



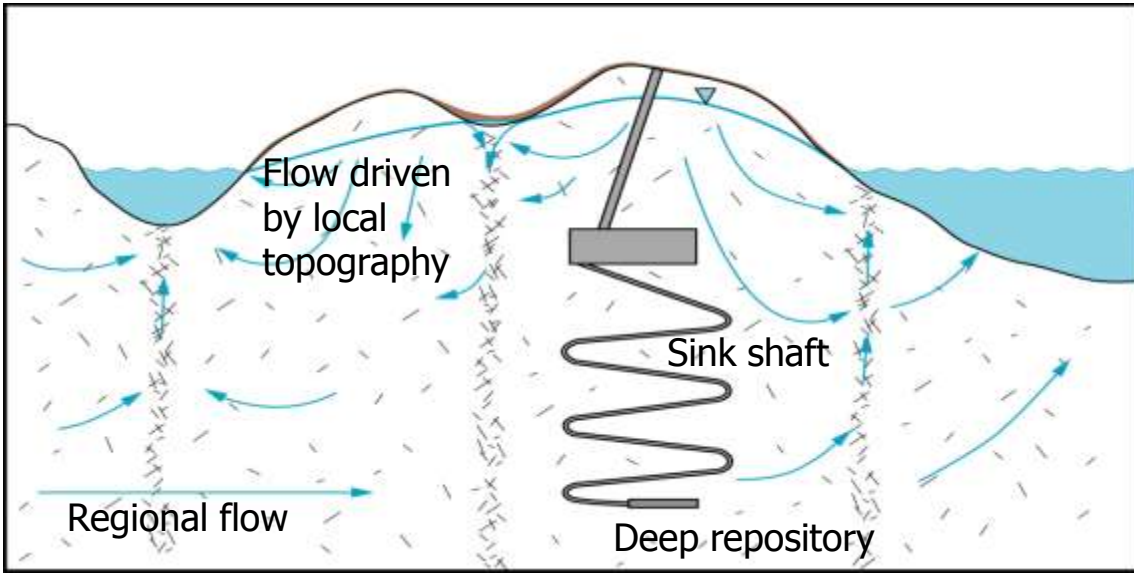
Assessing the behaviour and fate of mercury should it be released from a disposal facility

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Fate of mercury released from a deep repository in hard rock

- Hg may be released from the repository near-field by:
 - Diffusion through near-field barriers
 - Advective groundwater flow through the repository
 - Flow of vapour by gas released from the repository
- Hg will diffuse into the surrounding rock into the passing groundwater
- Hg may undergo geochemical changes:
 - In redox state
 - Of aqueous speciation
 - Precipitate as solid minerals
 - Adsorb to mineral surfaces
 - Form or adsorb to colloidal material in the groundwater
 - Biomediated methylation
- Physical and chemical retention
 - Matrix diffusion
 - Sorption
- Dilution by groundwater



- Further biogeochemical reactions when released into the biosphere:
 - Oxidation by mixing with surface water
 - Redox cycling in sediment/lake bottom waters
 - Retention in sediments, organic soils etc
 - Biomediated methylation
 - Evaporation to atmosphere
 - Transfer between organisms at different trophic levels
 - Bioaccumulation of HgMe
 - Attenuation in anoxic surface sediment
 - Long-term embedding into deeper sediments

