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Using the EMEP intensive measurement periods to evaluate a new parameterization of coarse nitrate

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Outline

- Coarse nitrate formation
- Old parameterization
- New kinetic parameterization
  - Description of the method
  - Evaluation of model results
- New equilibrium parameterization
  - Description of the method
  - Evaluation of model results

Coarse nitrate formation on dust and sea-salt

- Coarse nitrate forms when nitric acid reacts with sea-salt and/or dust:

$$2\ HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O \quad (1)$$

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \quad (2)$$

- The most reactive parts in dust are calcite ($Ca(CO_3)$) and dolomite ($CaMg(CO_3)_2$)

Coarse nitrate in the model today

- Coarse nitrate in the EMEP model only depends on HNO_3, with a reaction rate coefficient k_{RH}

  $k_{RH} = 1.0 \times 10^{-4}$ for RH>90%

  $k_{RH} = 5.0 \times 10^{-6}$ for RH<90%

- The model run with this parameterization is later referred to as E_std

New kinetic parameterization

- Kinetic method: assumed total reaction in forward direction of reactions 1 and 2, with a reaction rate that depends on aerosol surface and the sticking coefficient γ of HNO_3

$$k = \left(\frac{d}{2D_g} + \frac{4}{\nu\gamma} \right)^{-1} A$$

The different model runs

- E_std: model run with old parameterization
- E_d: model run with reactions on dust only
  - E_d_ca60
- E_ss: model run with reactions on sea-salt only
- E_d_ss: model run with reactions on both dust and sea-salt

Coarse nitrate in model results compared to measurements

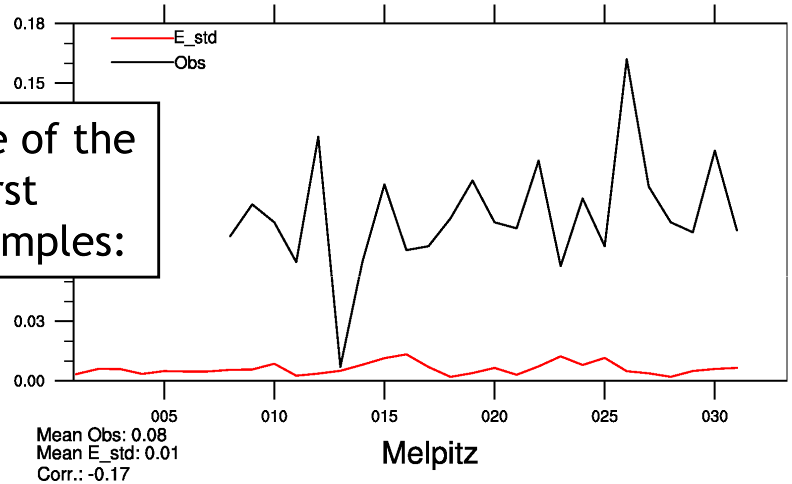
Station ID	Obs μg(N) m^{-3}	Bias (%) E_std	Bias (%) E_ss	Bias (%) E_d	Bias (%) E_d_ss	Correlation E_std	Correlation E_ss	Correlation E_d	Correlation E_d_ss
June 2006									
CH02	0.10	-60	-100	-97	-96	-0.28	-0.03	0.56	0.53
GB36*	0.51	-71	-96	-100	-94	0.01	0.39	-0.18	0.39
NL11*	0.03	67	-63	-98	-61	0.22	-0.15	0.32	-0.12
FI17	0.10	-3	-92	-99	-92	0.35	0.66	0.00	0.66
IT01	0.36	-64	-97	-94	-91	0.17	-0.06	0.36	0.22
NO01	0.11	-54	-91	-100	-91	0.64	0.62	0.13	0.62
DE44	0.12	-33	-96	-99	-96	0.17	0.56	-0.13	0.54
ES17	0.20	-55	-95	-85	-79	0.16	-0.46	0.84	0.75
January 2007									
CH02	0.29	-79	-97	-100	-98	0.39	0.52	0.30	0.53
NL11*	0.08	-64	-89	-100	-89	0.11	0.06	0.13	0.06
FI17	0.06	-27	-96	-100	-95	-0.03	0.05	0.07	0.05
IT01	0.30	-30	-87	-99	-85	0.06	0.22	0.00	0.21
NO01	0.002	-21	-74	-95	-74	0.22	0.33	0.14	0.33
DE44	0.10	-50	-90	-100	-95	0.24	0.39	0.15	0.39

