Combining it all: Mercury risk assessment - local

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WCC Science Ambassador Programme
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Content

- Regulatory developments
- Scope of the RA
- Effects assessment
- Exposure assessment
- Risk characterisation
- Companies’ achievements
Regulatory developments

- **PARCOM 90/3:**
  “...mercury based chlor-alkali plants shall be required to meet by 31 December 1996 a standard of 2 g/t capacity...for emissions to atmosphere, this shall include mercury and hydrogen.”
Regulatory developments

- PARCOM 90/3 also:

“RECOMMENDS that existing mercury cell chlor-alkali plants be phased out as soon as is practicable. The objective is that they should be phased out in 2010.”
Regulatory developments

- European Union

- BREF:
  - provides guidance
  - No binding emission limits
  - Indicates what can be achieved
  - Plant by plant: local conditions
  - Pressure: emissions below 1.0 g/t
Regulatory developments

- Best Available Technique (BAT) is:
  - Membrane
  - Diaphragm (asbestos free)
- Strict emission controls (e.g. mercury balance)
- Guidance on best achievable emission levels: estimate: 0.2-0.5 g Hg/t capacity
Euro Chlor commitments

1. No installation of new mercury cells
2. No shipment of mercury cells to other parties
3. Mercury emission reduction (conditional):
   - 1 g Hg/t Cl₂ cap by end 2007
   - further reduction if shutdown > 2010 for some plants
Euro Chlor commitments

4. Reporting of individual plant emissions
5. End of existing mercury plants (conditional): by end of 2020 with package of measures
6. Safe disposal of metallic mercury from shutdown cells (12,000 tonnes)
Scope of the local RA

- Standard plant (200,000 t Cl\(_2\) cap), emission of 1.9 Hg/t Cl\(_2\) cap
- 1.7 to air
- 0.1 to water
- 0.1 to products
- Elemental, inorganic, organic
Hg ads = Mercury adsorbed onto sediment particles and insoluble mercury compounds such as sulphide
Local scenario targets:

- **To water: inorganic Hg:**
  - aquatic compartment
  - sediment

- **To air: elemental Hg deposited as inorganic Hg:**
  - Soil (conversion to organic Hg)
  - vegetables, etc.

- **Humans: mainly oral intake, foodbasket + local food**
Effect Assessment: PNEC

PNEC’s needed for:

- Aquatic compartment ecotox data
- Aquatic – sediment EP + test
- Terrestrial – plants ecotox data
- Predators literature
- Human (TDI) WHO - RIVM
PNEC Aquatic: Effects Data

- 23 studies on fish
- 35 studies on invertebrates
- 36 studies on algae
- Acute and chronic studies
- Freshwater and marine: same sensitivity
- All studies validity checked (classes 1-4)
PNEC Aquatic - Results

- **Fish**: lowest chronic NOEC: 0.5 µg/L

- **Invertebrates**: lowest chronic NOEC: 0.25 µg/L

- **Algae**: lowest chronic NOEC: 0.9 µg/L

Proposed overall NOEC algae (Safety factor 2): 0.4 µg/L

(41 weeks, growth and reproduction of P. promelas, val. 1)

(112 d., C. fornicata-mollusc, val. 1, crustaceans and other invertebrates similar sensitivity)

(10 d., F.serratus, val. 2)

LOEC, 15% inhibition: 0.77 µg/L, 13 d. Isochrysis galbana, val. 2)
Aquatic PNEC evaluation

- Lowest value NOEC 0.25 µg/L
  - chronic data for 3 taxonomic groups; safety factor = 10: 0.025 µg/L
- Many data, also chronic NOEC’s allow statistical extrapolation based on species sensitivity:
  - RIVM: 0.23 µg/L
  - Euro Chlor: 0.47 µg/L (taxonomic grouping, only val. 1 + 2)
Sediment Toxicity

- Chronic test: 28 d. *C. riparius* (mosquito larvae)
- NOEC of 1000 mg/kg DW (nominal), 930 mg/kg DW (measured)
- Major route of exposure through waterphase, chronic sediment value, many aquatic toxicity data available: safety factor of 10
- PNEC = 93 mg/kg DW (31.2 mg/kg WW)
Fish-eating Predators

- Not relevant for inorganic (ionic) mercury
- Inorganic mercury can be transformed into organic mercury in sediment, fish
- Highly dependent on local conditions
- No PNEC for predators available

Producers advised to handle locally on a case-by-case basis
PNEC – Terrestrial: Plant testing

