HEAVY METALS IN WASTEWATER
REMOVAL AND ANALYSES

RAMBOLL

HEAVY METALS AND THEIR SOURCES

- The most commonly encountered toxic heavy metals in wastewater:
  - Arsenic, Lead, Mercury, Cadmium
  - Less common: Chromium, Copper, Nickel, Zinc
- Sources
  - Industrial sources: e.g. Printed board manufacturing, metal finishing and plating, semiconductor manufacturing, textile dyes
  - Street runoffs
  - Landfills

PROBLEMS CAUSED BY HEAVY METALS

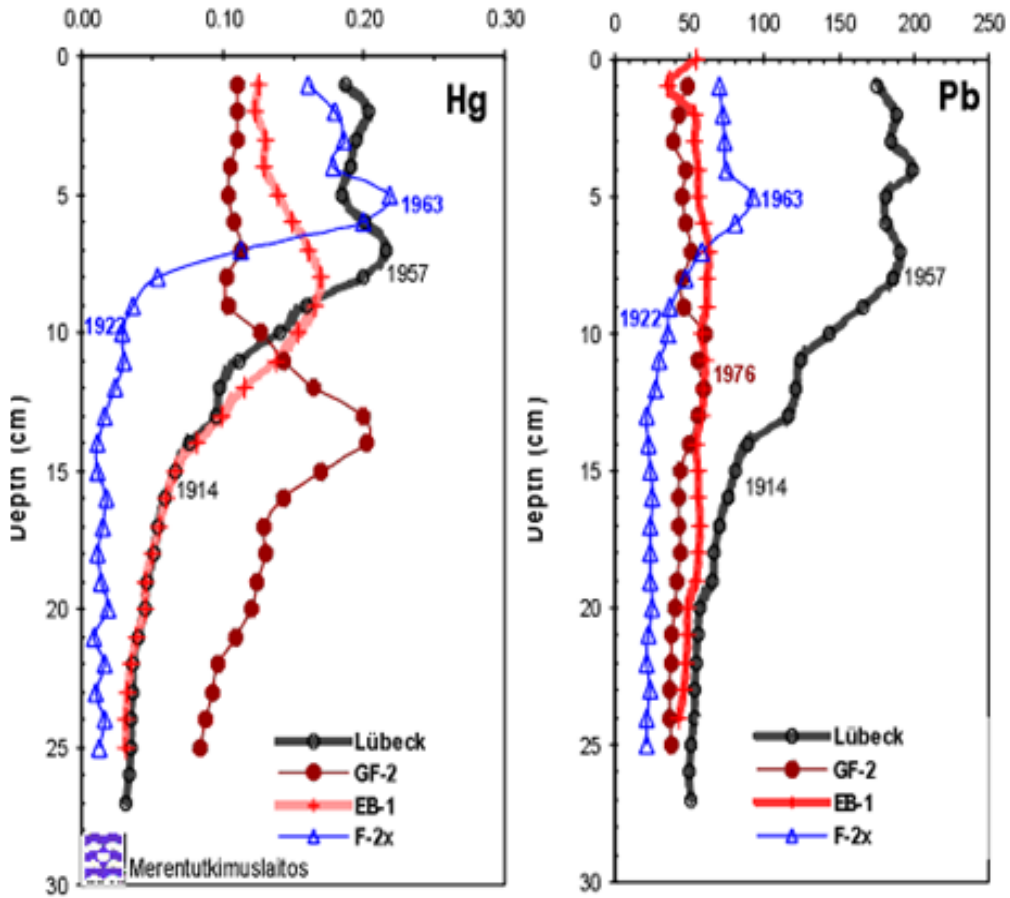
- Many heavy metals are essential trace elements for humans, animals and plants in small amounts
- In larger amounts cause acute and chronic toxicity.
- Linked to learning disabilities, cancers and even death
- Heavy metals have inhibitory effects on the biological treatment process at the wastewater treatment plants
- Limit the use of biosolids as fertilizer and may inhibit the digestion process in biogas plant


Kuva:Pasi Valkama

	EU (mg/kg)	Suomi (mg/kg)	Saksa (mg/kg)	Hollanti (mg/kg)	Esimerkki Suomi (mg/kg)	Esimerkki Hollanti (mg/kg)
As	----	25	40	15	----	9
Cd	20 - 40	1,5	1,5	1,25	0,5 - 1	1,5
Cr	--	300	---	75	21 - 53	43
Cu	1000 - 1750	600	---	75	143 - 496	390
Hg	16 - 25	1	1	0,75	0,41 - 0,80	1,1
Ni	300 - 400	100	60	30	16 - 44	30
Pb	750 - 1200	100	150	100	19 - 47	134
Zn	2500 - 4000	1500	---	300	330 -2495	994

