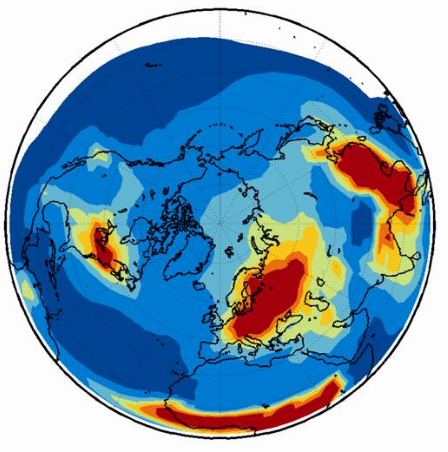
Regional photochemical sources of tropospheric ozone in ETR and Siberia



A.M.Obukhov Institute of Atmospheric Physics RAS

Yury Shtabkin, Konstantin Moiseenko, Andrey Skorokhod, and Elena Berezina

INTRODUCTION

• Effect of photochemically active species emissions on near-surface air composition in industrial regions is non-local and in many cases can be traced in transcontinental scale.

• Largescaled plumes of polluted air defined by observations of tracer species on background stations and calculations with chemical-transport models are examples of this effect.

• In this work we use GEOS-Chem chemical transport model to make an assessment of influence have anthropogenic and biogenic emissions in Europe, ETR and Siberia on total ozone generation taking into account common non-linear properties of O_3–NO_x–CO–VOC system.

THEORETICAL BASIS OF USED METHODS

Radical-chain mechanism of VOC oxidation in O_3 –NO_x –CO–VOC system

Reactions		Type
$O_3 + h\nu + H_2O \rightarrow 2\ OH + O_2$	**(R1)**	initiation reactions
$CH_2O + h\nu \rightarrow 2\ HO_2 + CO$	(R2)	
alkenes + $O_3 \rightarrow HO_2$, organic radicals	(R3)	
$RH + OH + O_2 \rightarrow RO_2 + H_2O$	(R4)	continuation reactions
$RO_2 + NO + O_2 \rightarrow \alpha NO_2 + \beta HO_2 + CARB$	**(R5)**	
$HO_2 + NO \rightarrow NO_2 + OH$	**(R6)**	
$NO_2 + h\nu + O_2 \rightarrow NO + O_3$	(R7)	
$HO_2 + HO_2 \rightarrow H_2O_2$	(R8)	termination reactions
$HO_2 + RO_2 \rightarrow ROOH$	(R9)	
$OH + NO_2 \rightarrow HNO_3$	**(R10)**	
$RO_2 + NO \rightarrow$ organic nitrates	**(R11)**	

In low polluted air ($NO_x < 0.5$ ppb) sink occurs by R10 & R11 $\rightarrow NO_z$

$$\mathbf{NO_z = NO_y - NO_x}$$

ASSESSMENT CRITERIA

1) The method of emission reduction – numerical assessments of atmospheric response (AR) [Wild et al., 2001]

$$AR_{REG} = \chi(O_3)_0 - \chi(O_3)_{REG}$$

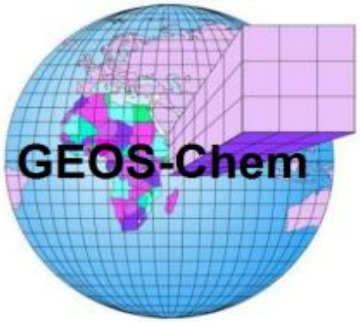
2) The first derivative of AR in NO_x – ozone production efficiency (OPE) [Trainer et al., 1993]

$$\text{OPE} = \frac{\partial \text{AO}}{\partial NO_x} \approx \frac{\Delta O_3}{\Delta NO_z}$$

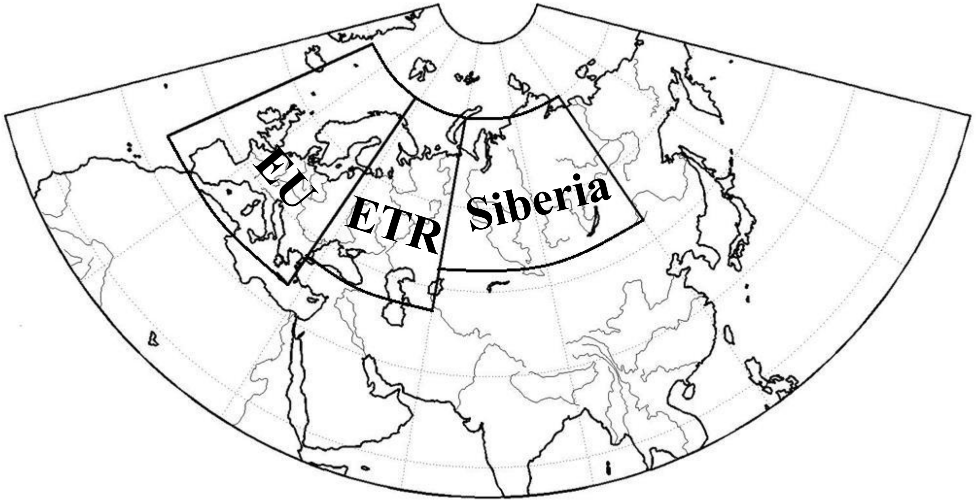
Within Eulerian approach the value $\Delta O_3/\Delta NO_z$ is defined as the slope of regression line from measurements or model calculations data in (NO_z , O_3) axes.