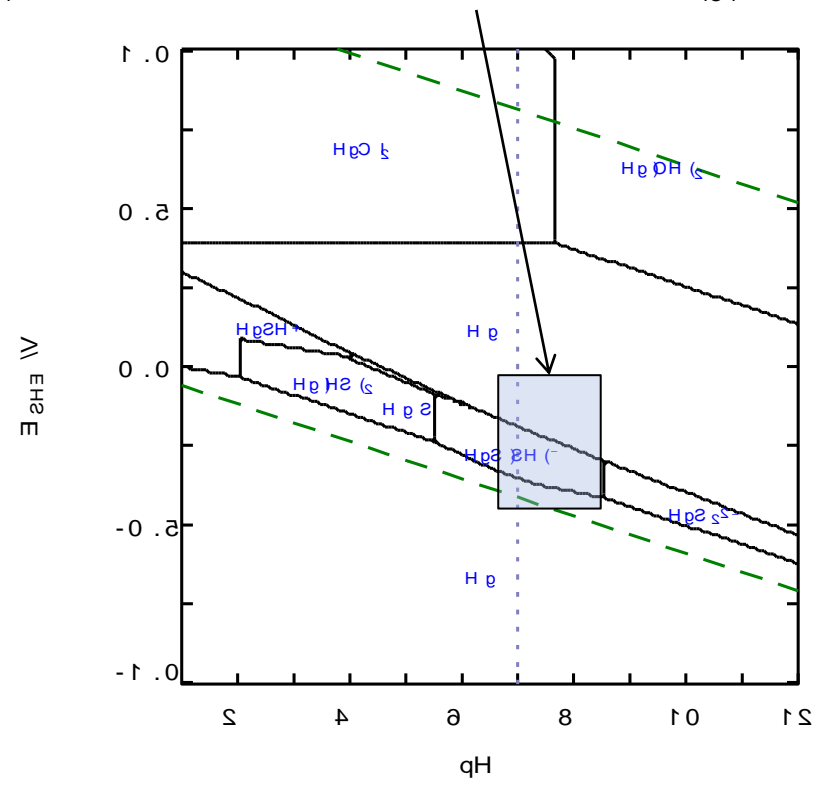
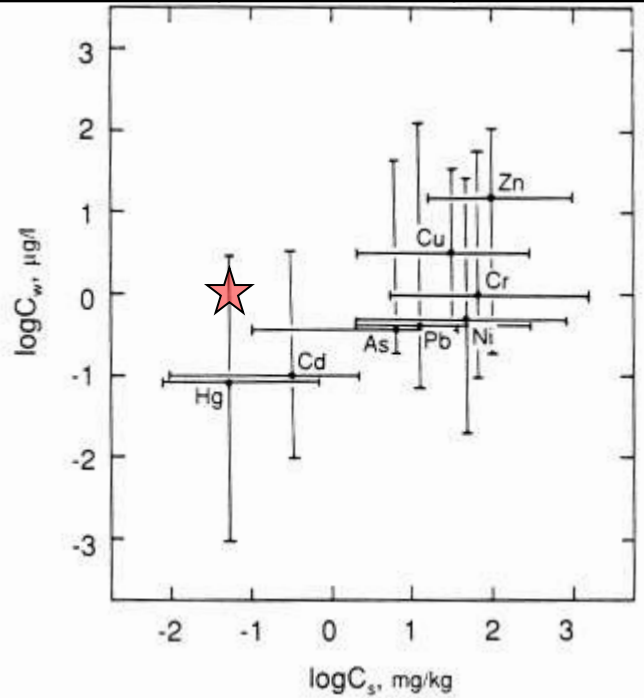
Background concentrations and chemical speciation of mercury in the groundwater in hard rock

SGU measured data in Swedish drill holes in rock

Percentile	Hg-tot (ng/l)	HgMe (ng/l)
50%	0,4	0,06
90%	6	1,24
Max	482	1,4

$\text{Fe}^{2+}_{TOT} = 5000 \text{ mM}$
 $\text{Fe}^{3+}_{TOT} = 200 \text{ mM}$

Expected geochemical window in deep hard-rock
 $\text{Fe}^{2+}_{TOT} = 1000 \text{ mM}$
 $\text{Fe}^{3+}_{TOT} = 1000 \text{ mM}$



Chemical speciation and sorption

- Mercury in form of Hg(II) is effectively sorbed to mineral surfaces, organic material, soil, sediments etc
- Speciation calculations demonstrate that mercury are likely to be dominated in solution by dissolved Hg^0 or different anionic species, e.g. $\text{HgS}(\text{SH})^-$
- Sorption of dissolved Hg^0 is expected to be very low or zero
- Sorption of anionic species, e.g. $\text{HgS}(\text{SH})^-$, is unknown, but can be expected to be very small
- With minimal sorption, no or very small chemical retention of mercury in the rock can be expected

