

On the observability quest for chemistry data assimilation and emission inversion

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1. Introduction

2. What needs to be observed?

Central case ozone photochemistry

3. When can emissions be quantified?

Initial? Boundary? Domain emissions?

4. A practical approach for a full fledged CTM

Where and what to observe to predict

5. Conclusions

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3. When can emissions be quantified?
4. A practical approach for full fledged CTMS
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Critical questions

(>20 a old, yet not fully answered)

1. With **O(100) prognostic variables**, and only few observations, why do you expect chemistry data assimilation to be successful?
2. How do you plan to **avoid artificial chemical imbalances** by “correcting” through single observations?(Push from a slow manifold)
3. Why do you improve initial values, while the **system is controlled by emissions?**

An observability quest:

→ Do we observe sufficiently complete?

Introduction: Setting the scene: stratospheric chemistry example

167 gas phase reactions + 10 heterogeneous reactions on polar strat. clouds

Table 1. Photolysis reactions included in the SAC

represents constituents that are not considered in the reaction scheme.

Reaction
(R1) $O_2 + h\nu \rightarrow O(^3P) + O(^3P)$
(R2) $O_3 + h\nu \rightarrow O(^3P) + O_2$
(R3) $O_3 + h\nu \rightarrow O(^1D) + O_2$
(R4) $H_2O + h\nu \rightarrow H + OH$
(R5) $H_2O_2 + h\nu \rightarrow OH + OH$
(R6) $NO_2 + h\nu \rightarrow O(^3P) + NO$
(R7) $NO_3 + h\nu \rightarrow NO_2 + O(^3P)$
(R8) $NO_3 + h\nu \rightarrow NO + O(^3P)$
(R9) $N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
(R10) $N_2O_5 + h\nu \rightarrow HNO_3 + NO_2$
(R11) $HNO_3 + h\nu \rightarrow NO_2 + OH$
(R12) $HNO_4 + h\nu \rightarrow NO_2 + OH$
(R13) $Cl_2O_2 + h\nu \rightarrow Cl_2 + O_2$
(R14) $Cl_2 + h\nu \rightarrow Cl + Cl$
(R15) $OCIO + h\nu \rightarrow Cl + O$
(R16) $HCl + h\nu \rightarrow H + Cl$
(R17) $HOCl + h\nu \rightarrow OH + Cl$
(R18) $ClONO + h\nu \rightarrow Cl + NO$
(R19) $CH_3Cl + h\nu \rightarrow CH_3 + Cl$
(R20) $CCl_4 + h\nu \rightarrow CCl_3 + Cl$
(R21) $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$
(R22) $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$
(R23) $CHF_2Cl + h\nu \rightarrow CHF_2 + Cl$
(R24) $CF_2Cl + h\nu \rightarrow CF_2 + Cl$
(R25) $CH_3CCl_2 + h\nu \rightarrow CH_3CCl + Cl$
(R26) $BrO + h\nu \rightarrow Br + O$
(R27) $BrCl + h\nu \rightarrow Br + Cl$
(R28) $HOBr + h\nu \rightarrow OH + Br$
(R29) $BrONC + h\nu \rightarrow Br + NO$
(R30) $CH_3Br + h\nu \rightarrow CH_3 + Br$
(R31) $CF_2ClF + h\nu \rightarrow CF_2Cl + F$
(R32) $CF_3Br + h\nu \rightarrow CF_3 + Br$
(R33) $HNO_4 + h\nu \rightarrow NO_2 + OH$
(R34) $ClONO + h\nu \rightarrow Cl + NO$
(R35) $N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
(R36) $CH_2O + h\nu \rightarrow H + HCO$
(R37) $CH_2O + h\nu \rightarrow H_2 + CO$

Table 2. Gas phase reactions that are included in the reaction scheme.

Reaction
(R38) $O(^3P) + O_3 \rightarrow O_2 + O_2$
(R39) $O(^1D) + O_2 \rightarrow O(^3P) + O_2$
(R40) $O(^1D) + O_3 \rightarrow O(^3P) + O_2$
(R41) $O(^1D) + O_3 \rightarrow O(^3P) + O_2$

Table 3. Heterogeneous reactions included in the SACADA reaction scheme. The notation "(c)" indicates a species in the condensed (liquid or solid) phase. The term "products" represents constituents which are not considered in the reaction scheme.

Reaction	Uptake coefficient		
	liquid/STS	NAT	ice
(R168) $BrONO_2 + H_2O(c) \rightarrow HOBr + HNO_3$	$f(t, p_{H_2O})^a$	-	0.26
(R169) $N_2O_5 + H_2O(c) \rightarrow HNO_3 + HNO_3$	$f(t, p_{H_2O})^a$	0.0004	0.02
(R170) $ClONO_2 + H_2O(c) \rightarrow HNO_3 + HOCl$	$f(t, p_{H_2O}, p_{HCl})^b$	0.004	0.3
(R171) $ClONO_2 + HCl(c) \rightarrow Cl_2 + HNO_3$	$f(t, p_{H_2O}, p_{HCl})^b$	0.2	0.3
(R172) $HOCl + HCl(c) \rightarrow Cl_2 + H_2O$	$f(t, p_{H_2O}, p_{HCl})^b$	0.1	0.2
(R173) $N_2O_5 + HCl(c) \rightarrow HNO_3 + \text{products}$	-	0.003	0.03
(R174) $HOBr + HCl(c) \rightarrow BrCl + H_2O$	0.01	-	0.3
(R175) $ClONO_2 + HBr(c) \rightarrow BrCl + HNO_3$	-	0.3	0.3
(R176) $HOCl + HBr(c) \rightarrow BrCl + H_2O$	-	-	0.05
(R177) $BrONO_2 + HCl(c) \rightarrow BrCl + HNO_3$	0.3	-	0.3

a: as recommended by Sander et al. [2006]

b: Shi et al. [2001], as recommended by Sander et al. [2006]

(R71) $OH + HO_2 \rightarrow H_2O + O_2$	(R141) $Br + HO_2 \rightarrow HBr + O_2$
(R72) $OH + H_2O_2 \rightarrow H_2O + O_2$	(R142) $BrO + HO_2 \rightarrow HOBr + O_2$
(R73) $HO_2 + O_3 \rightarrow OH + O_2$	(R143) $Br + O_3 \rightarrow BrO + O_2$
(R74) $HO_2 + HO_2 \rightarrow H_2O + O_2$	(R144) $CH_2O + Br \rightarrow HBr + HCO$
(R75) $NO_2 + O(^3P) \rightarrow NO + O(^3P)$	(R145) $Br + OCIO \rightarrow BrO + ClO$
(R76) $NO_3 + O(^3P) \rightarrow NO_2 + O(^3P)$	(R146) $BrO + NO \rightarrow Br + NO_2$
(R111) $CH_3Cl + OH \rightarrow H_2O + CH_3O$	(R147) $BrO + ClO \rightarrow Br + OCIO$
(R112) $CHF_2Cl + OH \rightarrow H_2O + CHF_2$	(R148) $BrO + ClO \rightarrow Br + Cl + O_2$
(R113) $CH_3CCl_2 + OH \rightarrow H_2O + CH_3CCl$	(R149) $BrO + ClO \rightarrow Br + Cl + O_2$
(R114) $Cl + HO_2 \rightarrow HCl + O_2$	(R150) $BrO + BrO \rightarrow Br + Br + O_2$
(R115) $Cl + HO_2 \rightarrow OH + ClO$	(R151) $O(^3P) + O_2 \rightarrow O_3$
(R152) $Cl + HO_2 \rightarrow OH + ClO$	(R152) $N_2O_5 + HCl(c) \rightarrow HNO_3 + HNO_3$

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How can the observation configuration be optimized?

