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Trends and source apportionment of atmospheric heavy metals in Finland

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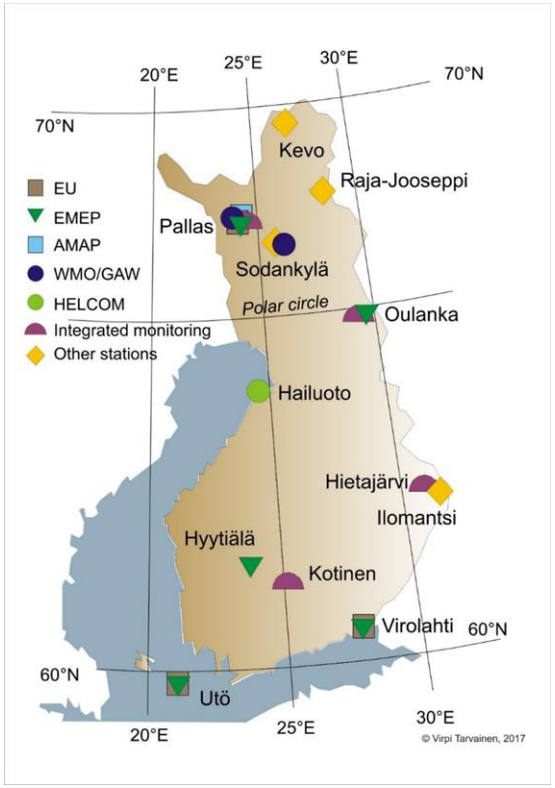
Joint Task Force ICP Waters and ICP Integrated Monitoring

4.6.2019 Helsinki

Background

- Sub-arctic site Pallas, measurements since 1996
- Heavy metals presented here: Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn in PM, and gaseous Hg (TGM)
- Trend analysis with Generalized Least-Squares (GLS) regression with classical decomposition and AutoRegressive Moving Average (ARMA) errors applied for monthly mean values
- Source apportionment with Positive Matrix Factorisation (PMF)
- Directives and programs
  - EMEP, AMAP, IM, GOS4M programs
  - Directive 2008/50/EC on Ambient Air Quality and Cleaner Air for Europe (CAFÉ) relating to e.g. Pb
  - Directive 2004/107/EC relating to As, Cd, Hg, Ni and PAHs in ambient air (PM10, deposition)
  - Directive 2015/1480

Measurement site



Atmospheric measurements at Pallas:
CO_2, CH_4, N_2O, O_3, SO_2, NO+NO_y, SF_6, CO, H_2, VOC, PAH, POPs, EC/OC, PM_{10}, $PM_{2.5}$, ^{222}Rn, main ions, fluxes…

International programs:
WMO/GAW, ACTRIS, IASOA, AMAP, EMEP, ICP Forests, ICP IM, FinLTSER, ICOS, LTER-Europe, ILTER, WFD, PEEX, GMOS, GOS4M, AnaEE, GAPS, MONET-EU

Lohila et al. (2015) Boreal Env.Res. 20, 431–454

Sampling

HM in PM, 1996=>

- Teflon filters
- Weekly sampling
- Air flow 17 l/min
- PM10 inlet (IVL PModel S10)

TGM, 2007=>

- Tekran 2537A, 2537X
- 5 min sampling
- Flow 1.0-1.5 l/min
- Int. calibration every 25 or 71 h

Analysis

Pretreatment of filters

- HF/HNO3 acid digestion according to Jalkanen et al. (1996-2009) at FMI
- Microwave-assisted HNO_3+H_2O_2 digestion according to EN 14902:2005 (2010-2018) at SYKE

