MINAMATA ONLINE

SEASON 1 - 2020

Implementation Review and Support: Article 12 Contaminated Sites



SPEAKERS

This session will outline how the Minamata Convention sets out obligations with respect to the management of contaminates sites (Article 12) and how it provides relevant technical guidance. The session will also include presentation on case studies on conceptual models, remediation technologies, monitoring and risk management.



Claudia ten Have

Senior Policy and Coordination Officer, Minamata Convention on Mercury



Thursday, 26 November 2020

10h00-11h00 CET

16h00-17h00 CET



Rocío Millán

Research Center for Energy, Environment and Technology – CIEMAT



Eisaku Toda

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Please register for the WebEx session using the links above.

Check the Minamata Online calendar

for other upcoming events and the presentations and video recording from the previous sessions.







THIS SESSION WILL COVER

- Overview Minamata Convention addressing the life cycle of mercury
- Section 1: Article 12 Contaminated sites
- Section 2: Guidance on the management of contaminated sites
- Section 3: Case studies
- Questions and Answers

Logic of the Minamata Convention

Control Measures

Keep mercury underground

Art. 3.3: No new primary mines

Art. 3.4: Existing mines - 15 years

Reduce the use and presence of mercury in the economy, industry and society

Art. 3.5 (a): <u>Stocks</u>

Art. 3.5 (b): Excess mercury from decommissioned chlor-alkali facilities

Art. 3.6 – 3.10: Trade of mercury

Art. 4: Mercury-added Products

Art. 5: Manufacturing Processes

Art. 7: ASGM

Art. 10: Interim Storage

Art. 11: Mercury wastes

Art. 12: Contaminated sites

Reduce mercury to the environment

Art. 7: ASGM

Art. 8: Emissions

Art. 9: Releases



Enabling / Supportive Context

Art. 13: Financial Mechanism

Art. 14: Capacity-building, technical assistance and technical transfer

Art. 15: Implementation and Compliance Committee

Art. 16: Health aspects

Art. 17: Information Exchange

Art. 18: Public information, awareness and education

Art. 19: Research, development and monitoring

Art. 20: Implementation plans

Art. 21: Reporting

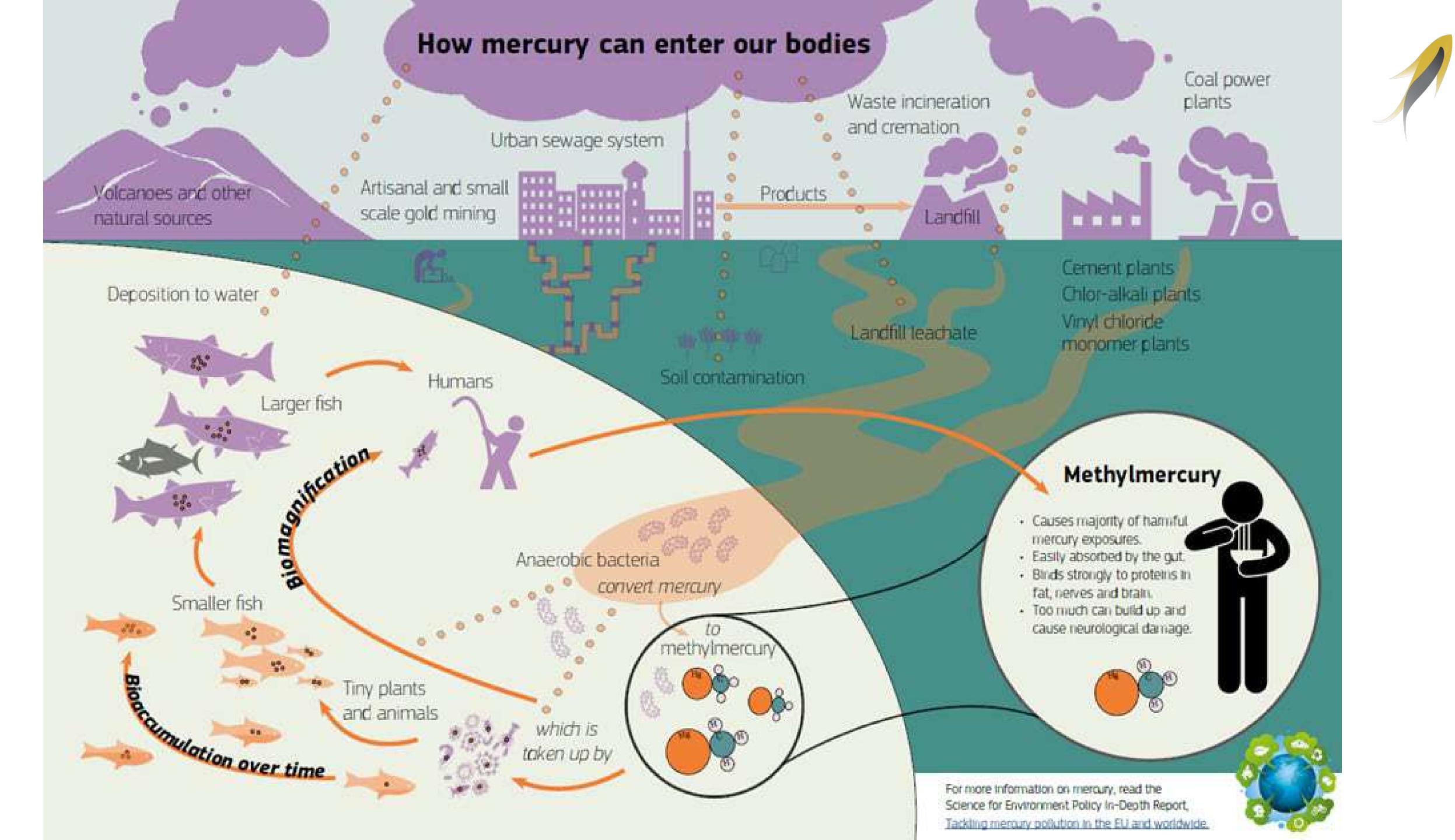
Art. 22: Effectiveness evaluation

Art. 23: Conference of the Parties

Art. 24: Secretariat

Arts. 25-35: Various procedural articles









ARTICLE 12 – Parties' Obligations

- 1. Each Party shall endeavour to develop appropriate strategies for identifying and assessing sites contaminated by mercury or mercury compounds.
- 2. Any actions to reduce the risks posed by such sites shall be performed in an environmentally sound manner incorporating, where appropriate, an assessment of the risks to human health and the environment from the mercury or mercury compounds they contain.
- 4. Parties are encouraged to cooperate in developing strategies and implementing activities for identifying, assessing, prioritizing, managing and, as appropriate, remediating contaminated sites.



ARTICLE 12: Development of Guidance

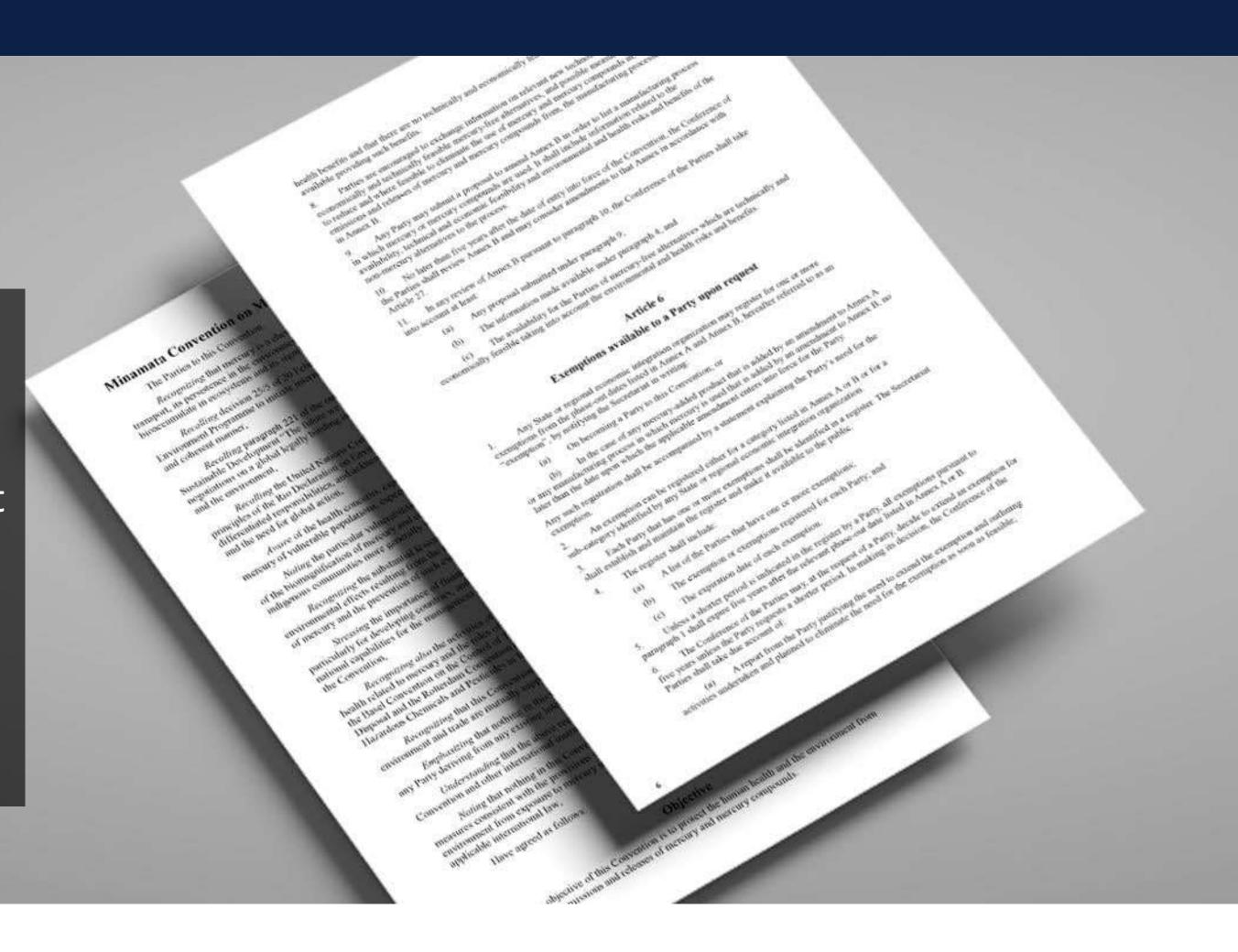
Para 3: The Conference of the Parties shall adopt guidance on managing contaminated sites that may include methods and approaches for:

- (a) Site identification and characterization;
- (b) Engaging the public;
- (c) Human health and environmental risk assessments;
- (d) Options for managing the risks posed by contaminated sites;
- (e) Evaluation of benefits and costs; and
- (f) Validation of outcomes.