Sorption of mercury

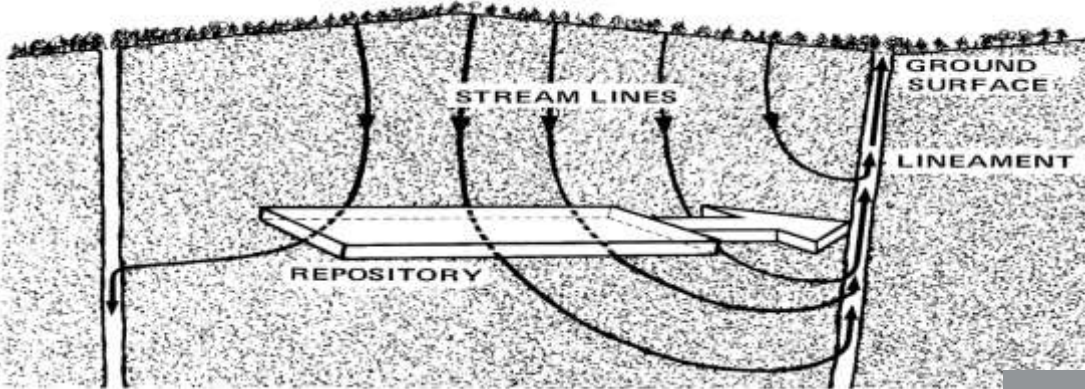
(Estimated values, from Lyon et al, 1998)

	K_d (Hg ⁰) (l/kg)	K_d (Hg ^{II}) (l/kg)	K_d (CH ₃ Hg ⁺) (l/kg)
Soil	1 000	58 000	7 000
Suspended sediment	1 000	100 000	100 000
Suspended solid biotic material	1 000	200 000	500 000
Bentic sediment	3 000	50 000	3 000

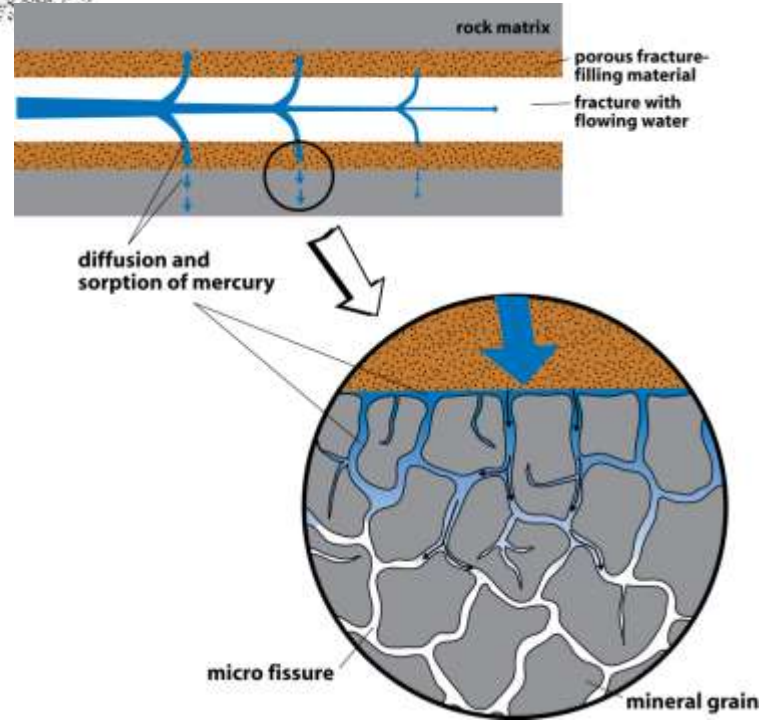
(From Allison och Allison, 2005)

Type of value	Soil – water [l/kg]	Suspended particles – water [l/kg]	Dissolved organic compounds – water [l/kg]	Sediment – water [l/kg]
Hg				
Median	6 300	200 000	200 000	79 400
Range	150 – 630 000	15 800 – 794 000	200 000 – 398 000	6 300 – 1 000 000
Number of measurements	17	35	3	2
CH ₃ Hg ⁺				
Median	630	250 000	-	4 000
Range	20 – 63 000	15 800 – 1 500 000	-	630 – 100 000
Number of measurements	11	2	-	4