THE OCCURRENCE OF HEAVY METALS IN NATURE AND WASTEWATERS

- Many heavy metals occur also naturally
- Contribution from human activities important for lead, cadmium and nickel.
- Measurements from the bottom sediments of the Golf of Finland suggest that highest pollution occurred during 1970-1980, a 40% decrease in recent sediments
- The heavy metal concentrations in treatment plant sludges have decreased

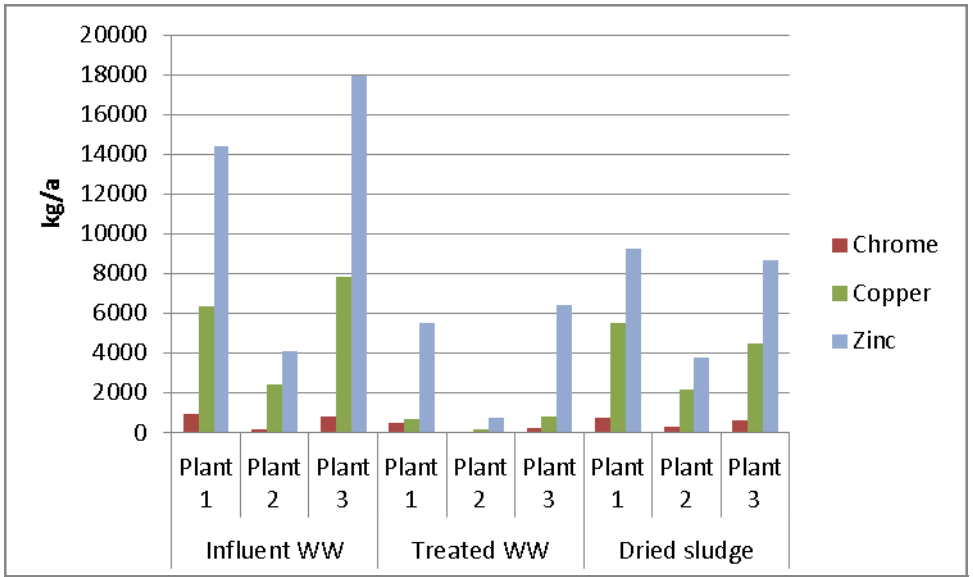


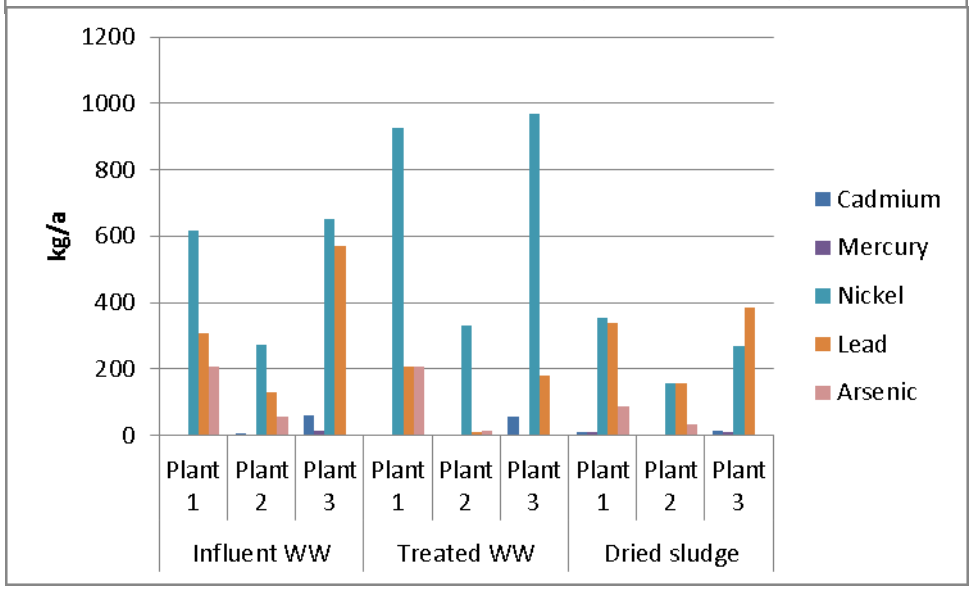
WAYS OF MINIMIZING THE CONCENTRATIONS OF HEAVY METALS

