Seasonal changes in stable nitrogen isotopic composition in fine aerosols at a rural background station Košetice (Central Europe).

Petr Vodička[1,2], Kimitaka Kawamura[2], Jaroslav Schwarz[1],

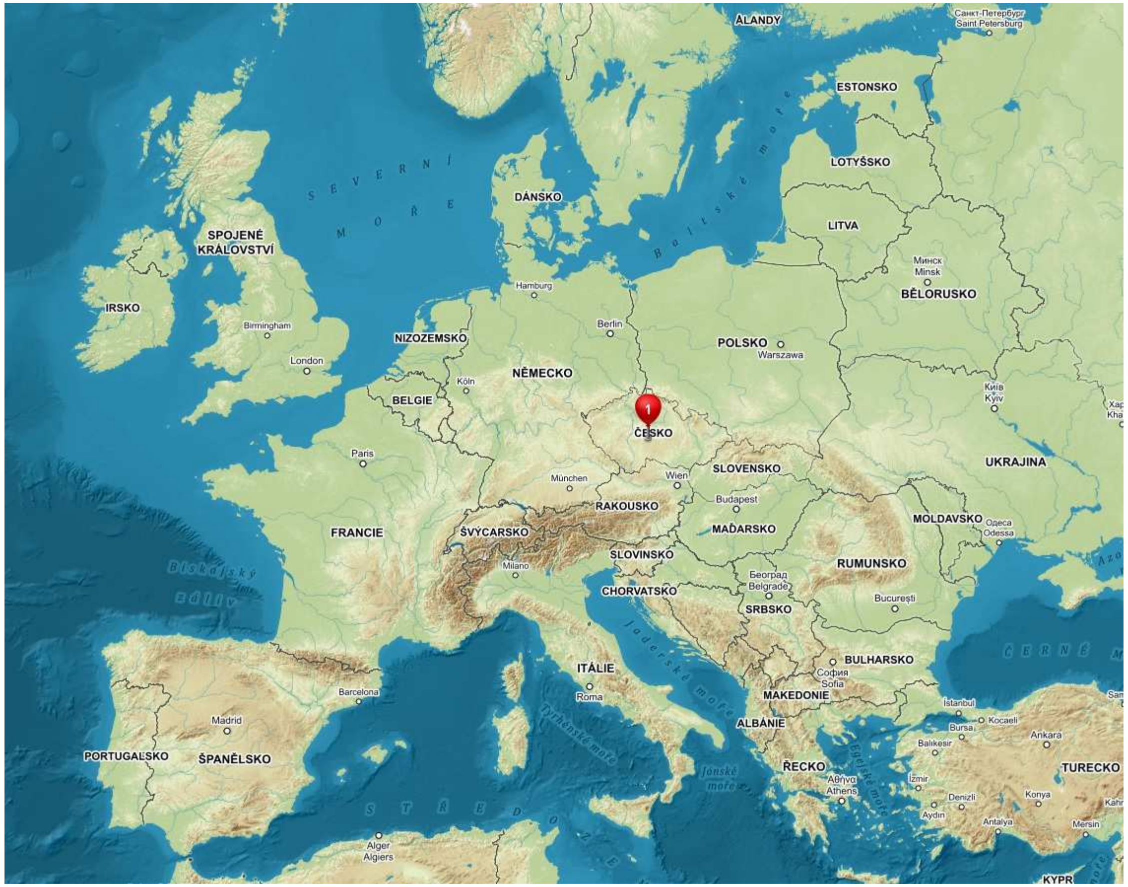
Bhagawati Kunwar[2], Vladimír Ždímal[1]

1) Institute of Chemical Process Fundamentals of the Czech Academy of Science, Department of Aerosols Chemistry and Physics, Czechia
2) Chubu Institute for Advanced Studies, Chubu University, 1200 Matsumoto-cho, Kasugai 487–8501, Japan

EGU2020-3469

Site – Košetice Observatory

Central European rural background site
Characteristic: agricultural landscape and forests, out of range of major soureces of pollution
location: N: 49° 34' 24.13'' E: 14° 4' 49.67'' Altitude: 534 m ASL



Sampling

- PM1 aerosol fraction, quartz fiber filters
- Period: 27 Sep 2013 – 9 Aug 2014 (every 2nd day)
- 146 samples with 24-h time resolution