Given CTM (here RACM and EURAD-IM) acting as tan.-lin. model operator \mathcal{L} :

$$\delta \mathbf{c}(t_F) = \mathcal{L}_{t_I, t_F} \delta \mathbf{c}(t_I), \quad \mathcal{L}_{t_I, t_F} = \left. \frac{\partial \mathcal{M}_{t_I, t_F}}{\partial \mathbf{c}} \right|_{\mathbf{c}(t_I)}$$

1. Berliner et al., (1998) Statistical design:
 “Minimize” the analysis error covariance matrix \mathbf{A} (say, via trace):

$$\min_{\mathbf{H}} \mathbf{A} = \mathbf{B} - \underbrace{\mathbf{B} \mathbf{H}^T (\mathbf{H} \mathbf{B} \mathbf{H}^T + \mathbf{R})^{-1} \mathbf{H} \mathbf{B}}_{\text{to be maximized by } \mathbf{H}}$$

For this find maximal eigenvectors as observation operators \mathbf{H} , which configure observations.

$$\mathcal{L}_{t_I, t_F} \mathbf{B} \mathcal{L}_{t_I, t_F}^T \mathbf{H}^T = \lambda \mathbf{H}^T$$

2. Palmer (1995) Singular vector analysis:
 Observe maximal SV configuration:

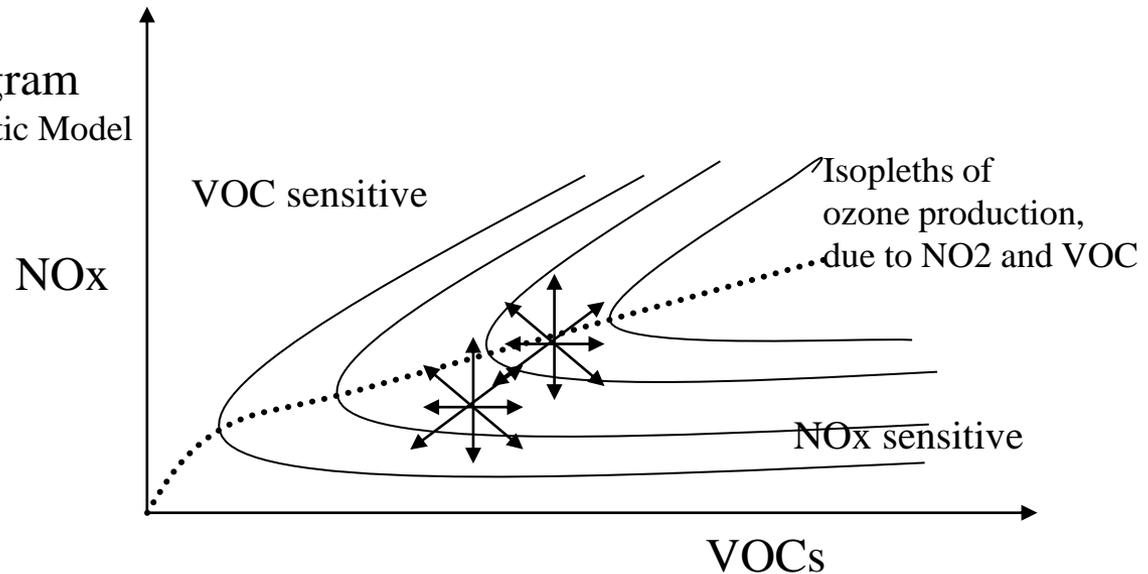
$$\max_{\delta \mathbf{c}(t_I)} \frac{\|\delta \mathbf{c}(t_F)\|_{\mathbf{B}}^2}{\|\delta \mathbf{c}(t_I)\|_{\mathbf{B}}^2} = \max_{\delta \mathbf{c}(t_I)} \frac{\delta \mathbf{c}(t_I)^T \mathcal{L}_{t_I, t_F}^T \mathbf{B} \mathcal{L}_{t_I, t_F} \delta \mathbf{c}(t_I)}{\delta \mathbf{c}(t_I)^T \mathbf{B} \delta \mathbf{c}(t_I)},$$

A prototype non-linearity example: Ozone production from NO_x and VOCs

$E_{\text{empirical}}$ K_{kinetic} M_{model} A_{approach} scheme

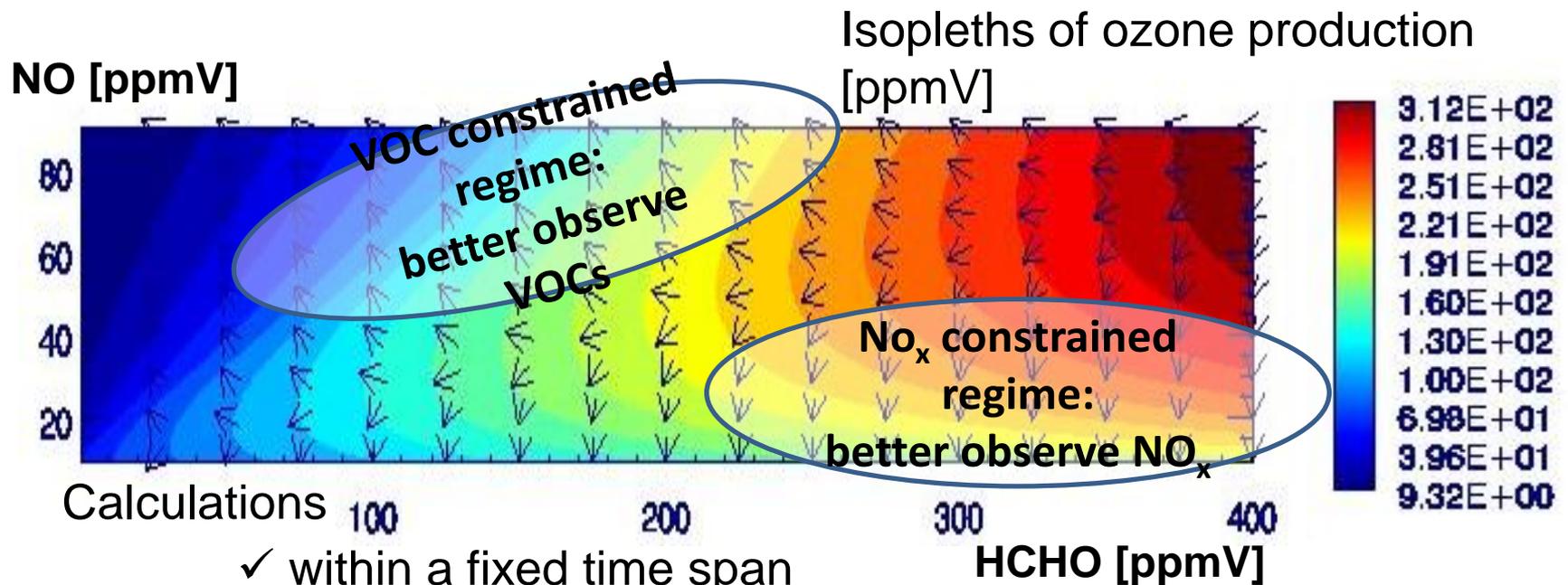
- Nitrogen oxides and numerous hydrocarbons act highly nonlinearly as precursors of ozone.
- Chemical conditions are either controlled by NO_x or VOC deficit, delineating the “chemical regime”.
- Both 4D-var and Kalman filter should start with the proper chemical regime.

EKMA diagram
(Empirical Kinetic Model
Approach)



2. What should be observed?

Is NO_x always the controlling key to ozone production?
And consequently, its observation the key to better forecast?

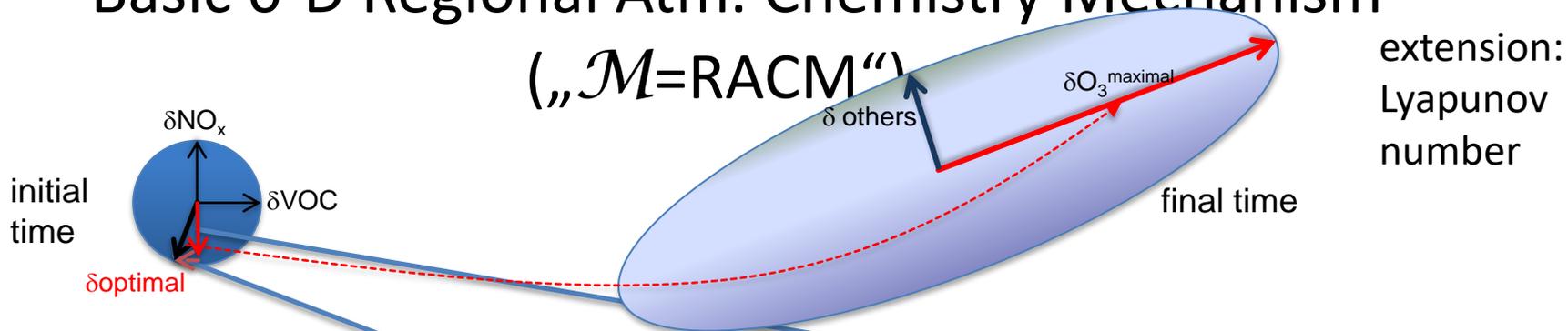


- ✓ within a fixed time span
- ✓ initial concentrations of **NO / HCHO were varied**
- ✓ change of final concentration is given by colour
- ✓ gradients (SVs) of maximyl ozone production given by arrows

What should be observed?

