# Minamata Convention: Initial Assesment of Turkey

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Inventory Mercury Training Meeting

29 – 31/01/2018, Hilton Garden Inn Eskişehir

# Lecture 4

## Minamata Convention and International Regulations, Global Mercury Parnerships, monitoring of mercury

# UNEP Global Mercury Partnership

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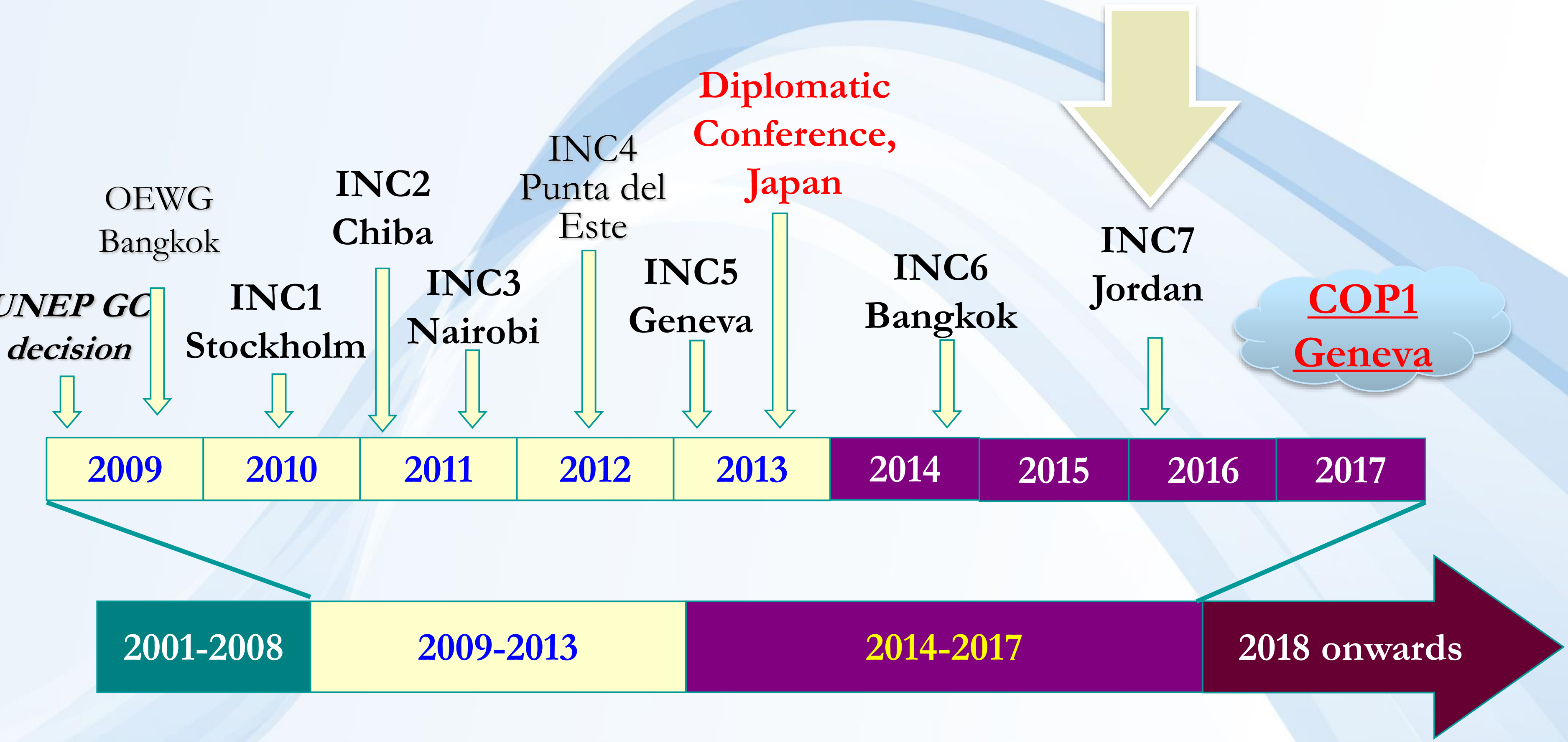
# Mandate and objectives

***of the Global Mercury Partnership***

- **Mandate**: to deliver immediate actions
- **Overall Goal:** to protect human health and the global environment from the release of mercury
- **Means:** by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land.

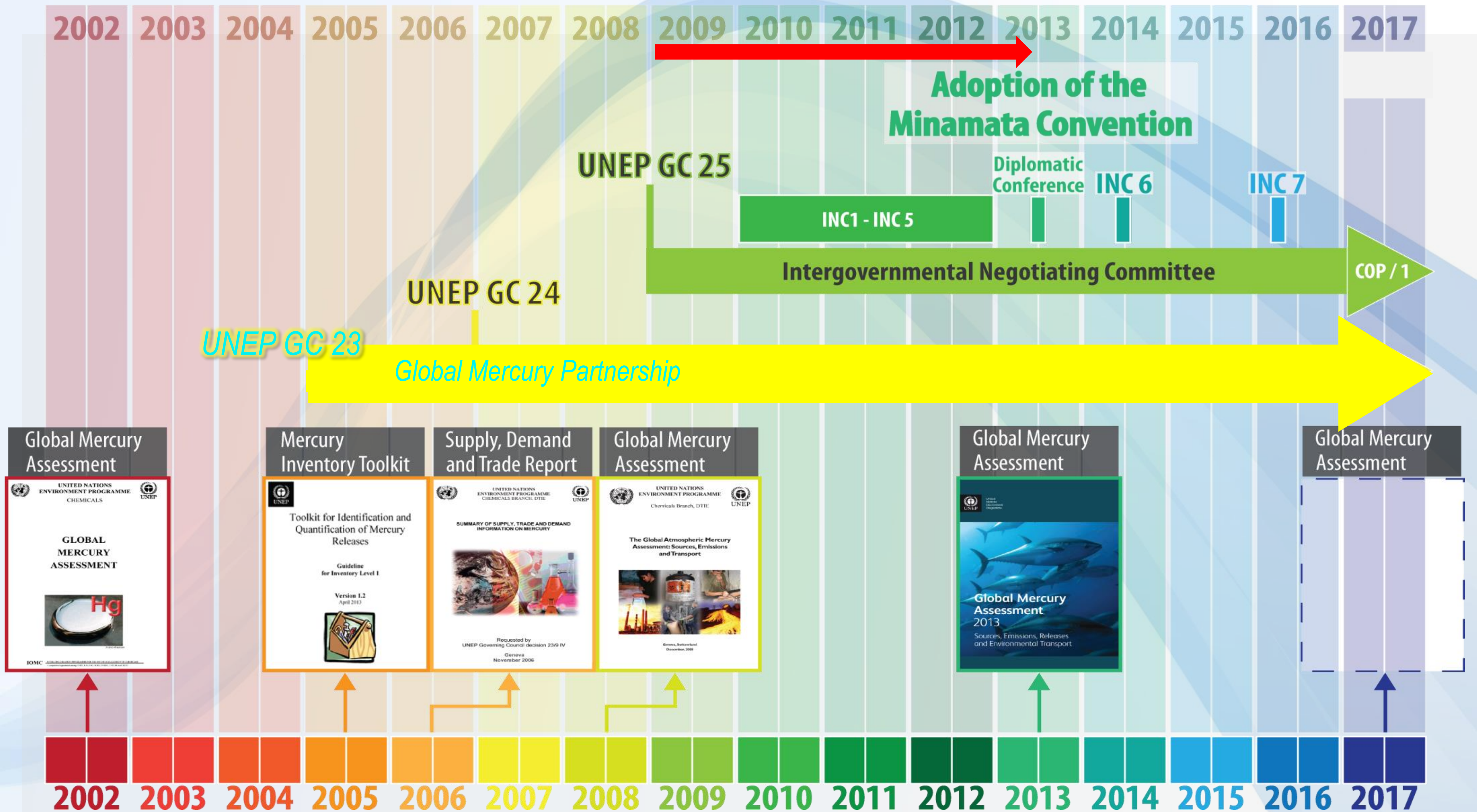
# Main steps of the negotiations process