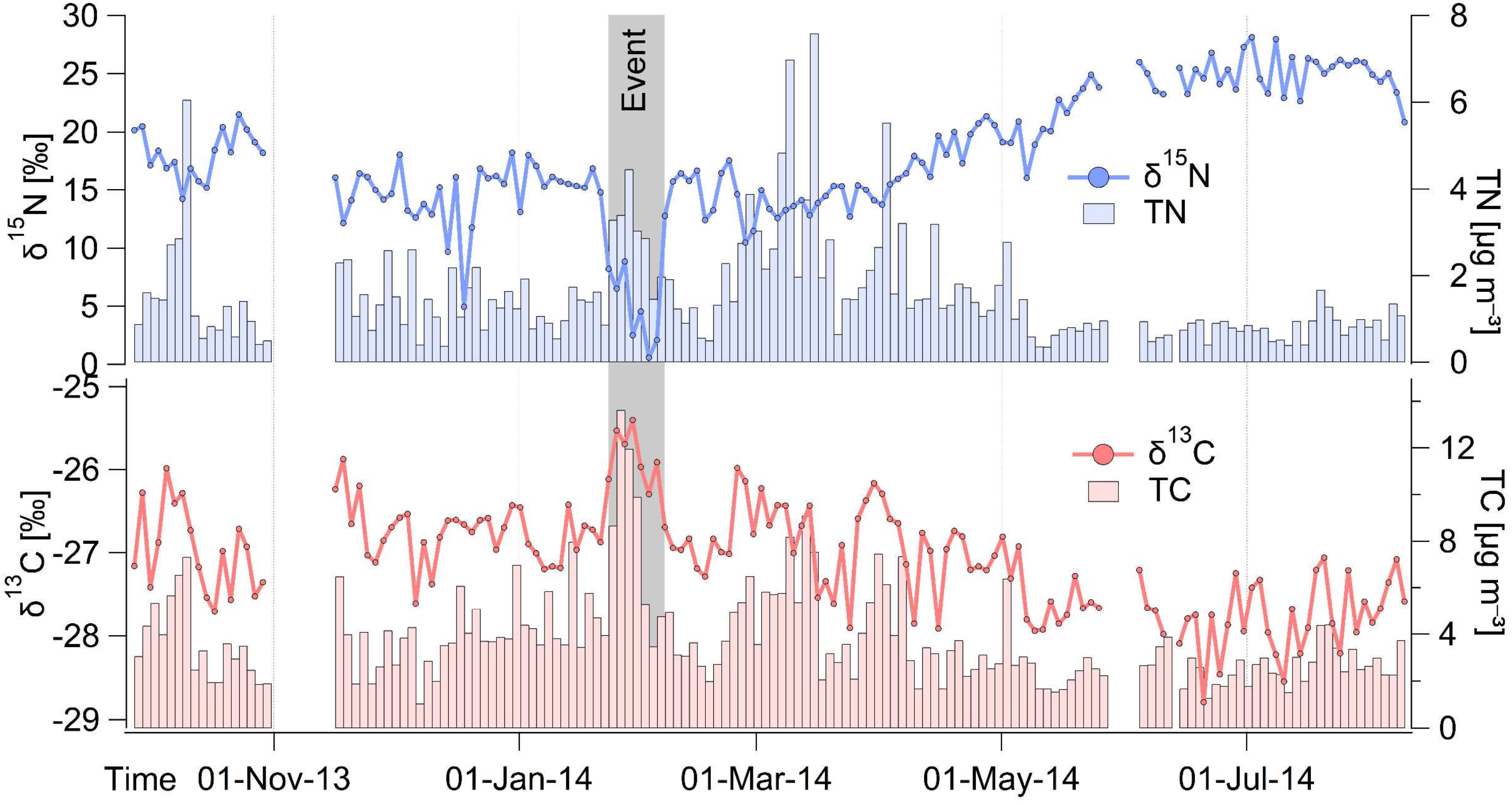
Analyses

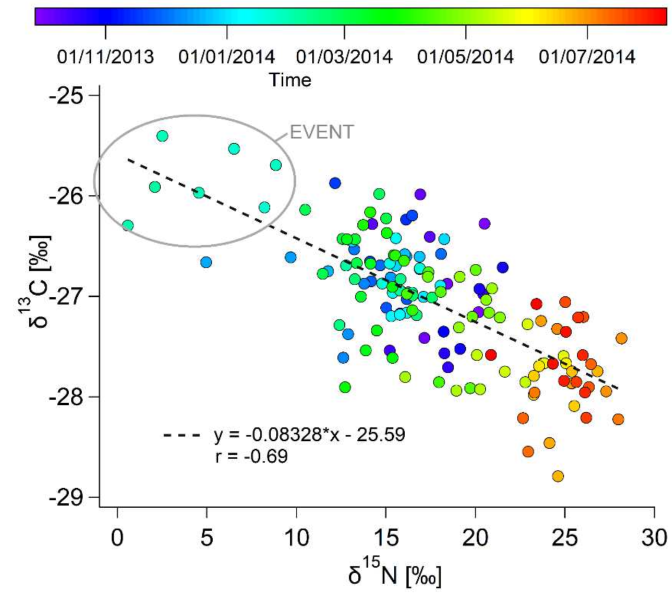
- TC, TN, $\delta^{13}C$ and $\delta^{15}N$
- PM1 mass weight (±1 μg)
- Ion chromatography: anions (SO_4^{2-}, NO_3^-, Cl^-, NO_2^-, oxalate) and cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+})
- $OrgN = TN – 14*[NO_3^-/62 + NH_4^+/18]$
- meteorological data (wind speed and direction, relative humidity, temperature, pressure, solar radiation) and trace gasses (SO_2, CO, NO, NO_2, NO_X, O_3).

Time series - TN, $\delta^{15}N$ (blue), and TC, $\delta^{13}C$ (red)

