

# Indicators to discriminate point sources and diffuse sources of pesticides in groundwater

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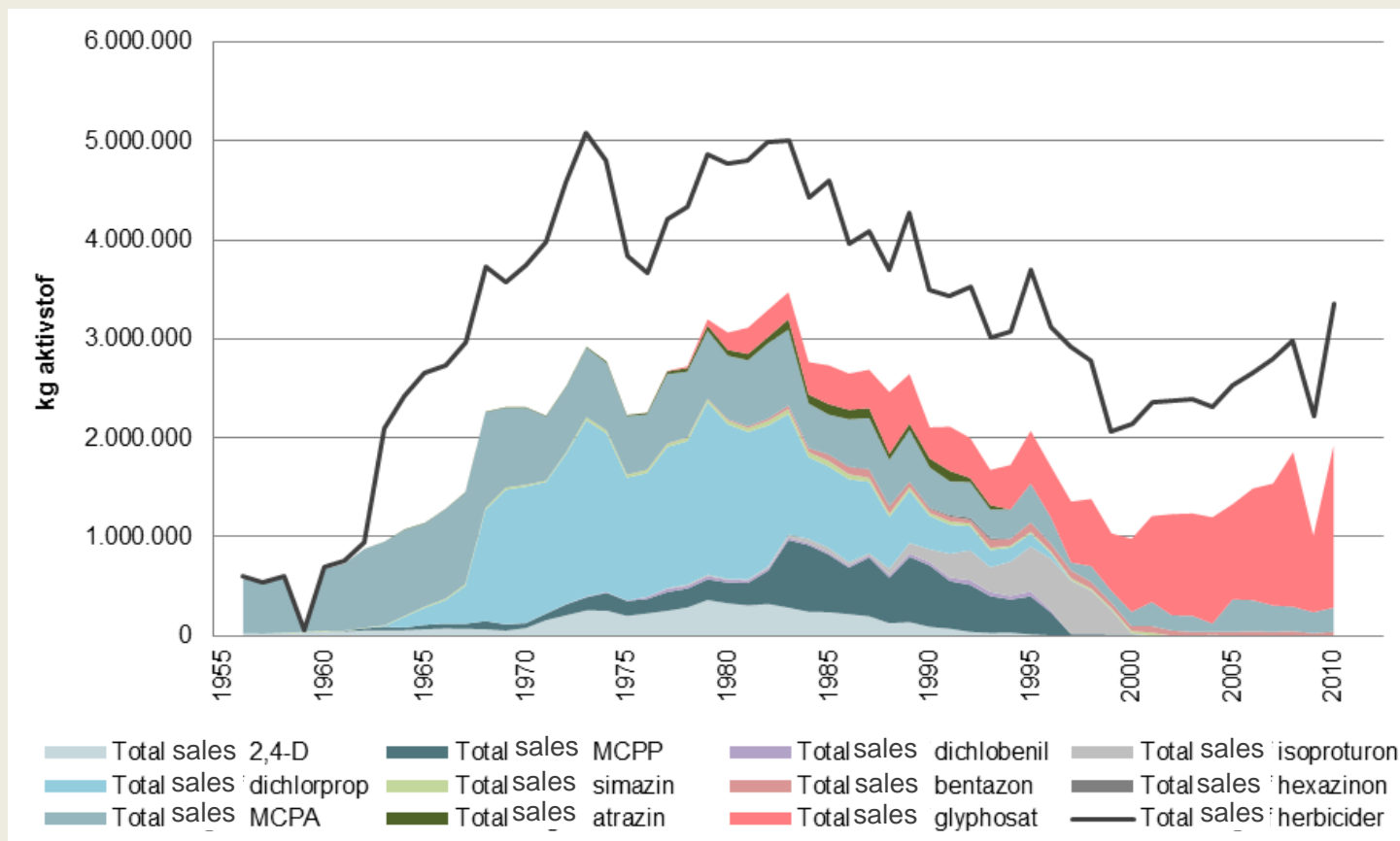
Geological Survey of Denmark and Greenland  
Danish Ministry of Energy, Utilities and Climate



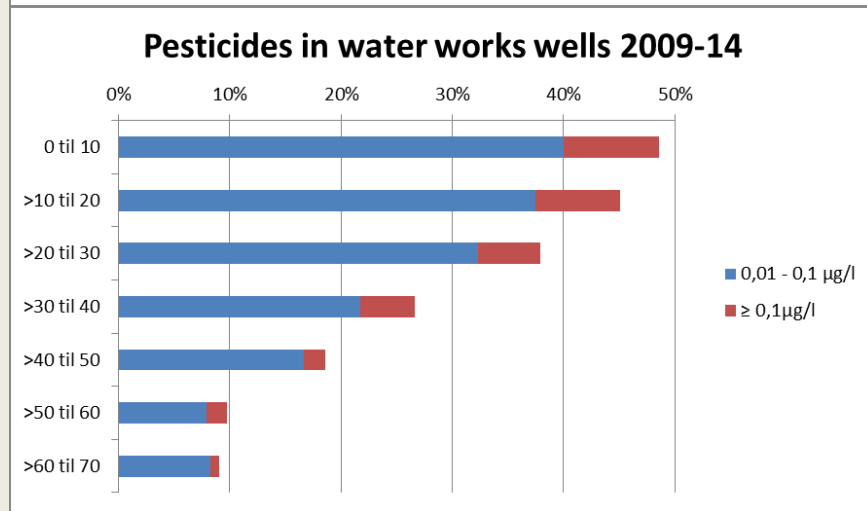
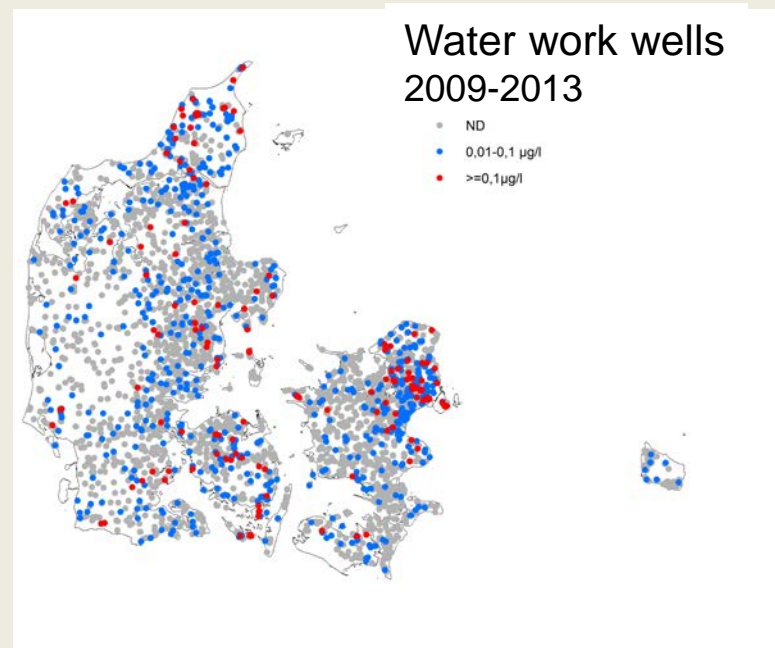
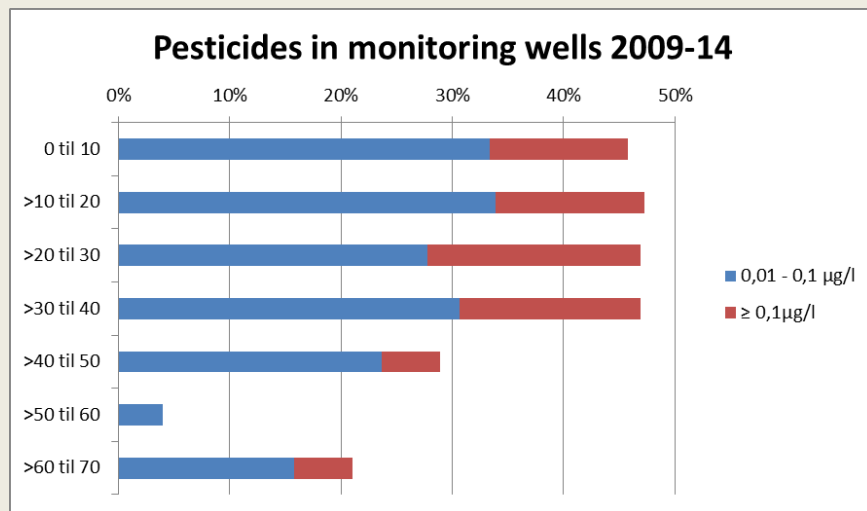
Miljøministeriet  
Miljøstyrelsen

