヤ地域の汚染された土壌は継続的に浸食され川と洪水が起きる平原へ連続的な水銀放出の源となっている。

また、イドリヤ市は住民の生活の質を継続的に向上するために環境問題の重要性を指摘しており、2009 年に設定されたイドリヤ市環境保護プログラムの戦略目標には効果的な環境管理システム、環境汚染物質の減少、電気、ガスなどのインフラ、廃棄物管理、持続的なエネルギー利用、天然資源の保護、生物の多様性の設定、さらには意識の向上と情報伝達などが含まれている。スロベニア政府は現在イドリヤ水銀遺産マネジメントセンターという名称の新しい公共機関を設立中である。この機関の運営は UNESCO の世界遺産リスト登録への申請に向けての管理計画と協調するもので、スロベニアとスペインによって UNESCO の世界遺産リストに推薦された国際的なプロジェクト、“水銀の遺産 アルマデンとイドリヤ”は、未来を目指した行動の計画である。

約 500 年もの間イドリヤ水銀鉱山は、イドリヤ地方で唯一の開発の原動力であった。1970 年代の水銀市場の危機とその結果としてイドリヤ水銀鉱山の不振は、より環境にやさしいテクノロジーや産業に尽力した。その結果町の様相は様々な観点で変貌した。水銀採鉱の半世紀の間イドリヤの町に独特で明確な形を与えた豊かな科学的、技術的、文化的な遺産は計り知れない価値の遺産であり、我々は来たるべき世代に対し保存する道を見出すべきである。



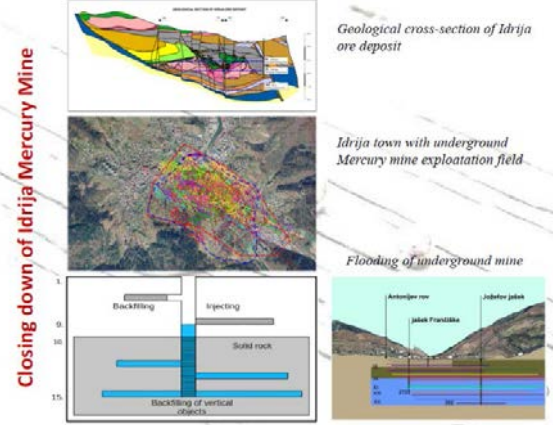


### Idrija Mercury Mine Milestones (1/2)

- 1490 native mercury ( $Hg^0$ ) was discovered in Idrija
- 1508 rich cinnabar ore was discovered
- 1970 beginning of first ecological research activities in Idrija due to  $Hg^0$  pollution
- 1977 temporary cessation of Hg production
- 1986 decision on the final termination of Hg production and the gradual, complete and permanent closure of mine
- 1987 "Long-term Program for the Complete and Permanent Shutdown of the Idrija Mercury Mine"
- 1983-1995 minimal Hg production
- 1995 systematic monitoring of Hg pollution in Idrija region
- 2004 last Hg stock of Idrija Mine was sold

### Idrija Mercury Mine Milestones (2/2)

- 2004 "Act on the Prevention of Effects of Mining Activities in the Idrija Mercury Mine" (Slovene National Assembly)
  - to include the rehabilitation of mining losses,
  - to eliminate the effects of mining activities on the health of former miners,
  - after the completion of shutdown works, the registered activities of the mine are to be changed for the purposes of
    - (1) maintaining of the unflooded part of the pit – and (2) monitoring
- 2006 Mining Project „Monitoring of the Affected Area of the Idrija Mercury Mine after the Completion of Shutdown Works“
- 2007 Program for maintenance of the unflooded part of the pit and monitoring after the completion of shutdown works in the Idrija Mercury Mine in the Phase of Gradual Shutdown in the period from 2008 – 2012 (approved by the Slovene Government)
- 2009 completion of the shutdown works in the mine
- 2009 decision of the Slovenian Government on the Idrija Mercury Mine liquidation



### Mercurialism (miners' disease)

= poisoning with vapours of elementary mercury

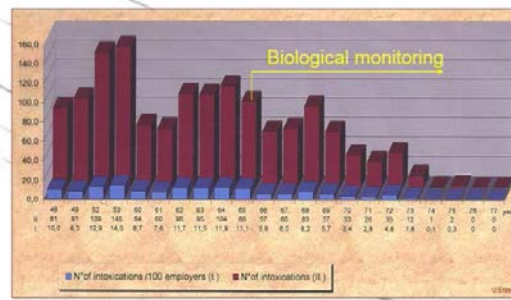
Occupational exposure to inorganic Hg (symptoms, consequences)

THE HEALTH SAFETY PROGRAMME FOR WORKERS EXPOSED TO ELEMENTAL MERCURY AT THE MERCURY MINE IN IDRIJA (1965 →)

- air monitoring and mercury emission controls
- technical measures for the reduction of  $Hg^0$  in the working environment
- personal safety equipment
- estimation of the intensity of external monthly exposure
- periodic rotation of workplaces and the reduction of daily exposure to mercury
- medical surveillance of workers exposed to elemental mercury ( $Hg^0$ ):
  - medical examinations
  - biological monitoring
  - assessment of work ability



### Occupational mercury intoxications in Idrija Mercury Mine from 1946 to 1977



### Total Hg production in the Idrija Mercury Mine 1490 - 1995 (Mlakar 1974, Cigale 1997)

	Ore (t)	Hg in ore (t)	Hgcomm (t)
Hg production	12 206 224	135 142	100 074
Hg (cinn. & othe)	551 508	10 516	7 618
TOTAL	12 575 732	145 568	107 692

Environmental pollution (~ 38.000 tons Hg)



Sole founder and owner of Idrija Mercury Mine is the Republic of Slovenia.

### Mercury research in Slovenia initiated by the Jožef Stefan Institute in the early 1960s

... to address the health status of the miners.

#### Mercury Environmental Pollution Monitoring:

- air
- water
- sediments
- soils
- plants
- animals
- old attic dust
- humans











**Idrija is traditionally preserving:**

- Heritage (of Mercury) and
- Knowledge and know-how (about Mercury).

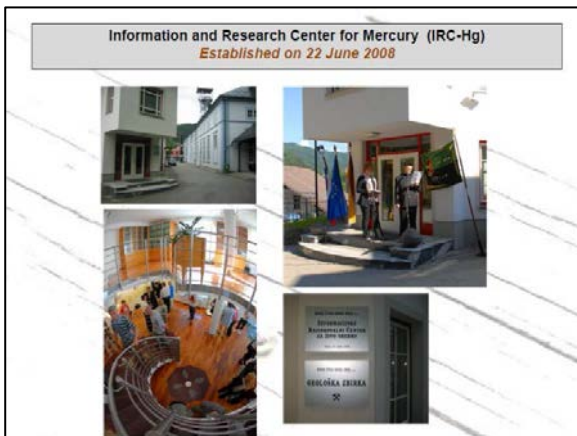
**In Light of:**

- Closing of Idrija Mercury Mine
- Changing of global perception on Mercury (EU Mercury Strategy, EU Mercury Convention)
- Preparation of Managing plan for UNESCO

**Information and Research Centre for Mercury (IRC Hg) has a good foundation for development within Idrija Mercury Heritage Management Centre.**

**Guidelines for IRC Hg future development:**

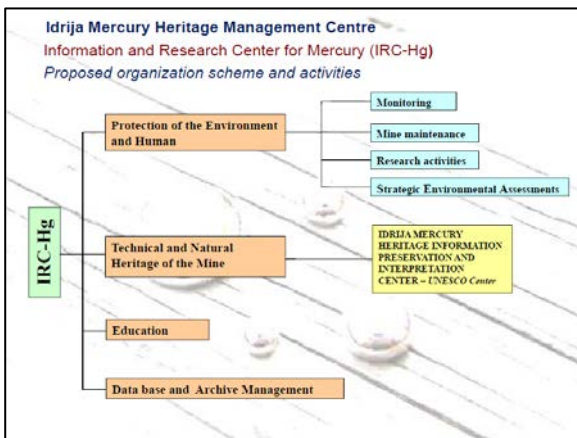
- Continuing existing activities (Heritage conservation and interpretation, monitoring the process of closing Idrija Mercury Mine and Mine maintenance),
- Active Research and Scientific Cooperation with Institutes (especially Jožef Stefan Institute).



**Information and Research Center for Mercury**

**The principal objectives**

- to associate existing know-how and scientific and research activities on mercury,
- building ties with domestic and foreign institutions,
- to deal with various activities, including monitoring, communication, database and archive management and teaching,
- drawing up a wide range of scientific programmes that are based on geology, mining, metallurgy, ecology and health,
- presentation of the unique features of the ore deposit, mining and processing of the ore and environmental issues.

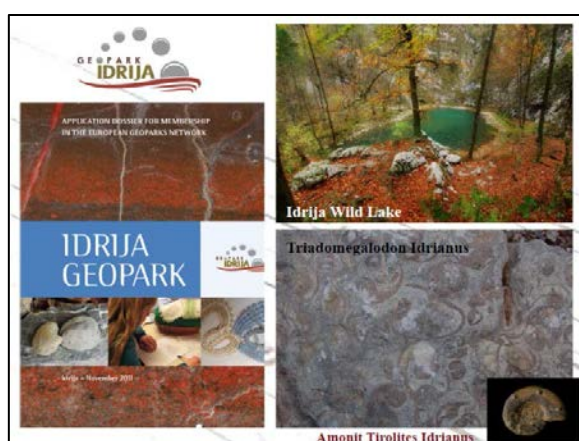
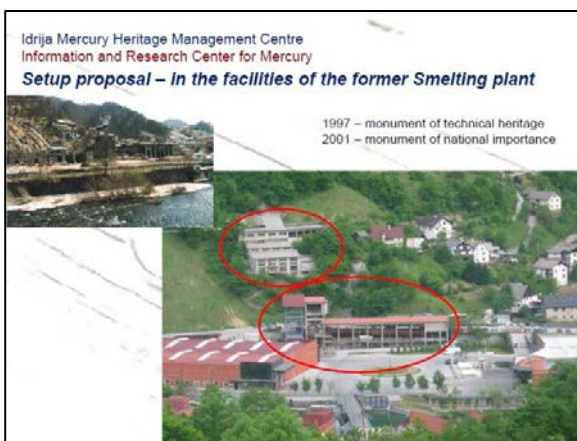


**Nomination for inscription on UNESCO's World Heritage List**

**Heritage of Mercury**

Gewerkenegg Castle, 16th Ct.

Klavže - water barrier, 18th Ct.



**Economic and Social Transition during Mine Closure**  
**New Technologies and Industries**

**KOLEKTOR**

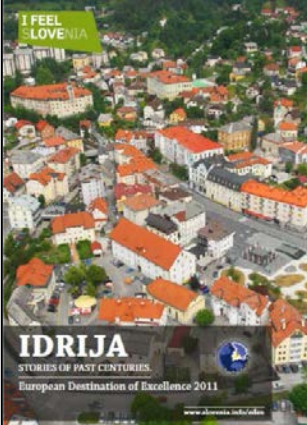


**Mercury Mine:**  
 1964: 1350 employees  
 1977: 350 employees  
 2011: 15 employees

**Kolektor:**  
 1964: 40 employees  
 1977: 500 employees  
 2011: 1200 employees

Social responsibility

**IDRIJA**  
 STUDIES OF PAST CENTURIES  
 European Destination of Excellence 2011



**IDRIJA**  
 Alpine Town of the Year 2011

500-years of mining and mercury extraction represent an environmental burden in the immediate and broader area of the town of Idrija.

The principal purpose of the rehabilitation and recultivation of an environment degraded by mining is by all means to ensure public health, safety and prosperity, as well as environmentally stable conditions.

**Thank you very much for your attention**

ご静聴ありがとうございました

## **Mercury fate and transport in the wider Idrija Region and the Gulf of Trieste; from environmental measurements to modelling tools**

**Milena Horvat<sup>1</sup>, Dušan Žagar<sup>2</sup>, Rudolf Rajar<sup>2</sup>, Matjaž Četina<sup>2</sup>,  
David Kocman<sup>1</sup>, Jože Kotnik<sup>1</sup>, Nives Ogrinc<sup>1</sup>**

<sup>1</sup>: *Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana*

<sup>2</sup>: *Faculty of Civil Engineering and Geodesy, University of Ljubljana; Slovenia*

Mercury (Hg) mining activities in Idrija, Slovenia, have resulted in significant environmental contamination. Hg contaminated soils, Hg-laden material and tailings continue to supply Hg to the local river system and to the Gulf of Trieste in N Adriatic, some 100 km downstream from the mercury mine. Due to the abundant precipitation, steep slopes and highly erodible underlying lithology, this region is especially prone to erosion. In the last 10 years numerous measurement campaigns were implemented and used for the validation of modeling tools to better describe and simulate the fate and transport of mercury in the catchment area, estuarine and the coastal environment of the Gulf of Trieste. Such an approach has been demonstrated to be an efficient tool for the resource management planning, including remediation in the riverine and coastal environment.

The presentation will provide examples of recent developments in the use of Erosion Potential Method (EPM) in a Geographic Information System (GIS) environment (Kocman and Horvat, 2009, 2011) which was used to estimate mercury delivery to the receiving water body associated with the contaminated soil loss from the Idrijca River catchment draining the area of the mine. Surface geology and soils, topographic features, climate, and land use were taken into consideration and validated against mercury measurements in soils and suspended solids delivered to the riverine system. Based on the spatial distribution of mercury in catchments soils the average annual Hg load to the Idrijca River system was predicted at 933 kg. Due to the high variability in spatial distribution of mercury in soil areal loads vary significantly and are the highest in the area surrounding the mine ( $5 - 20 \text{ mg Hg m}^{-2} \text{ yr}^{-1}$ ). In addition, based on the site-specific empirical correlations between the measured Hg emission fluxes and the parameters controlling the emission, a mercury emission model was developed within GIS to simulate non-point source mercury emissions at the catchment scale. The most contaminated areas surrounding the mine that represent less than 5 % of the catchment contributes 25 % of total annual mercury load to the Idrijca River

system. In this way, spatial distribution and significance of most polluted sites that need to be properly managed were assessed.

In the marine environment, the fate and transport model PCFLOW3D previously developed (Rajar et al., 2004, 2006; Žagar et al. 2006, 2007) has been improved in order to (1) forecast water circulation in the areas under study in adequate spatial and temporal resolution, (2) simulate transport and fate of pollutants on the basis of measured and modelled input parameters and (3) perform nearly real-time short-term simulations. Previous studies (Žagar, 1999, Rajar et al., 2000) showed high impact of wind induced waves and currents on bottom sediment resuspension and transport, particularly in the northern, shallow part of the Gulf. Therefore, the PCFLOW3D model has recently been upgraded with a module for prediction of wave parameters and wave-induced bottom shear stress from wind speed and direction measurements at the buoy positioned near the coastline. The module is based on an artificial neural network algorithm. The improved model allows for simulation of more environmental parameters and to account for the impact of several new variables on mercury transformations in much better horizontal and vertical scale (approx. 150x150 m and the layer thickness is 1 m). Such a model allows for an effective use in the advanced integrated monitoring system in which the measurement data from buoys and robots are transferred via web-interfaces from the AmI database to PCFLOW3D and the modelling results are then fed back to the database. GIS models are applied to simulate conditions in the background areas and to determine riverine inputs. Using all the described improvements and the significantly larger quantity and better quality of input data, it is expected to increase the accuracy of mercury transport and transformations simulated with the PCFLOW3D model.

## Acknowledgement

The EU FP7/2007-2013 (grant agreement n° 212790 – HYDRONET) and the ARRS of the R Slovenia is acknowledged for financial support.

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- Rajar R, Žagar D, Širca A, Horvat M. 2000. Three-dimensional modelling of mercury cycling in the Gulf of Trieste. *Sci. total environ.* 260, 109-123.



Rajar R., Žagar D., Četina M., Akagi H., Yano S., Tomiyasu T., Horvat M. 2004. Application of three-dimensional mercury cycling model to coastal seas. *Ecol. model.*, 171/1/2, 139-155.

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Žagar, D. (1999) Development and application of a three-dimensional model to simulate mercury transport and transformation process in the marine environment, *Acta Hydrotechnica*, 17, 27. 68.

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Žagar D., Petkovšek G., Rajar R., Sirknik N., Horvat M., Voudouri A., Kallos, G. B., Četina M.. 2007. Modelling of mercury transport and transformation in the water compartment of the Mediterranean Sea. *Mar. Chem.*, 107/1, 64-88.

### 広域イドリヤ地方とトリエステ湾での水銀の命運と輸送; 環境測定からモデル化手法まで

スロベニアのイドリヤにおける水銀鉱山活動は、深刻な環境汚染を引き起こした。水銀は、土壌を汚染し、水銀を含む物質及びテレーリング（尾鉱）は水銀鉱山から数 100 km にわたって、地域の河川系、さらには北アドリア海のトリエステ湾に水銀を供給し続けている。豊富な雨量、険しい勾配、受食性の高い岩質のせいで、この地域は特に浸食されやすい。過去 10 年間に膨大な計測の運動が履行され、最終結果の予測と水銀が流域、河口、トリエステ湾の沿岸の環境にどのように運ばれるかをよりよく説明するための検証に使用された。これらの取り組みは河川と沿岸環境の修復を含む資源の管理計画にとり効率的な道具になることを示してきた。

今回の発表では、地理情報システム（GIS）環境におけるエロージョン・ポテンシャル法(EPM)を用いた最近の研究の例を示す(Kocman and Horvat, 2009, 2011)。海洋環境では動態と輸送モデル PCFLOW3D が既に開発されていて(Rajar et al., 2004, 2006; Žagar et al. 2006, 2007)、さらに改良され、以下を可能にしている。（1）適正な空間的かつ時間分解能における研究が行われている地域の水の循環の予測（2）測定値と入力されたモデル値を基とした運送と命運のシミュレーション（3）現実に近い短時間のシミュレーションの実行。先の研究(Žagar, 1999, Rajar et al., 2000)では、沈殿土砂上の再懸濁と輸送における風に引き起こされた波と流れによる影響の大きさを示した。また、更なる改良を加え、膨大な量とより良い質の入力データのを用いて、PCFLOW3D モデルでシミュレートされた水銀の輸送と変換の正確さが増加することが予測される。



### Mercury fate and transport in the wider Idrija Region and the Gulf of Trieste; from environmental measurements to modelling tools

Milena Horvat

Dušan Žagar, Rudolf Rajar, Matjaž Četina,  
David Kocman, Jože Kotnik, Nives Ogrinc



### Contents

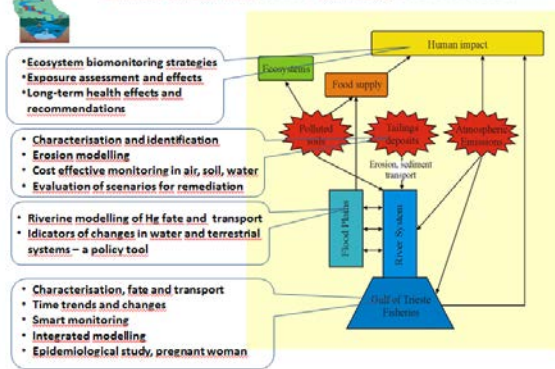
- Mercury contamination the river catchment and the coastal environment
- River modeling systems for spatial planning and management
- Coastal modeling systems: case study - GLP terminals in the Gulf
- Future perspectives: smart monitoring strategy

### The extent of Hg pollution from Idrija

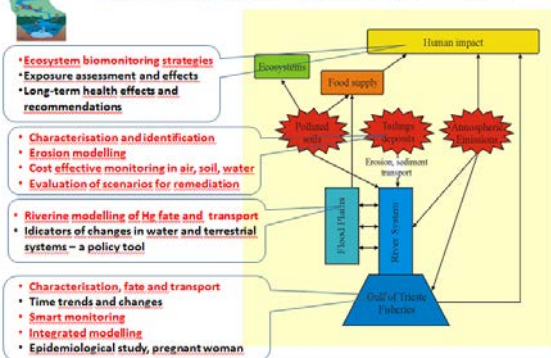


37.000 tons of Hg released in 500 years

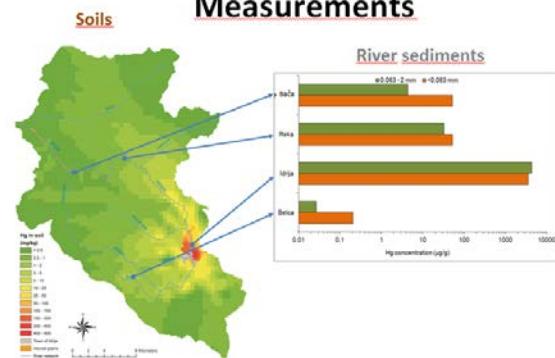
### What have we done during 1995-2010?



