14th International HCH and Pesticides Forum

Relevance of mercury contaminated sites for global mercury release and implementation synergy of Minamata & Stockholm Convention

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Short History of Mercury

Early use	BC 1500-	Religious or “health” uses in Egypt, China, Tibet.
		Ornaments in Greek
		Cosmetics in Egypt and Roman empire
	BC 500-	Alchemy: mercury & other metal relation (one aim: gold from Hg)
	8th century	First (?) recognized Hg pollution in Japan Use of large amount of Gold/Hg amalgam for Gold plating of Great Buddha in Nara. Evaporation of Hg and exposure. ⇒ Workers intoxication; Palace closed
Economic Industrial uses	1400-	Medical uses
	1800-	Dental amalgams, Industrial uses
	1956	Official confirmation of first Minamata disease patients
Env. Sound Manag.	1992	Enforcement of the Basel Convention
	2002	UNEP Global Mercury Assessment
	2006	Strategic Approach to International Chemicals Management
	2009 9/2017	UNEP: Global Convention on Mercury COP 1 Minamata Convention

Mercury Contaminated Sites in the Minamata Convention

MINAMATA CONVENTION ON MERCURY

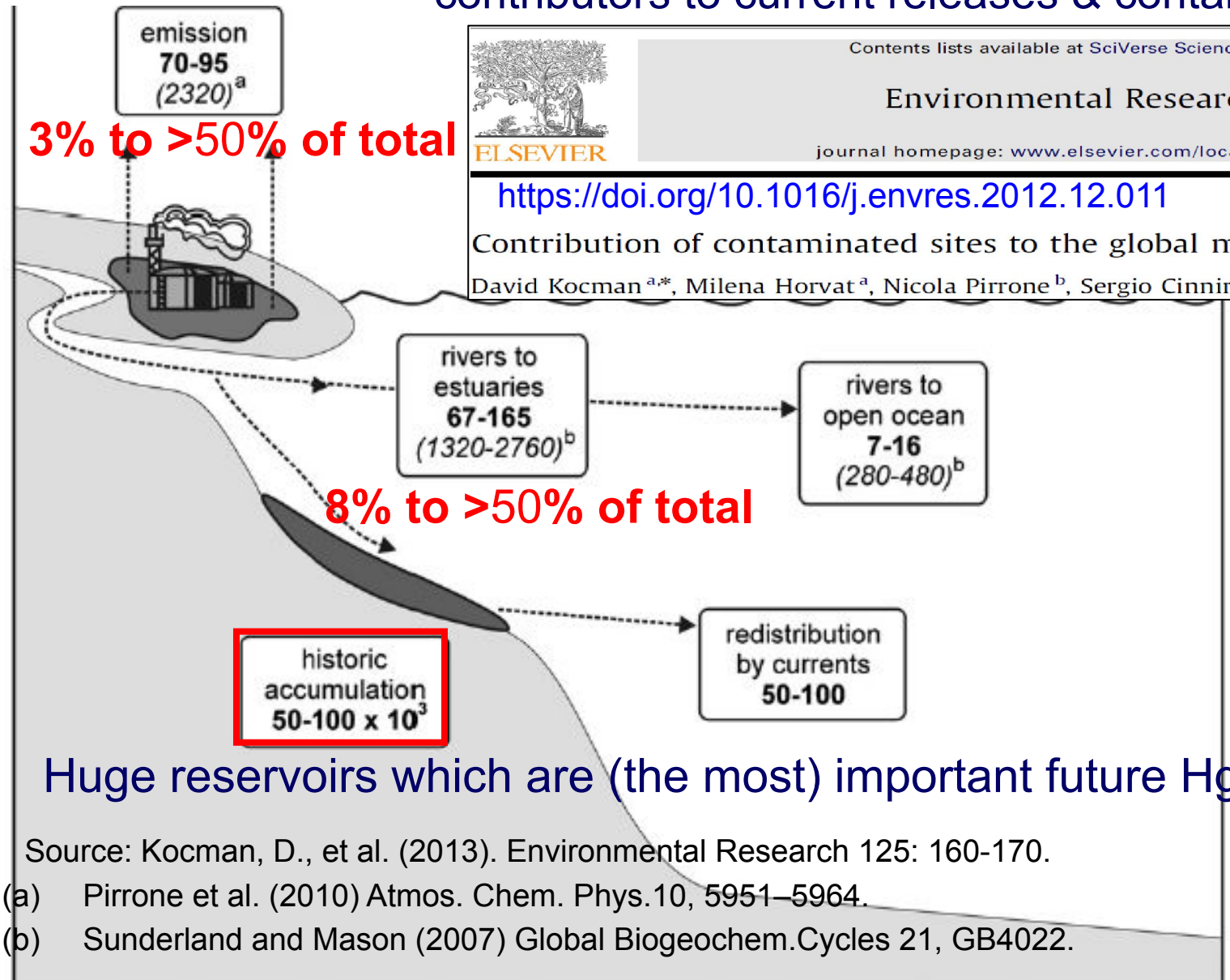
- The Minamata Convention: Various elements of mercury contaminated sites under Article 11 (Waste) and Article 12 (Contaminated Sites).
- **The Treaty calls on Parties to 'endeavor' to take action to address contaminated sites.** The parties are encouraged to:
  - cooperate in the formulation of strategies and the execution of activities to identify measure,
  - classify depending on priorities,
  - manage and, as appropriate, remediate