UNEP MINAMATA CONVENTION ON MERCURY

# Road to Minamata and beyond

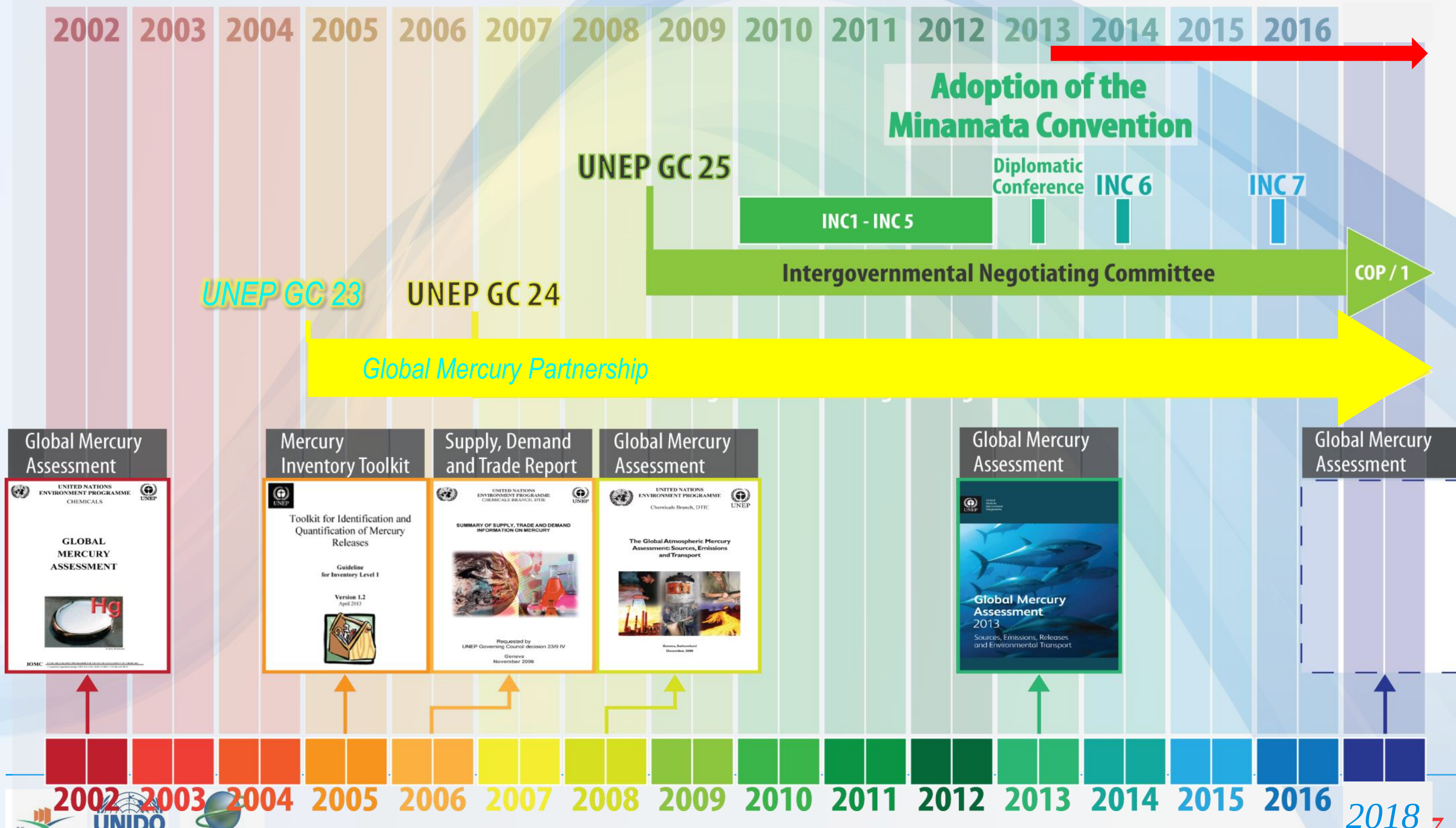
**2009-2013 during negotiations towards Minamata Convention GMP helped guide the negotiation process, provided technical information and scientific rationale.**



UNEP

# Road to Minamata and beyond

## The GMP supports countries with technical assistance and guidance in ratifying and implementing Minamata Convention




UNIDO gef

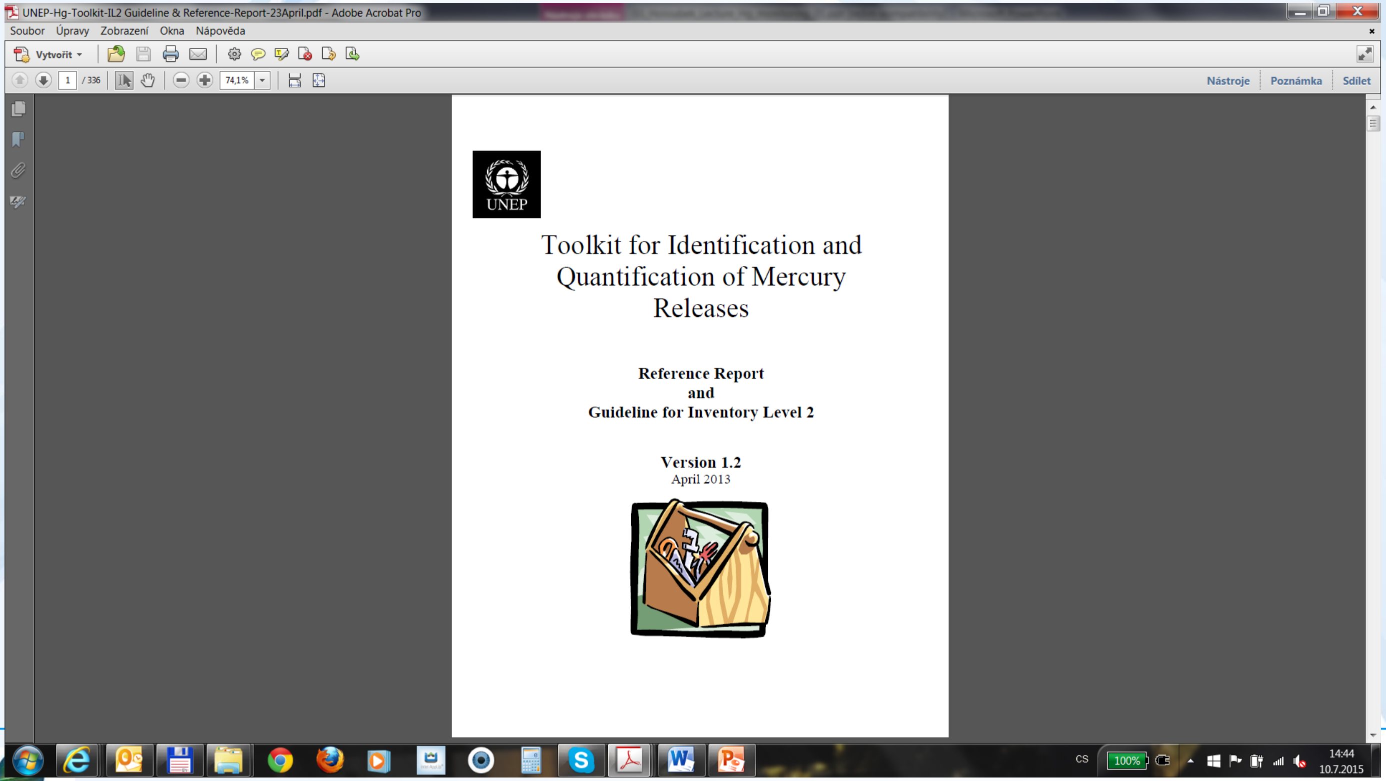
# Global Mercury Assessment

UNEP's Global Mercury Assessments provide authoritative information on anthropogenic sources of mercury emissions to inform policymakers, researchers and the general public.

# Mercury Inventory Toolkit

**UNEP's Mercury Inventory Toolkit** is intended to assist countries in developing national mercury release inventories.

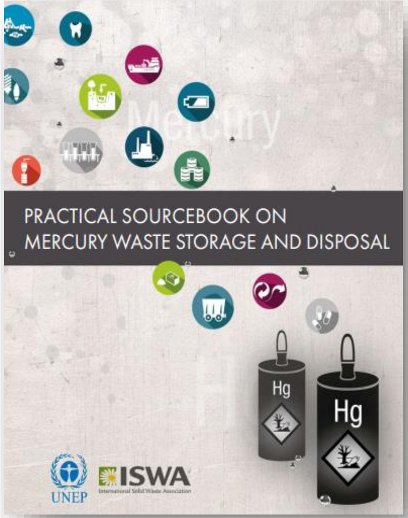
The Toolkit provides a standardized methodology, enabling countries to produce consistent and well-document inventories.



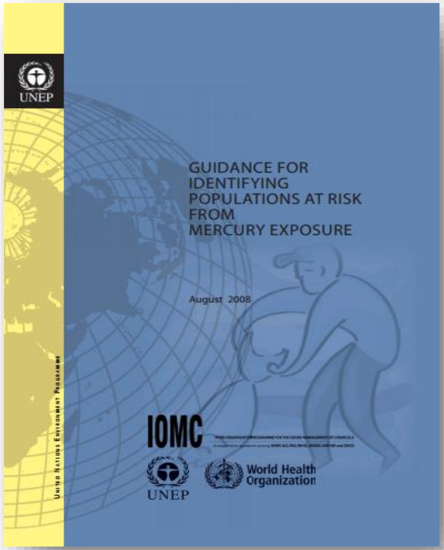

UNEP
Waste management
Coal combustion
Products
GMP
Cement
Transport and fate
Artisanal and Small Scale Gold Mining
Chlor-alkali
Supply and storage