Retention by matrix diffusion during transport in hard rock

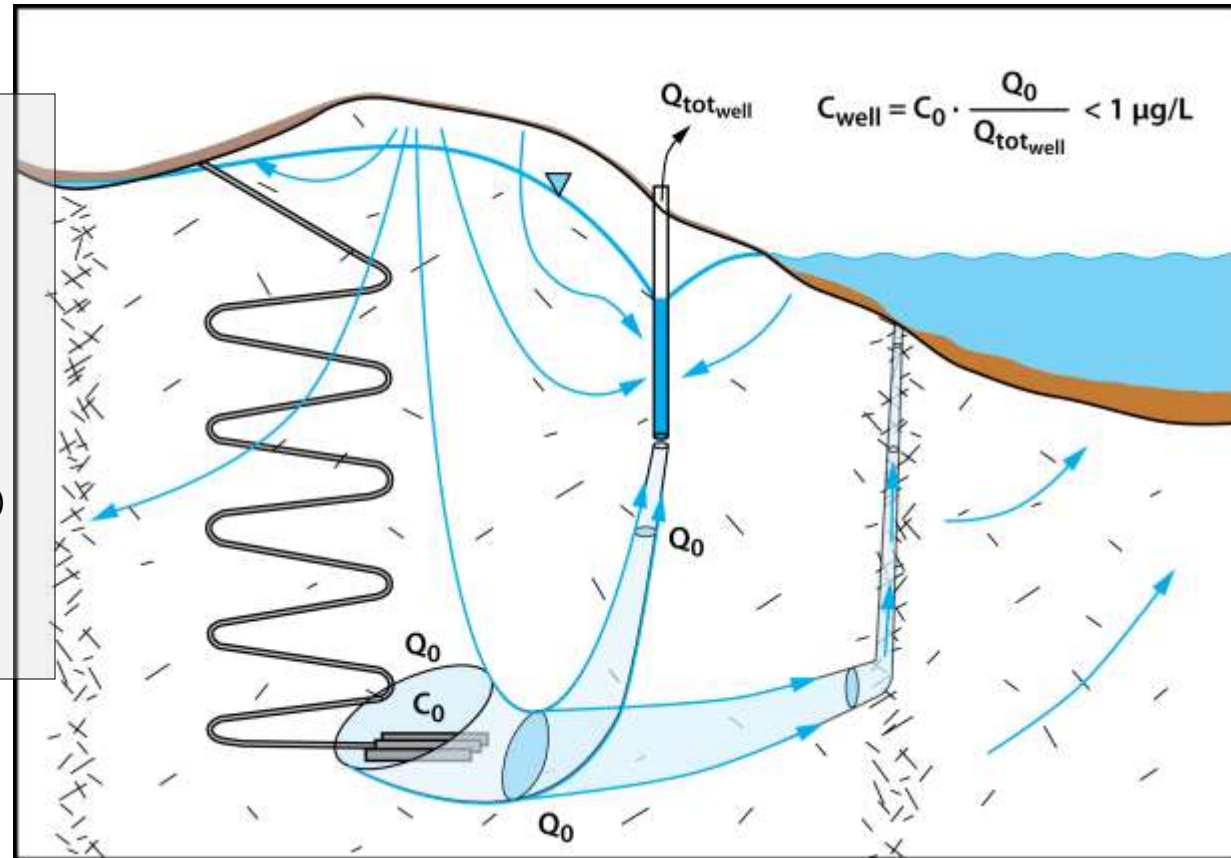


Source: SKB



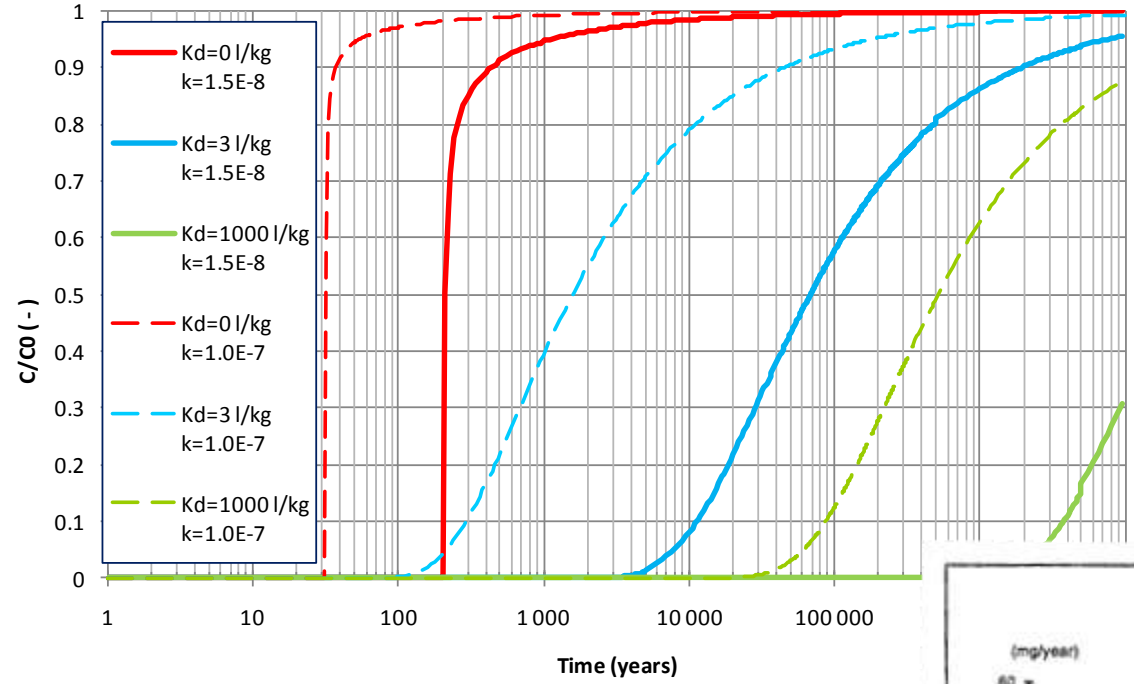
Limiting well scenario

- Assume Hg solubility as Hg(I)
50 µg/l (high)
- Diffusive release and film resistance give
15 – 50 mg/year from near field
- Advective release disregarding the near
field barriers give 25-50 mg/year
- Well capacity sufficient to supply small
farm, 6 m³/day