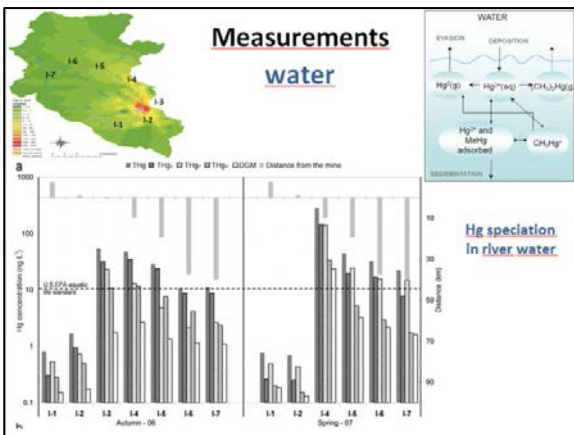
### What have we done during 1995-2010?



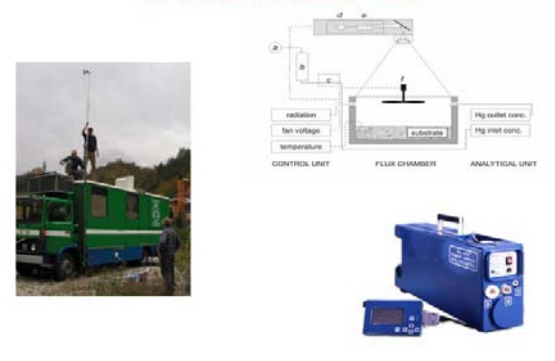
### Measurements



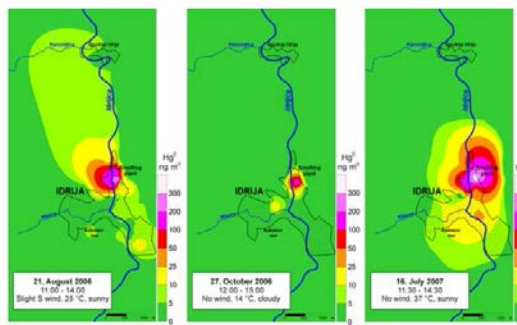
### Measurements water



### Measurements - air



## Measurements - air



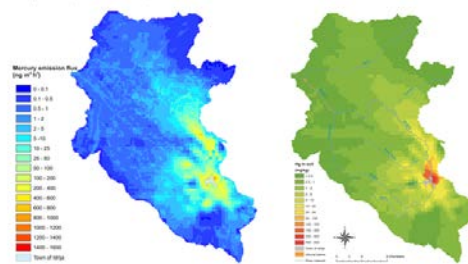
## Quantification of Hg releases from contaminated sites – modeling approach

## Hg atmospheric emission

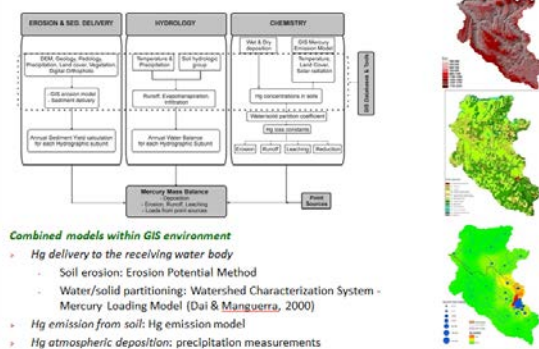
Emissions depend on substrate, Hg content, soil temperature, solar radiation, soil moisture

## Hg release to aquatic systems

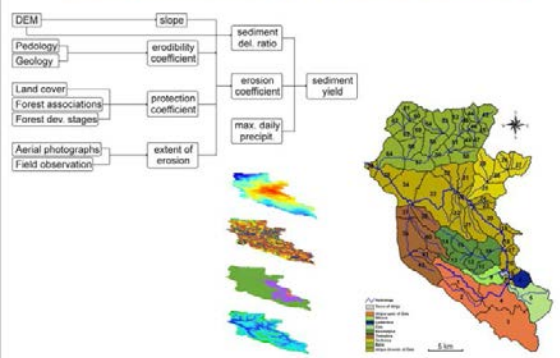
Erosion and runoff depend on land cover/use, geology, pedology, topography, precipitation...



## Modeling framework – GIS approach

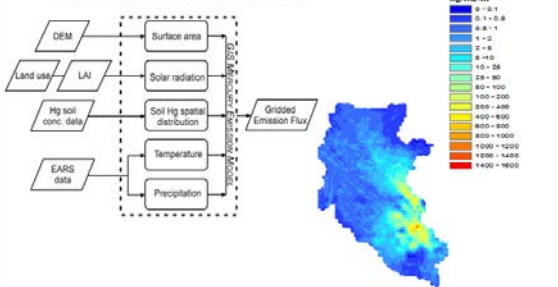


## Erosion Potential Method, GIS parameters extraction

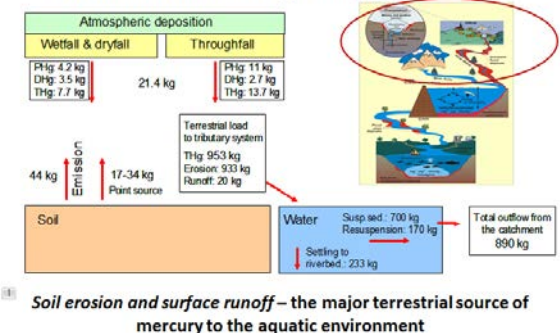


## GIS mercury emission model

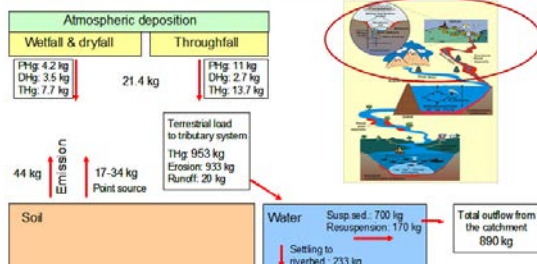
- Hg emission from soil =  $f(\text{soil Hg content, temperature, solar radiation, precipitation})$



## Annual mass balance of Hg in the Idrija catchment

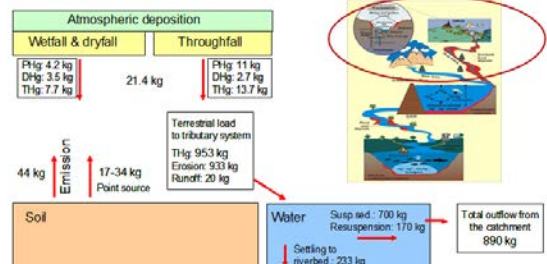


## Annual mass balance of Hg in the Idrija catchment



98 % of Hg in particulate phase

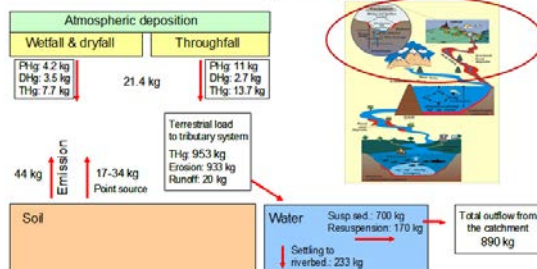
## Annual mass balance of Hg in the Idrija catchment



Importance of the hot spots: e.g. 25 % of total annual load from the area representing < 5%, 50 % of total emission to the atmosphere from the point sources



## Annual mass balance of Hg in the Idrija catchment

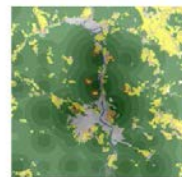


Extreme hydrological conditions: contaminated riverbed sediment resuspension

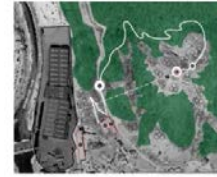
## Possible measures to reduce the release of Hg from the "hot" spots



## 1. Forestation



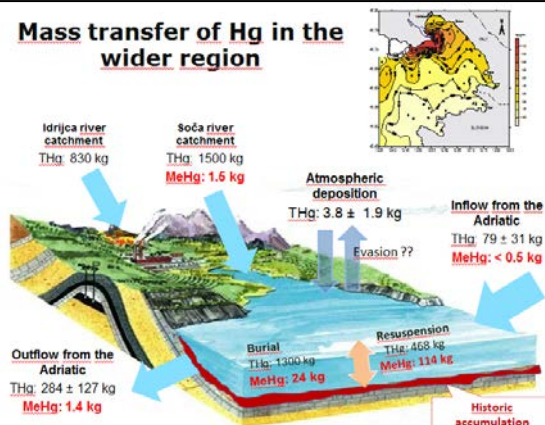
## 2. Physical elimination



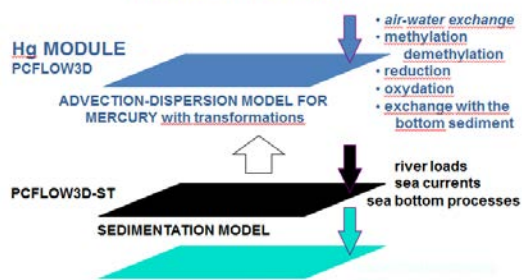
- Changes in land use - replacement of agricultural or bare landscapes to forest
- Scenario: reduction of terrestrial load up to 30 %

- Removal of the top soil layer, surface leveling and forestation
- Scenario: reduction of Hg emission up to 50 %

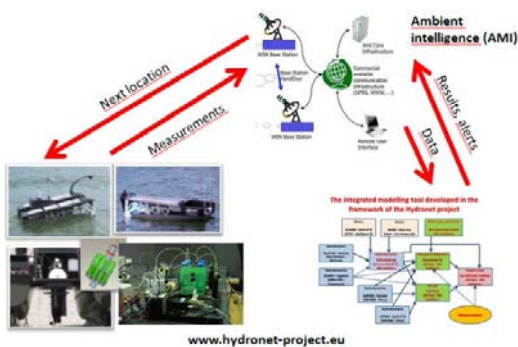
## Mass transfer of Hg in the wider region



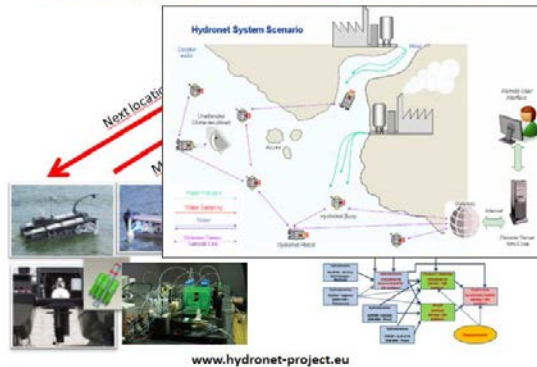
## CONCEPT OF THE 3D WATER MODELING SYSTEM (MARINE ENVIRONMENT)



## Modelling using „automated“ measurements



## Modelling using „automated“ measurements

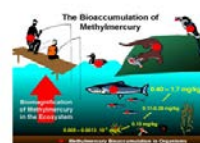
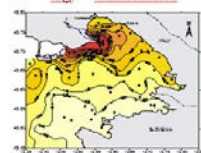


## Need for (nearly) real-time modelling

- A perpetual/averaged year (season...) does not exist.
- Variability in nature is extremely high:
  - Air-sea fluxes change with wind (hourly !)
  - Transformations depend on BGC parameters (daily !)
  - Transport depends on meteorology and hydrology (daily !), etc...
- The data collected „automatically“ by the floating robots can thus only be used in models with:
  - Fine spatial resolution and
  - Real-time hydrodynamic fields
  - Particularly important in small (costal) areas...

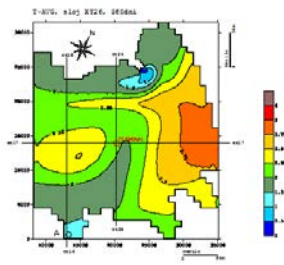
## Gas terminals in the Gulf of Trieste?!

## Hg in sediments

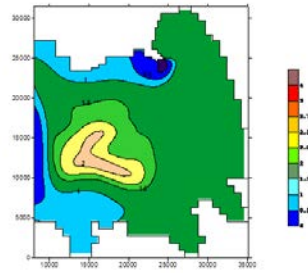


## MeHg in fish

0.40 mg/kg → 0.56 mg/kg



Qualitative distribution of MeHg in the surface layer (1 m) caused by one-year operation of the offshore terminal (percentage of the initial input – 81 kg). The discharge of Soča River is changing by seasons, inflow with no MeHg. Location of mariculture is marked by (A).



NEW LOCATION OF THE OFFSHORE TERMINAL: Qualitative distribution of MeHg in the surface layer (1 m) caused by one-year operation (percentage of the initial input – 50 kg). The discharge of Soča River is changing by seasons, inflow with no MeHg.

### The model(s) are capable of:

- ✓ Nearly real-time simulations (daily !) of hydrodynamic fields in selected areas,
- ✓ Transport/dispersion (and basic transformation) simulations based on hydrodynamic quantities,
- ✓ The simulation results provide support to the Ambient Intelligence tool and the robots,
- ✓ Using today's measurements for tomorrow's simulations.





## Mercury concentration in fish muscle (*Pargus major*) based on current seawater characteristics of Minamata Bay

Akito Matsuyama

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In Minamata Bay, the dredging project involving sediment with a mercury concentration of more than 25 ppm was implemented from 1977 until 1990. Then, currently, *Sebastiscus marmoratus*, and *Pseudolabrus japonicus* are specified as a monitoring fish for mercury pollution in Minamata Bay. Recently, average values of total mercury concentration in fish muscle for 3 years (2008-2010) of these fishes were 0.36 ppm and 0.20ppm, respectively. On the other hand, the average values of total mercury concentrations of these fishes in Japan are 0.12 ppm and 0.04 ppm respectively. FDA (2001, 2004) and Health Canada (2008) suggested that a part of mercury accumulated in fish is derived from seawater. Therefore, to evaluate absorption and accumulation of mercury in fish, the fish cage experiment using young fish (red sea bream) and a special fish food that do not include mercury was carried out for 2 years continuously in Minamata Bay and Nagashima (control). As a result, there was no difference on mercury accumulation in fish muscle (red sea bream) between Minamata Bay and Nagashima. Therefore, generally, in case of red sea bream, it seems to be most mercury that was accumulated in fish muscle is not from seawater, then it was reconfirmed that most mercury that was accumulated in fish muscle is from diet in the sea based on our results.

### 水俣湾の現在の海水特徴に基づく魚（マダイ）筋肉中の水銀濃度

水俣湾では 1977 年から 1990 年にかけて水銀濃度 25ppm を超える堆積物を埋め立てるため浚渫工事が行われた。現在カサゴとササノハベラが水俣湾の水銀汚染観察対象魚とされている。

この 3 年間（2008～2010）、この魚の筋肉における水銀濃度平均値はそれぞれ 0.36ppm、0.20ppm であった。一方、日本におけるこの魚の一般的な水銀濃度平均値は各々 0.12ppm、0.04ppm である。FDA と Health Canada では魚の水銀蓄積の一部は海水によるものとしている。

よって、魚の水銀蓄積とその吸収を評価するため真鯛の稚魚と水銀を含まない特定の餌を使用し、魚ケージによる実験を 2 年間連続で水俣湾と長島（対象地）の海水域で行った。

その結果、魚（真鯛）の筋肉における水銀蓄積には水俣湾と長島間での違いは認められなかった。よって真鯛に関しては、魚の筋肉に蓄積される水銀のほとんどは海水によるものではなく、そのほとんどは海から採取される食物によることが再確認された。

## Mercury concentration in fish muscle (Pargus major) based on current seawater characteristics of Minamata Bay

National institute for Minamata disease  
Epidemiology department Risk evaluation section

Akito Mtsuyama

### Background (1)

- Dredging project for elimination of mercury in Minamata Bay already finished at 1990. However, currently, sediment that contains less than 25 ppm as mercury is remain in Minamata bay. As a result, currently, total mercury concentration in sediment /Minamata Bay is almost less than 10 ppm.
- In order to grasp the condition of mercury pollution in Minamata Bay, nowadays, *Sebastiscus marmoratus* and *Pseudolabrus japonicus* are specified as a monitoring fish in Minamata Bay.



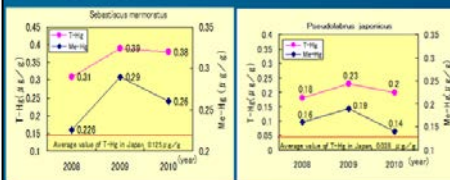
*Sebastiscus marmoratus*



*Pseudolabrus japonicus*

Chronologically variation of mercury concentration in fish muscle on the monitoring fishes (*Sebastiscus marmoratus* and *Pseudolabrus japonicus* 2008-2010).

※Japanese regulatory standards of T-Hg and Me-Hg in fish muscle are  $0.4 \mu\text{g/g}$ ,  $0.3 \mu\text{g/g}$  respectively



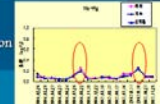
(Ministry of Health, Labour, and Welfare. Results of investigation on mercury that was accumulated in seafood, 2004)

### Background (2)

#### ■ Typical data of dissolved mercury concentrations of sea area in the world

	(A) diss-Hg ng/L	(B) diss-methyl ng/L	(C) SS-Hg ng/L	(B)/(A) %
Northern Adriatic Sea (Pavesi et al., 2002)	$1.8 \pm 1.40$	$0.02 \pm 0.03$	$4.94 \pm 0.94$	1.1
Mediterranean Sea (Al-Ram et al., 2003)	$0.29 \pm 0.082$	$0.038 \pm 0.008$		13
Western Mediterranean (Cossa et al., 1997)	$0.51 \pm 0.25$	nd		
Chesapeake Bay (Robert P. Mason et al., 1998)	4.0 or less	$0.02 \pm 0.02$		1.25
New York-New Jersey Harbor (Preston N. Bittow et al., 2007)	$0.78 \pm 0.08$	$0.02 \pm 0.002$	$27.6 \pm 0.0$	2.6
Nagashima fish cage (2 years average)	$0.22 \pm 0.06$	$0.02 \pm 0.01$		10.0
Minamata fish cage (2 years average)	$0.45 \pm 0.10$	$0.10 \pm 0.07$		22.2

■ From mercury monitoring in Minamata bay for 5 years continuously, dissolved methylmercury concentration was a high level in summer in comparison with other seasons as a special tendency.