# Delivery mechanism

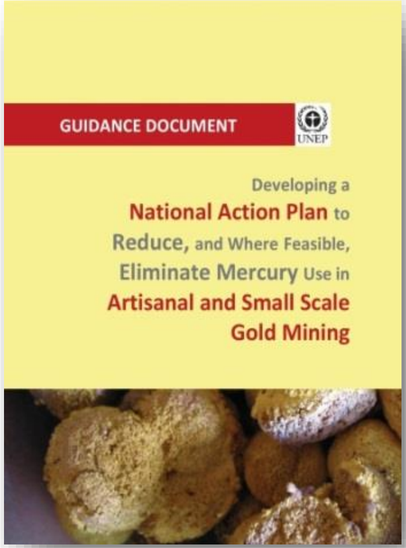
- Development of guidance materials




**Practical Sourcebook on Mercury Waste Storage and Disposal**



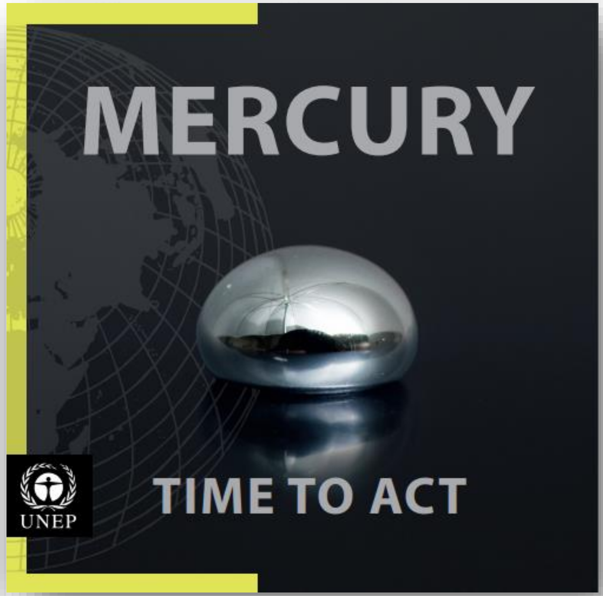

**Guidance for Identifying Population at Risk from Mercury Exposure**

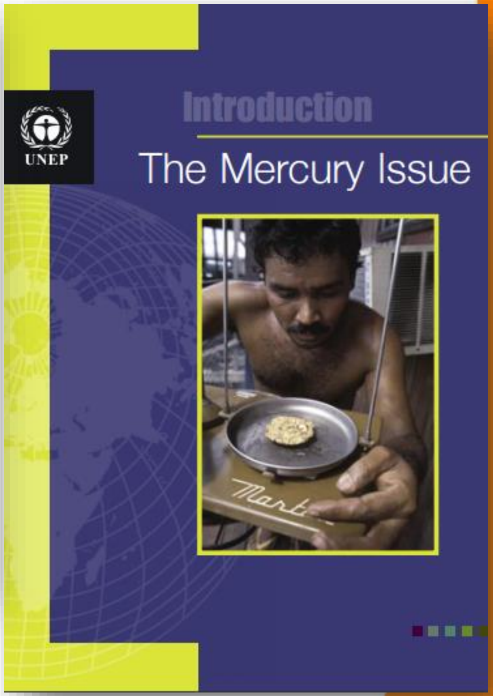



**ASGM NAP Guidance**

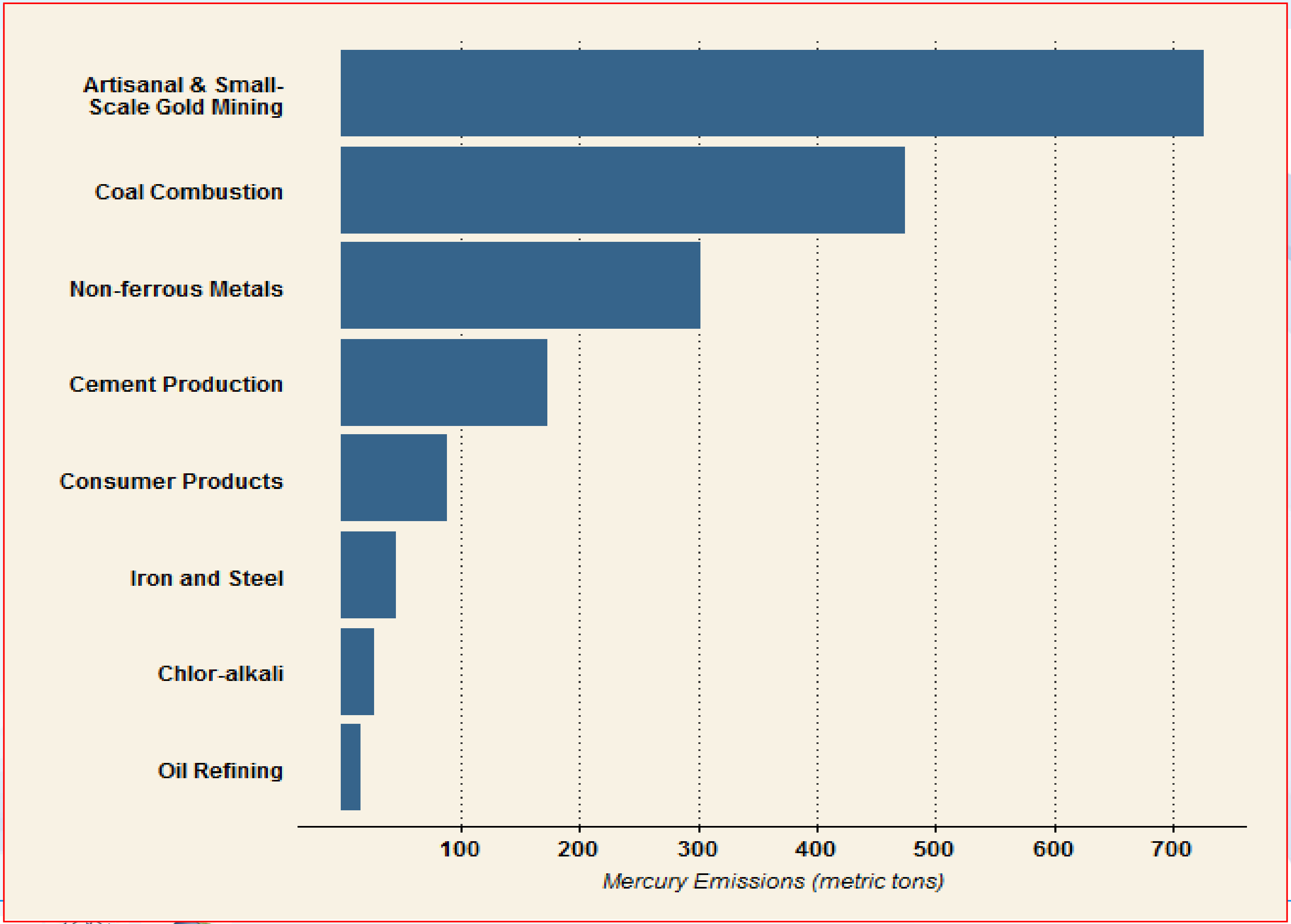
# Delivery mechanism

- *Advocacy, awareness raising*

# Global Anthropogenic Atmospheric Emissions (UNEP, Global Mercury Assessment, 2013)

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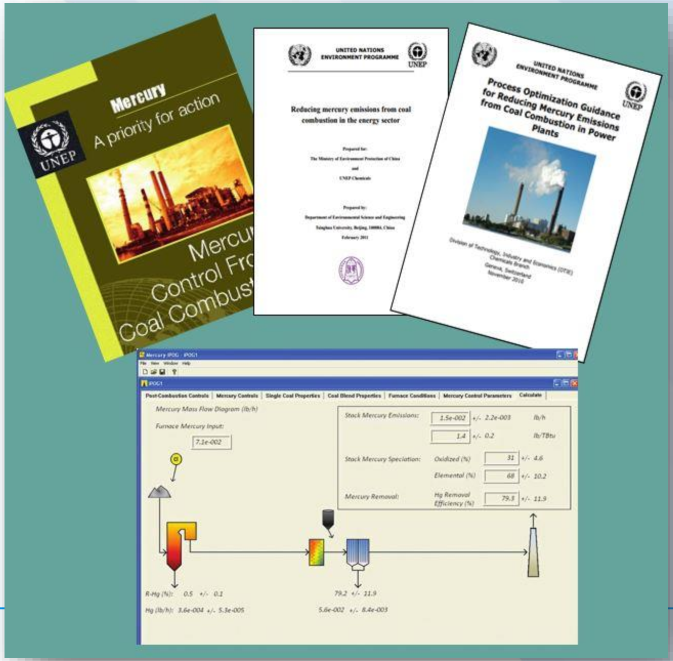
# Partnership activities can support Governments in implementing the Minamata Convention by providing

- Information necessary for prioritizing actions
- Technical guidance, capacity building and awareness raising relevant to the Minamata Convention on Mercury
- Expertise in providing guidance as requested by the INC and COP

# Mercury Control from Coal Combustion partnership can assist countries to

- Characterize and assess the coal-fired power sector
- Analyze mercury content of coals
- Measure emissions of mercury from selected power plants
- Develop proposals for measures to reduce Hg emissions/releases (action plans)
- Develop emissions inventories based
- Demonstrate mercury reductions



# Mercury partnership in Artisanal and Small-scale Gold Mining area can assist countries by providing

- Draft guidance document and assistance in the development of ASGM National Action Plans under the Minamata Convention
- A platform for partners to share information and jointly develop interventions to reduce mercury use in ASGM
- Technical solutions and monitoring of the success of the Convention

*Mercury use in Tanzania*

# Mercury in Products partnership can assist countries by providing

- Information on product alternatives (batteries, lamps, measuring devices in health care, dental amalgam)
- Prioritized project proposals on mercury-added products and assistance seeking appropriate funding
- Incorporating a lifecycle management approach to manufacturing, use and disposal of mercury added products
- Information on case studies and best practices on use of alternatives

UNEP Global Mercury Partnership

What is mercury?

Mercury is a toxic element. Although mercury occurs naturally, the levels in our air, water, land, food and bodies have increased, due in part, to use and releases from mercury-containing products.

Once released into the environment, mercury and its compounds can build up in fish, wildlife and humans. Even small amounts of mercury and its compounds can impact human health and the environment .

Mercury uses and alternatives

The use of mercury in products can lead to releases of the metal during manufacture, usage, recycling and disposal. Mercury is used worldwide in many products, such as batteries, fever thermometers, blood pressure devices, thermostats, medical equipment, dental amalgam, lamps, electronics, paints, fungicides, household appliances and switches. Transitioning away from mercury-added products to mercury-free alternatives is an opportunity to reduce the amount of mercury that gets into the environment and our bodies. For many products, effective mercury-free alternatives are available.

In 2008, UNEP published a report entitled, "Report on the Major Mercury-Containing Products and Processes, their Substitutes and Experience in Switching to Mercury-Free Products and Processes."

This brochure condenses the information in the 2008 report into a concise reference guide on mercury products and their alternatives.