contaminated sites.

Mercury Contaminated Sites – Release Contribution

Release (t) (Kocman)
(*Other studies*)

Releases from mercury contaminate sites are relevant contributors to current releases & contamination of fish



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Contribution of contaminated sites to the global mercury budget

David Kocman [a,*], Milena Horvat [a], Nicola Pirrone [b], Sergio Cinnirella [c]

Huge reservoirs which are (the most) important future Hg sources.

Source: Kocman, D., et al. (2013). Environmental Research 125: 160-170.

(a) Pirrone et al. (2010) Atmos. Chem. Phys.10, 5951–5964.

(b) Sunderland and Mason (2007) Global Biogeochem.Cycles 21, GB4022.

Mercury Contaminated Sites-Sources

Mercury contaminated sites are generated along the life cycle of Hg:

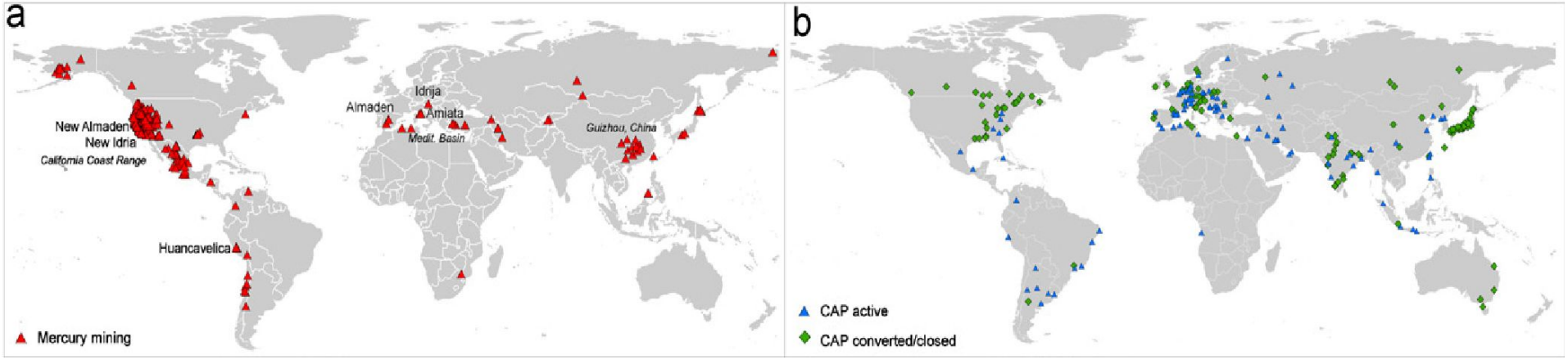
- Mining sites of Hg (and some other mining sites);
- (Former) use of mercury in manufacturing of products
  - Prod. of pesticides, medical devices, thermometers, light bulbs, hats
- Sites of (former) mercury use in industry
  - Chloralkali sites; acetaldehyde; vinyl acetate; PVC (acetylene proc.)
- Application and storage/disposal sites of mercury pesticides;
- Gold/precious metal mining including artisanal gold mining (ASGM)
- Sites of mercury recycling
- Non-ferrous metals processing; oil/gas industry
- Disposal sites of mercury & mercury containing produc
- Graveyards (dental amalgam)

Mercury Contaminated Sites – Major Point Sources

Global distribution of contaminated sites:

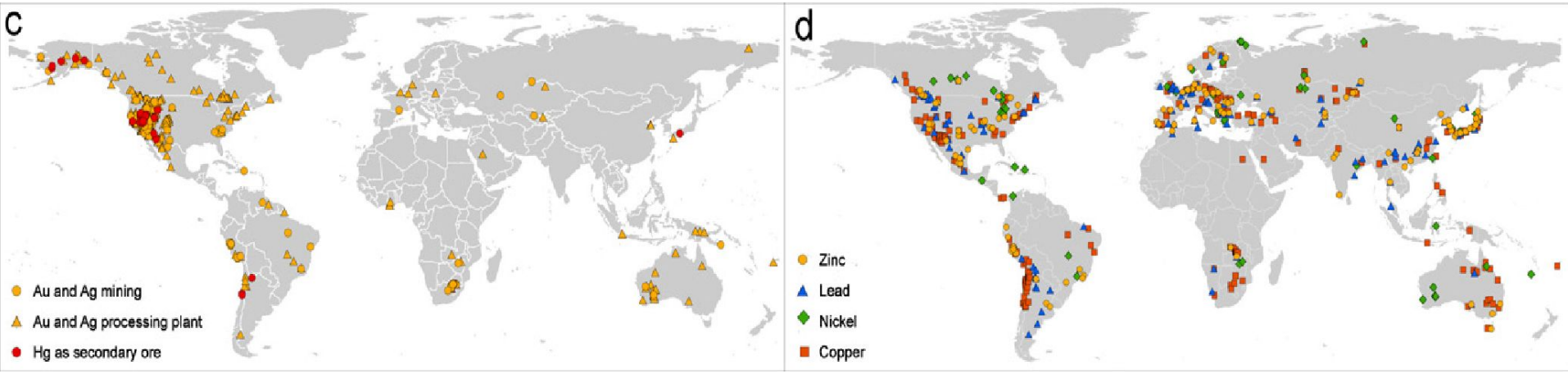
a) Primary mercury mining

(b) Chlor-alkali plants



c) Large-scale precious metal mining

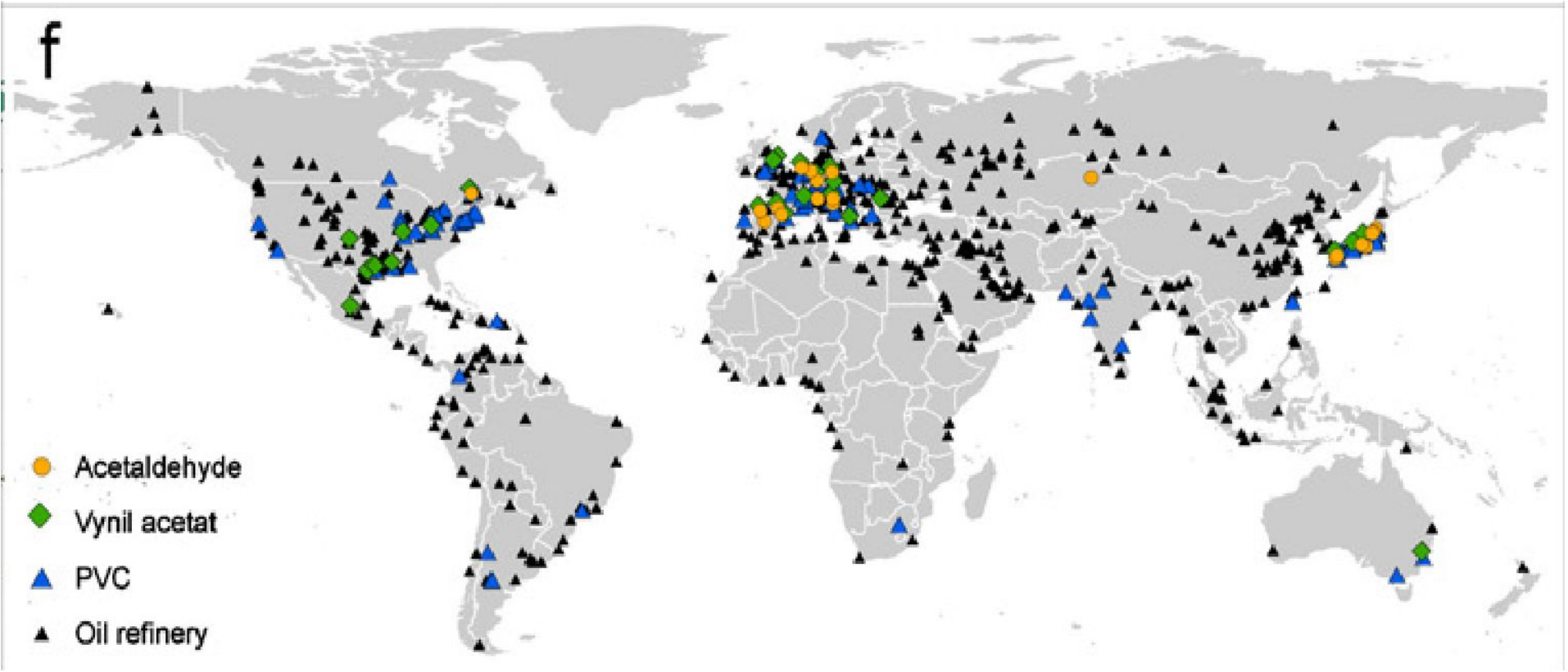
(d) Non-ferrous metals processing



Source: **Kocman, et al. (2013).** "Contribution of contaminated sites to the global mercury budget." Environmental Research 125: 160-170.