Basic 0-D Regional Atm. Chemistry Mechanism

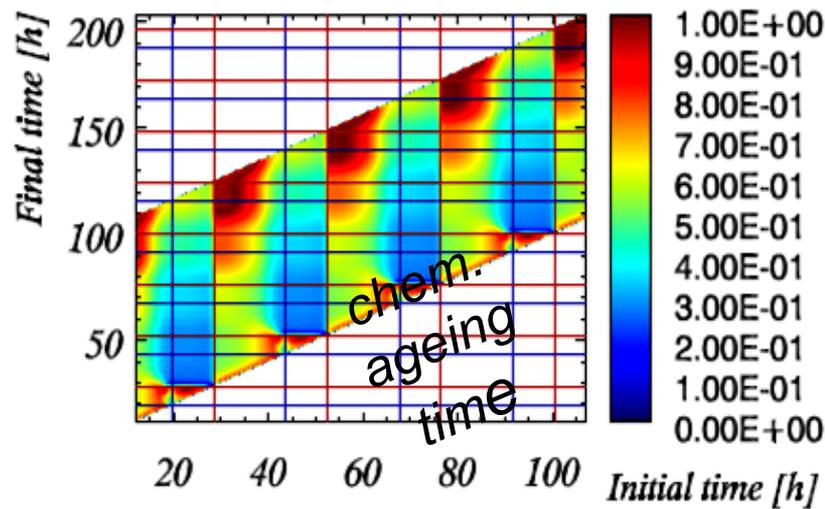
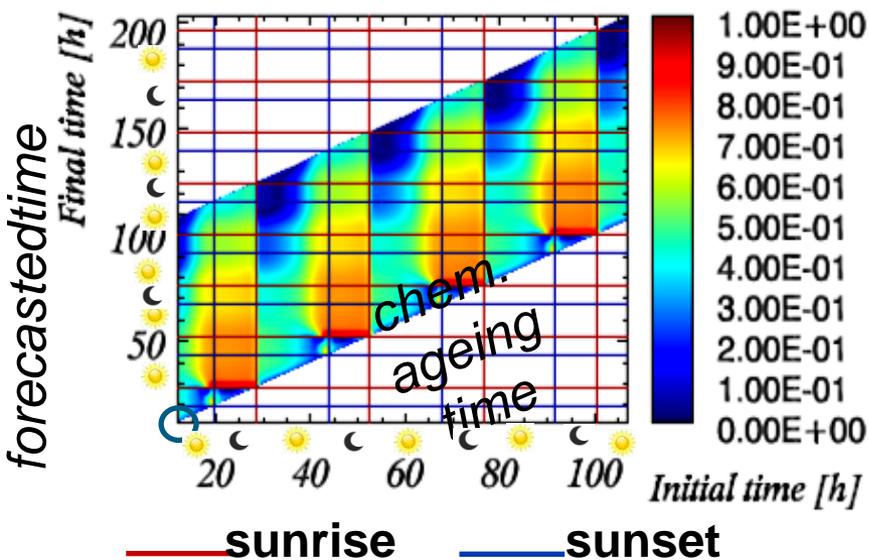
(„ \mathcal{M} =RACM“)



- **Optimal perturbations (Singular Vectors) for scenario MARINE**

1st Grouped Singular Vectors (δ VOC)

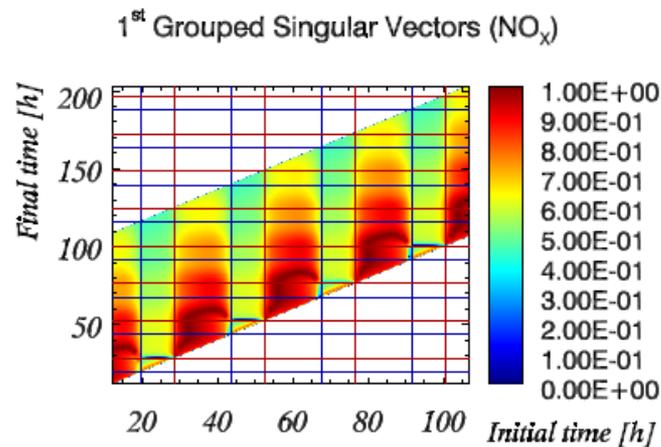
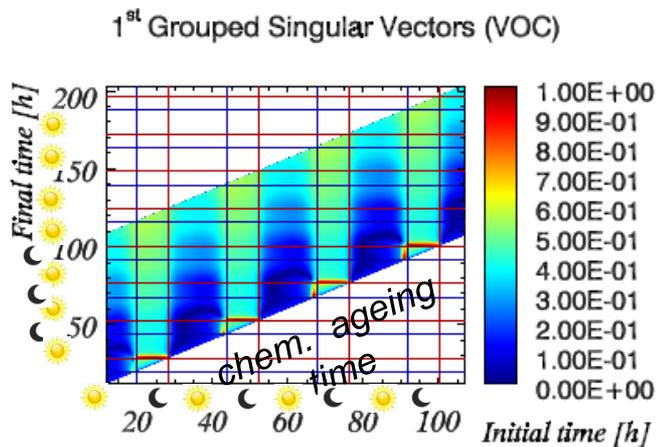
1st Grouped Singular Vectors (δ NO_x)



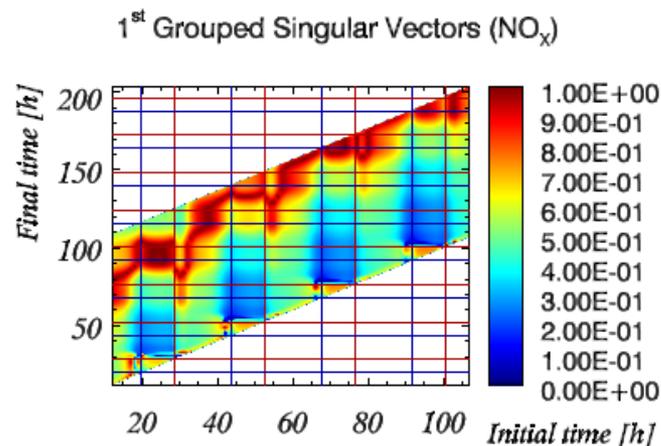
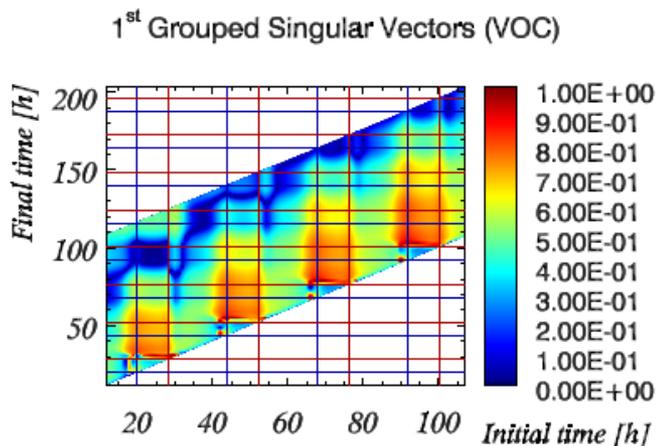
not — very important to observe

SV components for initial values VOC (left) and NO_x (right) for scenarios “free troposphere” and “urban plume”

free troposphere



urban plume



— sunrise — sunset

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- 3. When/where can emissions be quantified?**
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In the troposphere, for **emission rates**, the product
*(paucity of knowledge * importance)*
 is high