UNEP GLOBAL MERCURY PARTNERSHIP

The overall goal of the partnership is to protect human health and the global environment from the release of mercury and its compounds by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land. In order to contribute to this overall goal, the partnership area on mercury in products strives to phase out and eventually eliminate mercury in products and to eliminate releases during manufacturing and other industrial processes via environmentally sound production, transportation, storage and disposal procedures.

For more information, please contact:

United Nations Environment Programme (UNEP)
Division of Technology, Industry & Environment
Chemicals Branch
11-13 chemin des Anémones
1219 Châtelaine/Geneva
Switzerland
E-mail: mercury.chemicals@unep.org

For further information, please visit:
www.unep.org/hazardoussubstances

This brochure was developed by the United Nations Environment Progamme (UNEP) Global Mercury Partnership Area on Products to:

- provide a concise list of mercury-free alternatives to mercury-containing products;
- encourage the reduction or elimination of mercury in products where effective substitutes exist.

LIST OF ALTERNATIVES TO MERCURY-ADDED PRODUCTS

# Mercury Reduction in Chlor alkali partnership can assist countries by providing

- Information on the current global inventory and plans of conversion to mercury-free technology

- Technical assistance to chlor alkali plants that plan to convert

# Mercury Supply and Storage Partnership can assist countries to

- Identify and characterize new primary mercury mining
- Collaborate with industry on ESM and storage of mercury; sectors: chlor-alkali, non-ferrous, gas production
- Assess options for the management, storage and final disposal of surplus mercury
- Review regulations and strengthen collaboration to facilitate the implementation of trade measures
- Promote transparency and traceability throughout the whole lifecycle of mercury to address potential illegal sources

## Kyrgyz Republic:

- Assist in the transition away from mercury mining
- Identify economic alternatives to mercury

Container for safe storage (EU project MERSADE)

# Mercury Waste Management partnership can assist countries by:

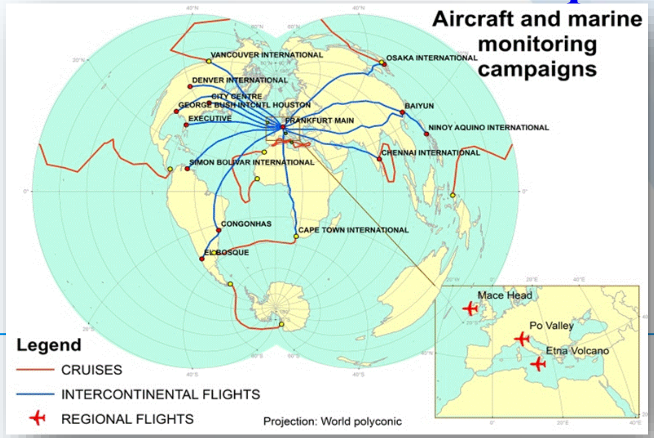
- Reviewing existing regulation and waste management infrastructure

- Providing information on technologies and costs to implement ESM of mercury waste

- Providing information on success stories and case studies in developed and developing countries

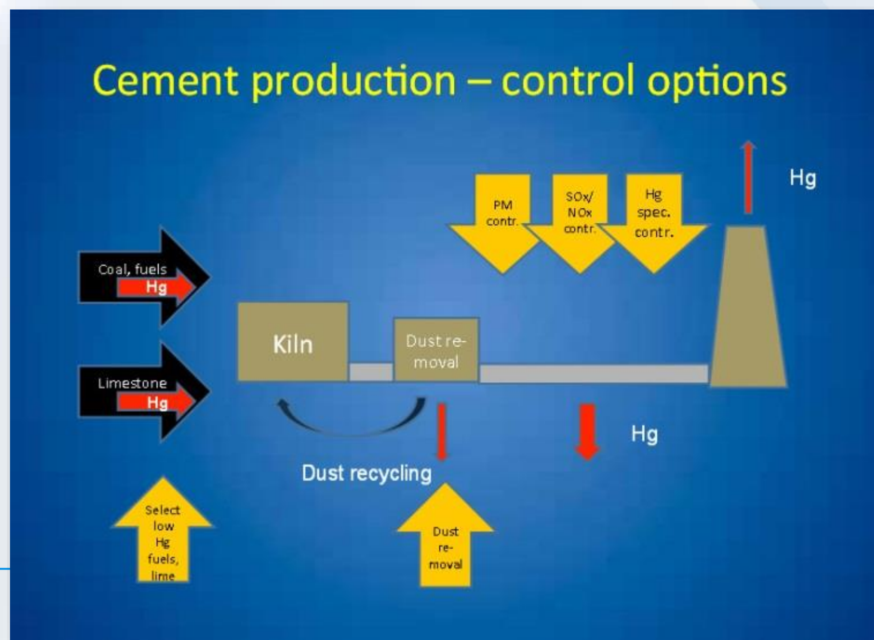
# <u>Fate and Transport</u> partnership can assist countries by :

- Accelerating the development of sound scientific information in global mercury cycling;
- Enhancing compilation and sharing of information among stakeholders;
- Providing technical assistance and training;
- Enhancing the development of a globally-coordinated mercury observation system, including air and water ecosystems.
- Enhancing the exchange of information and cooperation with relevant organizations.



# Mercury Reduction from Cement Industry partnership can assist countries to:

- Establish sectoral mercury inventories and baseline scenarios for the industry.
- Encourage use of most appropriate technique to reduce or minimize mercury releases into the environment.
- Increase the awareness of the cement industry to mercury as a pollutant through increased outreach efforts.



# *Thank you for your attention!*

See Partnership website for details or email
metals.chemicals@unep.org

www unep.org/chemicalsandwaste/Mercury/GlobalMercuryPartnership

# The UNECE Convention on Long-range Transboundary Air Pollution

- UNECE – Geneva Convention
- 8 protocols (POPs, Gothenburg P, Heavy Metals)
- Negotiations since early 70's
- 1998 HMP adopted, in force since 29.12.2003, 31 Parties
- Aims:
  - to control emissions of HMs caused by anthropogenic activities subject to long-range transboundary atmospheric transport, and
  - to reduce the significant adverse effects on human health and environment
- Basic obligations:
  - emission reduction compared to base year
  - emission limit values (ELVs) for dust
  - use of BAT
  - No lead in petrol
  - management measures for products
  - recommendation for reducing emissions from dental amalgam

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# What is different for point sources in comparison to the future Hg Convention?

- Concerning point sources:
  - Different Definition of BAT

  …taking into account economic and technical considerations for a given party or a given facility within the territory of that party…

  - Different source categories
  - Higher capacity thresholds
  - Different ways to reduce emissions
    - adopt a [national] goal [or target or outcome]  for controlling and/or reducing emissions to the atmosphere from these sources (either in aggregate or by source category;
    - establish emission limit values(or equivalent technical measures to be applied to these installations),
    - require the use of BAT/BEP at these installations.
    - apply multi-pollutant control strategies
  - Guidelines to assist Parties to reduce emissions are developed later

# Mercury Export Ban

Regulation (EC) No 1102/2008 of the European Parliament and of the Council of 22 October 2008 on the banning of exports of metallic mercury and certain mercury compounds and mixtures and the safe storage of metallic mercury (Text with EEA relevance)

# EU Chemical Policy - REACH

**Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)**

- **Adopted on 30/12/2006**
- **Gradual entry into force**
- **REACH replaces about 40 pieces of EU legislation including some on mercury, specifically**
- **Applies to all chemicals**
- **Industry responsible to manage risks posed by chemicals**
- **European Chemicals Agency (ECHA) with a central coordination and implementation role in the overall process.**

# Mercury in REACH

Annex XVII – refers to restrictions on the manufacture, placing on the market and use of 52 different groups of dangerous substances

a) Contains mercury compounds
b) As of 1 June 2009 will also contain provisions related to the EU Directive 76/769/EEC on restrictions on the marketing and use of certain dangerous substances and preparations as amended

# Control measures

- **Compliance with the requirements** – nationally (various bodies required to inspect (environmental inspections, hygiene institutes, COI) and evaluate national reports

- **EU level** – based on national reporting, verified by measurement and values from national and European registers – if not in compliance – infringements or fines

- **Directive 2007/51/EC** of the European Parliament and of the Council of 25 September 2007 amending Council Directive 76/769/EEC relating to restrictions on the marketing of certain measuring devices containing mercury (Text with EEA relevance)

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# Unresolved issues by EU legislation

- **Dental amalgam** – review ongoing, phase down/ban in some cases of EU countries
- **Button cell batteries** – alternatives available, but collection scheme may be resource intensive

# Case Minamata (1953 – 1973), Japan

50´s and 60´s – Japan – mass poisoning by Hg and its compounds.

The first surrounding of Bay Minamata in 1953.

During the following three years was confirmed that the primary source is connected with the wastewaters from chemical company Chisso-Nippon Chemical Plant (production of acetaldehydes, vinylchlorides), which were released more than 30 years to this bay with hogh contents of Hg compounds , which were on water and sediments transformed to methylated form.

Mono- and dimethylmercury concentrated in plankton and via bioaccumulation in fish were transferred to human bodies.

# Case Minamata (1953 – 1973), Japan

Most affected just fishermen and members of their families who were great consumers of fish.

116 cases were detected, 71 from them died, from year 1956 died 1 784 people.

The victim died as a result of hardening of the brain cell lysis in the centers of vision, hearing and balance.

Other people suffered "only" an incurable damage to the nervous system and resulting disability.

Since this event was talking about so-called Minamata disease.

# *Minamata (1953 – 1973, Japan)*

# Monitoring of Hg emissions

Monitoring of mercury emissions is an essential part of overall BAT and BEP implementation for controlling mercury emissions to the environment and for maintaining high operating efficiency of the abatement techniques used.

Monitoring of mercury emissions should be conducted according to overall best practices using approved/accepted methods.