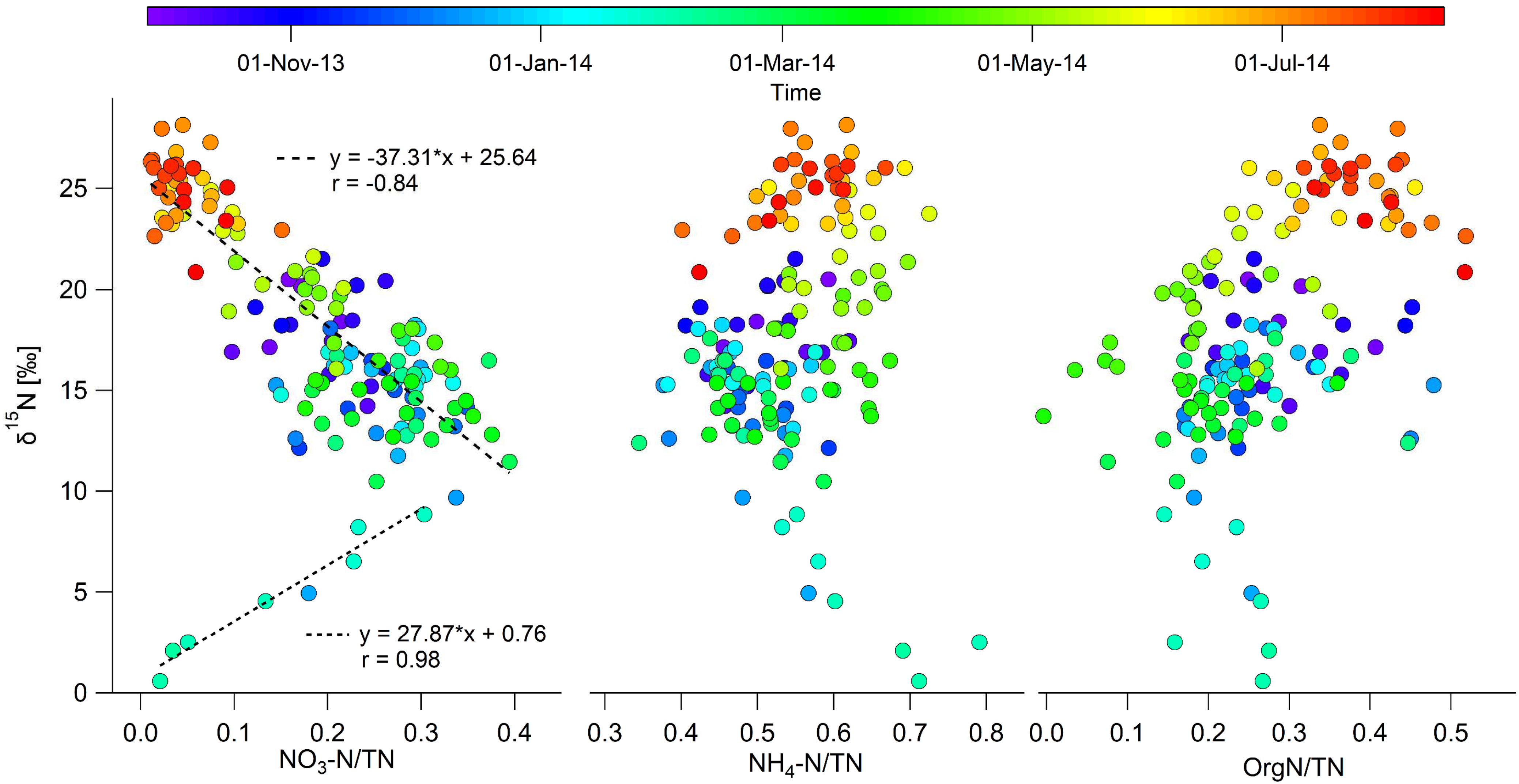
$\delta^{15}N$
Min.: 0.6‰
Max.: 28.2‰

$\delta^{13}C$
Min.: -28.9 ‰
Max.: -25.4 ‰



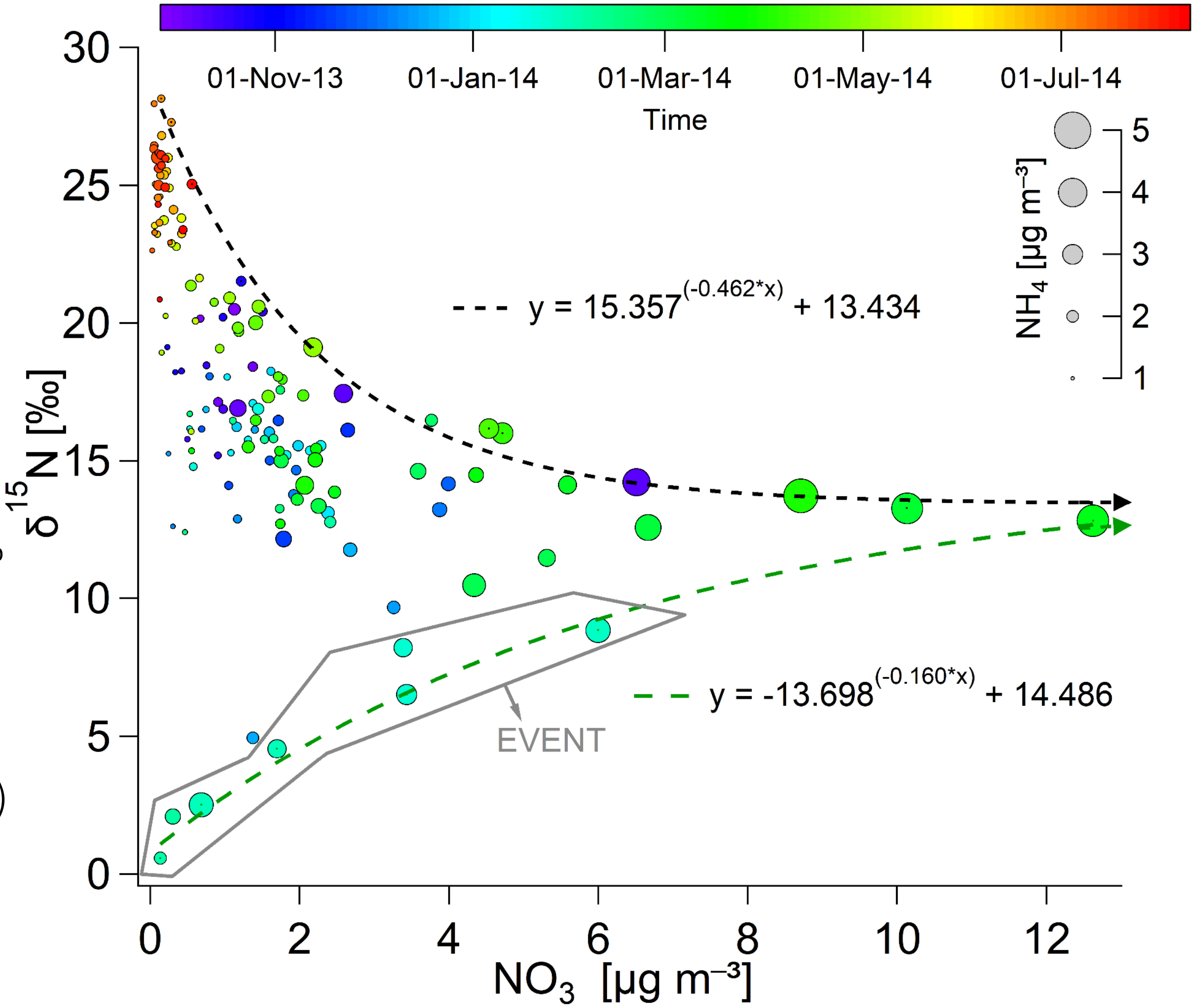


$$\delta^{15}N_{TN} = \delta^{15}N_{NO3}*f_{NO3} + \delta^{15}N_{NH4}*f_{NH4} + \delta^{15}N_{OrgN}*f_{OrgN}$$