Emission Rate Optimization

minimize cost function

$$\begin{aligned}
 J(\mathbf{x}(t_0), \mathbf{e}) = & \frac{1}{2}(\mathbf{x}^b(t_0) - \mathbf{x}(t_0))^T \mathbf{B}_0^{-1}(\mathbf{x}^b(t_0) - \mathbf{x}(t_0)) + \\
 & \frac{1}{2} \int_{t_0}^{t_N} (\mathbf{e}_b(t) - \mathbf{e}(t))^T \mathbf{K}^{-1}(\mathbf{e}_b(t) - \mathbf{e}(t)) dt + \\
 & \frac{1}{2} \int_{t_0}^{t_N} (\mathbf{y}^0(t) - H[\mathbf{x}(t)])^T \mathbf{R}^{-1}(\mathbf{y}^0(t) - H[\mathbf{x}(t)]) dt
 \end{aligned}$$

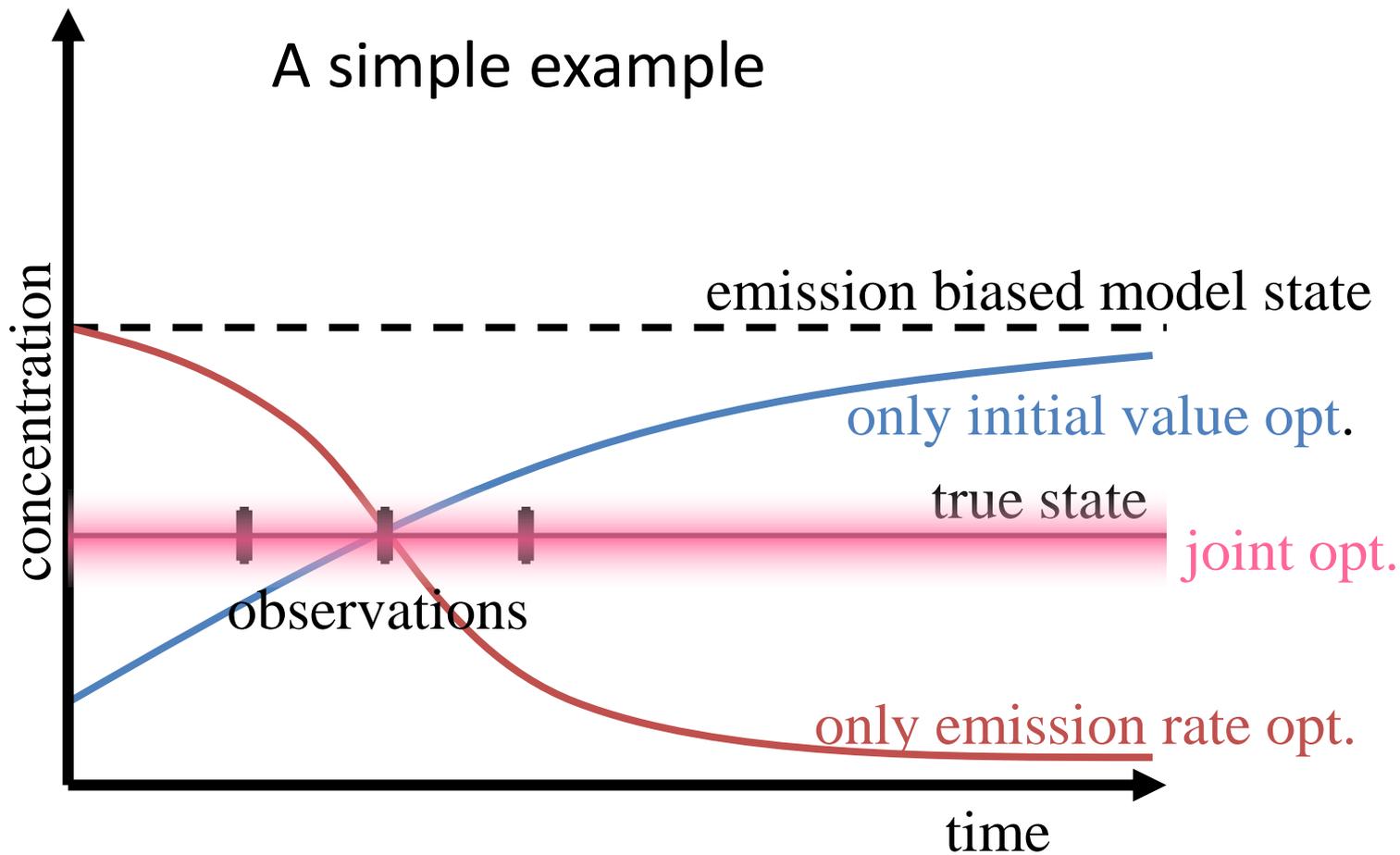
deviations from background initial state

deviations from a priori emission rates

model deviations from observations

- $\mathbf{x}^b(t_0)$ background state at $t = 0$
- $\mathbf{x}(t)$ model state at time t
- $\mathbf{e}_b(t_0)$ background emission rate at $t = 0$
- $\mathbf{e}(t)$ emission rate field at time t
- \mathbf{K} emission rate error covariance matrix
- $H[\]$ forward interpolator
- $\mathbf{y}^0(t)$ observation at time t
- \mathbf{B}_0 background error covariance matrix

1. What should we optimise, only state variables?
2. What should be best observed?



Is this achievable within a limited time interval?

Can a finite assimilation window suffice to estimate emissions?

A prepended safeguarding study

Wu, Xueran, B. Jacob, and H. Elbern: Optimal control and observation locations for time-varying systems on a finite-time horizon, SIAM J. Control Optim., 54, 291-316, 2016.

- Result:

For time-varying systems in Hilbert spaces, the existence and convergence of the optimal locations based on the linear-quadratic control on a **finite-time horizon** is demonstrated subject to conditions.

- Approach:

The optimal location of observations for improving the estimation of the state at the final time is considered as the **dual problem to the LQ optimal problem of the control locations**. (Kalman smoother and filter)

Is the information needed available?

Observation location impact assessment on parameter optimisation by Ensemble Kalman Smoother

We seek to infer **normalised sensitivity maps**, which exhibit the control capacity of observations on parameters to be optimised: here **emission rates** and **initial values**

Extended model with emission rates

$$\begin{pmatrix} \delta c(t) \\ \delta e(t) \end{pmatrix} = \begin{pmatrix} M(t, t_0) & \int_{t_0}^t M(t, s) M_e(s, t_0) ds \\ 0 & M_e(t, t_0) \end{pmatrix} \begin{pmatrix} \delta c(t_0) \\ \delta e(t_0) \end{pmatrix} \cdot$$

extended state vector concentrations emissions (formally made prognostic)

Typically, there is no direct observation for emissions.

$$\delta y(t) = [H(t), 0_{n \times n}] \begin{pmatrix} \delta c(t) \\ \delta e(t) \end{pmatrix} + \nu(t), \quad (2)$$

where $0_{n \times n}$ is a $n \times n$ matrix with zero elements.

Is the information needed available?

observability Gramian: Exhibiting the control capacity of observations on parameters to be optimised

Here, infer **normalised sensitivity maps**, for **emission rates** and **initial values**

Costly:

calculate the **observability Gramian** matrix (control theory) by forward and adjoint model M , observation operators H , and observation error covariance matrix.

$$\mathcal{G} = \begin{pmatrix} H(t_0)M(t_0, t_0) \\ H(t_1)M(t_1, t_0) \\ \vdots \\ H(t_N)M(t_N, t_0) \end{pmatrix}, \rightarrow \mathcal{G}^T \mathcal{R} \mathcal{G}$$

Is the information needed available?

