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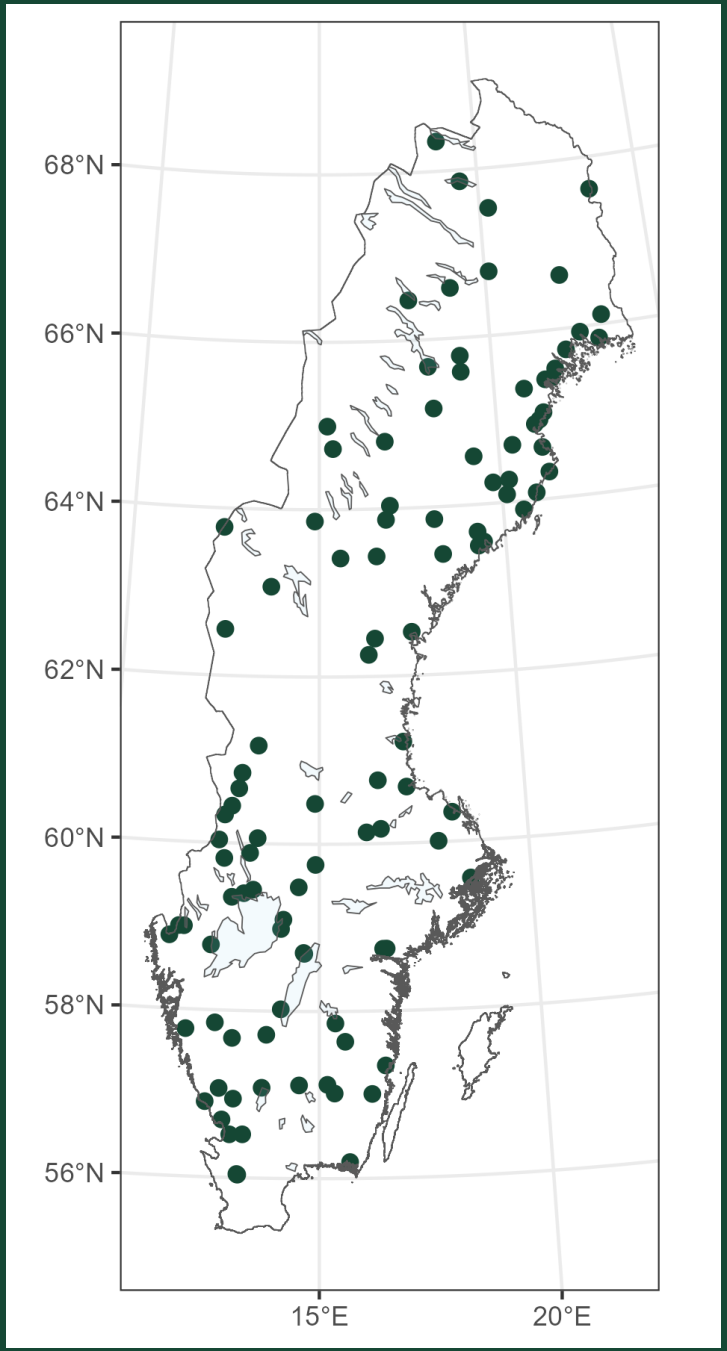
Dissolved organic matter charge dynamics over three decades

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[1]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden. [2]Norwegian Institute for Water Research, Oslo, Norway. [3]Department of Soil and Environment, Swedish University of Agricultural Sciences, Sweden.

Dissolved organic matter charge dynamics over three decades

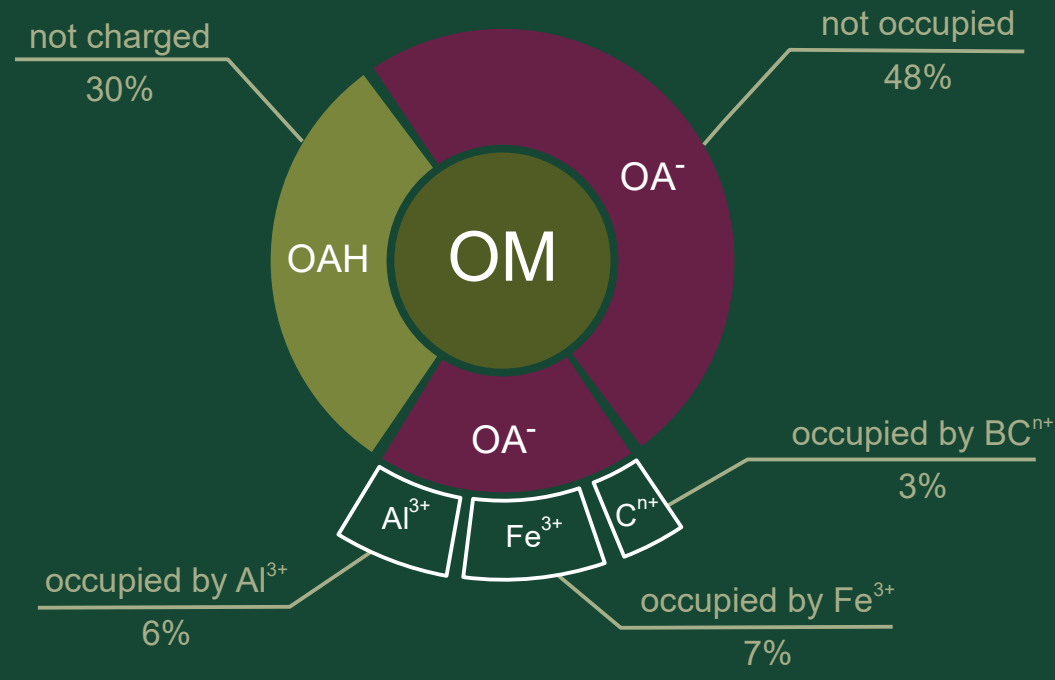
- Chemistry timeseries data from 110 river monitoring stations across Sweden (>42 000 samples)



Dissolved organic matter charge dynamics over three decades

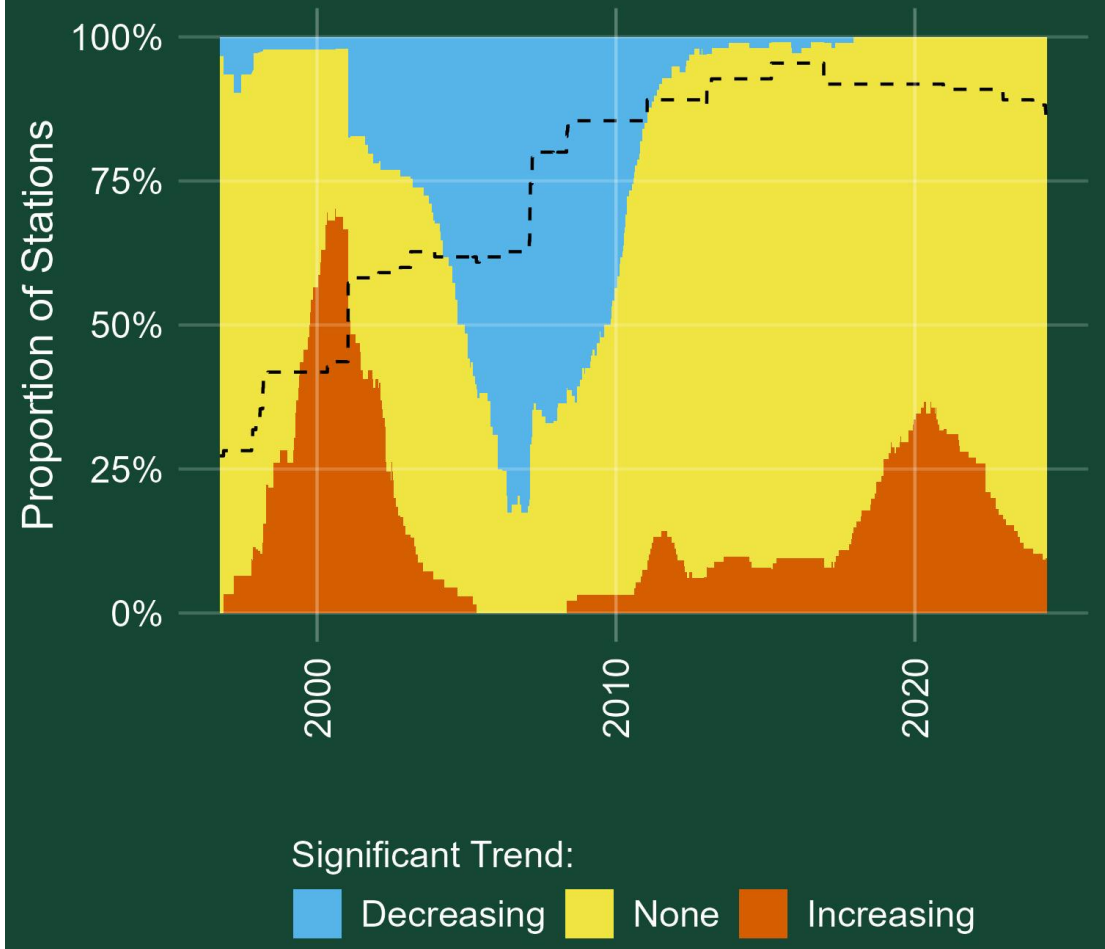
- Chemistry timeseries data from 110 river monitoring stations across Sweden (>42 000 samples)
- Chemical equilibrium modelling for each sample optimizing for the best fit site density (SD) of organic matter