Representative, reliable and timely data obtained from mercury emissions monitoring is needed to evaluate and ensure the effectiveness of the mercury emission control techniques in use at a facility.

All relevant sources of mercury emissions should undertake mercury emissions monitoring.

# Monitoring of Hg emissions

The first step in conducting mercury emissions monitoring is to take direct measurements of them mercury concentrations in the applicable gas streams to establish a performance baseline.

Subsequently, more measurements are taken at specific time intervals (e.g. daily, weekly, monthly) to characterize the mercury concentration in the gas at that point in time.

Monitoring is then conducted by compiling and analyzing the emissions measurement data to observe trends on emissions and operating performance.

Should the measurement data indicate any areas of concern, such as increasing mercury concentrations over time or peaks of mercury emissions associated with certain plant operations, swift action should be taken by the facility to rectify the situation.

# Monitoring of Hg emissions

The selection of a measurement or monitoring approach should begin with consideration of the intended outcomes.

Short term measurements may be needed to provide quick feedback for process optimization, or long term monitoring may be desirable for emissions inventory reporting.

Continuous emissions monitoring may be needed to control the process if mercury emissions are highly variable, for example due to rapidly changing mercury contents in the feed materials.

In addition, site-specific characteristics may need to be taken into account when selecting the most appropriate monitoring method and planning for the sampling campaign.

# Monitoring of Hg emissions

Depending on the process, mercury may be present to a variable extent as particulate-bound mercury, gaseous elemental mercury ($Hg^0$) and/or in the ionized gaseous forms, $Hg^{(I)}$ or $Hg^{(II)}$.

The partitioning may even vary significantly among facilities conducting similar processes.

For some processes, it may be useful to measure these different mercury species individually, for example, to inform decisions on effective control technologies or to conduct risk assessments.

The sampling point should be easily accessible, meet occupational health and safety requirements, meet regulatory requirements, and allow for the retrieval of representative samples.

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# Monitoring of Hg emissions

Ideally, the same sampling points should be used for subsequent sampling campaigns to provide comparability between results.

To prevent dilution of the samples and avoid false low results, ambient air should not infiltrate the sampling points.

Preferably, the gas velocity flow profile should be considered when identifying the sample location to avoid areas of flow disturbance, which would affect the representativeness of the sample.

Detailed information on the design and installation of measurement points are available in the European guideline EN 15259:20073 "Air Quality-Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report".

# Monitoring of Hg emissions

The guideline is applicable for continuous as well as discontinuous measurements.

To provide representative data, the sample timing, duration and frequency should be determined by considering various parameters, including the measurement and monitoring method used, the facility operating conditions and site-specific process variations and requirements to show compliance under the applicable regulatory process.

Samples should be taken at steady-state conditions representative of normal facility operations.

If the emissions are highly variable, or emissions are from a batch process, longer sample duration should be used or more samples collected (e.g. samples taken across the entire batch) to provide a reliable average measurement.

# Monitoring of Hg emissions

Also, low concentrations of mercury in the sample stream may necessitate longer duration to provide a total sample mass above the method detection limit.

Furthermore, periodic composite samples (e.g. over ½ hour, 12 hours, 24 hours) provide more representative results compared to random grab samples.

Mercury emissions can vary significantly within a single facility over time or among facilities conducting similar processes due to variable mercury content in the materials entering the process.

Mercury concentrations can change rapidly in the fuel, raw materials or other inputs, such as waste.

# Monitoring of Hg emissions

During the emissions measurement procedure, the mercury content in the process inputs should also be documented to assist with quality assurance.

When conducting sampling, care must be taken, as far as possible, to ensure that the process is operating at normal steady state, mercury concentrations in European Committee for Standardization, "EN 15259:2007: Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report", August 18, 2007.

http://standards.cen.eu/dyn/www/f?p=204:110:0::::FSP_PROJECT:22623&cs=106F3444821A456A90F21590F3BFF8582

the input streams are representative of normal feeds, and that fugitive emissions are minimized.

# Monitoring of Hg emissions

If the operating conditions are not typical, extrapolation of the sampling data may provide results with a large margin of error.

Operating conditions should be documented before, during and after the sampling campaign.

Specific parameters, such as the volumetric gas flow rate, gas temperature, water vapor content of the gas, static pressure of the gas duct, and atmospheric pressure, should be accurately recorded to allow for conversion of the measured mercury concentrations to standard reference conditions (0 °C, 1 atm, measured or reference oxygen content and on a dry gas basis).

# Monitoring of Hg emissions

The quantity of mercury emitted over time can be determined by multiplying the mercury concentration in the exhaust gas by the stack volumetric gas flow rate, as follows:

For example:

$$EHg = CHg \times F \times T$$

Where:

EHg = Annual emissions of mercury ($kg\ y^{-1}$)
CHg = Mercury concentration in the gas stream ($kg\ m^{-3}$)
F = volumetric flow rate of the gas stream ($m^3\ h^{-1}$)
T = operating time per year ($h\ y^{-1}$)

# Monitoring of Hg emissions

Most direct emissions monitoring methods rely on sampling at a point source, such as a stack.

Measurement of diffuse emissions, including fugitive emissions, is normally not practiced and methodologies that do exist for measuring diffuse emissions typically produce results with high uncertainty.

Thus, it should be noted that emissions monitoring results from point sources may not provide complete data on the total mercury emissions from a facility.

Monitoring method selection should be based on various criteria, such as: site characteristics; process specifics; measurement certainty; cost considerations; regulatory requirements; and, maintenance requirements.

To compare the facility's mercury emissions over time, consistent sampling methods should be used in subsequent years.

# Direct measurements methods

Direct measurement methods are generally considered as the most reliable techniques for mercury emissions monitoring.

When correctly conducted, these methods can provide representative, reliable data to allow for more precise estimation of a facility's actual mercury emissions.

Short Term Measurements

Impinger Sampling

Impinger sampling of mercury emissions from a stationary source is conducted by manually collecting a sample of exhaust gas from an outlet such as a stack or duct with an isokinetic sampling system, whereby the sample gas stream that is extracted is of the same velocity as the main stream.

# Impinger sampling

The isokinetic sampling accounts for changes in gas flow rate and for some particulate loading in the gas.

However, this method is not suitable for gases with heavy particulate loading.

This method requires the use of an intricate sampling train to recover mercury from the gas stream into a solution that is then sent for laboratory analysis.

While this method allows for good accuracy in mercury concentration measurement, it requires continuous attendance during the sampling period.

An advantage of this method is that recovery is possible for both mercury in gaseous form and mercury bound to particulate matter.

Because of the complexity of this procedure, source testing tends to be performed only periodically (e.g. once or twice per year).

# Existing reference methods

- **Method EN 13211:2001/AC: 20055 - Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury**
- **Method EN 14385:20046 - Air quality - Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V.**
- **US EPA Method 297 - Metals Emissions from Stationary Sources.**
- **Method ASTM D6784- 02 (Reapproved 2008)8 - Standard test method for elemental, oxidized, particle-bound and total mercury in flue gas generated from coal-fired stationary sources (Ontario Hydro Method)**
- **JIS K02229 (Article 4(1) – Methods for determination of mercury in stack gas (wet absorption and cold vapor atomic absorption method)**

# Sorbent trap sampling

Sorbent traps provide an average mercury concentration measurement over a sampling period, similar to the impinger methods.

In addition, sorbent traps provide more stable mercury retention and a simpler sampling protocol which allows for unattended operation of the sampling over extended periods.

Sorbent traps are used to measure mercury emissions from point sources with low particulate matter concentrations.

Typically, duplicate samples are extracted in parallel using probes inserted into the gas stream.

The probes contain sorbent traps which accumulate mercury from the gas. The sorbent material used is mainly halogenated carbon. Standard sorbent traps are intended to measure gaseous mercury but due to the operation of the sampling method, particulates containing mercury can be drawn into the sorbent traps. This particulate is analyzed and the measured amount is added to the carbon bed amounts to form the total mercury value. However, the sorbent trap method does not collect particulates isokinetically so it is not an accurate method for measuring particulate bound mercury.

# Sorbent trap sampling

## Existing reference methods:

- **US EPA Method 30B11 – Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps**
- **JIS K0222 (Article 4(2) – Methods for determination of mercury in stack gas (Gold amalgamation and cold vapor atomic absorption method)**

# Instrumental testing

Instrumental testing can be used for short term measurements of vapor phase mercury concentrations in gas.

In this method, a gas sample is continuously extracted and conveyed to a mobile analyzer which measures elemental and oxidized mercury ($Hg^0$ and $Hg^{2+}$), either separately or simultaneously.

The mobile analyzer uses a measurement technique similar to that used in continuous emissions monitoring.

US EPA Method 30A12 - Determination of Total Vapor Phase Mercury Emissions From Stationary Sources (Instrumental Analyzer Procedure)

Method 30A is a procedure for measuring total vapor phase mercury emissions from stationary sources using an instrumental analyzer. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury continuous emissions monitoring systems and sorbent trap monitoring systems at coal-fired combustion sources. Quality assurance and quality control requirements are included.

# Long term measurements

Sorbent Trap Monitoring Systems

Sorbent trap monitoring systems are used to monitor mercury emissions from point sources with low particulate matter concentrations.

These systems are permanently installed at a suitable sampling point to provide consistent, representative samples and operated on a continuous basis over a set time period, such as 24 hours up to 168 hours, or even 14 days for samples of low mercury concentration.

As with other extractive methods, the location of the sample point should be carefully chosen to provide representative and useful data.

Cost for installing a sorbent trap monitoring system is estimated at about US$ 150 000. Using US data from 2010, annual operating costs for the sorbent trap monitoring system for coal-fired power plants are US$ 26 000 to $ 36 000 and annual labor costs for operation are US$ 21 000 to $ 36 000.

