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# PRELIMINARY EVALUATION OF CMAQ MODELLED WET DEPOSITION OF SULPHUR AND NITROGEN OVER BULGARIA

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**Abstract**: Wet depositions of sulphur and nitrogen by the WRF-CMAQ modelling system are compared to observations for the region of Sofia. Precipitation samples were collected and chemically analysed for the period March-June 2016. Sulphate is prevailing for the whole period (share of 34%), following by nitrate (share of 25%).
The precipitation amount on a monthly basis is overestimated by the model (average NMB 70%), thus a precipitation adjustment using observed values is applied as post-processing of CMAQ output data. This correction leads to improvement of simulated monthly depositions, especially for sulphur (NMB 9%). The effect on nitrogen deposition is not so clear, as the correction leads, in general, to underestimation of nitrogen depositions. Back trajectories for two selected periods with high sulphate concentrations suggest importance of emissions at local and regional scale. Further studies are needed to analyse other processes important for model wet deposition (emissions, transport etc)

***Key words:*** *model validation, precipitation chemistry*

## INTRODUCTION

The deposition of acidifying and eutrophying components in Bulgaria is a key factor for the health of forest ecosystems, which cover 31 percent of the country's area. In urban areas the atmospheric deposition may have adverse effects on buildings, vegetation and water quality. Monitoring data for deposition of pollutants in Bulgaria are, however, limited in number and on a non-regular basis. In fact, the region of South East Europe and especially Bulgaria is "white field" in global and European long-term databases on chemical composition of precipitations (EBAS database). The numerical modelling of transport processes, chemical transformation of pollutants and their deposition is powerful tool to fill in gaps in regions with lack of, or insufficient observations.
The objective of this work is to study the performance of the Bulgarian Chemical Weather Forecast System for the simulation of sulphur and nitrogen wet deposition for the region of Sofia, using recently obtained data for the chemical composition of precipitation samples.

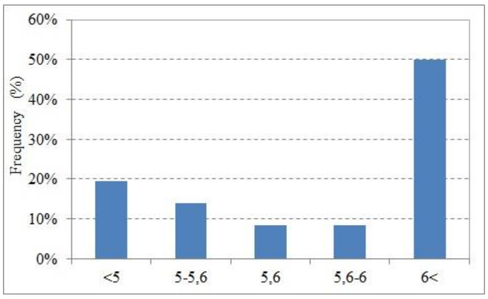
## METHODOLOGY

### The modelling system

The Bulgarian Chemical Weather Forecast System (Syrakov et al., 2013) is based on the state of the art WRF-CMAQ model chain. The Weather Research and Forecasting model WRF v3.6.1 (Skamarock and Klemp, 2008) is used as meteorological pre-processor to the Community Multiscale Air Quality (CMAQ) model, v4.6 (Byun and Schere, 2006). The model was run over 3 nested domains – Europe (81km horizontal resolution), Balkan Peninsula (27 km), and Bulgaria (9 km). The initial meteorological conditions are provided by the National Centers for Environmental Prediction (NCEP) Global Forecast Model (GFS) with resolution of 1°x1° in space and 6 hours in time. The chemical boundary conditions over the mother domain (Europe) are set according to the CMAQ's BCON profiles. The presumption is that the possible errors decrease inside the domains because of the continuous action of pollution sources.
The characteristics of some processes affecting wet deposition are as follows: for wet deposition of gases and particulates – RADM (Chang et al., 1987), for gas-phase chemistry CB4 mechanism, for inorganic aerosol thermodynamics/partitioning ISORROPIA 1.7 (Nenes et al.1998). CMAQ was run with the predefined configuration "cb4_ae4_aq".

The emissions are based on the inventory provided by the Netherlands Organization for Applied Scientific Research (TNO) for 2009 (Kuenen et al., 2014); for Bulgaria national emission inventories for 2010 have been exploited. Results from model domain Bulgaria have been used here.
The model wet deposition was estimated using CMAQ output as the sum of gas and aerosol species. For nitrogen the deposition flux includes nitrate ($NO_3^-$), ammonia ($NH_3^+$), ammonium ($NH_4^+$), NO, and $NO_2$. The sulphur wet deposition was estimated as the sum of $SO_4^{2-}$ and $SO_2$.