Site density: 13.7 μeq mg^{-1} C



Dissolved organic matter charge dynamics over three decades

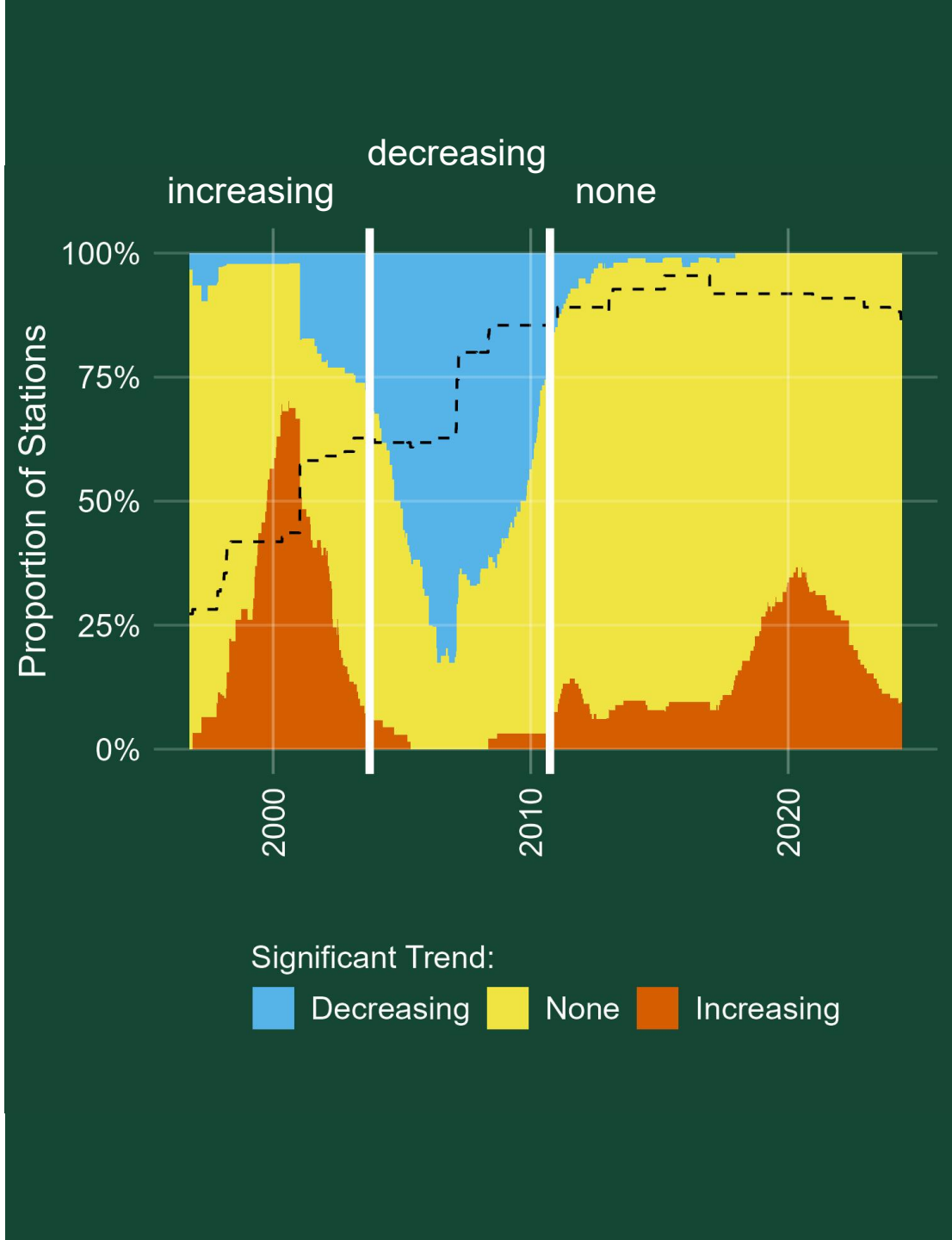
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- Focus on dominant trends in SD across all stations



Dissolved organic matter charge dynamics over three decades

- Chemistry timeseries data from 110 river monitoring stations across Sweden (>42 000 samples)
- Chemical equilibrium modelling for each sample optimizing for the best fit site density (SD) of organic matter
- Focus on dominant trends in SD across all stations
- Three distinct trend periods:

  increasing -> decreasing -> none



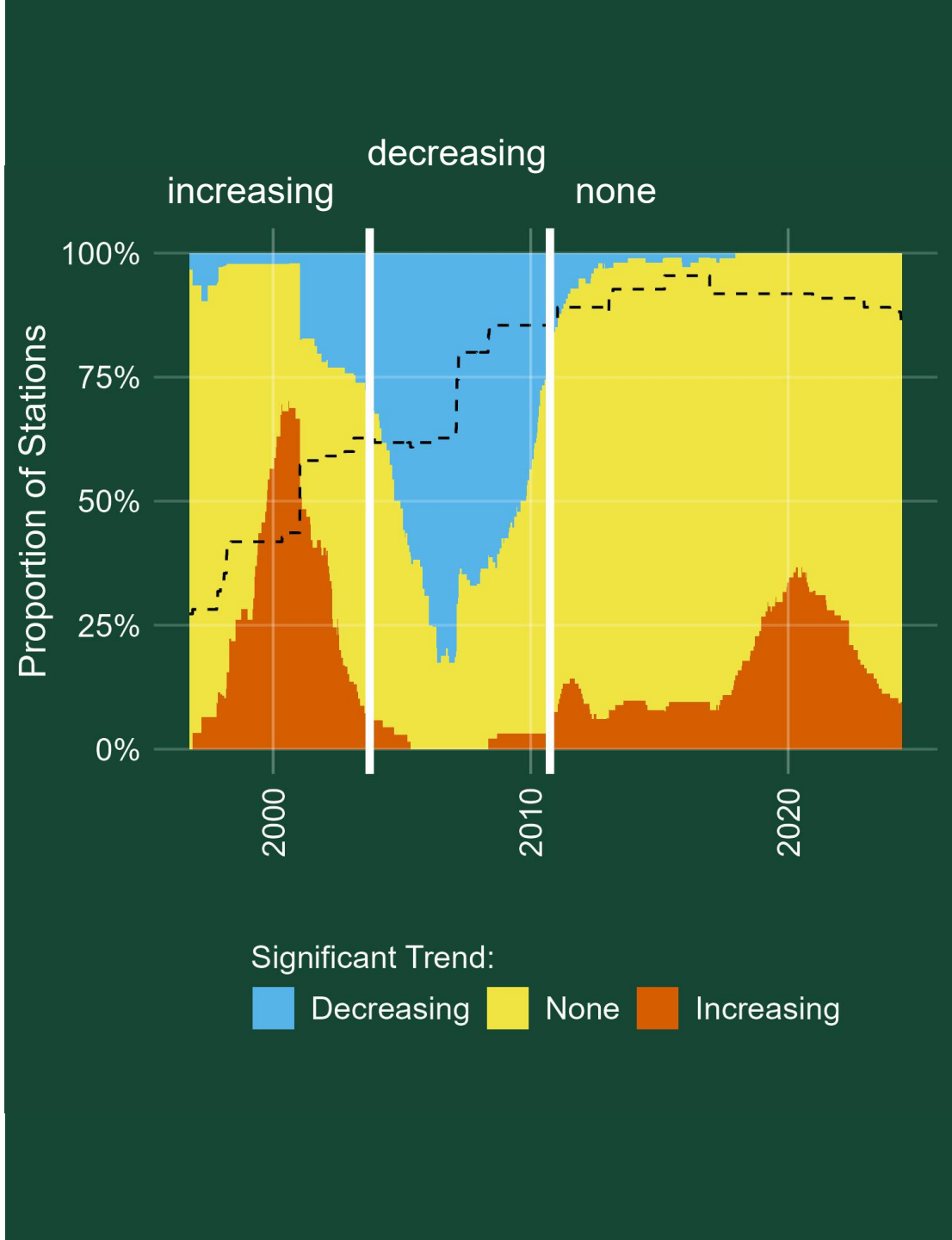
Dissolved organic matter charge dynamics over three decades

- Chemistry timeseries data from 110 river monitoring stations across Sweden (>42 000 samples)
- Chemical equilibrium modelling for each sample optimizing for the best fit site density (SD) of organic matter
- Focus on dominant trends in SD across all stations
- Three distinct trend periods:

  increasing -> decreasing -> none

What may be happening?