# Sorbent Trap Monitoring Systems

**Existing reference methods:**

**US EPA Method PS-12b15 (Performance Specification 12b) – Specifications And Test Procedures For Monitoring Total Vapor Phase Mercury Emissions From Stationary Sources Using A Sorbent Trap Monitoring System**

**This method is used to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapor-phase mercury emissions in stationary source flue gas streams.**

**This method is appropriate for long-term mercury measurements up to a sampling time of 14 days in order to monitor low levels of mercury emissions.**

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# Continuous measurements

## Continuous Emissions Monitoring Systems (CEMS)

Continuous emissions monitoring systems (CEMS) are used to monitor gaseous emissions from point sources over long durations.

This monitoring method does not measure particulate mercury.

With this automated method, representative samples are taken continuously or at set time intervals using a probe inserted into the gas stream.

CEMS are therefore useful for uninterrupted monitoring of mercury emissions, which can be variable over short time intervals due to changing mercury concentrations in raw materials, fuels or reagents.

For example, CEMS would be useful during the co-incineration of waste material as fuel because of the rapidly changing mercury content in the waste.

# Continuous Emissions Monitoring Systems (CEMS)

Due to regulatory monitoring and reporting requirements, there has been a growing use of this method in the US and the EU among certain sources over the last 10 years.

While the cost of installation and operation may be high compared to other methods, CEMS provide the greatest data quantity, generating real-time information over various types of operations and process fluctuations.

The location of the sample point should be carefully chosen to provide representative and useful data.

In a complex facility with multiple outlets potentially emitting mercury, the cost of installing CEMS on each outlet may be very high.

Using US data from 2010, the general cost of installing a new mercury CEMS in a coal-fired power plant is estimated at about US$ 500 000, with $ 200 000 for the system, including startup and training, and $ 200 000 to $ 300 000 for site preparation. At facilities with multiple stacks and where CEMS would be technically and economically viable, as well as informative, the CEMS should be located on the outlet emitting the bulk or largest mass of mercury emissions at the facility. While the CEMS in such a case would not provide information from all gas outlets, the resulting data may provide a useful real-time indication of process performance trends and mercury control efficiency.

# Continuous Emissions Monitoring Systems (CEMS)

**Existing reference methods:**

US EPA Method PS-12a17 (Performance Specification 12a) – Specifications And Test Procedures For Total Vapor Phase Mercury Continuous Emission Monitoring Systems In Stationary Sources

EN 14181:201418 – Stationary source emissions - Quality assurance of automated measuring systems

EN 14884:200520 – Air quality - Stationary source emissions - Determination of total mercury: Automated measuring systems

Method EN 13211:2001/AC: 200521 - Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury

JIS K0222 (Article 4(3) – Methods for determination of mercury in stack gas (Continuous monitoring method)

# Indirect measurements methods

**Mass balance**

$$M_{in} = M_{out} + M_{accumulated/depleted}$$

**Where:**

$M_{in}$ = mass of mercury entering the facility in the feedstock, fuel, additives, etc.

$M_{out}$ = mass of mercury leaving the facility in finished products, byproducts, wastes and emissions and releases

$$(M_{out} = M_{product} + M_{by\text{-}product} + M_{waste} + M_{emissions} + M_{releases})$$

$M_{accumulated/depleted}$ = mass of mercury accumulated or depleted within the facility

# Predictive emissions monitoring systems (PEMS)

## Emission factors

The general equation for estimating mercury emissions using an emissions factor is:

$$E_{Hg} = BQ \times CEF_{Hg} \text{ or}$$

$$E_{Hg} = BQ \times EF_{Hg} \times (100 - CE_{Hg})/100$$

Where:

$E_{Hg}$ = Emission of mercury (kg or other unit of mass)

BQ = Activity rate or base quantity (base quantity unit)

$CEF_{Hg}$ = Controlled emission factors of mercury (kg $BQ^{-1}$) [dependent on any emission control devices installed]

$EF_{Hg}$ = Uncontrolled emission factors of mercury (kg $BQ^{-1}$)

$CE_{Hg}$ = Overall emission control efficiency of mercury (per cent)

# Predictive emissions monitoring systems (PEMS)

## Engineering estimates

General estimates of mercury emissions can also be obtained using engineering principles, knowledge of the relevant chemical and physical processes, application of related chemical and physical laws, and familiarity with site-specific characteristics.

For example, annual mercury emissions from fuel use can be estimated as follows:

$$E_{Hg} = QF \times \%\,Hg \times T$$

Where:

$E_{Hg}$ = Annual emissions of mercury (kg $y^{-1}$)

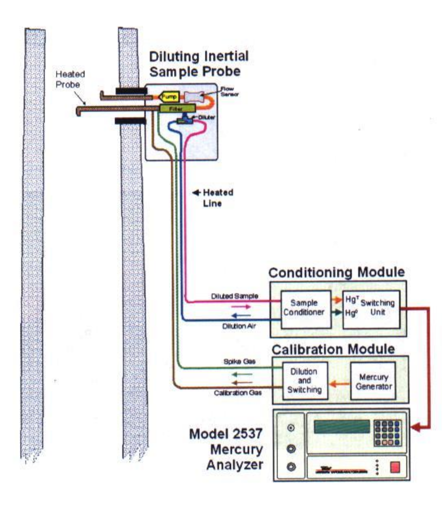
QF = Rate of fuel use (kg $h^{-1}$)

% Hg = per cent of mercury in fuel, by weight

T = operating time (h $y^{-1}$)

Engineering estimates should only be considered as rapid general approximations with a high level of uncertainty.

# Sampling of Hg emissions




Sampling of mercury emissions at the Kendal coalfired power plant in SouthAfrica, conducted under a UNEP project.

A probe with mercury traps is inserted into a sampling port in the stack to collect mercury present in the flue gas.

The mercury traps are subsequently analysed according to the US EPA Mercury Monitoring Toolkit sampling protocol.

# Atmospheric forms of Hg

Mercury in the atmosphere is in three primary forms.

Gaseous elemental mercury is the most common in anthropogenic and natural emissions to the atmosphere.

Gaseous oxidized mercury and mercury bound to particulates are less common.

The transport and deposition of atmospheric mercury depend greatly on whether the mercury is elemental or oxidized.

Elemental mercury stays in the atmosphere long enough for it to be transported around the world, whereas oxidized and particulate mercury are more readily captured in existing pollution control systems or deposited relatively rapidly after their formation.

As a result, most mercury in the air is in the gaseous elemental phase.

Relatively little elemental mercury is deposited directly, but instead must first be oxidized.

# Atmospheric forms of Hg

Although gaseous oxidized mercury is very important in mercury cycling between air and other environmental compartments, the process of oxidation in the air is poorly understood, with reactions and resulting compounds yet to be verified in observations.

When mercury moves from air to water and land, it is generally in an oxidized gaseous or particulate form, whereas when it is re-emitted to air it has been converted back to gaseous elemental mercury.

Sunlight appears to play a large role in both oxidation and reduction of mercury, but temperature and biological interactions are also likely to be involved to some degree.

Here, too, much uncertainty remains.

Nonetheless, the reactions are important in determining net deposition and fate of mercury.

# Atmospheric monitoring of Hg

Monitoring of mercury in air focuses on the three primary forms of mercury.

The measurement of gaseous elemental mercury is routine and robust.

Measuring gaseous oxidized mercury and particulate-bound mercury, however, is challenging.

Concentrations are typically very low, and these forms are chemically unstable, leading to high uncertainty in the measurements.

Nonetheless, these forms are critical for defining and modelling the fate and transport of airborne mercury.

In the past two decades, coordinated mercury monitoring networks and long-term monitoring sites have been established in a number of regions, measuring mercury concentrations in the air as well as deposition of mercury in precipitation.

In Europe and North America, high-quality, continuous monitoring has been going on for more than 15 years, especially in the Arctic. High quality monitoring has started more recently in East Asia and South Africa, as part of a global effort to expand the coverage provided by long-term monitoring sites.

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# Atmospheric Hg measurements and trends

Monitoring stations around the world have provided information about trends in atmospheric mercury, though the time periods vary depending on how long the site has been active.

Overall, a declining trend in background mercury levels over the past decade has been recorded from monitoring stations in many regions.

Other regions, however, show an increase in mercury levels.

The sites also provide information about geographical patterns, reflecting both background levels of mercury and local and regional influences.

Mercury concentrations at remote sites in Asia are higher than in other regions of the Northern Hemisphere.

Coastal cities in China have lower levels than inland sites, likely due to the influence of relatively clean air over the ocean.

# Atmospheric Hg trends

*Trends in atmospheric measurements of mercury*

| *Site(s)* | *Period* | *Measurement* | *Trend* |
|---|---|---|---|
| Mace Head, Ireland | 1996-2011 | Gaseous elemental mercury | Decrease of 1.4-1.8% per year |
| North America, rural sites | 1995-2005 | Total gaseous mercury | Decrease of 2.2% to 17.4% in total |
| High Arctic, sub-Arctic, mid-latitudes | Up to 20 years of records | Total gaseous mercury | Decreasing trend at some stations, increasing at others |

# *Atmospheric Hg monitoring programmes*

The European Monitoring and Evaluation Programme (EMEP)

Three monitoring networks currently operate in North America, providing good coverage of Canada and the United States: the Mercury Deposition Network, the Canadian Air and Precipitation Monitoring Network, and the Atmospheric Mercury Network. More recently, new sites have been established in Mexico, extending coverage on the continent.

Monitoring of mercury in the air and in precipitation has been underway in Asia for nearly a decade.

The monitoring network of the Arctic Monitoring and Assessment Programme (AMAP) includes air and deposition monitoring sites located in Arctic regions of Canada, Greenland, Iceland, Norway, Russia, and Sweden.