- Maximum concentration in well,
0,01 µg/l (disregarding background load)
- Roughly equals 90-95 percentile in rock
groundwater
- Equals 1% of the drinking water criteria



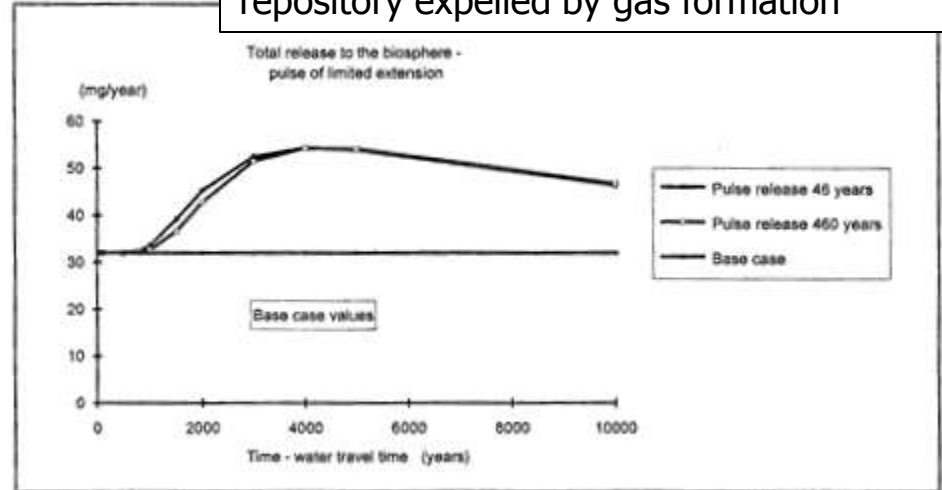
Calculated breakthrough curves for mercury from repository to fracture zone or a well considering the retention by matrix diffusion and sorption

Continuous release by advection and diffusion "Base case". Distance to well 100 m. Neglecting dilution effect.