- Pulse of relatively highly charged OM before 2003 related to recovery from acidification
- Supported by the covariation with mobilization of DOM related explanatory variables in period 1: 1995 – 2003.




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1. Background
2. Research Question
3. Methods
   a) Overview of methods
   b) GAMM trend analysis
4. Results
   a) Main results: SD trends across Sweden
   b) Results summary
5. Discussion
   a) Potential Interpretation
   b) Broader Implications





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Background: DOC Quality and its charge properties

- Hruska et al., 2001
  Triprotic acid analog model, quantified site density = 8.6 µeq/(mg of TOC)

- Sjöstedt et al., 2010
  Stockhom-humic model with a parameter for active organic acid sites
  SD= 11.5 µeq mg^{-1} C

- DOC's character is changing: less color (Eklöf et al, 2020)

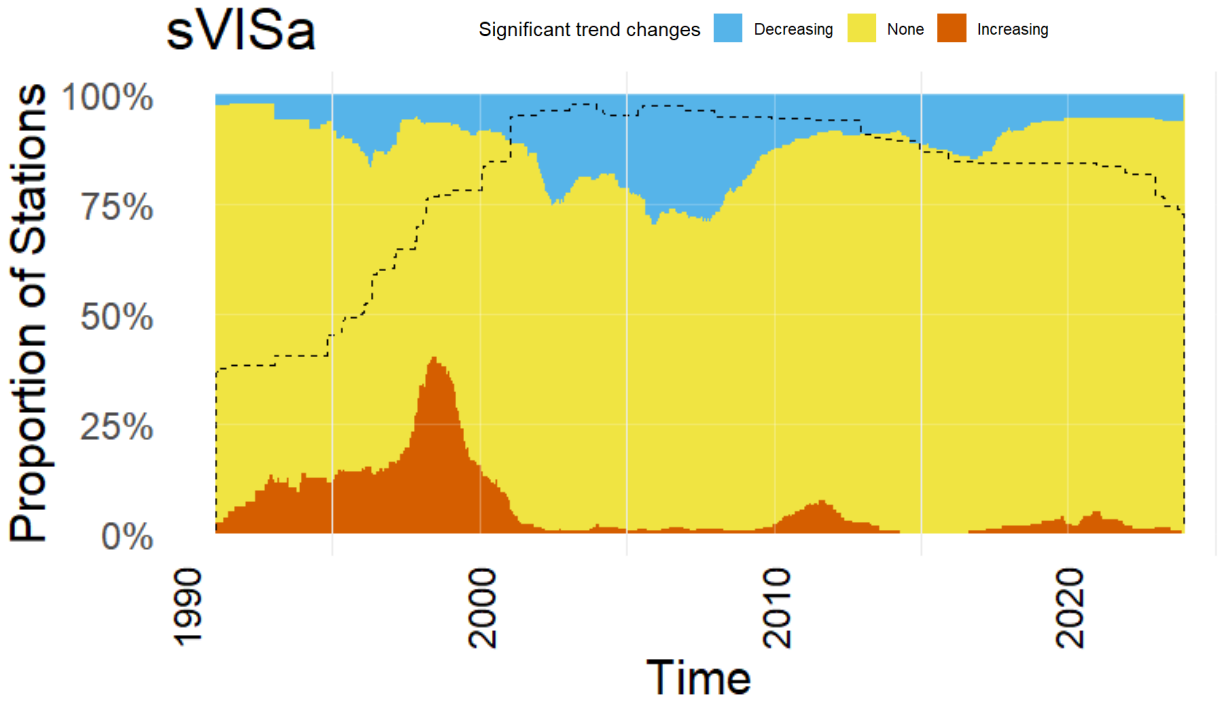


Figure 2 *(Above): Proportion of stations with increasing (orange), decreasing (blue) or no significant (yellow) trends in sVISa (absorbance 420mm / TOC) across Sweden.*

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Research Question

- Charge properties are often assumed to be invariable across time and often space, therefore we wanted to verify this in the monitoring data collected across Sweden since 1990:
- **What are the trends in organic charge properties as SD across Swedish rivers in the past 30 years?**
- Hypothesis:
  - As DOC quality has changed, likely SD would also have changed across the Swedish landscape.
  - We can see variability on SD depending on the method used and the dataset – so consistency is key to get a accurate picture of trends in SD.

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Methods

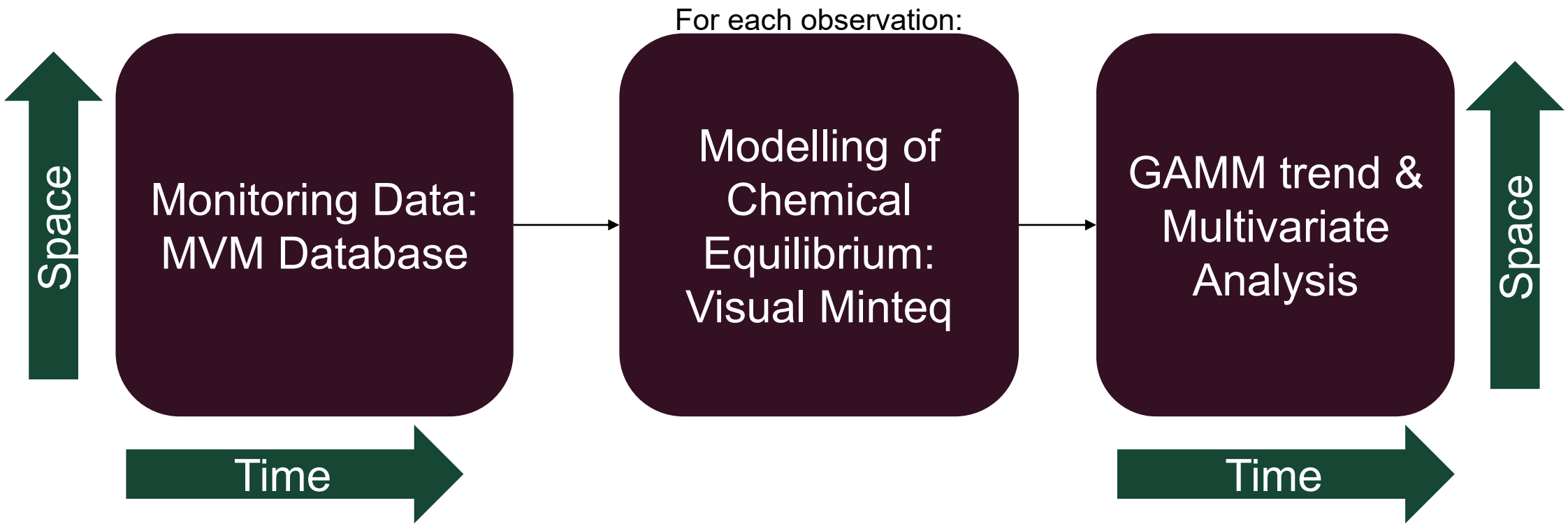


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Chemical Equilibrium Modelling

- Visual MINTEQ: include modelled speciation of aluminium and iron
- At the end of the titration curve (pH 5.6): known pH and pCO2
- Stockholm Humic Model: discrete site approach for proton and metal binding
- Optimizing SD for single samples based on minimizing charge difference

Constant Input	Varying Input	Output
pH, pCO2, temperature	Base cations (Ca, Mg, Na, K) NH_4 Anions (SO_4, NO_3, Cl) Al, Si, F, Fe TOC	Organic charge Optimized SD Metal speciation

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Data

- **Water chemistry** (measured): sVISa, TOC, SO4, alkalinity, Abs420, field pH
- **Water chemistry** (calculated): ionic strength, ANC, BC
- **Water chemistry** (modelled): OA-Al/SD, OA-Fe/SD, OA-BC/SD, OA^-/SD, OAH/SD
- **General**: area, elevation, area above high coastline
- **Land cover**
- **NDVI**
- **Peat and ditches**: peat cover, ditch density, % ditches in peat
- **Hydrology**: spec. Q, Q
- **Atmospheric deposition**: S dep. N. dep.