# Herbicides sold in DK 1955-2010

The herbicides sold are not necessarily those we find in ground water



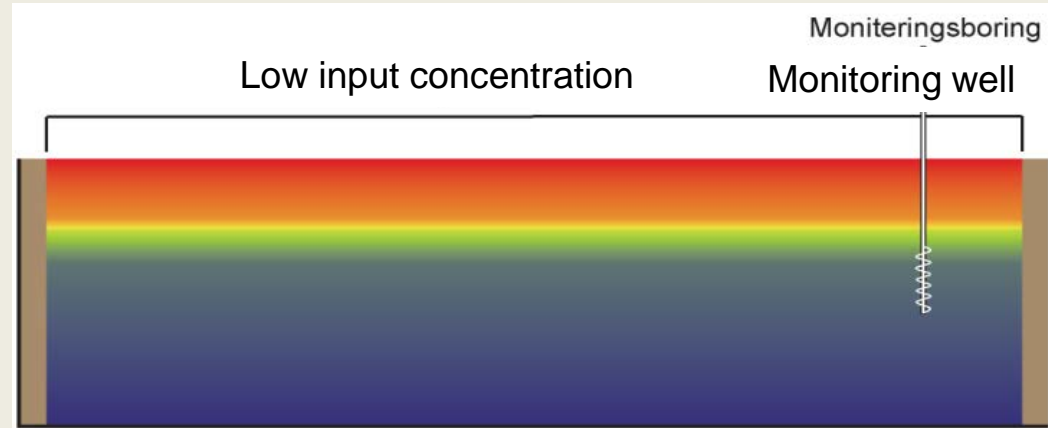
# Pesticides in Danish Groundwater



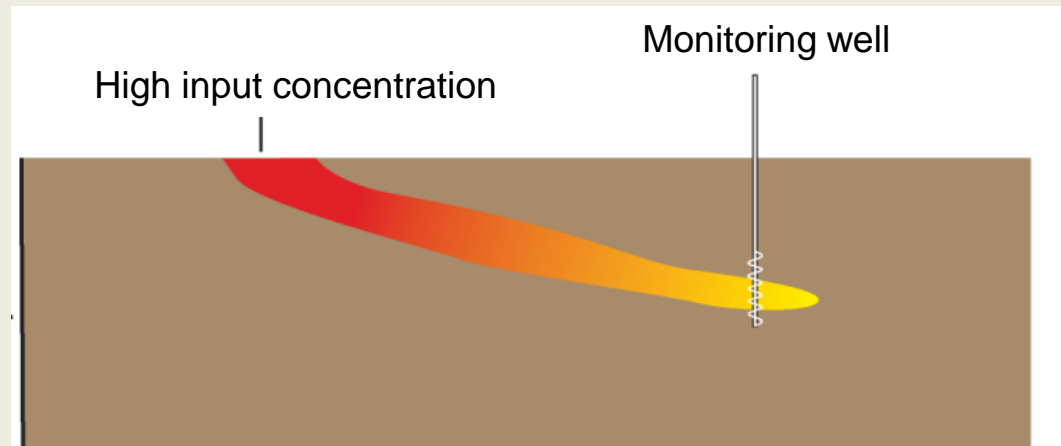
- 12 % of water work wells have > 0,1 µg/l of pesticides
- 50 % of all groundwater monitoring wells have at least one detection of a pesticide

# Point and diffuse pesticide loads

Diffus:  
Intentional spread in environment



Point source:  
Non-intentional spread in environment



# Project Idea

Given a pesticide is found in a ground water sample!

Is it possible to tell if it originates from a point source or a diffuse source.??

Pragmatic indicators were established to support decision on relevant reaction.