**Observational data**
The observational data consist in daily precipitation samples collected with a wet only deposition sampler WADOS according to EMEP methodologies (EMEP, 2001) at the Central Meteorological Observatory Sofia (42.655 N, 23.384 E, at 586 m a.s.l.). Collected daily samples are further analysed for acidity-pH, electrical conductivity-EC, main anions $Cl^-$, $SO_4^{2-}$ , $NO_3^-$, cation $NH_4^+$ and elements Ca, Mg, K, Na, Fe, Si, Zn. Chemical analysis is performed by Ion Chromatograph (ICS 1100, DIONEX), ICP OES (Vista MPX CCD Simultaneous, VARIAN) and Spectrophotometer S-20. For the period from March to June 2016, 36 precipitation samples were collected and analysed.



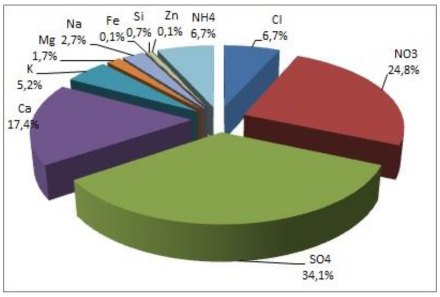
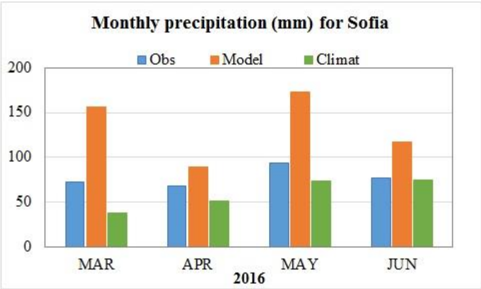



**Figure 1.** Chemical analysis of the samples. Frequency distribution of pH (left) and Percentage contribution of individual ions to total ionic composition (right)

The pH values for the period from March to June 2016 were in the range (4.7 - 7.6). The pH frequency distribution is presented in Fig. 1 (left). From all precipitation samples 33% are in acidic range (below 5.6) and 58% are in alkaline range. Only 8% of precipitation events are in neutral range.
The percentage contribution of each ion to total ionic composition/mass is shown in Fig.1 (right). The contribution of sulphate and nitrate (the acidifying components) are 34.1% and 24.8%, respectively. 33.8% of the total ionic mass are on alkaline cations ($NH_4^+$, Ca, Mg, K, Na, Fe). This explains the higher percentage of precipitation samples with pH value above 5.6 (58%).
The concentration of main anions and cations in precipitation samples followed the order: $SO_4^{2-}$>$NO_3^-$> Ca > $NH_4^+$, $Cl^-$ > K > Na > Mg >Si > Fe, Zn.

**Precipitation adjustment**
Wet deposition estimated by the model is sensitive to simulated precipitation amounts. To account for these errors, a correction is applied as post-processing to CMAQ estimated wet depositions. The precipitation bias adjustment follows the work by Appel et al., 2011, where the modelled wet depositions are linearly corrected by the ratio of the observed to estimated precipitation. Thus, two model data sets are available – the first one with no post-processing for adjustment of CMAQ wet deposition data, and the second one with precipitation adjustment.

**RESULTS AND DISCUSSION**
**Precipitation**
Model performance on precipitation amounts is shown in Fig. 2. Note that the whole period was marked by precipitations above the climate values. The model overestimates the precipitation for all months, more significant in April and May, it also produces higher monthly variability than the observed ones.