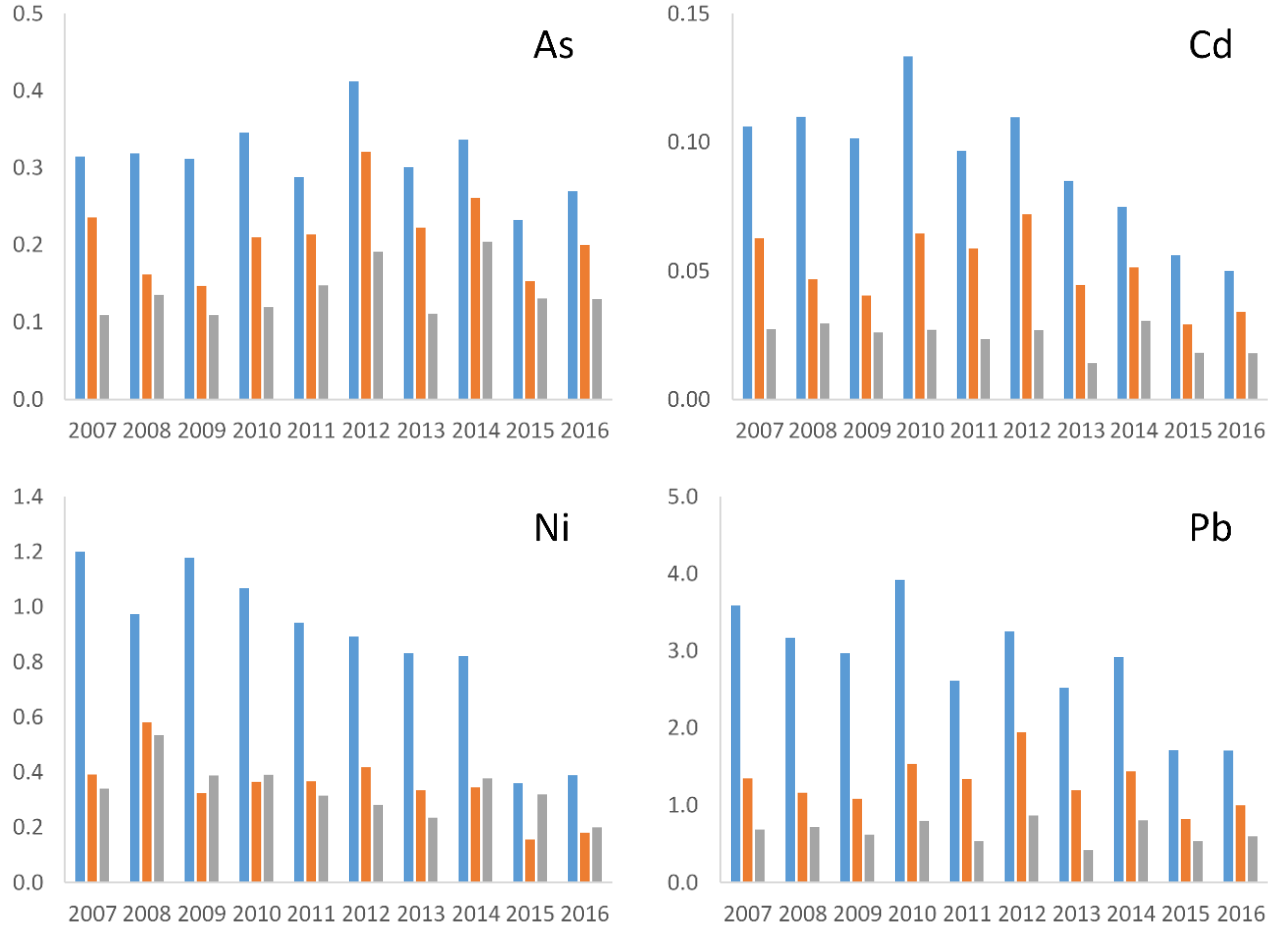
Analysis FMI/SYKE

- ICP-MS (PerkinElmer Elan 5000/6000/DRCII, Thermo iCAP Q)

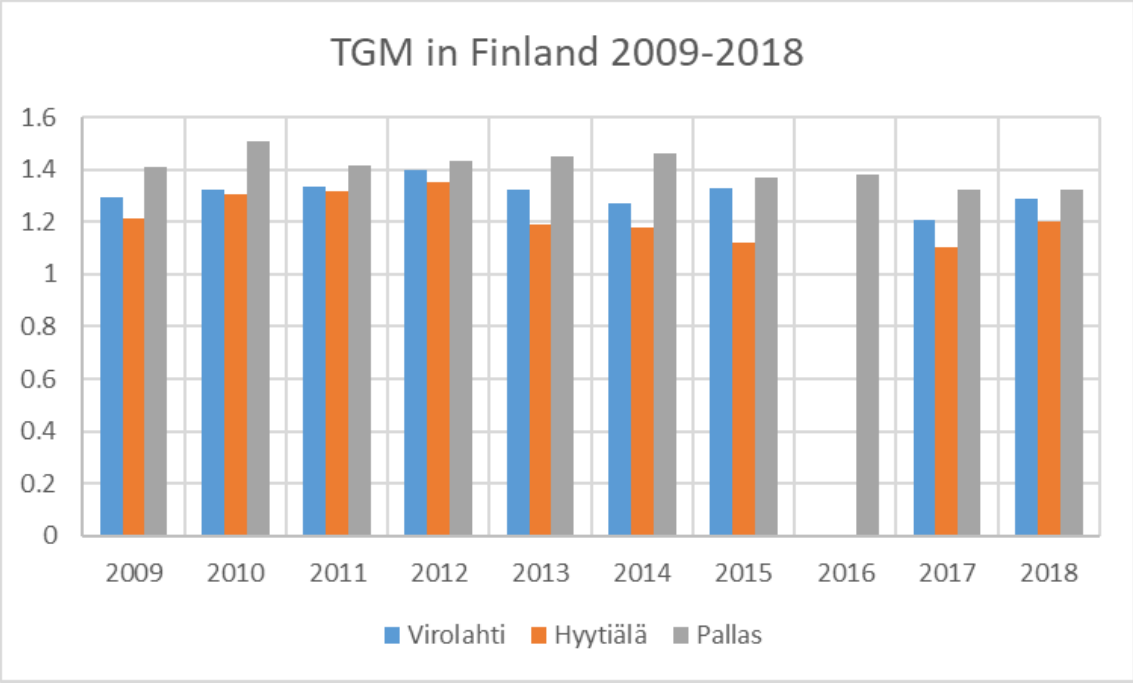
SYKE laboratory

Jalkanen et al. (1996). Simple Method for the Dissolution of Atmospheric Aerosol Samples for Analysis by Inductively Coupled Plasma Mass Spectrometry *J. Anal. At. Spectrom* 11(5):365-369

The annual PM10 concentration (in ng m^{-3}) of As, Cd, Ni and Pb at Finnish background stations in south to north order: Virolahti (blue), Ähtäri (orange) and Pallas (grey)