# Questions

## **Identify differences in findings from point and diffuse pesticide sources :**

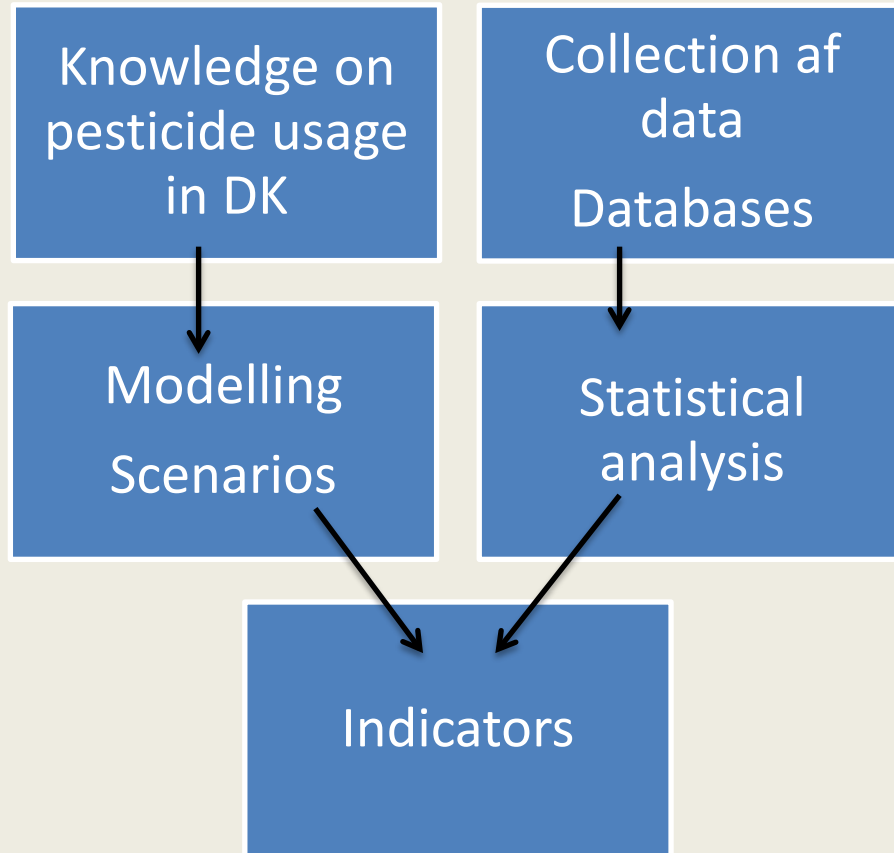
- Which compounds occur
- Concentrations found
- Coexistence of substances
- Variations in time and space

## **Modelling controlling factors influence that might indicate the source of the pesticides present in groundwater:**

- Specific chemical properties
- Geology og hydrogeology
- Type of well
- Usage and regulation



# Methods



# Available data

- Only samples with at least one detected pesticide or relevant metabolite were compared ( $> 0,01 \mu\text{g/l}$ )
- Known point sources (43 thorough mapped sites by regional authorities)
- Only diffuse sources : Shallow groundwater ( $< 6 \text{ m}$ ): in agricultural monitoring areas (520 samples from 1997- 2011)
  - Only below conventional agricultural fields
- Waterworks wells 7.272 samples
- Groundwater monitoring wells 3.811 samples
- All other Available samples (AA) 9.213 samples
- In Denmark the analytical programs of all datasets largely are comparable



- 2,4-D
- Atrazine
- Bentazon
- Dichlobenil
- Dichlorprop
- Glyphosat
- Hexazinon
- Isoproturon
- MCPA
- MCPP
- Simazine

## Pesticides in special focus

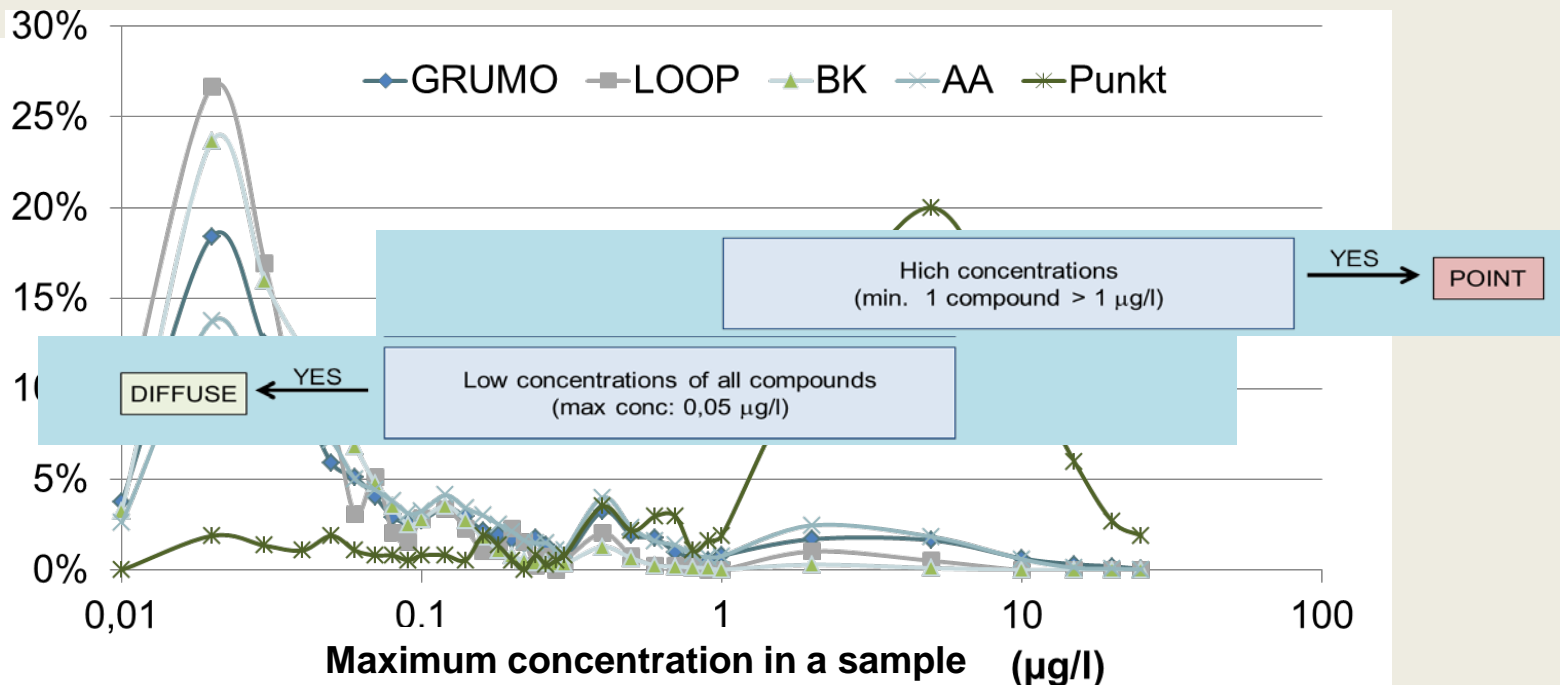


# Results

# Difference in distribution of concentration

Statistical test samples:

- Sum of pesticides
- Max single pesticide



Groundwater monitoring

Agricultural monitoring

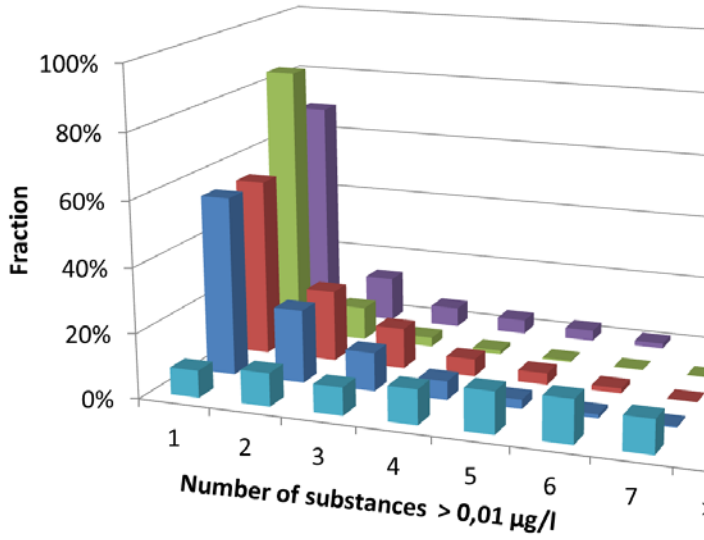
Water work wells

Additional analysis

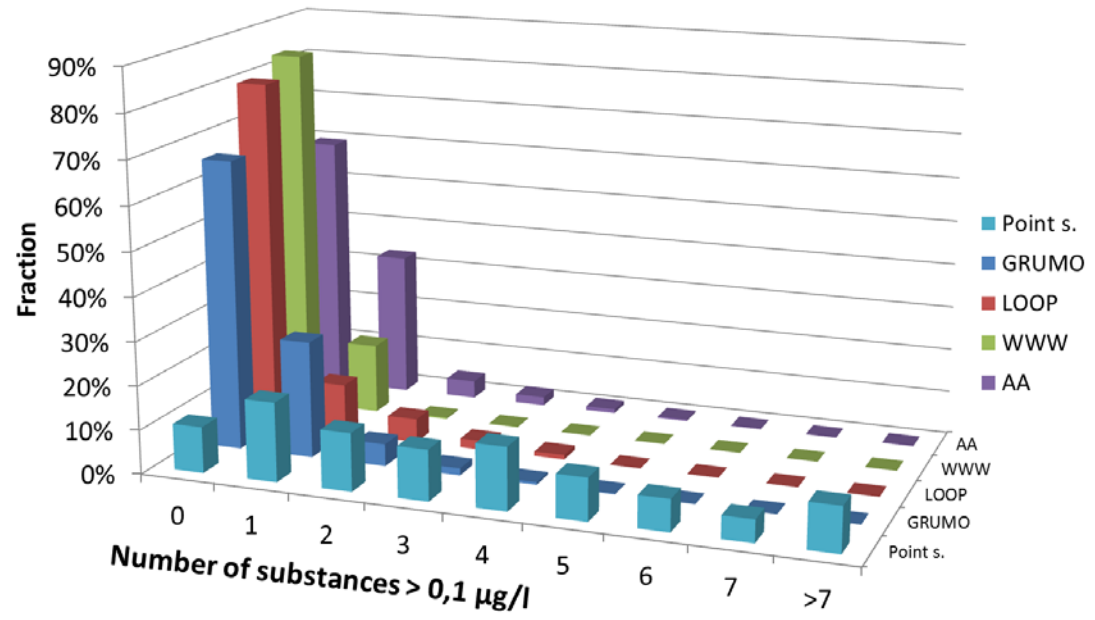
Point sources near, close, general

# Differences in number of compounds in a sample

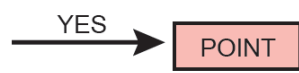
Number of substances in a sample > 0,01 µg/l



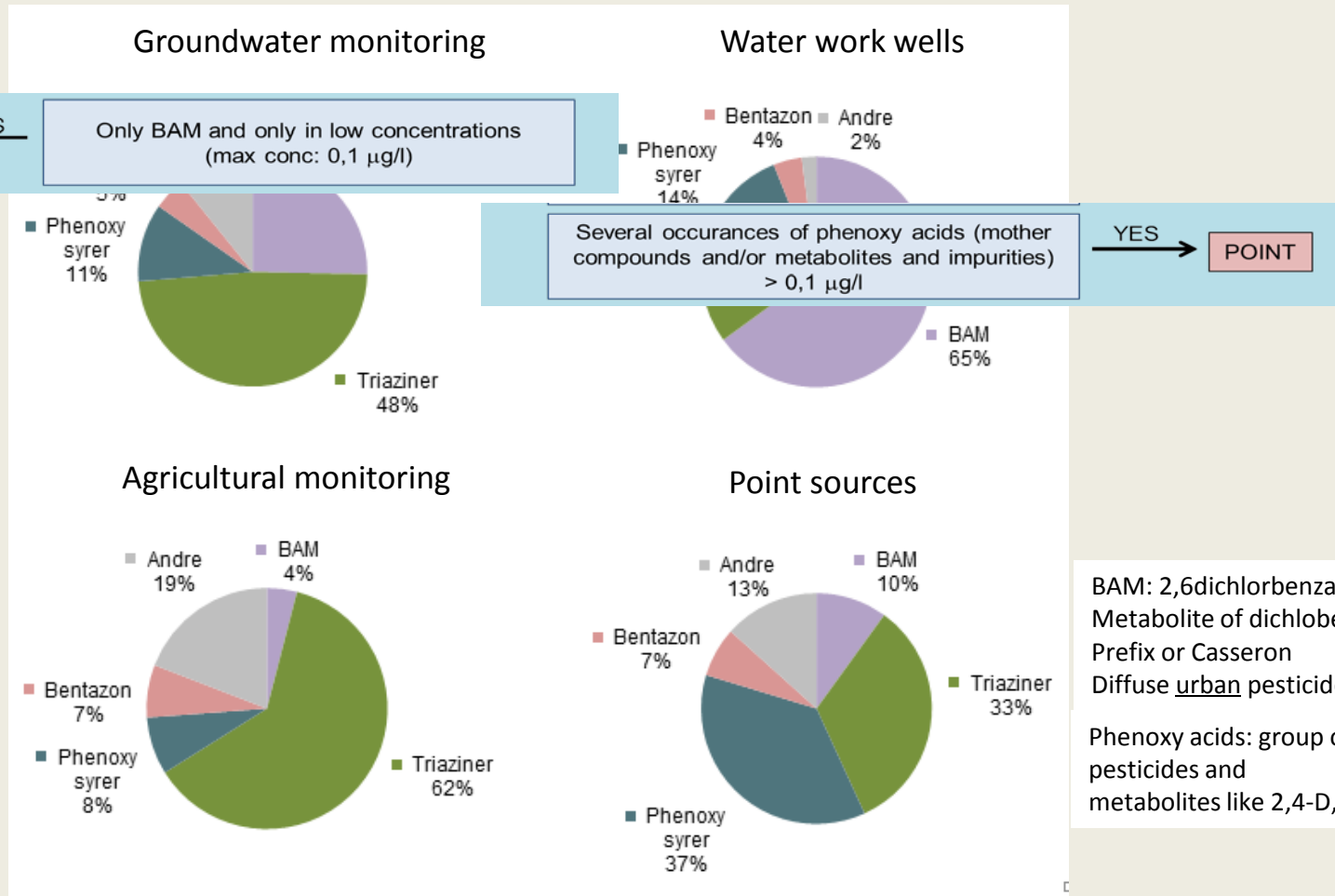
Number of substances > 0,1 µg/l in a sample