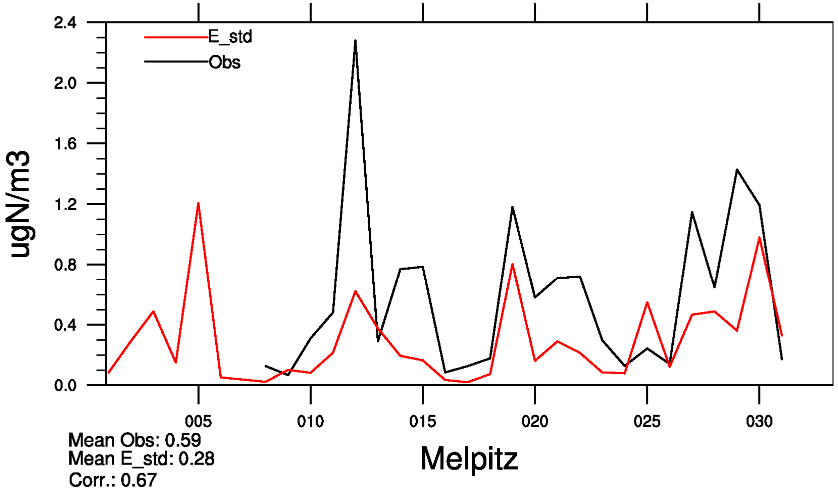
- Temporal correlation improves
- There is a negative bias in the new parameterization

5% Ca^{2+} in coarse dust compared to measured (PM10-PM1) Ca^{2+}, 2007

Na⁺ in coarse sea-salt compared to measured (PM10-PM25) Na+, 2007

One of the worst examples:

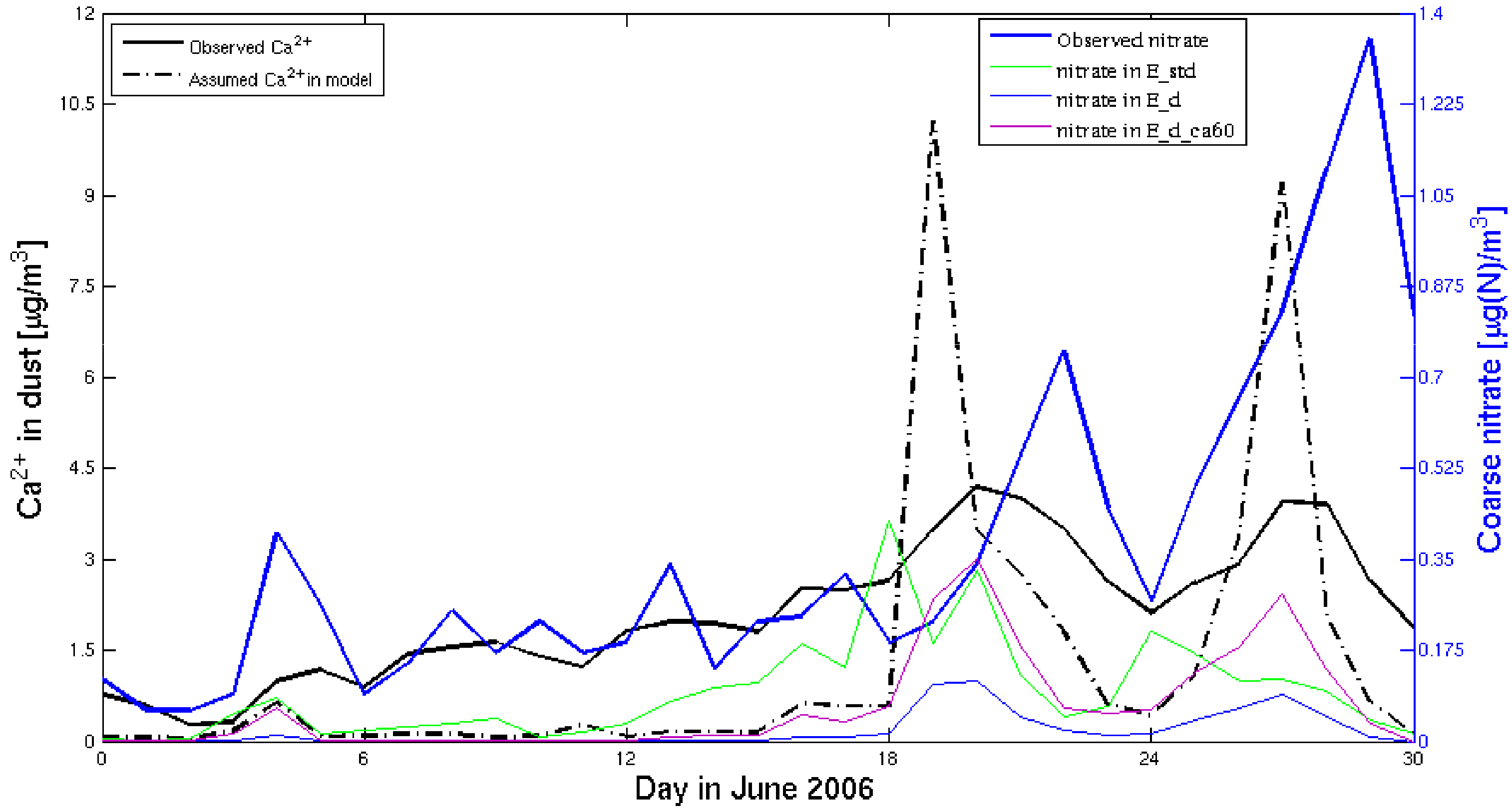




- Can the low value of 5% Ca^{2+} in coarse dust compared with measurements explain the high negative bias?
- Underestimation of coarse sea-salt may be a reason for underestimating coarse nitrate formation

Coarse nitrate on dust, 2006

Montelibretti (IT01)



- Assuming more Ca^{2+} content in dust did not explain the negative bias in the dust parameterization