Guidance on the Management of Contaminated Sites

- Adopted by COP-3 in 2019
- Covers the identification, assessment, management and remediation of sites contaminated by mercury and mercury compounds

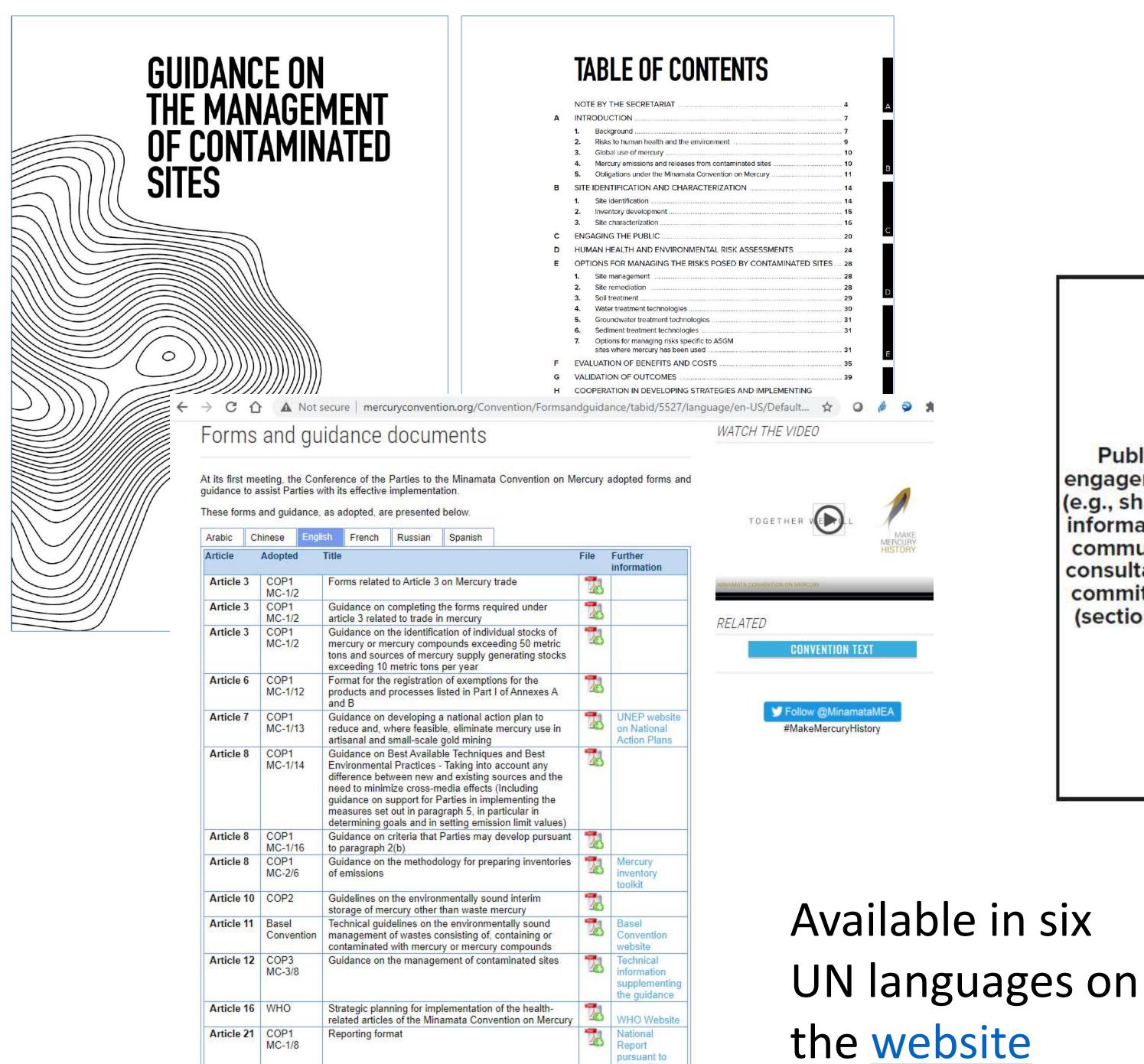




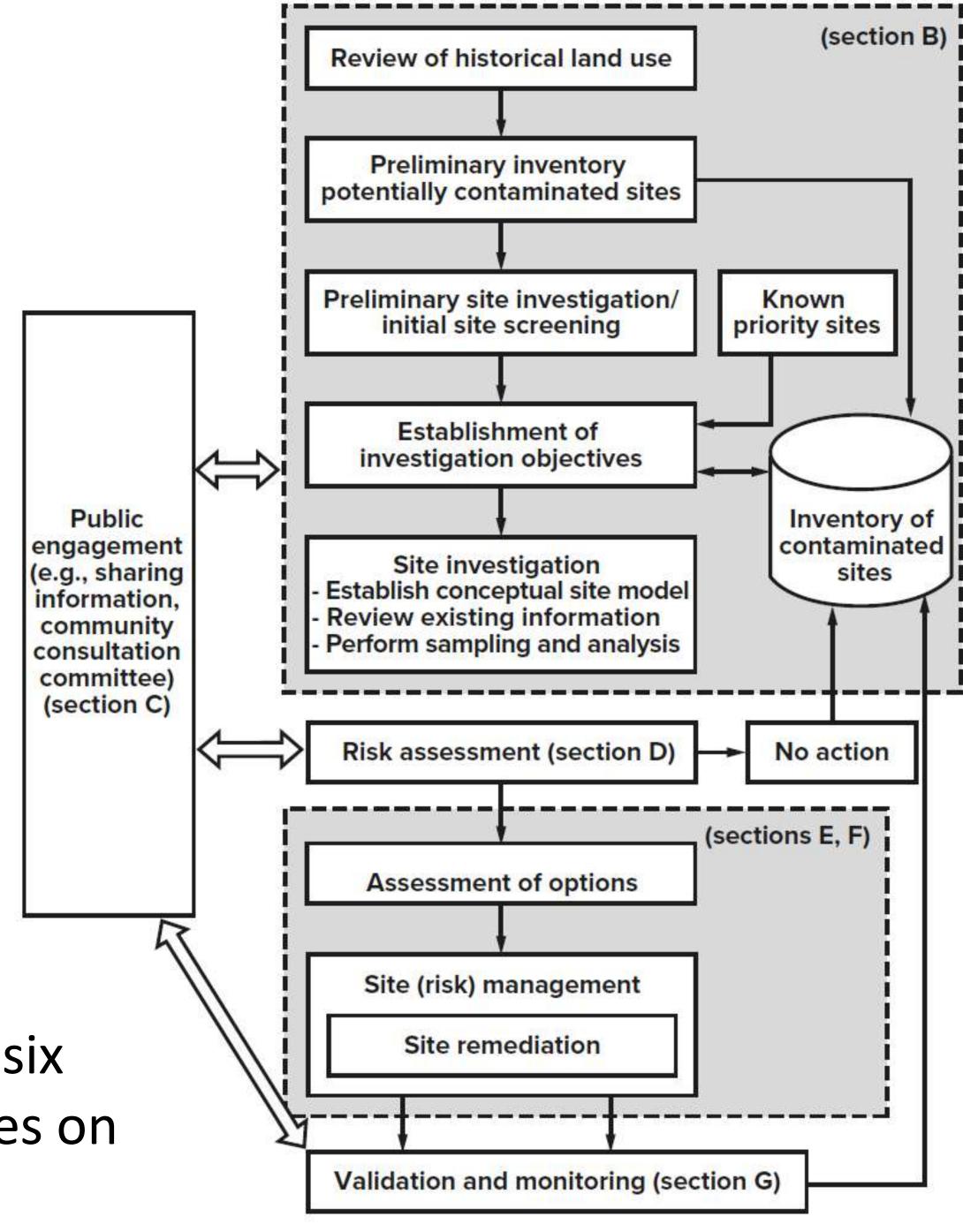
COP Decision MC-3/6

The Conference of the Parties,

- Adopts the guidance on the management of contaminated sites;
- Notes the importance of capacity-building, technical assistance and technology transfer, as appropriate and in accordance with articles 13 and 14 of the Minamata Convention;
- Encourages the Parties to take the guidance into account in identifying, assessing and managing, and, as appropriate, remediating sites contaminated by mercury or mercury compounds;
- Requests the Secretariat to continue to collect technical information that supports the guidance, in cooperation with experts nominated by Governments, relevant networks and others, and to make such information available to parties;
- Notes that the guidance may need to be revised in the future in the light of experience in its use to
 ensure that it continues to reflect best practice.



Report pursuant to Article 21



Site identification and characterization



Site identification

Review of historical and current land use – look into possible sources including:

- Mercury storage
- Manufacturing of mercuryadded products
- Use of mercury in manufacturing processes
- ASGM activities using mercury or primary ore rich in mercury in which the mercury is mobilized
- Primary mercury mining and abandoned, historical mines not managed in accordance with modern practices
- Point sources of emissions and releases
- Waste treatment and disposal

Contaminated sites may also be identified when land use changes or actions such as excavation and construction take place.