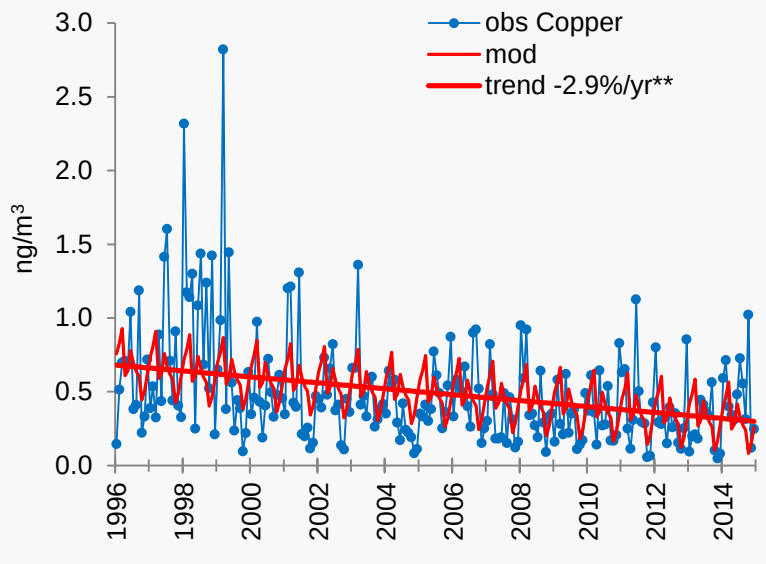


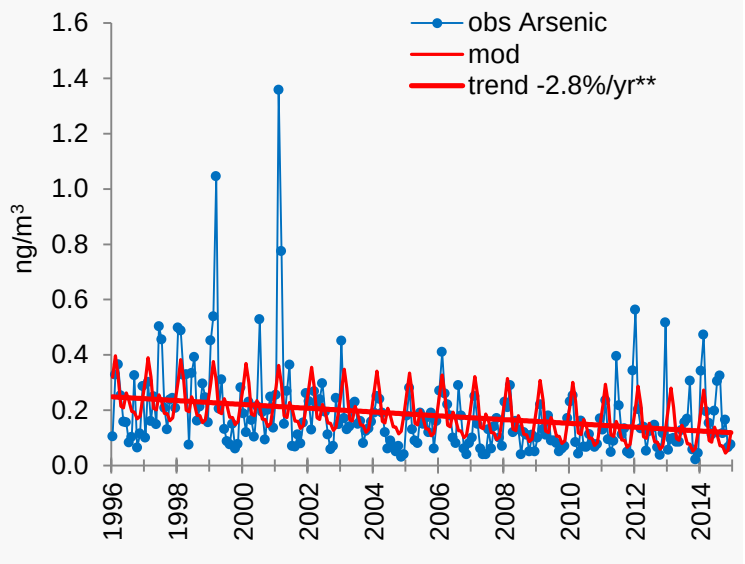
Mercury shows different behaviour

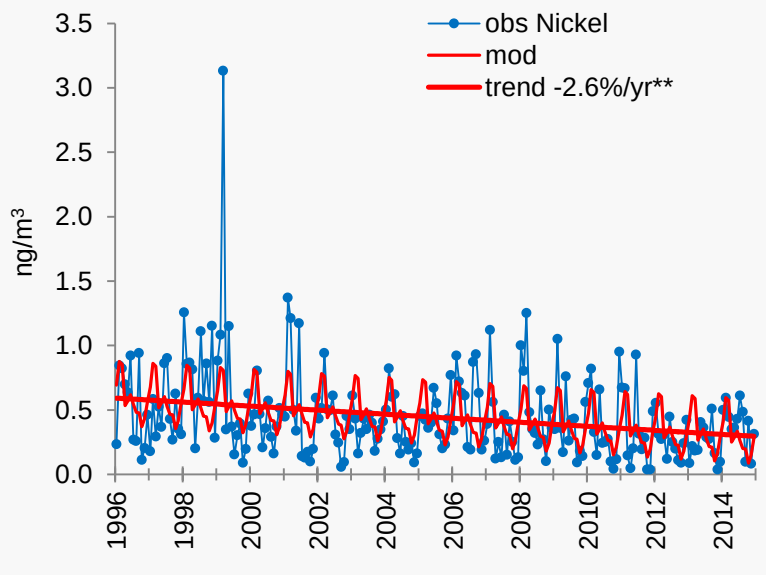


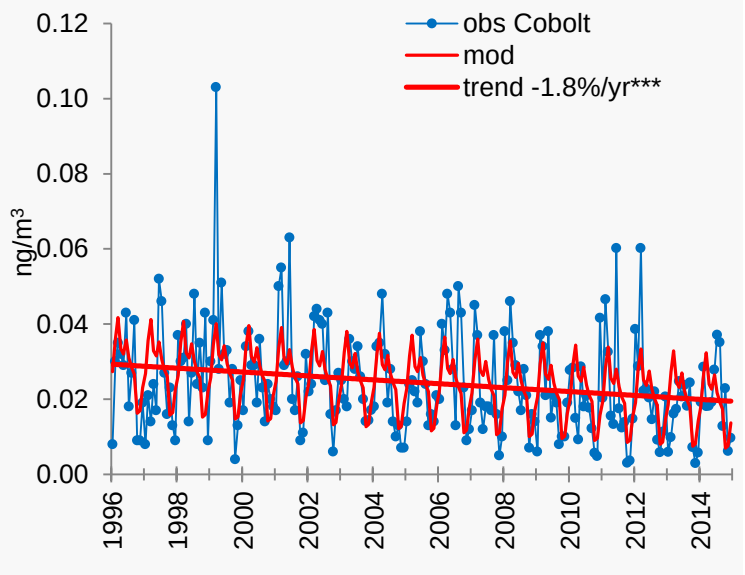
Jiskra M, Sonke JE, Obrist D, Bieser J, Ebinghaus R, Lund Myhre C, Aspmo Pfaffhuber K, Wängberg I, Kyllönen K, Worthy D, Martin LG, Labuschagne C, Mkololo T, Ramonet M, Magand O, Dommergue A (2018) A vegetation control on seasonal variations in global atmospheric mercury concentrations. Nature Geoscience, 11, 244–250.

HM air concentrations and trends (1/3)