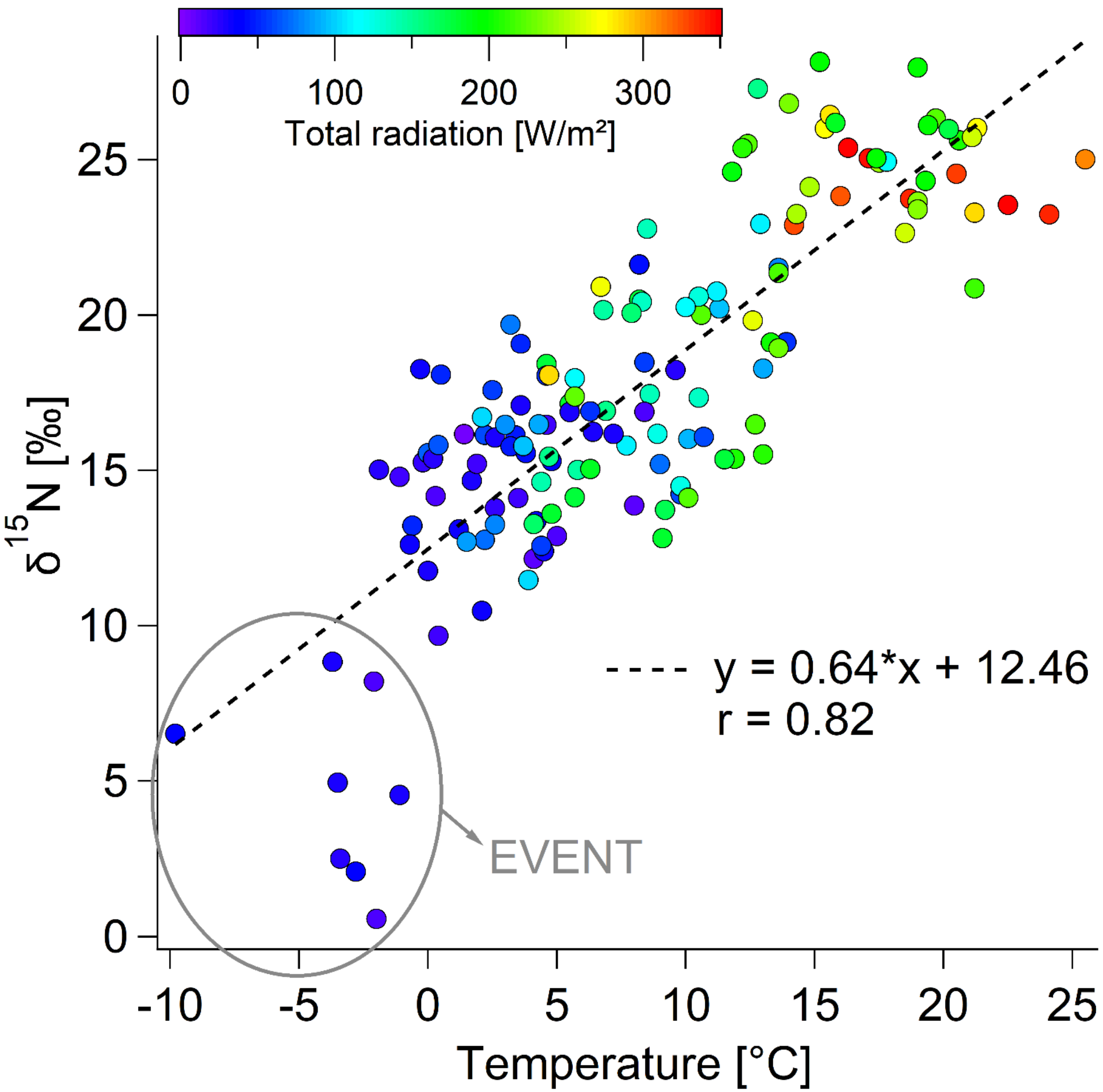


$\delta^{15}N$ vs. NO3

- NO_3 in PM1 mainly from NH_4NO_3
- $NH_4NO_3(s,aq) \leftrightarrow NH_3(g) + HNO_3(g)$
- NO_3 amount drive an exponential changes in $\delta^{15}N$
- NO_3 reach values around 14‰ … similar to other studies where sources are coal or biomass burning.
- Different process (mechanism) during the Event and the majority of data



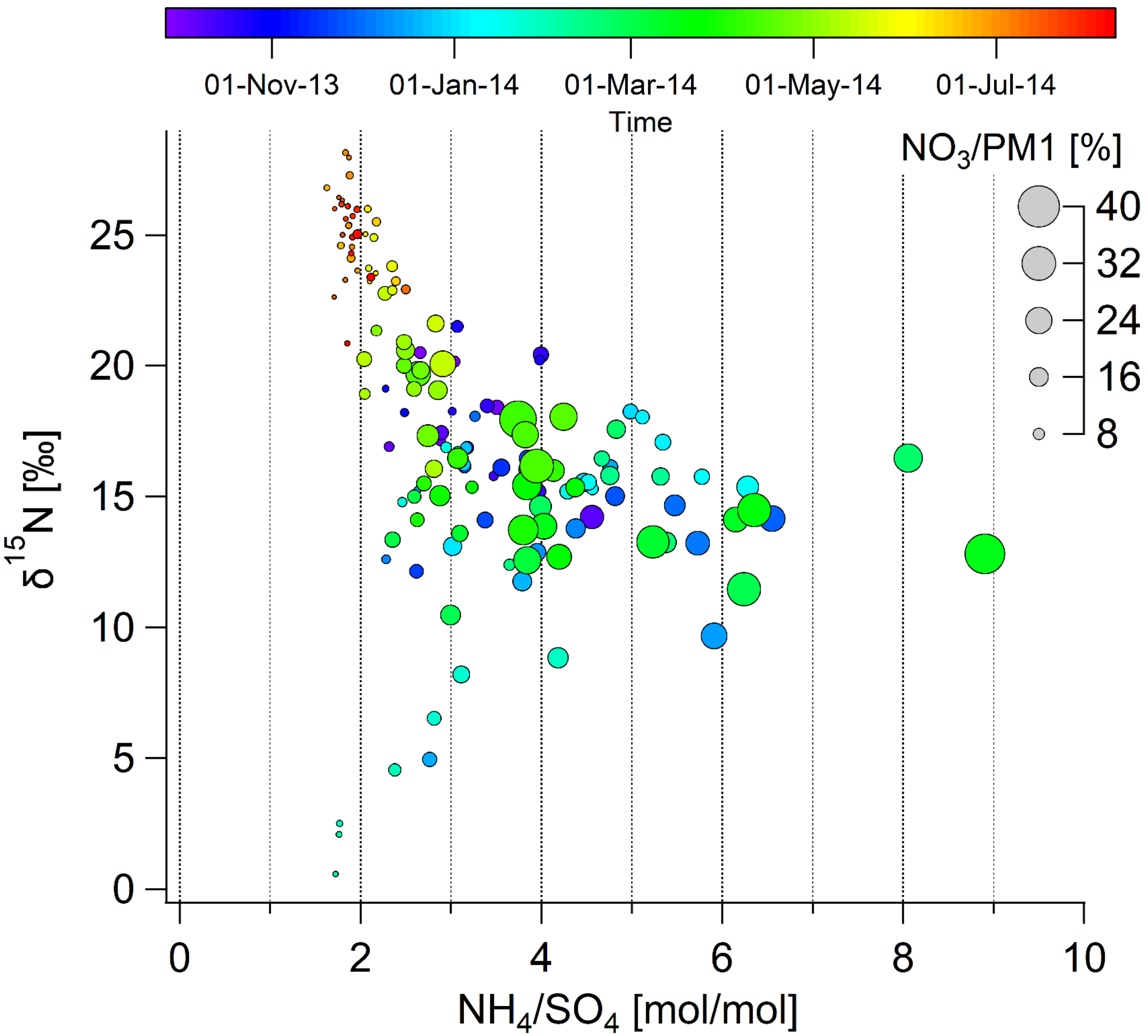
$\delta^{15}N$ vs. temperature



- Studies> diff. dependence of $\delta^{15}N$ on temp. for NO_3 and NH_4
- Temp. drive equilibrium $NH_3(g) \leftrightarrow NH_4(p)$. … it is stopped in winter and summer