Inventory development

Inventory of suspected and confirmed contaminated sites can contribute to using a risk-based approach in managing the contaminated sites.

As an example, the government of Western Australia uses the following seven classifications.

- Contaminated –
 remediation required;
- Contaminated restricted use;
- Remediated for restricted use;
- Possibly contaminated
 investigation
 required;
- Decontaminated;
- Not contaminated unrestricted use;
- Report not substantiated

Site characterization

Suspected contaminated sites can be further characterized by phased investigation.

The development of a **conceptual site model (CSM)** for the site is an essential step in site characterization and assessment.

- Overview of historical, current and planned land uses
- Detailed description of the site and its physical setting that is used to form hypotheses about the release and ultimate fate of contamination at the site
- Sources of contamination at the site, the potential chemicals of concern and the media that may be affected
- Distribution and chemical form of contaminants within each medium
- How contaminants may be migrating from the source(s), the media and pathways through which migration and exposure of potential human or ecological receptors could occur, and information needed to interpret contaminant migration, such as geology, hydrogeology, hydrology and possible preferential pathways
- Information on climate and meteorological conditions that may influence contamination distribution and migration
- Where relevant, information pertinent to soil vapour intrusion into buildings
- Information on human and ecological receptors and activity patterns at the site or at areas affected by the site

Site investigation involving sampling and analysis of soil, sediment, groundwater and other media may be conducted for site characterization.

Engaging the public

- Whenever possible, Parties could consider strategies to promote public engagement, particularly on sensitive issues such as the presence of nearby contaminated sites, to ensure the successful management of issues and sites.
- The focus of public engagement is to ensure that people (or groups) who could be affected by, involved in or interested in an action are informed and that their views are considered in the decision-making process.
 - Community outreach targets different levels:
 - > Landowners or residents living near or on the site
 - Communities affected by pollution from the sites
 - > Industries in the area who might be affected by the pollution
 - > Site managers and workers employed at currently active sites
 - Etc. etc.
- Different methodologies for engaging the public may be appropriate, depending on the phase of the process (site identification, investigation, remediation, aftercare, etc.).
 - > The process of engaging the public could begin with giving information to the community involved.
 - Effective communication, along with a two-way process of transmitting and receiving information, is important for increasing understanding among stakeholders.
 - > Public engagement activities should include public meetings, which may be held at central community locations, or, in some cases, at the affected site.
 - > A useful engagement mechanism can be the establishment of a community consultation committee where technical, practical and anecdotal information can be exchanged between the authorities, the site contractors and the community to ensure a shared understanding of proposed activities at the contaminated site.

Human health and environmental risk assessments

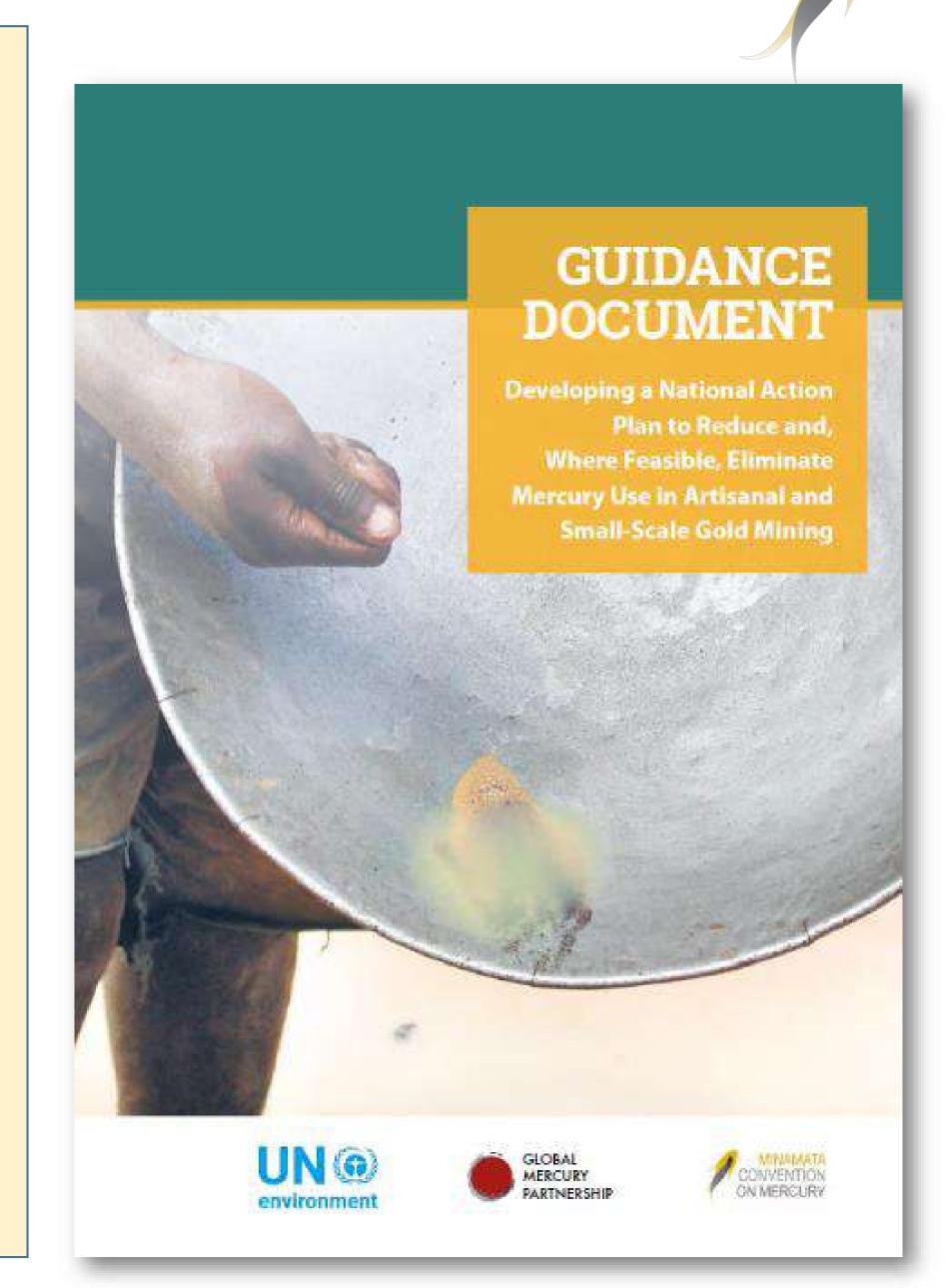
- Risk assessment will help to answer the following questions:
 - > Does the site present a risk to the human population and/or to the biota?
 - ➤ What is the magnitude of the risk?
 - > Can the site risk be adequately managed without site remediation (in the near term or over a longer period), or should the site be remediated to reduce the risk (in the near term or the long term)?
 - > If the site is not remediated, could the risk increase and/or spread?
- Risk assessment is generally carried out in four clearly defined stages.
 - ➤ Identification and characterization of the scope Priority on human health in many cases, but may also cover terrestrial animals and aquatic biota. Consider extent of contamination, proximity to human populations, depth to groundwater, proximity to surface water or sensitive habitats.
 - ➤ Analysis of the hazard level and toxicity The human health hazards of mercury and mercury compounds are well recognized and documented. The environmental effects of mercury exposure, particularly on high-level predators, can include decreased reproductive success and impaired hunting ability.
 - Analysis of exposure: The goal is to estimate the rate of contact between the identified contaminants and humans or the environment. This may involve exposure measurements such as testing of water supplies, locally grown food, seafood, and human scalp hair and urine. Measurements of mercury levels in sediments and fish and other biota can identify potential ecologic effects.
 - > Analysis of risks: The results of the previous stages are combined to objectively estimate the probability of adverse effects on human health and the environment under the specific conditions of the site. Risk = Hazard x Exposure

Options for managing risks posed by contaminated sites

- Site management includes actions taken to reduce exposure of humans and the environment to the mercury.
 - > Restrict the use of the site and impose spatial planning rules in accordance with the risk present on the site.
 - > If the water supply is contaminated, an alternative water supply or water treatment may be needed.
 - > Isolate the contamination on site in a containment facility pending later remediation.
 - > Periodically monitor the site to ensure that mercury is not migrating off site or developing the potential to affect the environment beyond the site boundaries.
- Site remediation includes actions taken to remove, control, contain or reduce contaminants or exposure pathways.
 - ➤ The decision to remediate requires consideration of factors including the desired outcome, the level of contamination, the likely exposures resulting from the contamination, the feasibility of remediation options, cost-benefit considerations, the potential adverse effects of any actions, availability of relevant technology, and the financial resources available for remediation.
 - > On-site soil treatment may be considered to either remove the contaminant or reduce the associated hazard.
 - > On-site containment of the mercury-contaminated area may be a viable option in certain circumstances Physical barriers, in situ injection of stabilization chemicals into the soil
 - > If in-situ treatment of the contaminated soil to remove the contamination is not feasible, another option is to excavate the contaminated soil and remove it from the site for treatment off site.
 - Relevant technologies:
 - ✓ Soil treatment solidification and stabilization, soil washing and acid extraction, thermal treatment and vitrification, as well as electrokinetics and in-situ thermal desorption.
 - ✓ Water treatment precipitation/coprecipitation, adsorption and membrane filtration

Options for managing risks specific to ASGM sites

- Identification of mercury-contaminated **ASGM sites** can follow the same preliminary site identification, detailed site identification and site characterization processes as any other mercury contaminated site, but additional complexity arises when the site is active, occupied and in a dynamic state of contamination.
- For public engagement, additional measures may need to be considered.
 ASGM sites can have a mix of transient and established workers. ASGM activities are also considered illegal in some locations, which can act as a barrier to effective engagement. Public engagement activities should occur within the context of the Party's National Action Plan under article 7.
- Reducing or eliminating the use of mercury in ASGM is the preferred approach, as preventing contamination is invariably cheaper than remediation.
- Using a holistic approach with community support under the National
 Action Plan, the problems associated with dynamic mercury contamination
 can be reduced or even eliminated, allowing the site contamination to be
 managed effectively.