# Atmospheric Hg monitoring programmes

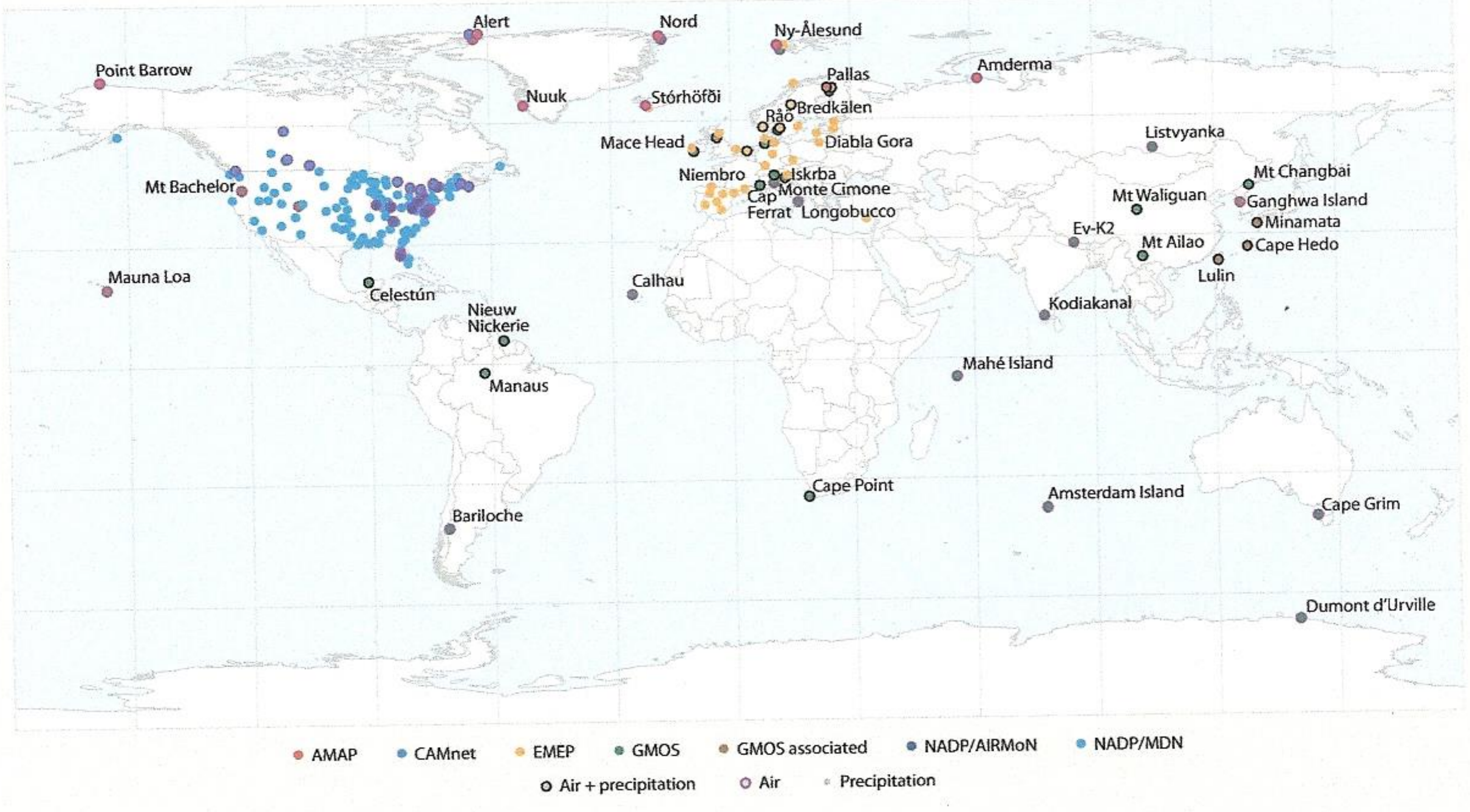
Building on existing national and regional monitoring networks, the European Union-financed project "Global Mercury Observation System" (GMOS) started in November 2010.

Its goal is to develop a coordinated global system for monitoring mercury, including a large network of ground-based monitoring stations.

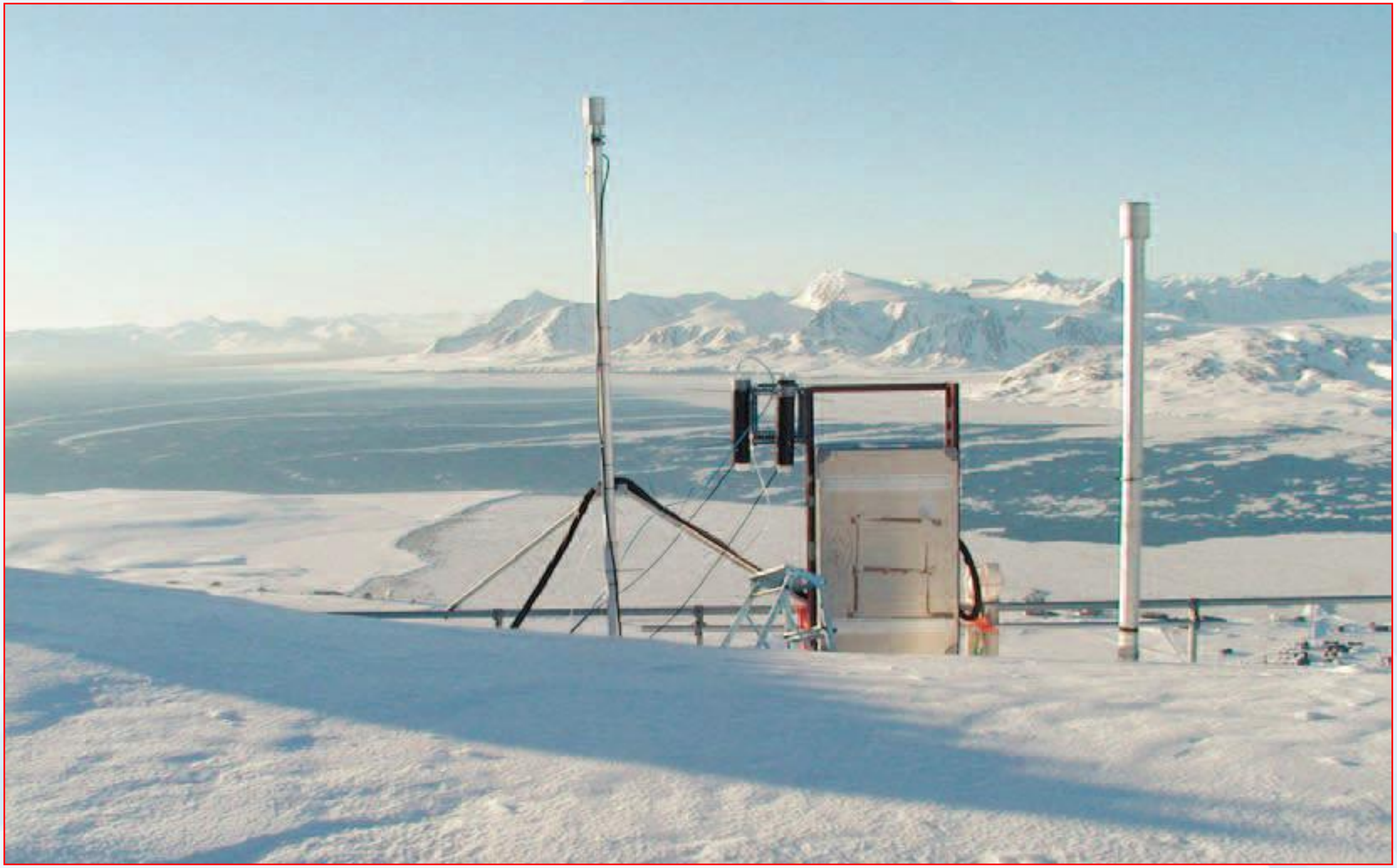
New sites are being installed in regions where few monitoring stations exist, especially in the Southern Hemisphere.

Two sites have been established in Antarctica, one on the Antarctic Plateau and one on the coast.

