

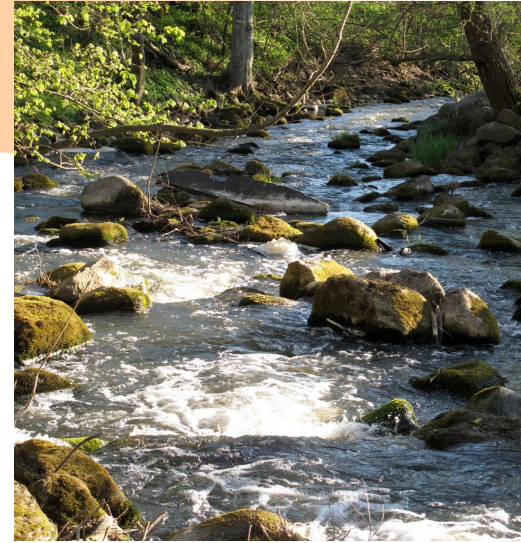
Monitoring long-term trends of pesticides in surface waters

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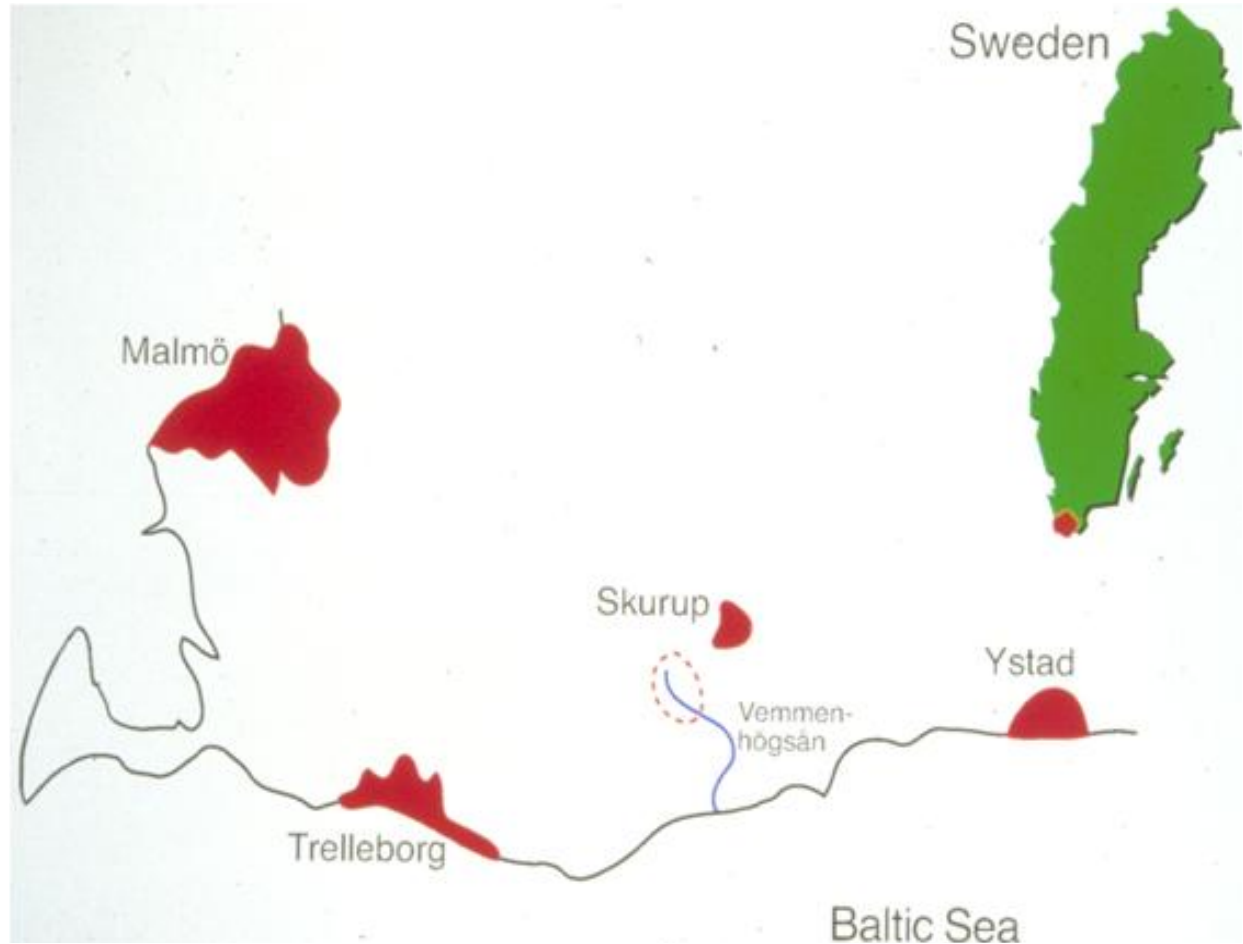
Pesticide monitoring – many different reasons