Evaluation of benefits and costs

- Assessment of the cost and benefits of site management or remediation should consider:
 - > Costs associated with contaminated site identification and assessment.
 - > Costs associated with management or remediation of contaminated sites.
 - > Impact of site-related mercury exposure on the local population and the local environment
 - ✓ Direct costs such as medical monitoring or care for people with adverse health effects
 - ✓ Indirect costs such as loss of income associated with contaminated fish that cannot be caught or sold, or lost cropland
 - ✓ Some costs relate to non-market outcomes such as morbidity, brain damage, the loss of natural resources, clean water or ecological value.
- Financing of contaminated site management and remediation should reflect the polluter pays principle whenever possible.
 - > This may require a legal and regulatory framework that places the onus of expenditure for site assessment, management, remediation, waste treatment and disposal on those responsible for the pollution.
 - > In the absence of an established legal framework, parties would need to take a case-by-case approach.
 - > In some cases, different levels of government may be responsible for the financing framework for contaminated sites.
 - > Many national polluter-pays models for contaminated sites include provisions similar to the "orphan site" provisions of the European Union model.



CASE STUDIES



Useful information for using the guidance



- ➤ Technical information collected in the process of developing the guidance on the management of contaminated sites was compiled in a COP information document UNEP/MC/COP.3/INF/13.
- It includes a glossary of terms:
 - ✓ Conceptual site model: a visual representation and narrative description of the physical, chemical and biological processes that may occur, are occurring, or have occurred, at a site.
 - ✓ Contaminated site: A location where as a result of human activity an unacceptable hazard to human health and ecosystems exists. Local contamination (contaminated sites) is a problem in restricted areas (or sites) around the source, where there is a direct link to the source of contamination. (European Environment Agency)
 - ✓ Site characterization: Action to determine the contamination levels of and key risks posed by individual site. This involves phased investigation from preliminary site investigation or initial site screening to detailed site investigation.
 - ✓ **Site management:** A set of actions taken to reduce exposure of humans and the environment to the contaminants present at the site. Site remediation may be one of the management options, but in a narrower sense the word site management may be used to refer to options for controlling exposure other than remediation options.
 - ✓ **Site remediation:** Actions on the site aimed at the removal, control, containment or reduction of contaminants so that the contaminated site, taking account of its current use and approved future use, no longer poses any significant risk to human health or the environment. (Proposed EU Soil Framework Directive)

Existing guidance and technical tools



General or cross-cutting guidance

- > Canadian Council of Ministers of the Environment (CCME) (2016). <u>Guidance Manual for Environmental Site Characterization in Support</u> of Environmental and Human Health Risk Assessment.
- > IPEN (2016). Guidance on the Identification, Management and Remediation of Mercury-Contaminated Sites.
- Kovalick W., Montgomery, R., Developing a Program for Contaminated Site Management in Low and Middle Income Countries. The World Bank (2014).
- Mediterranean Action Plan/United Nations Environment Programme (MAP/UNEP) (2015). <u>Guidelines on Best Environmental Practices</u> for Environmentally Sound Management of Mercury-Contaminated Sites in the Mediterranean.
- > World Health Organization. Regional Office for Europe (WHO/EURO) (2013). Contaminated Sites and Health

Site identification and characterization

- ➤ Guérin V., Laperche V., Grangeon S., Hubé D. (2014) Characterisation of Mercury Contaminates Sites
- Australian National Environmental Protection Council (1999). NEPM Schedule B (1) Guideline on Investigation Levels for Soil and Groundwater.

Site management and remediation

- > ADEME, BRGM, Interactive tool for pre-selection of pollution control techniques, available in French only,
- ➤ Merly, C. and Hube, D. (2014). Remediation of Mercury-Contaminated Sites.
- NICOLE (Network for Industrially Co-ordinated Sustainable Land Management in Europe) (2015) Report: Risk-based Management of Mercury Impacted Sites
- ➤ United States Environment Protection Agency (US EPA) (2007). <u>Treatment Technologies for Mercury in Soil, Waste, and Water</u>.

Case studies

France submitted the following case studies

- Case studies on background mercury levels and conceptual model of mercury transfer to the food chain from Laperche V., R. Maury-Brachet, F. Blanchard, Y. Dominique, G. Durrieu, J.-C. Massabuan, H. Bouillard, B. Joseph, P. Laporte, N. Mesmer-Dudons, V. Duflo et L. Callier (2007) "Répartition régionale du mercure dans les sédiments et les poissons de six fleuves de Guyane". Rapport BRGM/RP-55965-FR.
- A case study on Restoration of Surface water bodies contaminated by mercury. State of the art of available methods and applicability in the French Guiana context from Laperche V. Touzé S. (2014) "Restauration de l'état des masses d'eau de surface contaminée par le mercure Etat de l'art des méthodes existantes et adaptabilité dans le contexte guyanais". Rapport final. BRGM/RP-64032-FR.
- A case study on groundwater Characterisation at chloralkali site

Canada submitted the following case studies

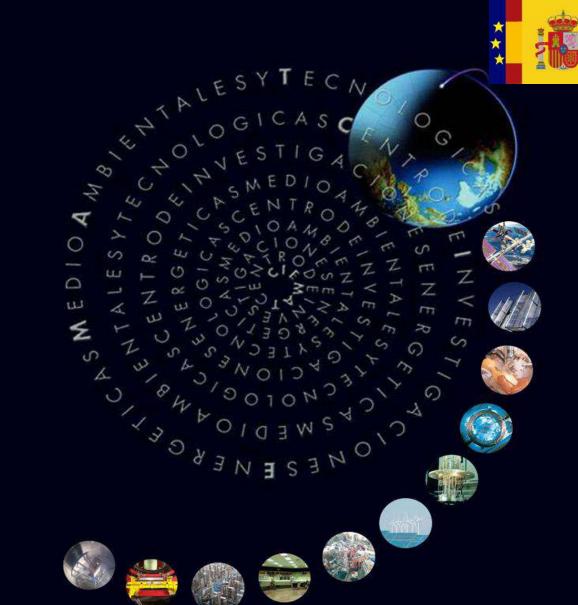
- Hydrometric monitoring stations using servo-manometers: Prior to 1997, Quebec hydrometric monitoring stations were operated using mercury servo-manometers. Due to large fluctuations in water levels, mercury was, in some cases, released from the instrument and ended up in the nearby sediments. Since 1997, all hydrometric sites in southern Quebec have been decontaminated.
- Chlor-alkali facilities: Due to the absence of environmental regulations prior to the 1970s, the lands of former industrial plants in Quebec could be contaminated with mercury. At one chlor-alkali production facility, 360,000 cubic metres of mercury-contaminated soil was treated using a physical separation process to recover liquid mercury and placed in a specially constructed containment cell located on the same property. As sediments of the river downstream of the facility were also found to be contaminated with mercury, they were dredged and added to the containment cell.
- Harbours and lighthouses: The surrounding soils and sediments around lighthouses and harbours may be contaminated with mercury due to the use of mercury containing products (e.g. paint, fungicide, lightbulbs, batteries) used in the construction, operation, and use of these structures. In many cases, the soils and dredged sediments are placed in specialized containment cells on or offsite.
- A description of the successful remediation of certain federal contaminated sites in Canada can be found on website. While these sites are not all mercury-contaminated sites, they may be helpful case studies to draw upon when preparing the draft guidance document.

Switzerland submitted the following case studies

- A major chlor-alkali plant of the CABB Company is situated in Pratteln in the canton of Basel-Landschaft. It is the only one in Switzerland that is still in use. Since about 2015, however, mercury has no longer been used for the chlor-alkali process.
- > At Lonza site in the canton of Valais, mercury was mainly used in the production of acetaldehyde from acetylene.

GOBIERNO

DE ESPAÑA



Contaminated sites. Case study: Almadén

Dr. Rocio Millán
CIEMAT – Environmental Department
Head of Soil and Geology Research Division
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CIEMAT: Public research organisation under the Spanish Ministry of Science and Innovation **focusing on energy and environment.** The activity is structured around projects which form a bridge between R&D&I and social interest goals. Work force: 1,400 employees

Departamento de Medio Ambiente / Environmental Department

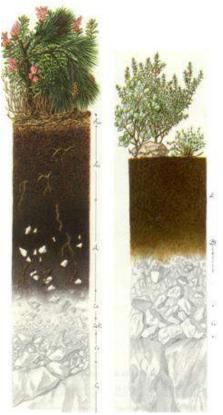
División de Suelos y Geología Ambiental / Soil and Environmental Geology Research Division

Unidad de Conservación y Recuperación de Suelos / Soil Conservation and Recuperation Research Unit





- Soil conservation (National parks, Antartica, etc).
- Recuperation of abandoned (marginal) soils.
- Characterization, rehabilitation and monitoring of contaminated sites.
- Sustainable agriculture.
- > Propose solutions for the treatment and reuse of organic waste (circular economy).







