



Airborne Ammonia and Ammonium within the Northern Adriatic Area, Croatia

A. Alebic-Juretic
Teaching Institute of Public Health,
Rijeka, Croatia



Introduction

- Growth in population and standard led to increased pollution, but also deposition
 - Regional protocols with emission ceilings
 - By 2010 predicted relative to 1999:
 - 63% reduction in SO_2 (75% to 1980's)
 - 41% reduction in NO_x
 - 17% reduction in NH_3
-

The city of Rijeka



The city of Rijeka

- Rapid industrialization in 1970's
- Monitoring programme since 1980
- One of the most polluted in mid 1980's
- Start of precipitation analysis
- Different chemical composition of rainwater even within city area
- 70% reduction in SO_2 emission and ambient levels by 1995.
- 45% reduction in S-SO_4 deposition by 1995.

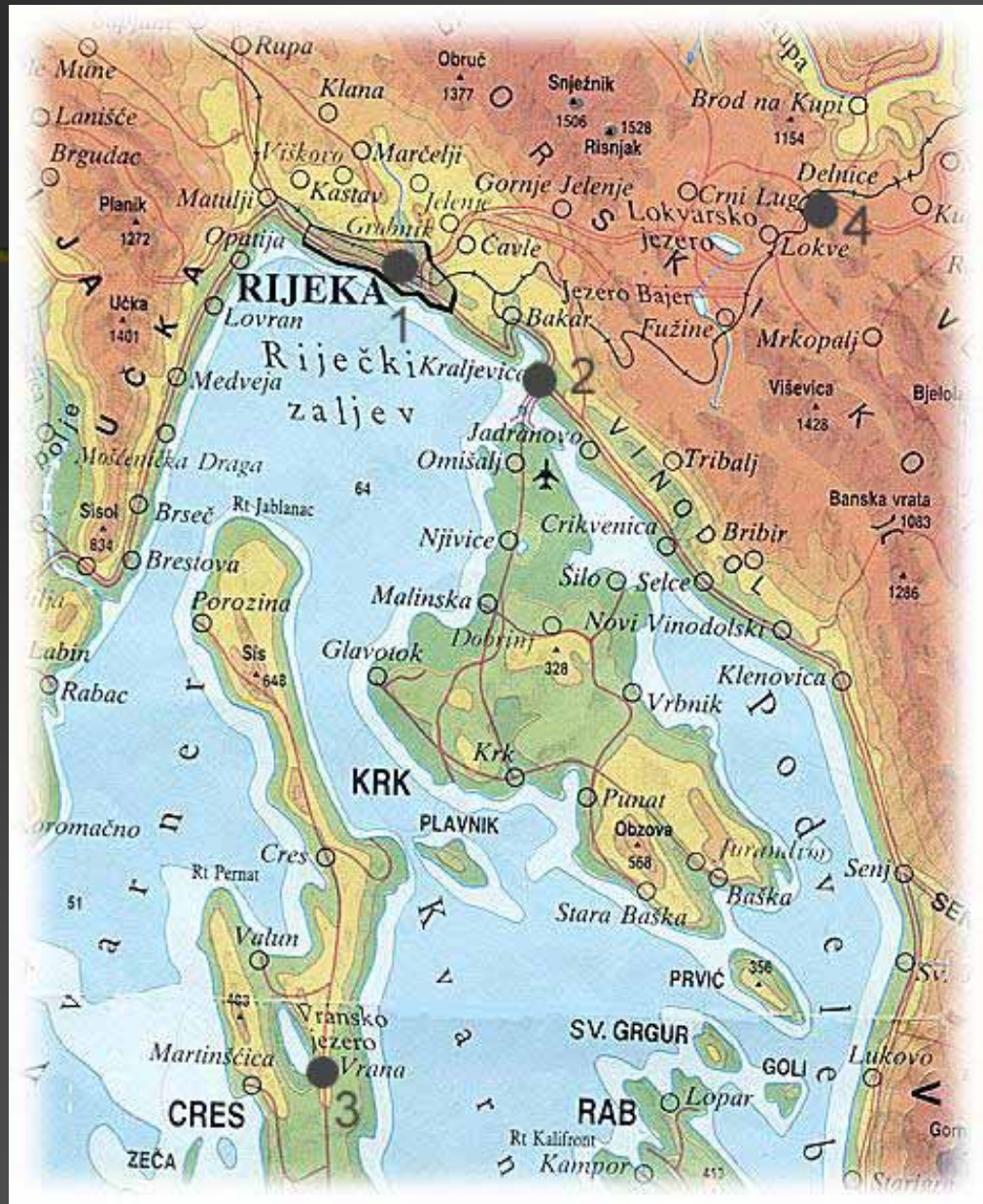
Locations of sampling sites

Distance from Rijeka:

Site 2: ~ 20 km

Site 3: ~ 80 km

Site 4: ~ 50 km



The Kvarner Bay area



Site 1: The city center of Rijeka



Site 2: Kraljevica



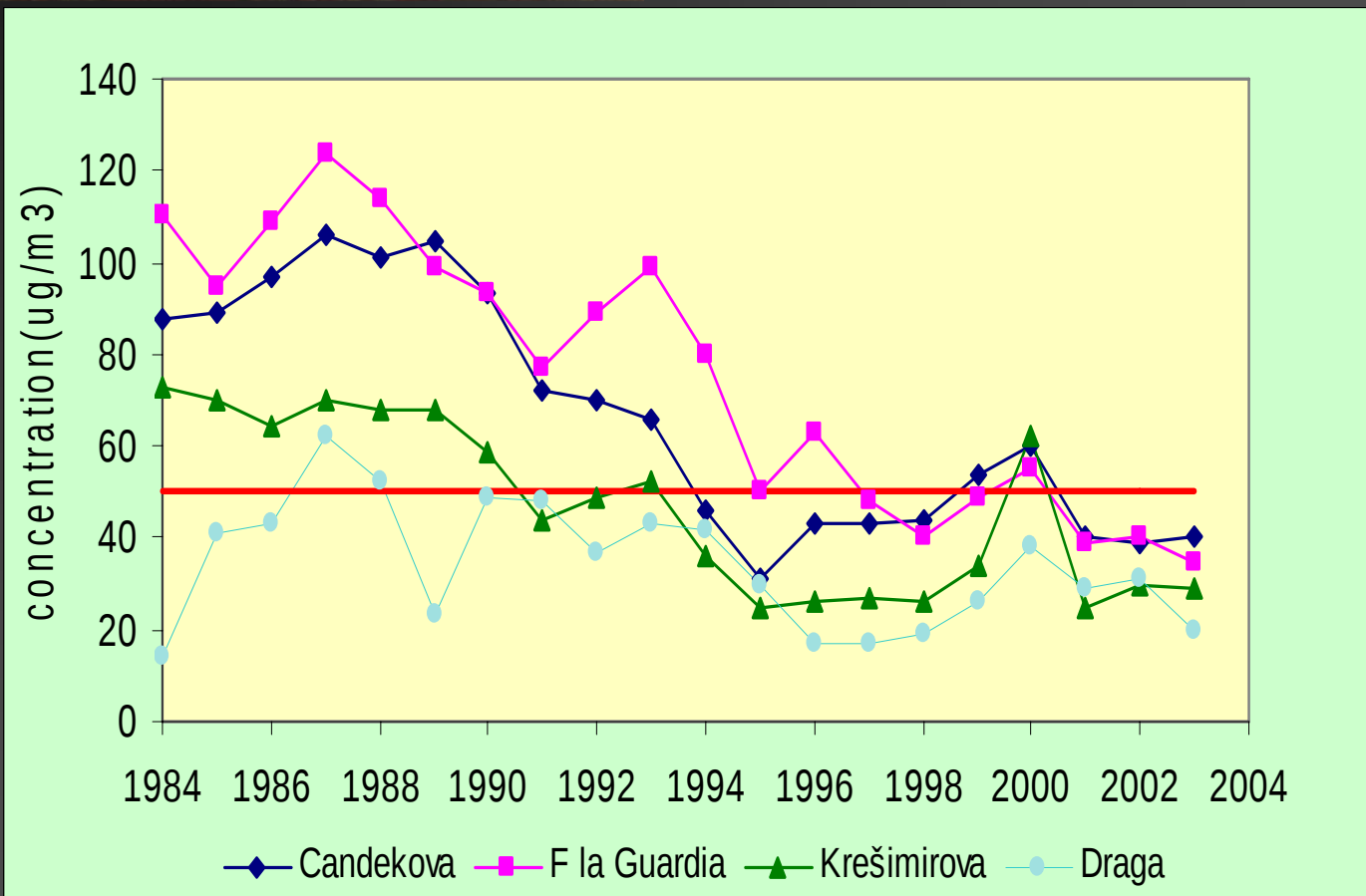
Site 3: Island of Cres



Site 4: Delnice

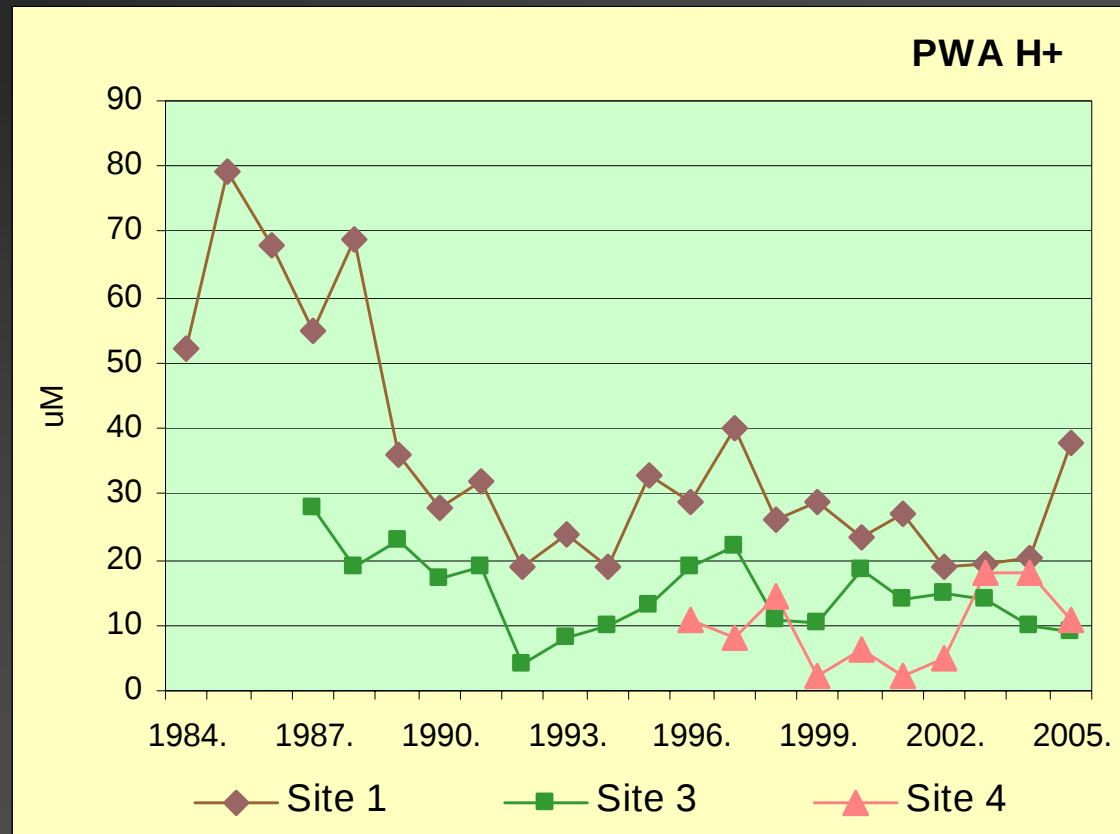


Trends in ambient SO₂ concentrations



Hydrogen ion (precipitation weighted average-PWA)

Site 1: 80 → 20 μM
Site 3: 30 → 10 μM
Site 4: no trend



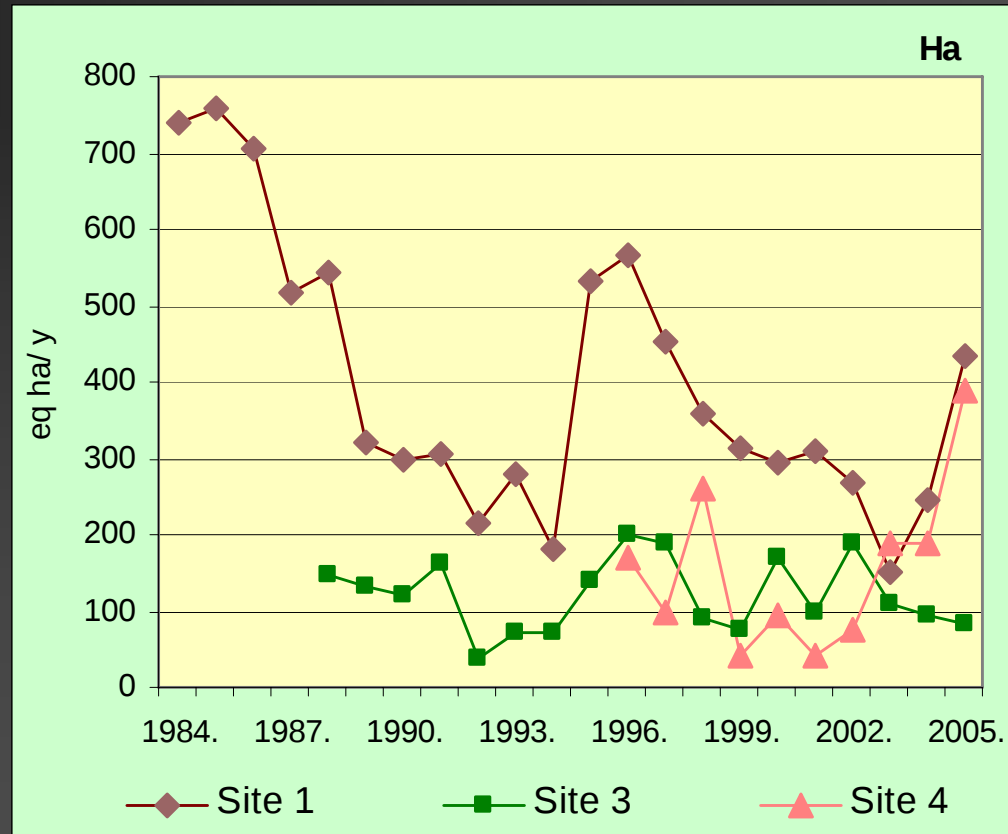
Deposition of hydrogen estimated from pH (Ha)

Site 1: overall decline

Site 3: no trend

Site 4: rise

Last two years?



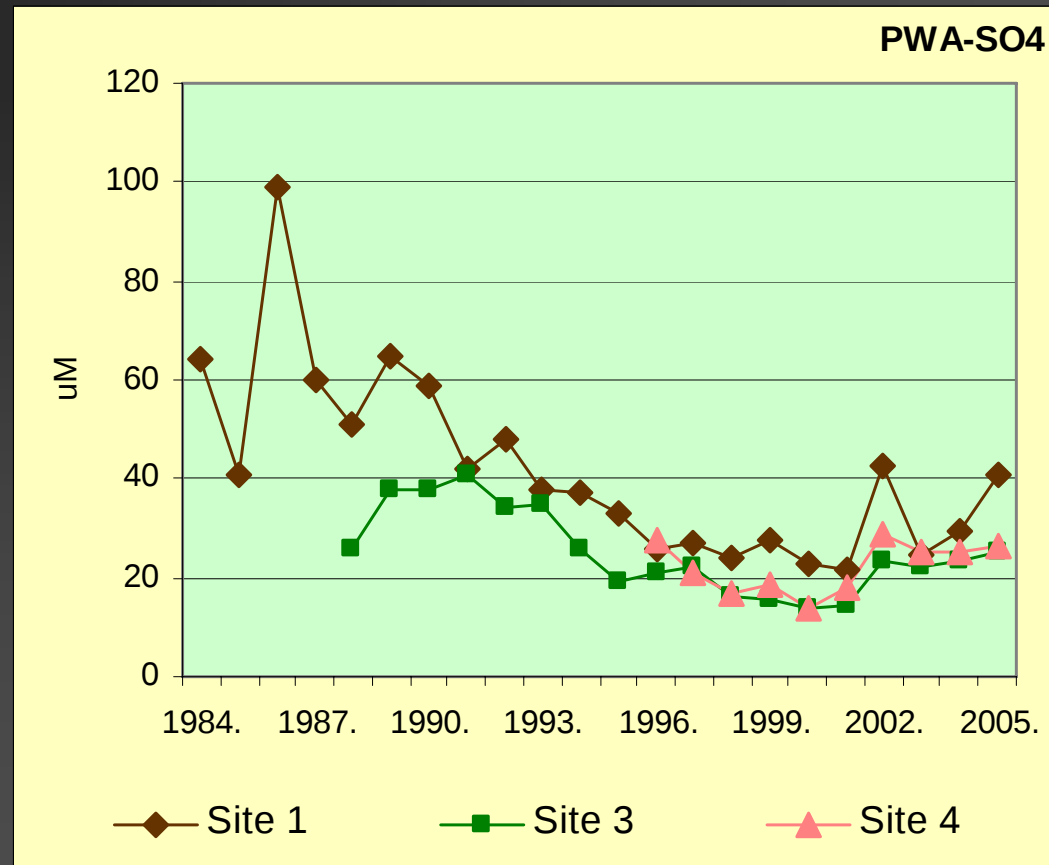
Sulphates

PWA concentrations (μM)

Site 1: 100 $\rightarrow$ 20 μM

Site 3: 40 $\rightarrow$ 20 μM

Site 4: $\sim$ 20 μM



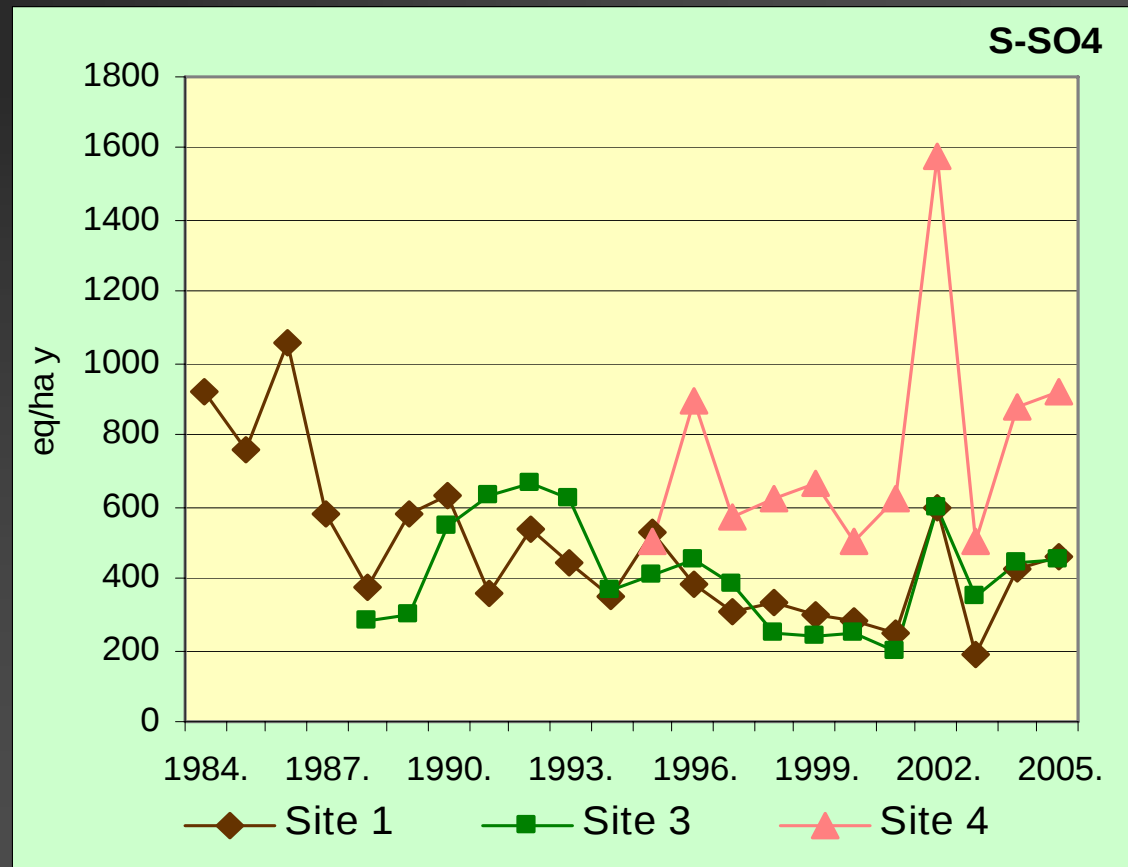
Deposition of S-SO₄ (eq/ha y)

Site 1: 1000-→200
eq/ha y

Site 3: 600-→300
eq/ha y

2004 and 2005?