- To investigate pesticide fate in the actual field situation
 - Go beyond the the well-controlled conditions common for most environmental fate studies
- Investigate the development over time
 - Follow-up on regulatory decisions (eg drinking water directive, WFD)
 - Follow-up on the registration process and policy changes
- Develop scientific understanding
 - Calibration/validation of exposure models (regional/catchment scale)



The Vemmenhög catchment

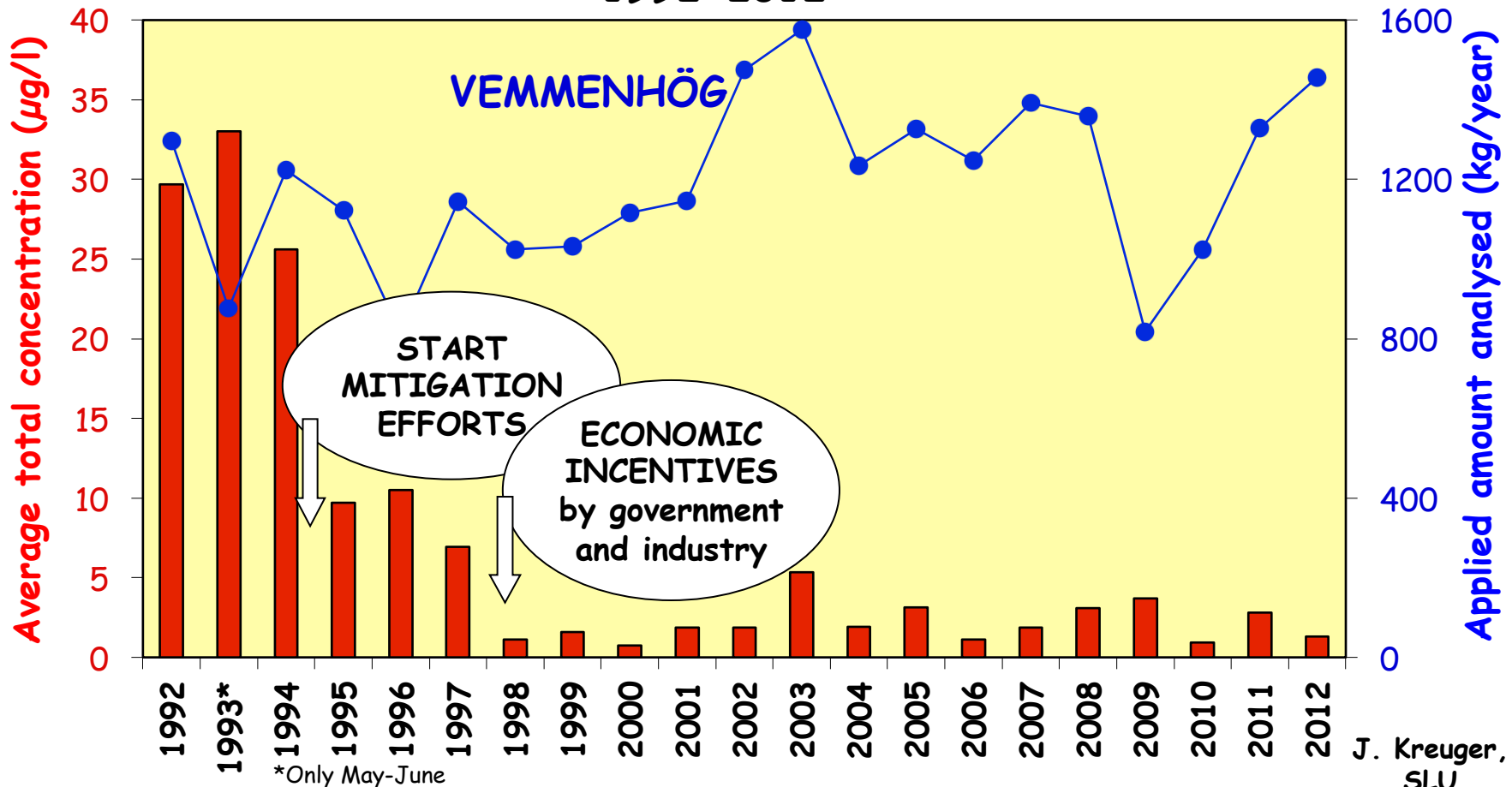
- Monitoring of pesticides in stream water from an agricultural catchment in southern Sweden
- Started in 1990, now >20 years of data