- Producers: 726 mg/kg DW
- Decomposers:
  - microorganisms: 800 µg/kg DW
  - invertebrates-soil dwelling organisms: 6.2 mg/kg DW (LC50: 26.6 mg/kg DW)
- Primary consumers: no reliable data
- TGD: lowest LC50/1000: 26.6 µg/kg DW

Background concentrations in soil:
- 300 µg/kg DW (highest average): 300 µg/kg DW used as PNEC
Secondary Consumers – Terrestrial Predators

- Study on mink only: 8.5 mg/kg feed (long-term NOEC)
- ‘Mainly aquatic species, but sensitive’
- Safety factor 100:

\[ \text{PNEC}_{\text{pred-terrestrial}} = 85 \, \mu g/kg \text{ feed} \]
Humans

Data Sources:

- WHO-ICPS – Integrated Criteria Document (RIVM, NL)
- TDI inorganic mercury: 4 µg/kg bw (Slooff et al., 1995)
- TDI organic mercury: 0.08 µg/kg bw (Slooff et al., 1995)
Exposure assessment

- Aquatic: measurements for water phase, EP calculations for sediment
- Soil: model calculations (EPA: COMPDEP)
- Humans: food basket calculations

- Italics: will be illustrated
Emissions - aquatic

Mercury levels in receiving water based on BAT or real emission data

$\text{PNEC} = 0.47 \, \mu g/l$
## Human exposure - DI

<table>
<thead>
<tr>
<th>Daily intake route</th>
<th>Concentration</th>
<th>Unit</th>
<th>DI</th>
<th>Unit</th>
<th>DI/ kg BW</th>
<th>Dose</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>0.05</td>
<td>µg/l</td>
<td>2</td>
<td>L/d</td>
<td>0.02857</td>
<td>0.001429</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
<tr>
<td>Fish</td>
<td>300</td>
<td>µg/kg</td>
<td>0.115</td>
<td>kg_wwt_/d</td>
<td>0.00164</td>
<td>0.492857</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
<tr>
<td>Leaf crops</td>
<td>1400</td>
<td>µg/kg</td>
<td>1.2</td>
<td>kg_wwt_/d</td>
<td>0.01714</td>
<td>0.6</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
<tr>
<td>Root crops</td>
<td>3</td>
<td>µg/kg</td>
<td>0.384</td>
<td>kg_wwt_/d</td>
<td>0.00549</td>
<td>0.016457</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
<tr>
<td>Meat</td>
<td>5</td>
<td>µg/kg</td>
<td>0.301</td>
<td>kg_wwt_/d</td>
<td>0.0043</td>
<td>0.0215</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
<tr>
<td>Dairy products</td>
<td>1</td>
<td>µg/kg</td>
<td>0.561</td>
<td>kg_wwt_/d</td>
<td>0.00801</td>
<td>0.008014</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
<tr>
<td>Air *</td>
<td>0.14</td>
<td>µg/m³</td>
<td>20</td>
<td>m³/d</td>
<td>0.28571</td>
<td>0.03</td>
<td>µg.kg_bw_-1.d_-1</td>
</tr>
</tbody>
</table>

**Total daily intake**

1.17 µg.kg\_bw\_-1.d\_-1

*Bioavailability 0.75*
# Summary - inorganic mercury

<table>
<thead>
<tr>
<th>Type of scenario</th>
<th>DI</th>
<th>TDI</th>
<th>DI / TDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human health</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Public</td>
<td>0.62 µg/kg bw.d</td>
<td>4 µg/kg bw.d</td>
<td>0.16</td>
</tr>
<tr>
<td>General public - close</td>
<td>1.17 µg/kg bw.d</td>
<td></td>
<td>0.29</td>
</tr>
<tr>
<td>Occupational</td>
<td>3.12 µg/kg bw.d</td>
<td></td>
<td>0.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of scenario</th>
<th>PEC</th>
<th>PNEC</th>
<th>PEC/PNEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic compartment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquatic organisms</td>
<td>0.006 µg/l (median - bioavailable n=40)</td>
<td>0.47 µg/l (bioavailable soluble fraction)</td>
<td>0.013</td>
</tr>
<tr>
<td>Fish-eating predators</td>
<td>94% &lt; 0.47 µg/l(n=53)</td>
<td>94% &lt;1</td>
<td></td>
</tr>
<tr>
<td>Aquatic sediments</td>
<td>not relevant</td>
<td>31.2 mg/kg (w.w.)</td>
<td>0.007</td>
</tr>
<tr>
<td>0.22 mg/kg (w.w.) (median level)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17 mg/kg (w.w. - 94%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Terrestrial compartment |    |     |          |
| Soil dwelling organisms | 207-221 µg/kg soil (d.w.) | 300 µg/kg soil (d.w.) | <1 |
| Plants | 6500 µg/kg (w.w.) | no adequate data | - |
| Terrestrial herbivores | 0.14 µg/m3 air | 85 µg/kg feed w.w. | >1 |
| Terrestrial predators (meat) | 207-500 µg/kg feed (w.w.) | | |