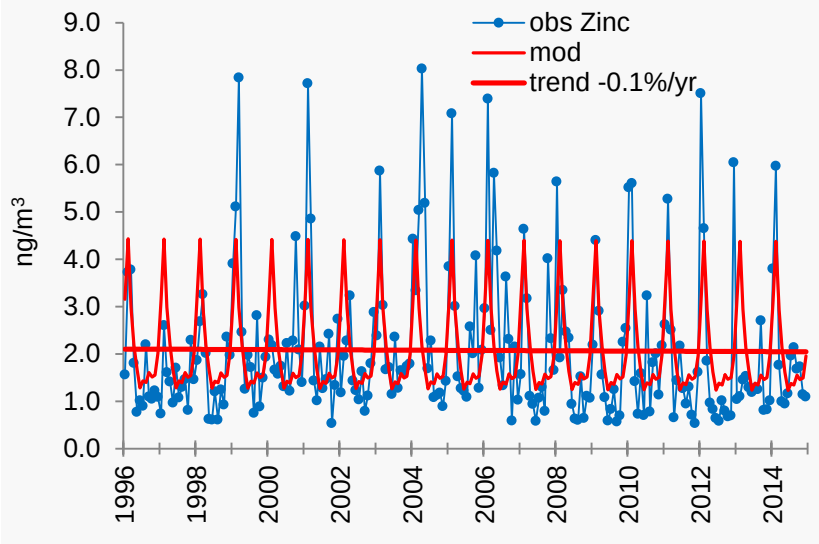


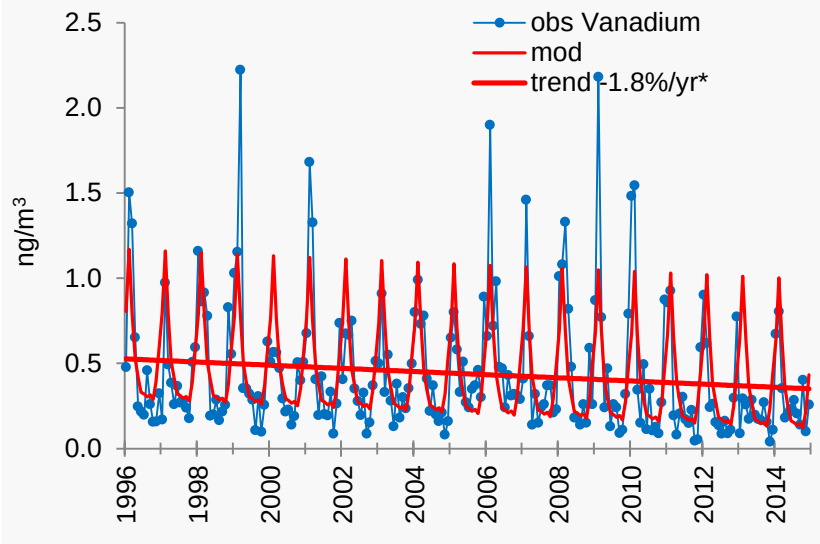


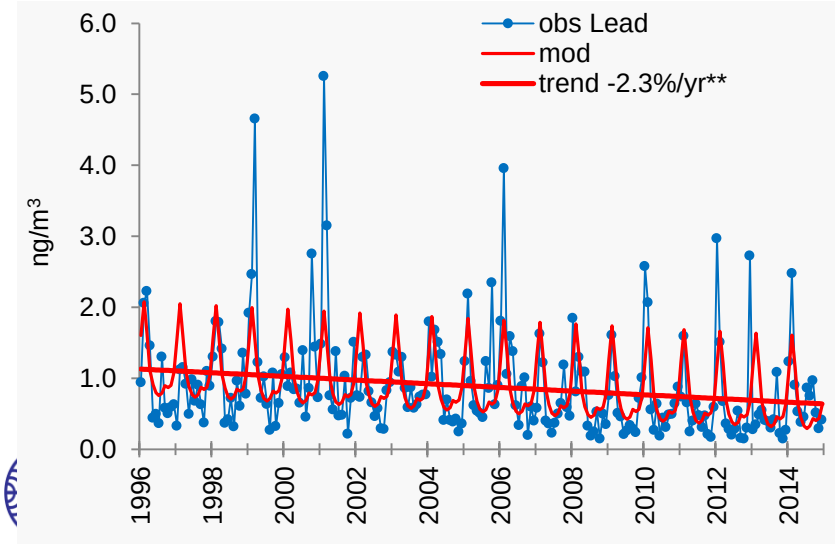


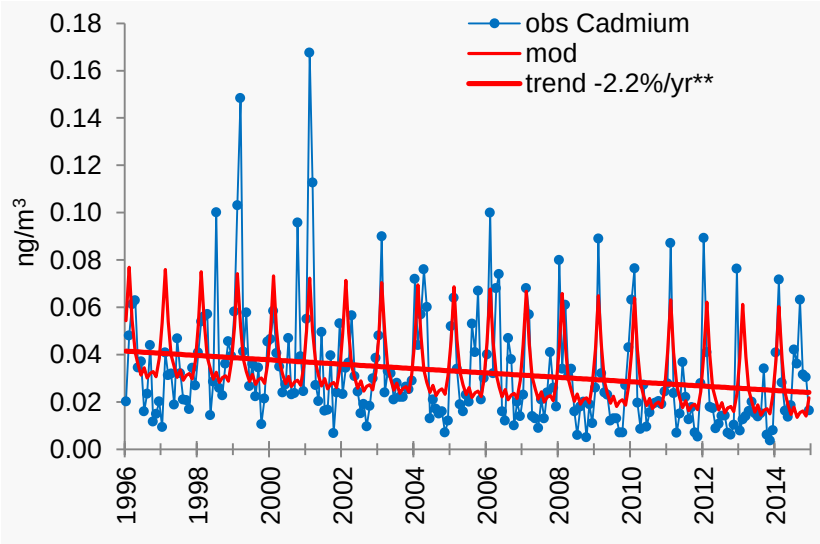


HM air concentrations and trends (2/3)