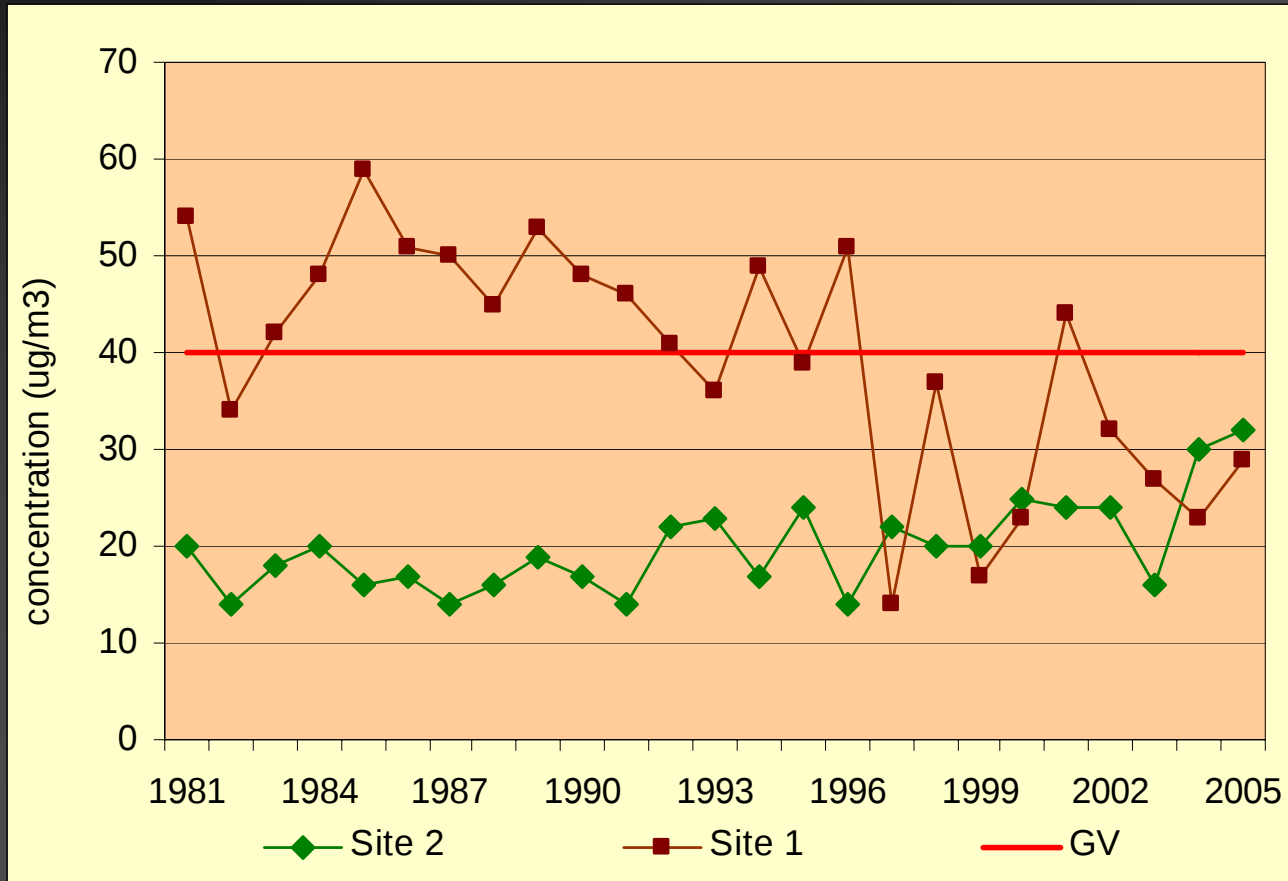
High deposition of
minerals in 2002.



Nitrogenous species

- Slow decrease in ambient NO_2 , almost constant NH_3
 - Emissions of NO_2 :
 - 1989: 4594 t/a (4 industrial sources)
 - 1995: 2764 t/a (-40%), 76% of total 3627 t/a
 - 2000: 3218 t/a (+67%), 53% of total 6047 t/a
 - Ambient NO_2 and NO_3^- in precipitation do not confirm the increased emissions
-

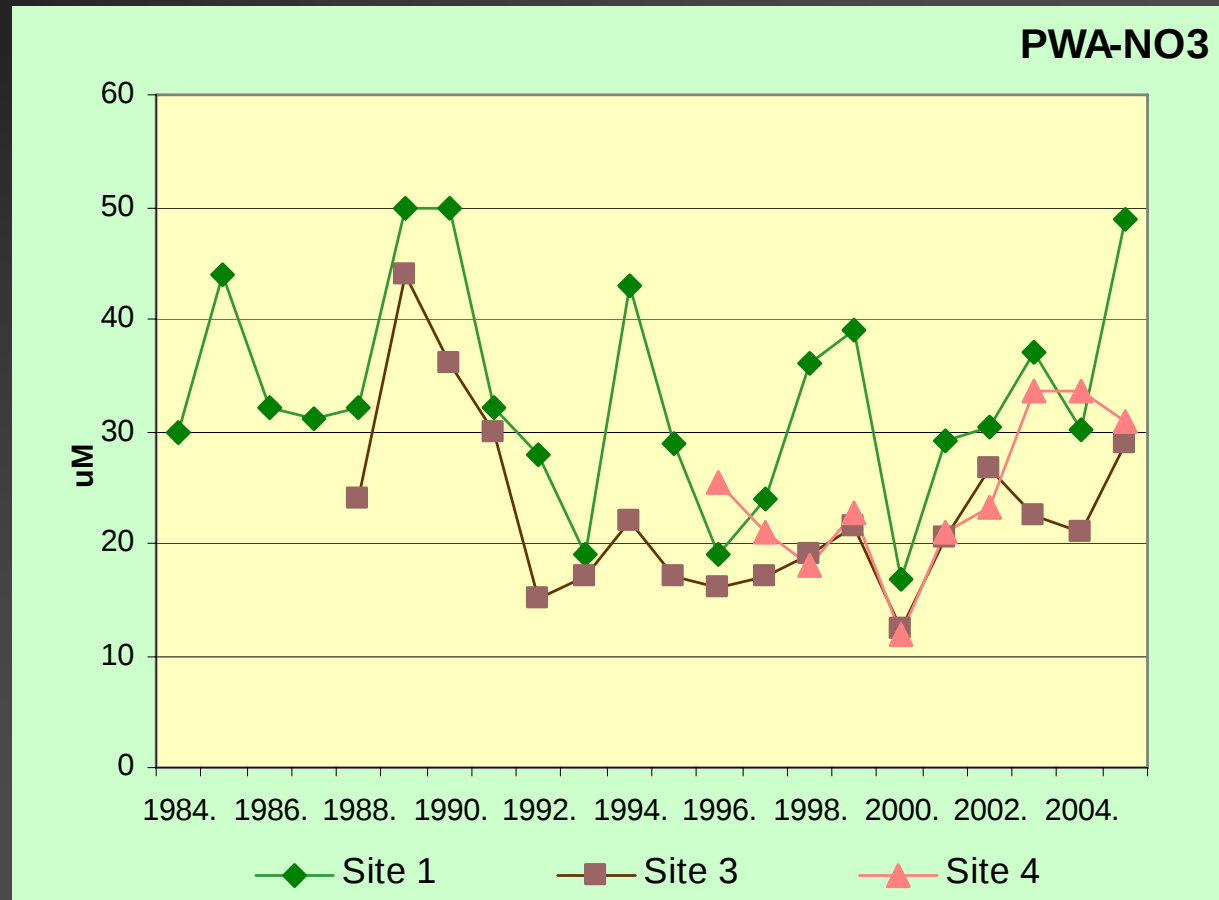
Annual mean NO₂ concentrations



Nitrate

PWA concentrations

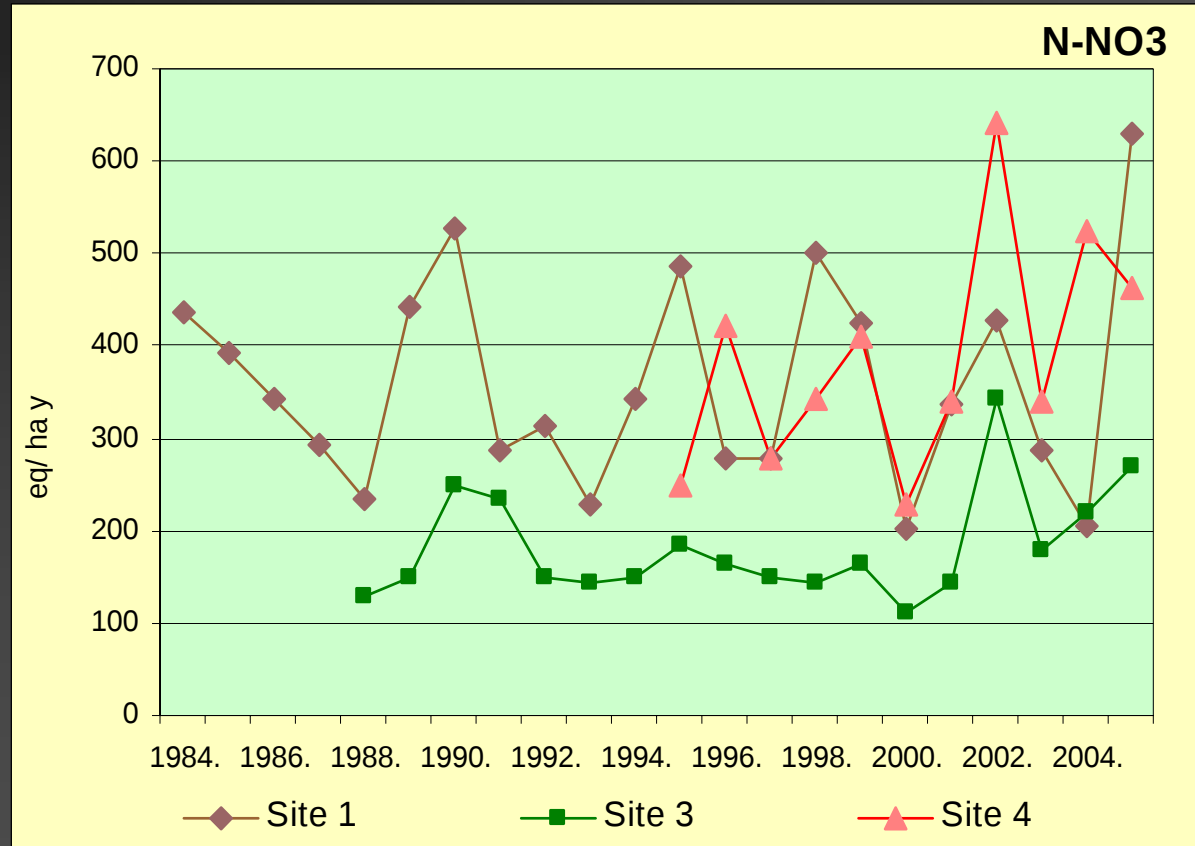
Overall:
Site 4- rise
year 2000 ?