Co-existence of many compounds  
(min. 4 compounds > detection limit and/or  
min. 2 compounds > groundwater quality level)



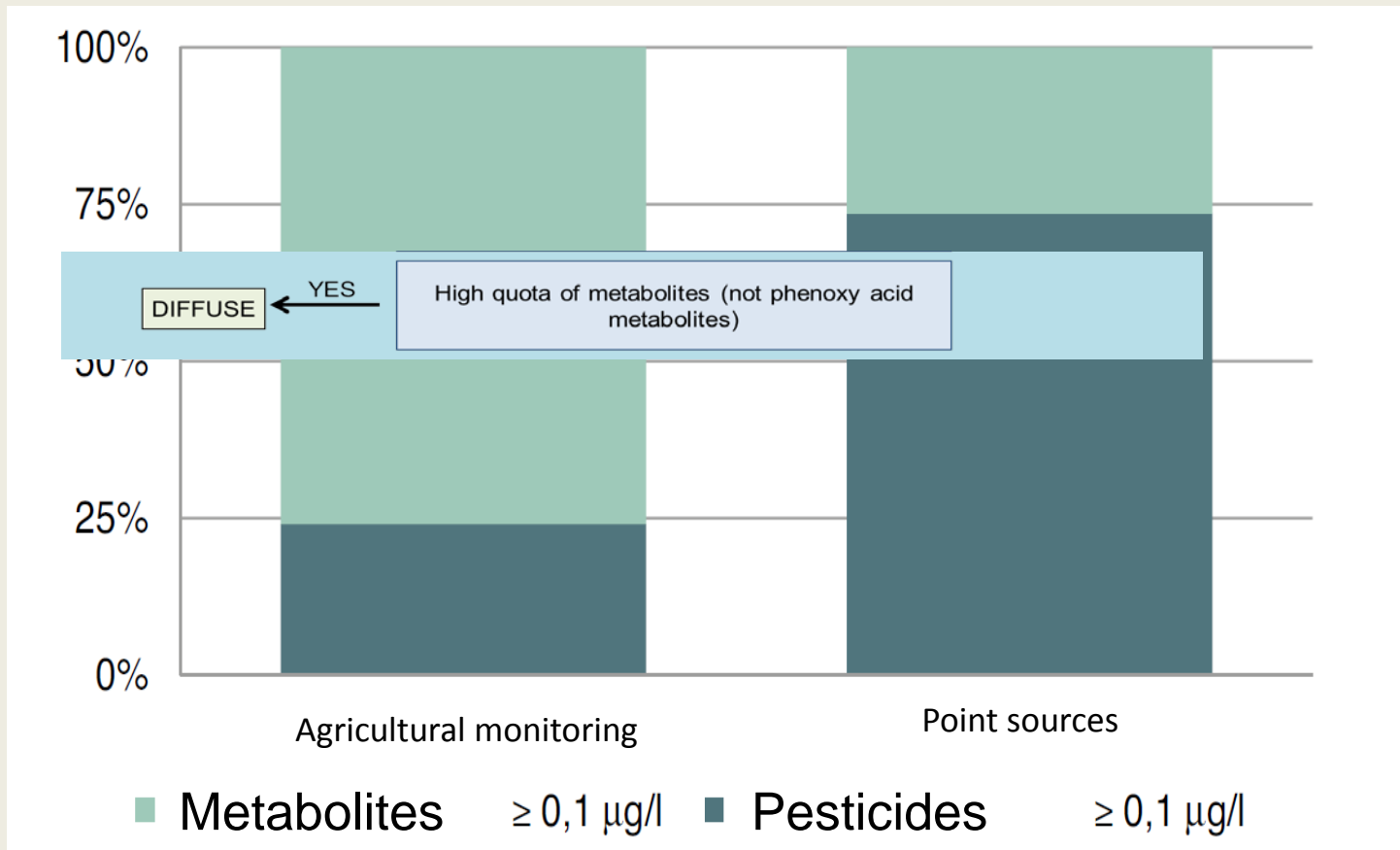
# Difference in occurrence of specific compounds and their concentrations



BAM: 2,6dichlorbenzamid  
Metabolite of dichlobenil in  
Prefix or Casseron  
Diffuse urban pesticide