Degree of Freedom for Signal (DFS)

Define the *relative improvement covariance matrix*
(scaled forecast – analysis error covariance matrix from KS)

$$\begin{aligned}\tilde{P} &= P^{-\frac{1}{2}}(t_0|t_{-1})(P(t_0|t_{-1}) - P(t_0|t_N))P(t_0|t_{-1}) \\ &= I - (I + P^{\frac{1}{2}}(t_0|t_{-1})\mathcal{G}^\top \mathcal{R}^{-1}\mathcal{G}P^{\frac{1}{2}}(t_0|t_{-1}))^{-1} \\ &= I - (I + VSS^\top V^\top)^{-1} = \dots = \\ &= V(I - (I + SS^\top)^{-1})V^\top \\ &= \sum_{i=1}^r \frac{s_i^2}{1 + s_i^2} v_i v_i^\top,\end{aligned}$$

singular value s_i
singular vector v_i
decomposition

Is the information needed available?

Degree of Freedom for Signal (DFS)

Separation in terms of initial values
and emission rates

separate singular vector sections
initial values,
emission rates

$$\tilde{P} = \begin{pmatrix} \tilde{P}^c & \tilde{P}^{ce} \\ \tilde{P}^{ec} & \tilde{P}^e \end{pmatrix} = \sum_{i=1}^{2n} \frac{s_i^2}{1 + s_i^2} \begin{pmatrix} v_i^c \\ v_i^e \end{pmatrix} (v_i^{c\top}, v_i^{e\top}) \in R^{2n \times 2n},$$

$$\|\tilde{P}^c\|_1 = \sum_{i=1}^{2n} \frac{s_i^2}{1 + s_i^2} \text{tr}(v_i^c v_i^{c\top}), \quad \|\tilde{P}^e\|_1 = \sum_{i=1}^{2n} \frac{s_i^2}{1 + s_i^2} \text{tr}(v_i^e v_i^{e\top}).$$

Is the information needed available?

Sensitivity by partial singular vectors

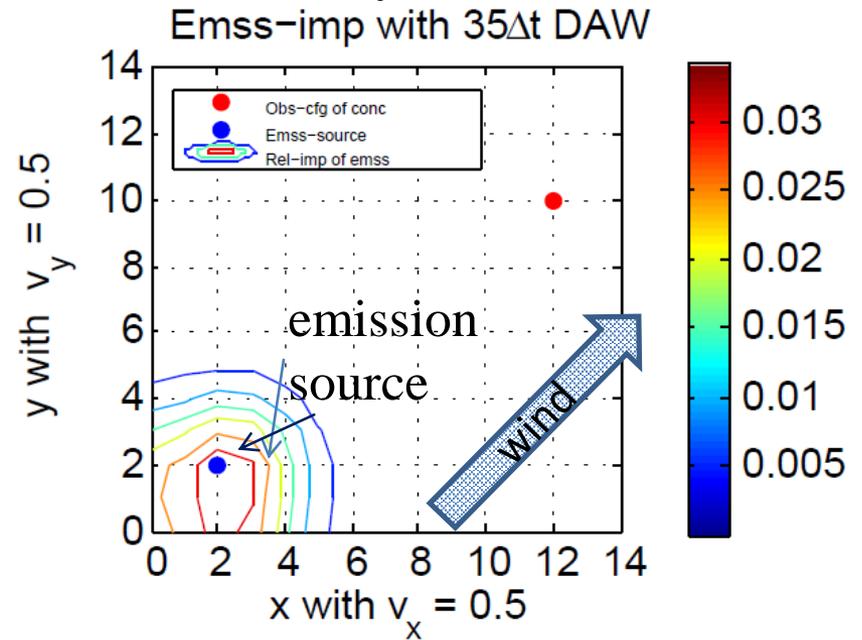
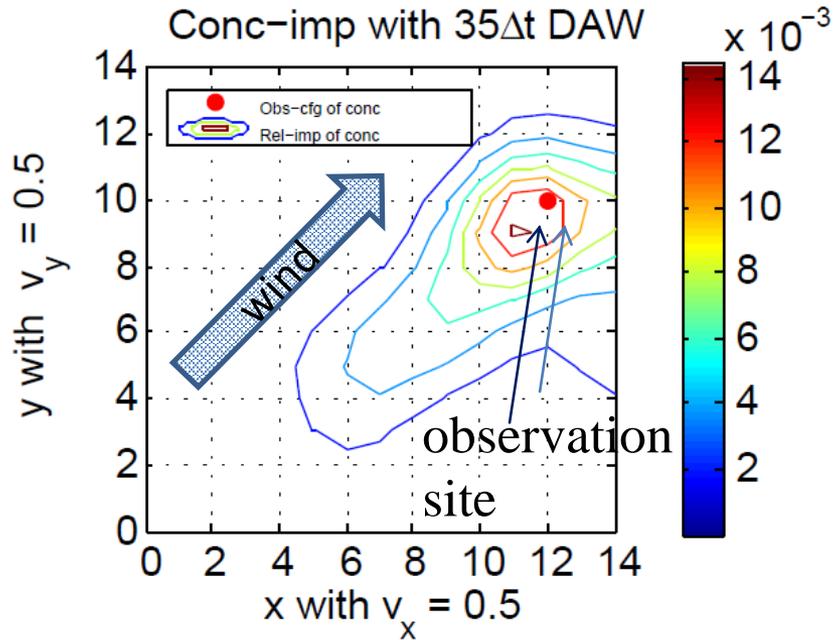
a simple example

Given:

1 observation site 1 windward emission source location
 assimilation window: advection time source → observation (35 units)

Question:

can **both** initial values and emission rates be analysed?