Mercury Contaminated Sites – Major Point Sources

Potentially mercury contaminated sites by major mercury releasing industries (Acetaldehyde, Vinyl acetate, PVC (acetylene process) and oil refineries) - in addition to the chloralkali sites.



Source: **Kocman, et al. (2013).** "Contribution of contaminated sites to the global mercury budget." Environmental Research 125: 160-170.

Mercury Contaminated Sites – Release Contribution

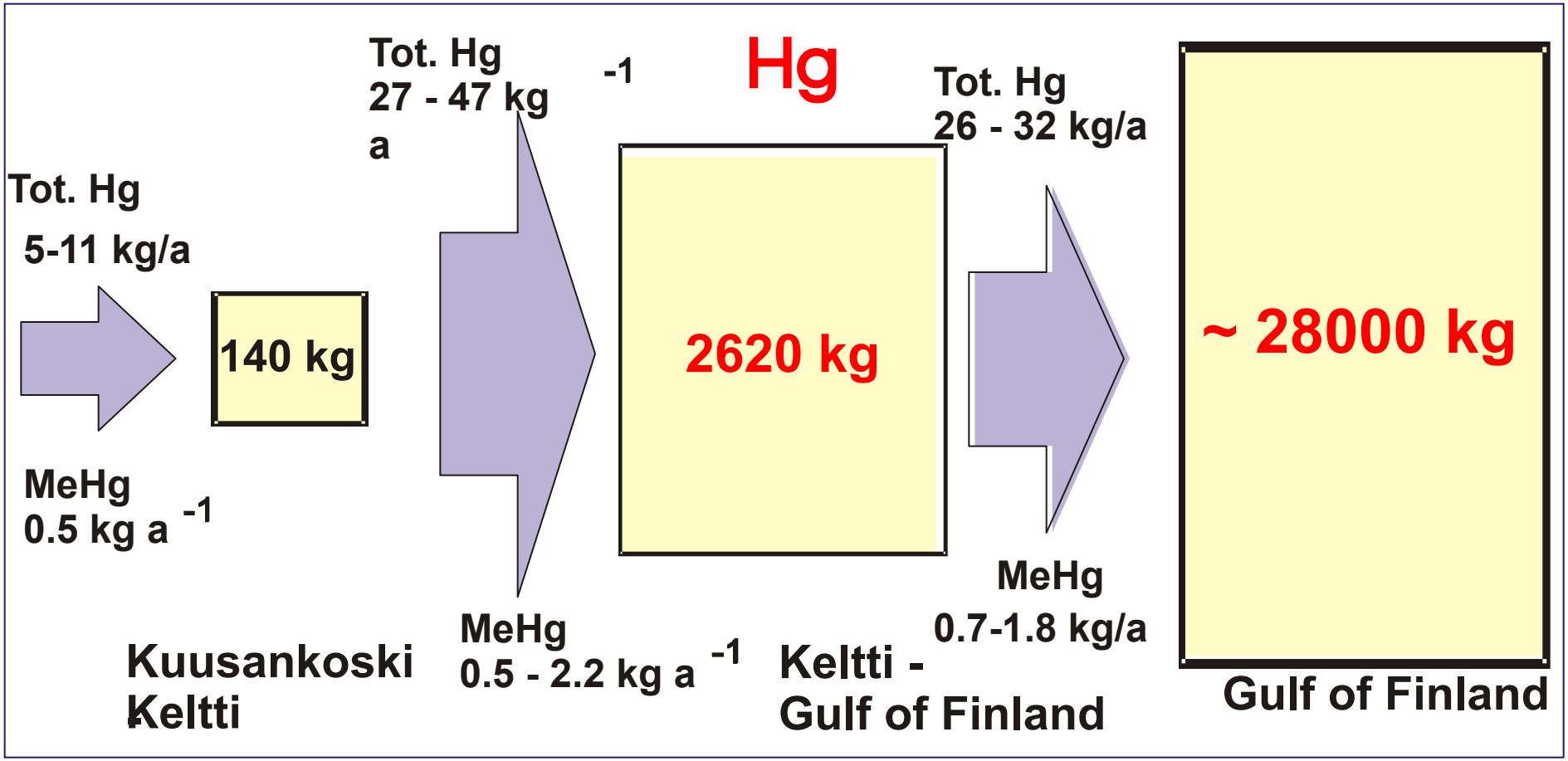
- Historic releases from primary Hg mining, chloralkali industry, large scale precious metal production has been quantified in studies.