Phenoxy acids: group of  
pesticides and  
metabolites like 2,4-D, MCPA

# Difference in fraction of active compounds - metabolites



Share of compounds with concentrations  $\geq 0,1 \mu\text{g/l}$

# Input to scenario models

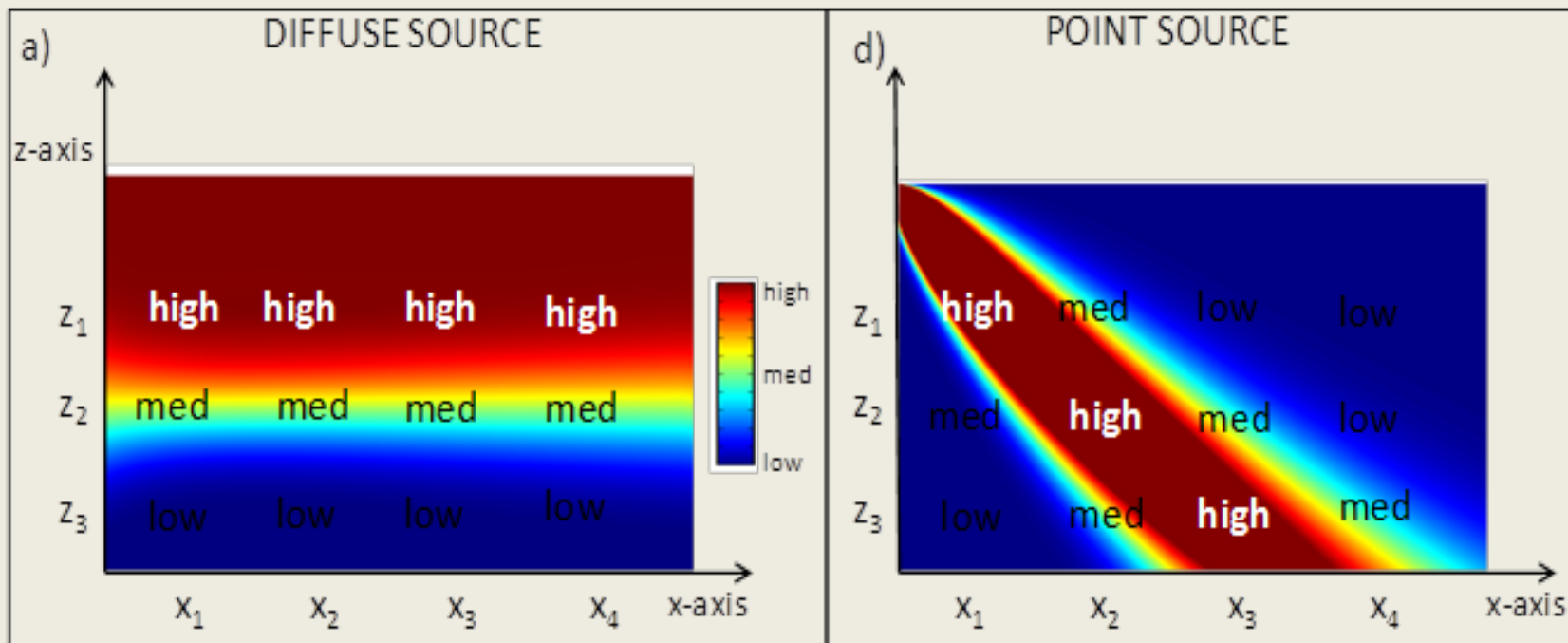
- Type of pesticide
- Pesticide concentration
- Varying input function fore diffuse source (simulating shift in pesticide application)
- Area of point source
- Location of point source
- Location and depth of water work wells
- Location and depth of monitoring wells
- Dispersivity
- Pumping rate in water works wells
- Infiltration
- Geology

scenario	Pesticide & characteristics	Decay coeff. (1/yr)	Sorption coeff. (Kd) (sand, clay) (L/kg)	Input conc. (kg/l)	Source input function	Source size (m)	Point source location, x (m from pumping)	Depth of pumping well (top screen in)	Monitoring well location (x,y in m and mbs)	Longitudinal (α <sub>L</sub> , transverse vertical) dispersivity (m)	Pumping rate, Q (l/s or l/min)	Recharge (m/yr)	Geology (Figure 1)	
base_d	bentazone	0	0,0	0,0	1975-present									
A1_d		0,02												
A3_d	MCPP	0,002	0,1, 0,5	0,03	1955-1997									
A4_d		0,0002												
A5_d	glyphosate	0,003	150, 300	0,03	1975-present									
A6_d		0	5, 100											
base_p	bentazone	0	0,0	50	1980-present									
A1_p		0,02												
A3_p	MCPP	0,002	0,1, 0,5	100	1960-present	10	2500	-40	4000, 10-12	5, 0,01	20	0,34	1	
A4_p		0,0002												
A5_p	glyphosate	0,003	150, 300	100	1980-present									
A6_p		0	5, 100											
base_d	bentazone	0	0,0	0,1	1975-present									
B2_d		0,02												
B3_d	MCPP	0,02	0,1, 0,5	0,03	1955-1997								0,34	1
B4_d		0,0002												
B5_d	glyphosate	0,003	150, 300	0,03	1975-present									
B6_d		0	5, 100											
base_p	bentazone	0	0,0	0,1	1975-present									
B1_p		0,02												
B2_p		0,02												
B3_p	MCPP	0,02	0,1, 0,5	0,1	1975-2012								0,34	1
B4_p		0,0002			3 months/yr									
B5_p	glyphosate	0,003	150, 300	0,1	1975-2012									
B6_p		0	5, 100		1 year every day									
base_d	bentazone	0	0,0	50	1980-present								0,34	1
D1_d		0												
D2_d		0												
D3_d		0												
D4_d		0												
D5_d		0												
D6_d		0												
D7_d		0												
D8_d		0												
D9_d		0												
D10_d		0												
D11_d		0												
D12_d		0												
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D75_d		0												
D76_d		0												
D77_d		0												
D78_d		0												

**78 simulations**

**Identify important factor or not**

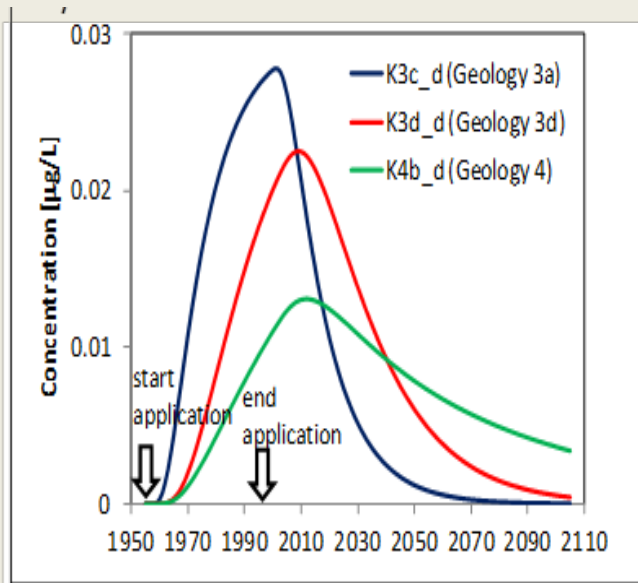
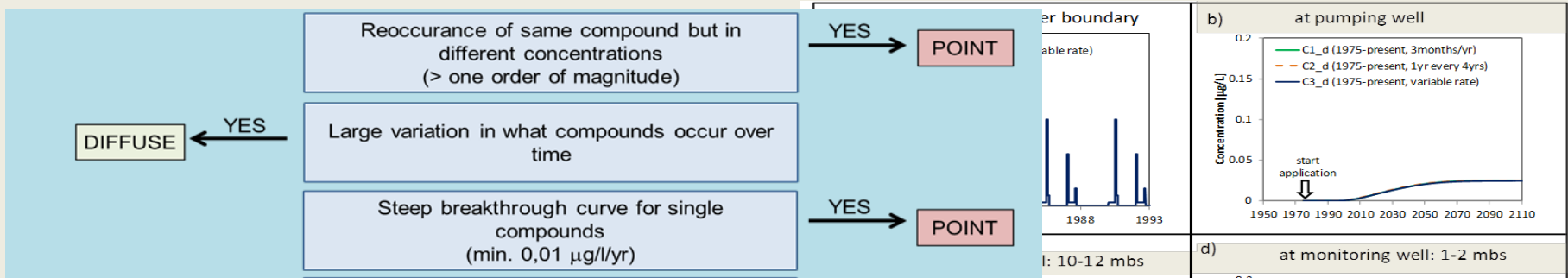
# Spatial differences