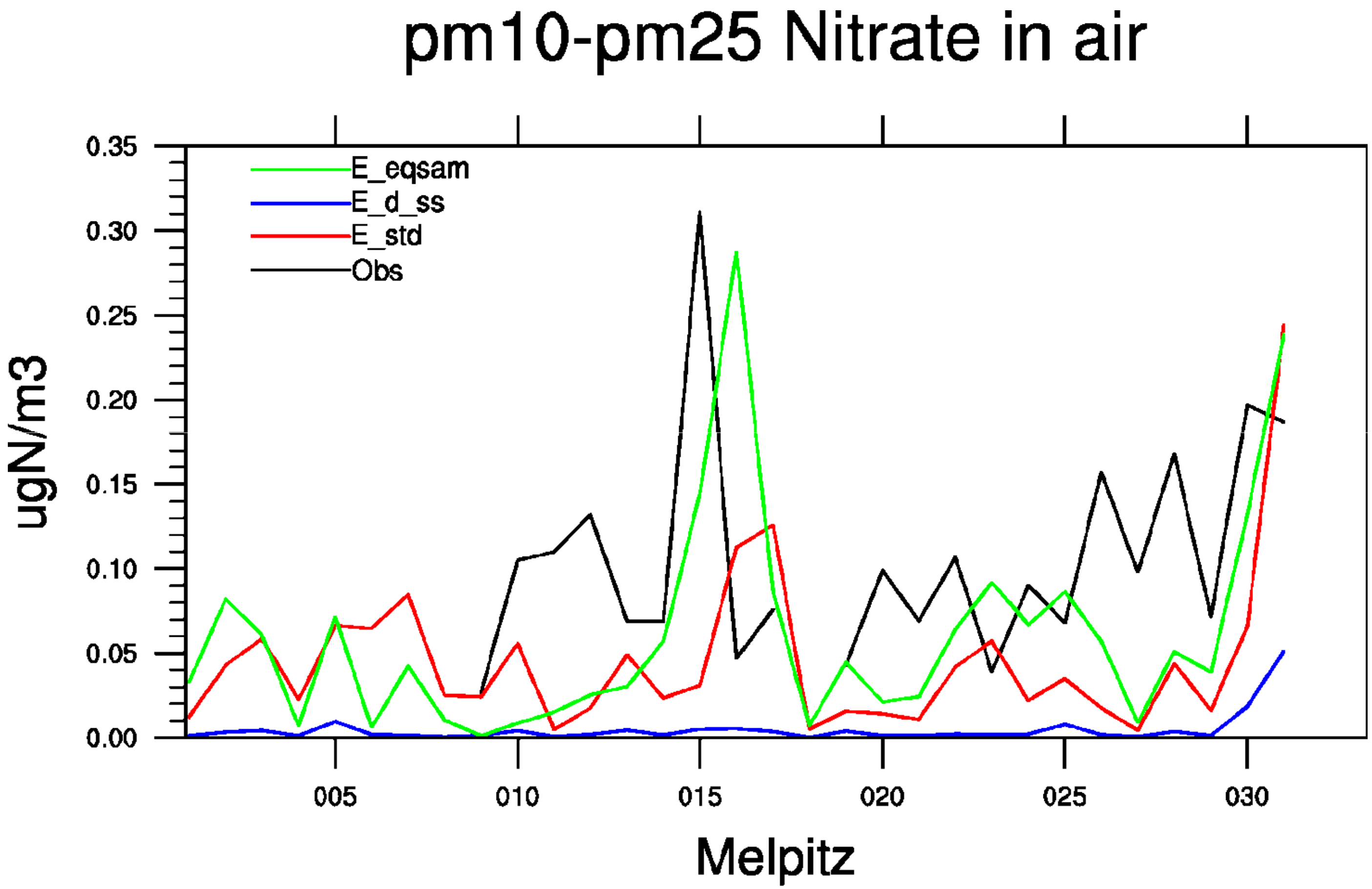
Equilibrium method

- Assume that formation of coarse nitrate on sea-salt and dust reaches equilibrium within the 20-minute time step in the EMEP model
- Use the equilibrium module EQSAM to calculate the equilibrium
- First let the photochemistry work, then let fine aerosols reach equilibrium, before letting coarse aerosols reach equilibrium
- This model run is later referred to as E_eqsam

Station ID	Obs $\mu g(N)\ m^{-3}$	Bias (%) E_std	Bias (%) E_d_ss	Bias (%) E_eqsam	Correlation E_std	Correlation E_d_ss	Correlation E_eqsam
June 2006							
CH02	0.10	-60	-96	-90	-0.28	0.53	-0.20
GB36*	0.51	-71	-96	-82	0.01	0.39	-0.02
NL11*	0.03	67	-67	89	0.22	-0.12	-0.04
FI17	0.10	-3	-88	-96	0.35	0.77	0.05
IT01	0.36	-64	-91	-100	0.17	0.22	-0.20
NO01	0.11	-54	-91	-91	0.64	0.62	0.20
DE44	0.12	-33	-92	-92	0.17	0.54	0.41
ES17	0.20	-55	-80	-95	0.16	0.75	0.60
January 2007							
CH02	0.29	-79	-98	-76	0.39	0.53	0.56
NL11*	0.08	-64	-89	-12	0.11	0.06	0.30
FI17	0.06	-27	-95	-27	-0.03	0.05	0.00
IT01	0.30	-30	-85	-27	0.06	0.21	-0.05
NO01	0.002	-21	-74	-37	0.22	0.33	0.41
DE44	0.10	-50	-95	-30	0.24	0.39	0.33