Results long-term monitoring

A 90% reduction in pesticide concentrations

Average total pesticide concentration May-Sept
1992-2012



J. Kreuger,
SLU

Avoid point sources – education of farmers

- Safe storage of pesticides
- Safe places for filling and cleaning spraying equipment
- No "beauty-treatment" on farmyards

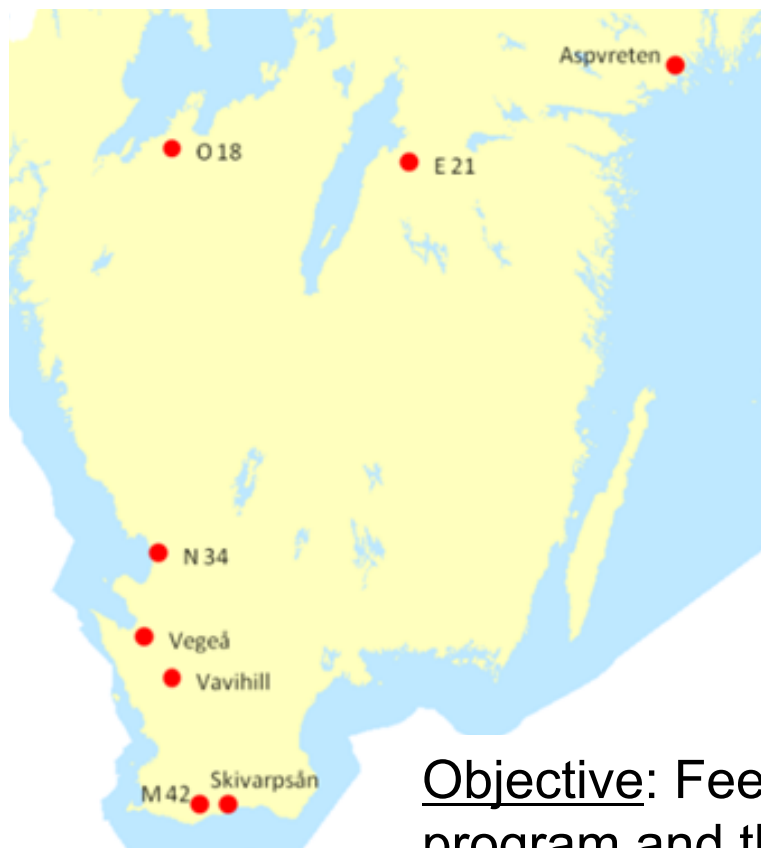


One mitigation option applied was the use of safe places for filling and cleaning spraying equipment (e.g. biobeds)

Pesticides in water from

- Diffuse sources
 - Processes influenced by soil and weather conditions, the intrinsic properties of the pesticide, management practices (*EU regulation 1107/2009*)
- Semi-point and point sources
 - Unregulated applications, e.g. on surfaces with no active soil such as farmyards, or practices, e.g. effluents from greenhouses
 - Spillage during application, filling and cleaning spraying equipment, waste disposal, accidents (*EU directive 2009/128*)

Current Swedish pesticide monitoring program in agricultural areas – from 2002



- **Surface water:**
 - Västergötland (O18)
 - Östergötland (E21)
 - Halland (N34)
 - Skåne (M42)
 - Skivarpsån
 - Vegeå
- Streams draining small catchments (8-16 km²)*
- Rivers (100-500 km²)*

Objective: Feed-back on the national risk-reduction program and the regulatory process, as well as the basis for information to farming community