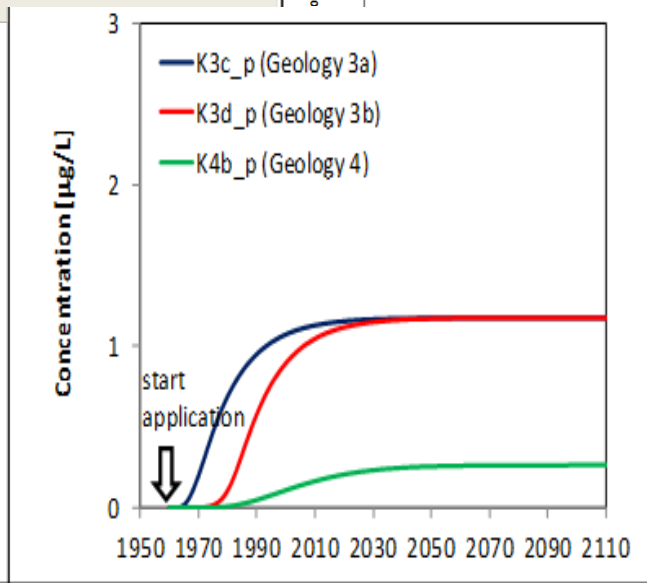
Horizontal variation of same compound(s) within 100 m in deep wells (>10 m)	YES →	POINT
Occurance of a compound in an abstraction well which is not present in more shallow wells (The wells should be in hydraulic contact)	YES →	POINT



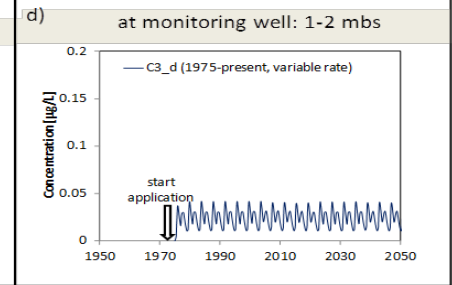
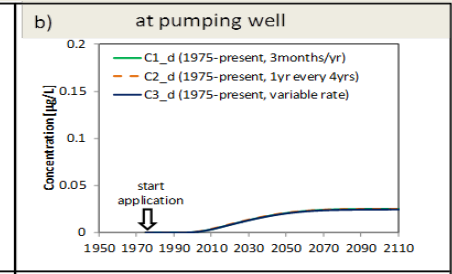
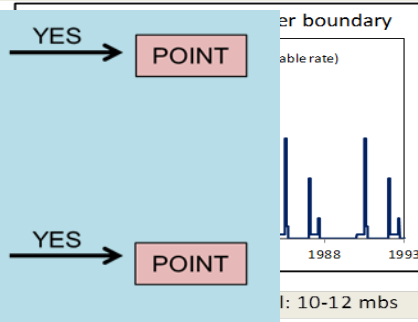
# Differences in trends, model results



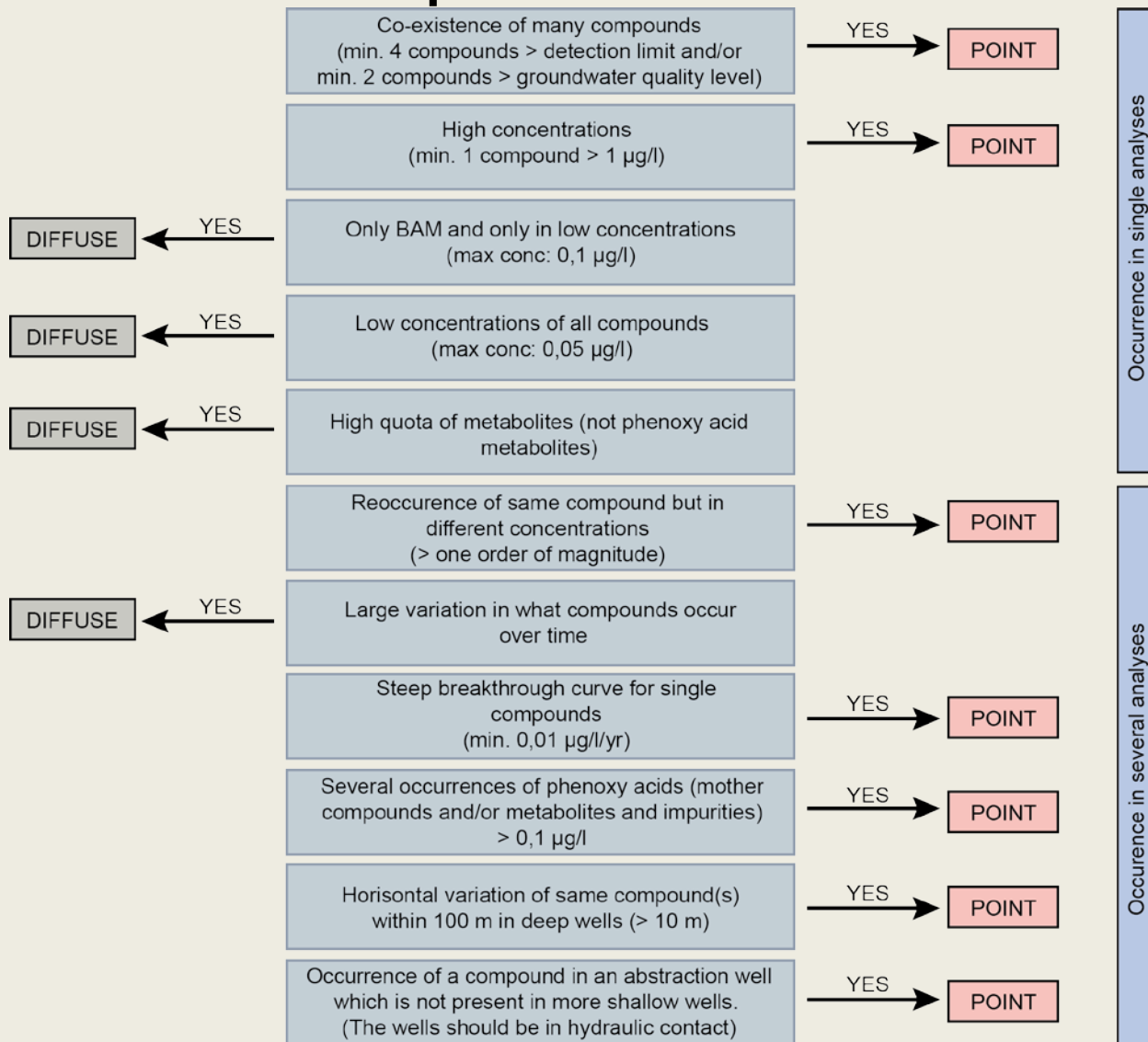
**Diffuse source trend**  
~ 0,001 µg/l/y