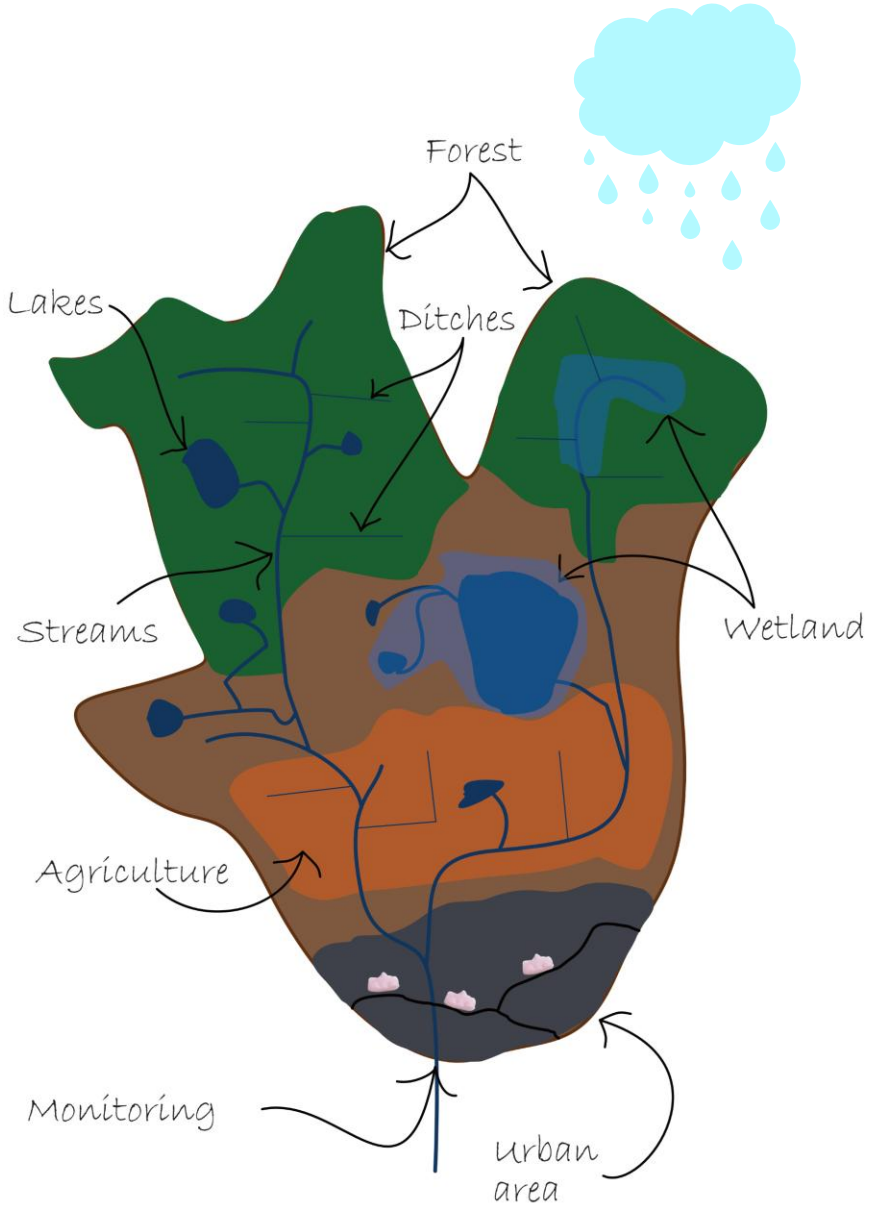
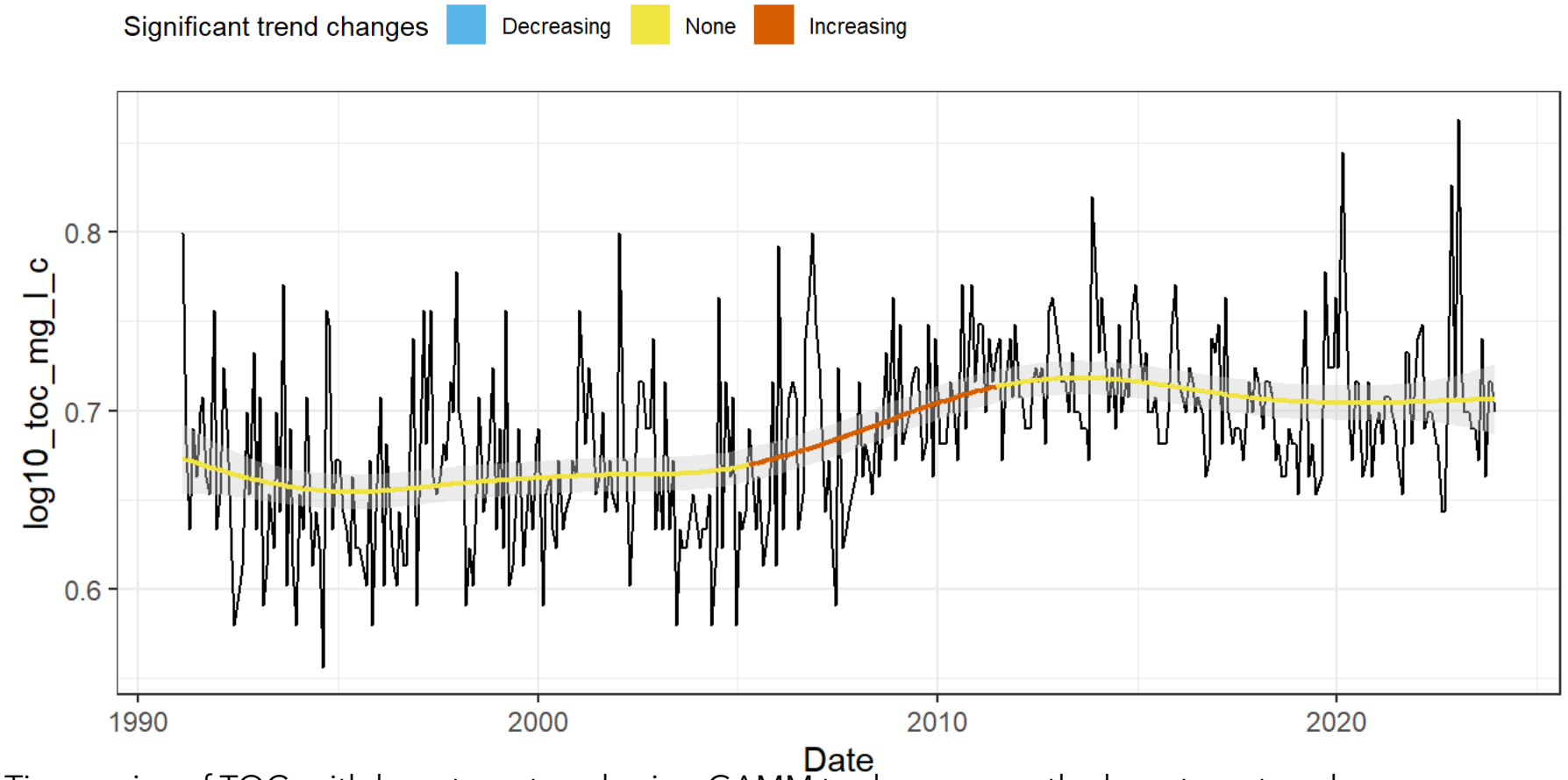


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GAMM trend analysis

- Decomposition into long-term trend, seasonality accounting for autocorrelation



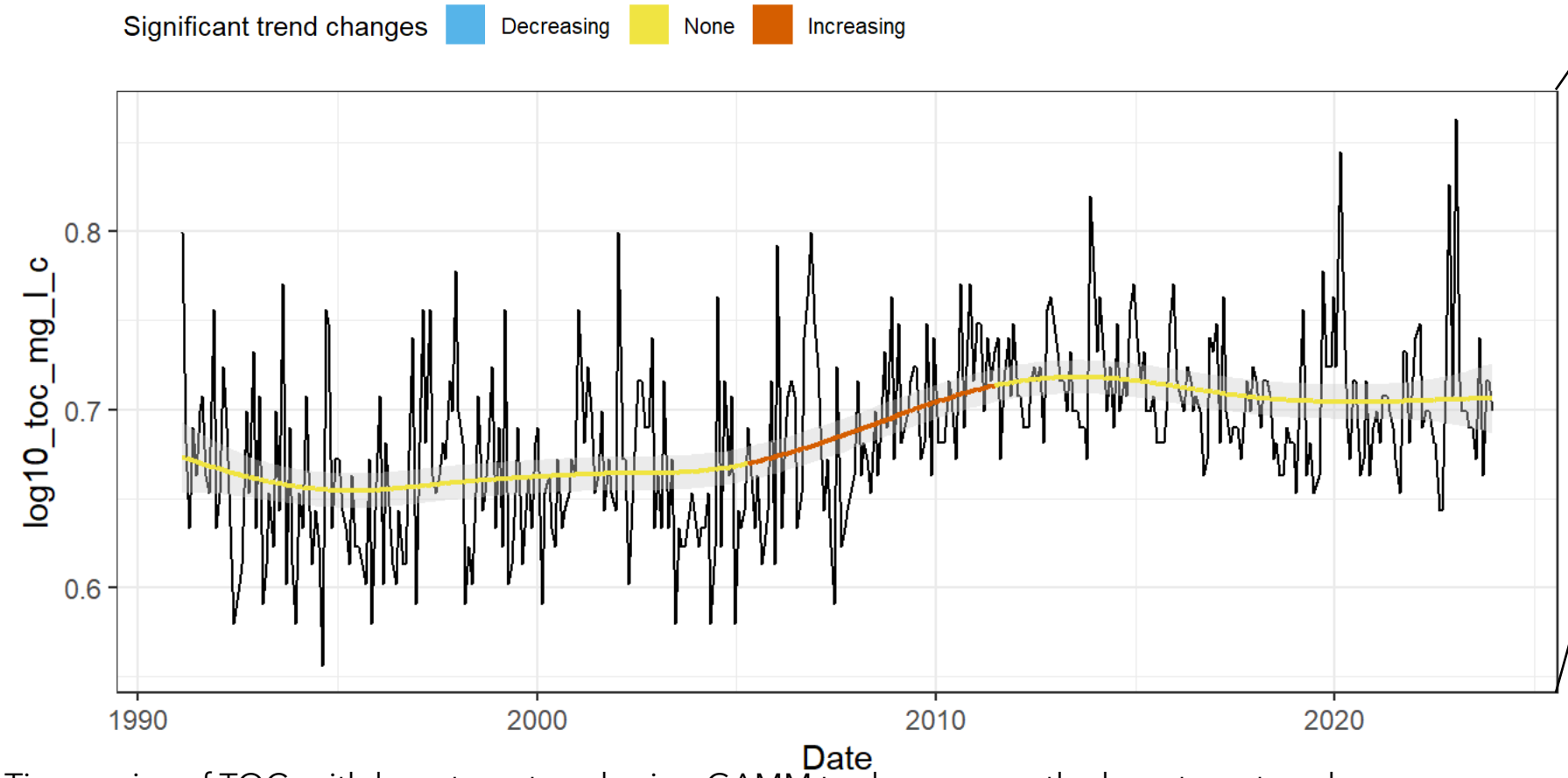
Time series of TOC, with long term trend using GAMM to decompose the long-term trend.