maximal sensitivities: ini. val. $P^c = 0.45$

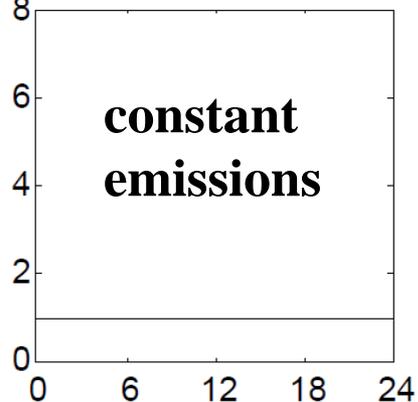
emi rate $P^e = 0.55$

Answer: Yes, both sensitivities are of same order from Wu et al. 2019

4. Is the information needed available? Sensitivity by partial singular vectors

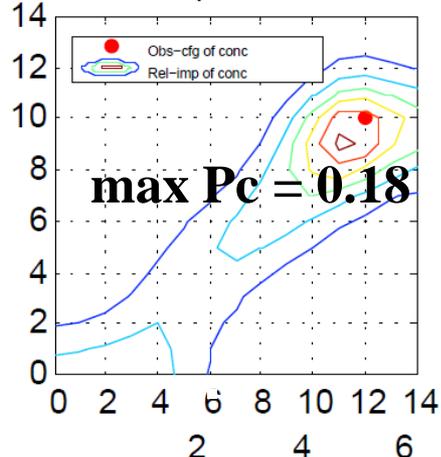
emission variation + 48 time units

Emission profile



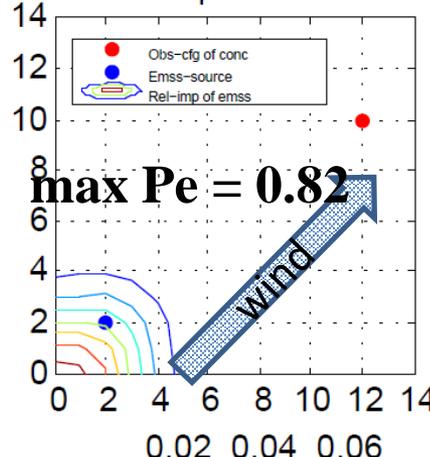
**constant
emissions**

Conc-imp with 48Δt DAW



max $P^c = 0.18$

Emss-imp with 48Δt DAW



max $P^e = 0.82$

maximal

ini. val. $P^c = 0.18$

emi rate $P^e = 0.82$



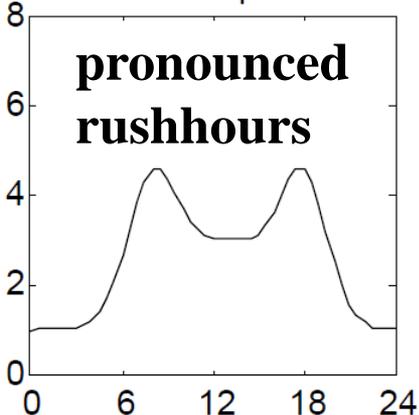
longer data

assimilation window

favours emission

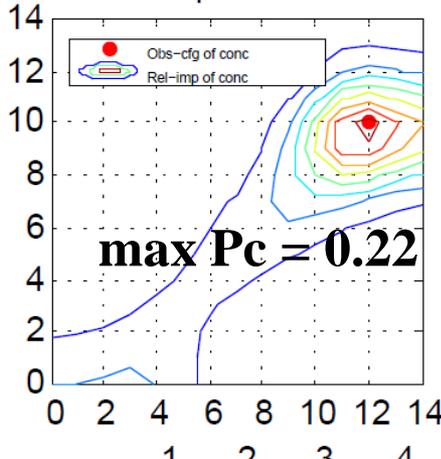
sensitivity

Emission profile



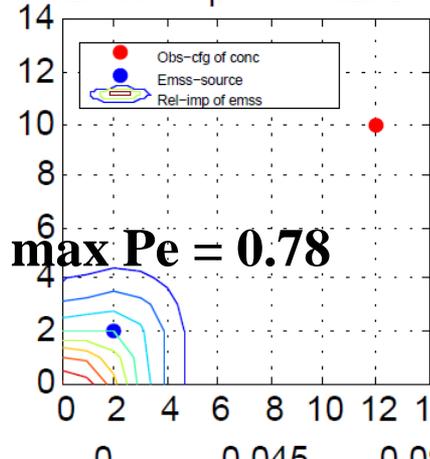
**pronounced
rushhours**

Conc-imp with 48Δt DAW



max $P^c = 0.22$

Emss-imp with 48Δt DAW



max $P^e = 0.78$

maximal

ini. val. $P^c = 0.22$

emi rate $P^e = 0.78$



characteristic

emission features

favour

observability

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ZEPTEP-2 campaign

- **ZEP**pelin based **T**ropospheric photochemical chemistry exp**ER**iment:
 - 17.10.2008 – 08.11.2008
 - In-situ obs **OH, O₃, HONO, NO, NO₂, CO,...**
 - 25 flights in 100 km diameter around Friedrichshafen (southern Germany)
 - soundings of **vertical profiles**



EUropean Air pollution Disperion- Inverse Model

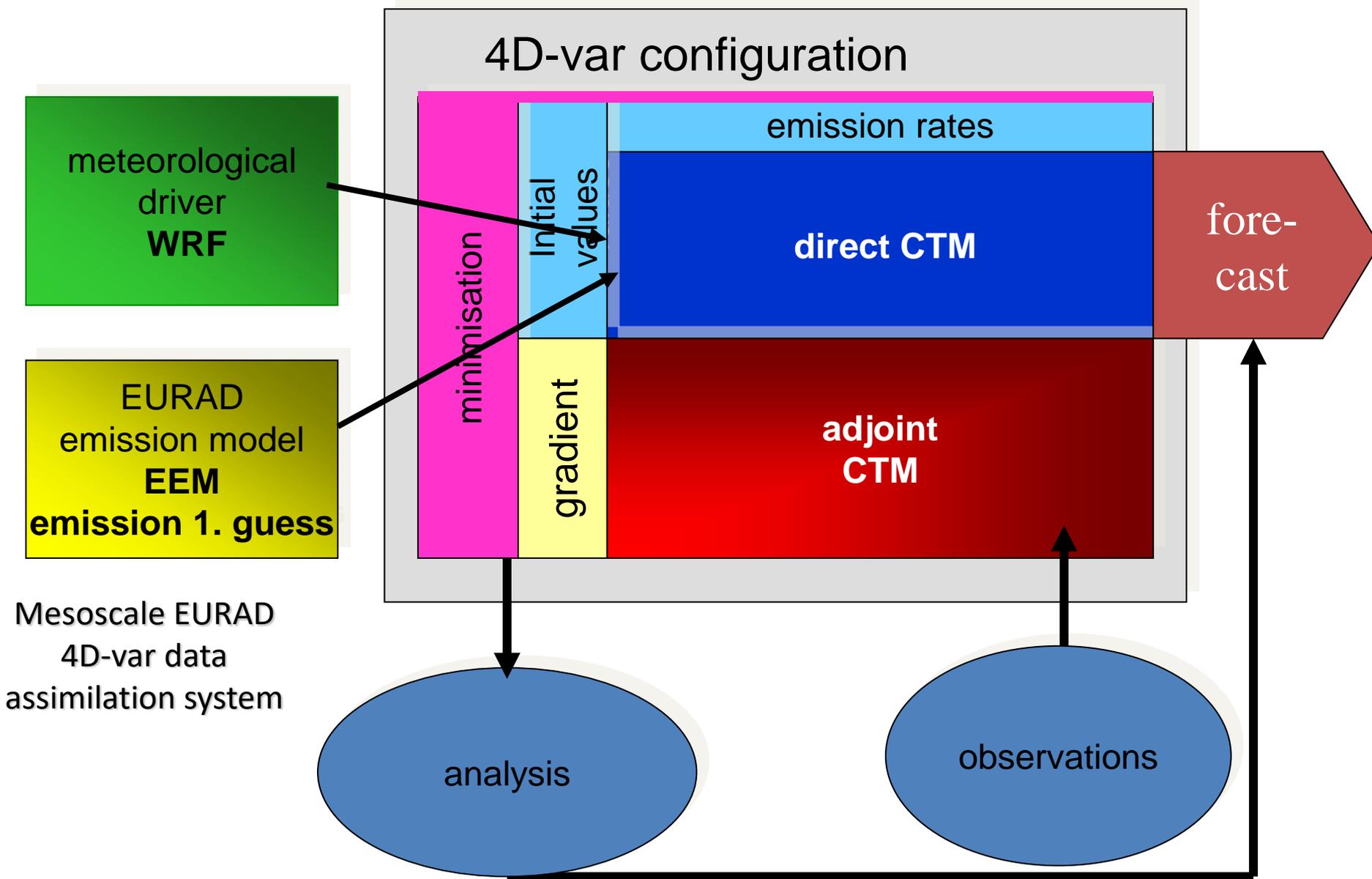
EURAD-IM



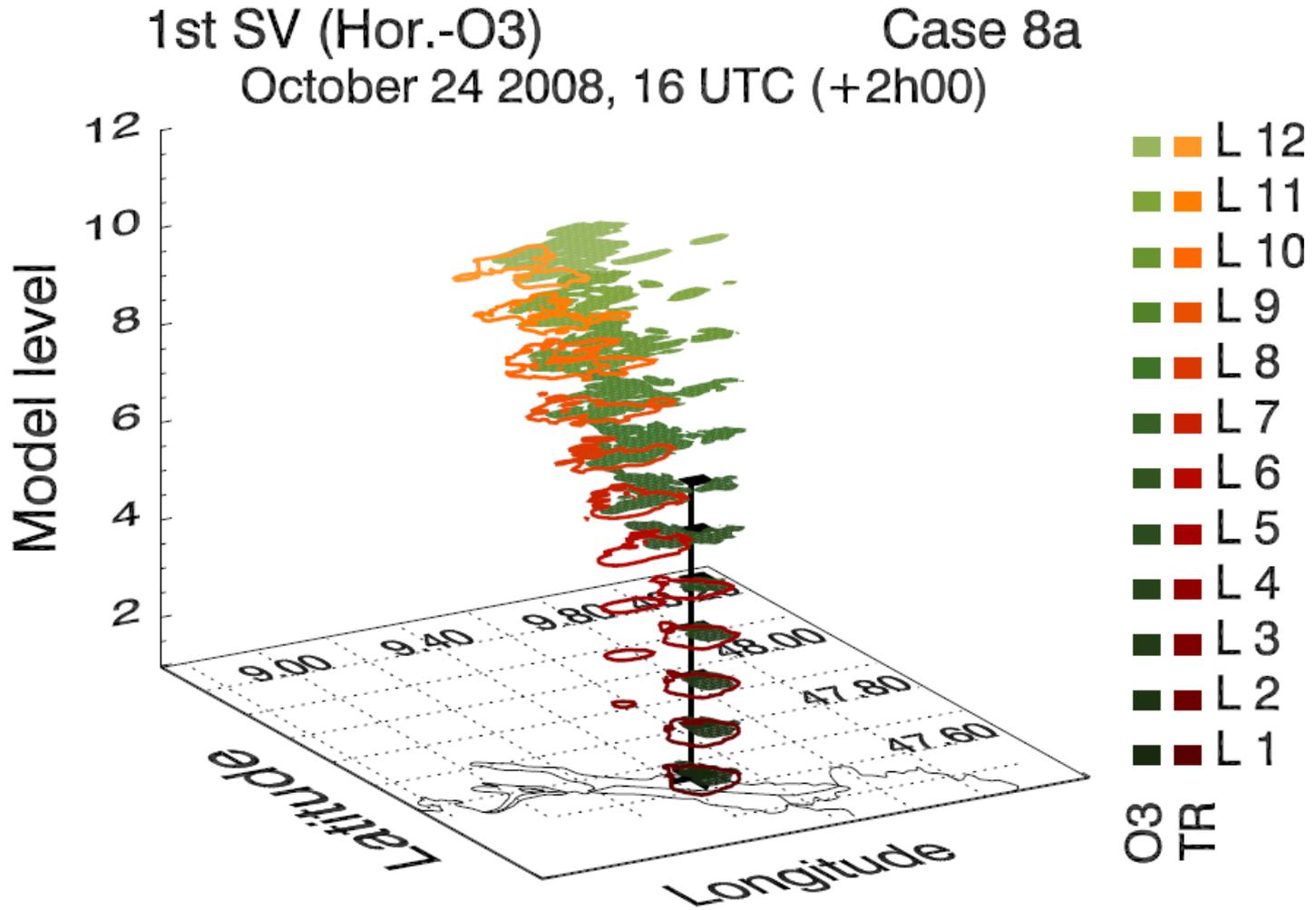
Involved in chemistry data assimilation directed
European activities