# Hg monitoring networks



# The mercury background air monitoring station at Zeppelin mountain, Svalbard



# RECETOX - Research Centre for Toxic Compounds in the Environment, Masaryk University, Brno, CR

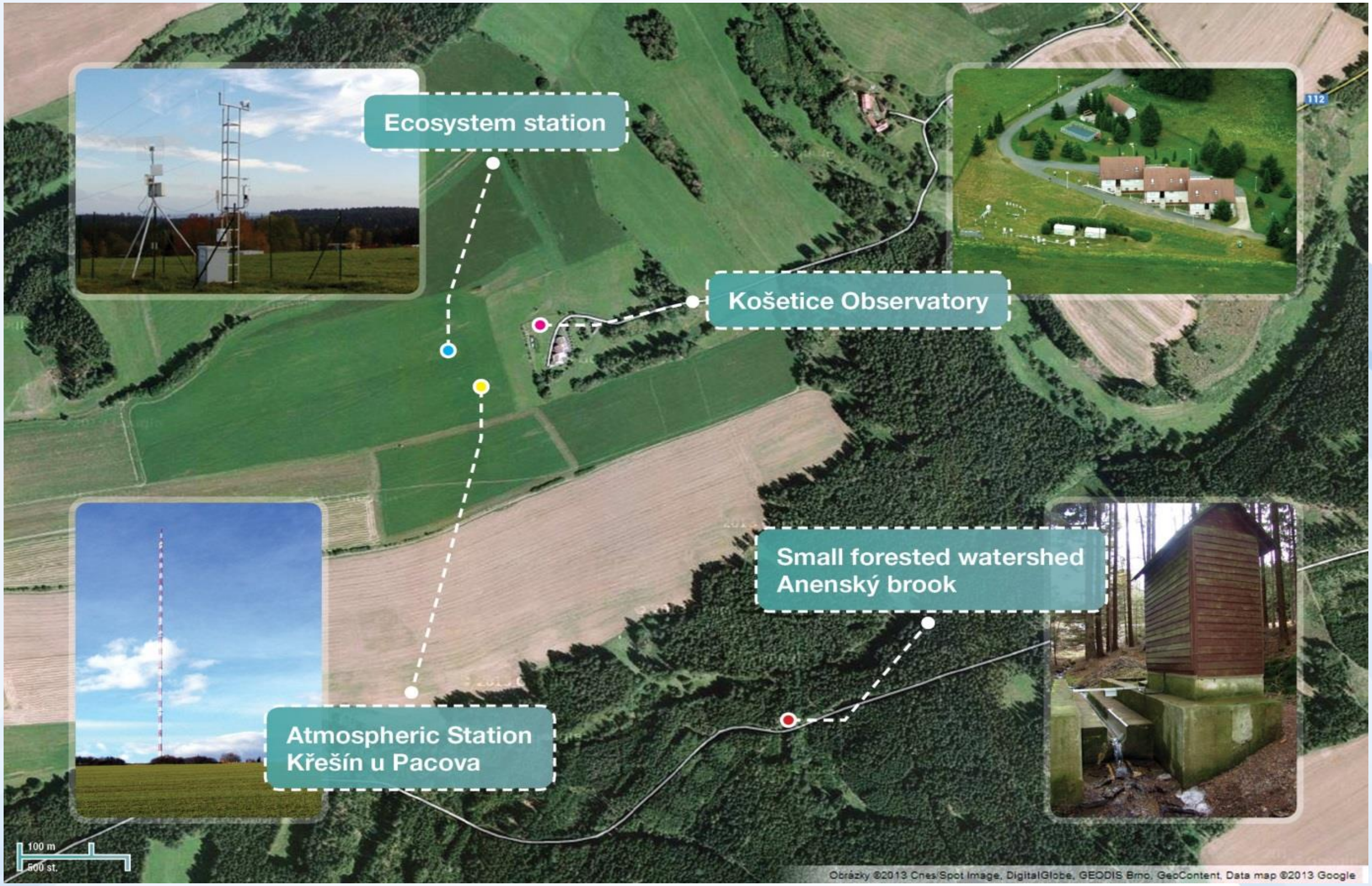
# National Centre for Toxic Compounds

*www.recetox.muni.cz/nc*

- Part of the RECETOX
- The bilateral agreement between MoE CR and MU Brno

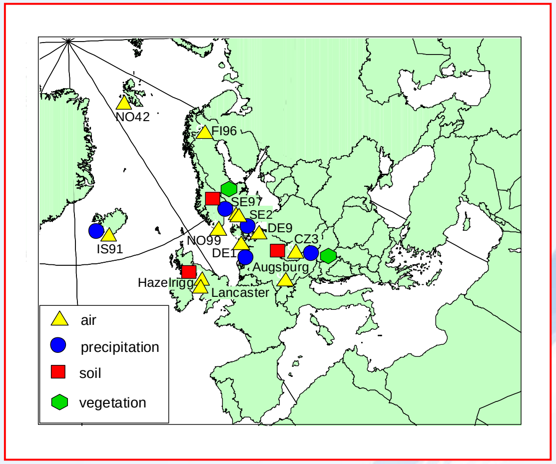
- Established at 2006 as the National POPs Centre
- From 2014 covers all chemical conventions nin the CR including Minamata (synergism)
- Centre serve as a platform for information transfer between science and decision making sphere fro these chemical conventions (technical, datas, epertise etc.)
- POPs and chemicals issueas are complex and interministerial – coordination is done by interdependent Council of National Centre for Toxic Compounds

# National Atmospheric Observatory (NAO) Košetice



# Superstation concept - Observatory Košetice, CR

## EMEP POPs Network

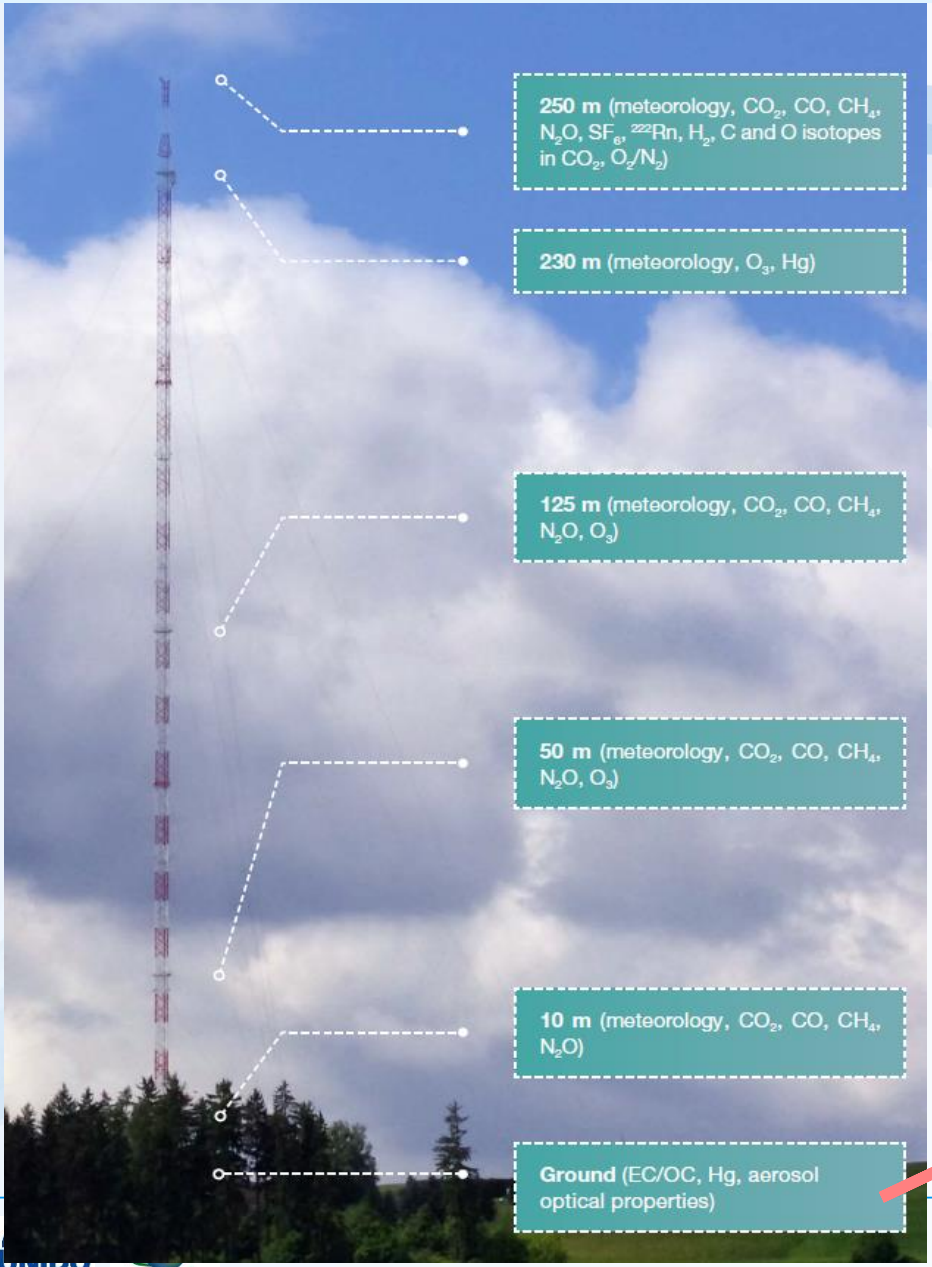


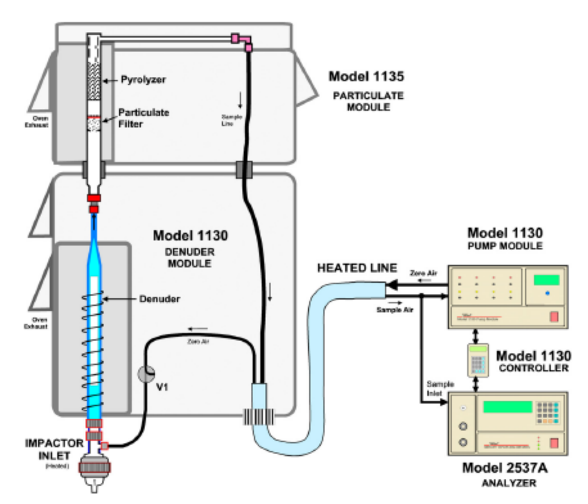

## Integrated POPs monitoring - Observatory Košetice

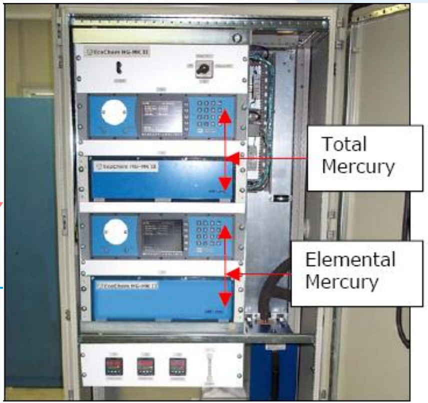
Comparison of existing programmes (EMEP, GAPS, MONET) and approaches (active vs. passive)

# National Atmospheric Observatory (NAO) Košetice

# National Atmospheric Observatory (NAO) Košetice



# Teşekkür Ederim