Rock porosity 0,001
 Gradient 0,001 m/m
 K-rock $1e-8$ m/s
 K-fracture $1e-7$ m/s
 Fracture fraction 5%

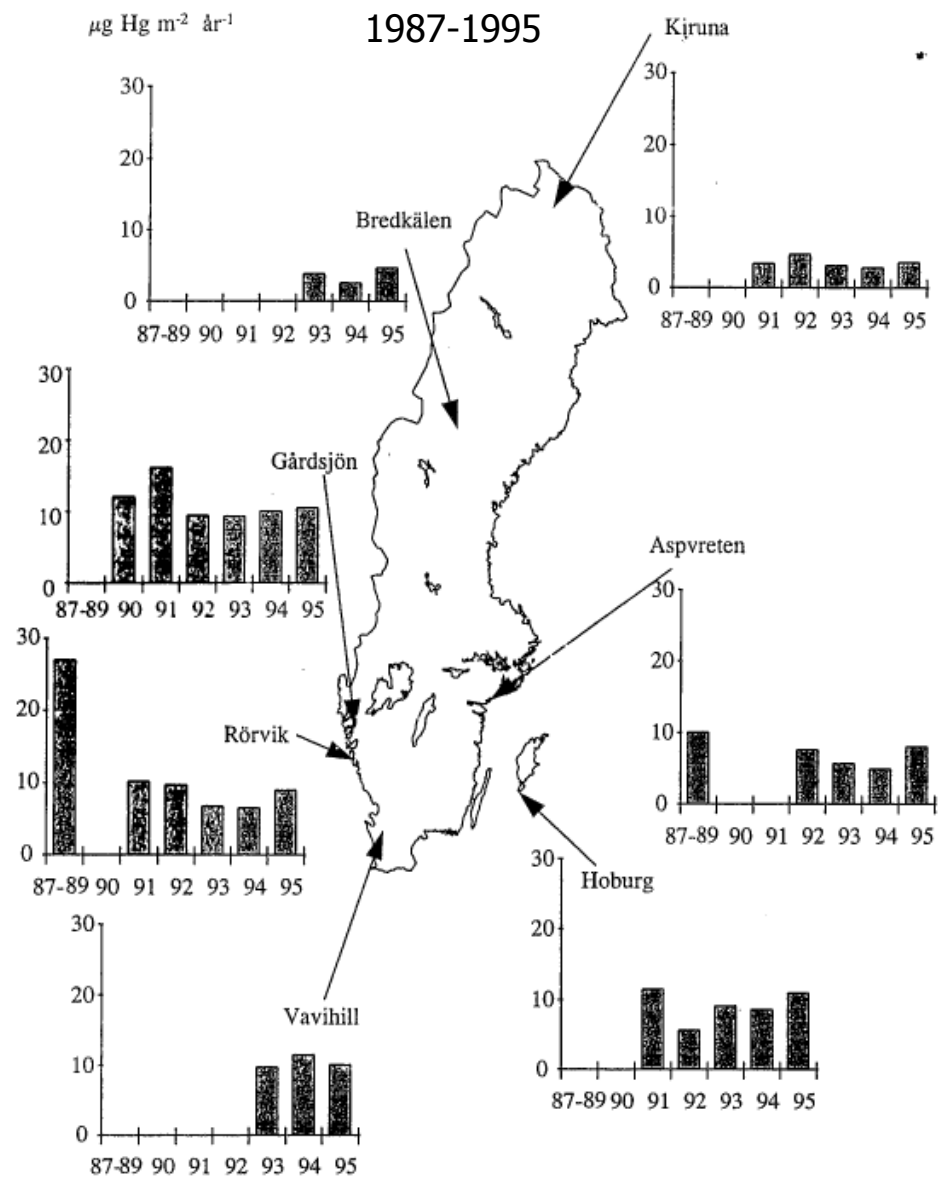
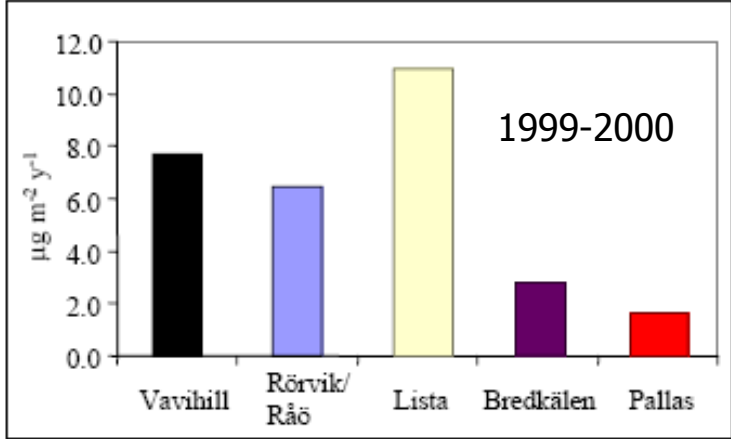
Extreme scenario – all pore water in the repository expelled by gas formation