Stream water sampling in catchments

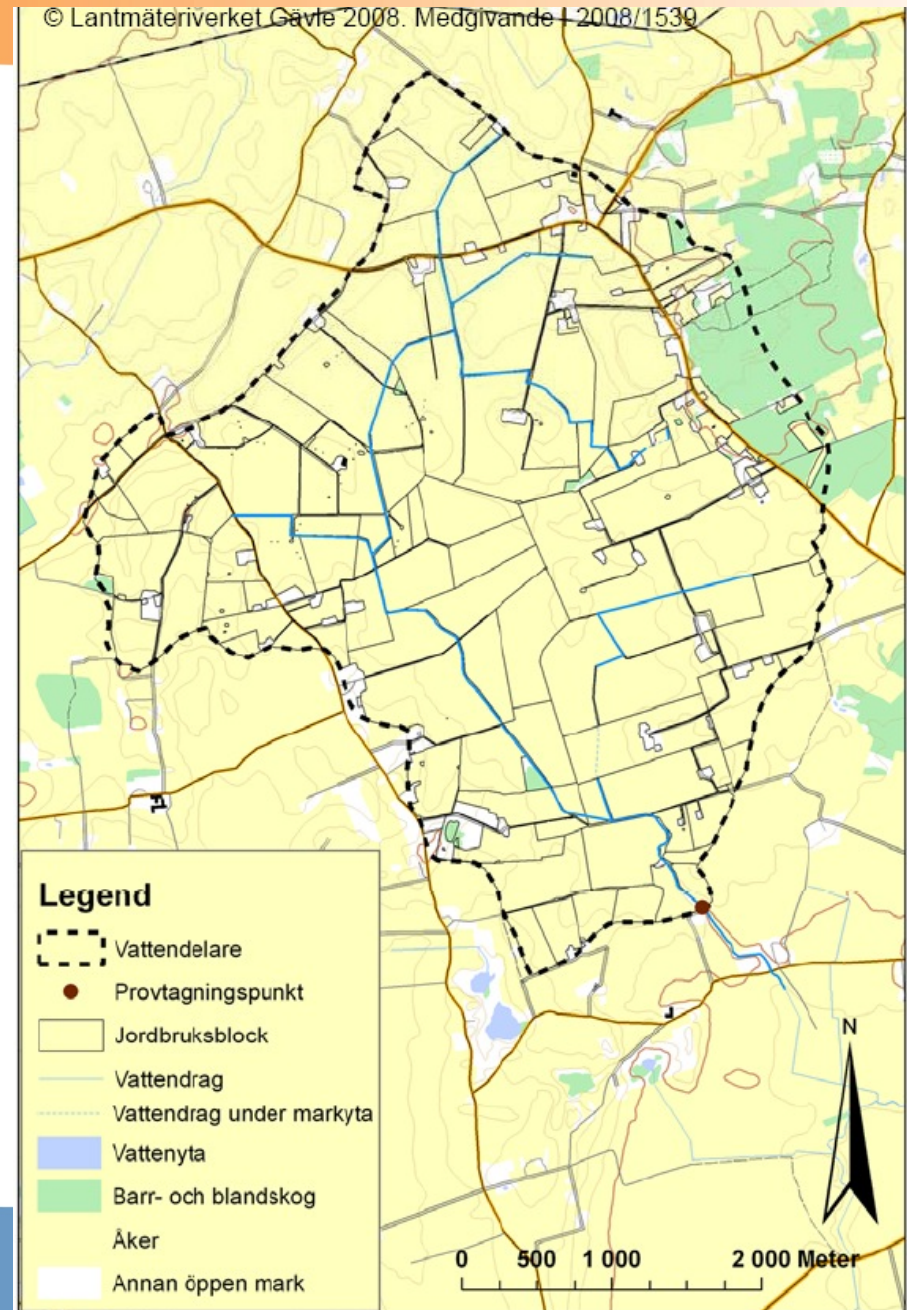


- Automatic water sampling
- Time paced weekly composite samples (1 sub-sample each 90 min during the week) during main growing season
- During later years also bi-weekly composite samples during winter season – 2 catchments
- Continuous water flow measurements



Catchment inventory

- Yearly interviews with farmers in the catchments on the use of pesticides (& crops and nutrients) – which pesticides, when, where and how much
- Gives good background for interpretation and method development