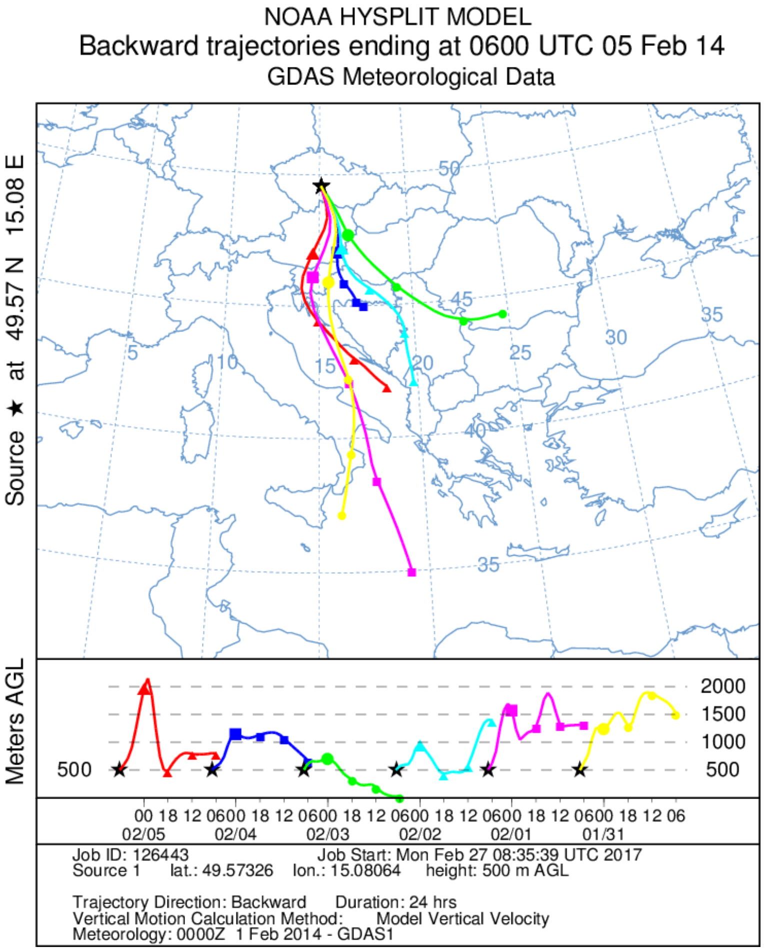
Corr.>	$\delta^{15}N$ vs. Temp.	$\delta^{15}N$ vs. NO3-N/TN	$\delta^{15}N$ vs. NH4-N/TN
Year	**0.82**	**-0.77**	**0.42**
Autumn	**0.58**	-0.39	0.16
Winter	0.30	-0.04	-0.30
Spring	**0.52**	**-0.73**	**0.60**
Summer	-0.21	-0.26	**0.52**
Event	-0.43	**0.98**	**-0.86**

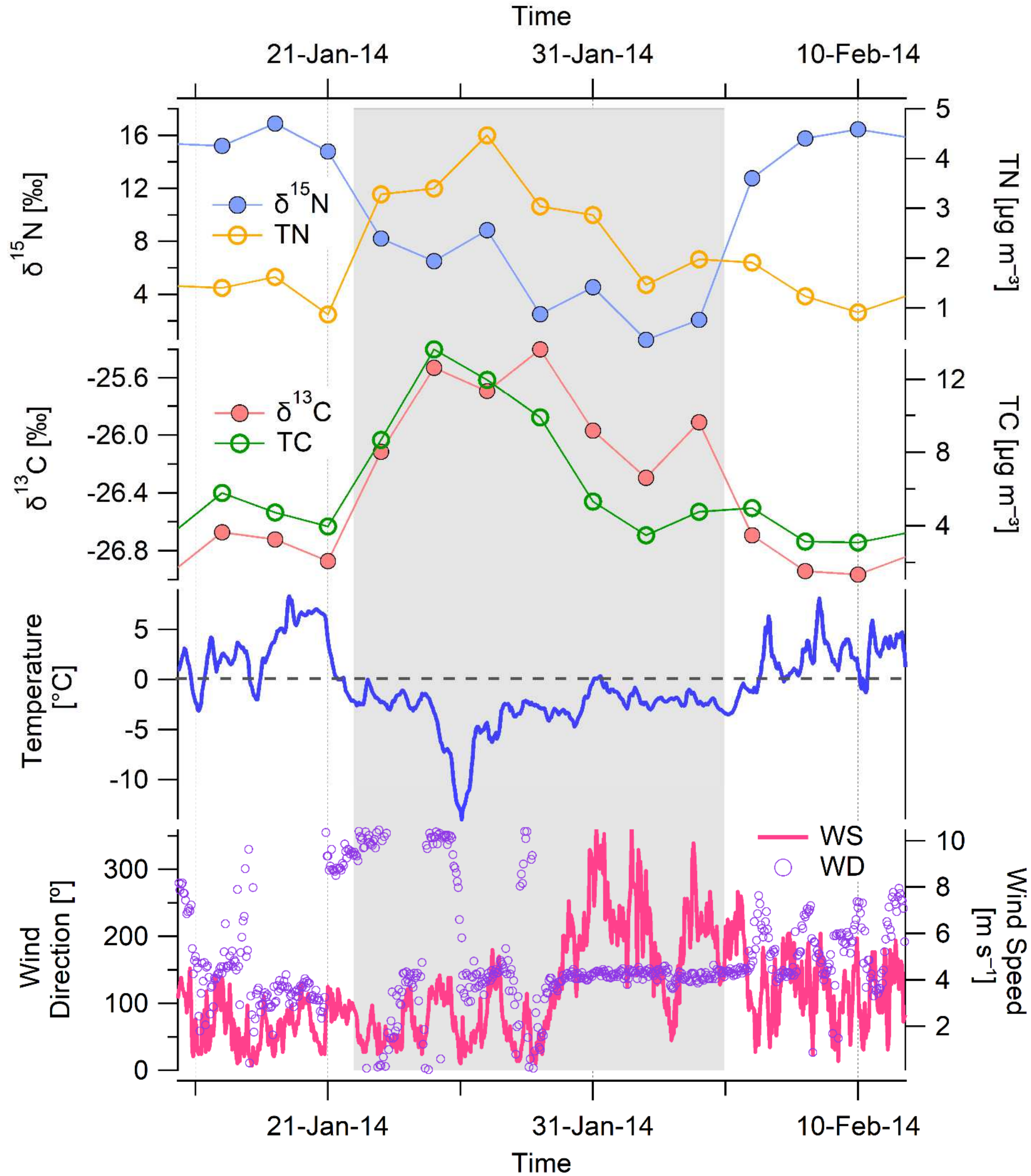
$\delta^{15}N$ in TN and molar ratios of NH_4^+/SO_4^{2-}