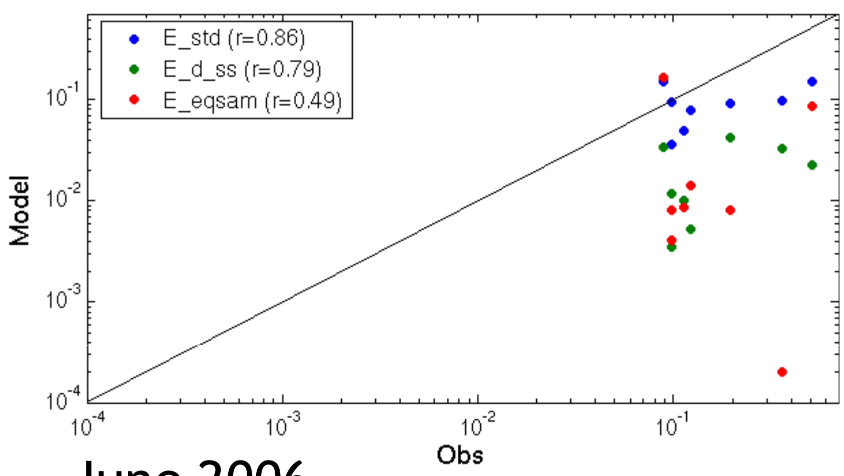
- The equilibrium method improves temporal correlation and the bias in winter

Coarse nitrate at Melpitz in 2007

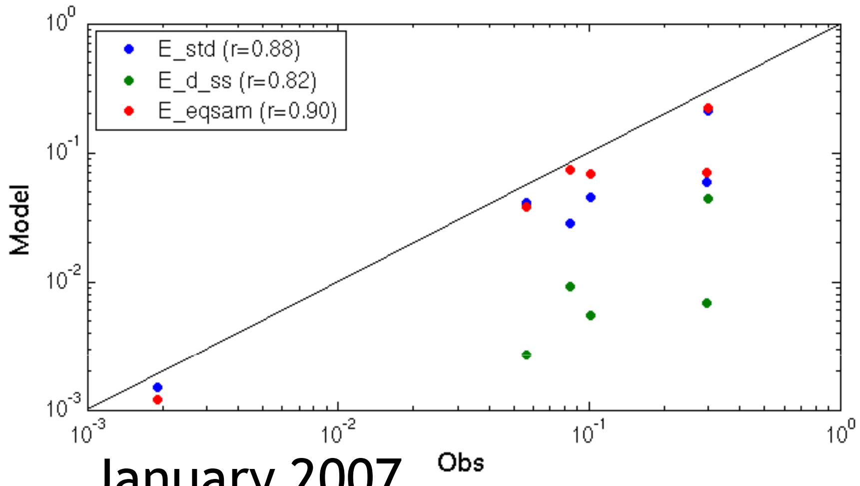


- The equilibrium method improves both correlation and bias at Melpitz (DE44)

Spatial correlation of coarse nitrate



June 2006



January 2007

- Good spatial correlation, especially in January
- Small improvement in spatial correlation indicates that the formation of coarse nitrate is mainly driven by HNO_3
- The spatial correlation of dust and sea-salt limits the spatial correlation of coarse nitrate

Summary

- Inclusion of coarse nitrate formation on dust and sea-salt with the kinetic approach improves the temporal correlation but gives a high underestimation of coarse nitrate
  – Several sensitivity tests were performed, but neither of them could explain this high negative bias
  – Comparison with other model studies of coarse nitrate formation on dust and sea-alt reveals a rather small production of coarse nitrate in this study
- Inclusion of coarse nitrate formation on dust and sea-salt assuming equilibrium improves the result in winter