### Background(3) and Study Objective

Currently, Minamata fisheries cooperative esteem fish cultivation and seaweed cultivation in Minamata Bay. On the other hand, influences of seawater quality of Minamata Bay as for fishes and so on in Minamata bay were worried. Especially, influences of mercury in Minamata Bay are very important.



- Based on above mentioned, in order to contribute people in Minamata city, we should grasp whether seawater quality of Minamata Bay that contains mercury affects to fishes or not.

### General concepts of mercury accumulation in fishes

○ Dissolved mercury in seawater is absorbed from fish gill and then, since marine fishes drink seawater to keep water content constant in their body, there is a possibility that dissolved mercury in seawater is absorbed from intestinal tract of fish. Also, dissolved mercury is absorbed from fish body surface too.

(FDA 2001, 2004 J. Mactz et al.)

○ Inorganic mercury in seawater is organized on surface of gill, intestinal tract, etc by microorganisms activity, then sign is recognized that it was absorbed to fishes.

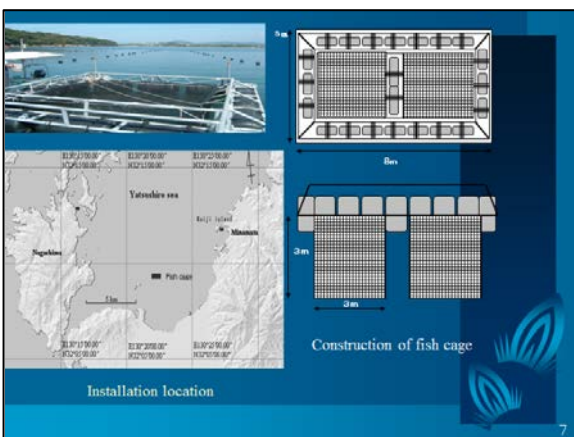
(NIHS 1997)

○ Even if inorganic mercury in seawater is absorbed in fishes, it is not organized in fishes.

(Kikuchi et al 1981 Rucker et al 1979)



However, the investigation related to mercury accumulation of fishes in general sea area that has comparatively high mercury level is rare.



### Conditions of fish cage experiment

<Installation location>  
Minamata Bay, Nagashima (as a control)

<Fish species>

Red sea bream (mean body weight  $112.4 \pm 15.3$  g, n=10, mean body size  $8 \pm 0.4$  cm)  
※ 300 red sea bream (*Pargus major*) were introduced into each fish cages.

<Experimental term and design>

first time 2009 end of February to end of September

second time 2010 middle of March to middle of December

All test fish were fed synthesized food with almost no mercury at feeding rate 2% every week day.

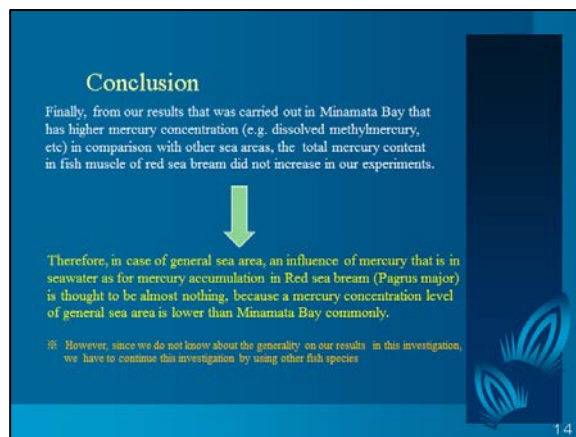
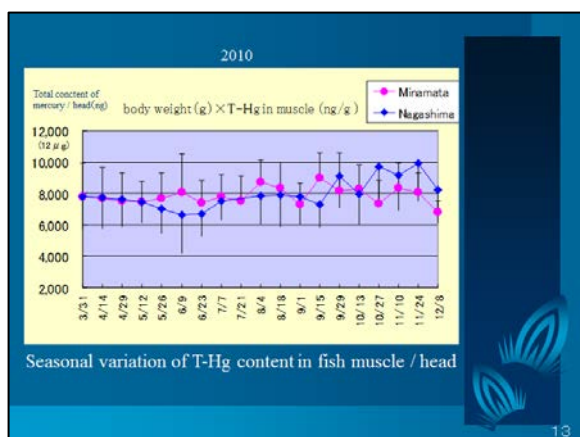
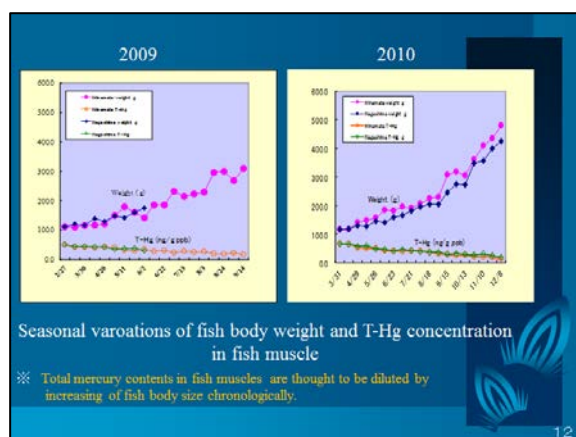
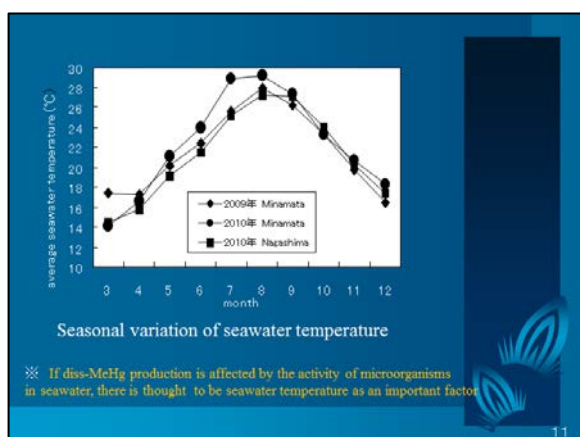
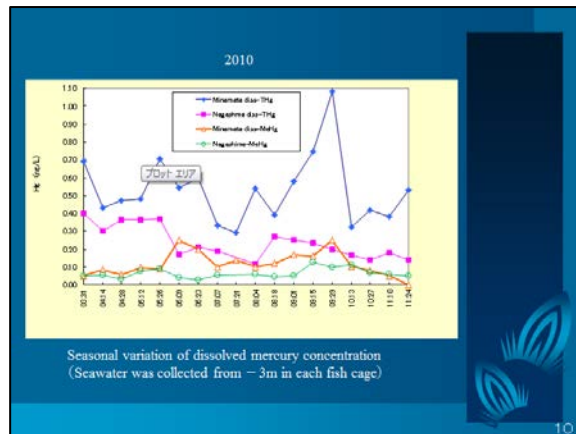
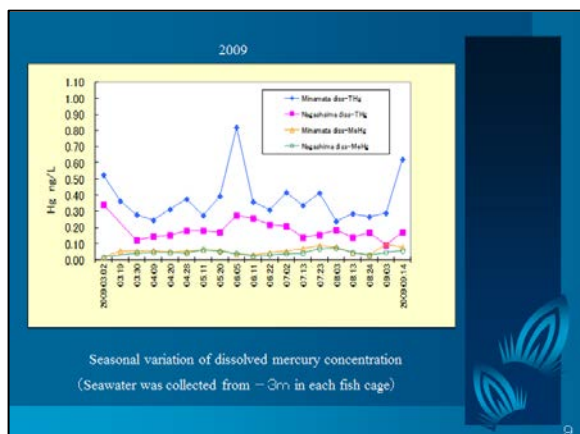
※ The special food that is not contain mercury is made by Faculty of Fisheries, Kagoshima University

<Sample collection>

Ten fish were randomly collected from both fish cages every 10 days. Also, simultaneously, the seawater samples were collected at 3m depth using a teflon. Bailers from each fish cage.

<Analysis and measurement>

Fish\*\*\*body size, body weight, THg : MeHg in fish muscle  
Seawater\*\*\*temperature,  $\text{Ca}^{2+}$ , pH, dissolved THg, dissolved MeHg, SS weight, THg : MeHg in SS



## **Mercury in contaminated coastal sediments: novel approaches in source appointment**

**Nives Ogrinc<sup>1</sup>, Milena Horvat<sup>1</sup>, Jože Kotnik<sup>1</sup>, Jadran Faganeli<sup>2</sup>,**

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Contamination with mercury (Hg) on coastal sediments is initially suspected based on historical land use such as mining or industrial activity. Hg mining results in a legacy of contamination that can occur on large distances from the source. The Gulf of Trieste represents an ideal case study where large quantities of Hg have been released into the environment of Hg mines due to inefficient mining procedures and incomplete extraction of Hg in Idrija mining district. Several research studies were performed in order to track the transport and transformation pathways of Hg in this Hg contaminated coastal region (Horvat et al., 1999, Covelli et al., 2001). It was found that Hg was methylated and demethylated everywhere in the gulf sediments (Hines et al., 2000). The freshwater to marine gradient is dynamic, exhibiting seasonally and horizontally variable rates of sulfate reduction and Hg transformation. Hg mobilization and methylation were driven by S cycling, but coastal demethylation may significantly attenuate the accumulation of methylmercury (MeHg). In general concentrations of MeHg correlates well with total Hg in sediments in non-contaminated environments (Ogrinc et al., 2007), however this is not always the case in polluted coastal environments, indicating that environmental factors play an important role in mercury fate and transport. As expected, the ratio between MeHg and total Hg in sediments is low with an average value of 0.32. Novel instrumental techniques based on stable isotope fractionation were also applied in order to trace the sources of Hg in surficial sediments of the gulf (Foucher et al., 2009). It was found that the Hg isotopic composition of river sediment was similar to that of cinnabar ore from upstream. We concluded that sediments throughout the watershed of Soča/Isonzo River to the Gulf of Trieste were dominated by Hg exported from the headwaters near the Idrija Hg mine progressively decreasing from > 90% in the northern part to < 45% in the southern Gulf.

### **References:**



Covelli, Stefano, Faganeli, Jadran, Horvat, Milena, Brambati, Antonio. 2001. Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea). *Appl. geochem.*, 16/4, 541-558.

Foucher Delphine, Ogrinc, Nives, Hintelmann Holger. 2009. Tracing Mercury Contamination from the Idrija Mining Region (Slovenia) to the Gulf of Trieste Using Hg Isotope Ratio Measurements. *Environ. Sci. Technol.*, 43 (1), 33-39.

Hines, Mark, Horvat, Milena, Faganeli, Jadran. 2000. Mercury biogeochemistry in the Idrija river, Slovenia from above the mine into the Gulf Trieste. *Environ. Res.* 83/A, 129-139.

Horvat, Milena, Covelli, Stefano, Faganeli, Jadran, Logar, Martina, Fajon, Vesna, Rajar, Rudolf, Širca, Andrej, Žagar, Dušan. 1999. Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *Sci. Total Environ.*, 237/238, 43-56.

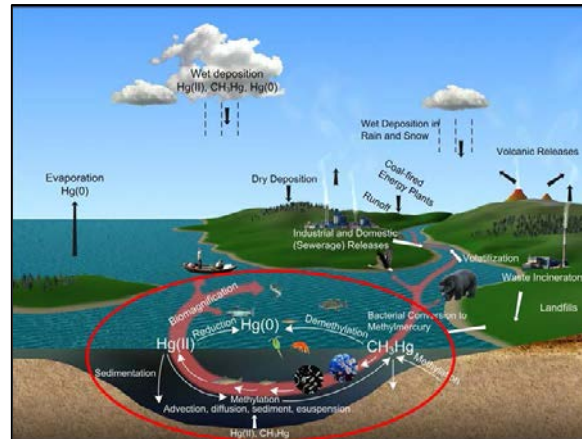
Ogrinc, Nives, Monperrus, Mathilde, Kotnik, Jože, Fajon, Vesna, Vidimova, Klara, Amouroux, David, Kocman, David, Tessier, Emmanuel, Žižek, Suzana, Horvat, Milena. 2007. Distribution of mercury and methylmercury in deep-sea surficial sediments of the Mediterranean Sea. *Mar. Chem.* 107/1, 31-48

### 汚染された沿岸沈殿物中の水銀：起源選定の新しいアプローチ

沿岸部底質中の水銀汚染は、当初、鉱工業活動などの歴史的な土地利用によるものと考えられた。水銀採掘は発生源から広範囲の汚染という負の遺産を残した。トリエステ湾はイドリヤ鉱業地区の非効率の採掘方法と不十分な水銀抽出により、大量の水銀が環境に流出した典型的な事例である。輸送経路および汚染沿岸部での水銀の変容経路の様々な研究が行われ（Horvat et al.,1999, Covelli et al.,2001）、水銀のメチル化、脱メチル化は湾内底質の至る所で起きていることが分かった（Hines et al., 2000）。淡水から海水への勾配は変化に富み、硫酸還元や水銀変容は季節および水深による変動が見られる。水銀動態とメチル化は S サイクリングによって起こるが、沿岸部での脱メチル化はメチル水銀の蓄積をかなり抑制している可能性がある。通常、メチル水銀濃度は汚染のない環境では底質中の総水銀に相関するが（Ogrinc et al.,2007）、汚染沿岸部では必ずしもそうではなく、環境要因が水銀の最終形態や輸送に大きな役割を果たすことを示唆している。また、河川底質中の水銀同位体組成は上流からの辰砂鉱石と同様であることが分かった。このことから我々は、ソカ/イゾンツォ川の分水地点からトリエステ湾にいたる底質は、イドリヤ水銀鉱山近くの源流から運ばれた水銀がおそらく北部では 90%以上から湾南部では 45%以下のレベルで、蓄積していると結論づけた。

## Mercury in contaminated coastal sediments: novel approaches in source appointment

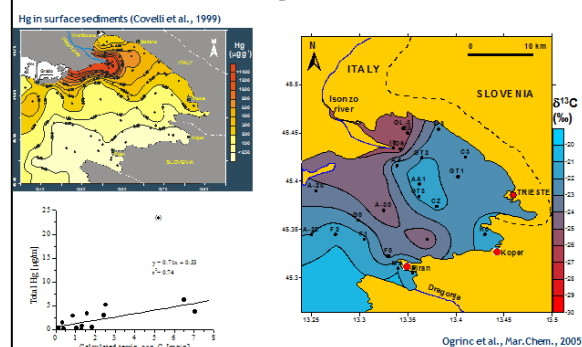
N. Ogrinc, M. Horvat, J. Kotnik,  
Jožef Stefan Institute, Ljubljana, Slovenia  
J. Faganeli  
National Institute of Biology, Piran, Slovenia  
M. Hines  
University of Massachusetts, Lowell, USA  
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Trent University, Peterborough, Canada



### Hg speciation in surface deposits of marine system

Location	THg (nmol g <sup>-1</sup> dry wt)	MeHg (pmol g <sup>-1</sup> dry wt)	MeHg/THg (%)	Reference
San Francisco, CA	1.1 (0.10-3.50)	2.5 (<0.1-17.0)	0.20	Conaway et al., Mar.Chem., 2003
Lavaca Bay, Texas	1.79 (0.03-3.92)	12.5 (0.14-51.7)	0.70	Bloom et al., ES&T, 1999
Chesapeake Bay, Maryland	2.25 (0.05-6.15)	14 (0.50-50.0)	0.62	Mason et al., Environ.Toxicol. Chem., 1999
Scheldt River Estuary, Belgium	2.31 (0.76-4.73)	13.9 (7.00-24.6)	0.60	Baeyens & Leermakers, Mar. Chem., 1998
Venice Lagoon	6.5 (0.50-17.0)			Berto et al., STOTEN, 2006
Kastela Bay, Adriatic	11.0 (2.50-30.7)	48 (15-100)	0.44	Mikac et al., Wat. Res., 1985
Minamata Bay, Japan	16.2 (1.70-24.1)			Tomiyasu et al., STOTEN, 2006
Gulf of Trieste, Adriatic	26.2 (0.05-117)	84.5 (1.00-301)	0.32	Covelli et al., Appl. Geochem., 2001

### Relation between Hg and OC - Gulf of Trieste



- $K_D$  values for Hg(II): range  $10^3$ - $10^5$
- $K_D$  values MeHg: range  $10^{1.5}$ - $10^{3.5}$
- $K_D$  values for Hg(II) and MeHg:  
10-100 less than those in oxic overlaying water
- Concentrations in pore waters:  
5 - 50 pM for Hg(II) and 1- 30 pM for MeHg
- MeHg/THg: 5 - 50%, most values 10 and 30%

### MeHg cycling and production

#### The net production of MeHg:

- Loadings of Hg(II)
- Partitioning of Hg species with solid-phase OM
- Effect of sulfide on speciation of Hg complexes
- Availability of labile organic substrates
- Temperature
- Sediment disturbance (bioturbation)

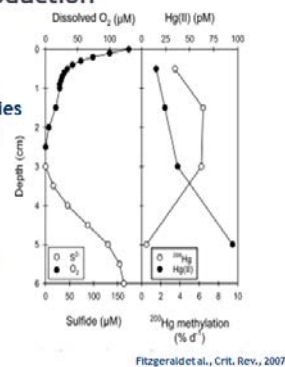
#### Solid-phase MeHg:

- Methylation/demethylation reactions
- Adsorption/desorption mechanisms
- Diffusional/advective processes

### MeHg cycling and production

**HgS<sup>0</sup> - Hg-S complex most available for bacteria**  
Hg(SH)<sub>2</sub><sup>0</sup> - the dominant species in contaminated organic-rich sediments  
(Drott et al., ES&T, 2007)

HgHS<sub>2</sub><sup>-</sup> - formed deeper in sediments; less bioavailable



### Demethylation of MeHg

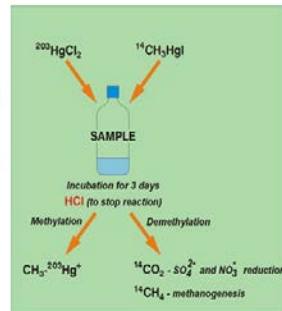
- Microbial mediated process
- Reductive demethylation (CH<sub>4</sub> is synthesized from the Me group): Hg-polluted sediments
- Rate constants are 10-1000 times greater comparing to Hg methylation

### Protocols for methylation/demethylation studies

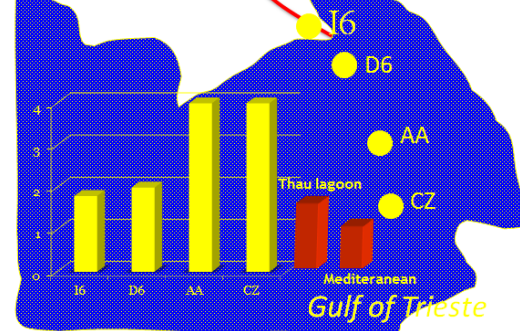
Stable isotopes of Hg:  
 $^{199}\text{Hg}$   
(CNRS UMR, University of Pau)

Radioactive isotope  $^{197}\text{Hg}$   
formed from  $^{196}\text{Hg}$

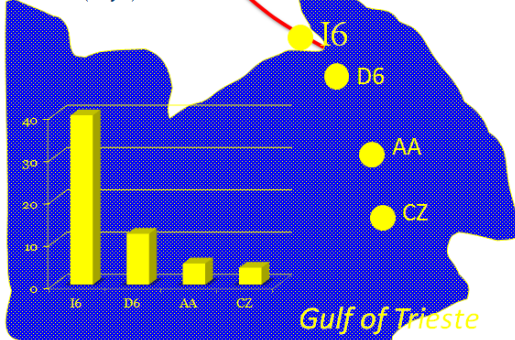
Gulf of Trieste  
Thau lagoon  
Grado lagoon  
Mediterranean deep-sea



### Hg Methylation (day<sup>-1</sup>)



### Hg Demethylation (day<sup>-1</sup>)



### Diffusional sediment-water fluxes of MeHg from coastal marine deposits

Location	Sediment-water flux (pmol m <sup>-2</sup> d <sup>-1</sup> )	Reference
Continental shelf (NW Atlantic)	9	Hammerschmidt & Fitzgerald, GCA, 2006
Mediterranean Sea	16	Ogrinc et al., Mar.Chem., 2007
San Francisco Bay, CA	30	Choe et al., Limnol.Oceanogr., 2004
New York/New Jersey Harbor	44	Fitzgerald et al. Mar.Chem., 2007
Long Island Sound, CT/NY	47	Hammerschmidt et al., Mar.Chem., 2004
Lavaca Bay, TX	210	Gill et al., ESBT, 1999
Gulf of Trieste, Adriatic	2156	Covelli et al., ECSS, 1999

### Hg - tracer for anthropogenic sources

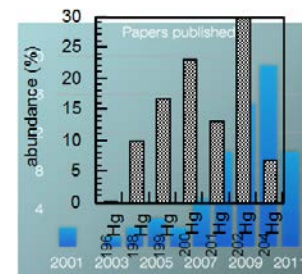
- Over 5x10<sup>6</sup> metric tons of Hg ore, mostly cinnabar, were excavated for 500 years.
- Hg historical trend well correlated with excavation.
- Hg accumulation range from 1.77 to 31.5 mg m<sup>-2</sup> yr<sup>-1</sup>.