METHODS

1) Emission inventories:
Anthropogenic (EDGAR, http://edgar.jrc.ec.europa.eu)
Biogenic (volatile organic compounds (VOC) oxidation, MEGAN, http://bai.acd.ucar.edu/MEGAN/)
Wildfires (GFED, http://www.globalfiredata.org)



2) Global chemical-transport model GEOS-Chem (http://acmg.seas.harvard.edu/geos).



Geographical areas selected for calculations: EU - Europe (35-75 N, -15 – 27 E), ETP - European territory of Russia (41-75 N, 27-60 E), Siberia (49-75 N, 60- 120 E).

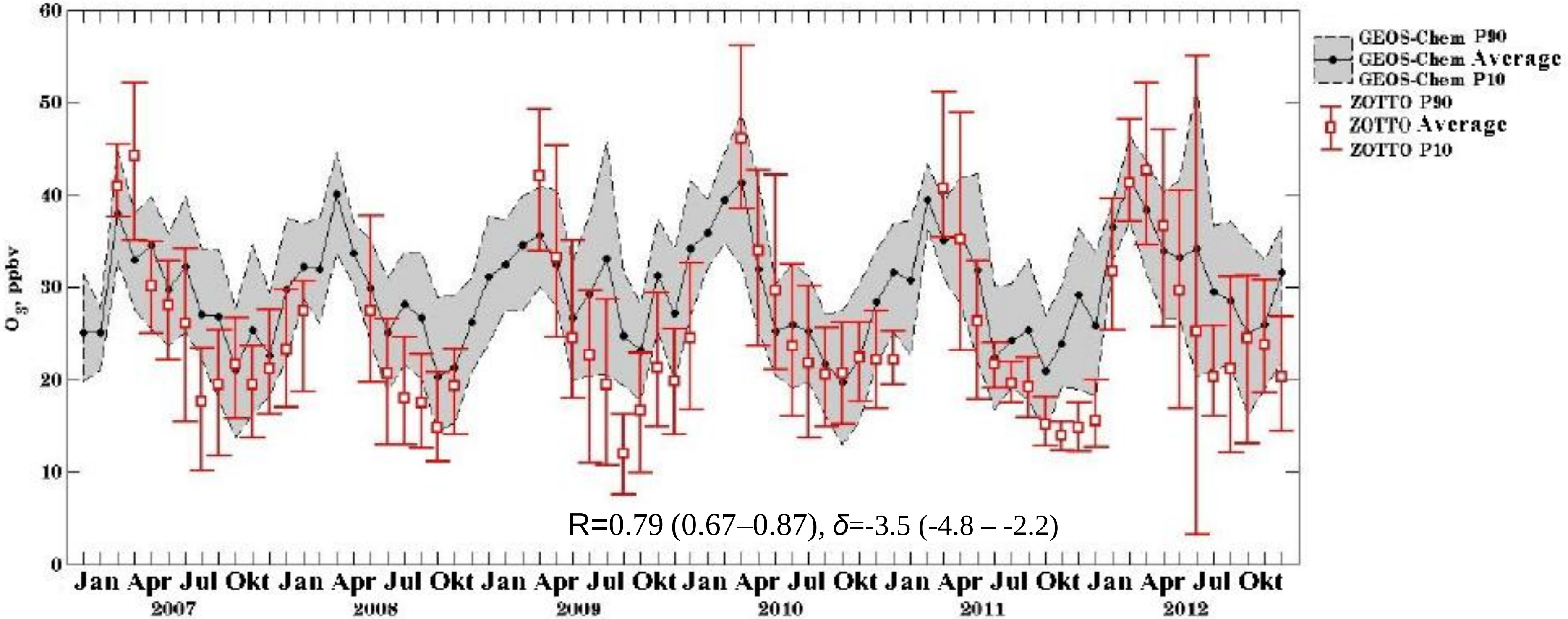
ZOTTO

ZOTTO measurements: CO_2, CH_4, CO, Ozone, NO_x and aerosols at different heights, meteorology at different heights and on the ground (Temperature, Wind, Humidity), biweekly flask sampling at 301 m height and various irregular ecosystem measurements