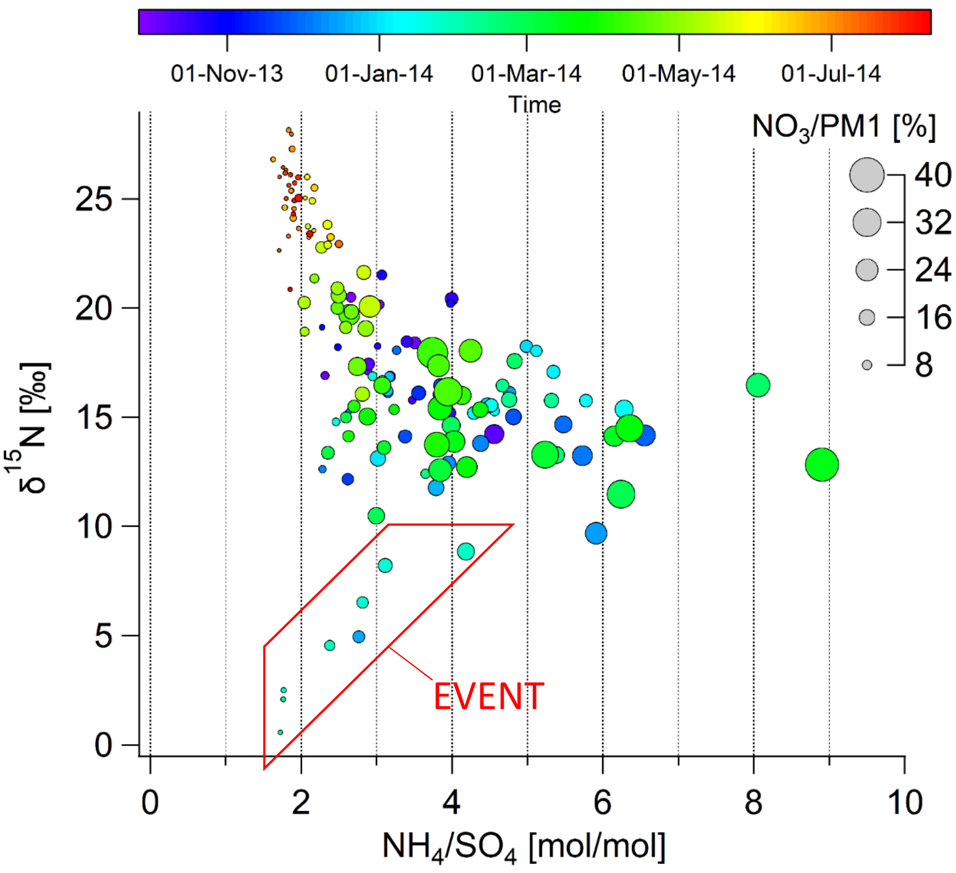
- Summer corr. $\delta^{15}N$ vs. NH_4(r=0.40) and SO_4^{2-} (r=0.51)
- Summer ratio below 2 => not enough NH_3 in gas phase = > excluding NO_3 from aerosol phase and disrupt thermal equilibrium NH_3(g) ⟷ NH_4(p).
- Silvern et al. (2017) - organic aerosols can retarding H_2SO_4-NH_3 thermal equil. under ratio of below 2, even when enough NH_3.
- Summer coating of particles by organic supported by corr. with temp (r=0.39), and O_3 (0.66)
- Event…