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GAMM trend analysis

- Decomposition into long-term trend, seasonality accounting for autocorrelation



Time series of TOC, with long term trend using GAMM to decompose the long-term trend.

TOC trends for 316 stations

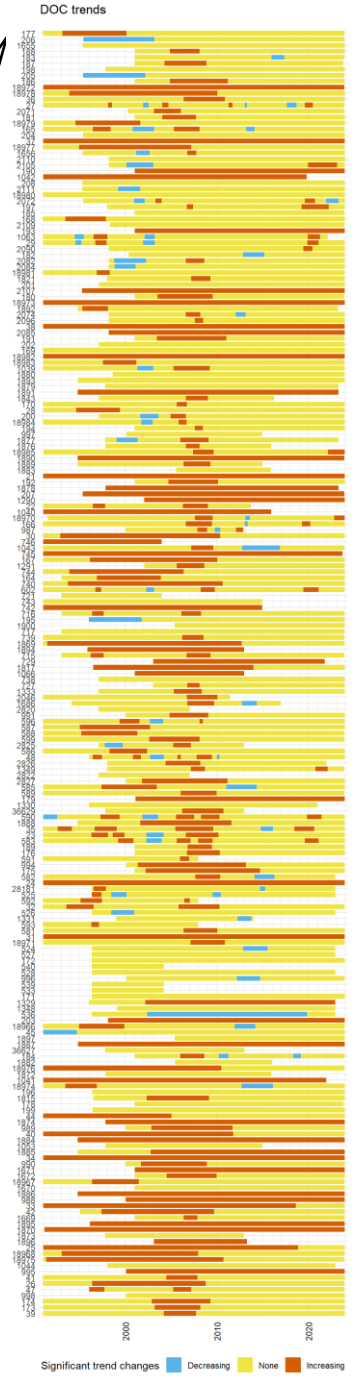
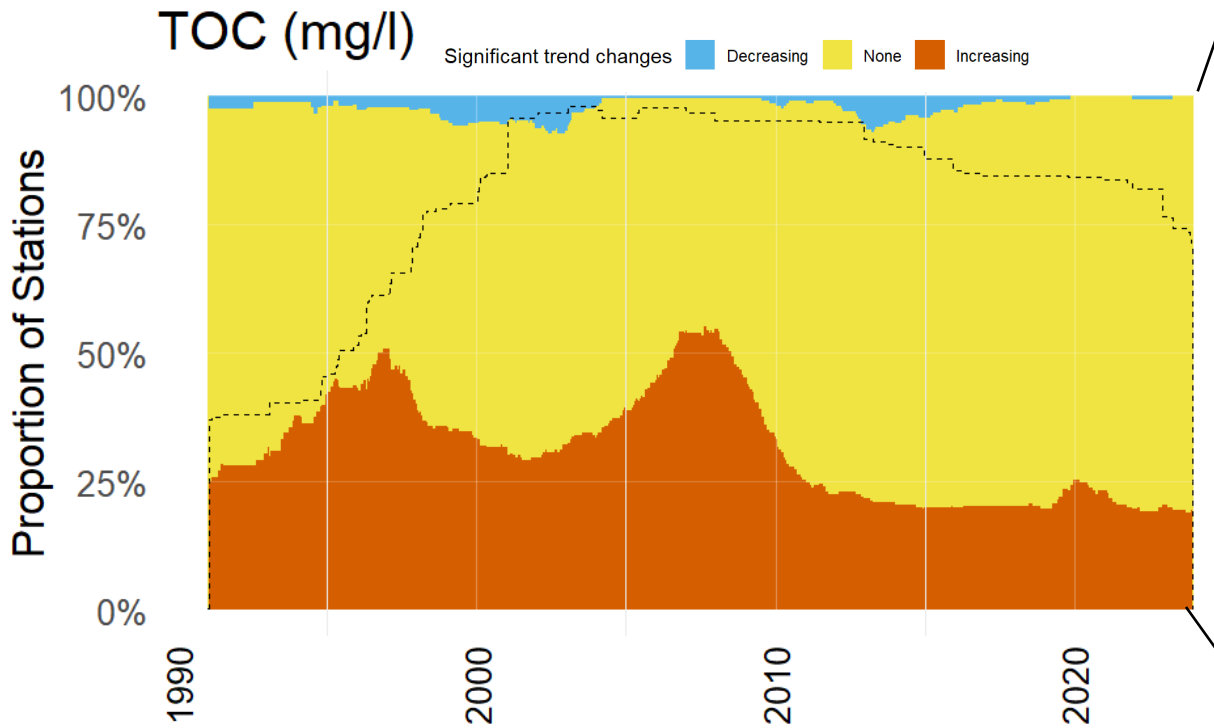


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GAMM trend analysis

- Decomposition into long-term trend, seasonality accounting for autocorrelation
- Visualization of trends across time series with varying time range.