zottoproject.org

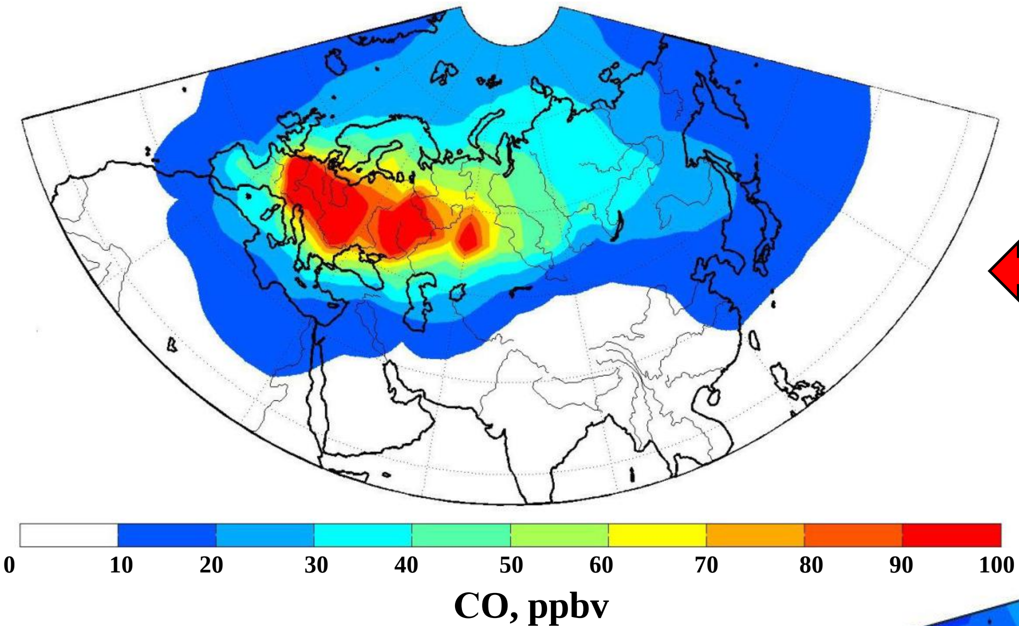
Background character of the station provide an excellent opportunity to study regional as well as long-range impact of various climatically important sources of pollutants including regional industry and wildfires.

GEOS-Chem vs ZOTTO



Ozone concentration at a height of 6 m above the ground observed at ZOTTO in 2007-2012. P10,90 - percentile, □ - average. The solid and dashed lines - GEOS-Chem model calculation (monthly averaged concentrations at the first model level, ~ 58 m above the ground).

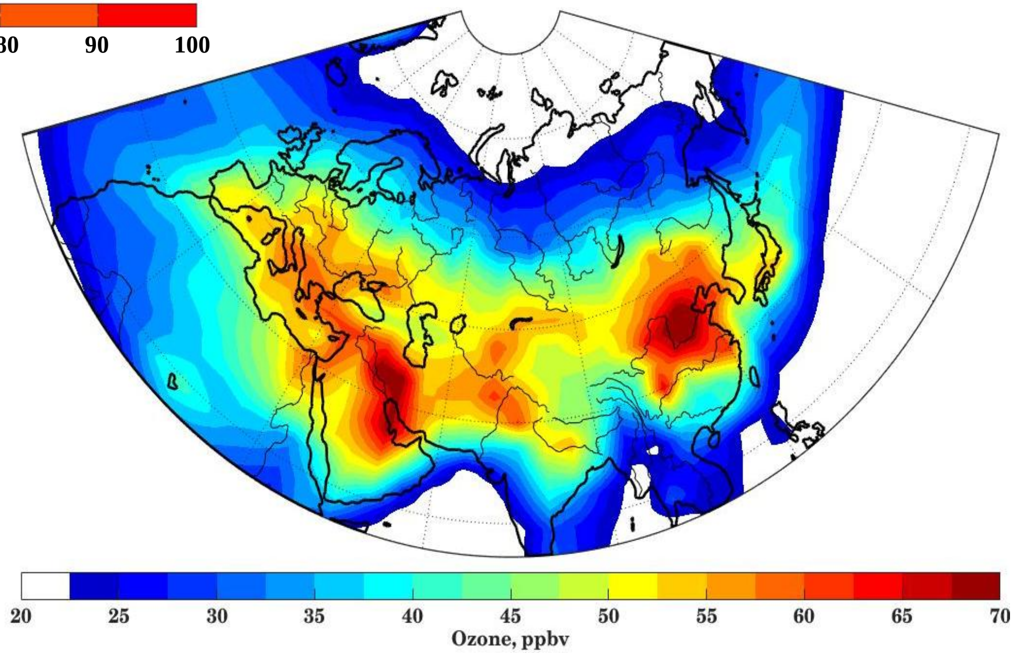
MODEL EXPERIMENT (I)



Atmospheric response on anthropogenic emissions in near-surface CO field

$$AO_R = \chi(CO)_0 - \chi(CO)_{REG}$$

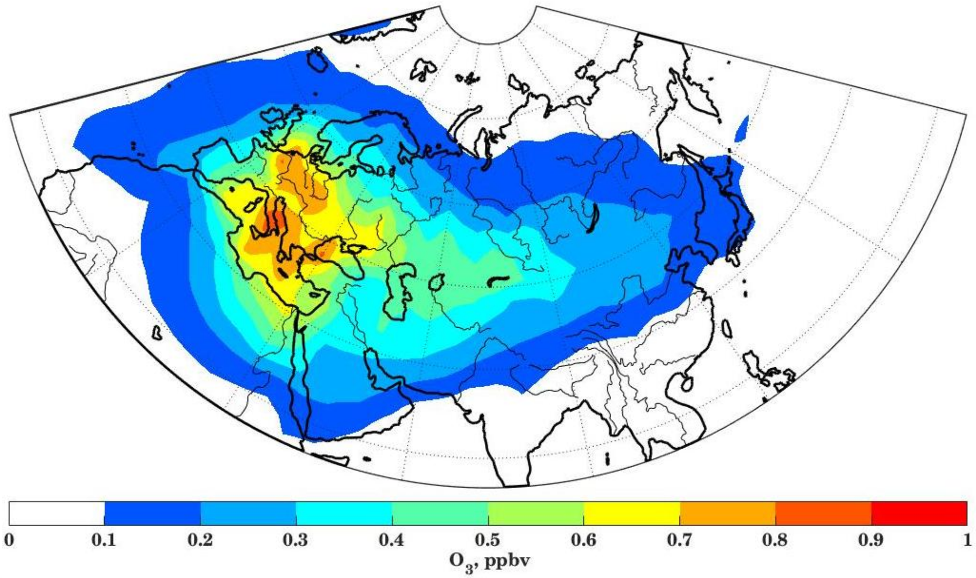
Averaged for summer 2007 ozone concentration