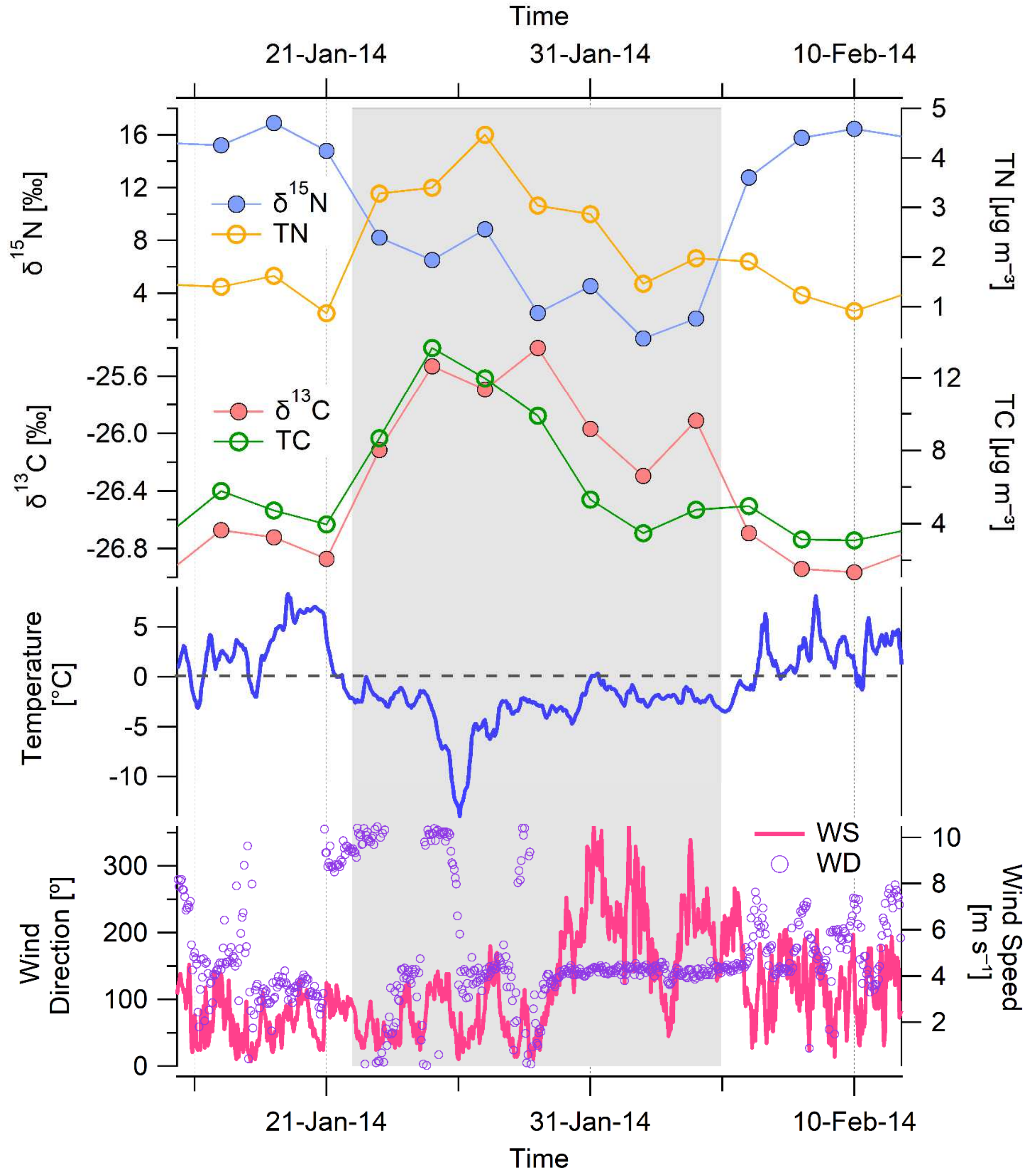
Winter Event



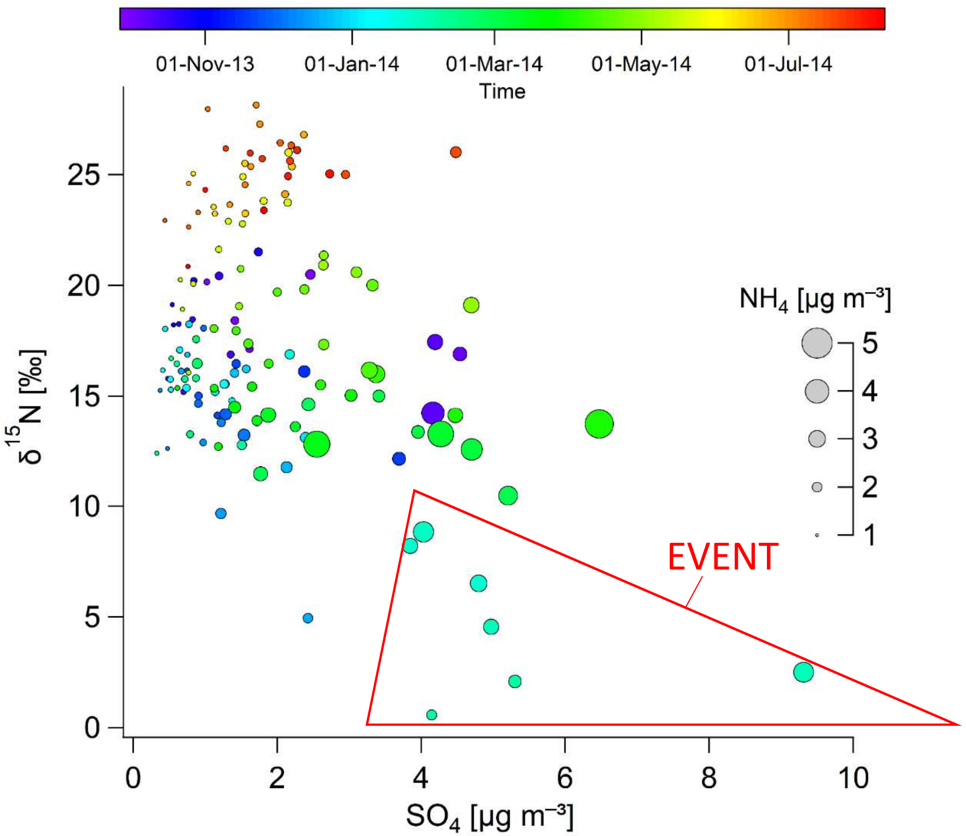


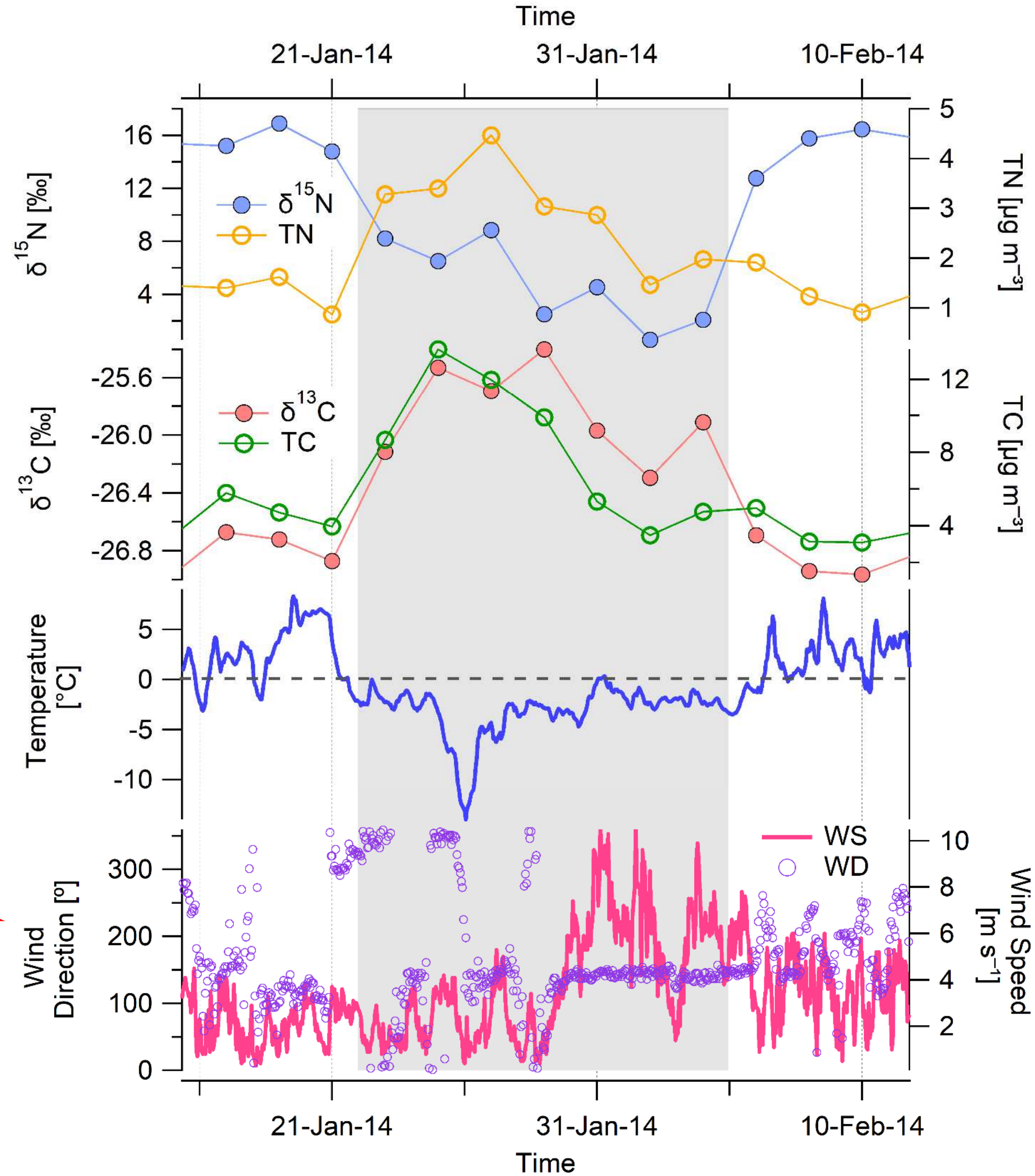
Winter Event





Winter Event

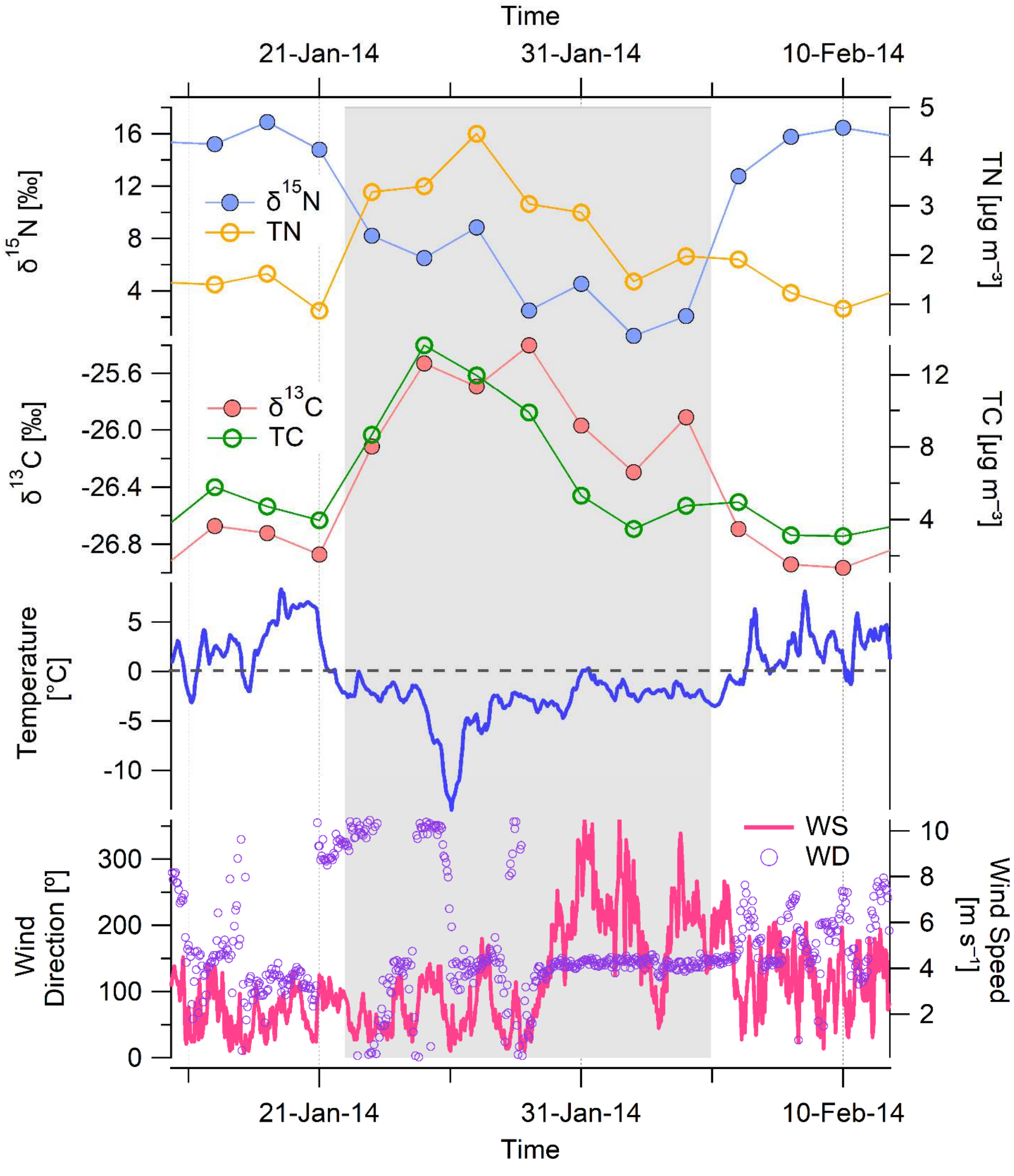




Winter Event

- ^{15}N - mixture of aerosols from heating (higher amounts of NO_3^- and δ^{15}N in TN (ca. 14‰)), which are gradually replaced by ^{15}N-depleted agricultural aerosols.

- Whole process results from low temperatures which first support dry deposition of NH_3 followed by unidirectional (kinetic) reaction of lighter isotope $NH_3(g) \rightarrow NH_4^+(p)$, originating mainly from agriculture sources in SE directions from the Košetice station.



Conclusions

- Clear seasonal pattern of $\delta^{15}N$ in TN – the main and gradual changes during spring (opposite in autumn).
- comparison with IC shows different dependence of $\delta^{15}N$ for NO_3 and NH_4 nitrogen
- ^{15}N enrichment mechanism is controlled by temperature, NO_3 concentrations and therm. equilibrium between $NH_3(g) \leftrightarrow NH_4(p)$.
- The highest winter NO_3 conc. (mainly NH_4NO_3) => $\delta^{15}N$ around 14 ‰ => value represented nitrogen from coal and biomass burning
- Summer: $NH_3(g) \leftrightarrow NH_4(p)$ therm. equilibrium suppressed. The most enriched ^{15}N represents aged $(NH_4)_2SO_4$ and Org.N
- Event - unidirectional (kinetic) reaction of lighter isotope $NH_3(g) + H_2SO_4 \rightarrow (NH_4)_2SO_4$ (p). (low temperature, NO_3 excluded from partitioning in aerosol) >> probably agriculture nitrogen (cow waste).

Reference:

Vodička, P., Kawamura, K., Schwarz, J., Kunwar, B. and Ždímal, V.: Seasonal study of stable carbon and nitrogen isotopic composition in fine aerosols at a Central European rural background station, Atmos. Chem. Phys., 19, 3463–3479, 2019.