Determination of sedimentation rate

Covelli et al., Mar. Geol., 2006

### Hg isotope system

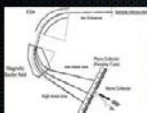
- 7 stable isotopes
- Hg forms covalent bonds, rich redox chemistry, bioaccumulates
- relatively new field, first reliable measurements reported in ~2000



Future perspectives!

### Equipment

- Multicollector Inductively Couple Plasma Mass Spectrometry MC-ICP/MS: isotope ratio precision: 0.001%



- single collector ICP/MS: precision of 0.1%
- BUT: requires ~ 10-20 ng of Hg for a single measurement!!
- exact concentration matching: standard/sample within 10%

### Data reduction

Standard bracketing approach:

$$\delta^{202}\text{Hg} (\text{‰}) = \frac{^{202}\text{Hg} / ^{199}\text{Hg}_{\text{sample}}}{^{202}\text{Hg} / ^{199}\text{Hg}_{\text{standard}}} - 1$$

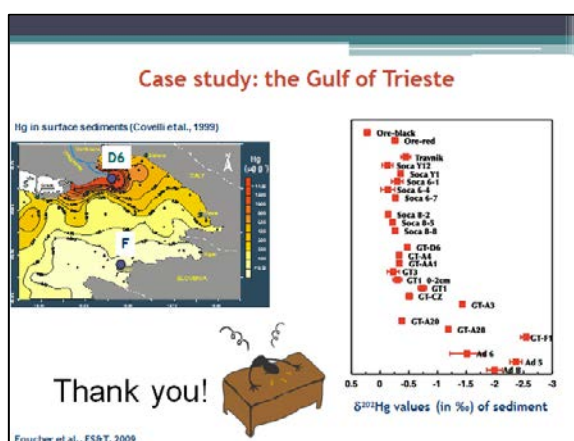
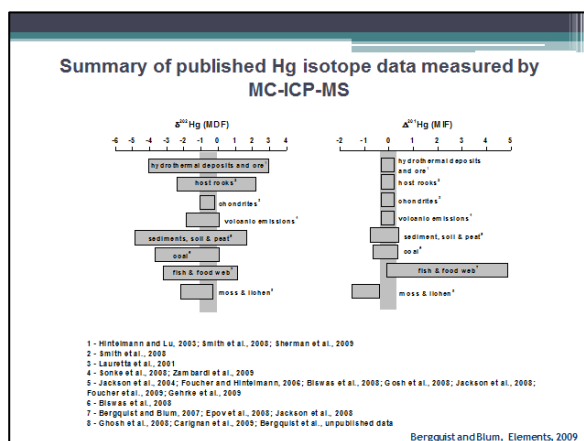
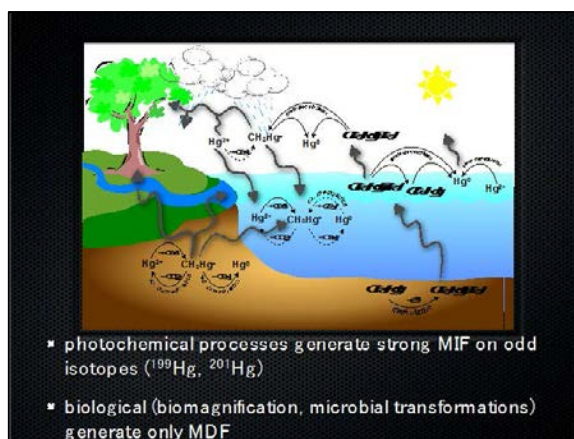
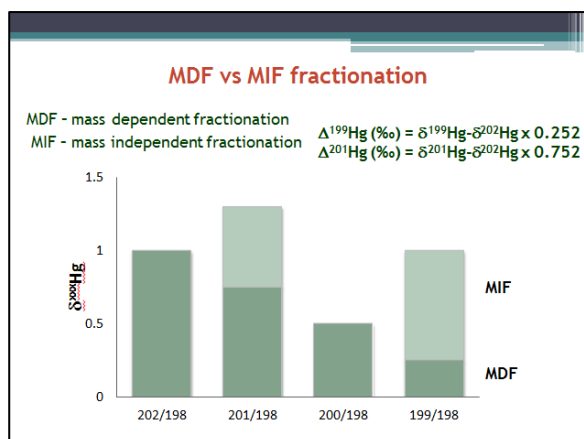
$\delta^{202}\text{Hg} (\text{‰})$  -3.0 -2.0 -1.0 0.0 +1.0

enrichment of the sample with lighter isotopes

enrichment of the sample with heavier isotopes

Isotopic Reference Standard





## Mercury pollution by many small-scale gold ore smelters in Talawaan River, North Sulawesi, Indonesia.

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A new gold ore deposit was found in the Talawaan region, North Sulawesi, Indonesia, in 1996, which was followed by establishment of a great number of small-scale gold ore smelters upstream in the Talawaan River from 1998 to 2000. The smelters distribute in a triangular-shaped region around Dimembe, Talawaan and Tatelu Villages, which we named AT (auriferous triangle). In order to evaluate mercury behavior in the environment after release from the smelters, we determined the methylmercury (MeHg) as well as total mercury (THg) levels in sediments at more than 10 stations along the Talawaan River in 2010 and 2011. Furthermore, we conducted to catch some species of fishes along the stream to clarify the bio-accumulation of mercury

Geometric means of sediment T-Hg and MeHg concentrations in the river were 0.31 µg/g and 0.92 ng/g, respectively. The maximum THg and MeHg levels were both detected inside AT, as 3.25 µg/g and 9.20 ng/g. MeHg distributions were highly correlated with those of T-Hg, which implies that MeHg was generated from the elemental mercury derived from the artisanal gold mining waste materials. In addition, MeHg concentrations in sediment samples were correlated with amounts of ignition loss.

Some carnivorous fish showed high value of Hg, and the accumulation of MeHg in fishes in this area in the food web was observed. Thus, we infer that metallic mercury diffusion from mining into the environment causes bio-accumulation of MeHg in the Talawaan watershed

### インドネシア、北スラウェシ、タラワン川の多くの小規模の金鉱石精錬所による水銀汚染

1996 年インドネシア、北スラウェシのタラワン地域で新たな金の鉱床が発見された。そしてその後 1998 年から 2000 年にかけてタラワン川上流に非常に多くの小スケールの金鉱石製錬所が作られた。製錬所は、我々が AT（金を産する三角形）と名付けたディメンベ、タラワンそしてタテル村の周りの三角形の地域に分布している。製錬所から放出された後の環境中での水銀の動きを査定するために、我々は 2010 年から 2011 年までタラワン川に沿って 10 か所以上においてメチル水銀と総水銀レベルを測定した。さらに、我々は水銀の生物濃縮を明らかにするために流れに沿って幾種類かの魚の捕獲を指揮した。

川の堆積物の総水銀とメチル水銀濃度の幾何平均値は、それぞれ 0.31  $\mu\text{g/g}$  と 0.92  $\text{ng/g}$  であった。総水銀とメチル水銀レベルの最高値は 3.25  $\mu\text{g/g}$  と 9.20  $\text{ng/g}$  で、両者ともに AT 内で検出された。メチル水銀の分布は総水銀の分布と密接な関係があり、メチル水銀は小規模金採鉱からの廃棄物から出てきた元素水銀から作り出されることを示唆している。加えて、堆積物サンプル中のメチル水銀濃度は強熱減量と相互に関連がある。

幾種類かの肉食性魚類は、高い水銀値を示し、この地域における食物連鎖中のメチル水銀の蓄積が観察された。このように我々は鉱山から環境中への金属水銀の拡散がタラワン流域のメチル水銀の生物濃縮を引き起こしていると推論する。



## Mercury pollution by many small-scale gold ore smelters in Talawaan River, North Sulawesi, Indonesia.

<sup>1</sup>K. Mori, <sup>2</sup>M. T. Lasut, and <sup>1</sup>Y. Yasuda

<sup>1</sup> National Institute for Minamata Disease, Japan

<sup>2</sup> Marine Science Department, Faculty of Fisheries and Marine Science, Sam Ratulangi University, Indonesia

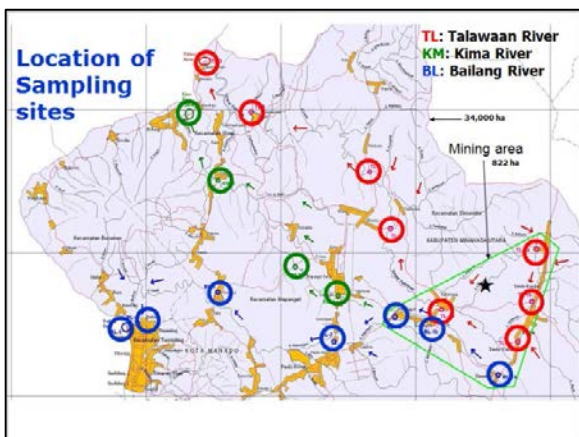
## Japan and North Sulawesi



## Talawaan gold mining area



Watershed covers 34,000ha  
Three rivers flow-out from the gold mining area:  
Talawaan River, Kima River and Bailang River  
Mining area: 822 ha, includes 8 villages,  
2,500-3,000 laborers  
Method: Mercury amalgamation (1994 trommel),  
Cyanide (58 CII-ponds) Both are used in  
combination  
Earning: 30 billion Rp (more than 400 million Yen) per  
year  
Mercury consumption: 2kg Hg / trommel x 500 trommel  
x 200 days = 200 t Hg / year (Indonesian  
Government Report)  
Mercury discharge to atmosphere: 11.2 t / year



A new gold ore deposit was found in the Talawaan region, North Sulawesi, Indonesia, in 1996, which was followed by establishment of a great number of small-scale gold mines upstream in the Talawaan river from 1998 to 2000.

The gold mines distribute in a triangular-shaped region around Dimembe, Talawaan and Tatelu Villages, which we named AT (auriferous triangle).

From 2004, government has integrated the factories at the small area.

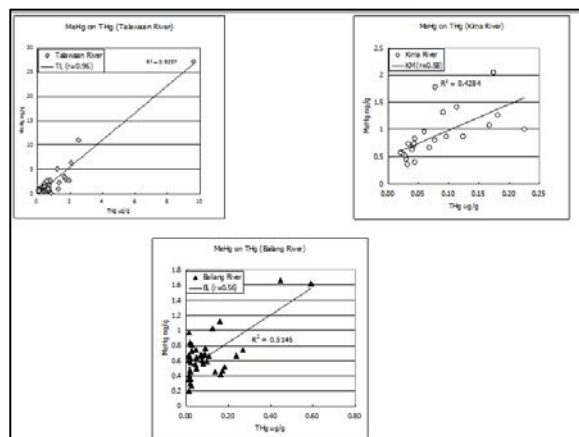
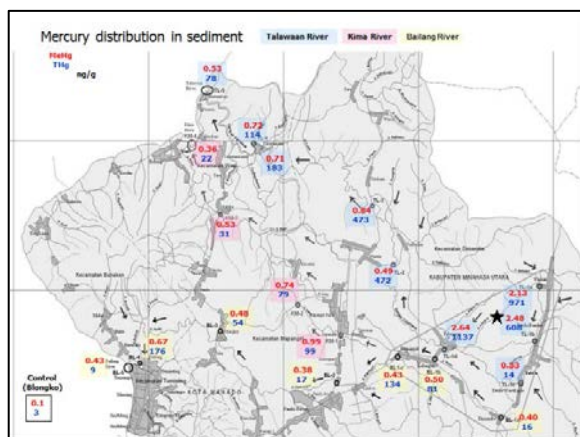
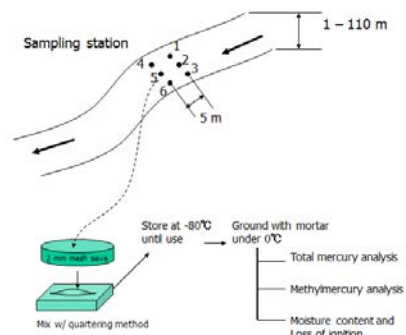
Mercury distribution changed and concentrated?





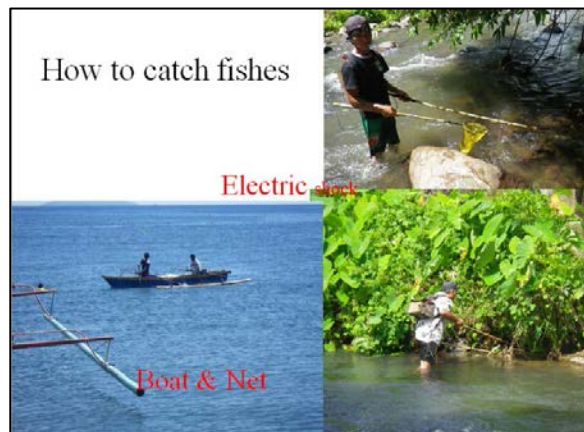
In order to evaluate mercury behavior in the environment after release from each mine, we determined the methylmercury (MeHg) as well as total mercury (THg) levels in sediments at more than 10 stations along the Talawaan River.

### Sampling Procedures for Sediments

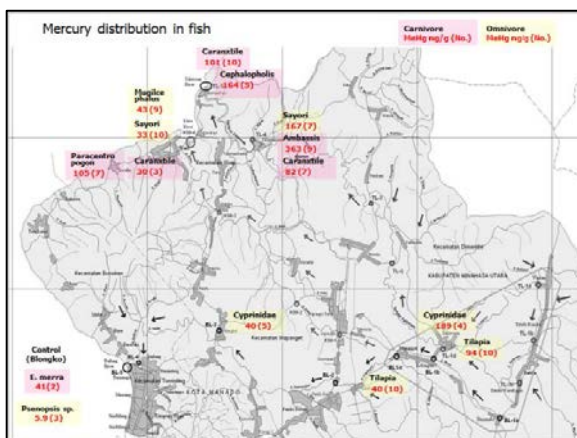


- Mercury concentration of fishes  
for bio-accumulation analysis
- Stomach contents of fishes  
for food web analysis

### How to catch fishes



### Stomach Contents of fishes



### Results

- Sediment mercury
  - Geometric means of THg 0.31 μg/g
  - MeHg 0.92 ng/g
  - The maximum THg 3.25 μg/g
  - MeHg 9.20 ng/g.
- MeHg distributions were highly correlated with those of THg
- Bioaccumulation of MeHg in fishes was observed.
  - Carnivorous fishes show high value of mercury concentration.



## **Biomarkers of low level mercury exposure: exposure, impact and genetic susceptibility**

**Janja Snoj Tratnik<sup>1</sup>, Ana Miklavčič<sup>1</sup>, Simona Jurković Mlakar<sup>6</sup>, Darja Mazej<sup>1</sup>, Mladen Krsnik<sup>2</sup>, Joško Osredkar<sup>2</sup>, Fabio Barbone<sup>3</sup>, Marika Mariuz<sup>3</sup>, Francesca Valent<sup>3</sup>, Katia Sofianou<sup>4</sup>, Zdravko Spirić<sup>5</sup>, Janja Marc<sup>6</sup>, Milena Horvat<sup>1</sup>**

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<sup>3</sup>: Unit of Hygiene and Epidemiology, University of Udine, Udine, Italy

<sup>4</sup>: Institute of Child Health, "Aghia Sophia" Children's Hospital, Athens, Greece

<sup>5</sup>: Institute for Applied Ecology, Oikon Ltd., Zagreb, Croatia

<sup>6</sup>: University of Ljubljana, Faculty of Pharmacy, Department of Clinical Biochemistry, Slovenia

Speciation of mercury (Hg) in biological samples is often disregarded when assessing methyl mercury (MeHg) exposure. To evaluate how good measure of prenatal low-level exposure to MeHg is total mercury (THg) concentration, we have assessed the relation between these two species of mercury in available biological samples. THg was determined in 2153 scalp hair samples, 1654 umbilical cord blood samples, 1081 maternal blood samples, and 1051 breast milk samples in pregnant/lactating women from Slovenia, Croatia, Italy and Greece. MeHg was determined in approx. 30 % of the samples. As it is well known that selenium (Se) can play a protective role against Hg toxicity in organisms, Se was determined in all samples together with THg in order to find an evidence for such connection. In a subset of samples, THg and MeHg were determined also in placenta, fetal membranes, meconium and pubic hair. In order to observe gene-environment interactions, the glutathione S-transferase class - theta 1 (*GSTT1*) and - mu 1 (*GSTM1*) gene deletion variants were studied in a subset of participating women. The study was implemented within the EU 6<sup>th</sup> framework programme PHIME.