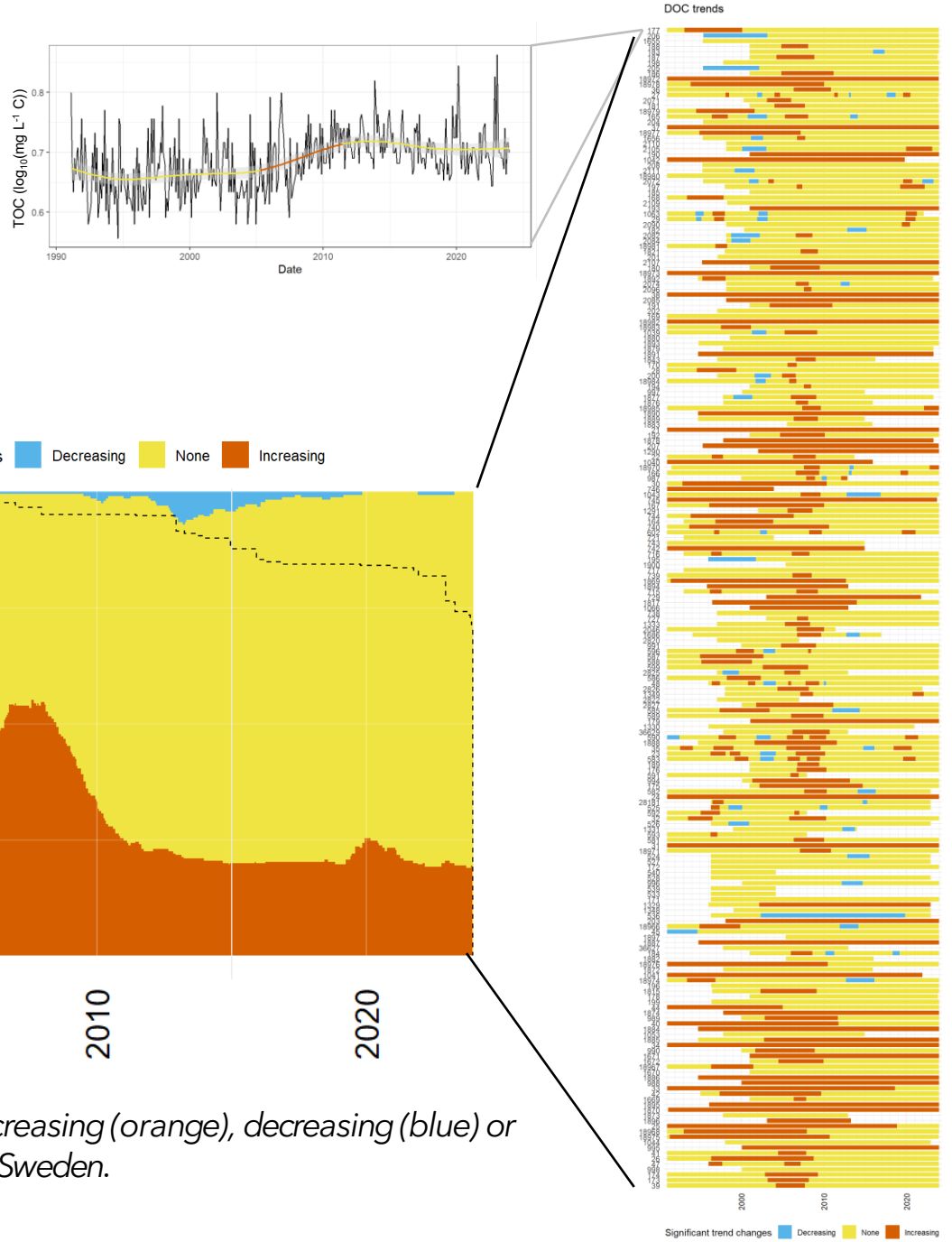


Figure above: Proportion of stations with increasing (orange), decreasing (blue) or no significant (yellow) trends in TOC across Sweden.

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Multivariate analysis: OPLS

- Orthogonal least square analysis was used to look into the drivers of linear SD changes within each period, ancillary data summarized for each catchment.
- Linear trends were summarized using Sen slope estimates.

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Results

- Quantification of SD (site density)
- SD vs charge density
- **SD trends**
- Spatial distribution of SD
- Possible drivers of SD trends

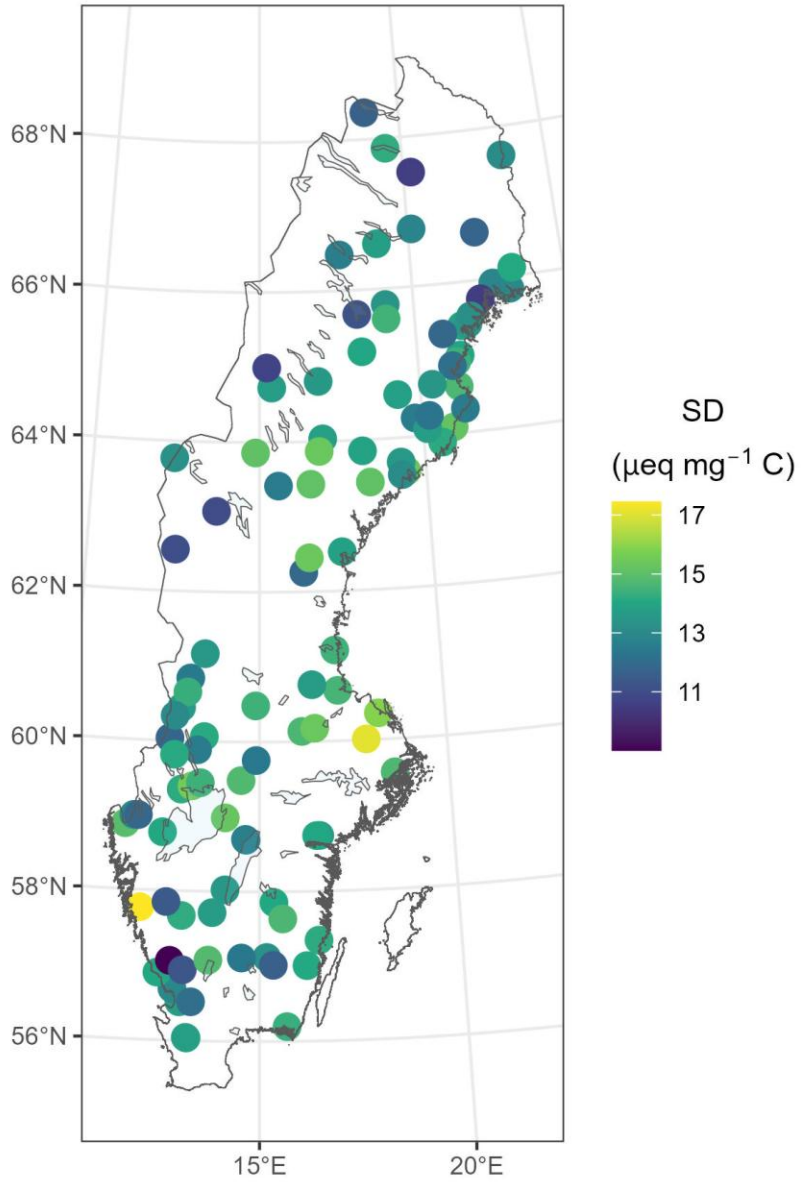


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Site density

Table 1: P25, P50 (median), and P75 for the period October 2010 to October 2024, calculated from the station-wise mean at pH 5.6.

Variable	Unit	P25	P50	P75
$OMCD_{5.6}$	µeq mg^{-1} C	5.9	6.6	7.0
SD	µeq mg^{-1} C	12.7	13.7	14.3
Percentage of SD occupied by Al (OA-Al/SD)	%	3.7	5.8	8.7
Percentage of SD occupied by Fe (OA-Fe/SD)	%	6.0	7.3	8.1
Percentage of SD occupied by Al and Fe together ((OA Al + Fe)/SD)	%	11.3	13.4	15.1
Percentage of SD not dissociated (OAH/SD)	%	28.8	30.0	31.3
Percentage of SD that is charged (OA^-/SD)	%	46.9	48.4	49.2
Percentage of SD complexed by other cations than Fe and Al (O-BC/SD)	%	2.2	3.1	4.1
Percentage negative charge contributed by OM compared to total negative charge (OA-/Total-)	%	11	17	30



Station-wise mean for SD for the period October 2010 – October 2024.

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Site density vs Charge density

- R^2 = 0.97; marginal R2 = 0.99
- Highly correlated SD and CD
- Intercepts: Different metal complexation for each station