Deposition $N\text{-NO}_3^-$:

All rise

If 2002 excluded:
Site 1 decline



Ammonia

■ Sources:

- Industry, traffic, wood burning
- Bacterial decomposition of urea
- Natural and fertilized soil

■ Emission:

- 1989: 993-1329 t/a from coke battery
 - Other industrial sources and traffic ?
 - 1995: estimated 51-316 t/a from population
-

Chemical analyses

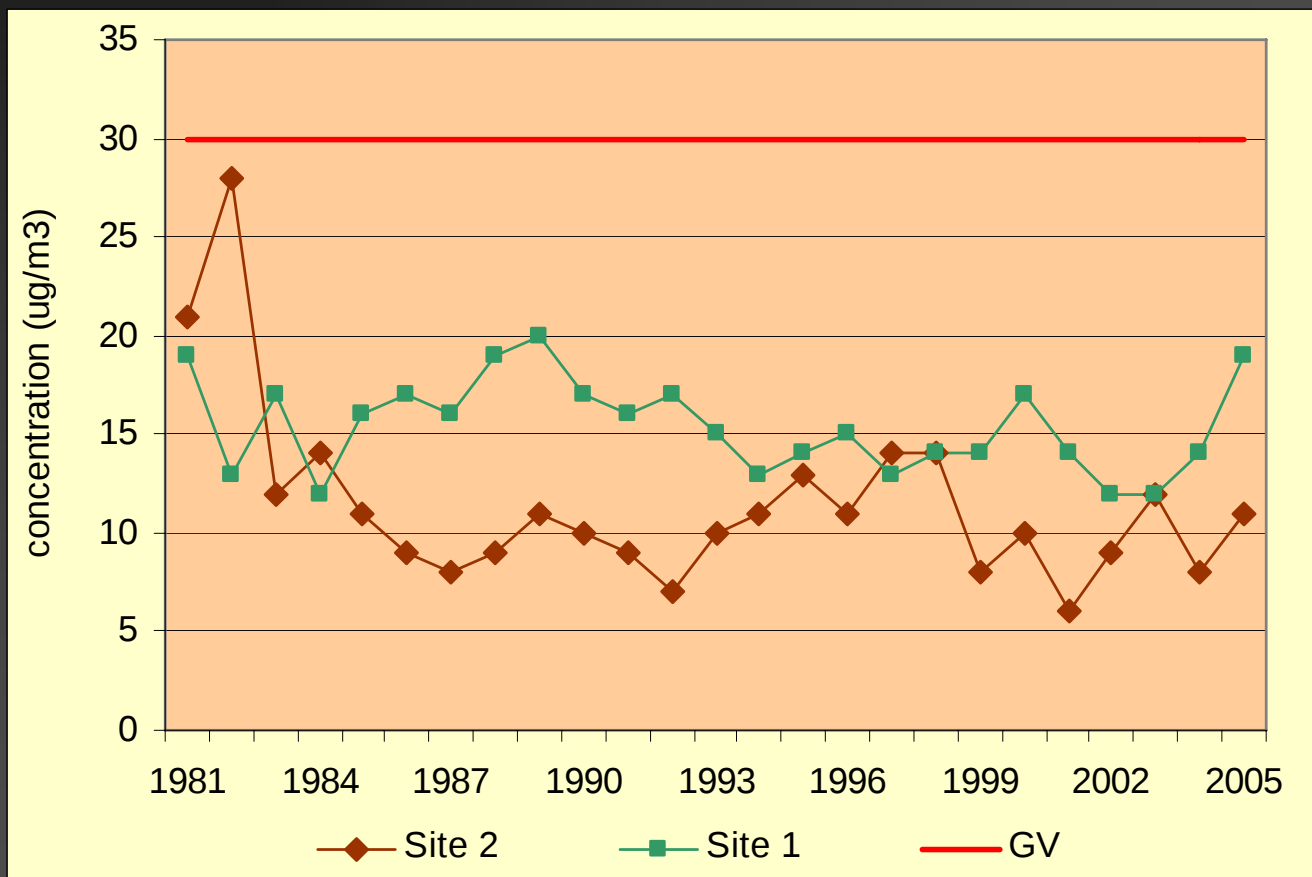
- Airborne ammonia:
 - Sampling: impingers with 0,06% H₂O₂
 - Determination: spectrophotometrically

 - Ammonium:
 - Sampling: open polyethylene buckets
 - Precipitation depth
 - Determination:
 - pH: pH meter
 - Nitrates: spectrophotometrically, LDL= 0.2 mg/L
 - Ammonium: spectrophotometrically, LDL=0.1 mg/L
-