Analytical program development

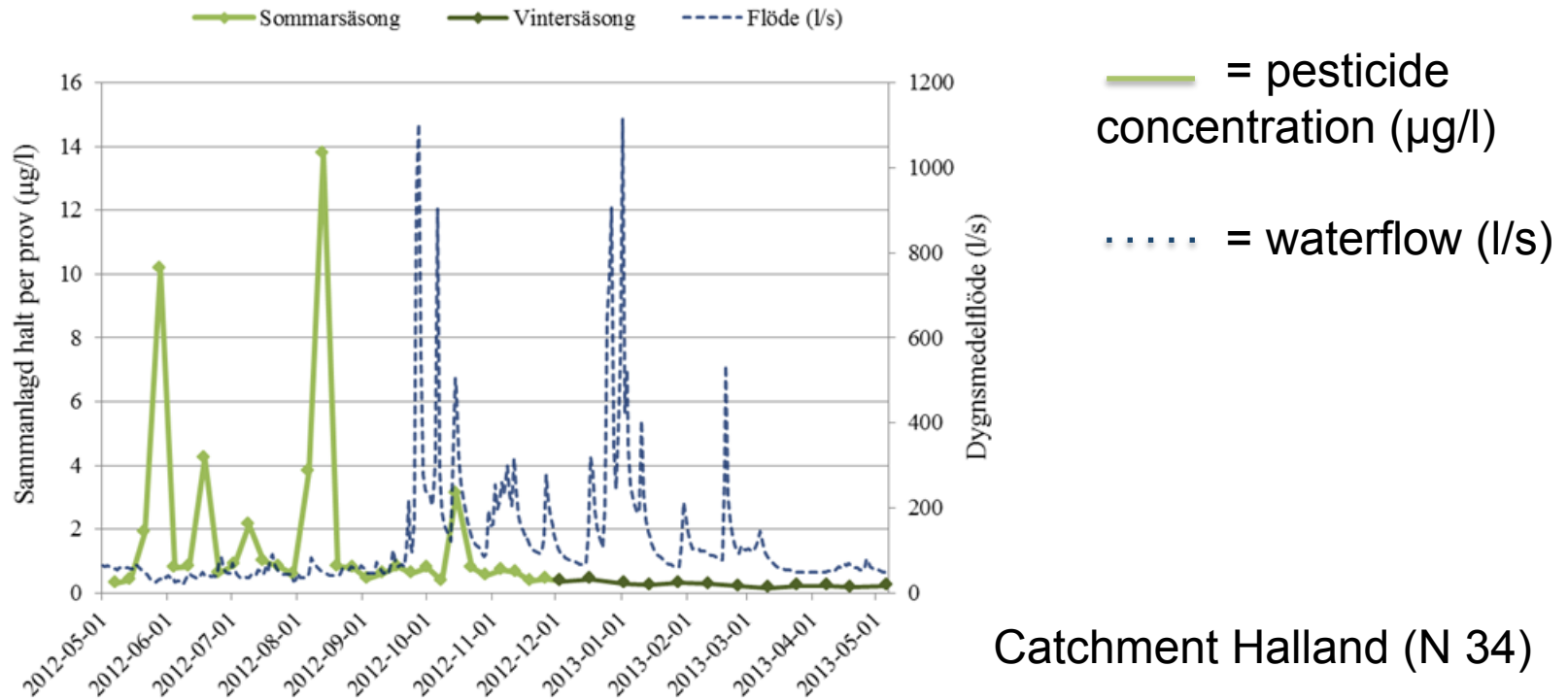
- New pesticides enter the market, old ones disappear
- The analytical program needs to be flexible
- Selection criteria:
 - Most heavily used (corresponds to ca. 90% of sold amounts in Sweden) and sprayed on large acreages
 - Superseded though still frequently detected
 - Included in Water Framework Directive (WFD)
 - Aquatic toxicity
 - List updated each year in co-operation with regulatory authorities and feedback from farmer interviews