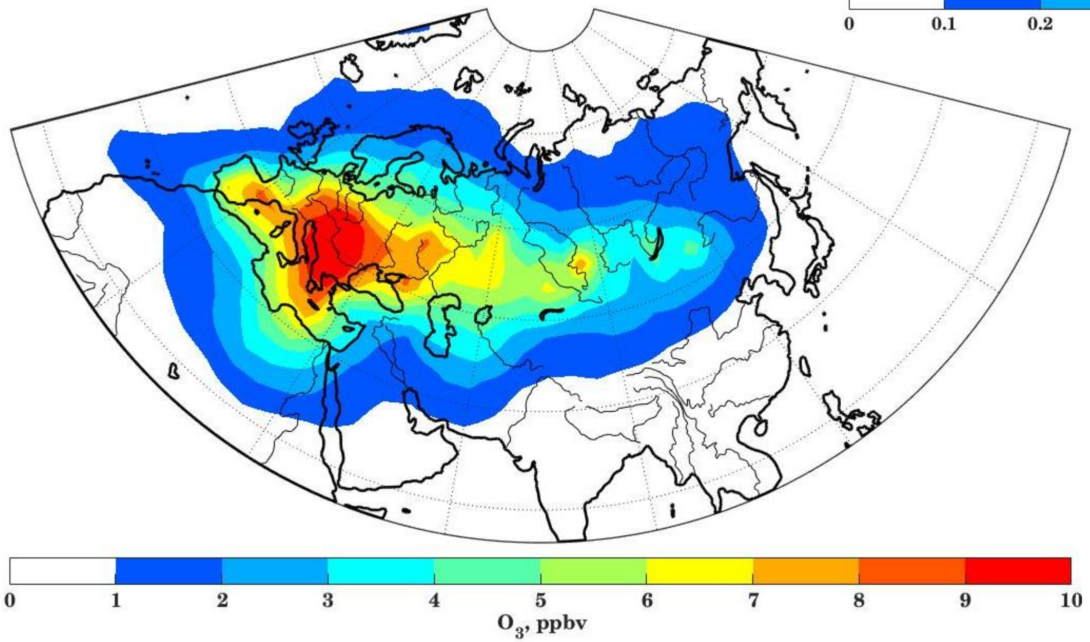
MODEL EXPERIMENT (II)