Mercury in gold mines







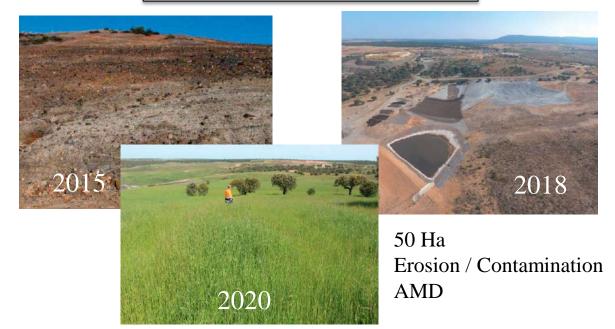




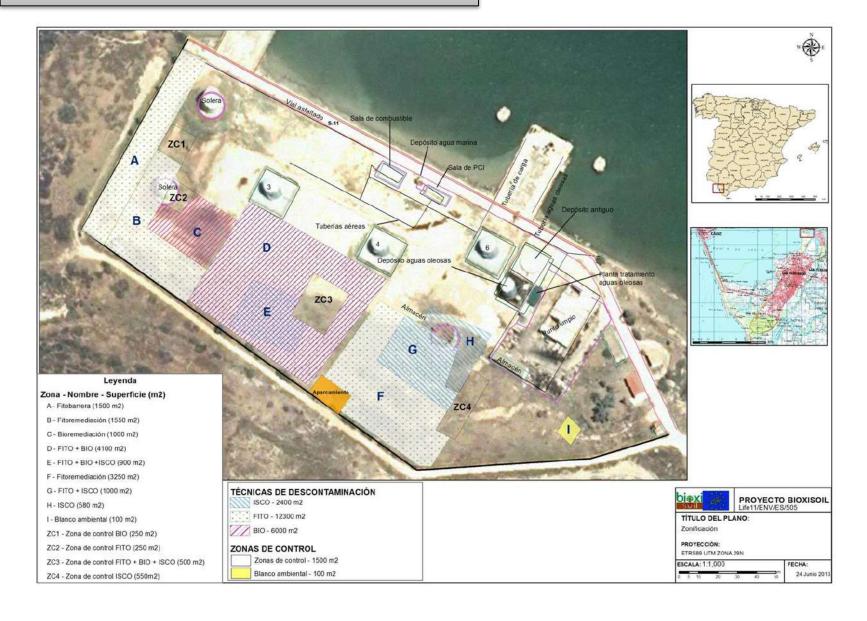
Mercury mines



Other mines: Uranium mine



Brownfields; industrial areas; Fuel plants



Spanish legislation

("Real Decreto 9/2005, por el que se establece la relación de actividades potencialmente contaminantes del suelo y los criterios y estándares para la declaración de suelos contaminados"; Ley 22/2011, "Residuos y suelos contaminados")

The toxicity threshold (*umbral de toxicidad*) for each contaminant is calculated from the normal value that is present in natural uncontaminated soils. From this geochemical background (*fondo geoquímico*), it is possible to establish the minimum threshold that represents contamination and define the levels of toxicity. These levels have to be contrasted with studies on the impact on humans, plants and animals.

The reference levels (*niveles de referencia*) that give the level of contamination. Involve alert, monitoring and control systems.

Above these guidelines are the levels of intervention (niveles de intervención) that already require corrective measures.

Mercury (Hg)	Reference level (mg/kg)	Level of intervention (mg/kg)	
Euzkadi	0.3	3	
Andalucía	1	10-15	



Madrid	Industrial use	Urban use	Other uses
Hg Reference level (mg/kg)	15	7	5

Contaminated sites recuperation

"Es mejor prevenir que curar" (prevention is better than cure)

Exploitation projects have to plan the actions to prevent and compensate the consequences of the exploitation that can result in damage to the environment and the population. It is needed to integrate the "exploitation plans" and the "rehabilitation / recuperation plans".

CONCEPTUAL MODEL

- ✓ Site information (past and recent);
- ✓ Legislation and normatives;
- ✓ Affected area (geology, hydrogeology, soil, flora, fauna, topography...);
- ✓ Risk sources and contaminants;
- ✓ Land uses;
- ✓ "Mosaic of situations" (urban and rural areas, forest, rivers, lakes, marine coast…);
- ✓ Transport and migration models;
- ✓ Exposure pathways and receptors ((bio)accumulation, toxicity, persistence);
- ✓ Environmental and population impacts and risks;
- ✓ Traditional and cultural issues
- **√**

General planning of a decontamination project

Phase 1. Preliminary evaluation

- -Contamination / Riskiness degree
- -Historical data / cultural data
- -Site characterization (environmental and population data)
- -Site inspection and in situ evaluation of the problem

Phase 2. Detailed research

- -Contamination type, location, extension and origin (sources)
- -Sampling and analysis

Phase 3. Planning and feasibility

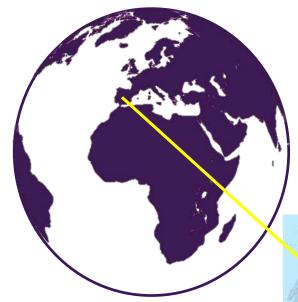
- -Risks evaluation. Urgent measures implementation
- -Clean-up or decontamination objectives. Maximum permissible contaminant levels
- -Alternatives evaluation (foreseeable behavior, potential feasibility, costs and monitoring)
- -Selection of the most recommended / feasible / available remedial actions

Phase 4. Action Plan

- -Practical planning of the most reliable selected alternative(s)
- -Pilot trials (if needed) and implementation
- -Study of technical parameters and **remediation** activities
- -Final results and environmental and population monitoring

Almadén



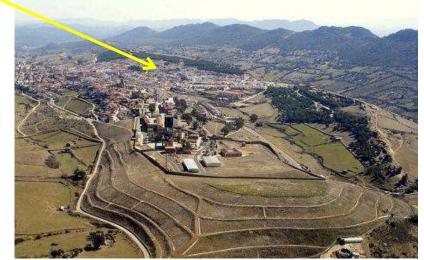


Almadén is located 300 km (SW) from Madrid, in the Province of Ciudad Real.

The mercury ores in this area are the main Hg concentration in the World. It was the oldest and biggest Mercury mine.

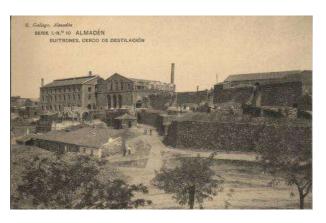












Almadén...a life around the Hg mine

Almadén, Idrija and Monte Amiata produced 99% of the primary mercury mined in Europe.

The Almadén mercury mine has been exploited over the past two millenniums. Well known during the Roman times.

Almadén provided nearly a third of the total known mercury produced in the world. (It has been estimated that in 2000 years of exploitation, 250.000 t of mercury have been extracted).



- ✓ 1997 Closure of the "El Entredicho" open pit.
- ✓ 1999 Closing of the Almadén mine initiated.
- ✓ 2001 Mine closed (mercury extraction terminated).
- ✓ 2003 2004 Primary mercury production ceased. Mining activities stopped.
- ✓ 2011 End of mercury export.



BUT... at present

Working staff reduced from >1200 to < 100. Population decreased:

1950: 12375

2000: 7152

2006: 6406

2012: 6175

2018: 5461

The unemployment rate increased



CIEMAT R&D activities

Site characterization

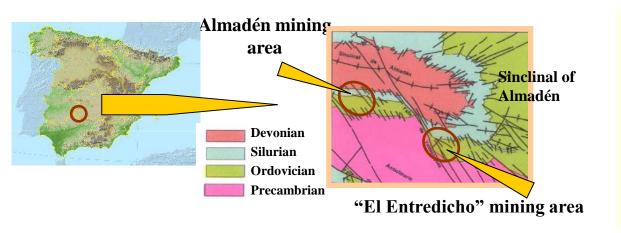
Environmental restoration

Environmental monitoring of Almadén mining district

Socio-economical alternatives (land uses, alternative activities)

Divulgation. Results dissemination. Formation.

Geological complexity of the Almadén area



Mercury mineralizations are restricted to the geological structure known as the Sinclinal of Almadén (quartzite formation ("Cuarcita del Criadero"). Secondary Hg mineralizations are linked to veins in quartzites, and to stockworks in Silurian and Devonian volcanic hosting rocks.

Quaternary deposits partially cover slopes under main relieves.

No Mesozoic nor Tertiary materials are present.

Climatic features in the Almadén area

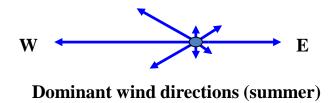
Mediterranean climate type: cool and wet winters, and hot and dry summers (representative for the southern *Meseta* (plateau) of the Iberian Peninsula).

Average annual rainfall:

613 mm (AUG, 7 mm; DEC, 84 mm) Max. in 24 h: 43 mm **Average annual temperature:**

16.3 °C

(JAN, 7.6°C; JUL, 26.9°C) Abs. max: 41°C; Abs. min: -3°C Almadén "Minas" (535 m a.s.l.) National Meteorological station



Average Relative Humidity (%)		Storms per year	Freeze days (T<0ºC) per year	Sunshine hours per year	
Annual 63	July 45	Dec. 82	17	47	2656

RELIEF and DRAINAGE NETWORK in ALMADÉN

According to strata disposition, main relieves have an E-W feature.

Highest altitudes (750-850 m a.s.l.): Lower-Ordovician quartzitic ranges (1).

Medium altitudes (600 m a.s.l.): Silurian or Devonian quartzites (2).

Valleys (380-500 m a.s.l.): correspond to shales within the Valdeazogues river (3).

Main drainage network is conditioned by E-W orientation of strata. The low permeability of substrate favours a dense drainage network.

Prince of its News

Prince of its News

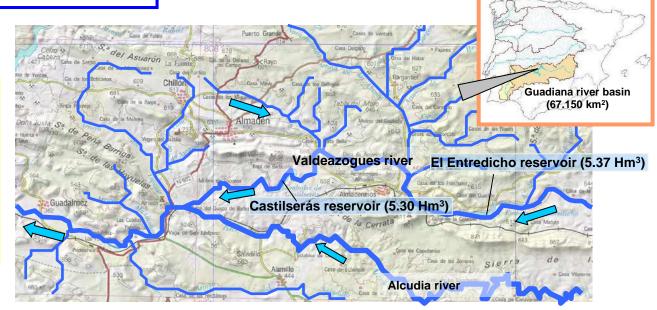
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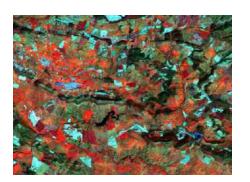
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Small rivers are located in the mining area.