Analytical methods

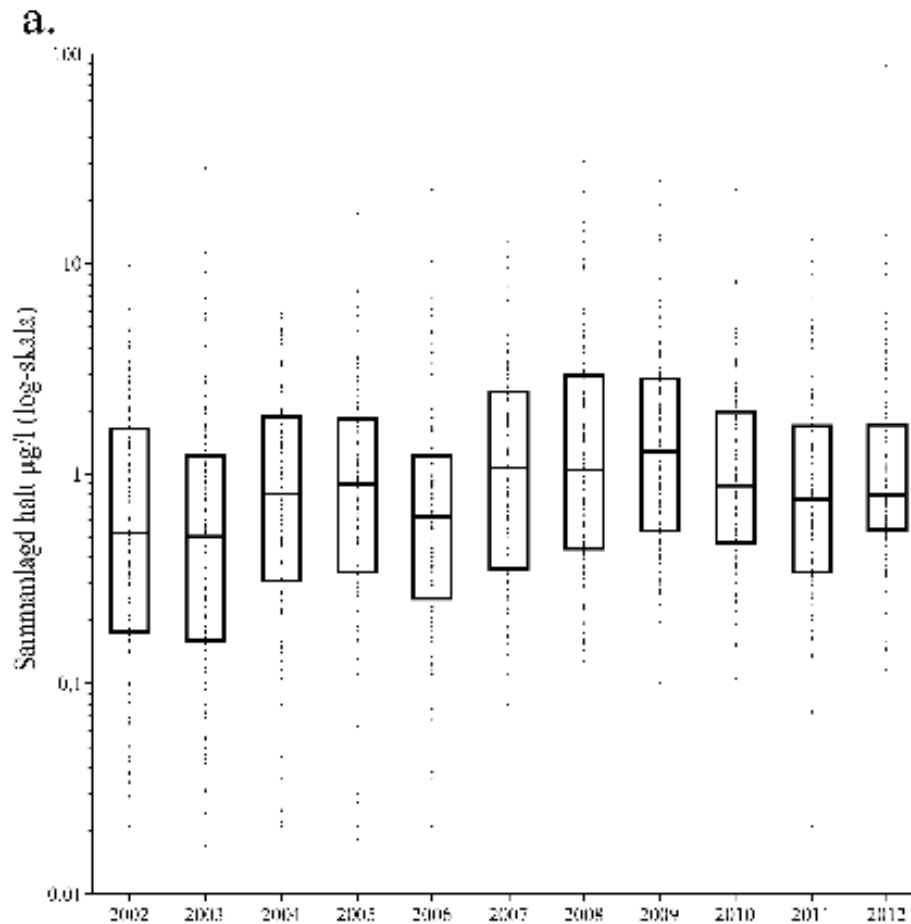
- On-line LC-MS/MS for a broad range of pesticides
 - Method description *Jansson & Kreuger, 2010, J. AOAC Intern., vol 93, 1732-1747*
- GC-MS for the most non-polar compounds
- Currently including ca 130 different pesticides in the monitoring program, incl. some degradation products
- LOD/LOQ levels are at the ng/l-level for most pesticides



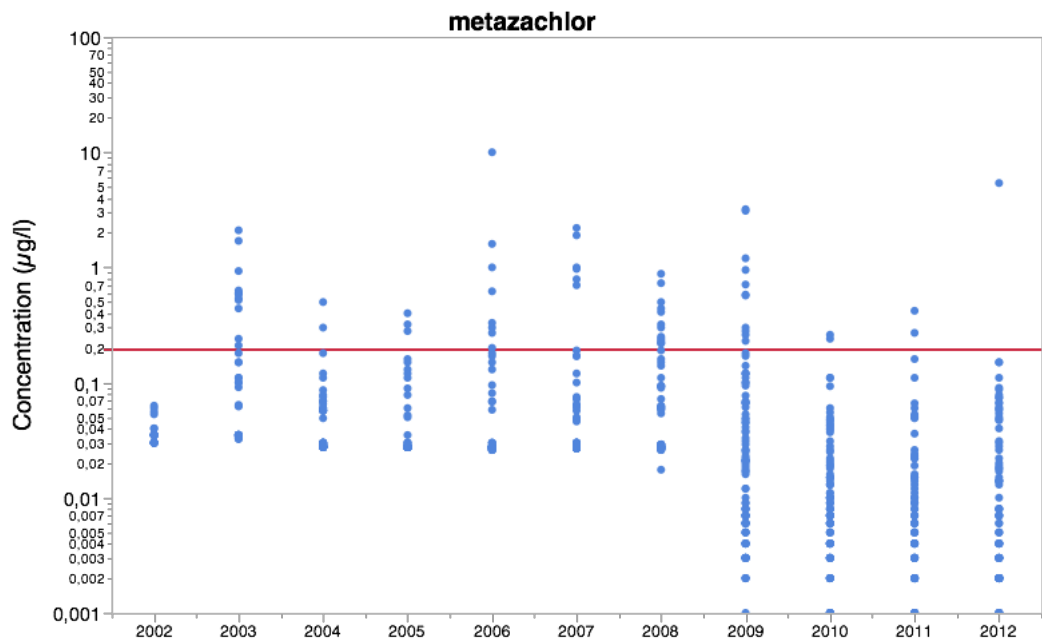
Summed weekly (summer) and bi-weekly (winter) average concentrations over a growing season (2012/2013)