- Pretreatment of industrial effluents
  - More cost-effective and easier treatment
  - Recovery possible
- Agreements for industrial effluents with fixed limits for heavy metals
- Control samples from effluents
- Examples of used limits
  - Cd < 0,01 mg/l; Ni < 0,5 mg/l
  - Pb < 0,5 mg/l; Zn < 3,0 mg/l

REMOVAL OF HEAVY METALS AT THE MUNICIPAL WASTEWATER TREATMENT PLANT

- Activated sludge process does not remove most of the heavy metals efficiently
- Inhibition at high concentrations
- More load mainly from the use of chemicals
- Heavy metals do not disappear nor react – they are either in the water or in the sludge!

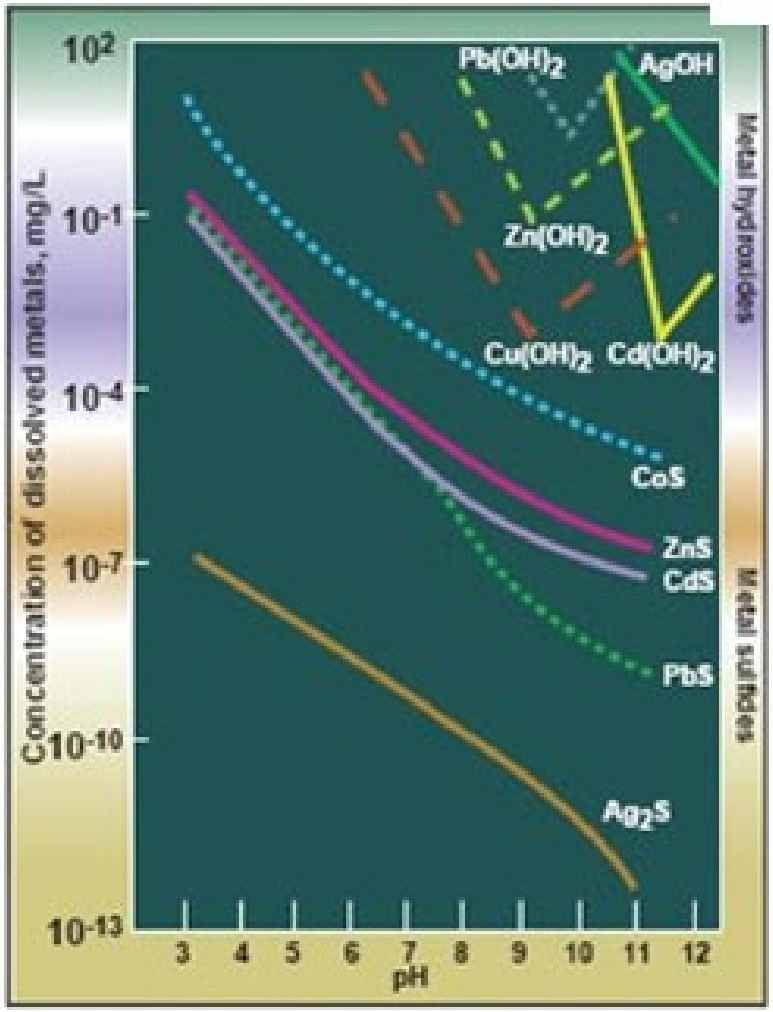




RAMBOLL

REMOVAL OF HEAVY METALS 1/3

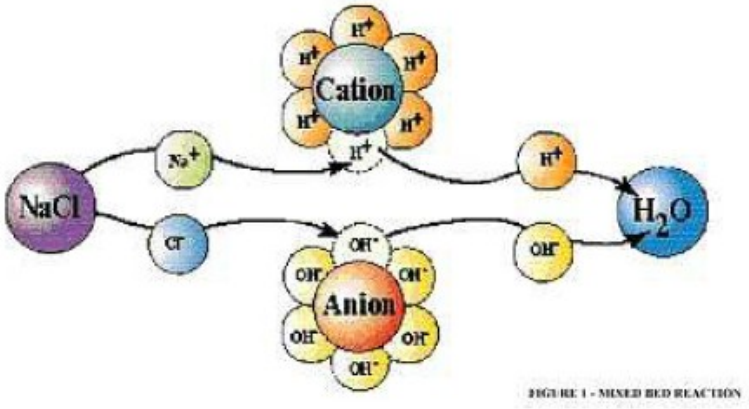
- Chemical precipitation
  - Hydroxide precipitation NaOH or Ca $(OH)_2$, pH 8 – 11
  - Addition of coagulants possible
  - + 99 % removal possible
  - - Requires high concentration, produces sludge, some metal hydroxides are amphoteric, inhibition by complexing agents
  - Also sulfide precipitation (possible using sulfate-reducing bacteria), chelates