CS category	Historical/present releases	References	Remarks
Primary Hg mining	20 Mg yr^{-1}	Hylander and Meili (2003)	Losses to air 10,000 Mg along 500 years
	10 Mg yr^{-1}	Ferrara et al. (1998a)	Almaden, Spain; losses to air
	10–40 Mg yr^{-1}	Wu et al. (2006)	China; losses to air (1995–2003)
	91 Mg yr^{-1}	Dizdarevič (2001)	Idrija, Slovenia; losses to air, soil and water; 45,500 Mg along 500 years
Chlor-alkali industry	163 Mg yr^{-1}	Pirrone et al. (2010)	Globally; losses to air
	144 Mg yr^{-1}	Concorde East-West (2006)	Europe; losses to products, air and water
	1400–2700 Mg	Qi et al. (2000)	China; losses to air, soil and water since 50s
	2000 Mg	Trip and Thorleifson (1998)	Canada; losses to air and water from 16 CAPs (1935–1998)
	3700 Mg	ACAP (2005)	Russia; losses to soils, waste and water from 7 CAPs (1951–1998)
Large scale precious metal production	196,000 Mg	Nriagu (1994)	Latin America; cumulative losses due to production of Au and Ag
	61,380 Mg		North America; cumulative losses due to production of Au and Ag
ASGM	640–1350 Mg yr^{-1}	Telmer and Veiga (2009)	Globally
	350 Mg yr^{-1}		Losses to atmosphere
	650 Mg yr^{-1}		Losses to hydrosphere
Non-ferrous metal production	275–310 Mg yr^{-1}	USGS (2004) Hylander and Herbert (2008)	Losses to air

Source: **Kocman, et al. (2013).** Contribution of contaminated sites to the global mercury budget. Environmental Research 125: 160-170.

Contaminated Site from Chloralkali Plant (Finland): Mercury Sediment Burden and Fluxes (2001)

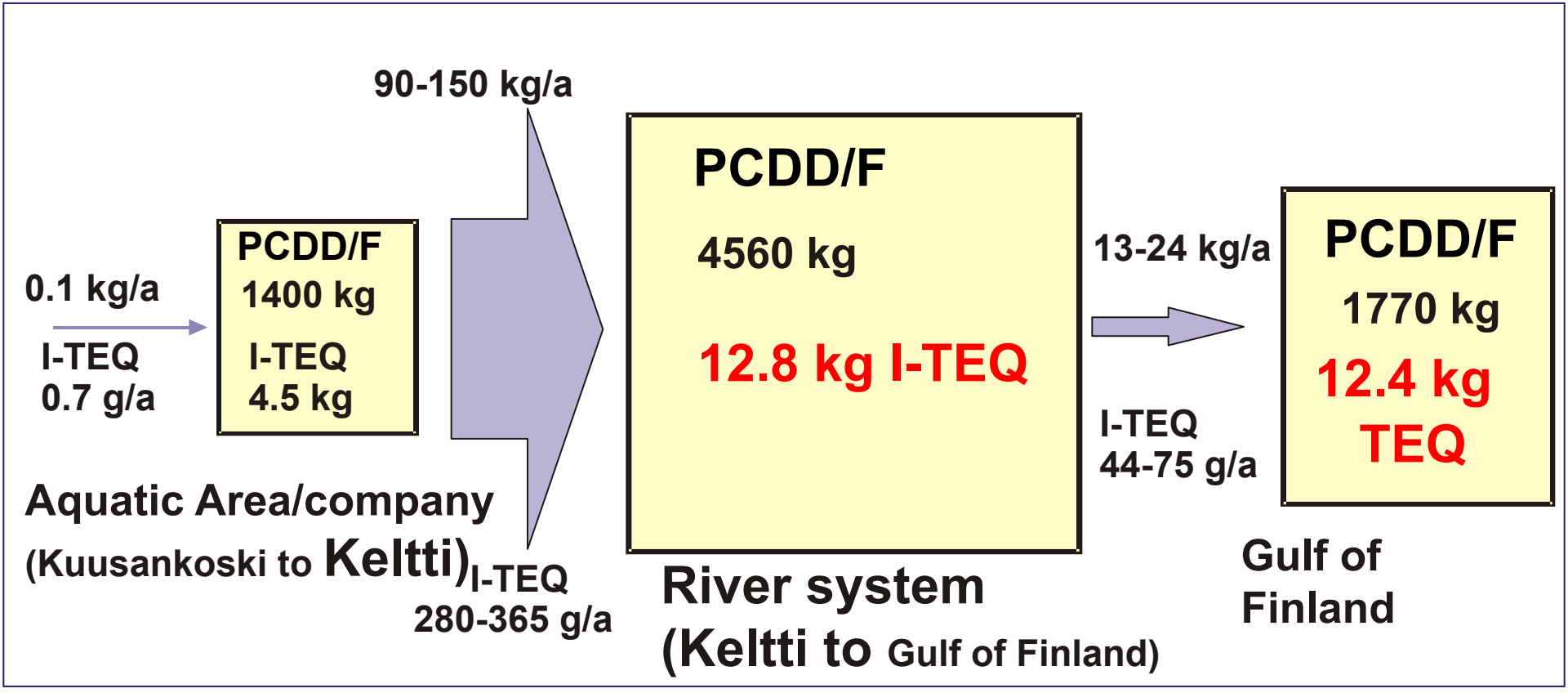
PxCP factory with **chloralkali production (1940-1984)** released more than 30 t mercury into River Kymijoki migrating into the Baltic.