Σ pesticide concentrations in the catchments (streams) 2002-2012



Annual median concentration - no trend during the past 11 years



Metazachlor – declining concentrations in surface water during the last 3 years due to lower doses being applied

← EQO = 0.2 µg/l

90th percentile concentration exceeded the Swedish EQO during 2003, 2008 and 2009

Metazachlor was used in two different products:

Butisan S (ca 1.5 kg a.i./ha) **until 2008, though old stocks still used in 2009**

Butisan Top (ca 0.75 kg a.i./ha, max 1 kg a.i./ha during 3 y) **from 2009**

RISK

Exposure

Toxicity

Swedish Environmental Quality Objectives (EQO) for surface waters (examples) www.kemi.se

Pesticide	EQO ($\mu\text{g/l}$)	Pesticide	EQO ($\mu\text{g/l}$)
fluroxypyr	100	aclonifen	0.12
glyphosate	100	tribenuron-methyl	0.1
clopyralid	50	pirimicarb	0.09
bentazone	30	metribuzin	0.08
mecoprop	20	sulfosulfuron	0.05
metamitron	10	triflusulfuron-methyl	0.03
MCPA	1	metsulfuron-methyl	0.02
fluazinam	0.4	terbuthylazine	0.02
isoproturon	0.3	rimsulfuron	0.01
fenpropimorph	0.2	diflufenican	0.005
metazachlor	0.2	esfenvalerat	0.0001

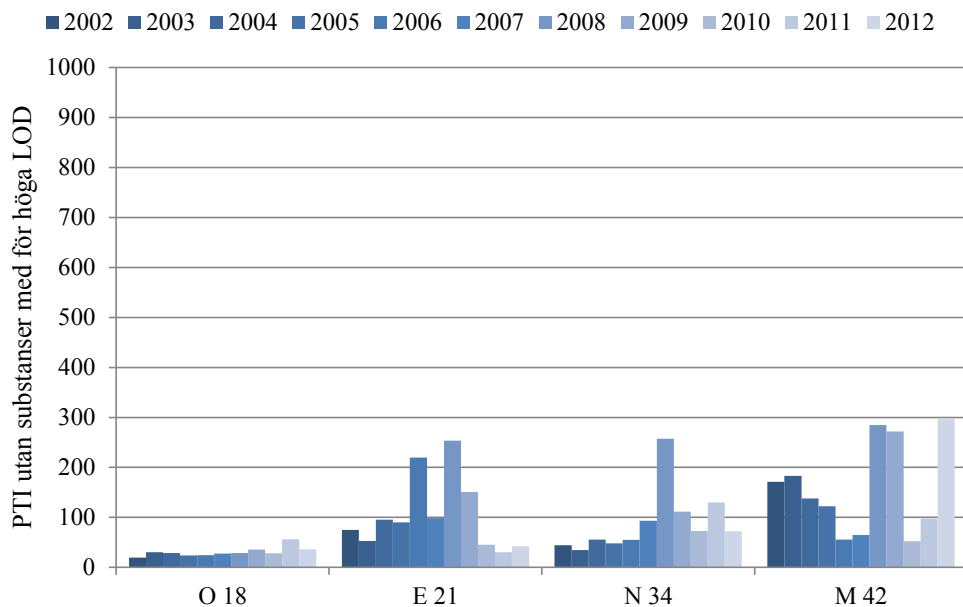
Risk-index based on monitoring data

- using a modified version of the US Pesticide Toxicity Index (PTI)

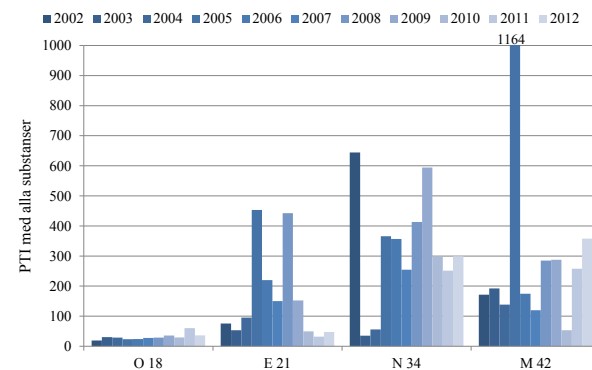
$$PTI = \sum_{i=1}^n \frac{Conc_i}{EQS_i}$$