SUMMER

AR on anthropogenic CO emissions in 3 regions

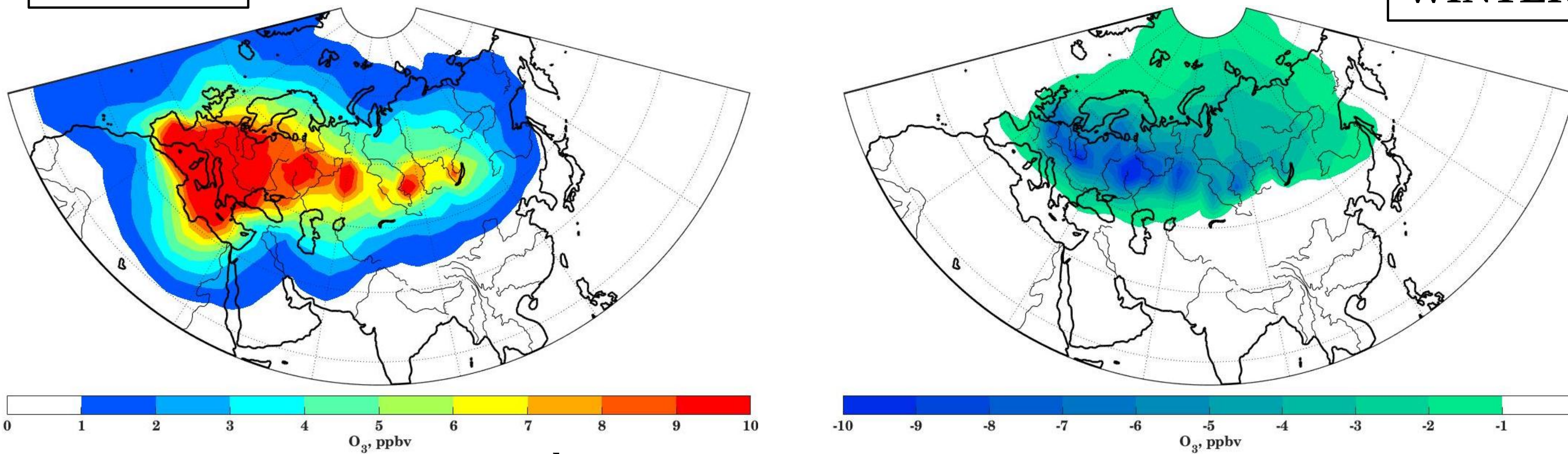


AR on biogenic VOC emissions in 3 regions

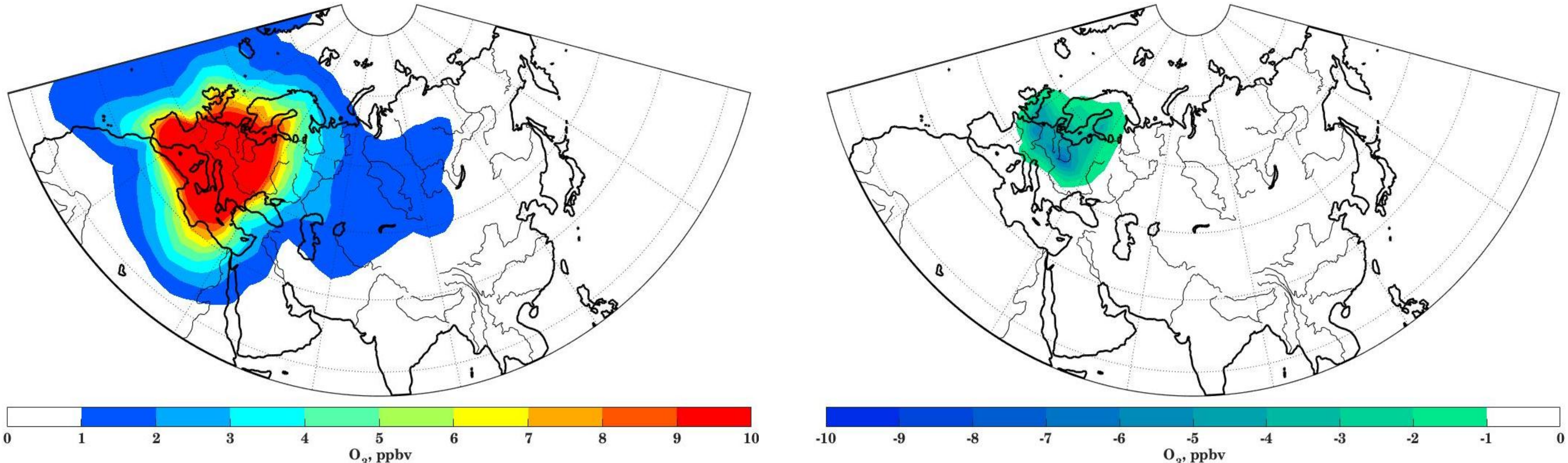


MODEL EXPERIMENT (III)