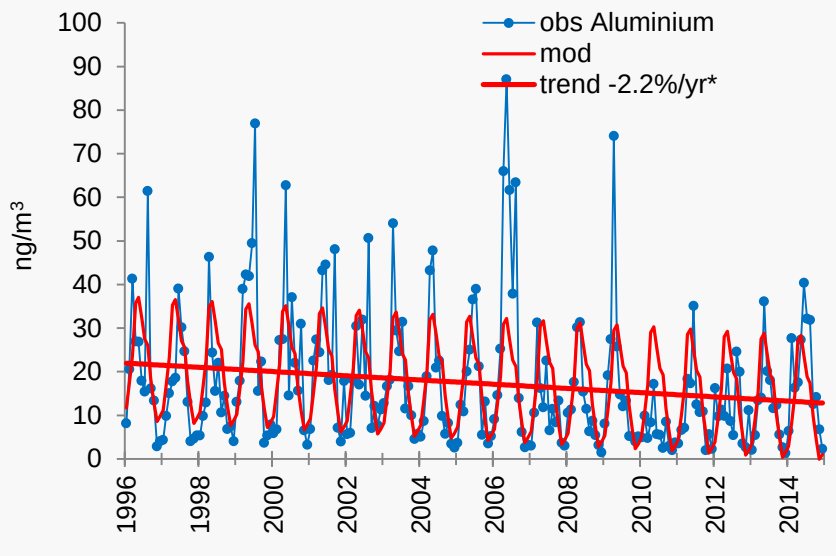


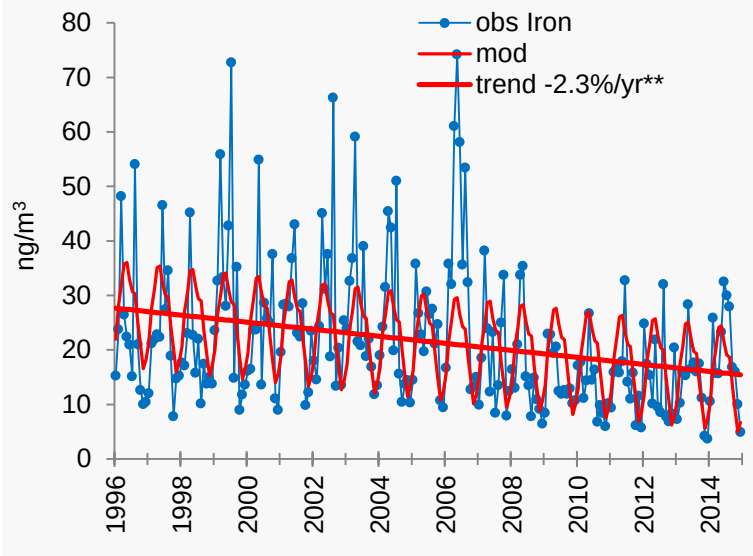


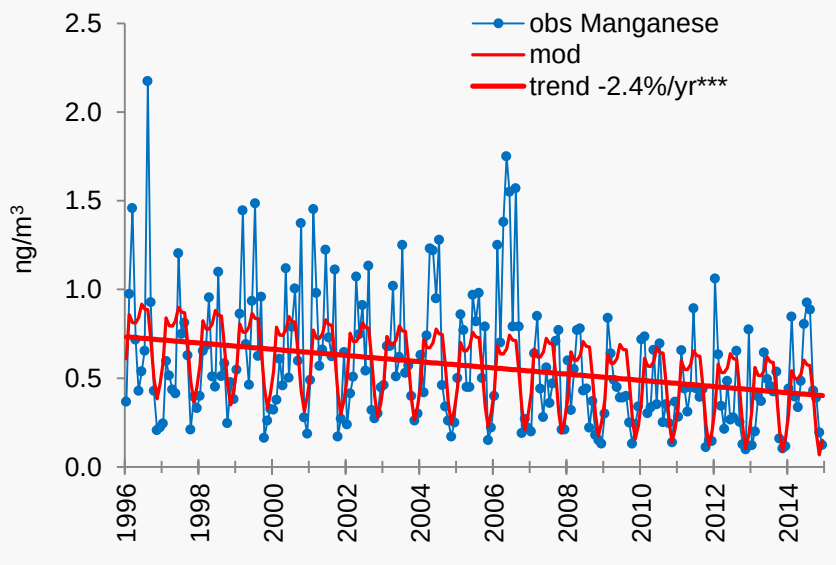


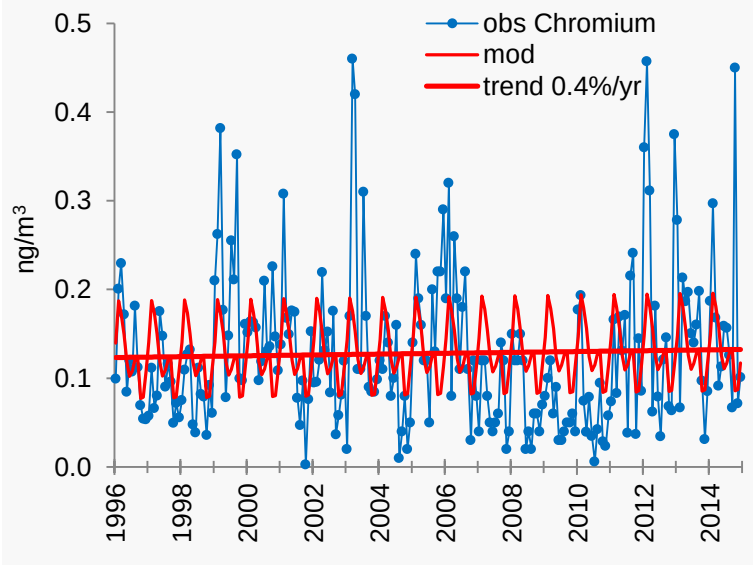


HM air concentrations and trends (3/3)