The proportion of MeHg in blood and hair was highly variable (14-100 % in blood and 19-100 % in hair) and THg concentration was found liable to overestimate MeHg exposure at low levels. Hair-to-blood MeHg ratio was highly variable as well (67 to 398). We found whole cord blood as the most suitable biomarker of prenatal exposure to MeHg. For accurate assessment of exposure, speciation analyses are required in blood samples, while in hair THg determination is sufficient as an approximate indicator of exposure due to fish consumption. Maternal scalp hair MeHg was associated more strongly with blood than pubic hair MeHg. The significance of placenta as an indicator of MeHg or inorganic Hg exposure is questionable, while meconium was found to indicate MeHg exposure to a certain extent, although a negligible proportion of mercury present as


MeHg in meconium indicated potential demethylation of MeHg in the fetus. Positive and significant linear correlation between Hg and Se was found in cord blood, maternal blood and breast milk. The strongest correlation was observed between inorganic Hg and Se in breast milk of the overall population. Hg and Se were found to be associated positively and significantly also in blood of children aged 6-11 from mercury mine area, but not in children from other areas in Slovenia, confirming the association of Se with *inorganic* Hg, which is the predominant species people are exposed to in the contaminated site. Se in maternal and cord blood, but not in milk, was significantly correlated with the intake of many food items in pregnancy. The strongest direct associations regarded cheese and some vegetables (artichokes and fennels). In addition, both Hg and Se in blood were significantly associated with fish consumption, possibly explaining correlations between these two elements found in selected biomarkers. Hg in milk was not associated with the frequency of fish consumption, but with the number of amalgam fillings. Pregnant women with homozygous deletion of *GSTT1* gene showed significantly higher MeHg (but not total Hg) in cord blood compared to women with the presence of *GSTT1* gene. When adjusted to Se levels in blood, positive and significant associations were observed also for MeHg in maternal blood. No significant differences of MeHg, THg and Se concentrations between *GSTT1* gene deletion variants subgroups were obtained.

#### 低レベル水銀曝露のバイオマーカー：曝露、影響と遺伝学的感受性

胎児の低濃度メチル水銀曝露の測定において、総水銀濃度が有効な指標であることを示すため、生体試料を用いて総水銀とメチル水銀の関係を調べた。スロベニア、クロアチア、イタリアおよびギリシャの妊婦および授乳中の母親から採取した 2153 件の頭髮試料、1654 件の臍帯血試料、1081 件の母体血液試料、1051 件の母乳試料で総水銀を測定、メチル水銀は約 30%の試料で測定した。セレンは生体内では水銀毒性に対する防御作用があることで知られているため、その関連性を調べるため、総水銀と合わせて全試料においてセレンを測定した。一部の試料で、胎盤、胎膜、胎便および陰髪についても総水銀とメチル水銀の測定を行った。

血液および毛髪中のメチル水銀の割合はばらつきが大きく（血液 14–100%、毛髪 19–100%）、総水銀濃度は低濃度でのメチル水銀曝露を過大評価しやすいことが分かった。毛髪対血液のメチル水銀の割合もばらつきが大きい（67–398）。全臍帯血が胎児のメチル水銀曝露に最も適した生体指標であることが分かった。メチルまたは無機水銀曝露の指標としては、胎盤の有意性は疑わしいが、胎便については、胎便内のメチル水銀が胎児のメチル水銀の脱メチル化の可能性を示唆するため、ある程度メチル水銀曝露の指標となることが分かった。臍帯血、母体血、および母乳において、水銀とセレンに有意な正の線形相関が見られた。特に母乳で無機水銀とセレンの高い相関性が見られた。水銀とセレンは、水銀鉱山地区の 6–11 歳の児童の血液にも高い相関性があるが、スロベニアの他の地区の児童にはなく、汚染地区の住民で無機水銀とセレンの関連性が確認できた。

 Institut "Jožef Stefan", Ljubljana, Slovenija



## Biomarkers of low level mercury exposure: exposure, impact and genetic susceptibility

Janja Snoj Tratnik<sup>1</sup>, Ana Miklavčič<sup>1</sup>, Simona Jurkovič Mikar<sup>2</sup>, Darja Mazej<sup>1</sup>, Mladen Krnjack<sup>3</sup>, Joško Osredkar<sup>4</sup>, Fabio Barbone<sup>2</sup>, Marika Mariuz<sup>2</sup>, Francesca Valent<sup>2</sup>, Katia Sofianou<sup>4</sup>, Zdravko Spirin<sup>2</sup>, Janja Marč, Milena Horvat<sup>1</sup>

<sup>1</sup> "Jožef Stefan" Institute, Department of Environmental Sciences, Ljubljana, Slovenia  
<sup>2</sup> University Medical Centre Ljubljana, Institute of Clinical Chemistry and Biochemistry, Ljubljana, Slovenia  
<sup>3</sup> Unit of Hygiene and Epidemiology, University of Udine, Italy  
<sup>4</sup> Institute of Child Health, "Aglaia Sophia" Children's Hospital, Athens, Greece  
<sup>5</sup> Institute for Applied Ecology, Oikon ltd, Zagreb, Croatia  
<sup>6</sup> University of Ljubljana, Faculty of Pharmacy, Department of Clinical Biochemistry, Slovenia

NIMD Forum 2012, Minamata, Japan

# OUTLINE

- Biomarkers of low-level mercury exposure in a general population (Mediterranean) as part of PHIME project
- **General aim:** *To evaluate how good measure of prenatal low-level exposure to methyl mercury (MeHg) is total mercury (total Hg) concentration*
- **Study description, study design**
- **Methods**
- **Results:**
  - \*Total Hg as a measure of MeHg exposure
  - \*Correlation between different biomarkers of exposure (hair, maternal blood, cord blood, milk,...)
  - \*Correlation between Hg and selenium (Se)
  - \*Gene-environment interaction (polymorphism)
- **Conclusions**

[illegible]

# Study design

- GENERAL population, random recruitment
- Only healthy pregnant women, living in non-industrial environment and non-professionally exposed included

Country	Mother-child pairs
Slovenia	300
Croatia	200
Italy	750
Greece	400

N = 1700

The flowchart illustrates the study design timeline. It begins with a timeline from 0 to 9 months, labeled 'Pregnancy'. At 9 months, a 'Delivery' event is marked. Following delivery, a 'Questionnaire: DETAILED Sampling: MAMA' is administered. Simultaneously, 'Sampling: HAIR BLOOD URINE' is performed, accompanied by an image of a child. At 0 months post-delivery, a 'Clinical examination Sampling: CORD BLOOD' is conducted, shown with an image of a newborn. At 12 months, the 'BAYLEY test DENVER II' is administered. Finally, at 6 months, 'Neuro-developmental and psychological get a few more...' are assessed, indicated by a dashed line and an arrow pointing to the right.

	Total mercury	Methyl mercury	Selenium
Blood	Acid digestion and detection by cold vapour atomic absorption spectrometry (CVAAS)	Acid leaching/ solvent extraction/ derivatization and detection by cold vapour atomic fluorescence spectrometry (CVAFS)	Inductively coupled plasma mass spectrometry (ICP- MS)
Breast milk	CVAAS	CVAFS	ICP-MS
Hair	Thermic decomposition, reduction and amalgamation of Hg, and detection by atomic absorption spectrometry (DMA)	evaporation of MeHg into the cystein-impregnated paper/ extraction into toluen and detection by gas- chromatography coupled with electron detection (GC-ECD)	-
Meconium & Placenta	DMA	GC-ECD	-

# Genetical analyses - glutathione S-transferase (GST) genes

- Glutathione (GSH) conjugation to electrophilic compounds (inorganic Hg, MeHg)
- GST1 deletion and GSTM1 deletion → lack of enzyme activity
- Ref. *Environmental Health Perspectives* 2010\*\*\*
- No GST-genetic studies have been done related to MeHg levels

**Interaction between GSTM1/GSTT1 Polymorphism and Blood Mercury on Birth Weight**

*Boo-Gul Kim, Yun-Gul Chung, Hyeyoung Park, Minu Ha, Boe Sang Kim, Naeyeon Chung, Young-Min Kim, Byoung-Hyun Kim, Young-Ju Kim, Byung-Ho Kim, Seung-Joon Yi, and Eun-Ha Yi*

Variations of glutathione transferase, either as a conjugator, a long-term liver enzyme, induce hepatocarcinoma or hepatocellular carcinoma, Seoul National University College of Medicine, Seoul, Korea; Department of Preventive Medicine, Gachon University College of Medicine, Incheon, Korea; Department of Obstetrics and Gynecology, Gachon University College of Medicine, Incheon, Korea; Department of National Science and Food Management, Ewha Woman's University, Seoul, Korea; Institute of Environmental and Industrial Medicine, Hanyang University, Seoul, Korea; Division of Child and Adolescent Psychiatry, Department of Obstetrics Medicine, School of Medicine, Ewha Woman's University; Ministry of Environment, Division of Environmental Health Policy, Seoulshin, Korea

## GSTT1/GSTM1 gene deletion polymorphisms – samples, method

Number of extracted DNA samples

Pregnant women (1 month before delivery –  $N_{\text{ex}}=214$ ) → 212 successfully extracted DNA (10 samples were excluded)

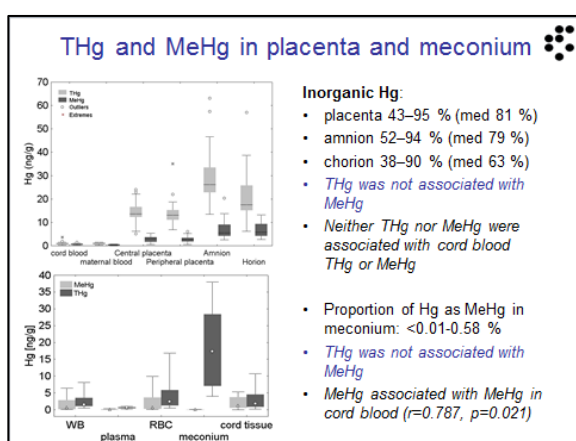
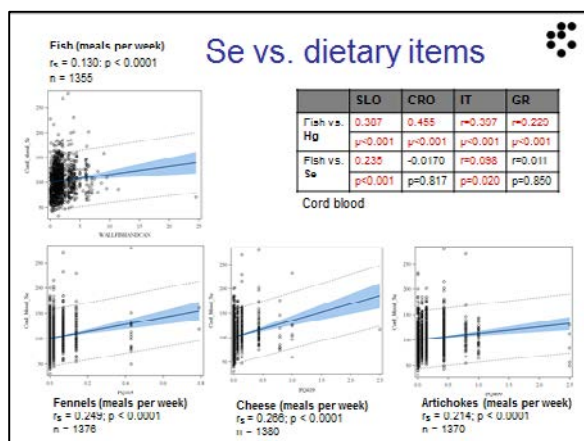
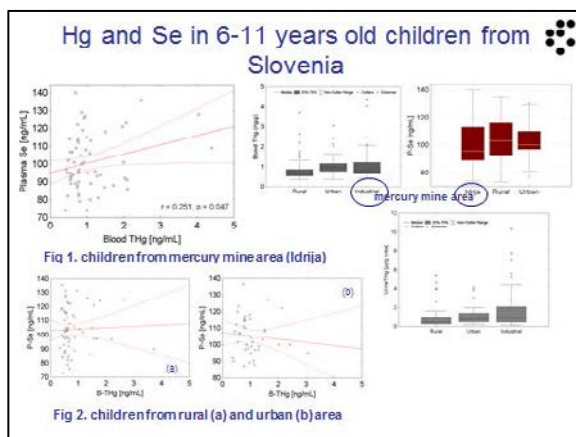
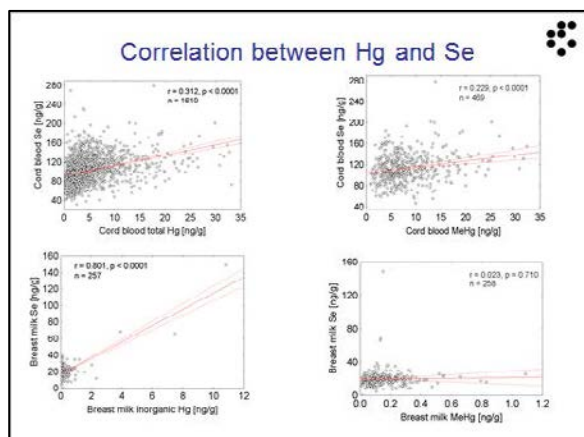
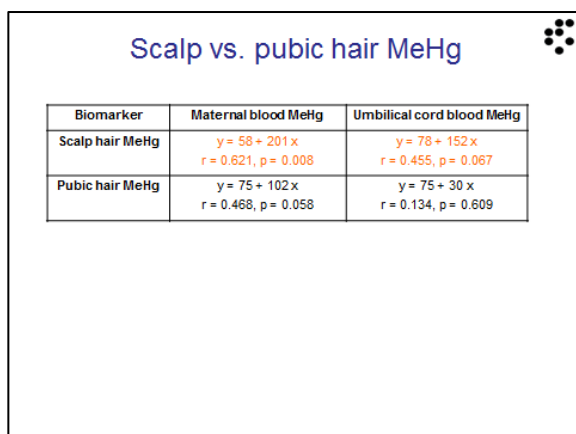
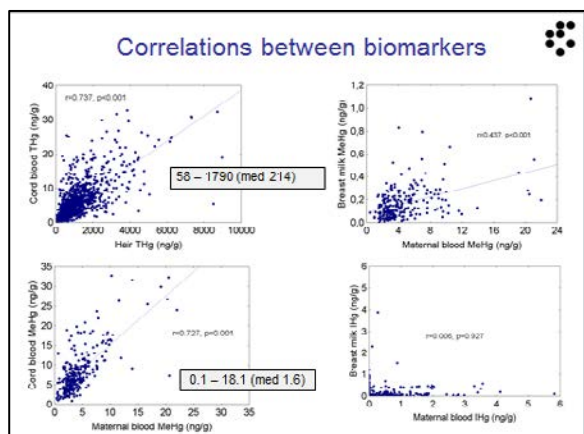
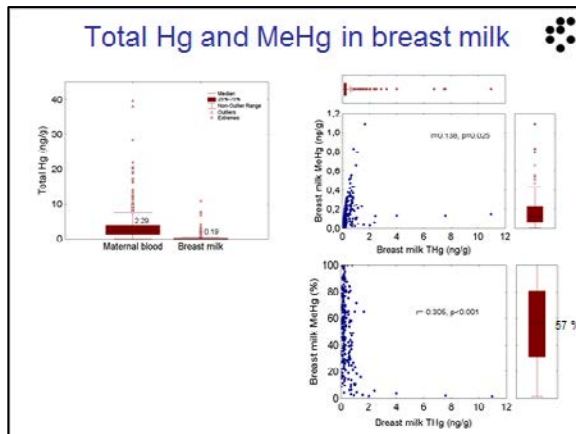
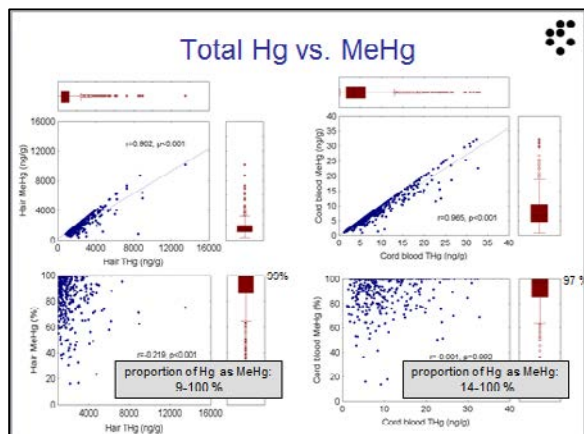
Fig. 1: Multiplex PCR products on 2% agarose gel (80V, 25min)

M, marker with lengths of 50, 150, 300, 500, 700bp; No. 952-962, ID of samples; SL1, negative control

Polymorphism	N of successfully genotyped (tot. 212)
GSTT1 <sub>del</sub>	211
GSTM1 <sub>del</sub>	211

A cartoon illustration of a person with brown hair tied in a bun, wearing a purple long-sleeved shirt and blue pants, sitting on a green chair at a desk. They are using a computer with a CRT monitor displaying a blue screen with white text. The desk is green and has a keyboard on it.





### Association of different biomarkers with potential source of exposure

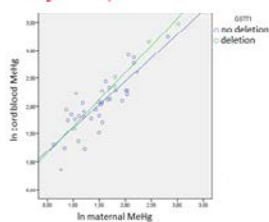
	Frequency of fresh fish consumption	No. of dental amalgam fillings
Cord blood	THg: $r=0.636$ , $p=0.048$ MeHg: $r=0.654$ , $p=0.040$	IHg: $r=0.024$ , $p=0.942$
Scalp hair	THg: $r=0.695$ , $p=0.026$ MeHg: $r=0.700$ , $p=0.024$	THg: $r=-0.471$ , $p=0.122$ MeHg: $r=-0.448$ , $p=0.144$
Placenta or foetal membranes	no data	IHg: $r<0.4$ , $p>0.05$
Meconium	THg: $r=0.656$ , $p=0.040$	no data
Breast milk	THg: $r=0.180$ , $p=0.070$	THg: $r=0.294$ , $p=0.003$
Urine (creatinine corrected)		THg: $r=0.295$ , $p<0.001$ $r=0.335$ , $p<0.001^*$

\*Study on 6-11 years old children

### Gene polymorphisms results

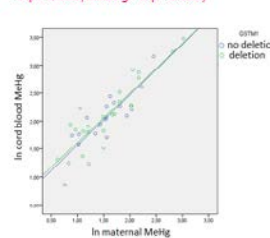
GSTT1 (cord blood vs maternal blood MeHg)

GSTT1 genotype (statistical significant difference between regression lines) (univariate analyses: cMeHg  $\rightarrow p=0.028$ ; mMeHg  $\rightarrow 0.105$ )



GSTM1 (cord blood vs maternal blood MeHg)

GSTM1 genotype (no statistical significant difference between regression lines) (cMeHg  $\rightarrow p=0.295$ ; mMeHg  $\rightarrow p=0.855$ )



No significant results between GSTM1/GSTT1 deletion variants and total Hg levels.

### Covariate analyses – with Se

The next model was shown to be significant ( $p<0.05$ ) in Hg/MeHg analysis:



### Conclusions

<b>Blood samples</b>	Speciation analyses required for accurate assessment of exposure to MeHg / inorg. Hg
<b>Cord blood</b>	THg is an appropriate indicator of MeHg prenatal exposure in general population
<b>THg in hair</b>	sufficient as an approximate indicator of exposure to MeHg resulting from fish consumption
<b>placenta</b>	questionable as an indicator of MeHg or inorganic Hg exposure
<b>Meconium</b>	found to indicate MeHg exposure to a certain extent; potential demethylation of MeHg in the fetus
<b>Breast milk THg</b>	indicates mainly inorg. Hg exposure
<b>Hg and Se</b>	associated in all biomarkers studied ... in BLOOD MeHg, in MILK inorg. Hg
<b>Maternal deletion of GSTT1</b>	associated with higher MeHg (but not total Hg) in cord blood
	Adjustment to maternal blood Se levels increases significant association with maternal blood MeHg concentrations

Thank you for your attention!



Gulf of Trieste

## National Environmental Health Survey - Mercury Concentration in Blood and Urine -

**Hyun Jeong Kim, Choong Hee Park**

*Department of Environmental Health Research, National Institute of Environmental Research*

The first stage of Korean National Environmental Health Survey(KoNEHS) Based on Environmental Health Act(2009) was conducted from 2009 to 2011 in order to find exposure status and pathways of environmental pollutants.

For annually 2,000 adults over the age of 19, total 6,000 people for three years, questionnaire for identifying the exposure factors and analysis of the 16 different toxic pollutants in human blood and urine were performed. The subjects have been selected among urban, rural and coastal areas and regions adjacent to air quality monitoring networks by securing representative concentration of environmental chemicals while considering socio-economical and environmental exposure impact factors.