Components of EURAD-IM chemistry 4D-var system

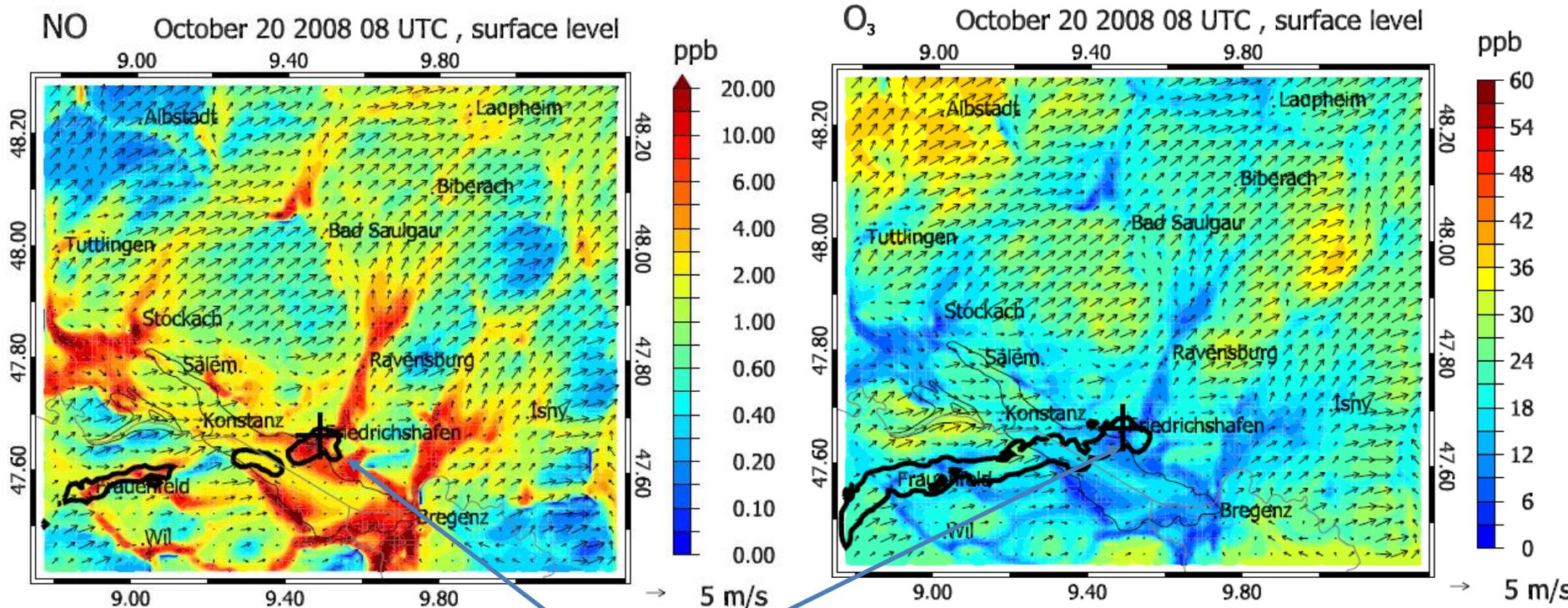


Where should be observed?



Where should be observed?

SV optimal placement of observation sites (solved by PARPACK)



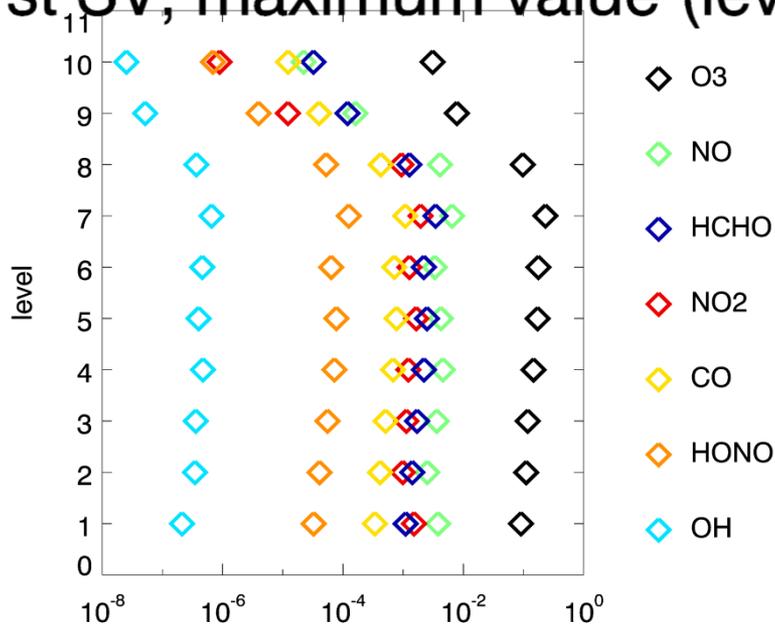
Optimal forecast target place +
 Initial concentrations and optimal horizontal placement of NO (left) and O₃ (right) at surface level . Isopleths of the optimal horizontal placement: black .
 from Goris and Elbern , GMD, 2015

What is important to observe for better O₃ prediction?

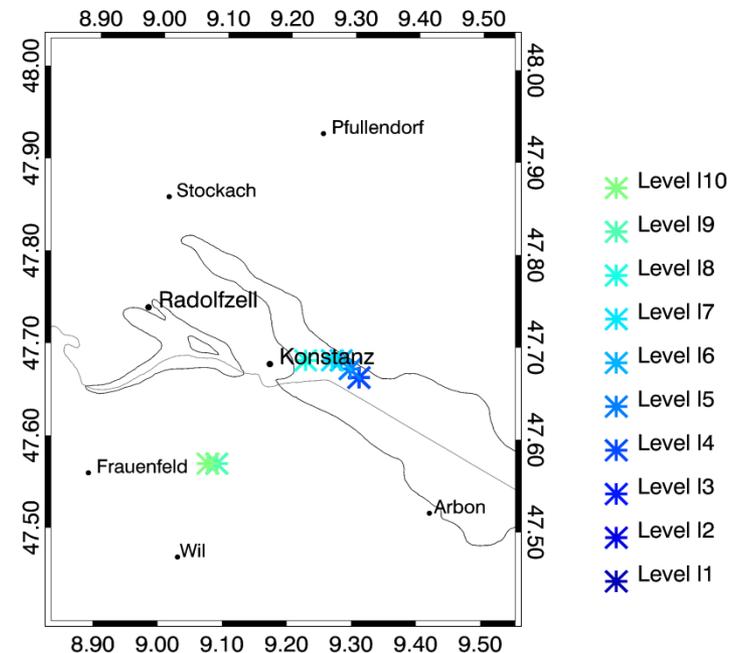
$\delta O_3 > \delta HCHO > \delta CO > \delta HONO > \delta OH$

with NO and NO₂ typically varying between $\delta O_3 > \delta NO_x > \delta HONO$
dependent on the specific chemical scenario.