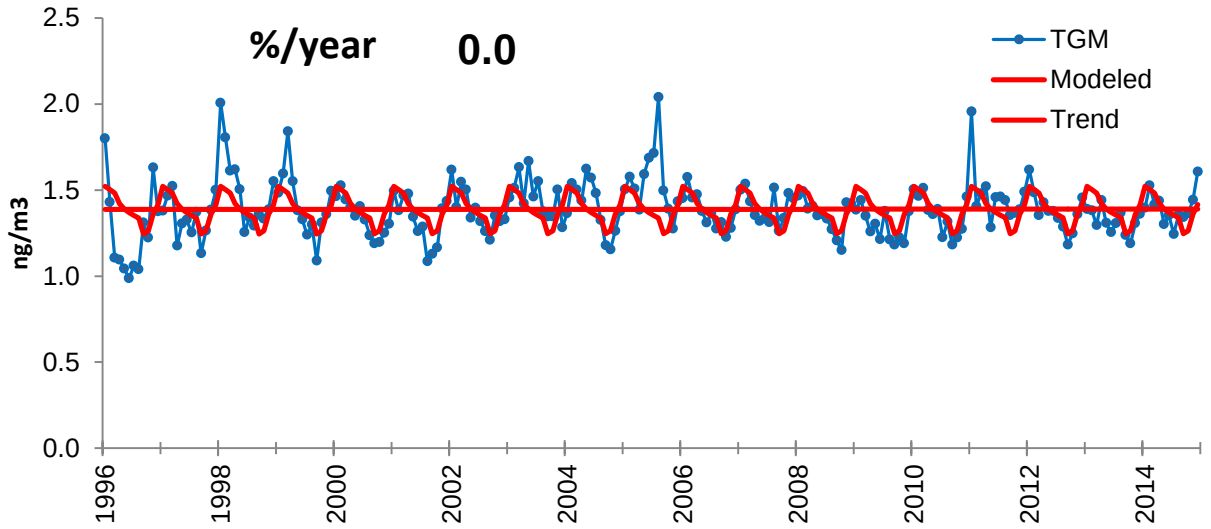




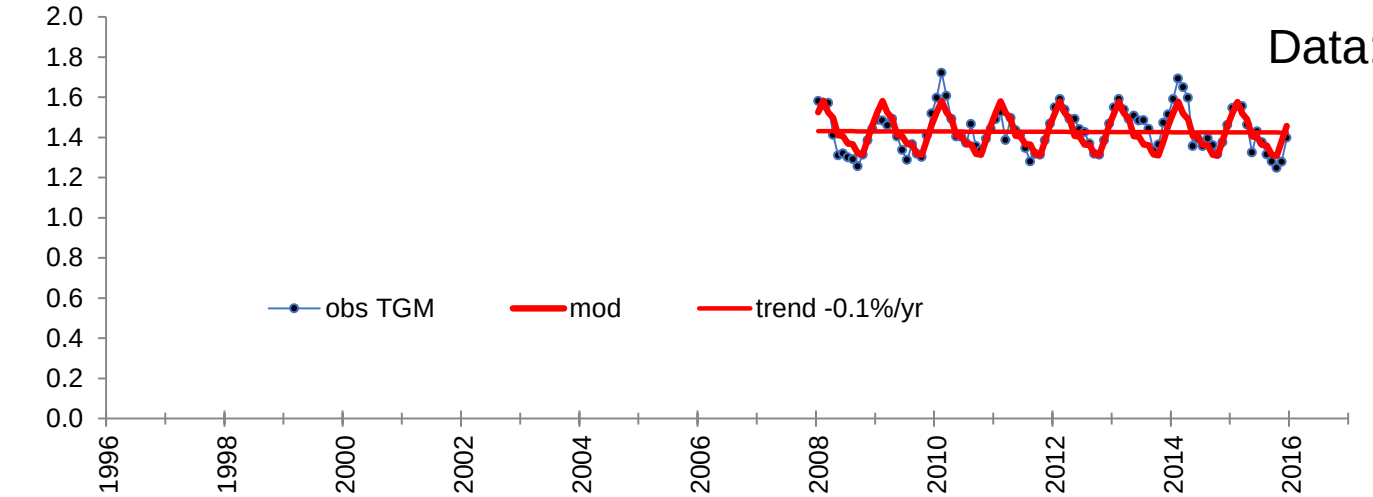




Total Gaseous Mercury



Data: IVL



Data: FMI

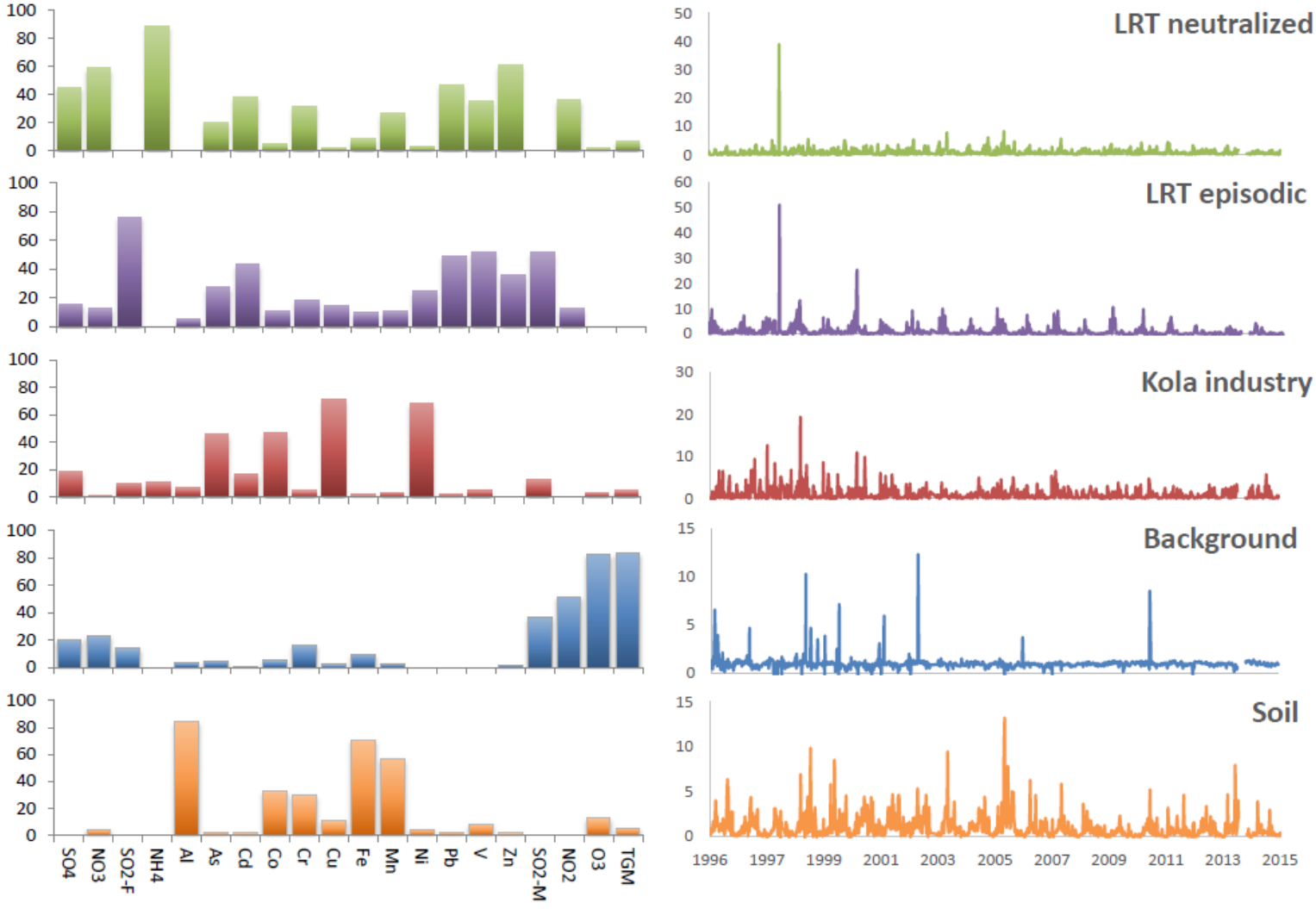
Summary of trends

The trend was calculated by Generalized Least-Squares (GLS) regression with classical decomposition and AutoRegressive Moving Average (ARMA) errors applied for monthly mean values (*see* e.g. Anttila and Tuovinen 2010).

	Change % year^{-1} 1996-2014	Significance
Al	-2.2 ± 2.1	*
As	-2.8 ± 1.7	**
Cd	-2.2 ± 1.6	**
Co	-1.8 ± 0.9	***
Cr	0.4 ± 2.5	-
Cu	-2.9 ± 2.1	**
Fe	-2.3 ± 1.5	**
Mn	-2.4 ± 1.2	***
Ni	-2.6 ± 1.6	**
Pb	-2.3 ± 1.7	**
V	-1.8 ± 1.4	*
Zn	-0.1 ± 1.8	-
TGM	0.0	-

Confidence levels
***, 99.9 %
**, 99 %
*, 95 %
-, not significant