SUMMER **WINTER**

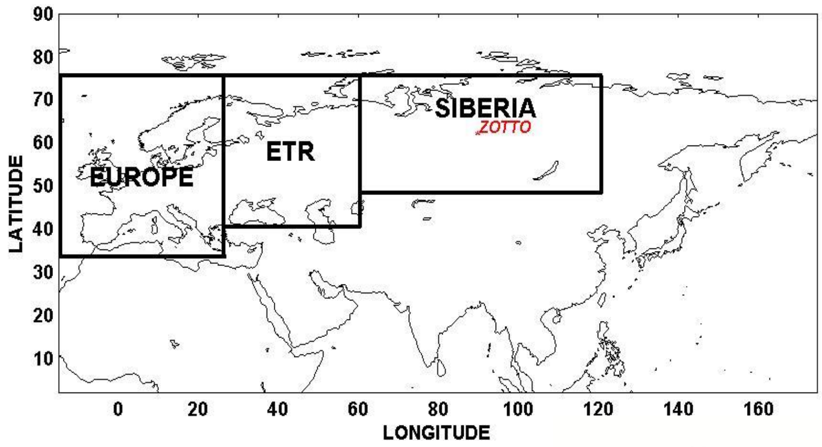


AR on anthropogenic NO_x emissions in 3 regions



AR on anthropogenic NO_x emissions in Europe

ZOTTO near-sutrface ozone sensivity to NOx and VOC emissions

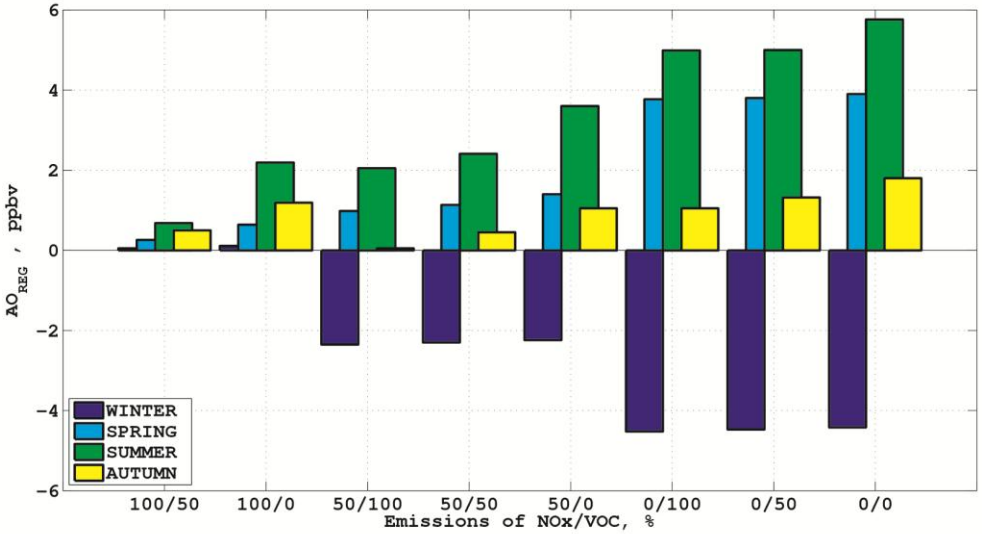


Geographical areas selected for ozone reduction calculations

Atmospheric response:

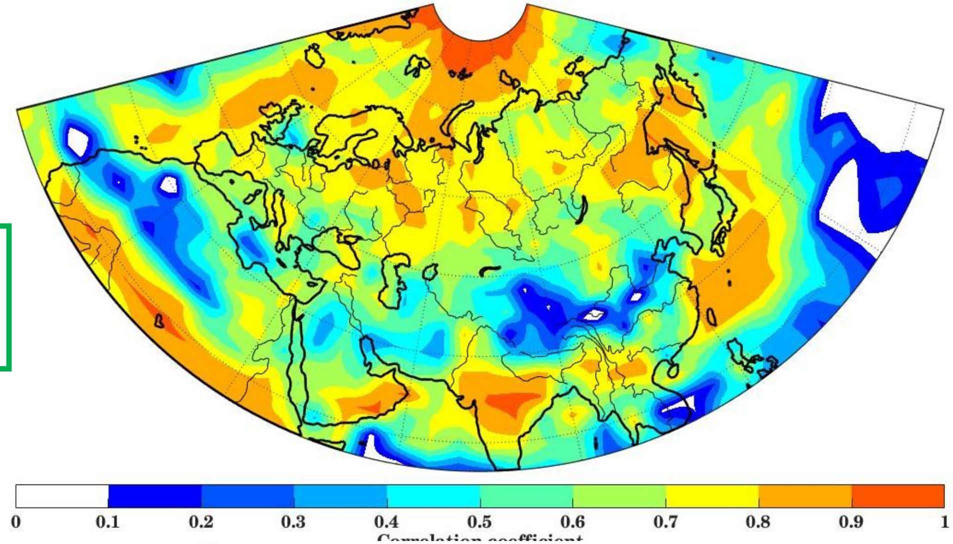
$$AO_R = \chi(O_3)_0 - \chi(O_3)_{REG}$$

Summary diagram of ozone reduction near ZOTTO station at different biogenic VOCs and anthropogenic NOx emission reduced values in Siberia, European Russia and Europe. An averaged values for all 2007 seasons are given.



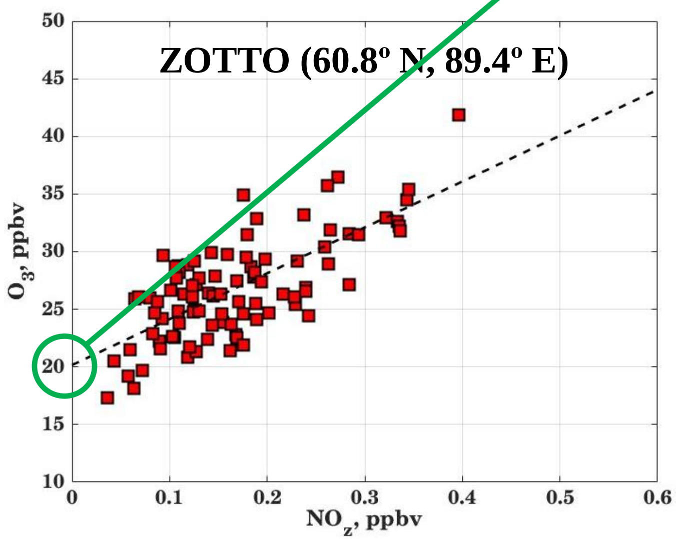
OZONE PRODUCTION EFFICIENCY (I)