Acknowledgement:

- project No. LM2015037 (the Ministry of Education, Youth and Sports of the Czech Republic)
- project "ACTRIS-CZ RI" (No. CZ.02.1.01/0.0/0.0/16_013/0001315)
- the Japan Society for the Promotion of Science (JSPS) through Grant-in-Aid No. 24221001

Email: vodicka@icpf.cas.cz

Thank you for your attention!

Spearman correlation coefficients (r) of $\delta^{15}N$ with various tracers. Only bold values are statistically significant (p-values < 0.05)

$\delta^{15}N$ vs.	Autumn	Winter*	Spring	Summer	Year*	Event
TN	-0.30	**-0.40**	**-0.70**	**0.36**	**-0.54**	**0.93**
TN/PM1	**-0.63**	**-0.50**	-0.02	**0.37**	**-0.35**	0.36
NO_3^--N/TN	-0.39	-0.04	**-0.73**	-0.26	**-0.77**	**0.98**
NH_4^+-N/TN	0.16	-0.30	**0.60**	**0.52**	**0.42**	**-0.86**
OrgN/TN	0.20	0.38	0.20	-0.33	**0.51**	-0.71
NO_3^-	**-0.41**	**-0.35**	**-0.80**	-0.03	**-0.78**	**0.96**
NH_4^+	-0.22	**-0.42**	**-0.61**	**0.40**	**-0.44**	0.75
OrgN	-0.26	-0.27	**-0.56**	0.30	**-0.25**	0.71
SO_4^{2-}	-0.07	**-0.38**	-0.30	**0.51**	0.03	-0.57
Cl^-	-0.37	-0.18	**-0.74**	**-0.37**	**-0.74**	**0.99**
O_3 (gas)	**0.45**	0.14	0.15	-0.02	**0.40**	-0.71
NO_2 (gas)	**-0.53**	**-0.34**	**-0.72**	0.20	**-0.64**	**0.86**
NO_2/NO (gas)	**-0.51**	-0.26	**-0.82**	0.14	**-0.76**	**0.82**
Temp.	**0.58**	0.30	**0.52**	-0.21	**0.77**	-0.43

$\delta^{15}N$ vs. OrgN

- Most samples in concentration range 0.1-0.5 ug/m3
- More driven by same changes like NH4, especially during summer
- With increasing NO3+NH4 also OrgN increase to values around 14 ‰ >> in this case probably OrgN connected with emissions from biomass burning.