**Summary - inorganic mercury**

- **DI**: Daily Intake
- **TDI**: Tolerable Daily Intake
- **PEC**: Predicted Environmental Concentration
- **PNEC**: Predicted No Effect Concentration
- **DI / TDI**: Ratio of Daily Intake to Tolerable Daily Intake
- **PEC/PNEC**: Ratio of Predicted Environmental Concentration to Predicted No Effect Concentration
<table>
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<th>TDI</th>
<th>DI / TDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human health</td>
<td>0.01-0.027 µg/ kg (b.w.)</td>
<td>TDI = 0.08 µg/ kg (b.w.)</td>
<td>0.13-0.34 consumption of local fish may increase DI</td>
</tr>
<tr>
<td>Terrrestrial compartment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil dwelling organisms (microorganisms, earth worms, insects), plants</td>
<td>7 µg/ kg soil d.w.</td>
<td>23 µg/ kg</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Terrestrial predators (meat)</td>
<td>7 µg/ kg w.w.</td>
<td>No adequate data</td>
<td></td>
</tr>
<tr>
<td>Aquatic compartment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquatic organisms</td>
<td>not relevant</td>
<td>no need 18-21 µg/ kg</td>
<td>not relevant</td>
</tr>
<tr>
<td>Fish-eating predators</td>
<td>not relevant</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Risk management: mercury balance

- Mercury Balance is assessed on a yearly basis in European chlor alkali plants since at least 1977.
- Since 2000 these data are sent to OSPAR every year. Data are consistent with national authority information.
- A guideline was developed and updated in June 2000 to match additional criteria asked by OSPAR (Env Prot 12 - Guidelines for Making a Mercury Balance in a Chlorine Plant - 3rd Edition).
Mercury balance and reducing emissions
Mercury balance

- To increase our credibility further, a guideline for preparing an audit of the mercury balance in a chlorine plant was written (Env Prot 17 - Audit Guidelines for Making a Mercury Balance in a Chlorine Plant) and approved by a well known third part organisation: TÜV, from Germany.

- An audit took place in Germany on the 20th December 2001, with the concluding remark:

"The audit guideline in all respects provides a specific working tool for the implementation of mercury balances, especially for those companies that do not yet have a management system. Even where management systems have already been introduced (e.g. ISO 9001, 14001), valuable implementation information can be integrated in the existing system".
Results: mercury emissions

Mercury Emissions 1977-2002
Euro Chlor: W. Europe

Mercury Emissions to Air, Water and in Products

Values in g. of Hg per tone of Chlorine Capacity

- Air
- Water
- Products

Years: 1977 to 2002

Chart shows mercury emissions in g. of Hg per tone of Chlorine Capacity for each year from 1977 to 2002.
Results: mercury emissions

EMISSIONS 1995 - 2002

g. of mercury per tone of chlorine capacity

<table>
<thead>
<tr>
<th>Year</th>
<th>g of Mercury/tonne of chlorine capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>2.70</td>
</tr>
<tr>
<td>1996</td>
<td>2.00</td>
</tr>
<tr>
<td>1997</td>
<td>1.40</td>
</tr>
<tr>
<td>1998</td>
<td>1.38</td>
</tr>
<tr>
<td>1999</td>
<td>1.34</td>
</tr>
<tr>
<td>2000</td>
<td>1.25</td>
</tr>
<tr>
<td>2001</td>
<td>1.15</td>
</tr>
<tr>
<td>2002</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Legend:
- Products
- Water
- Air
Results: mercury emissions
Conclusions

- Organic mercury formation in the environment and potential food-chain effects (toxicity to predators) could not be assessed in a generic local RA:
  - Case-by case local assessments, measurements in fish
- A few plants need to reduce emissions to water
- in practice all plants do!
Conclusions - continued

- Human health seems OK
- The BAT emission of 1 g/t Cl₂ cap poses no problem for most scenarios, but for some sites it might and some others are close
- Remaining uncertainties and concerns: need to continue reduction of emissions
Recommendations

- RA activity is very useful ‘homework’:
  - Hg difficult but risks quantified, prioritizes areas for improvement
  - Strengthens position towards stakeholders
- Know your science BUT know your limits AND be pragmatic
- Open interaction with stakeholders is beneficial for understanding and acceptance