As the Results of the analysis, the geometric mean of mercury concentration in blood was 3.08 ug/L and men's concentration, 3.65 ug/L, showed high level than women's, 2.65 ug/L. Mercury concentration in urine was 0.76 ug/g creatinine and the concentration of the 19~39 age group showed relatively higher level than others.

The results of this survey will be announced as national official statistics by generating representative value and reference value of in-vivo environmental toxic substances on general population and will be a reference to other domestic studies while contributing to the establishment and evaluation of environmental policy.

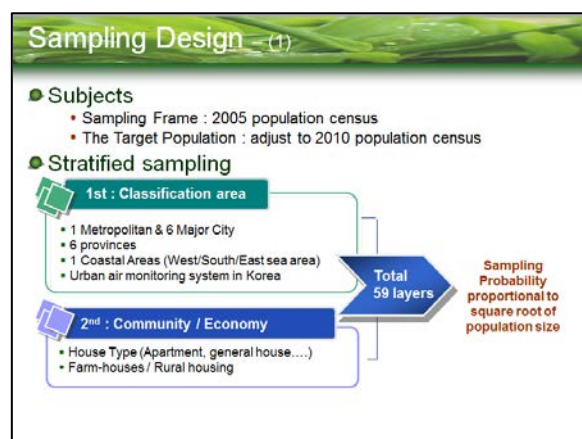
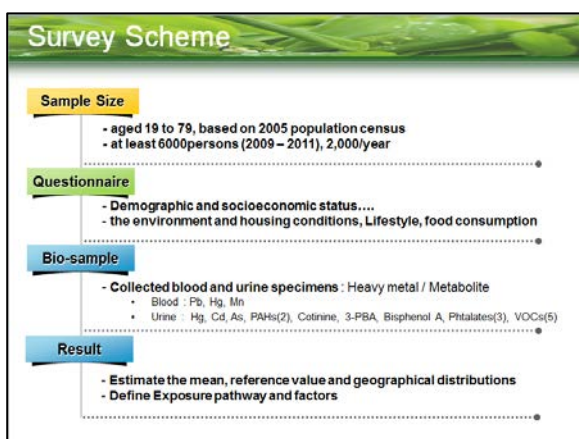
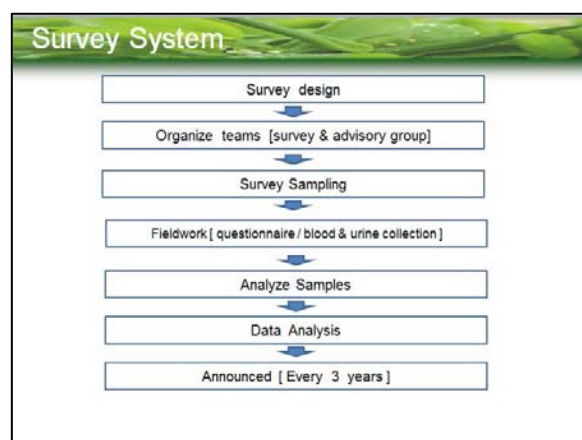
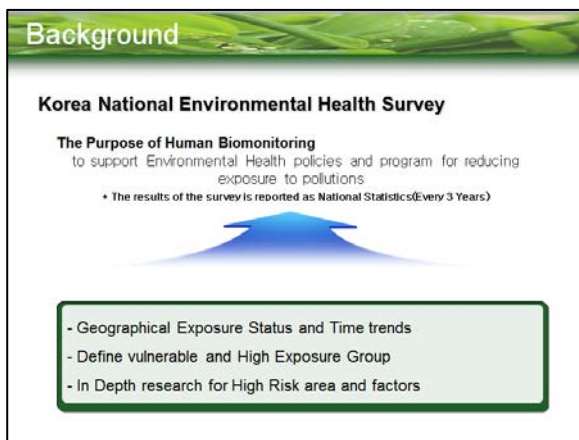
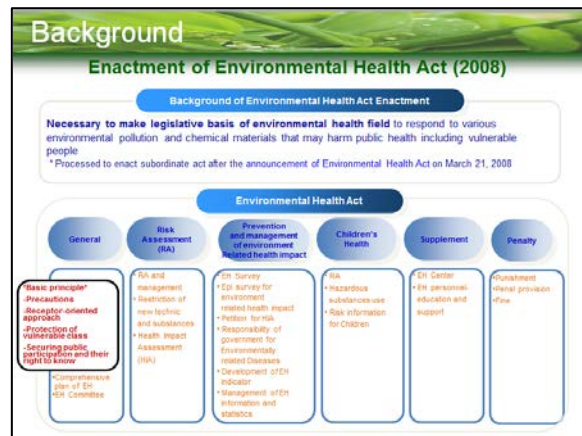
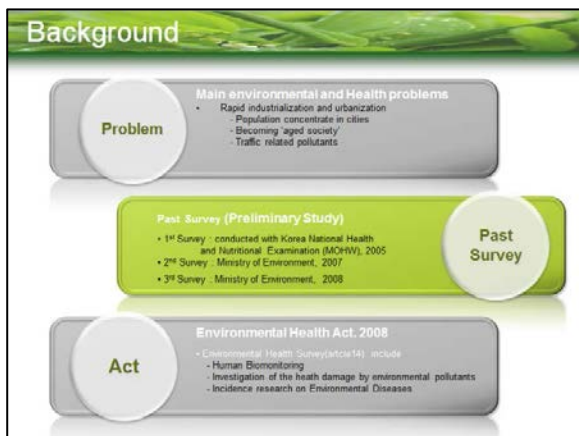
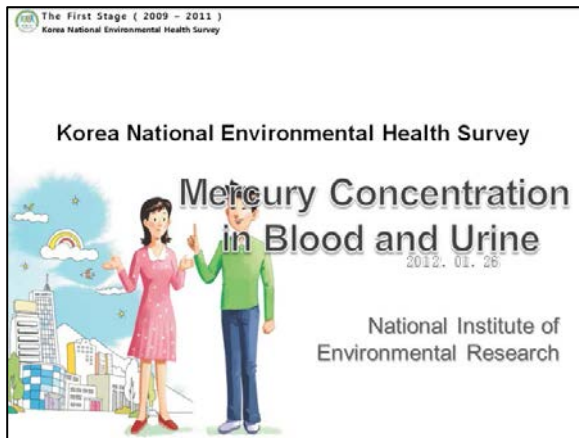
### 韓国環境保健調査-血液と尿中水銀濃度

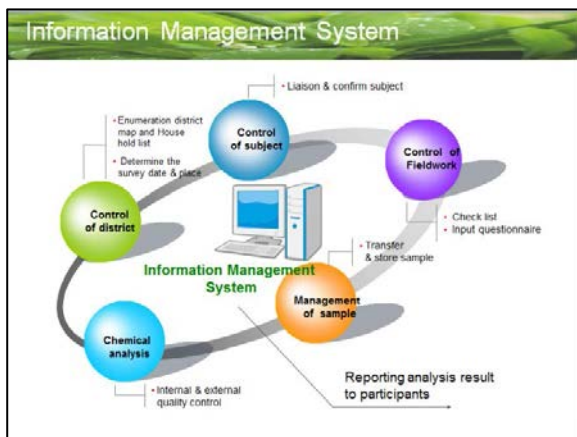
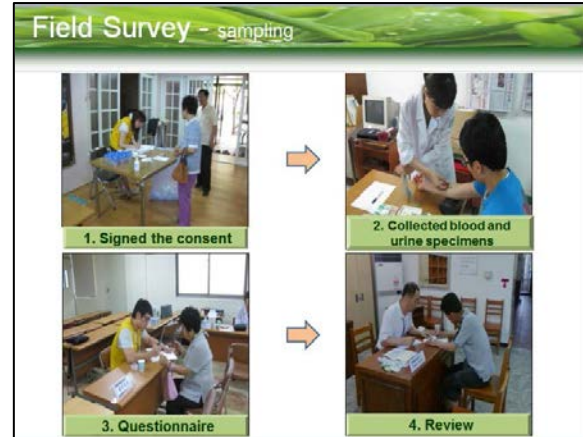
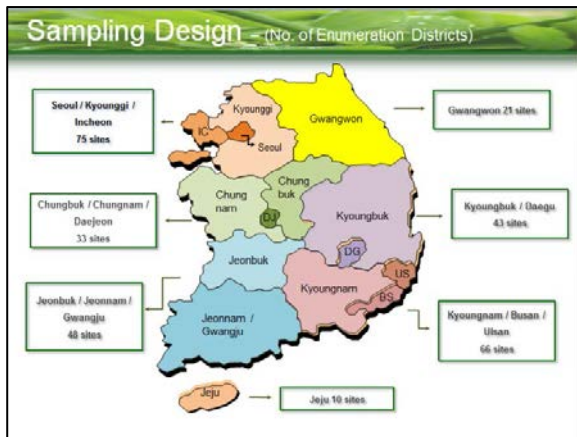
環境汚染物質の曝露状と経路を調べるために 2009 年から 2011 年にかけて環境健康法（2009）による第一回韓国全国環境健康調査がおこなわれた。曝露要因を見つけるために毎年 19 歳以上の成人 2,000 人、3 年間で 6,000 人を対象としたアンケート調査をし、血液および尿中における 16 種の有害汚染物質の分析を行った。

分析の結果、血中における水銀血中濃度の幾何平均は 3.08ug/L であり、男性の濃度は 3.65 ug/Lde で、女性の 2.65 ug/L より高い値を示した。尿中水銀濃度は 0.76 ug/L クレアチニンで、19 歳から 39 歳までの年齢グループによる濃度が、他のグループのものより比較的高い値を示した。

調査の結果は、体内環境毒性物質の代表値および基準値を算出したのち、全国の公式統計として発表し、ほかの国内研究の参考資料として、また環境政策の評価策定に役立てていきたいと考えている。



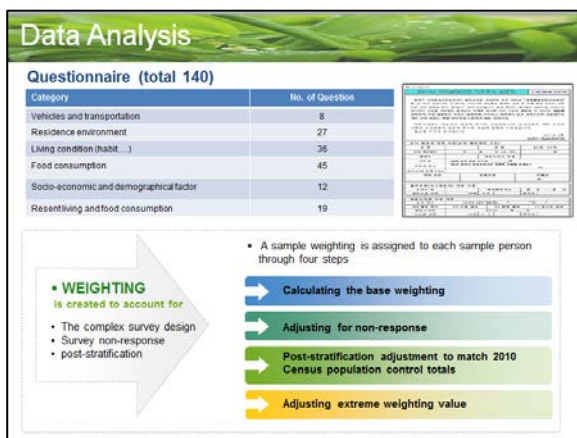




# Laboratory Analysis

	Chemicals	Method
Blood (3)	Metal	Pb GF-AAS
		Mn GF-AAS
		Hg CVAAS (Cold Vapor Atomic Absorption Spectrometer)
		Hg CVAAS (Cold Vapor Atomic Absorption Spectrometer)
		Cd GF-AAS
	Metal	As HG-AAS
		2-Naphthol GC-MS
		PAHs 1-Hydroxynaphene GC-MS
		Tobacco Smoke Cotinine GC-MS
		Phthalates Phthalates HPLC-MS/MS
Urine (14)	Environmental Phenols Bisphenol A HPLC-MS	
	Pyrethroid Pesticide 3-Phenoxycarboxylic acid GC-MS	
	VOCs	Mutagenic acid HPLC-MS/MS
		Isopropic acid GC-MS (99)
		Methylglucuronic acid HPLC-MS (10-11)
		Benzoic acid GC-MS (99)
		Phenylglyoxylic acid HPLC-MS (10-11)

➤ Assessment creatinine concentration range : 0.3-3 g/L (WHO, 1996)



### Result - Hg in Blood

Hg in Blood (μg/L)	Sample size	Arithmetic mean	Geometric mean (95%CI)	25th	50th	75th	95th
Total	6,298	3.97	3.08 (2.97-3.20)	1.99	3.65	4.76	9.9
Gender							
Male	2,924	4.74	3.65	2.33	3.60	5.74	12.1
Female	3,374	3.22	2.62	1.77	2.82	3.82	7.4
Age Group (years)							
19-29	747	2.87	2.35	1.59	2.33	3.40	6.5
30-39	1,180	4.62	3.22	2.16	2.26	4.08	16.6
40-49	1,333	4.34	3.45	2.29	3.40	5.29	10.2
50-59	1,495	4.89	3.75	2.37	3.62	5.94	12.7
60-69	1,110	4.08	3.05	1.88	2.90	4.89	10.2
70 and older	433	3.36	2.68	1.66	2.66	3.92	7.6
Region							
Urban	4,966	4.00	3.11	2.00	3.07	4.79	9.99
Rural	428	3.15	2.51	1.66	2.41	3.79	7.33
Costal	177	5.87	4.80	3.07	5.04	7.41	14.19
Air monitoring station area	727	4.68	3.38	2.19	3.33	4.87	10.29



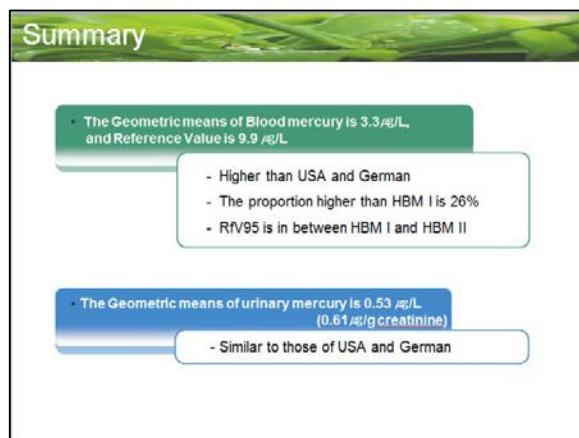
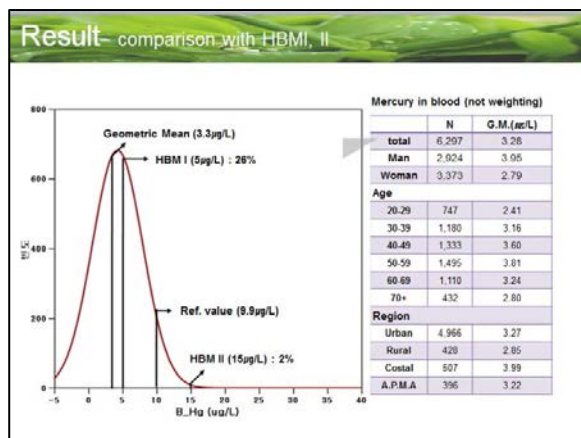
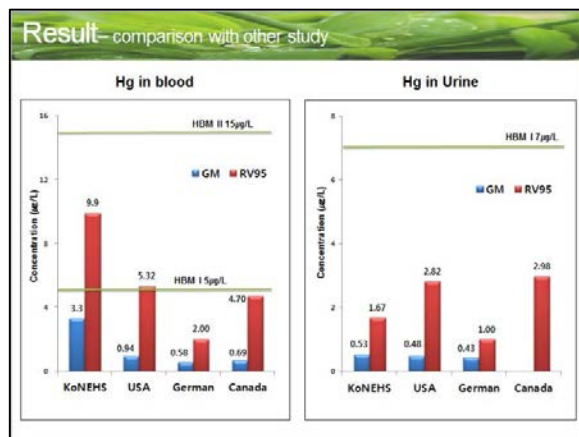


### Result- Hg in Urine( $\mu\text{g/L}$ )

Hg in Urine ( $\mu\text{g/L}$ )	Sample size	Arithmetic mean	Geometric mean (95%CI)	Percentile (95th)			
				25th	50th	75th	95th
<b>Total</b>	6,297	0.79	0.53 (0.51-0.56)	0.34	0.54	0.81	1.67
<b>Gender</b>							
Male	2,925	0.72	0.56	0.36	0.56	0.85	1.68
Female	3,372	0.68	0.51	0.32	0.51	0.78	1.67
<b>Age Group(years)</b>							
15-29	743	0.77	0.57	0.36	0.57	0.85	1.89
30-39	1,180	0.80	0.58	0.37	0.57	0.9	1.86
40-49	1,335	0.68	0.56	0.38	0.56	0.86	1.54
50-59	1,495	0.68	0.54	0.35	0.54	0.85	1.6
60-69	1,111	0.58	0.45	0.29	0.44	0.69	1.44
70 and older	433	0.52	0.40	0.26	0.41	0.6	1.26
<b>Region</b>							
Urban	4,963	0.79	0.53	0.34	0.53	0.81	1.68
Rural	429	0.68	0.53	0.33	0.54	0.82	1.63
Costal	177	0.81	0.58	0.37	0.60	0.98	1.90
Air monitoring station area	726	0.67	0.53	0.34	0.51	0.79	1.67

### Result- Hg in Urine( $\mu\text{g/g cr.}$ )

Hg in Urine ( $\mu\text{g/g cr.}$ )	Sample size	Arithmetic mean	Geometric mean (95%CI)	Percentile (95th)			
				25th	50th	75th	95th
<b>Total</b>	5,697	0.76	0.61 (0.59-0.63)	0.40	0.61	0.91	1.76
<b>Gender</b>							
Male	2,744	0.66	0.54	0.37	0.53	0.78	1.50
Female	2,953	0.86	0.69	0.45	0.69	1.02	1.97
<b>Age Group(years)</b>							
15-29	670	0.71	0.56	0.36	0.54	0.84	1.89
30-39	1,076	0.81	0.63	0.42	0.62	0.92	1.87
40-49	1,229	0.78	0.63	0.43	0.62	0.92	1.69
50-59	1,330	0.81	0.66	0.45	0.67	1.00	1.83
60-69	1,000	0.74	0.59	0.39	0.59	0.90	1.76
70 and older	392	0.69	0.56	0.35	0.55	0.84	1.71
<b>Region</b>							
Urban	4,400	0.76	0.61	0.40	0.60	0.91	1.77
Rural	401	0.78	0.62	0.42	0.66	0.91	1.71
Costal	159	0.89	0.72	0.54	0.73	0.98	2.05
Air monitoring station area	649	0.73	0.59	0.40	0.58	0.85	1.77





## Placental transfer of heavy metals and the changes in their body burden in infants during early-breastfeeding period

Mineshi Sakamoto

*Department of Epidemiology, National Institute for Minamata Disease*

Fetuses and breast feeding infants depend on their mothers for their nutrition, and they are exposed to heavy metals such as methylmercury, lead, arsenic, cadmium, and selenium through placenta and breast milk of mothers. Our study was performed to investigate the changes in heavy metals body burden in infants during early breastfeeding period in comparison with the metals transfer through the placenta. Blood samples were collected from 16 mother-child pairs; cord blood immediately after birth, maternal blood at 1 day after parturition, and infant blood at 3 months (most of the infants were breast-fed). Fetal levels of mercury, selenium, arsenic, and lead strongly reflected the maternal levels, and the placental transfer of methylmercury was especially high. However, the methylmercury level in infants after 3 months declined to about 50% of that in infants at birth. Selenium showed the similar but gentle changes to methylmercury. Se/Hg molar ratio in cord RBCs was significantly higher than that in maternal RBCs and the ratio in infants returned to similar ratio in maternal RBCs after 3 months. For lead and arsenic, the placenta barrier seemed to protect fetuses to some extent, and little change was observed during the breast-feeding period. The placenta barrier seemed to work strongest against cadmium among the metals, and the level was kept low during lactation. If no particular contamination of any metal exists in the environmental setting, metal exposure through breastfeeding need not be a concern.