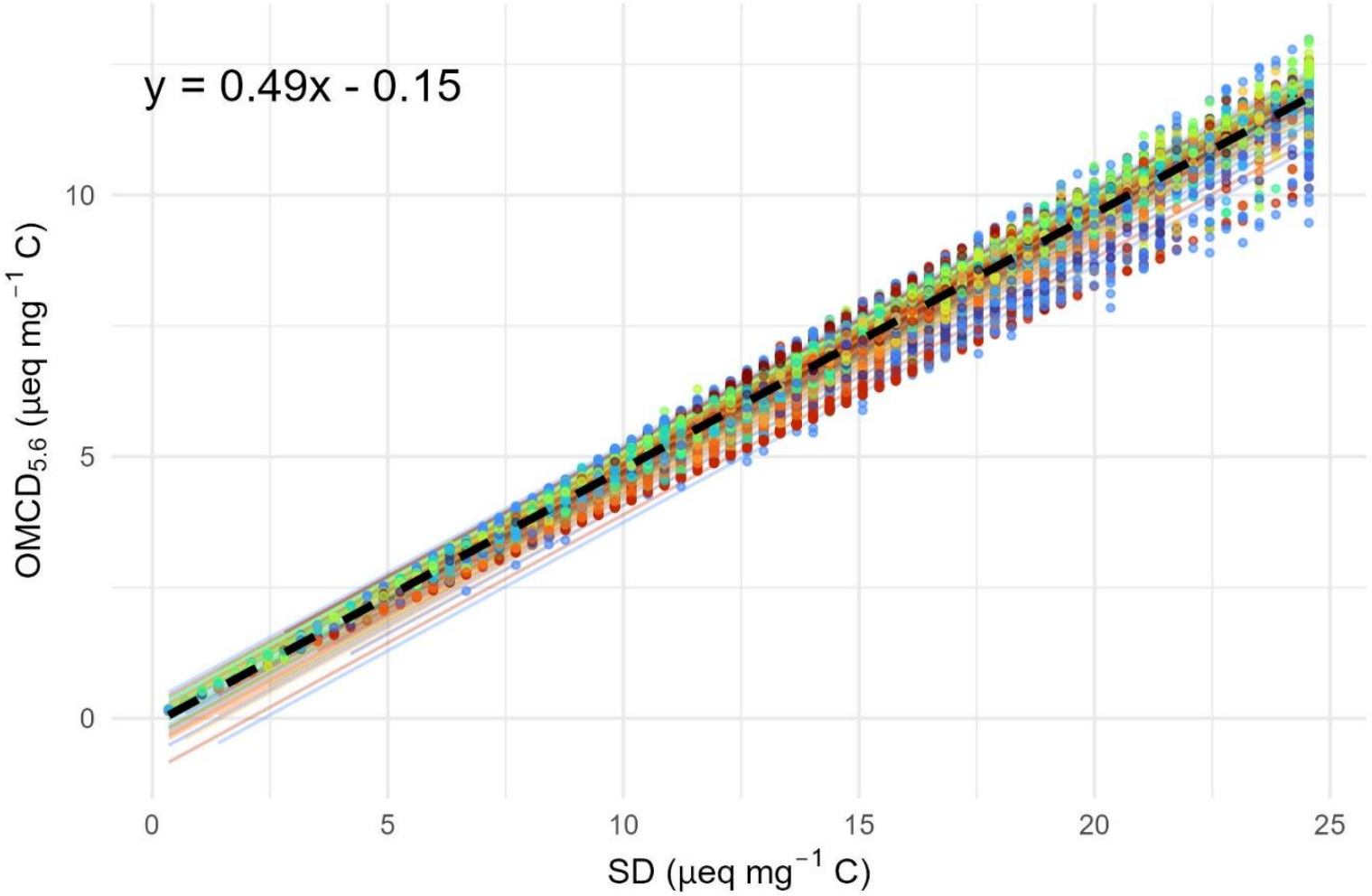


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Trends

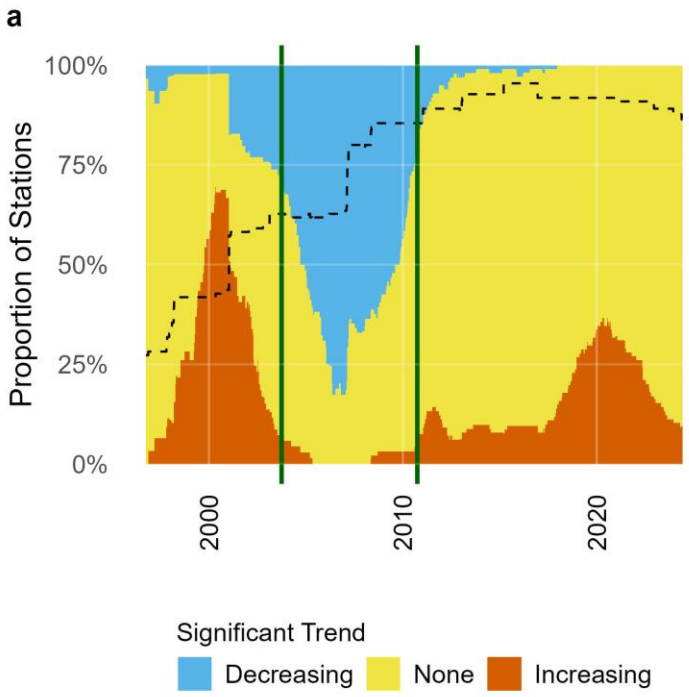
GAMM trend analysis summarizing long term trends in SD across 110 stations (a), and individual stations (b-e).

Dominat Trends:

Period 1 1995 - 2003: Increasing

Period 2 2003 – 2010: Decreasing

Period 3 2020 – 2024: None (Increasing)



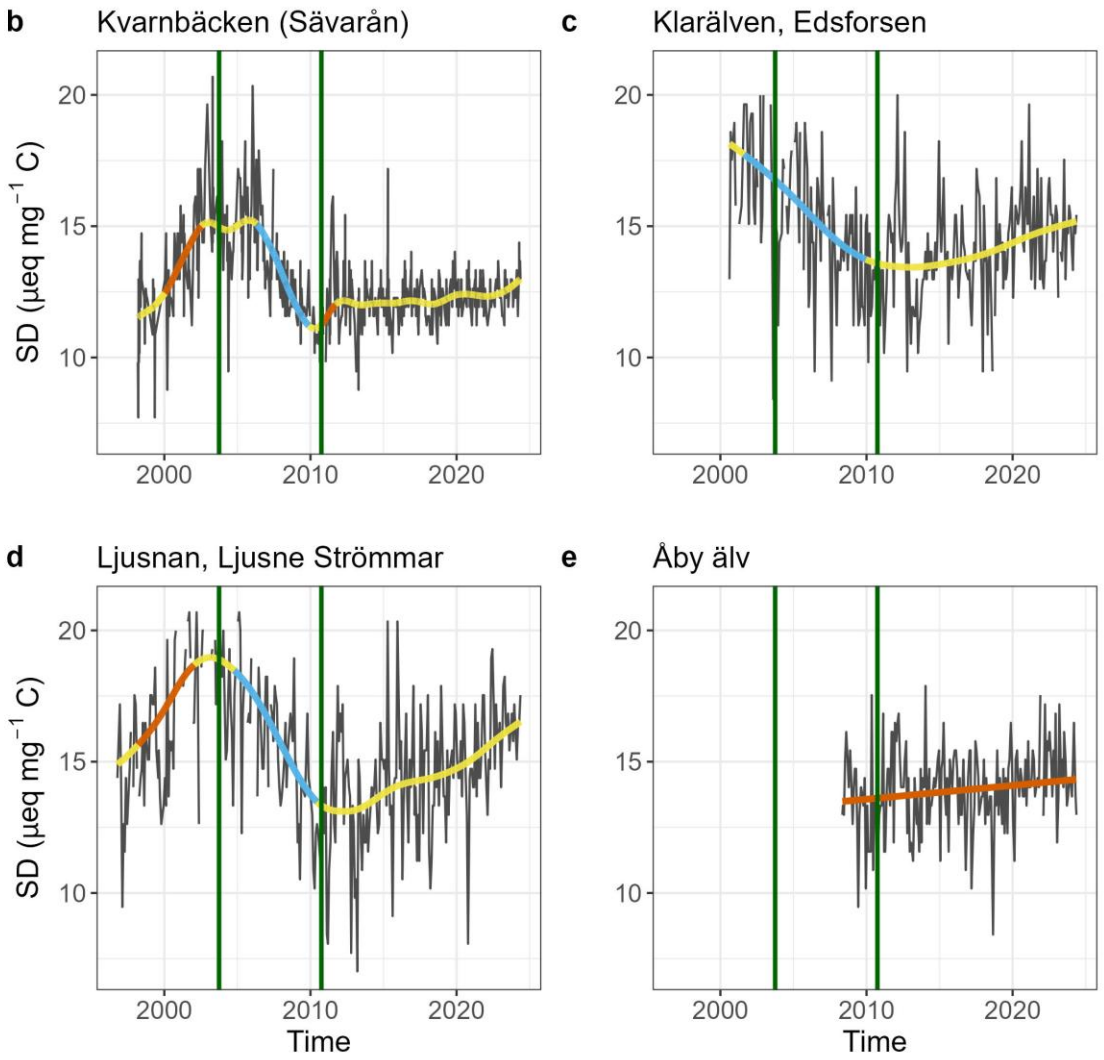
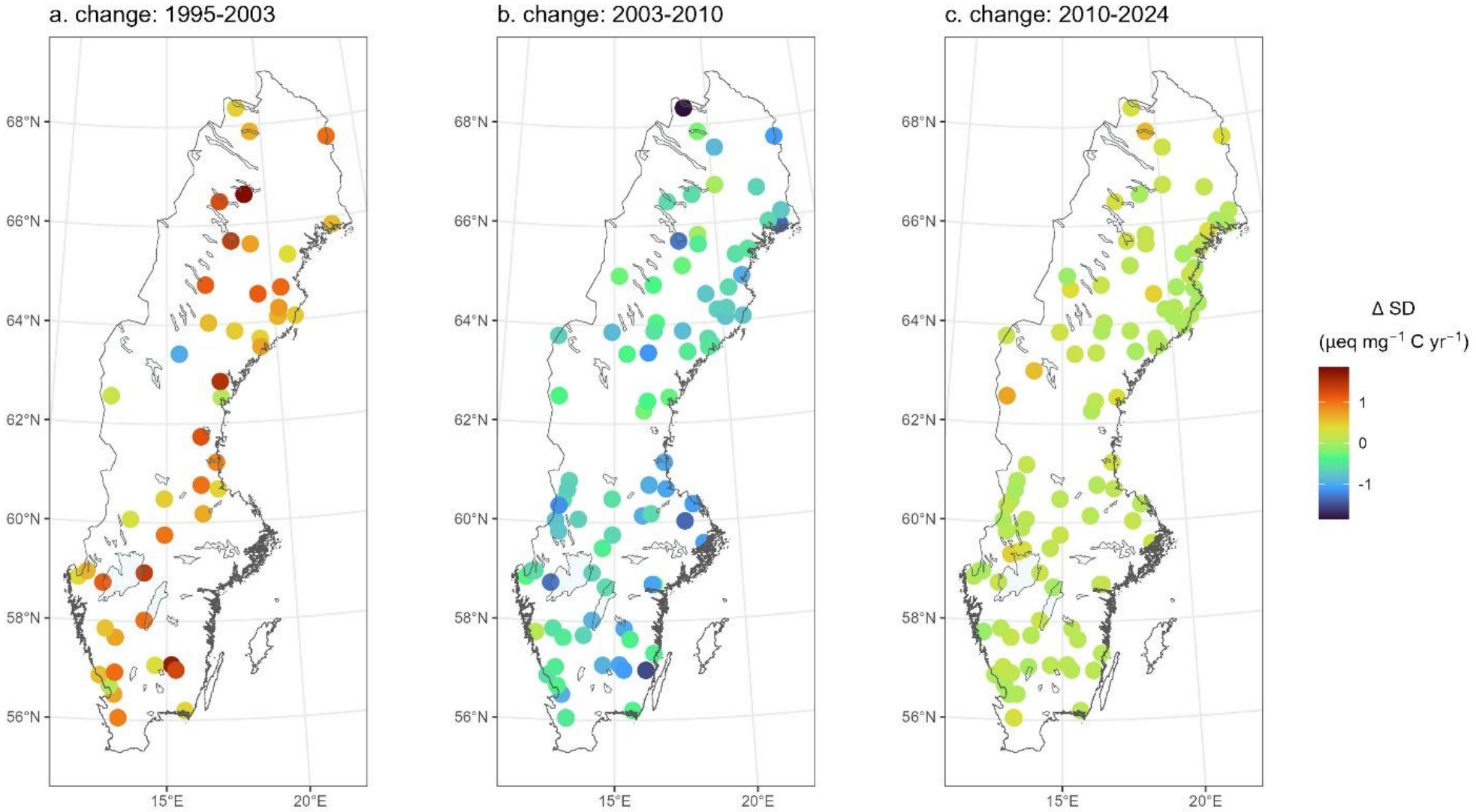