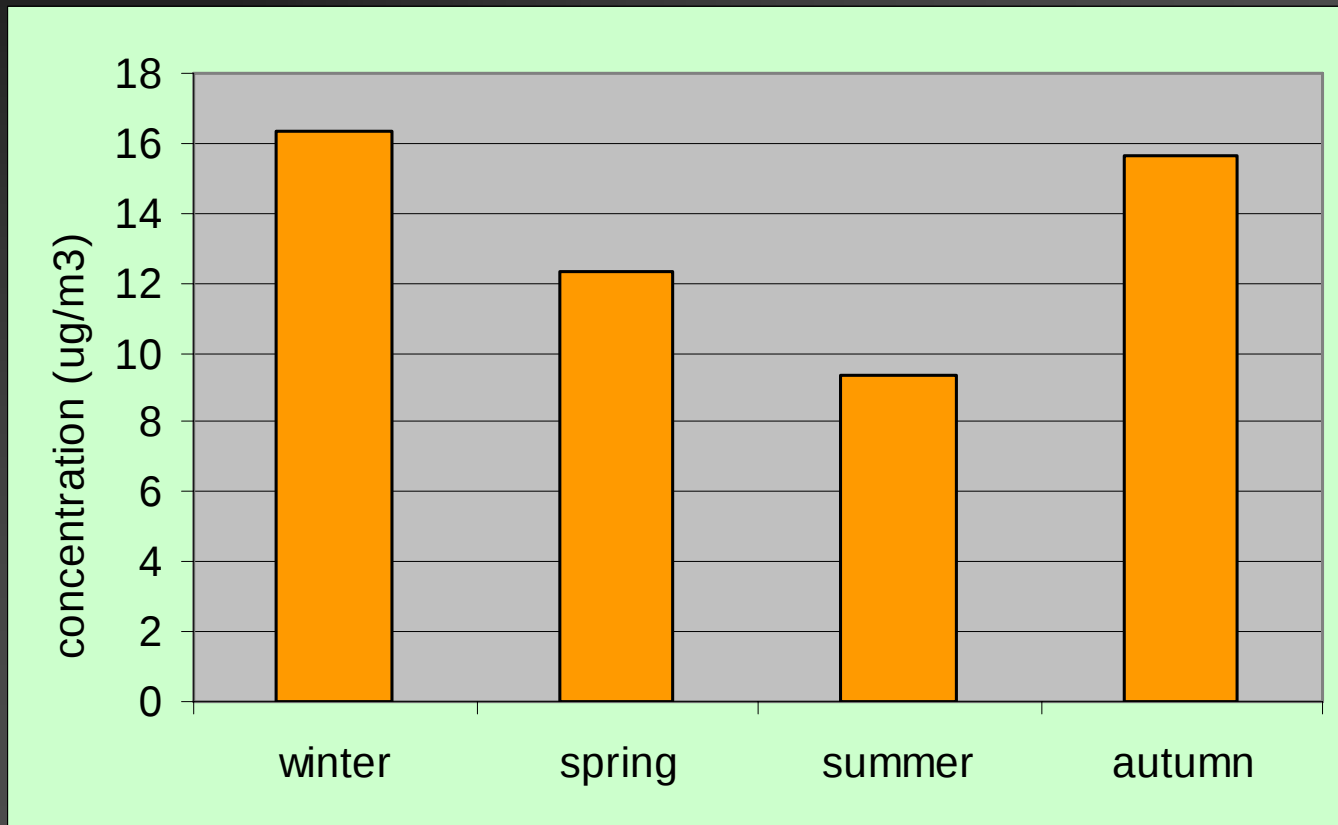


Ammonia

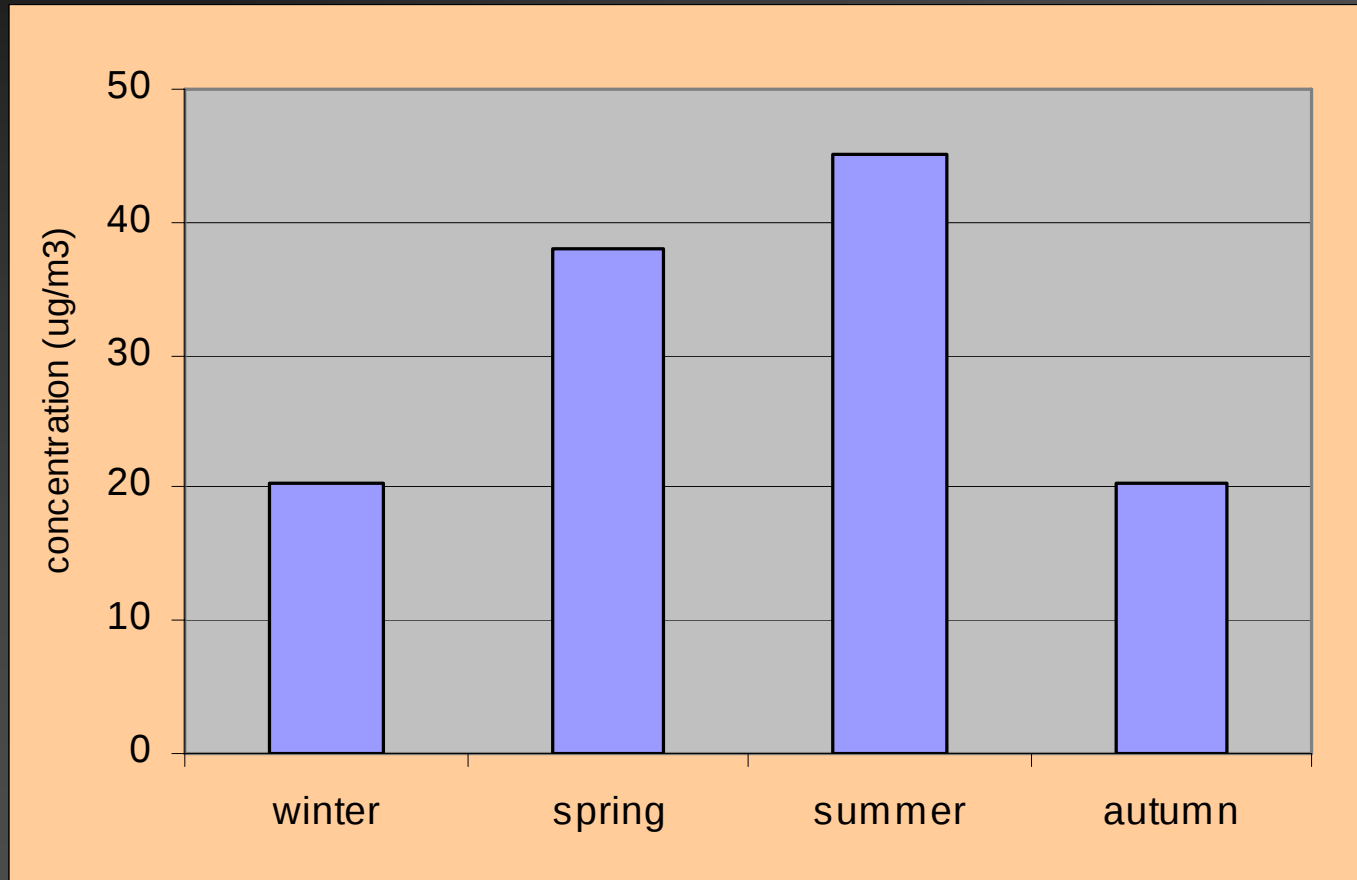
Annual means of NH_3 ($\mu g/m^3$)



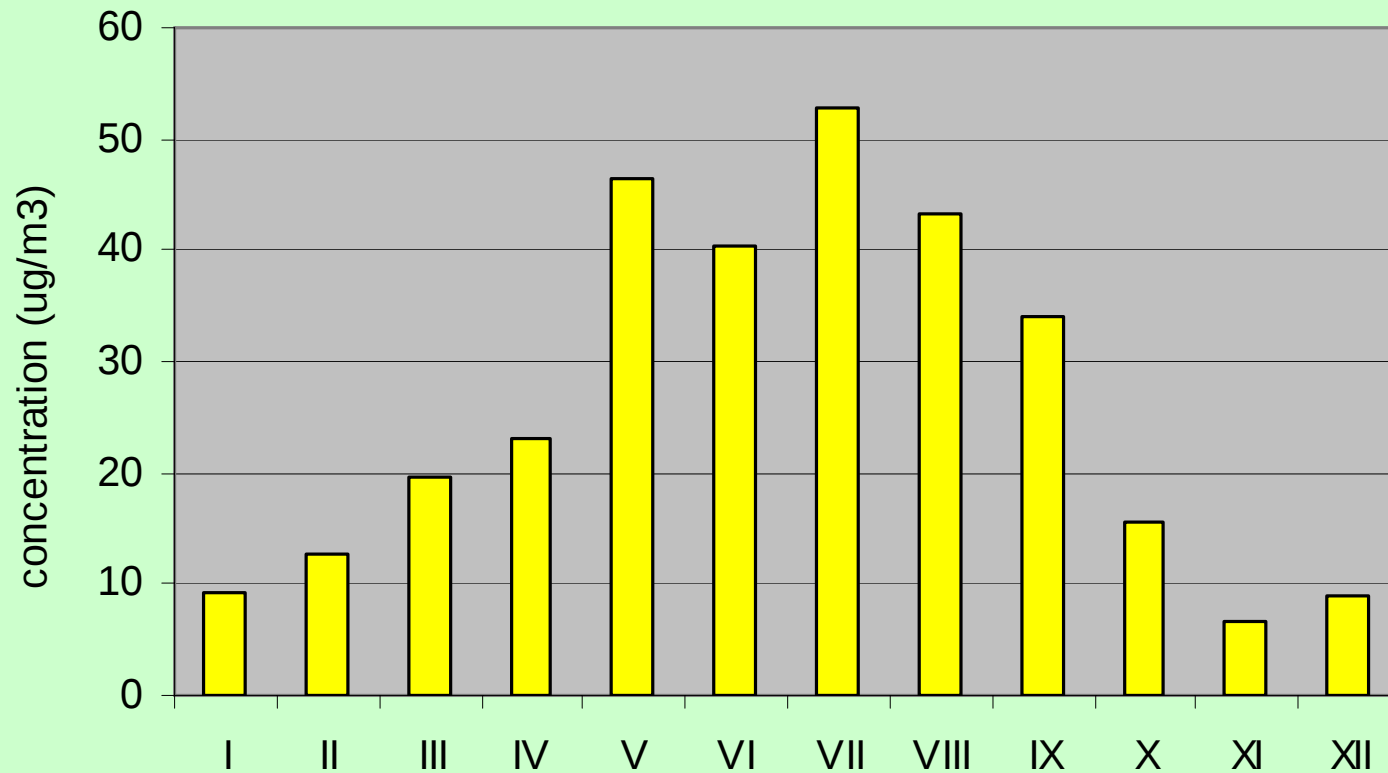
Site 2: Seasonal NH_3 concentrations, 2000-02