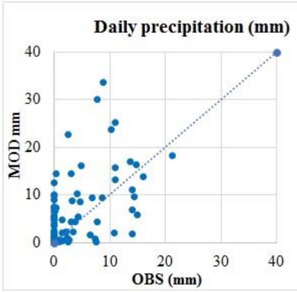
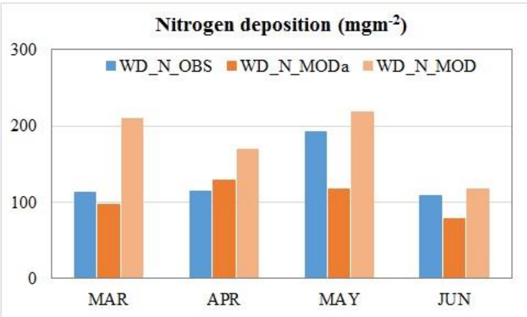



**Figure 2.** Monthly accumulated precipitations – observed, modelled and climate values (left), scatterplot of daily precipitations (right)

The average normalised mean bias (NMB) is 70.1%, with maximum value for March – 117%. The correlation coefficient for the daily values is 0.59, with lowest value for June (0.1). The complex terrain around Sofia contributes to highly irregular distribution of precipitation in summer, which could hardly be resolved by the used 9 km grid resolution. The local scale variability in June could be a reason for deficiencies in modelled precipitation in summer time.

**Monthly depositions**

Fig.3 shows monthly (March to June 2016) accumulated N and S depositions – observed and modelled by CMAQ in two versions - with and without precipitation adjustment. In Tables 1 and 2 the mean values and the relative NMB are given, respectively for N and S.



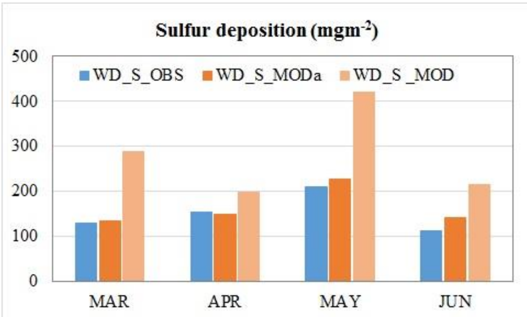



**Figure 3.** Monthly accumulated wet depositions ($mgm^{-2}$) of N (left) and S (right): observed (blue), modelled with adjustment (orange) and modelled without adjustment (light orange)

CMAQ modelled wet depositions are overestimating the observed ones, with average NMB of 87% for sulphur and 39% for nitrogen. The precipitation bias adjusted model depositions are closer to observed ones on monthly basis. S-deposition is still overestimated but the mean NMB is reduced significantly (9%), N-deposition is now underestimated with NMB of -17%. This suggests that the precipitation adjustment has clear positive effect on S-deposition, while not so for N-deposition. Precipitation amount is only one of the factors determining wet deposition.

**Table 1.** Wet deposition of Nitrogen: monthly values and bias for two model values

| | WD_N-obs ($mgm^{-2}$) | WD_N-mod ($mgm^{-2}$) | WD_N-mod-adj ($mgm^{-2}$) | NMB % | NMB-adj % |
|---|---|---|---|---|---|
| **MAR** | 112 | 209 | 96 | 86.37 | -14.21 |
| **APR** | 115 | 169 | 128 | 47.21 | 11.60 |
| **MAY** | 193 | 218 | 118 | 13.10 | -38.89 |
| **JUN** | 108 | 117 | 78 | 8.70 | -28.03 |
| **all** | 528 | 713 | 420 | 38.85 | -17.38 |

Other processes (chemistry and dispersion of pollutants, processing of emissions data) contribute also to modelled values and the results in this preliminary study pointing out for the importance of such processes especially for nitrogen. NMB for $NO_2$ and $SO_2$ in the air, based on model and observational data for the selected period, indicate strong underprediction for $NO_2$ (- 82%), $SO_2$ is overpredicted by 18%. Emissions from traffic, not accounted for in the model, are one probable cause for this discrepancy.

**Table 2** Wet deposition of Sulphur: monthly values and bias for two model options

| | WD_S-obs ($mgm^{-2}$) | WD_S-mod ($mgm^{-2}$) | WD_S-mod-adj ($mgm^{-2}$) | NMB % | NMB-adj % |
|---|---|---|---|---|---|
| **MAR** | 129 | 289 | 133 | 123.84 | 3.04 |
| **APR** | 152 | 198 | 150 | 29.58 | -1.76 |
| **MAY** | 210 | 421 | 227 | 100.47 | 8.32 |
| **JUN** | 111 | 215 | 142 | 93.39 | 28.05 |
| **all** | 602 | 1123 | 652 | 86.82 | 9.41 |

**Long range effects for two selected periods**

The origin of air masses for two selected periods was examined by means of back-trajectories (BT) produced by the model HYSPLIT (Stein et al, 2015, Rolph et al., 2017).