### 重金属の経胎盤移動と授乳早期の児における体内蓄積変動

胎児期及び乳児期に児は母親の栄養に依存し、これらの金属も母体経由で児へ移行するが、各金属で児への異なる曝露パターンを示した。特に妊娠後期の胎児脳は MeHg に対する感受性が高いと言われている上に、MeHg は母親より高い濃度で蓄積するので注意が必要であるが、通常での魚介類摂取における MeHg 曝露は比較的低濃度であることに加え、乳児期には生後 3 ヶ月で血中 MeHg 濃度が半減するので胎児期ほどの注意は必要ないと考えられる。Cd は胎盤透過性が非常に低く、血中 Cd 濃度は乳児期にも低いまま推移するという独特のパターンを示した。他の金属は、胎盤がこれら金属の胎児への移行をある程度制限する役割を果たしており、更に、乳児期においては大きな血中濃度の変動は無い。

以上より、胎児期には MeHg の曝露 に関する注意が必要であるが、特段の汚染が授乳中の母親に無い限り、乳児期には特定の金属が児に特に高濃度で蓄積する危険性は少ないと考えられた。

## Placental transfer of heavy metals and the changes in their body burden in infants during early-breastfeeding period.

M Sakamoto  
National Institute for  
Minamata Disease



## Background

- The developing brain in the late gestation and/or early-lactation periods is especially susceptible.
- Fetuses and breast-feeding infants depend on their mothers for their nutrition, and they are exposed to heavy metals such as methylmercury (MeHg), lead (Pb), arsenic (As), cadmium (Cd), and selenium (Se) through their mothers.
- We have recently reported the heavy metals transfer from mother to fetus (Ecotoxicol Environ Saf 2010). However, the changes in body burden of the metals in the breast-feeding infants are not well known.



## Objective

This study was performed to investigate the metals transfer through the placenta and the changes in heavy metals body burden in infants during early-lactation period.

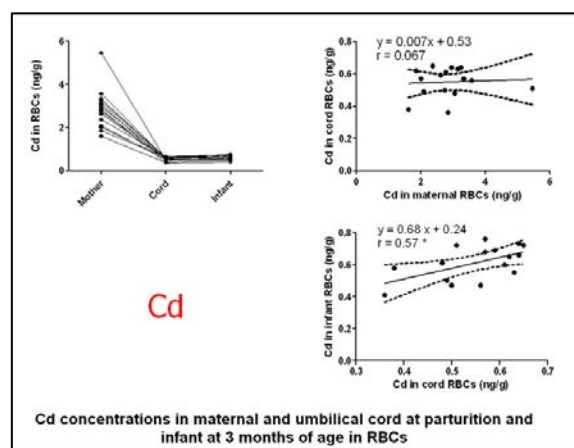
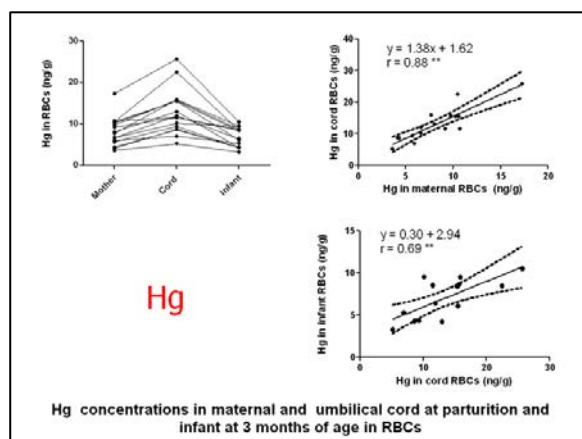
## Methods

- Blood samples were collected from 16 mother-child pairs; cord blood immediately after birth, maternal blood at 1 day after parturition, and infant blood at 3 months (most of the infants were breast-fed).
- Blood samples were obtained by venipuncture, and were centrifuged at 3000 rpm for 10 min to separate RBCs and plasma.
- Total Hg in RBCs was measured by cold vapor atomic absorption spectrophotometry (CVAAS), and other metals were analyzed using ICP-MS.

## Results

**Table 1. Average  $\pm$  SD (ng/g) of Hg, Pb, As, Cd, and Se in maternal, cord and infant (3 mo) RBCs.**

n=16	Hg	Pb	As	Cd	Se
Maternal RBCs	8.19 $\pm 3.43$	24.3 $\pm 10.8$	7.01 $\pm 4.45$	2.85 $\pm 0.89$	246 $\pm 27$
Cord RBCs	12.98 $\pm 5.42$	14.1 $\pm 4.3$	4.33 $\pm 2.97$	0.55 $\pm 0.09$	280 $\pm 40$
Infant RBCs	6.87 $\pm 2.37$	16.1 $\pm 2.0$	1.95 $\pm 0.67$	0.61 $\pm 0.11$	213 $\pm 30$





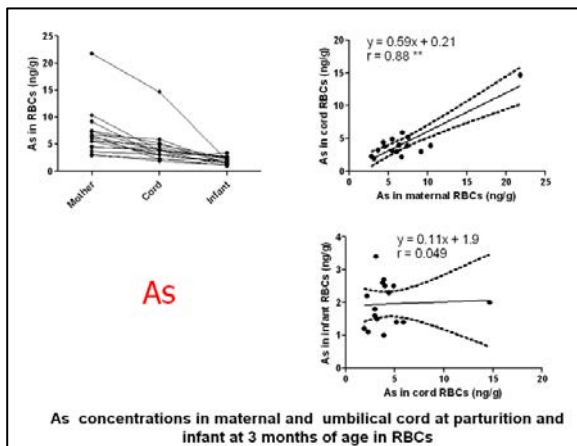
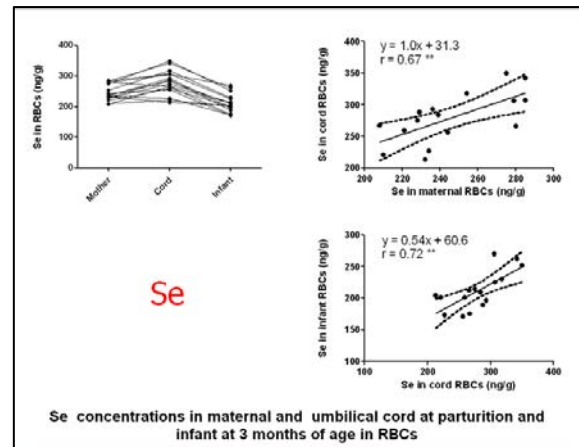
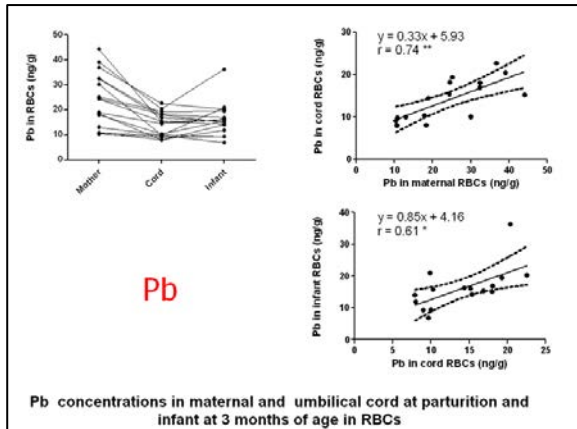
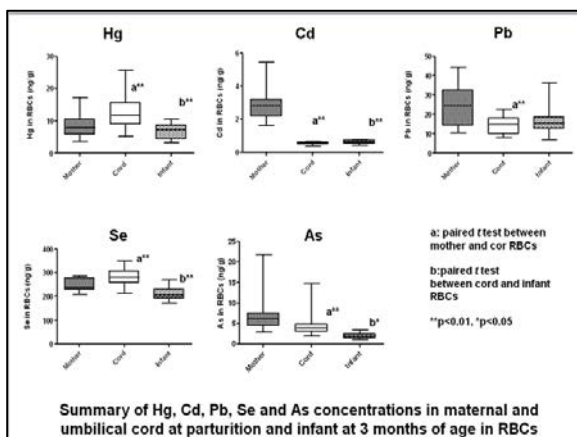


Table 2. Average  $\pm$  SD (ng/g) of Hg, Pb, As, Cd, and Se in maternal RBCs and milk.

	Hg	Pb	As	Cd	Se
Maternal RBCs=16	8.19 $\pm$ 3.43	24.3 $\pm$ 10.8	7.01 $\pm$ 4.45	2.85 $\pm$ 0.89	246 $\pm$ 27
Milk=9	0.46 $\pm$ 0.16	0.79 $\pm$ 1.3	1.45 $\pm$ 0.69	0.13 $\pm$ 0.09	18.7 $\pm$ 4.8
%	5.6	3.3	20.7	4.6	7.6



## Results & Discussion

- Heavy metals were transferred from mothers to infants with different patterns during gestation and lactation.
- Higher MeHg was accumulated in fetus compared to their mothers.
- However, the MeHg level in infants after 3 months declined to about 50% of that in cord level.
- Thus, mothers should limit their MeHg exposure during gestation, especially in populations consuming large amount of fish, but need not worry about MeHg transfer through breast-feeding.

## Conclusions

- Se and Hg showed similar changes during these periods, suggesting both metals may be transferred from mother to fetus through similar pathways or they were bound together as a MeHg-Se complex (MeHg-Se-Cys).
- For Pb and As, the placenta barrier seemed to protect fetuses to a some extent, and little change were observed during the breast-feeding period.
- Hg, Se, As, Cd and Pb concentrations in milk were much lower than those in maternal RBCs.
- Different from other metals, the placenta seemed to act effectively as a barrier against Cd, and the Cd transfer was also low during the breast-feeding period.

- Fetal exposure to Hg, Se, As, and Pb strongly reflected the maternal levels, and the placental transfer of MeHg was especially high. Therefore, pregnant women should pay attention to avoid high exposure to these metals, especially to MeHg.
- For Pb and As, the placenta barrier seemed to protect fetuses to a some extent, and little change were observed during the breast-feeding period. On the other hand, the MeHg level in infants at 3 months declined to about 50% of that in cord RBCs level. The transfer of Cd was very limited during both gestation, and the level was kept low during lactation.
- If there is no particular metal contamination, metal exposure through breast-feeding need not be a concern.



## **The blood mercury concentration in a coastal area and four cases of neuropsychological abnormal findings in children with high blood methyl-mercury concentration in Korea**

**Young-Seoub Hong**

*Department of Preventive Medicine, Dong-A University, Busan, Korea*


Many of previous studies reported that high blood mercury concentration increases the frequency of neural developmental disorder caused by mercury poisoning particularly in children because the development of brain and the nervous system is active during childhood. The health effects of mercury that have been reported in Korea are mostly occupational poisoning, and there have been few cases of health problems caused by non-occupational factors. We would like to suggest the level of the blood methyl-mercury concentration of the residents of coastal area, Korea, and introduce the observed four cases of neuro-psychological abnormal findings that were believed to have been induced by methyl-mercury. We performed thorough examination for four children whose mercury concentration (16.6  $\mu\text{g}/\ell$ , 15.4  $\mu\text{g}/\ell$ , 17.4  $\mu\text{g}/\ell$ , 20.6  $\mu\text{g}/\ell$ ) in the body exceeded the international standard in a community epidemiological survey on mercury exposure, and observed neuropsychological abnormal findings such as mild mental retardation, attention deficit hyperactivity disorder, and low attention concentration, so here we reported the cases. Based on this case report, efforts should be made to conduct expanded research as well as to reduce children's exposure to mercury and prevent related health problems in them.

### **韓国における沿岸地域の血中水銀濃度と高い血中メチル水銀濃度を示した子供達 4 ケースの神経心理学的異常の検出**

これまでの研究では、児童期には神経系統や脳の発達が生発であることから、児童の血中水銀濃度が高ければ、水銀中毒による神経発達障害が起こりやすいと報告されている。韓国で報告されている水銀の健康への影響は、そのほとんどが職業中毒であり、非職業要因による健康問題のケースはほとんど報告されていない。


我々は、体内水銀濃度が水銀曝露に関する国際基準を上回る 4 名の子供に水銀曝露に関する疫学的調査を行い (16.6  $\mu\text{g}/\text{L}$ , 15.4  $\mu\text{g}/\text{L}$ , 17.4  $\mu\text{g}/\text{L}$ , 20.6  $\mu\text{g}/\text{L}$ )、軽度の知的障害、注意力欠陥、多動性障害、注意集中力障害等の精神心理学異常所見を認めた。よってこのケースを報告する。

また今後は子供の水銀曝露や関連の健康障害を減らすために、この報告に基づいて更なる研究を重ねていくつもりである。



**Study 1:**  
The level of Blood Mercury, Methyl Mercury, Urine Mercury, and Hair Mercury of Coastal areas in Korea


# General Characteristics of Busan, Ulsan, and Gyeongnam Province



The first image is a map of South Korea with a red circle highlighting the southeastern region, which includes Busan, Ulsan, and Gyeongnam. The second image is a detailed map of this region, showing the coastline, major roads, and cities. The third image is a night view of the Busan skyline, featuring the Gyeongnam Expressway and the Busan Light Tower. The fourth image is a close-up view of a dish of sliced raw fish (sashimi) served with green vegetables and a red dipping sauce.


# Mercury & Methyl-Mercury Analysis

**Instrument: MTE 5700N, TMA-80**




- Specimen: Blood, Hair
- Method: Cold Amalgamation Method
- LOD: 0.0035 ng/L

**Instrument: NAC SP-300**



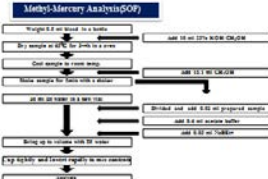
- Specimen: Urine
- Method: Cold Amalgamation Method
- LOD: 0.0021 ng/L

**Instrument: Brooks Rand, MFXN**



- Specimen: Blood
- Method: GC-CVAFS (Cold Vapor Atomic Fluorescence Spectrometry)
- LOD: 0.0001 ng/L

**Methyl-Mercury Analysis(GOR)**

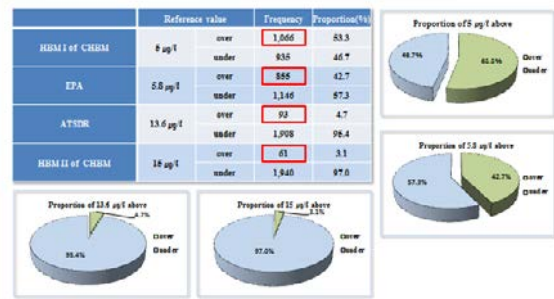


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graph TD
    A[Weigh 0.2 g of sample in a beaker] --> B[Boil sample in 10% HNO3 for 10 min]
    B --> C[Cool sample in clean water]
    C --> D[Boile sample for 10 min with a stirrer]
    D --> E[AS 80-1000-10-1 N/A 120]
    E --> F[Bring up to volume with DI water]
    F --> G[Asp. liquid and store liquid in clean container]
    G --> H[ANALYZE]
    H --> I[Print]
    I --> J[Save]
    I --> K[Exit]
    I --> L[Delete]
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Item	Blood Mercury ( $\mu\text{g/l}$ )	Methyl Mercury ( $\mu\text{g/l}$ )	Hair Mercury ( $\mu\text{g/g}$ )	Urine Mercury ( $\mu\text{g/g}$ )
No. of Subjects	2,001	400	1,200	1,933
Mean $\pm$ S.D.	0.06 $\pm$ 3.80	4.96 $\pm$ 3.48	2.03 $\pm$ 12.90	1.99 $\pm$ 2.97
GM(95% CI)	0.13(0.04-0.25)	4.07(3.00-4.37)	1.24(1.23-1.32)	1.81(1.40-1.88)
Range	0.00-65.70	0.53-35.30	0.12-429.17	0.00-73.86
Percentile				
1th	1.3	0.76	0.29	0.22
5th	2.1	1.31	0.45	0.54
10th	2.56	1.76	0.57	0.69
25th	3.8	2.4	0.83	1.01
50th	6.1	4.23	1.24	1.63
75th	7.8	6.37	1.91	2.14
90th	10.7	8.82	2.91	3.2
95th	12.2	10.6	3.86	4.09
99th	19.8	17.1	6.14	10.24

### The number of high-risk groups according to the international criteria



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### Blood mercury concentration according to related factors

Variable	Total GM (95%CI)	P-value	Male GM (95%CI)	P-value	Female GM (95%CI)	P-value
Age (years)						
20-29	3.80 (3.44-4.44)		3.82 (3.39-4.96)		3.59 (3.47-4.27)	
30-39	5.42 (4.81-6.06)		5.28 (5.13-5.25)		4.89 (4.68-5.40)	
40-49	5.30 (4.66-6.02)	<0.001	5.80 (5.57-7.00)	0.005	4.79 (3.92-5.64)	0.003
50-59	6.81 (3.37-6.71)		7.31 (6.42-8.33)		4.93 (4.17-5.83)	
60+	5.41 (4.83-6.99)		6.15 (5.19-7.36)		4.73 (4.17-5.42)	
Income (ten thousands won / month)						
<99	4.87 (4.35-5.56)		5.64 (4.49-7.07)		4.46 (3.39-5.11)	
100-199	4.80 (4.41-5.50)		5.54 (4.77-6.51)		4.37 (3.77-5.07)	
200-299	5.30 (4.57-6.16)	0.109	5.73 (4.73-6.96)	0.242	4.76 (4.03-6.00)	0.573
300-399	6.17 (5.36-7.07)		7.40 (6.34-7.00)		4.85 (4.12-5.80)	
400+	5.87 (5.27-6.54)		6.96 (6.02-8.00)		5.07 (4.37-5.89)	
Drinking status						
Current drinker	5.32 (3.41-6.23)		6.31 (5.79-6.92)		5.04 (4.24-5.80)	
Ex-drinker	4.80 (3.89-5.40)	<0.001	5.23 (4.18-6.80)	0.007	4.67 (3.18-5.22)	0.254
Non-drinker	4.63 (4.22-5.07)		5.23 (4.27-6.48)		4.62 (4.00-4.88)	
Residence						
Initial	4.42 (3.97-4.92)		5.09 (4.33-5.99)	0.015	3.82 (3.34-4.26)	0.004
Current	5.60 (5.26-5.95)	<0.001	6.20 (5.79-6.97)		4.92 (4.29-5.24)	
Annual Fish Consumption						
1Q (0-25%)	4.24 (3.78-4.78)		4.86 (3.79-5.72)		3.84 (3.47-4.21)	
2Q (25-50%)	5.18 (4.64-5.70)	<0.001	5.88 (4.98-6.92)	0.004	4.64 (4.04-5.82)	0.048
3Q (50-75%)	5.89 (5.28-6.52)		6.75 (5.86-7.76)		4.98 (4.34-5.72)	
4Q (75-100%)	5.89 (5.27-6.54)		6.81 (5.79-7.54)		5.24 (4.63-6.06)	
Per history of amalgam restoration						
Yes	5.29 (4.92-5.68)	0.001	6.04 (5.41-6.75)	0.760	4.69 (4.28-5.14)	0.730
No	5.27 (4.83-5.76)		5.87 (5.20-6.72)		4.54 (4.07-5.06)	

GM: Geometric Mean, 95%CI: 95% Confidence Interval  
P-value was calculated by ANOVA between blood mercury concentration and each group.