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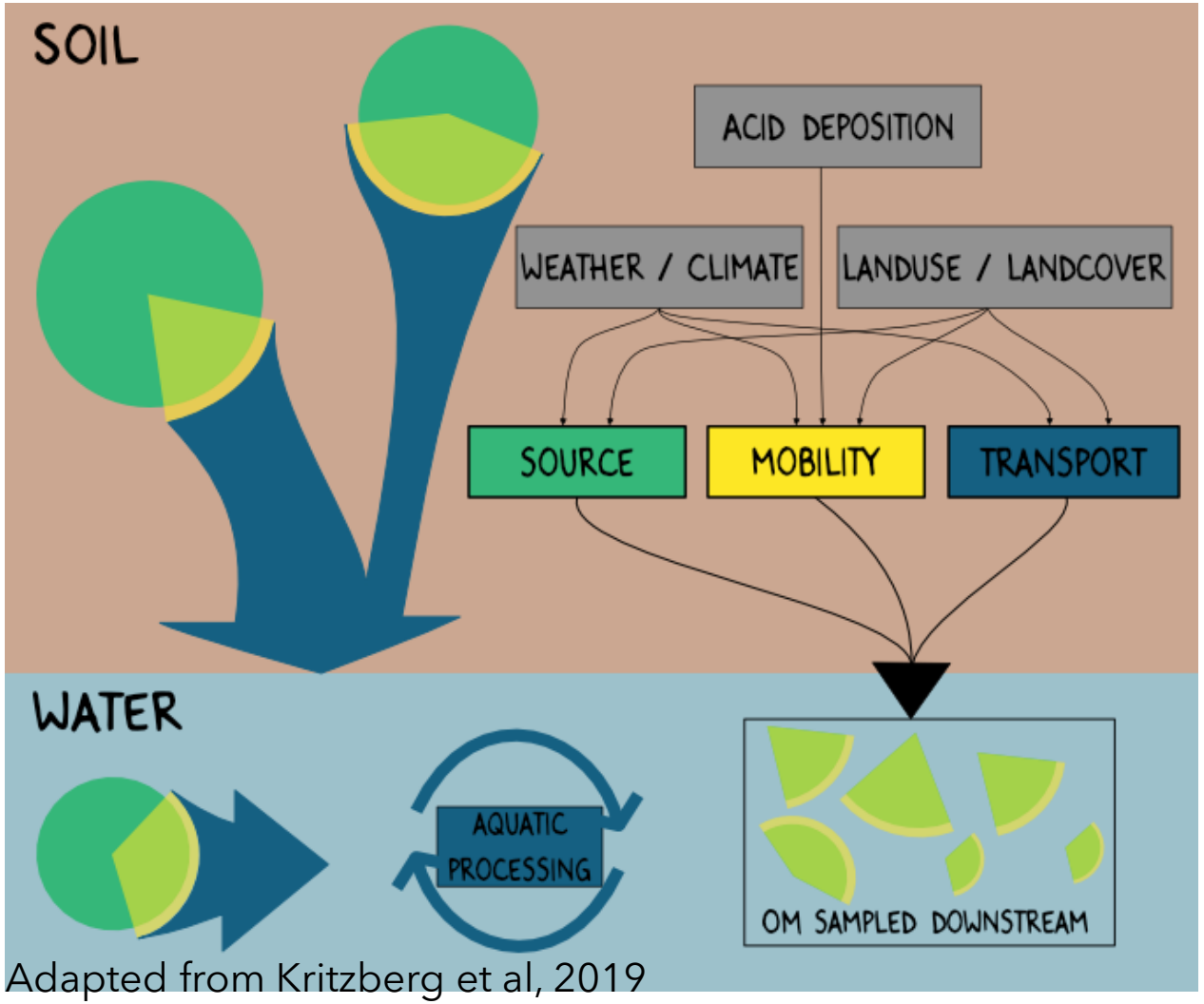
Spatial Distribution



Linear SD trends during the period 1995 – 2003 (a), 2003 – 2010 (b) and 2010 – 2024 (c).

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Drivers of SD



Adapted from Kritzberg et al, 2019

mean : 2010 - 2024		change: 1995- 2003		change: 2010 - 2024	
Variable	**VIP**	**Variable**	**VIP**	**Variable**	**VIP**
field pH	+2.02	ANC	-2.95	TOC	-2.19
alk	+1.84	Δalk	-2.84	Abs420	-2.12
ANC	+1.82	alk	-2.60	OA-/Total-	-2.07
precipitation	-1.79	ΔANC	-2.33	Al tot.	-2.03
BC	+1.72	ionic strength	-2.14	heathland	+2.03
ionic strength	+1.66	peat	-2.10	sVISa	-1.96
sVISa	-1.65	Δmean temp.	+1.54	forest	-1.91
elevation	-1.45	Δionic strength	-1.46	field pH	+1.68
Q	+1.42	ΔsVISa	+1.40	pine forest	-1.52
agriculture	+1.38	ΔNDVI	+1.40	bare soil	+1.51
water	+1.29	deciduous on wet	-1.37	mineral	+1.49
area	+1.24	BC	-1.34	ΔAl tot.	-1.46
< highest coastline	+1.22	Δspec. Q	-1.26	coniferous on wet	-1.43
OA-/Total-	-1.15	ΔP25 spec. Q	-1.21	ΔTOC	-1.39
SO4	+1.01	mixed forest	-1.16	Δfield pH	+1.36
		ΔOA-/Total-	+1.14	forest on wet	-1.32
		Δmax temp.	-1.11	NDVI	-1.21
		ΔQ	-1.07	alk	+1.20
		deciduous	+1.06	elevation	+1.14
		ΔP75 spec. Q	-1.03	S dep.	-1.08
				ΔAbs420	-1.06

VIP table for OPLSs with mean SD 2010 – 2024 (1st column), SD change 1995 – 2003 (2nd column), and SD change 2010 – 2024 (3rd column) as response variables. Explanatory variables are colored by association with the main determinants of OC quality: Source(green), mobility (yellow), and transport (blue).

Results summary

- SD has been changing cohesively across the country with a period of **increasing SD until 2003**, followed by a **decrease until 2010** and since remained stable with relatively small increases.
- The magnitude of SD trends within these periods has shifted from covariation with water chemistry and OM mobility related variables to OM source and transport related explanatory variables.

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Discussion



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Potential Explanation

- Pulse of **relatively highly charged DOM** was transferred from soils to surface waters during period 1.
- This pulse may have resulted from the release of DOM that had been temporarily stored in soils during the acidification era, due to stronger DOM sorption under acidic conditions and higher ionic strength.
- As ionic strength decreased, the more highly charged OM fraction may have been mobilized, leading to the observed effects. However, this pulse appears to have lasted only a few years, after which SD declined again during period 2.

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Back to the results

Broader Implications

- Changes in DOM quality influence charge, water colour, acidity, and metal binding, thereby affecting drinking water treatment, ecosystem health, and the transport of nutrients and contaminants.
- Improved representation of DOM charge characteristics in monitoring and modelling frameworks will therefore enhance our ability to manage water resources under ongoing environmental change.

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