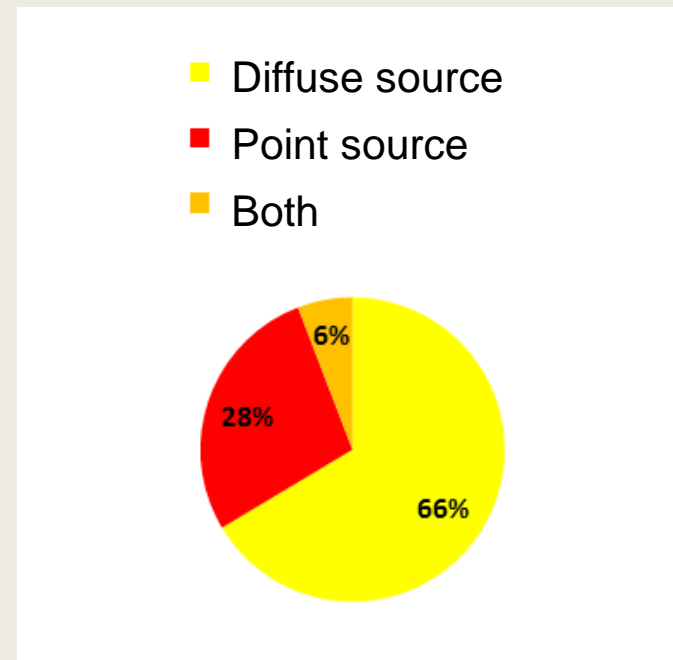
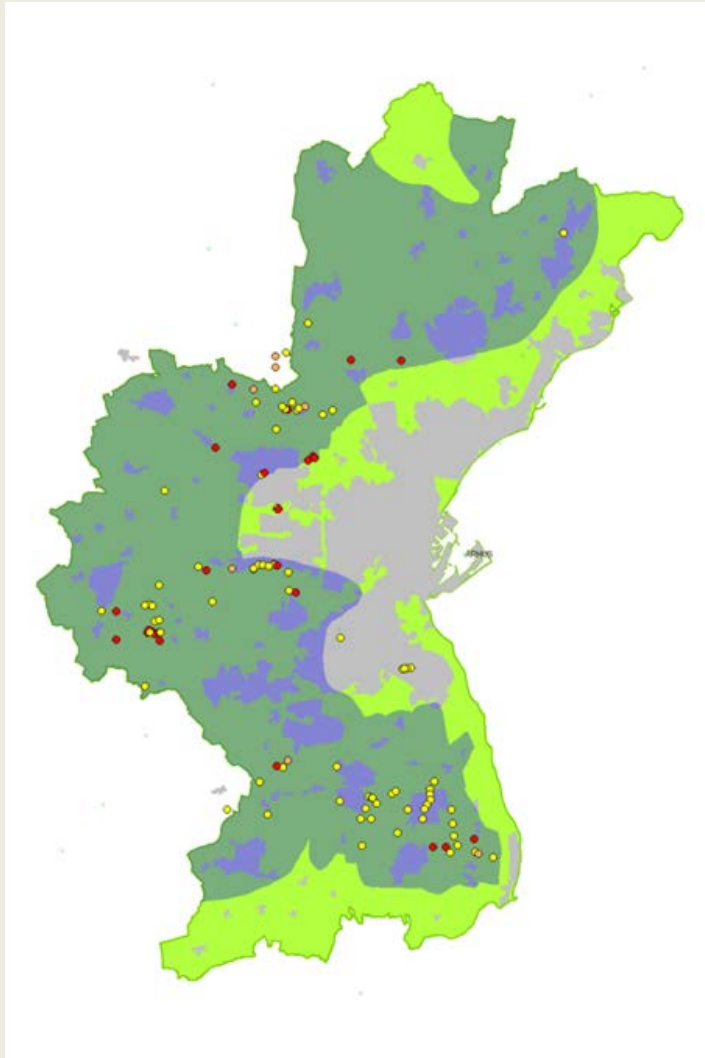
**Point source trend**  
> 0,01 µg/l/y



# Final Indicators for discrimination of diffuse and point sources



# Use of the indicator in Århus Municipality



# Example: Bam and phenoxy acids

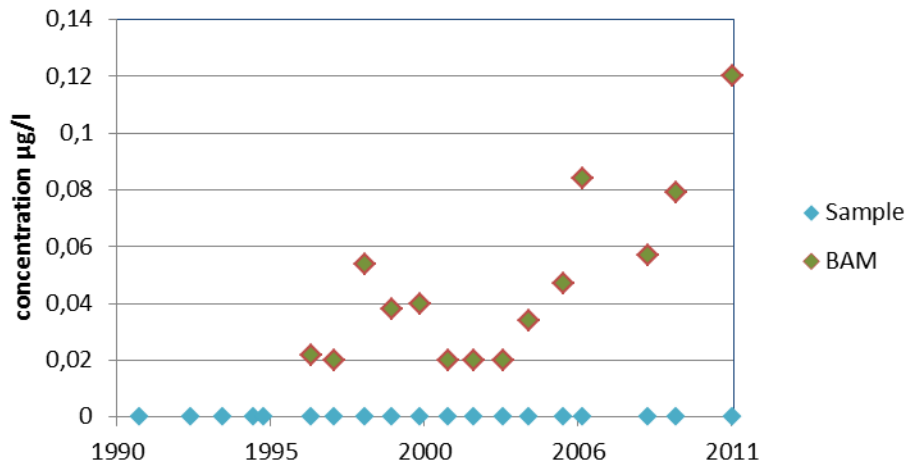
DIFFUSE\* ← YES

Only BAM and only in low concentrations  
(max conc: 0,1 µg/l)

Several occurrences of phenoxy acids (mother  
compounds and/or metabolites and impurities)  
> 0,1 µg/l

YES → POINT

### Diffuse sources



### Point source