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### Multiple regression analysis about related factor with the blood mercury

variable	B	SE	95% CI	t	p-value
Constant	0.363	2.050	0.21-0.39	6.74	<0.001
Gender					
Male	0.872	1.382	0.80-0.12	2.18	0.002
Female	0	1			
Age (years)					
60+	0.298	1.606	0.33-0.28	3.58	<0.001
50-59	0.193	1.053	0.32-0.26	5.20	<0.001
40-49	0.122	1.253	0.64-0.50	3.62	0.003
30-39	0.122	1.254	0.04-0.20	3.69	0.003
20-29	0	1			
Drinking status					
Current drinker	0.083	1.232	0.50-0.34	3.37	0.002
Ex-drinker	0.016	1.002	-0.07-0.09	0.23	0.819
Non-drinker	0	1			
Residence					
Current	0.083	1.245	0.05-0.14	3.83	<0.001
Initial	0	1			
Annual Fish Consumption					
4Q (75-100%)	0.137	1.256	0.46-0.14	3.84	<0.001
3Q (50-75%)	0.122	1.250	0.06-0.18	3.97	<0.001
2Q (25-50%)	0.084	1.254	0.02-0.14	2.77	0.006
1Q (0-25%)	0	1			
R <sup>2</sup>			0.243		

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### Distribution of total mercury concentration and the proportion of methylmercury/total mercury by sex

Groups	Males (n=200)		Females (n=200)	
	T-Hg level *	Proportion of 3.0-15.9 µg/l *	T-Hg level *	Proportion of 3.0-15.9 µg/l *
Quantile1 <sup>b</sup>	2.96 (2.69-3.23)	73.57 (68.97-78.17)	2.59 (2.43-2.75)	67.56 (63.87-71.56)
Quantile2 <sup>c</sup>	5.48 (5.33-5.64)	76.97 (72.70-81.23)	3.90 (3.76-4.04)	80.03 (76.04-84.02)
Quantile3 <sup>d</sup>	7.21 (7.01-7.40)	81.06 (79.56-86.45)	5.51 (5.33-5.69)	75.56 (72.09-79.64)
Quantile4 <sup>e</sup>	12.26 (10.92-13.60)	84.34 (83.34-88.54)	9.13 (8.38-9.89)	84.89 (81.09-88.60)

T-Hg: Total blood mercury, Me-Hg: Methylmercury.

\* Geometric mean; 95% Confidence Interval. \* The lowest group of total mercury level.

\* The intermediate group of total mercury level.

\* The high group of total mercury level.

\* The highest group of total mercury level.

#### Correlation between mercury indices

Variable	Blood mercury	Methylmercury	Urine mercury	Hair mercury
Blood mercury	1.000			
Methylmercury	0.969*	1.000		
Urine mercury	0.107*	0.090	1.000	
Hair mercury	0.802*	0.799*	0.107	1.000

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### Conclusion

- As this study targeted the residents of coastal areas, mercury exposure indices were higher than those observed across the nation or in some inland areas.
- The blood methylmercury concentration and the proportion of methylmercury/total mercury increased significantly depending on the amount of fish consumption, which is consistent with the results of previous studies from other countries.
- The blood mercury concentration of residents in the coastal areas of Korea is higher than the internationally recommended level. Therefore, comprehensive managements are needed.

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### Study 2: Four Cases of Neuropsychological Abnormal Findings in Children with High Blood Methylmercury Concentration

### Study 2 – Background & Introduction

- Many previous studies reported that high blood mercury concentration increases the frequency of neural developmental disorder caused by mercury poisoning particularly in children.
- The health effects of mercury that have been reported in Korea are mostly occupational poisoning, and there have been a few cases of health problems caused by non-occupational factors.
- In 2010, the community epidemiological survey on mercury exposure was performed by NIER, and four children whose mercury concentration exceeded the international criteria (15ppb) were found. Therefore, the children were requested to Dong-A University Hospital for thorough examination.

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### Admission evaluation

- Admission evaluation on the Environmental Clinics in Dong-A University Hospital
- Evaluation with Neurologist, Psychologist, Pediatrics



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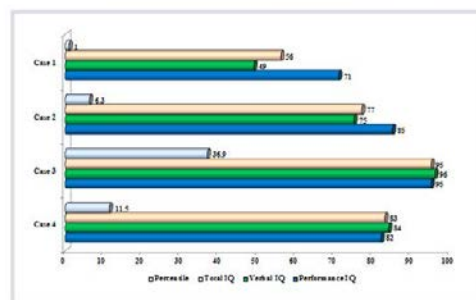


### Laboratory findings and blood metal concentration of cases at admission

	CASE1		CASE2		CASE3		CASE4		Reference
Age/Sex	9 years /Female		12 year/Male		10 years/Male		9 years/Male		
Heavy metal conc.	case	mother	case	mother	case	mother	case	father	
Blood Mercury( $\mu\text{g/l}$ )	21.4	8.48	12.7	-	21.61	22.47	18.56	22.68	WHO <5 HRM II <15
Blood methylmercury( $\mu\text{g/l}$ )	10.1	3.18	11.5	-	21.5	21.3	14.4	20.00	
Hair Mercury( $\mu\text{g/g}$ )	7.2	-	5.7	-	7.5	-	5.3	-	WHO <5
Urine Mercury( $\mu\text{g/l}$ )	2.39	6.33	4.44	-	3.58	1.69	1.77	4.51	HEMI <5 HEMI II <20
Blood Lead( $\mu\text{g/dl}$ )	1.21	-	1.97	-	1.51	-	1.09	-	12 vs Below < 15
Blood Cadmium( $\mu\text{g/l}$ )	0.82	-	0.78	-	0.86	-	0.20	-	WHO <5
History	Epilepsy								
Diet	high preference OF fish intake (shark, dombest)		high preference OF fish intake (shark, dombest)		high preference OF fish intake (shark, dombest)		high preference OF fish intake (shark, dombest)		
Lipid battery	TG increase		Total cholesterol, TG increase		Total cholesterol, TG increase		Total cholesterol, TG increase		
psychological and neurocognitive intelligence test	Mental retardation(mild), cognitive dysfunction, ADHD		ADHD(attention deficit hyperactivity disorder)		ADHD		Attention disability		

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### Cognitive function(IQ) test with K-WISC-III



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### Exposure to methyl-mercury through Shark meat fish intake



METHYLMERCURY LEVELS IN FISH

Species	Mercury concentration( $\mu\text{g/g}$ )				No. of Samples
	Mean	Median	Min	Max	
Mackerel King	0.73	NA	0.23	1.67	213
Shark	0.99	0.83	ND	4.54	351
Swordfish	0.97	0.86	0.10	3.22	605
Tilapia	1.45	NA	0.65	3.73	60

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### Discussion

#### COMPARING FAROE ISLAND STUDY

- Cohort of 1022 children born 1986-1987
- Exposure of mothers to methylmercury
- 903 children 7-year-old followed up
- Neuropsychological dysfunction(age7) : Language, Attention, Memory
- GM of hair mercury concentration in cohort was  $2.99\mu\text{g/g}$ , which was lower than that in our cases
- Maternal blood mercury concentration in cohort was  $22.9\mu\text{g/l}$ (the parents of Case 3 and 4 were  $22.47\mu\text{g/l}$  and  $22.68\mu\text{g/l}$ )

In our cases, it was hard to measure the level of perinatal mercury exposure, but based on available mercury exposure indices, neuropsychological abnormal findings observed in our cases are believed to correspond to the spectrum of various symptoms

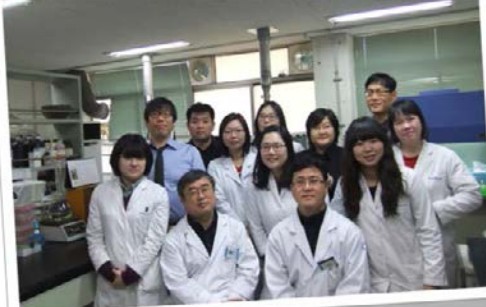
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### Conclusion

- We considered that fish consumption(shark) may be the main source of methyl-mercury exposure, and it can influence neuro-psychological symptoms in these cases. More vast studies are needed for the clarification of the causal relationship between mercury exposure and health problems in children using the neuro psychological test battery.
- This study provides meaningful findings for the control of mercury exposure in children. We expect to establish effective management guidelines pertaining to the blood mercury concentration of people in Korea.

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### ACKNOWLEDGEMENT !!



## Health effects of mercury in Almadén, the world's largest mercury mining district

**Pablo Higuera<sup>1</sup>; Santiago Español<sup>2</sup>; José M. Esbrí<sup>1</sup>; Sergi Díez<sup>3</sup>**

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<sup>2</sup>: Fundación Almadén

<sup>3</sup>: Environmental Chemistry Department, IDAEA-CSIC, Barcelona, Spain.

Almadén mercury mining district (south-central Spain) has been the world's largest producer of this element. The district includes a number of different mines and prospects, but the main source has been the Almadén mine, around which the town grown, so that general population has been always in close contact with the mine products, including mercury vapors spreading in the urban area. The three main sources of local mercury pollution have been the mine itself (affecting mainly to the mine workers), the metallurgical activity, and the main mine dump. Human exposure to mercury may occur via a variety of pathways, including occupational uses. In particular the town inhabitants have suffered intense exposure to mercury vapors, with the presence of other toxic species such as methylmercury only in relation with heavily polluted minor streams and in products (calcines) from metallurgy. Undoubtedly, the most intense exposure to mercury has been the one suffered by miners, historically affected by hydrargyris, the disease related to inhalation of gaseous mercury. The incidence of the disease declined sharply in the 50's, thanks to reducing miner's work from 20 to 8 days per month, and in recent times (1980-2003), with preventive health measures undertaken by the company medical staff. The mercury levels in the hair of residents living in Almadén showed higher levels than another area far away. Even though the fish consumption frequency is an important parameter, exposure to mercury due to residence is a key determinant that causes that the population most at risk is located in the vicinity of mining activities.

### 世界最大規模水銀鉱山地帯アルマデンにおける水銀の健康影響

アルマデン水銀鉱山地区（スペイン中南部）は世界最大の生産圏である。この地区にはたくさんの異なる鉱山があるが、しかしその主たるものはアルマデン鉱山で、その周辺には町が発達したため、一般住民は水銀蒸気を含む鉱山からの生産物と密接なかわりがあり、主たる水銀汚染源は鉱山そのものであり（主に鉱山労働者に影響を与えている）、精錬作業と主たる鉱山からの廃棄物である。住民も水銀蒸気への曝露に苦しんできた。最も強い水銀曝露のケースは抗夫であり、水銀ガスの吸入に関連した病気である。この病気のケースは 50 年代に急激に減少したが、これは、抗夫の労働時間が、月に 20 日間から 8 日間に減ったことと、会社の医療スタッフによる予防策による。アルマデンの住民の高い毛髪水銀レベルも鉱山活動に起因すると考えられる。



## Health effects of mercury in Almadén, the World's largest mercury mining district

Pablo Higuera, Santiago Español,  
José M. Esbrí, Sergi Díez

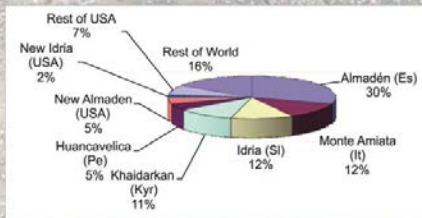
NIMD Forum 2012 - Current topics of mercury impact to human and environment.  
26-27 January 2012 - Conference Hall, Minamata Disease Archives, National Institute for Minamata Disease,  
Minamata City, Kumamoto, Japan

## Contents

- The Almadén mercury mining district
- Main local mercury sources
- Ways of exposure
- Health effects
  - Hydrargyris
  - Cardiovascular diseases
  - Genitourinary diseases
  - Cancer
  - Hair contents
- Conclusions

## The Almadén Hg District

- The largest and the longest in activity
  - Total production: around 400,000 tones – 9 Mflasks



## The Almadén Hg District

- The largest and the longest in activity
  - Mining history: since Romans times (c. year 0) to 2003 (closure of mines and metallurgical activity)



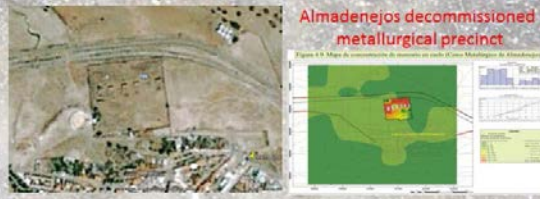
## Main local Hg sources

- Mining activity
- Metallurgy
- Main mine dump
- (Contaminated food)



## Main local Hg sources

- The only active sources for Hg exposition nowadays are non-reclaimed sites, Hg containing soils (including geochemical anomalies) and minor foods



## Ways of exposure

- Inorganic mercury ( $Hg_{vapor}$ ):
  - Miners: 8 days a month working schedule (since 1950's).  $Hg_{vapor}$  contents inside the mine well above  $100 \mu g m^{-3}$
  - General population: urban area around the mine.  $Hg_{vapor}$  contents in town well above  $1 \mu g m^{-3}$

## Ways of exposure

- Organic mercury
  - Local presence of Methylmercury (MeHg) in water of heavily polluted streams, coming from the mine/town area
  - Local presence of MeHg in metallurgy residua (calcines)
  - Presence of mercury (probably MeHg) in local wild food (crayfish, asparagus)



## Health Effects

- **Hydrargyris**
  - The disease caused by exposure (inhalation) of gaseous (inorganic) mercury
  - Affects Hg miners, dentists and XIX Cent. hatters
  - The main health concern in the Hg mining areas
  - Main symptoms (chronic exposure):
    - Hg temblor
    - Mouth health
    - Renal health
    - Hg **erethism** (behavior changes)



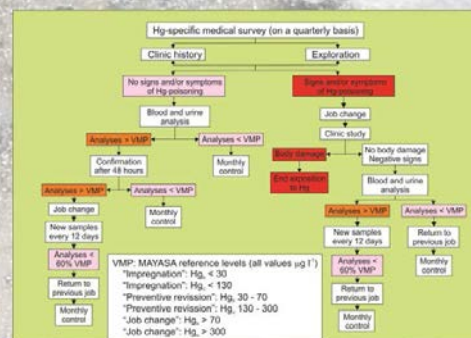
## Health Effects

- **Hydrargyris**
  - In Almadén, historic incidence was very high
  - By 1925 50% of the mine workers were affected by **hydrargyris**
  - In the 1950's, work schedule of the miners became 8 days a month, 6 hours a day, causing an important decrease of incidence
  - In the 1990's, hygienic and health normative in the mining company improved the efficiency of illness prevention

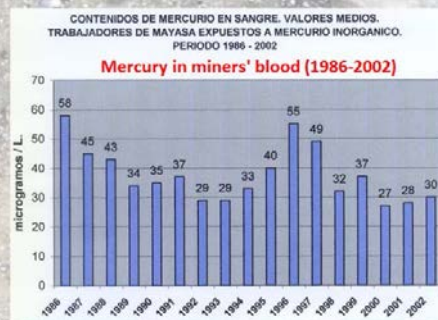
## Health Effects

- **Hydrargyris**
  - 1980-2003: Application of hygienic protocol MUONAS: *Metodología de Unidades Operativas, Niveles de Acción e Indicadores de Salud* / Methodology of operative units, action levels and health indicators
  - To be applied in Colombian gold artisanal mining areas

## Health Effects



## Health Effects



## Health Effects

- **Cardiovascular diseases**
  - García Gómez et al. (2007a):
    - Study of almost 4,000 miners (1895 to 1994)
    - A significant increase in mortality due to circulatory diseases was found (SMR 1.11, 95% confidence interval [CI], 1.02-1.20), especially for hypertension (SMR 2.78, 95% CI, 1.89-3.95), cerebrovascular diseases (SMR 1.17, 95% CI, 1.01-1.35), and other heart diseases (SMR 1.51, 95% CI, 1.29-1.76).

García Gómez, M., Boffetta, P., Caballero Klink, J.D., Español, S., Gómez Quintana, J. 2007a Cardiovascular mortality in mercury miners [Mortalidad por enfermedades cardiovasculares en los mineros de mercurio]. Medicina Clínica 128 (20), pp. 766-771

## Health Effects

- **Genitourinary diseases**
  - García Gómez et al. (2006):
    - Study of almost 4,000 miners (1895 to 1994)
    - A significant increase in mortality due to genitourinary diseases was found, being significant with respect to the total population for nephritis, nephrotic syndrome and nephrosis, with SMR of 1.69 an 95% CI 1.18 to 2.34.
    - Mortality excesses due to nephritis, nephrotic syndrome and nephrosis were higher in the metallurgy workers than in miners.

García Gómez, M., Boffetta, P., Caballero Klink, J.D., Español, S., Gómez Quintana, J. 2006 Genitourinary diseases mortality in mercury miners [Mortalidad por enfermedades genitourinarias en los mineros de mercurio]. Actas Urológicas Españolas 30 (9), pp. 913-920

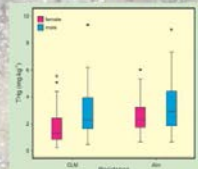
## Health Effects

- **Cancer**
  - García Gómez et al. (2007b):
    - Study of almost 4,000 miners (1895 to 1994)
    - Cancer mortality was significantly lower than expected, with an SMR of 0.72 (95% confidence interval, 0.63-0.82), mainly due to lower than expected mortality from colon and bladder cancer.
    - Deaths from liver cancer were slightly higher than expected (20 deaths vs. 17 expected).
    - Deaths from lung and central nervous system cancers were as expected
    - Mortality from kidney cancer was lower than expected.

García Gómez, M., Boffetta, P., Caballero Klink, J.D., Español, S., Gómez Quintana, J., Colin, D. 2007b Cancer mortality in mercury miners [Mortalidad por cáncer en los mineros del mercurio] Gaceta Sanitaria 21 (3), pp. 210-217.

## Health Effects

- Hair contents
  - Díez et al. (2011):
  - Comparison of local vs regional contents



**Table 1**  
Concentrations of  $\text{Hg}$  ( $\text{mg kg}^{-1}$ ) in the hair of studied participants with the description of variables of interest by area of residence.

	Total	Local	Almadén
	(n = 170)	(n = 100)	(n = 70)
Gender			
Females	8 (5)	8 (8)	8 (11)
Males	6 (3)	6 (6)	6 (6)
Age			
In years	Mean (sd)	30.9 (10.4)	33.6 (10.8)
In $\text{mg kg}^{-1}$	Mean (sd)	2.68 (1.67)	2.86 (1.56)
Median	2.32	2.31	1.79
IQR consumption	0.8 (1.0)	0.8 (1.0)	0.8 (1.0)

Díez, S., Esbró, J.M., Tobias, A., Higuera, P., Martínez-Coronado, A. 2011 Determinants of exposure to mercury in hair from inhabitants of the largest mercury mine in the world. *Chemosphere* 84 (5), pp. 571-577.

## Conclusions

- Exposure to gaseous, inorganic mercury, by mining and metallurgy in Almadén causes important increases in incidence of cardiovascular and genitourinary diseases, but not in cancer
- Mercury contents in hair are only slightly higher than for the regional area, possible in relation to ingestion of MeHg contaminated local food.

THANKS FOR YOUR ATTENTION!  
ご清聴ありがとうございました

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