- $Conc_i$ = Pesticide concentration $_i$
- EQS_i = EQS or national EQO for the pesticide $_i$
- n = Number of pesticides

Development of PTI in the four monitoring catchments 2002-2012

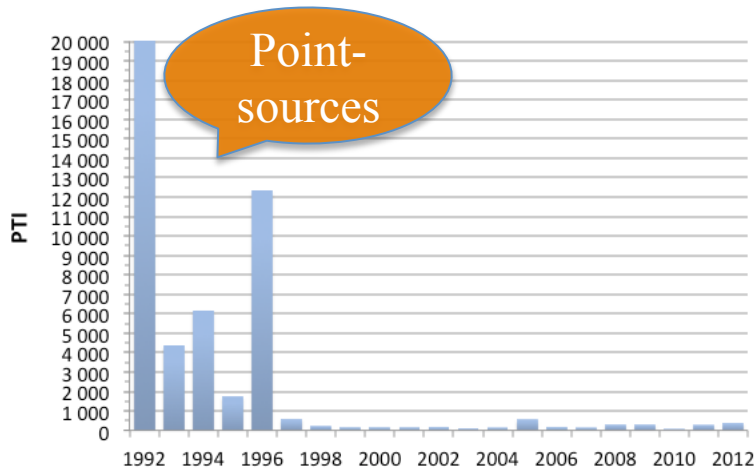


Including only pesticides with LOD below EQO during 2002-2012



Including also pesticides with LOD above EQO (mainly pyrethroids)

Development of PTI in the Vemmenhög catchment 1992-2012



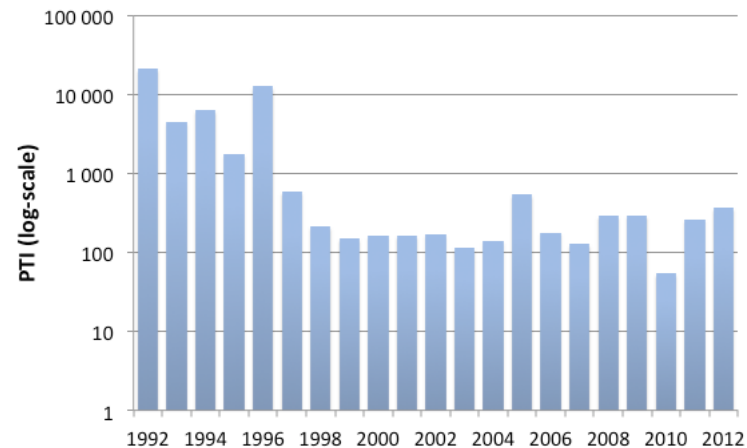
PTI - absolute values



PTI - log-scale



Following a 90 % decrease of measured pesticide concentrations in the stream, also the potential "risk" for aquatic organisms (measured as PTI) has decreased since mitigation measures started in the mid-90's - by 1-2 orders of magnitude!



Conclusions

- Results demonstrate a 90% decline in pesticide concentrations in surface waters when implementing best management practices and applying pesticides according to regulation
- Today many pesticide are detected in surface waters below EQO values, although some are frequently detected above the 0.1 $\mu\text{g/l}$ and a few also quite regularly above the EQO (i.e. pesticides with low EQO values)
- Much more difficult to reduce non-point source pollution – the importance of transport pathways in the agricultural landscape varies between different regions
 - i.e. mitigation options varies between regions and include a number of different options (e g buffer zones, drift reduction nozzles, timing of application, doses, Integrated Pest Management - IPM)

Questions?

Acknowledgement:

- The national pesticide monitoring programme is funded by the Swedish Environmental Protection Agency
- Information about pesticide research and monitoring at SLU www.slu.se/ckb (Centre for Chemical Pesticides)
- Publications downloadable from: <http://www.slu.se/ckb/miljoovervakning/publikationer>
- Data downloadable from: <http://jordbruksvatten.slu.se>

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