The first case period is from 02.03 to 13.03.2016, characterised by high sulphate concentrations (content in daily samples ranged from 0.86 to 4.64 $mgl^{-1}$). The modelled S wet deposition (204 $mgm^{-2}$) was overestimated by a factor of 2. The weather was marked by frequent passage of Mediterranean cyclones south of the country towards east (Bulletin-NIMH, 2016), and flow from SW turning later to SE-E.

Fig. 4, showing the frequency of HYSPLIT back trajectories for the period (02-13.03.17) and for two particular days, suggests influence of emissions at national and regional scale.

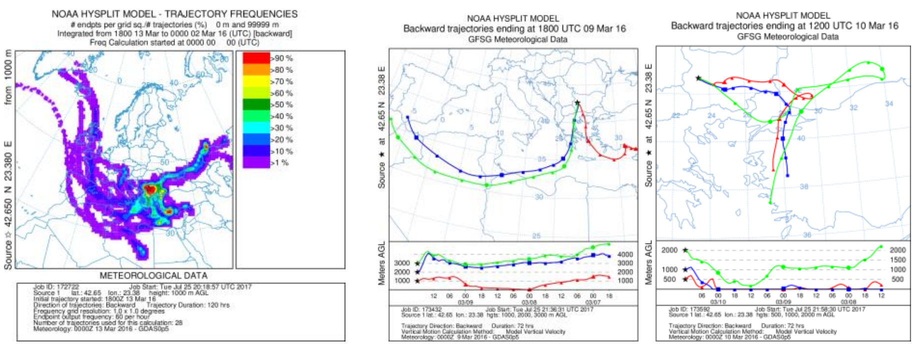



**Figure 4.** HYSPLIT back trajectories for Sofia: left – frequency of BT at 1000m agl for 02-13.03.2016; center and right: 3 days BT on 09.03.2016 18:00 and on 10.03.2016 12:00, arriving at heights 500, 1000 and 2000 m agl

In the second case period (09-11.04.17) wet depositions were well reproduced by the model, with NMB of about 10%. The pH was below 5.0 and the observed sulphur deposition about 60 $mgm^{-2}$. The weather in Bulgaria was determined by waste low pressure system centred over the Balkans and a high pressure system over Northern Africa extending towards north-east, producing NW flows near the ground and SW flows aloft (Bulletin – NIMH, 2016). The back-trajectories (Fig.5) suggest influence from Balkan countries from NW and W.

**CONCLUSION**

CMAQ estimated monthly wet depositions of S and N overestimate observed ones for the region of Sofia. Correction of modelled precipitation amount with observations leads to better performance of the model, especially for sulphur depositions. Sulphate is prevailing in precipitation samples for the studied period (March – June 2016). Model results for two case periods suggest both influences on local and regional emission sources.

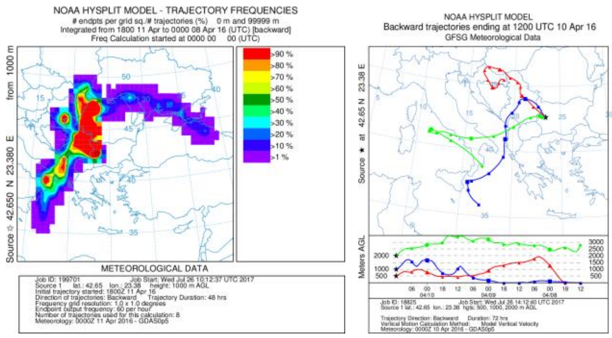



**Figure 5.** HYSPLIT back trajectories for Sofia: left – frequency of BT at 1000m agl for the period 08-11.04.2016; right: 3 days BT on 10.04.2016 12:00, arriving at heights 500, 1000 and 2000 m agl

As the analysis on modelling and observed depositions in Bulgaria started recently, the results in this work have to be treated as preliminary. Further studies on combining observations and CMAQ model data are necessary to investigate the relations between emissions, transport and depositions processes.

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