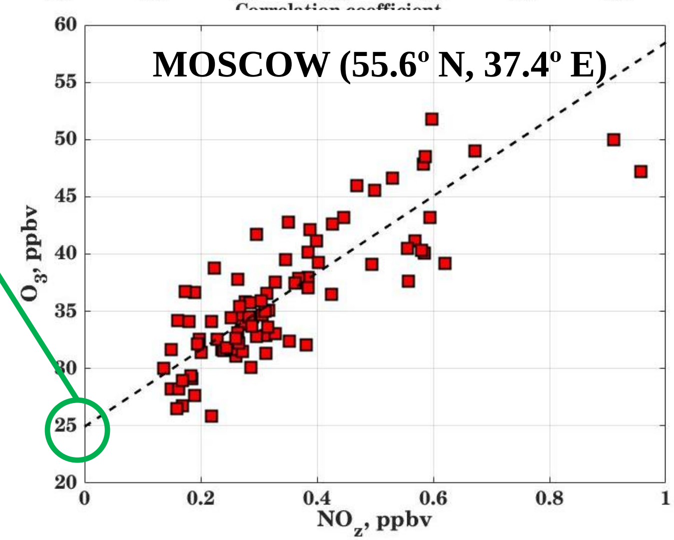
Correlation between ozone and NO_z



Ozone production efficiency (OPE):
$\delta_{NOx}O_3 \approx \Delta O_3/\Delta NO_z$

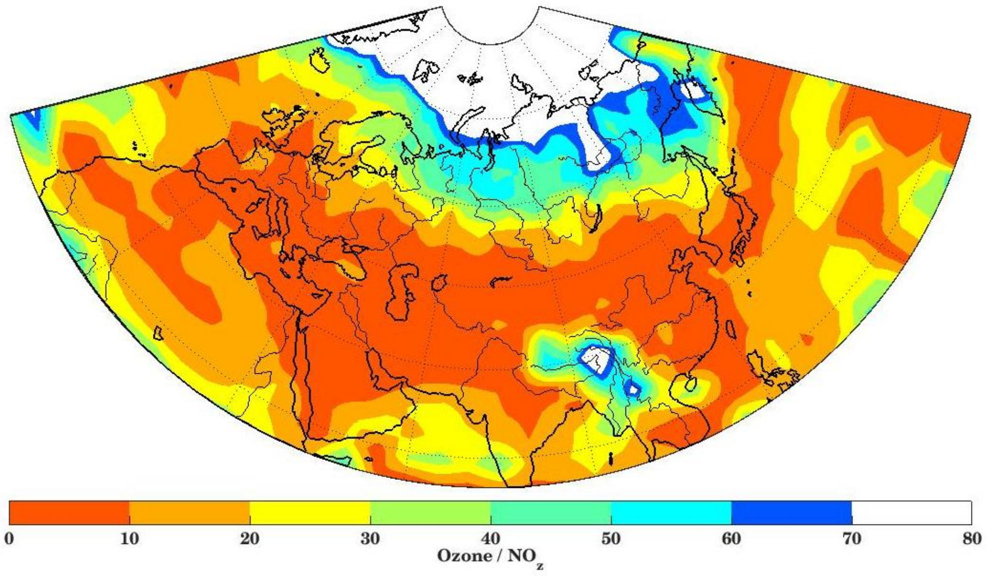
A) Regression: $O_3 = K{*}NO_z + Ozone_0$



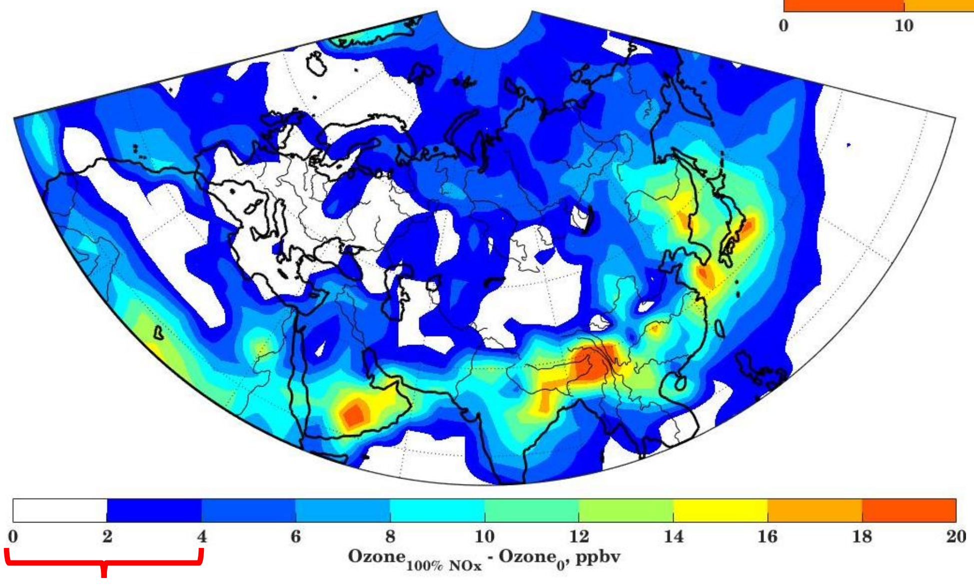


OZONE PRODUCTION EFFICIENCY (II)

Averaged for summer 2007 OPE field



Difference between summer O_3 fields calculated by model using reduction apporoach (100% reduced NO_x emissions) and Ozone$_0$ fields obtained by using regression (A)