Source: Verta et al. (2009) Environ Sci Pollut Res 16, 95-105. DOI 10.1007/s11356-008-0061-9

Contaminated Site from Chloralkali & PxCP Production: PCDD/F Sediment Burden and Fluxes (2001)

PxCP production (minor from chloroalkali process) (1940-84) discharged **30 kg I-TEQ** into the river Kymijoki of which 12 kg entered the Gulf of Finland



Verta et al. (2009) Environ Sci Pollut Res 16, 95-105.

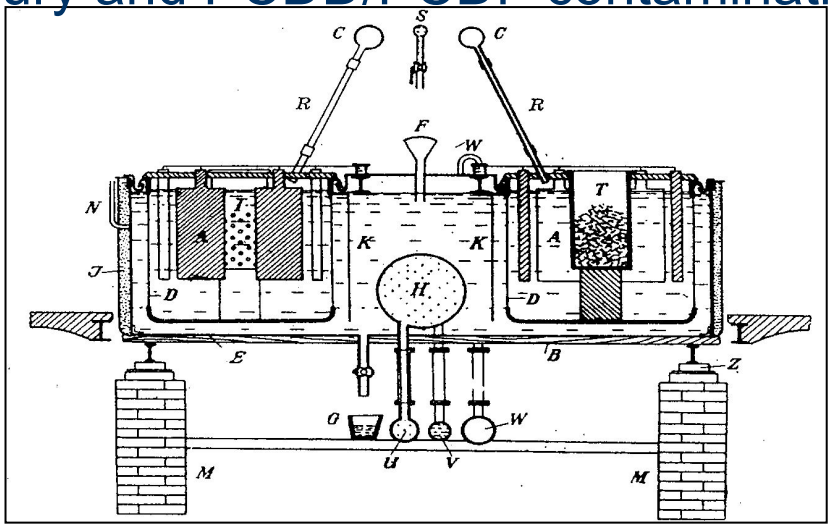
Synergy of Minamata & Stockholm Convention

MINAMATA CONVENTION ON MERCURY

STOCKHOLM CONVENTION

Chloralkali production with graphite electrodes

- In the chloralkali process with graphite electrodes (used 1890-1980s) high amount of PCDD/**PCDF** were formed and released (Emission level of pure sludge in Rheinfelden/Germany was 3.8 ppm TEQ).
- At some productions, larger PCDD/**PCDF** contaminated sites were generated depending on the management of the sludge with kg scale TEQ release to soils or sediments or deposition to landfills.
- Chloralkali using other technologies (**mercury**, membrane, diaphragm) have **significant lower PCDD/PCDF releases**. **But some can release mercury while others might release PFAS**. The technologies changed over time so that at some sites mercury and PCDD/PCDF contamination might occur together.