Atmospheric wet deposition in Sweden



In Sweden, Norway and Finland



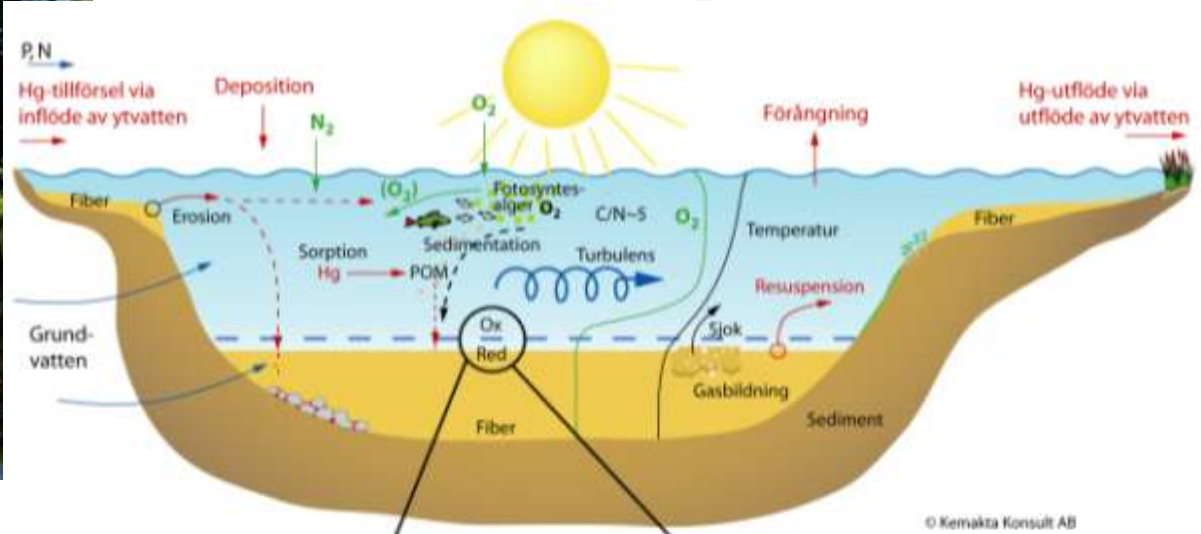
Source: IVL

Comparing calculated release with atmospheric deposition

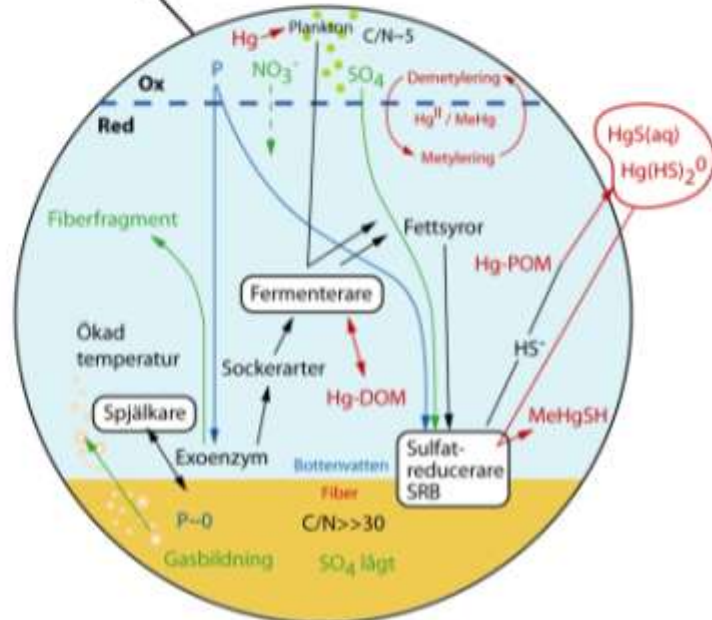
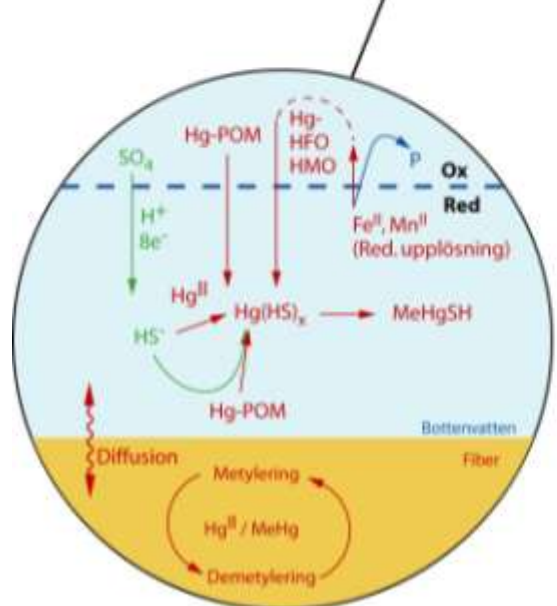
- Assuming an atmospheric deposition of $5 \mu\text{g}/\text{m}^2/\text{year}$
- Assume a lake of 1 km^2 , runoff area of 10 km^2
- Total Hg load equals $5 \text{ g}/\text{year}$ on the lake surface and 50 g in the runoff area