The main water flow is within the Valdeazogues river basin.

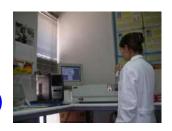
Dry summers and absence of important aquifers imply that most river beds are ephemeral streams.







Laboratory







Regional scale



Greenhouse









Field plots

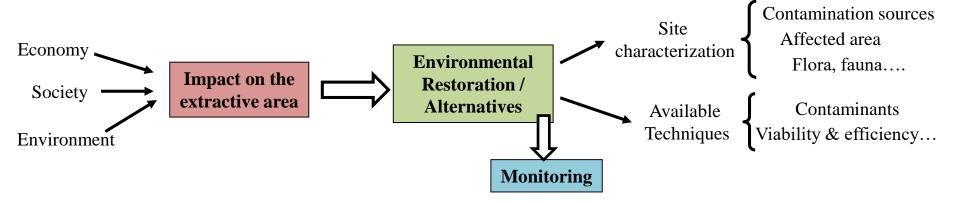


Lysimeter





Almadén study case



- Identification of mine structures and problems. Conceptual Model
- Selection of the most adequate techniques (barriers, bioremediation, phytotechnologies, soil amendments, soil washing, etc).
- Feasibility study and effectiveness of selected technique.
- Monitoring and control of conditions.
- Recommended strategies.



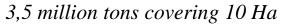












- ✓ Slope correction
- Drainage systems and pond (leachates storage and treatment)
- ✓ Soil amendments for mine tailing recovery
- ✓ Plant species selection for phytostabilization and landscape integration
- ✓ Monitoring points
- Reduction > 90% Hg in air and particles
- Landscape integration
- Visual impact reduction
- Social acceptation



Photos: MAYASA

"PARQUE MINERO DE ALMADÉN" - Almadén Mining Park

It was included on the **World Heritage** list with the name **Heritage of Mercury. Almadén and Idrija**. (UNESCO, 2012): "At both sites, the presence of mining infrastructure elements both underground and on the surface, the presence of technical artefacts linked to mining extraction, its upstream needs (hydraulic energy, wood) and its conversion into "quicksilver" (furnaces), its transport and its storage are authentic."



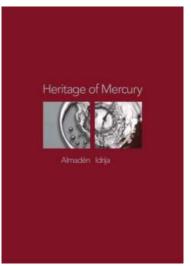
Facilities: Visitor's Centre; San Aquilino and San Teodoro shafts; Mining interpretation centre; Tour inside the mine; furnaces; Mercury Museum.....

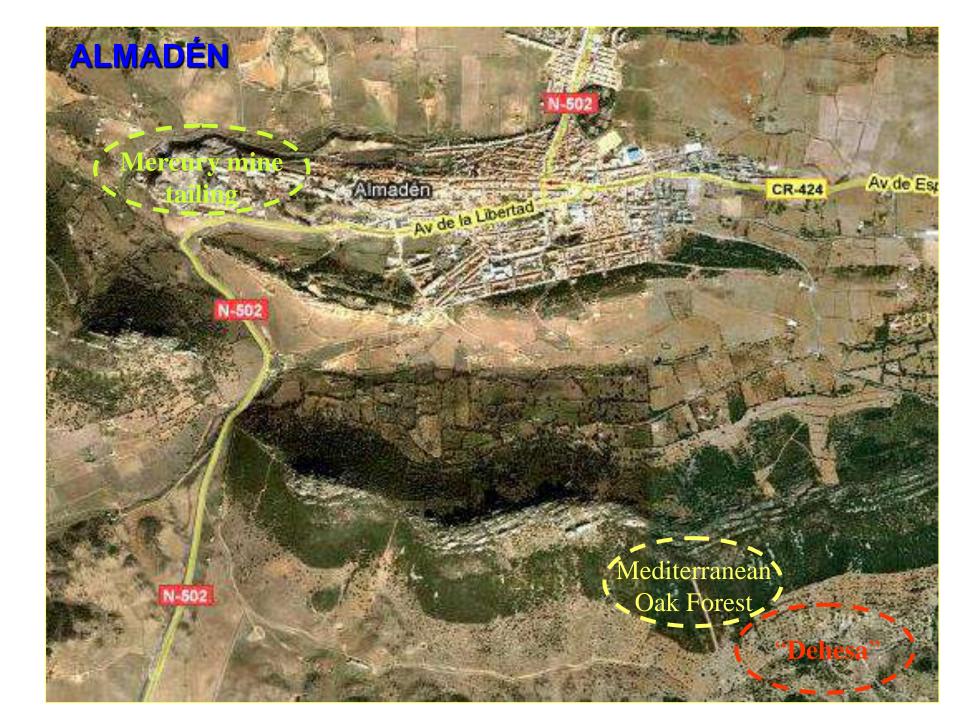




Come and visit it !!!!

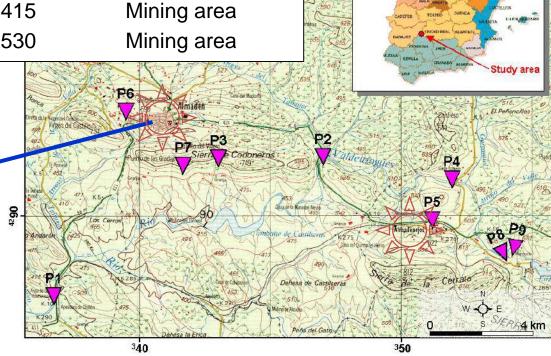






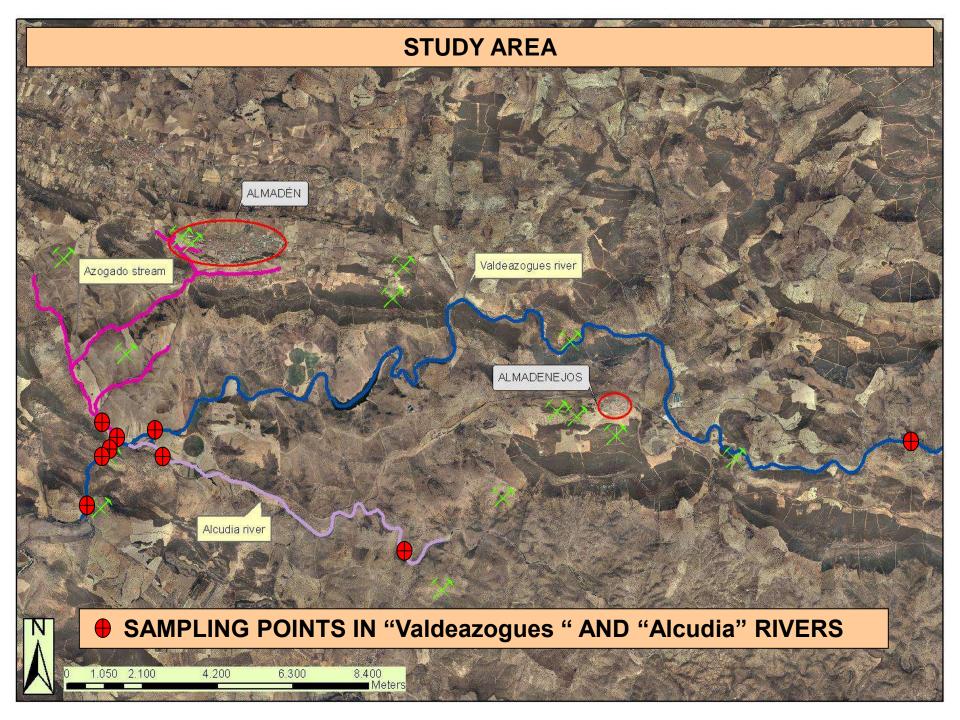
Plot	Location	Altitude (m a.s.l.)	Land use
P1	Valdeazogues river	368	River banks not used
P2	Source of Jardinillo	435	Not used open Mediterranean forest
P3	Sierra de Cordoneros	520	Pasture land with shrubs
P4	NE of Almadenejos	435	Crop cultivation
P5	Almadenejos smeltering site	508	Pig farming
P6	Almadén mercury mine	515	Mine dump
P7	Sierra de Cordoneros	505	Pasture land
P8	El Entredicho mine	470	Mining area
P9	El Entredicho mine	415	Mining area
P10	Las Cuevas mine	530	Mining area
		500	177 757 184

Experimental field plots



P10









Soil characterization and reference levels

Soil sampling in non-contaminated areas with the same geological substrates.

Under these conditions:

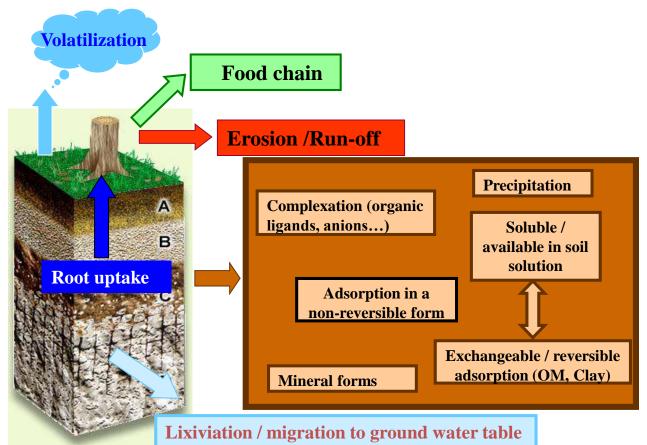
Reference level = Mean value (105 mg kg^{-1}) + 2 x standard deviation (175 mg kg^{-1})

Almadén reference level (MAYASA): 455 mg kg⁻¹

Hg <105 mg kg⁻¹: No action required

Hg 105 a 455 mg kg⁻¹: Research required. Remediation?