Seasonal NH_3 conc., remote site, 2000-02



Annual NH_3 profile, remote site, 2001

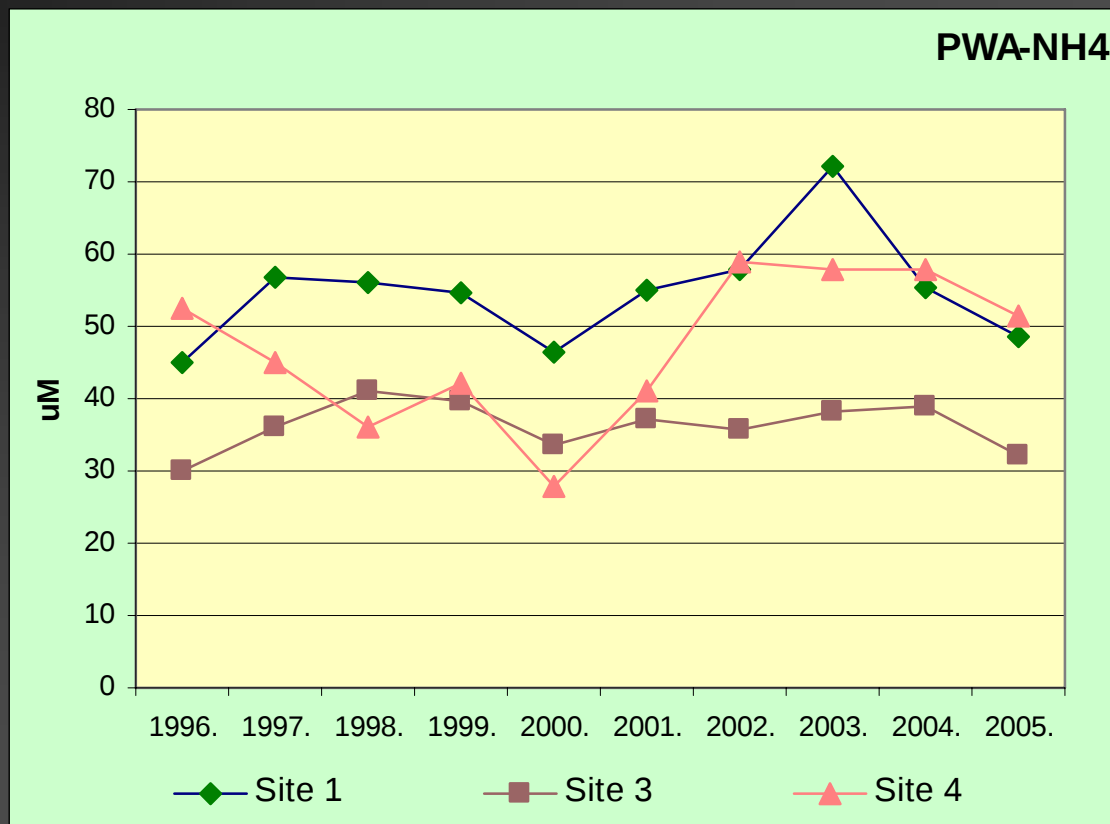


Precipitation

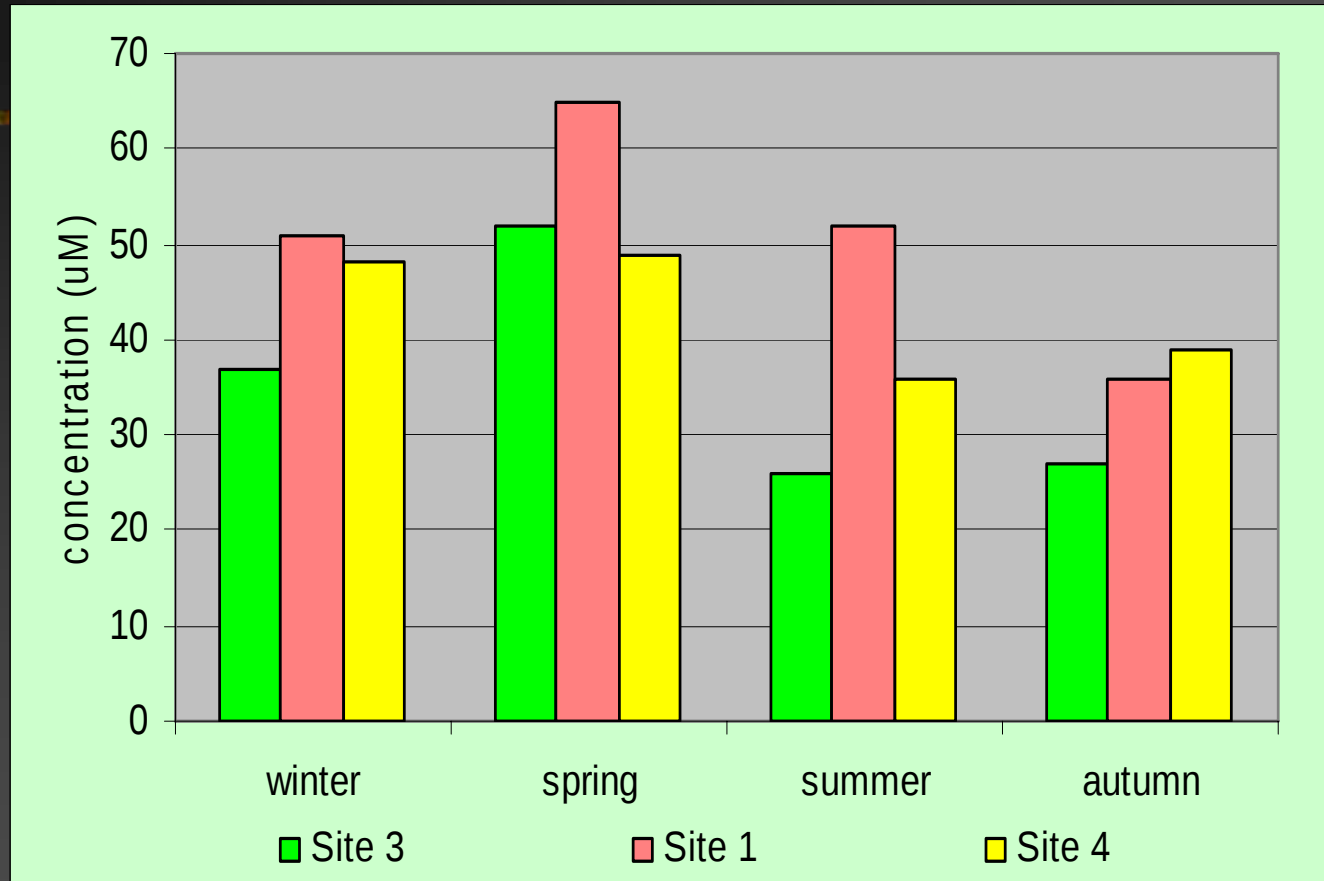


PWA concentrations of ammonium:

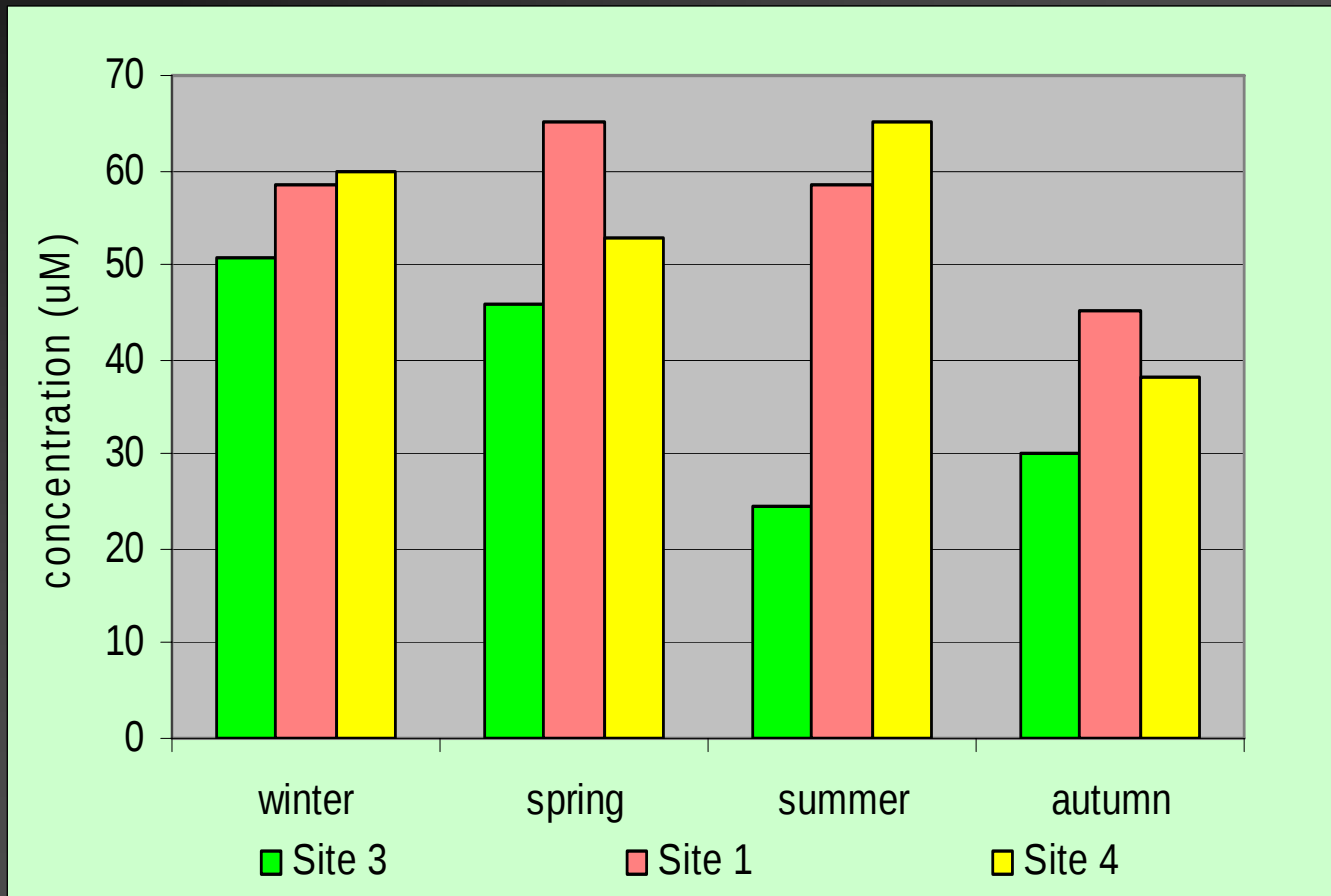
Upward trend
with and
without 2002.



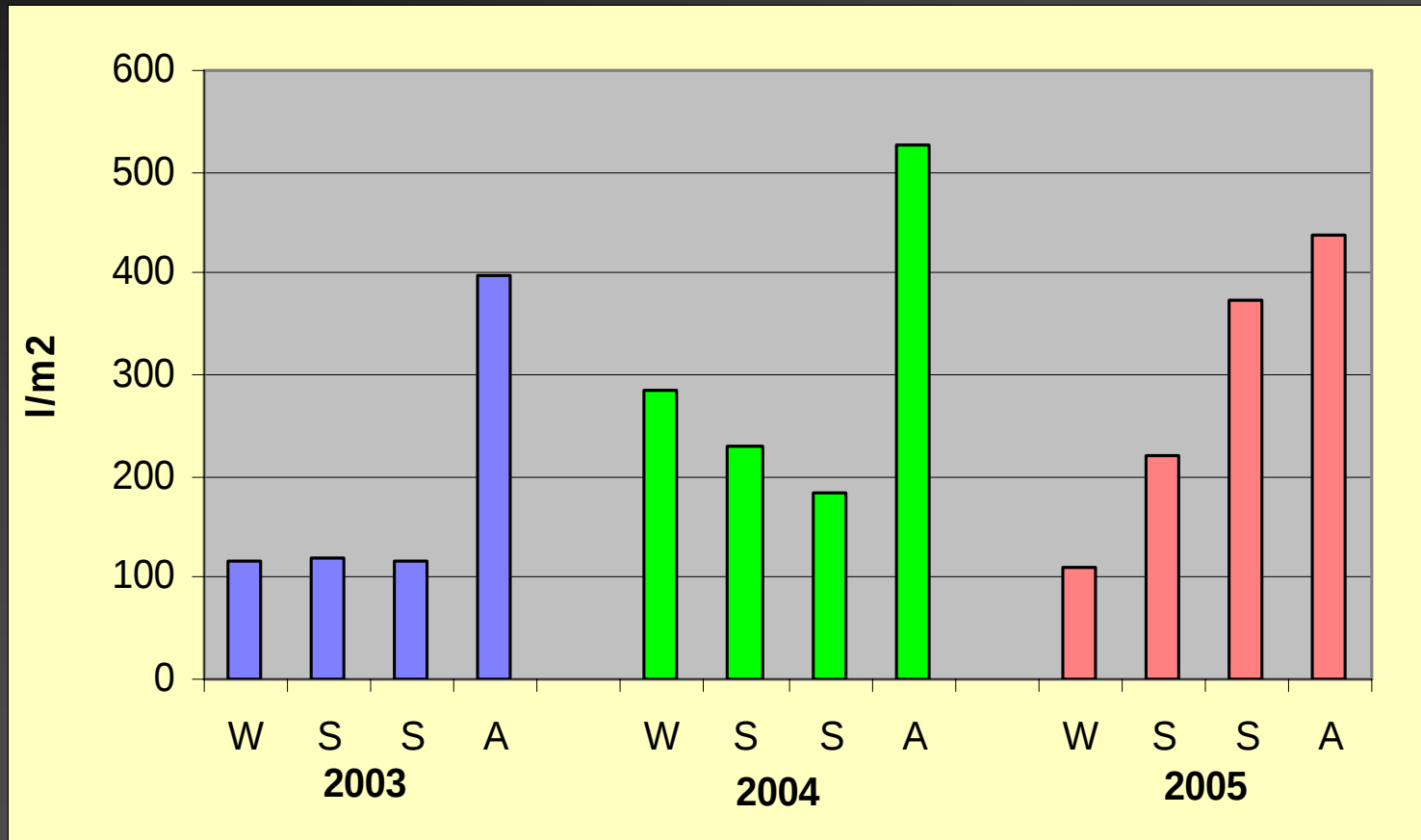
Seasonal distribution of ammonium (μM)-2005