1st SV, maximum value (level)



October 18 2008 12 UTC (H+02)



Orders of magnitude of different compounds (left) and position of maximal values (right) of maximal singular vector entries per model level
(from Nadine Goll, PhD thesis 2011)

Where should be observed?

Where is it important to observe for O₃ prediction?

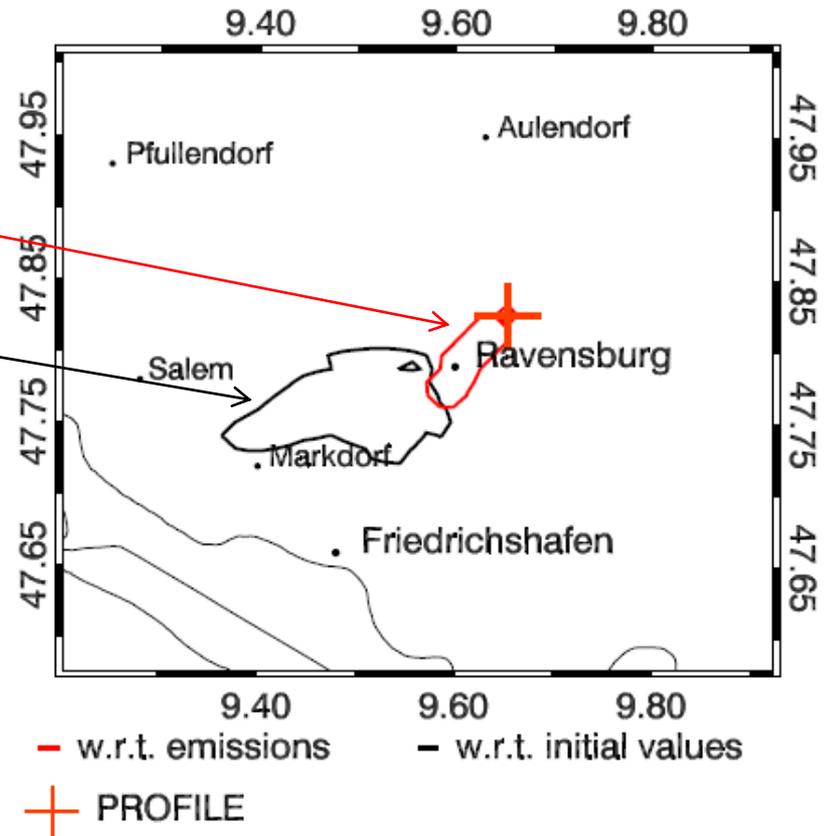
Example of maximal sensitivity contours of SV for

- emission rates (red) for flight
- HCHO initial values (black)

19.Oct. 2008, $t_i=14:00$, $t_f=15:20$ at

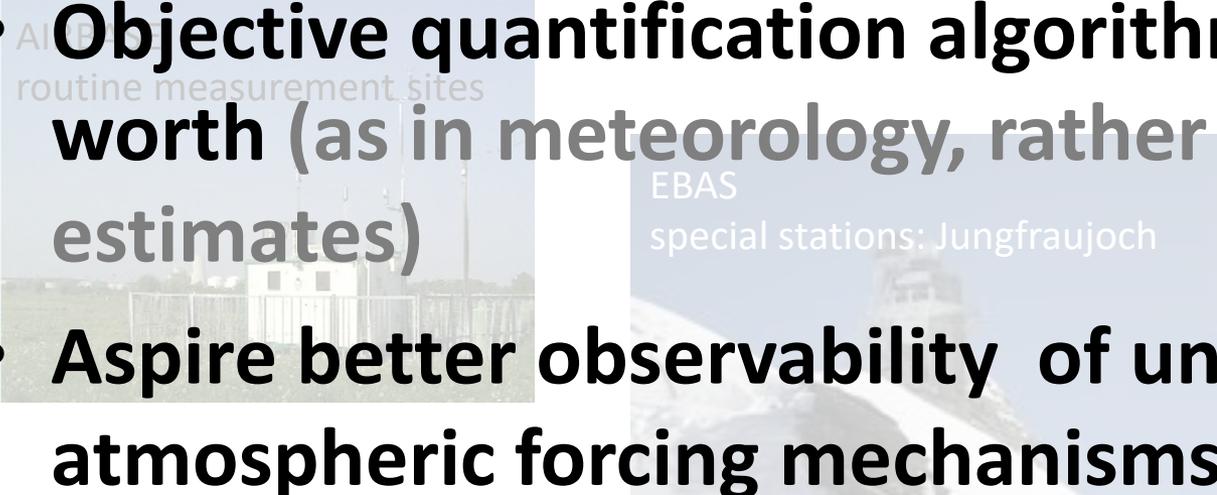
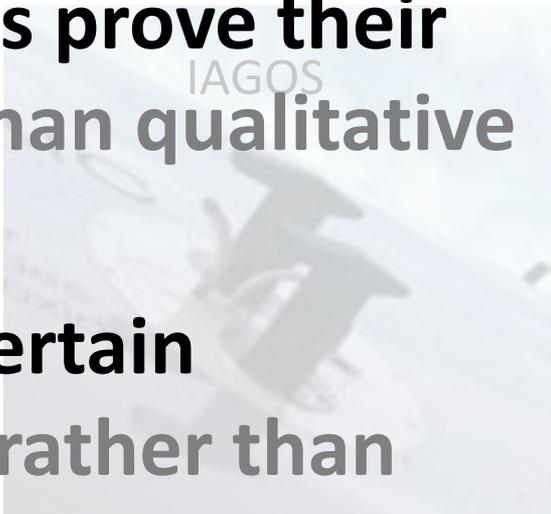
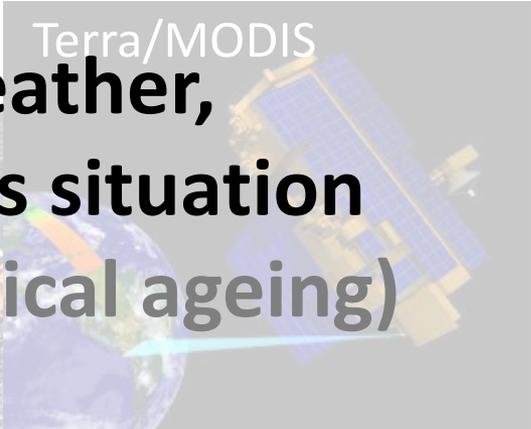
+ for final location.

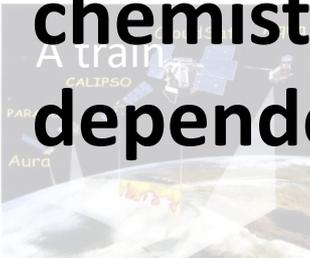
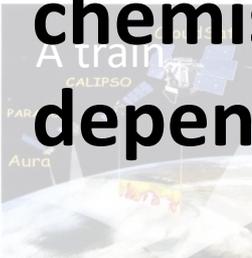
Emission sensitivity is concentrated in the Ravensburg urban area (inverse airshed).



1. Introduction
2. What needs to be observed?
3. When can emissions be quantified?
4. A practical approach for full fledged CTMS
- 5. Conclusions**

General conclusions/suggestions for future observation network design

- **Objective quantification algorithms prove their worth (as in meteorology, rather than qualitative estimates)**

- **Aspire better observability of uncertain atmospheric forcing mechanisms (rather than only state observations)**

- **Attention: being driven by the weather, chemistry network optimization is situation dependent (wind direction, chemical ageing)**




THANK YOU FOR YOUR ATTENTION