 $Hg > 455 \text{ mg kg}^{-1}$: Actions needed. Remediation necessary





SOIL

Organic matter content, pH, CEC, texture and soil depth, are the main influence parameters related with mercury behaviour. Relevant differences are observed depending on the soil type and the parent material (lithology).

Soil profiles (Soil samples form each one of the formal diagnostic horizon) / Soil top layer / Soil bulk and soil from rhizosphere

VEGETATION

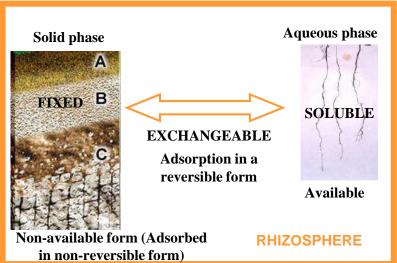
Incorporation (root / leaves).

Transfer factors (soil Hg total vs Hg available)

Translocation and distribution in plant

Bioaccumulation

Crops: Hg content in the edible part



METHODOLOGICAL PROCEDURE FOR SOIL SAMPLES

Soil sampling



Storage & transport



Pre-analyses treatment



Physical & chemical soil analyses

Soil profiles to a depth of > 100 cm Samples obtained with a metal cylinder (depth < 25 cm)

Samples obtained with a hoe (depth < 15 cm)

Samples stored in plastic bags, labelled and transported to laboratory (part of them at 4°C)

Samples are air-dried and sieved to separate fine earth fraction (<2 mm)

- Colour: Munsell Colour Table
- Texture (Bouyoucos)
- pH and EC (1:2.5 H₂O and satured paste)
- Organic matter (Walkley and Black; TOC)
- Carbonate content (Bernard calcimeter)
- Cation Exchange Capacity (EPA Method 9081)
- Soluble and exchangeable cations

DETERMINATION and DISTRIBUTION of MERCURY

Mercury content determination: Two Atomic absorption spectrophotometers (AMA – 254 Leco Instruments)



Periodical comparison between ICP-MS (Ciemat, UAM); Use of BCR / NIST reference materials; Intercalibration exercises

SEQUENTIAL EXTRACTION PROCEDURE IN SOILS SAMPLES (Sánchez et al., 2005)

Fraction	Extracting agent
Water soluble	H ₂ O
Exchangeable	1 mol·L ⁻¹ NH ₄ Cl (pH = 7)
Carbonates	1 mol·L ⁻¹ CH ₃ COONH ₄
Carbonates	$(pH = 4.5 HNO_3)$
Easily	Tamm's solution (oxalic
reducible	acid/ammonium oxalate, pH = 2.8)
Soluble in 6 M HCl	6 M HCI
Oxidizable	8.8 mol·L ⁻¹ H_2O_2 (pH = 2, HNO ₃)
- CARGILGOIO	1 mol·L ⁻¹ CH ₃ COONH ₄ (pH = 2 HNO ₃)
Final residue	Aqua regia / HF

SEP procedures: BCR (EUR 14763 EN); Giulio & Ryan (1987)

METHODOLOGICAL PROCEDURE for VEGETATION SAMPLES

Vegetation source



Vegetation sampling



Transport & storage



Pre-analysis treatment



Mercury content determination

Natural conditions: Field

Naturalized conditions: Lysimeter

Controlled conditions: Greenhouse and culture

chamber

<u>Herbaceous plants:</u> Roots + Aerial part

Woody plants: Branches with leaves and fruits

Samples are stored in paper bags, labelled and transported to laboratory

Roots and rhizosphere soils are stored in plastic bags in

fridge

Samples are air-dried and divided into different fractions (root, leaf, branch, fruit...)

Samples are washed into ultrasonic bath

Total mercury is determined in each plant fraction using an Advanced Mercury Analyser (AMA-254)

Field experiments and greenhouse studies (hydroponic cultures and pots filled with Almadén soil)



Rumex induratus (Almadén new – ecotype??)

- Found in mercury open pit and mine tailing.
- Arid conditions.
- High mercury root uptake and translocation capacity.
- Growth reduction less than 23%.
- 3-8 times less content in aerial part than *Marrubium* but higher biomass.
- Rumex more Hg tolerant than Marrubium.



Marrubium vulgare (Traditional medical uses!!!)

- Found in old metallurgical areas and mine activities zones (Hg soil: 500 mg kg⁻¹ dw).
- Poor biomass production.
- Mercury in plant (aerial part) 20-60 mg kg⁻¹ dw.
- Marrubium higher Hg content in plant than Rumex, but less root uptake and translocation capacity.
- Rumex induratus is capable of extracting more efficiently the available Hg.
- •The translocation of micronutrients is reduced due to high Hg content.

Riparian vegetation



Nerium oleander



Typha domingensis



Flueggea tinctoria

- ✓ Shrub and Macrophytes
- ✓ Water-sediment-plant interactions
- ✓ Hg uptake and translocation
- ✓ Rhizosphere role
- ✓ Microbiology
- Erosion control
- Ecosystem protection
- Phytobarriers? Rhizofiltration?
- Water treatments
- River crabs !!!



Tamarix canariensis

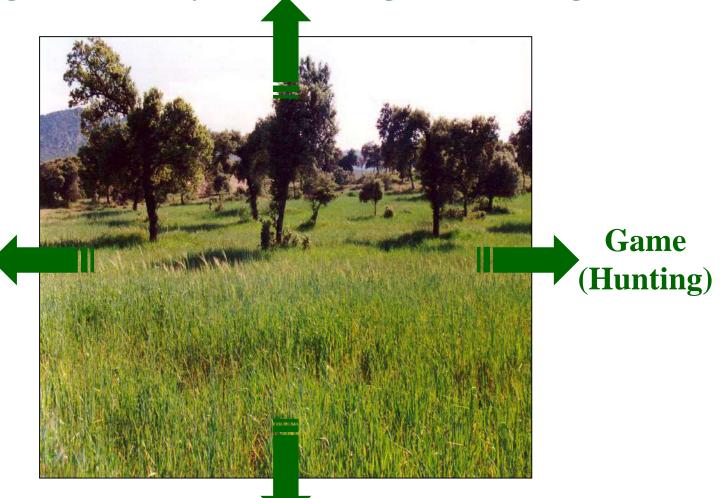


Phragmites australis

DEHESA DE CASTILSERAS... 9000 ha to be managed

......What is a "dehesa"?

Agriculture (dryland and irrigation farming)



Forestry (Wood, cork)

Cattle farming. Merine breed of sheep

LYSIMETERS from Almadén (located in CIEMAT)









And.... eggplant, wheat, chickpea, lettuce, potato, rape, lavender....

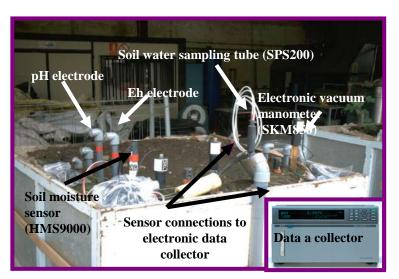


Close-to-real conditions (Mesocosmos).

Monitoring soil parameters in the soil profile (soil horizons); soil top layer; Bulk soil vs rhizhospheric soil.



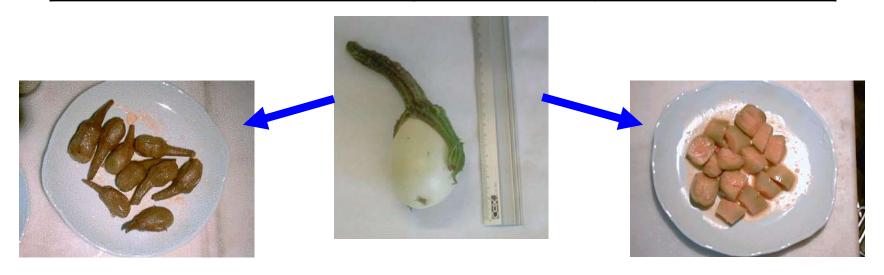
- ✓ Food and feed crops (including local cultivars).
- ✓ Industrial crops.
- ✓ Traditional medicinal plants.
- ✓ Nutrients vs contaminants (Hg).
- ✓ Fertilization effect on Hg uptake.
- •Best agronomical practices.
- •Impact on local diet....



Eggplant (Solanum melongena)

WHO (2011): 34.2 µg Hg/day (Person: 60 kg body weight and considering that 100% of Hg is retained in the body)

Eggplant	[Hg] (µg kg ⁻¹)	Maximum portion (kg fruit day ⁻¹)
Fruit with stalk and calyx	22.1 - 190.2	1.55 - 0.18
Fruit without stalk and calyx	16.8 - 65.4	2.04 - 0.52



- Sierra *et al.*, 2008. Potential use of *Solanum melongena* in agricultural areas with high mercury background concentrations. Food Chem. Toxicol 46 (6), 2143-2149.
- Millán et al., 2013. Could an abandoned mercury mine area be cropped?. Environ. Res. 125, 150-159.

Common vetch (Vicia sativa L.)

Lysimeter, greenhouse and field conditions

According to DIRECTIVE 2002/32/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 7 May 2002 on undesirable substances in animal feed:

Common vetch	[Hg] (mg kg ⁻¹)	Hg limit for animal nutrition (mg kg ⁻¹)	Consumption recommended YES	
Seeds	< 0.1 (0.02-0.006)	0.1		
Fodder	0.07 up to 0.48	0.1	NO	

- Sierra *et al.*, 2008. Evaluation of mercury uptake and distribution in *Vicia sativa* L. applying two different study scales: greenhouse conditions and lysimeter experiments. J. Geochem. Explor. 96, 203-209
- Millán et al., 2013. Could an abandoned mercury mine area be cropped? Environ. Res. 125, 150-159.