(Rast, 2013)

REMOVAL OF HEAVY METALS 2/3

- Ion exchange
  - High efficiency, fast process
  - Synthetic resins are most common
  - Research with natural zeolite
  - – cost-effective at high concentration, secondary pollution from regeneration
- Adsorption
  - Activated carbon – price increasing
  - Carbon nanotubes (CNT)
  - Low-cost or bioadsorbents (e.g. zeolite, clay; potato peels, eggshell, banana peels etc.)
  - Separation of biosorbents still a problem



REMOVAL OF HEAVY METALS 3/3

- Membrane filtration
  - Ultrafiltration, nanofiltration, reverse osmosis
  - Micellar enhanced (MEUF) = addition of surfactants to wastewater beyond the critical concentration, recovery and reuse of surfactant?
  - polymer enhanced (PEUF), research stage
  - NF&RO, high energy cost and membrane restoration
- Flotation
  - Ion flotation = imparting the ionic metals hydrophobic an d removal by air bubbles
- Electrochemical methods
  - Electrocoagulation (Fe or Al eletrodes)
  - Electroflotation (water eletrolysis)
  - Eletrodeposition (recovery)

REACHING VERY LOW LEVELS OF HEAVY METALS IN THE EFFLUENT

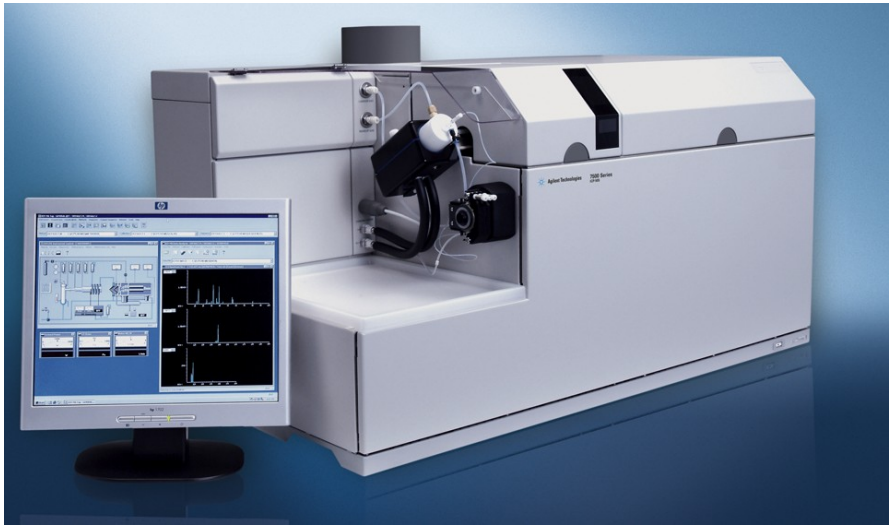
- EU priority substances with environmental quality standards:
  - Mercury < 5 µg/l ; 0,05 µg/l
  - Lead ; 7,2 µg/l
  - Cadmium < 10 µg/l ; 0,08 – 0,25 µg/l
  - Nickel ; 20 µg/l
- Concentrations in Finnish treated wastewater typically
  - Cd < 0,5 µg/l; Hg < 0,2 µg/l
  - Pb < 3 µg/l ; Ni < 10 µg/l

ANALYSING HEAVY METALS IN WASTE WATER

- Waste water samples are usually digested using microwave digestion in aqua regia or strong nitric acid
- Analyses of the elements are performed using ICP-MS technique
- Method is based on the SFS-EN ISO 17294-2 standard

ICP-MS (INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER)

- The digest solution is nebulized and sample aerosol is transported to argon plasma
- High temperature plasma produce the ions, which are introduced into the mass spectrometer
- The mass spectrometer sorts the ions according to their mass-to-charge ration and the ions are quantified with an electron multiplier detector



THANK YOU! KIITOS!