Chloralkali cell with graphite electrodes

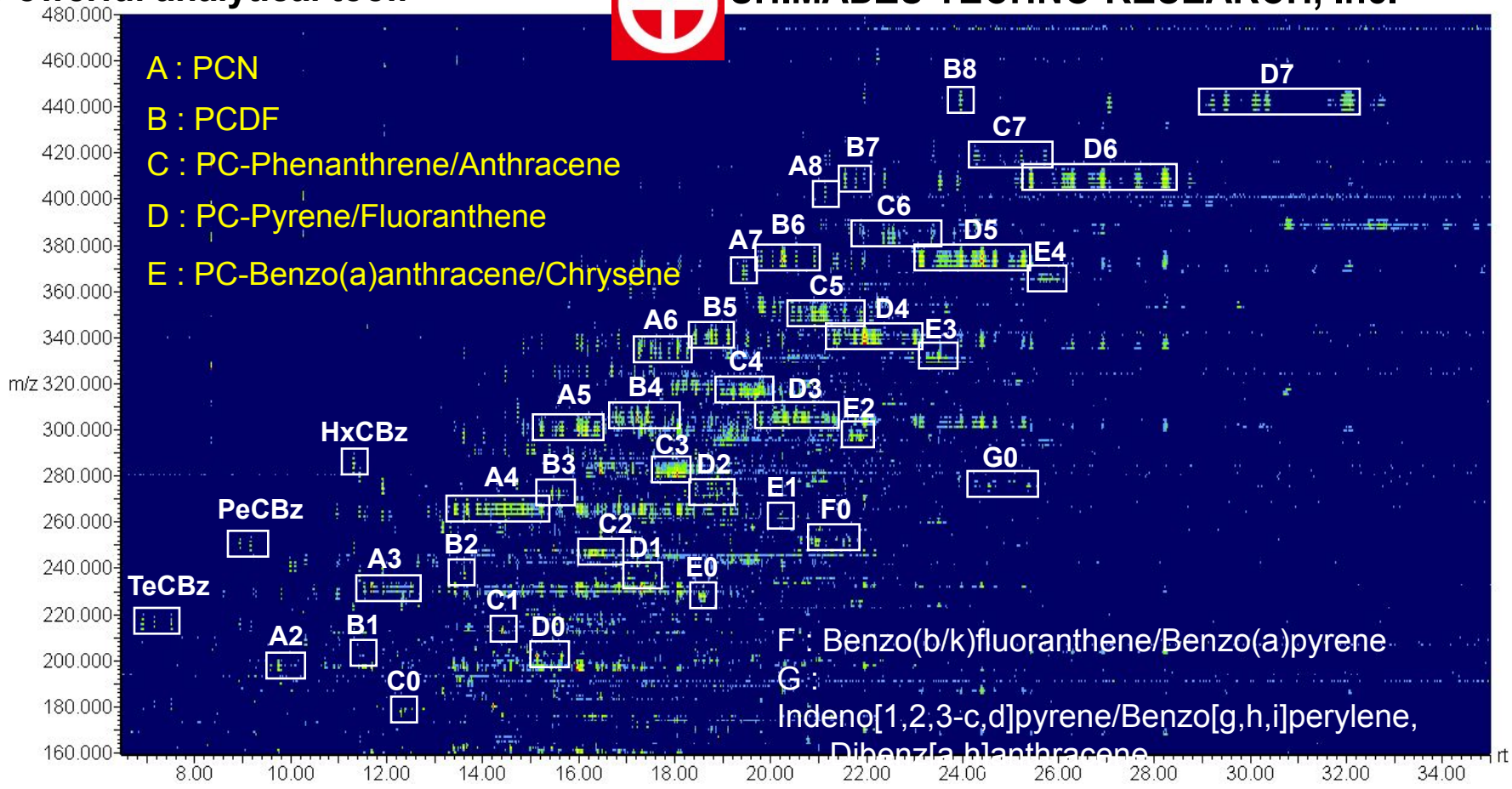
Weber et al. (2009) Env Sci Pollut Res Int. 15, 363-393.

PCDD/F and Chlorinated PAHs from Chloralkali Process (Graphite Electrode)