Preliminary results of source apportionment



Paatero et al. (1994) Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics, 5

Conclusions

- Almost all heavy metals (except Cr and Zn) in PM decreased significantly during 1996-2014; the decrease has been **34-55 %**
- **Mercury (TGM) has not decreased** during 1996-2014, nor during 2008-2016
- **No statistically significant increasing trends were observed**
- Major sources for HM at Pallas
  - Soil: Al, Fe, Mn
  - Kola industry: Cu, Ni, As, Co
  - LRT (episodic or neutralized): Cd, Cr, Pb, V, Zn
  - Background: TGM


Thank you for your attention!
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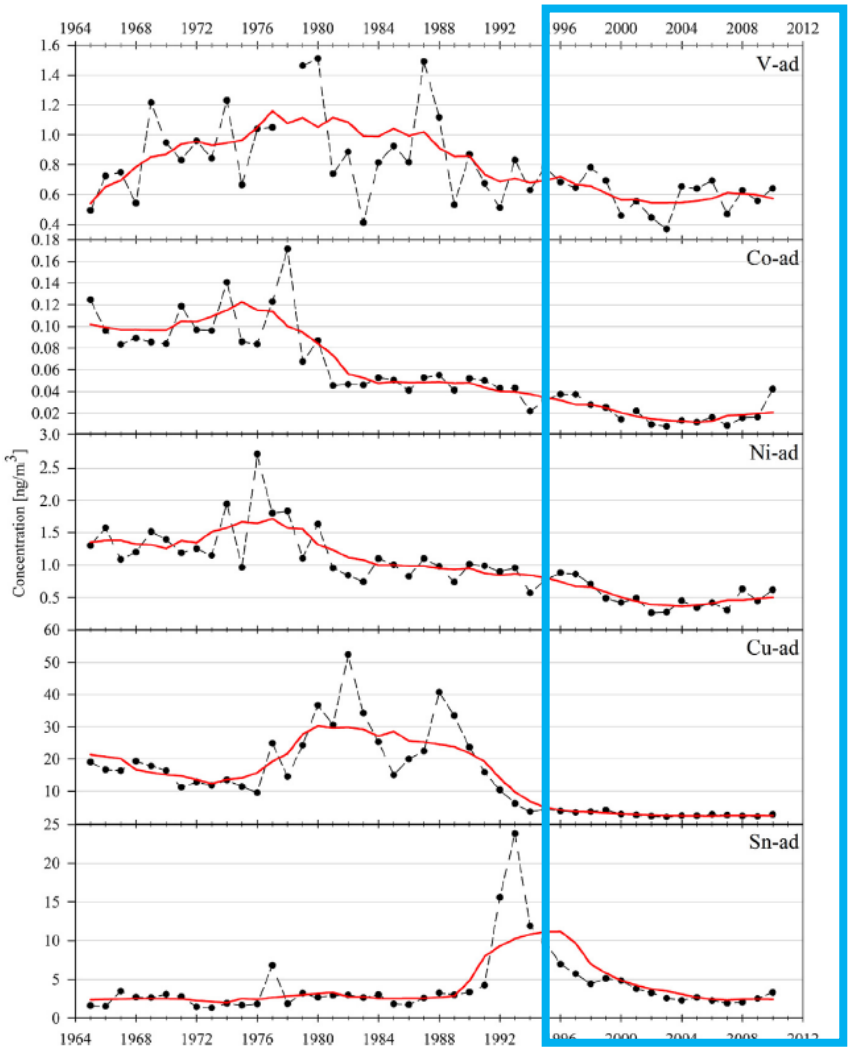
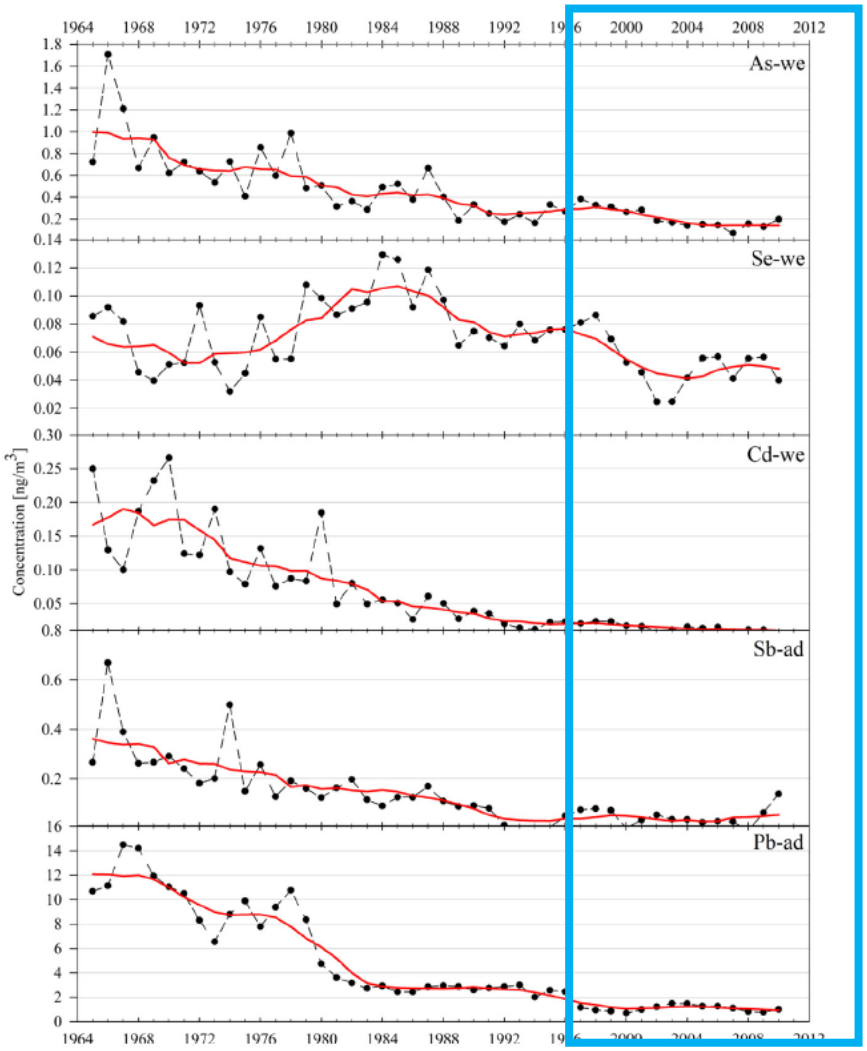
Photo: Hannu Mällinen