- Calculated release from a repository is about $0,05 \text{ g}/\text{year}$

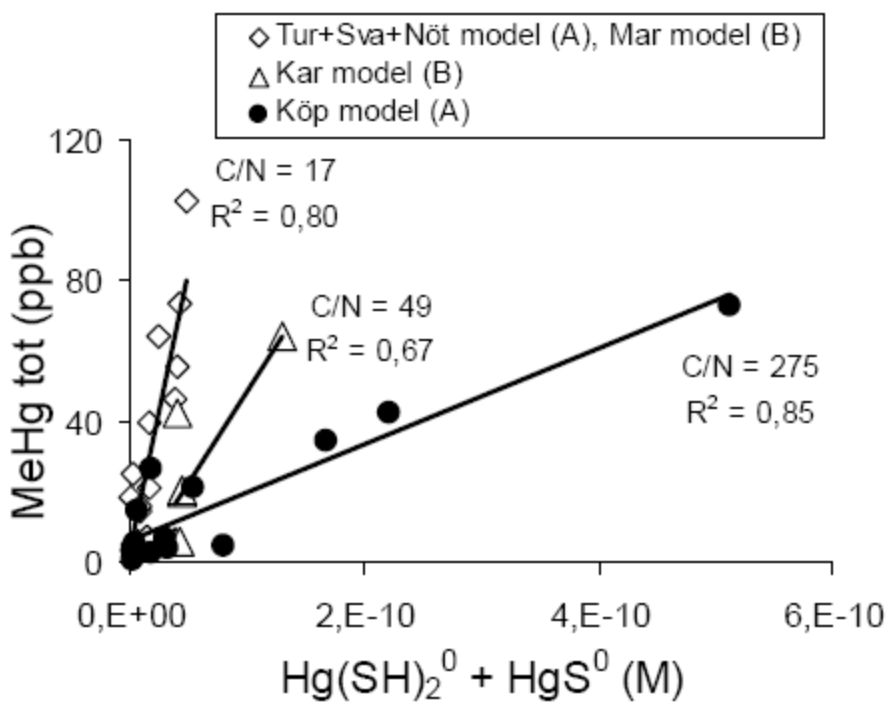
Conceptual model of a mercury lake



- Significant biogeochemical transformations are likely to occur when reducing conditions meet oxic conditions
- Lake sediments are very active environments
- Lakes and sediment often show seasonal cyclic conditions
- Mercury is likely to accumulate, at least partly, in anaerobic sediment
- Mercury methylation will occur in bottom water and upper sediment layer
- Net methylation of mercury = methylation – demethylation + inflow of $HgMe$ – outflow of $HgMe$



Observations on mercury methylation in different sediment systems



From Skyllberg et al (2006)

- Primary production and access to energy-rich organic material is an important factor for methylation – small eutrophic lakes may constitute a risk environment
- Strong relationship found between rate of methylation and the presence of neutral mercury sulphide complexes in the porewater
- Different rate constants apply to sweetwater (open symbols) and brackish water (filled symbols) systems

Box-model for mercury transfer in a lake