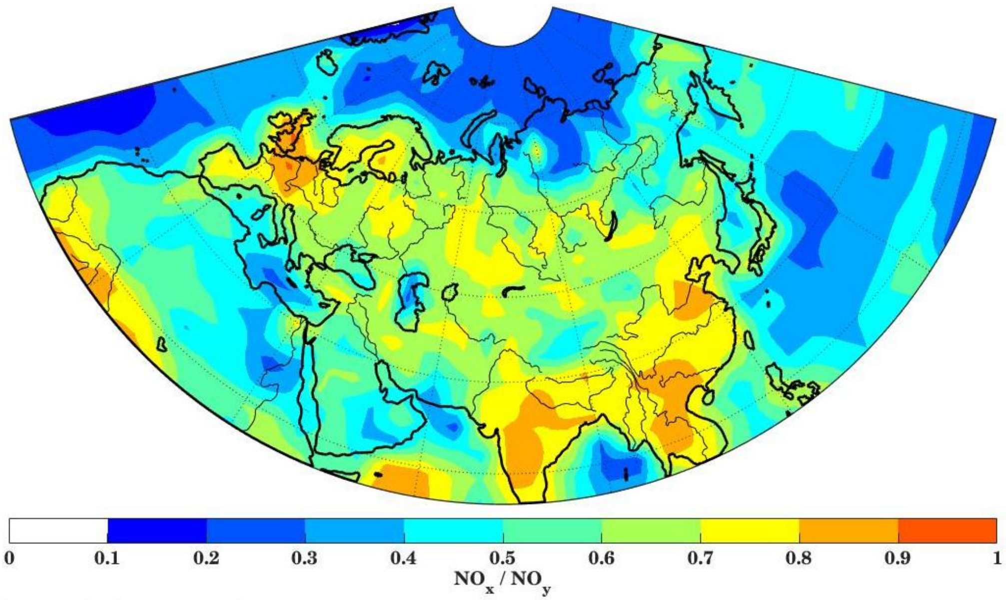
The limits of applicability of this approach

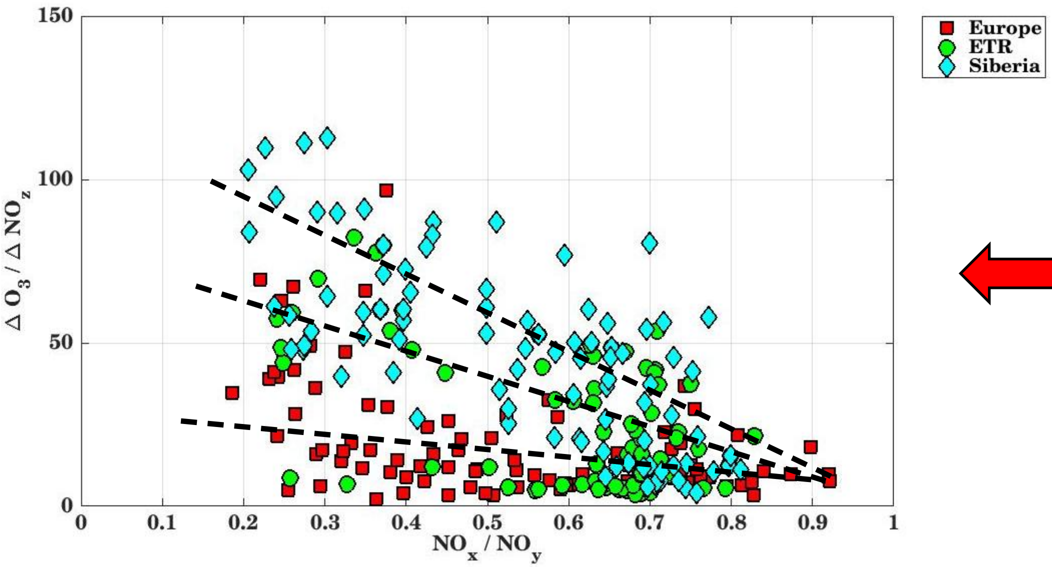
DEPENDENCE OF OPE ON THE AGE OF AIR MASS

Age of polluted air mass

$T = NO_X / NO_Y$

OPE decreases with the increase in NO_x emissions





Averaged for warm period values of OPE depending on age of polluted air mass

SUMMARY

• It was shown NO_x -sensitive ozone generation regime dominates over continental lower troposphere in photochemically active period of year. In these conditions AR O3 is determined by regional NO_x emissions, controlling intensity of ozone predictors oxidation reactions. The average value of regional sources impact over middle-latitude anthropogenically polluted air plume axis was about 10–15 ppbv, or ~20–30% of background near-surface ozone concentration in continental areas (35 – 55 ppbv).

• The highest AR_{O3} were obtained for Europe, in eastern regions on the plume axis response value decrease with decreasing of anthropogenic load.

• It was shown winter (OH-limited) ozone generation regime dominates over the continent during cold period. Ozone concentration decrease with increasing of NO, the main part of anthropogenic NO_x emissions.

• It was shown photochemical ozone production value has good correlation with air mass age, determined as NO_x /NO_y.

• It is important the continuation of studies of regional factors role in the balance of near-surface O_3 using air content complex monitoring data.

REFERENCES

- *Wild O. and Akimoto H.* Intercontinental transport of ozone and its precursors in a three-dimensional CTM // J. Geophys. Res. 2001. V. 106. P. 27729–27744.

- *Trainer M., et al* Correlation of ozone with Noy in photochemically aged air // J. Geophys. Res. 1993. V. 98. PP. 2917-2925.