47 years of near-total/water-extracted HM in Kevo





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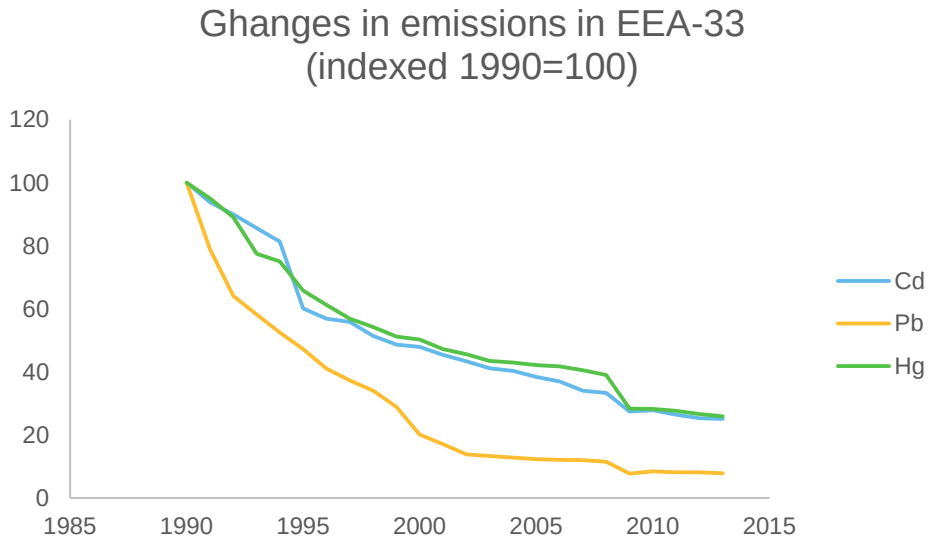
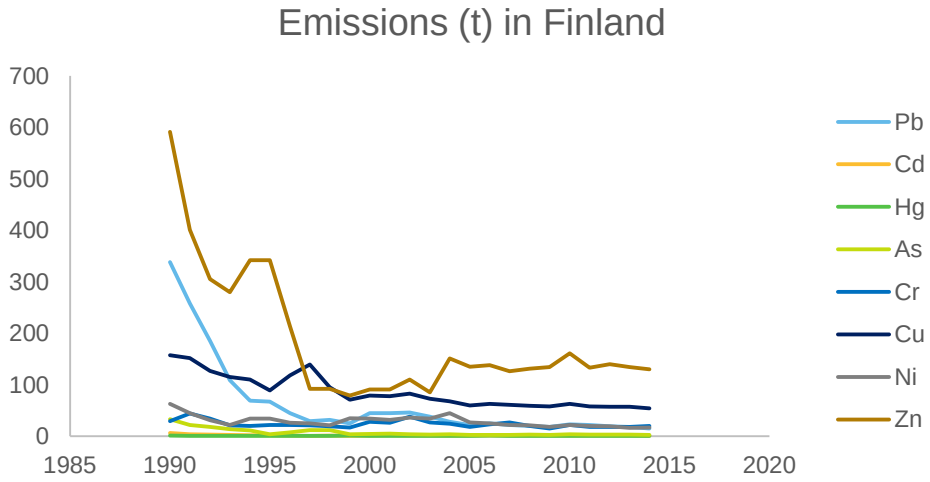
J.R. Laing et al. / Atmospheric Environment 88 (2014) 285–296

J.R. Laing et al. / Atmospheric Environment 88 (2014) 275–284

Atm. emissions of HMs





HM	Change (2005-2014)
Pb	-29 %*
Hg	-33 %*
Cu	-11 %**
Ni	-35 %**