2003-2005:



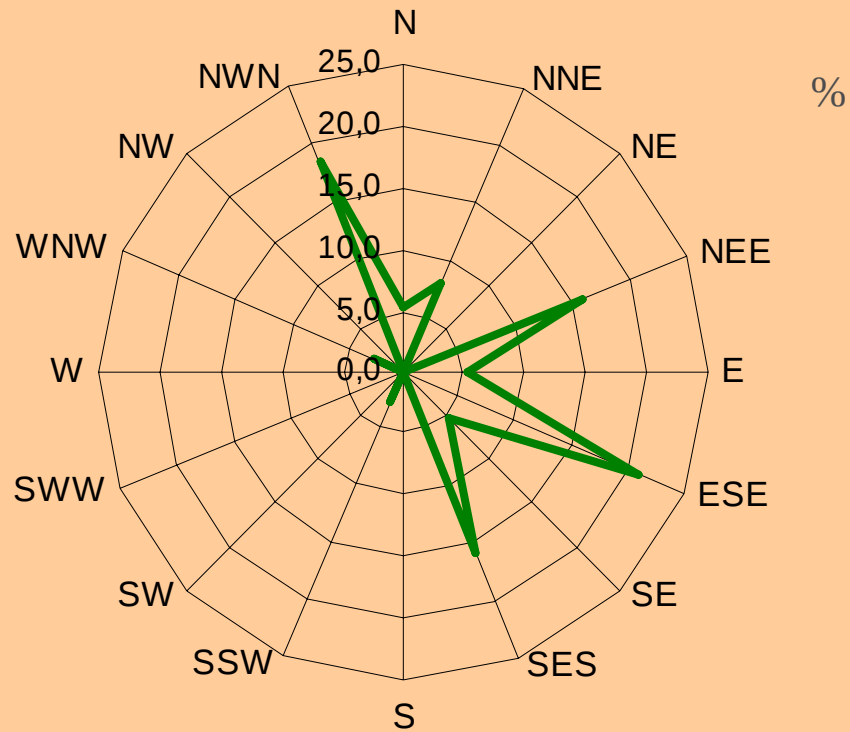
Site 1: Precipitation pattern



Air mass back trajectories

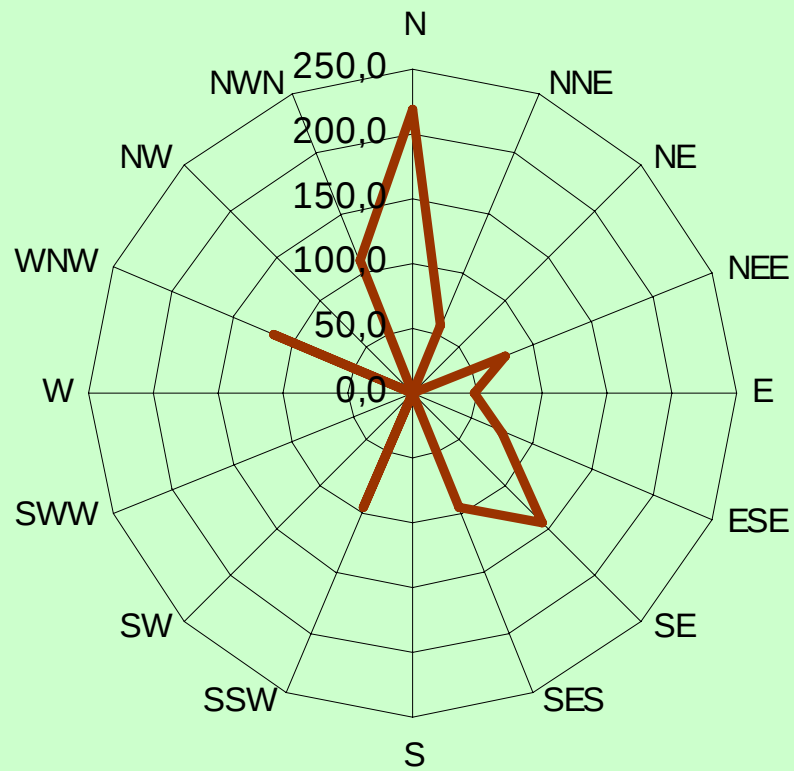
Site 1

Precipitation

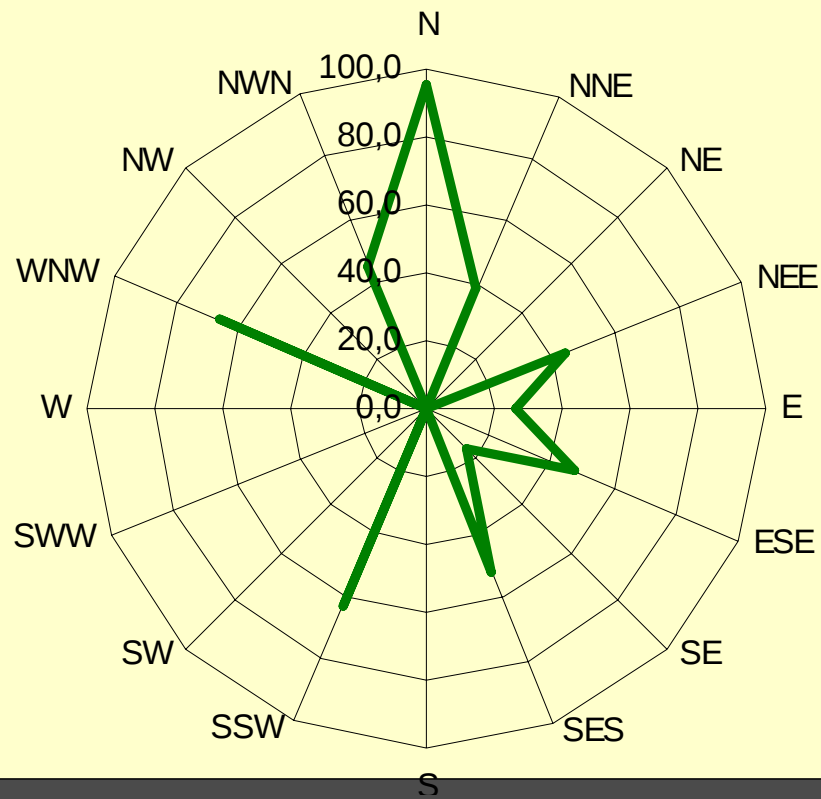


2003 year

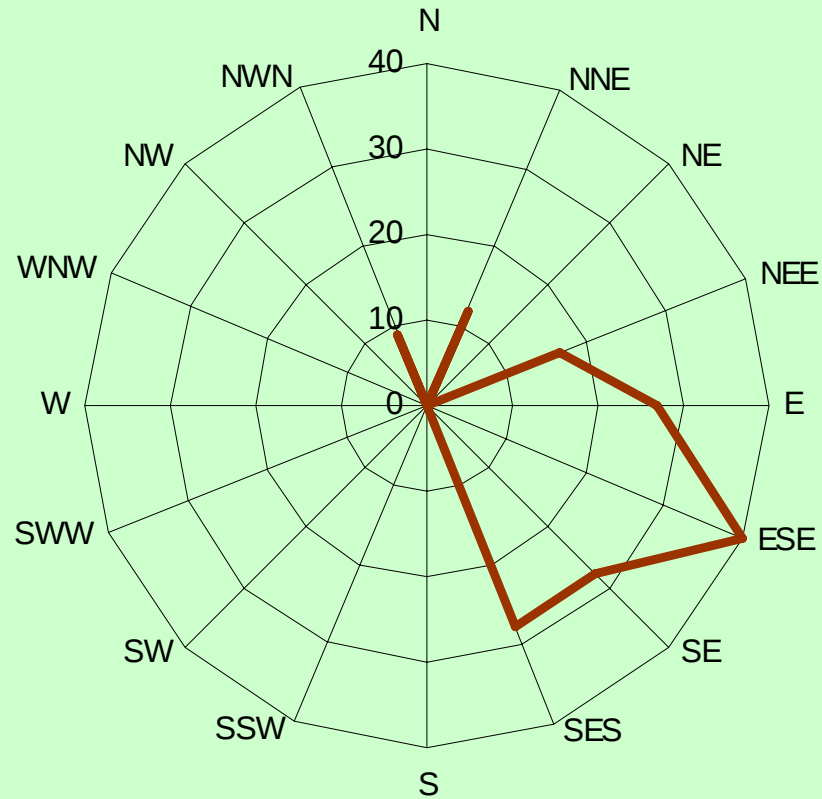
Ammonium (μM)



Nitrate (μM)