Lupine (Lupinus albus)

Lysimeter, greenhouse and field conditions

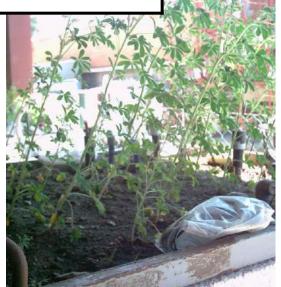
Animal feed (Directive 2002/32/EC Commission directive 2003/100/EC)

Lupine	[Hg] (mg kg ⁻¹)	Hg limit for animal nutrition (mg kg ⁻¹)	Consumption recommended
Seeds	0.01 - 0.03	0.1	YES
Fodder	0.06 - 0.14	0.1	NO

Human consumption

Lupine	[Hg] (mg kg ⁻¹)	Maximum portion (kg fruit day ⁻¹)
Seeds	0.01 - 0.03	3.97 – 1.38

WHO-IPCS Food Additives Series 52: Safety evaluation of certain food additives and contaminants (World Health Organization, 2004) where 42.6 µg Hg/day could be consumed.



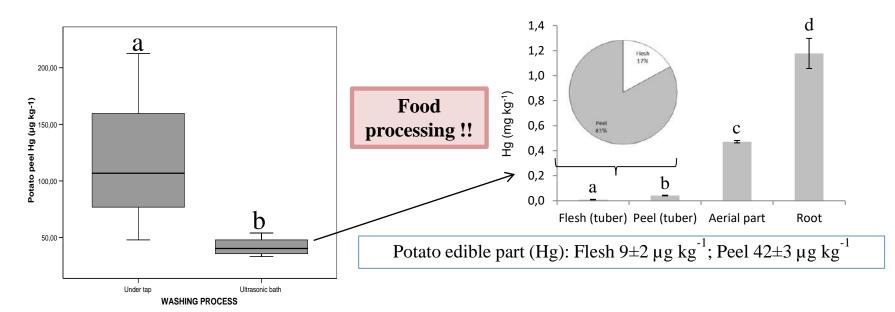
According to WHO-IPCS Food Additives Series: 52. Safety evaluation of certain food additives and contaminants. World Health Organization (Geneva, 2004), 42.6 µg day⁻¹ of total Hg could be consumed, so:

Crops	[Hg] µg kg ⁻¹	Maximum portion (kg grain day ⁻¹)	IN PRACTICE
LENTIL CHICKPEA	6 – 36	1.2 – 6.6	26 – 144 dishes/day
BARLEY	5 – 24	1.7 – 8.9	12 – 59 L beer/day



[•] Millán et al., 2013. Could an abandoned mercury mine area be cropped? Environ. Res. 125, 150-159.

Potato (Solanum tuberosum)



really

Hg Total in consumable products		In coction		<u>Fractions:</u> DYALIZABLE (Hg fraction absorbed in the body) and EXCRETA	
Processing method	[Hg] _{total} (μg kg ⁻¹)	Max. Portion (kg DW day ⁻¹)	Hg dyalizable (%)	Max. Portion considering % dyalizable (kg potato DW day ⁻¹)	•
Boiled peeled potato	3.8 ± 0.0	9.2	75.0 ± 37.2	12.2	
Boiled potato (+ salt)	4.5 ± 0.5	7.7	49.8 ± 14.4	15.3	9
Boiled potato (– salt)	6.7 ± 0.7	5.1	49.8 ± 14.0	10.2	

WHO 2011: 34,2 µg Hg día-1 (60 kg bw and if 100 % total Hg is retained in the body

[•] Sierra et al., 2017. Cultivation of Solanum tuberosum in former mining district for a safe human consumption integrating simulated digestion. J. Sci. Food Agric., 97, 5278-5286. DOI: 10.1002/jsfa.8412

Lavender (Lavandula stoechas)



 $[Hg]_{flowers+leaves}$ $0.03 - 0.55 \text{ mg kg}^{-1}$

Products



ESSENTIAL OIL; EAU DE COLOGNE; FRAGANCE



LAVENDER TEA



Lavender tea: 3.7 – 68.4 L day⁻¹ (no intoxication risk (OMS, 2011))

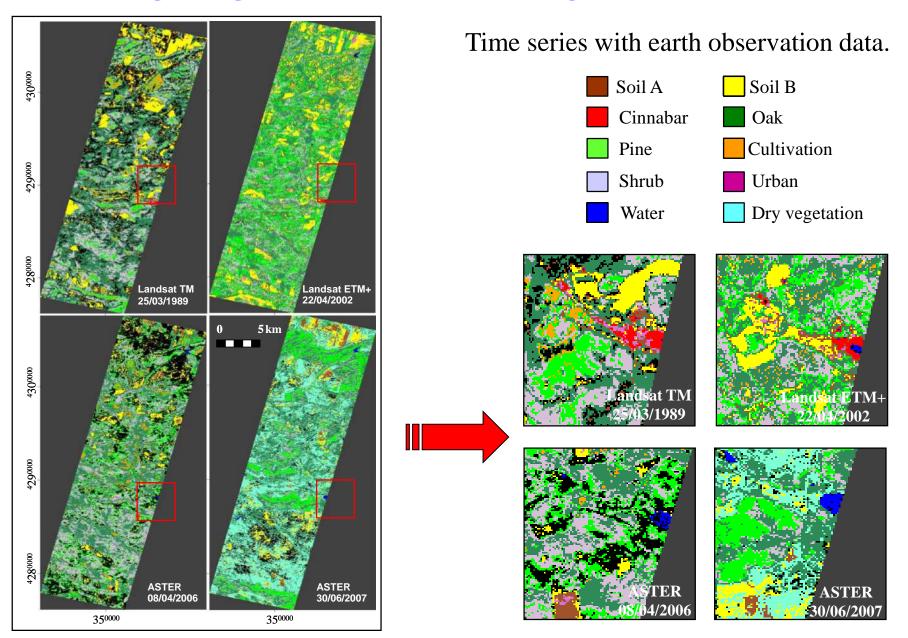
Cosmetic use: suitable (control and check updated regulations)

[Hg] lavender tea
[Hg] lavender essential oil
[Hg] eau de cologne, fragance

 $< 0.5 \mu g kg^{-1}$

• Sierra *et al.*, 2009. Mercury uptake and distribution in *Lavandula stoechas* plants grown in soil from Almadén district (Spain). Food Chem. Toxicol. 47, 2761-2767.

Monitoring using GIS and remote sensing.



• Schmid, T., Rico, C., Rodríguez-Rastrero, M., Sierra, M.J., Díaz-Puente, F.J., Pelayo, P., Millán, R., 2013. Monitoring of the mercury mining site Almadén implementing remote sensing technologies. Environmental Research, 125, pp. 92-102.

Dissemination. Divulgation. Formation

Capacitación en sitios contaminados: proyecto de mercurio em Latinoamérica. October 2017. CIEMAT, Madrid (Spain)



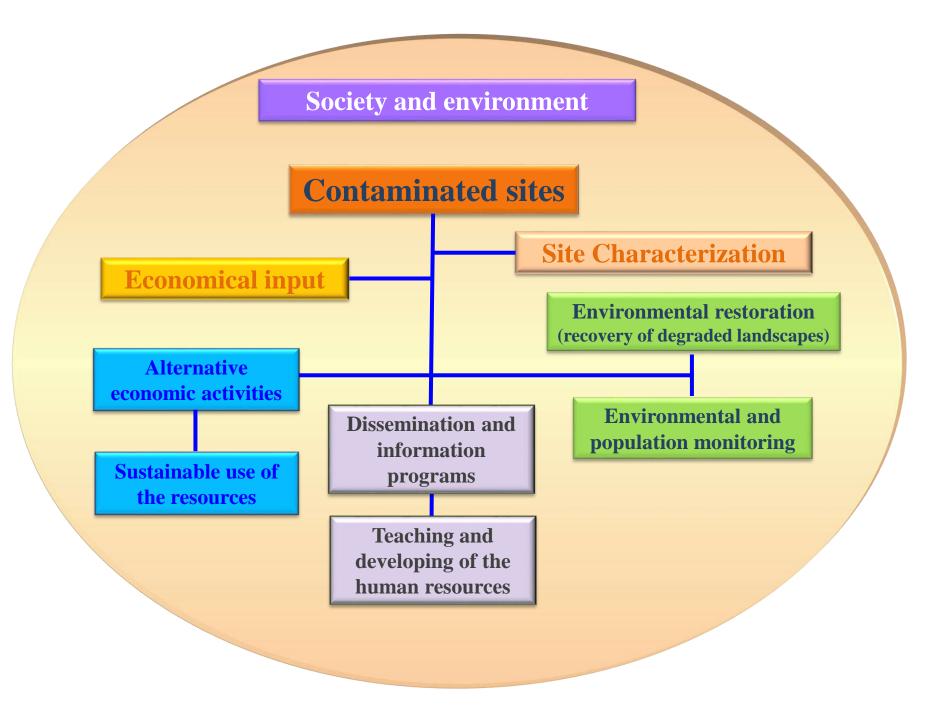
Capacitación en Desmantelamiento, Gestión de Residuos-sitios contaminados, asociados a la Industria Cloro-soda. February 2018. Montevideo (Uruguay).



Capacity building to promote trade of products that replace those with mercury to reduce marine pollution. July 2019. Viña del Mar (Chile)



And.... Courses, Training courses, Seminars, Conferences, Congress, Publications, Technical support, Researchers and students stay at CIEMAT...





Thank you for your attention Gracias por vuestra atención

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