GC-HRTOFMS Screening of pollutants in chloralkali residues

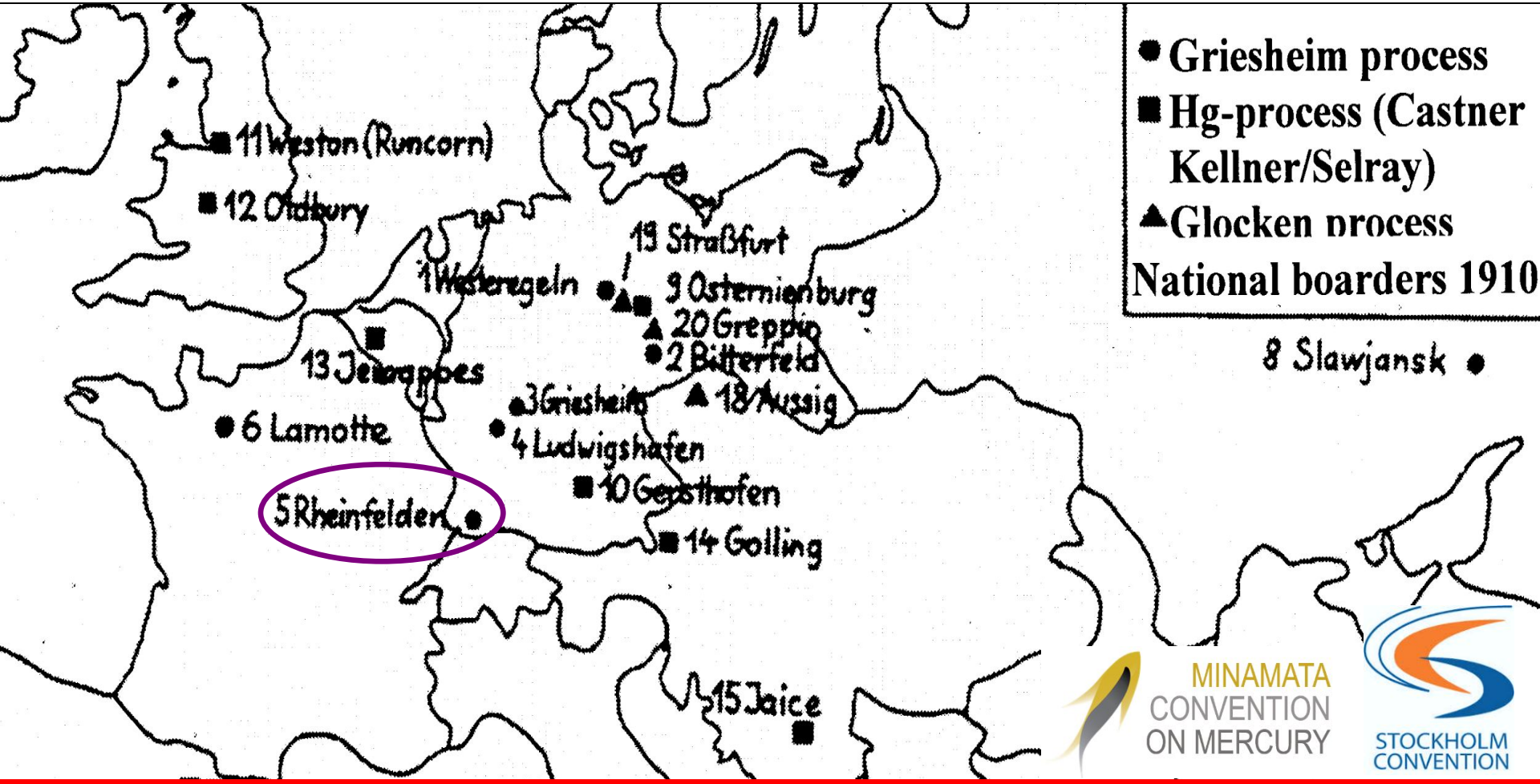
Powerful analytical tool!

SHIMADZU TECHNO-RESEARCH, Inc.



Takasuga et al. (2020) Emerg Contam 6, 133-142. https://doi.org/10.1016/j.emcon.2020.03.001

Chloralkali Plant Sites Europe (1910)



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- For the individual chloralkali plants, the history of the technology need to be assessed. In addition to assessment of mercury pollution, also PCDD/Fs, other UPOPs or POPs produced at sites need assessm.

HBN: World Chloralkali plant sites (2018)

Chlorine and Building Materials

A Global Inventory of Production Technologies, Markets, and Pollution

Phase 1: Africa, The Americas, and Europe

Chlorine and Building Materials

A Global Inventory of Production Technologies and Markets

Phase 2: Asia • Including Worldwide Findings

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Conclusion – Synergy of Minamata and Stockholm Convention

MINAMATA CONVENTION ON MERCURY

STOCKHOLM CONVENTION

- Mercury contaminated sites considerably contribute to environmental pollution and release of mercury likely becoming the most important source in future (Kocman et al. 2013 https://doi.org/10.1016/j.envres.2012.12.011).
- Major sites are Hg mining sites, use of mercury in manufacturing of products (pesticides, medical devices, thermometer, light bulb), sites of mercury use in industry (chloralkali sites, acetaldehyde, vinyl acetate, and PVC); application and storage/disposal sites of mercury pesticides; gold/precious metal mining including ASGM; sites of mercury recycling; non-ferrous metals processing; oil/gas industry (Kocman et al. 2013).
- Chloralkali production sites can also be contaminated with PCDD/PCDFs, other UPOPs or PFAS depending on the technology used in the past with highest PCDD/PCDF legacy from the former use of graphite electrodes.
- When assessing chloralkali production sites, also the technologies used in the past need to be assessed including the management of wastes.
- The historic assessment should also evaluate the past production portfolio at the individual sites including POPs pesticides or organochlorine chemicals with large formation and release of dioxins/UPOPs.

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THANK YOU FOR YOUR ATTENTION

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