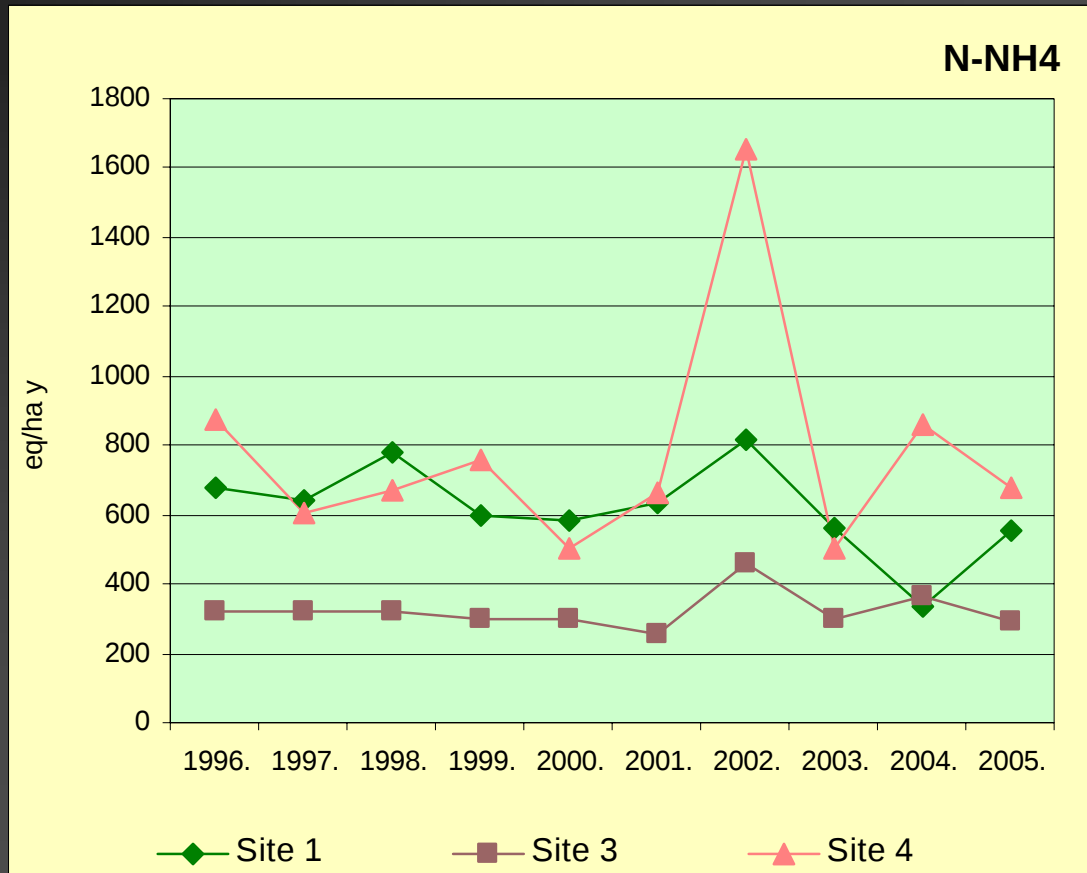


Sulphate (μM)



Deposition $N\text{-NH}_4^+$:

Site 1 decline
If 2002 excluded,
all decline



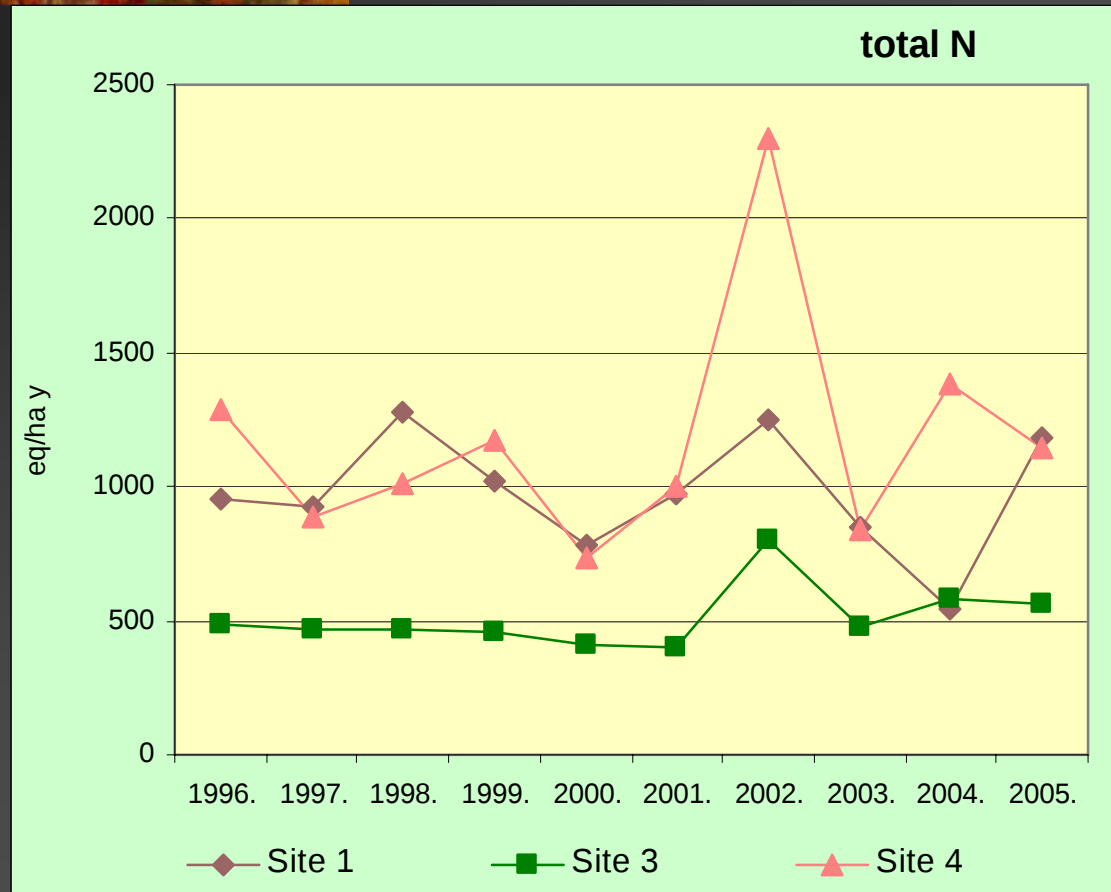
Total N

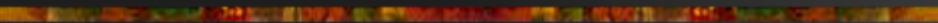
Deposition:

2/3 : N-NH₄

1/3 : N-NO₃

Slight rise in
both cases

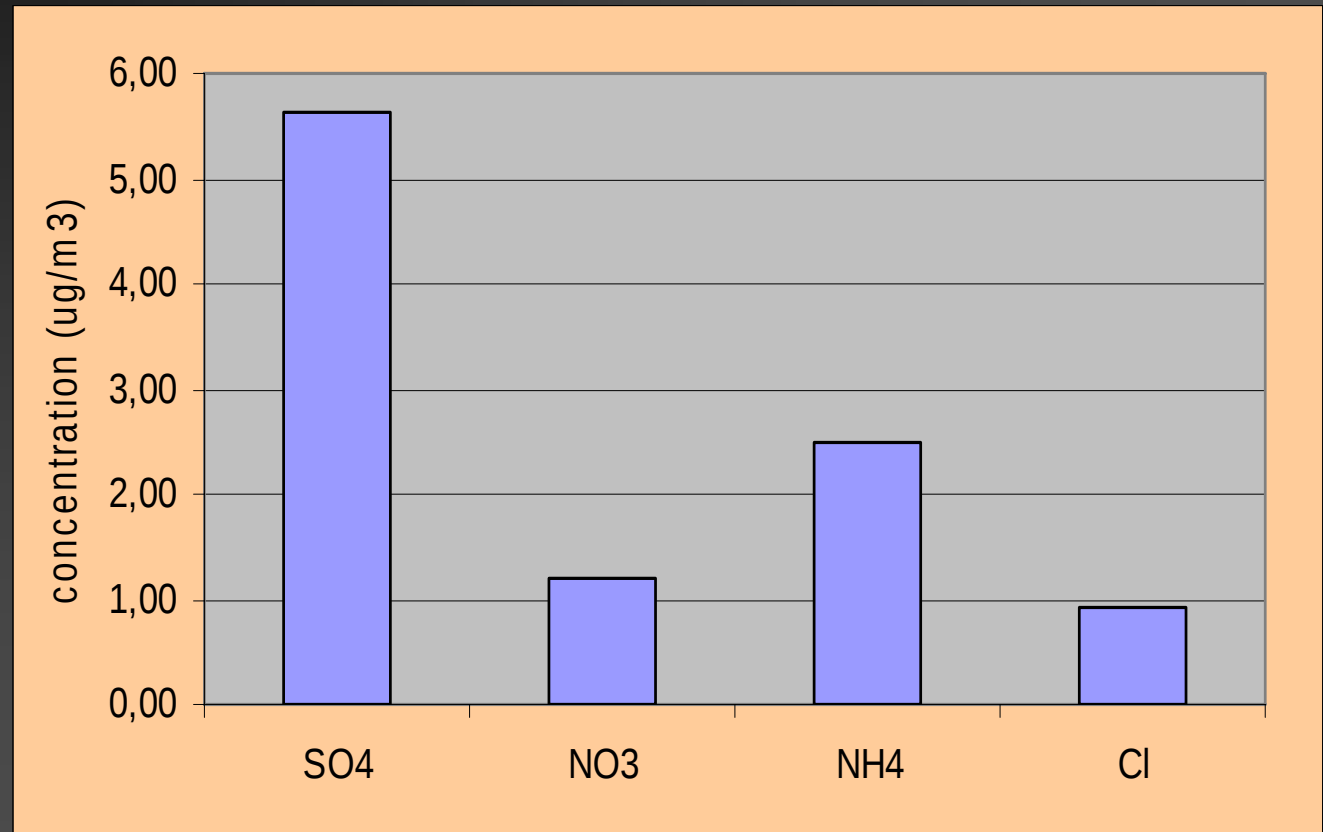


- 
- Generally, decline in PWA and deposition of N species less certain than H^+ and SO_4^{-2}
 - Austria: no trend in $N-NO_3$, slight increase in $N-NH_4$
 - Spain and Japan: no trend in N deposition
- 

Ammonium in PM₁₀

N=20

Summer
values



Conclusions:

- Airborne ammonia within the Rijeka bay are low with hardly any trend over 25 y period. A possible reason –reactivity?
- A weak decline in deposition of NH_4 , if 2002. data excluded
- Similar deposition of NH_4 (and NO_3) at Sites 1 and 4 due to different reasons:
 - Local washout of the atmosphere at Site 1
 - Higher precipitation depth at Site 4
- The latter confirmed by PWA concentrations

Source or sink?

