

Chapter 4

Evaluation of the Eulerian and Lagrangian models by measurements of VOC and CO.

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4.1 Introduction.

Comparison of models and evaluation of the models by comparison with measurements is essential during all stages of model development. As the previous generation of numerical models gradually are replaced by a new unified Eulerian model, evaluation of the model performance is particularly needed. In Simpson and Jonson (1998) results from the EMEP Lagrangian and Eulerian photochemistry models were compared. That comparison was carried out mainly for ozone. In Solberg et al. (1999) a preliminary evaluation of the models based on comparison with EMEP VOC measurements was carried out. The results of the comparison with VOC was not very encouraging for the Eulerian model; however, as pointed out then, the evaluation was preliminary and a more thorough inspection of the models and the performance was needed. Since then the Eulerian model has been revised, both with regard to the calculations of VOC as well as in general. Thus, a new model comparison and evaluation with the revised model was needed, and this is presented in the following. Figure 4.1 shows the location of the measurement sites used in these comparisons.

4.2 Model development

Whereas the Lagrangian oxidant model is unchanged since last year's report, the Eulerian model has been modified in several ways. Dry deposition of formaldehyde and acetaldehyde have been included, assuming a dry deposition velocity of 0.3 cm/s for both compounds. Wet deposition of formaldehyde is also included. The wet deposition is scaled according to the solubility of HCHO as described in Jonson et al. (1998). A value of

$$2.97 \times 10^3 \exp(7194(1/T - 1/298))$$

was used for the solubility of HCHO (where T is temperature). Note also that the dry deposition modifies the calculated concentrations both by the direct loss itself and also by the vertical concentration gradient estimated within the lowest model layer, as the measurements are compared with concentrations reduced to ground level.

4.3 Comparison between model calculations and measurements of VOC and CO

Aldehydes have proven particularly useful for oxidant model evaluation (Solberg et al., 2000) as they to a large extent are formed by atmospheric oxidation of other VOC and thus directly linked

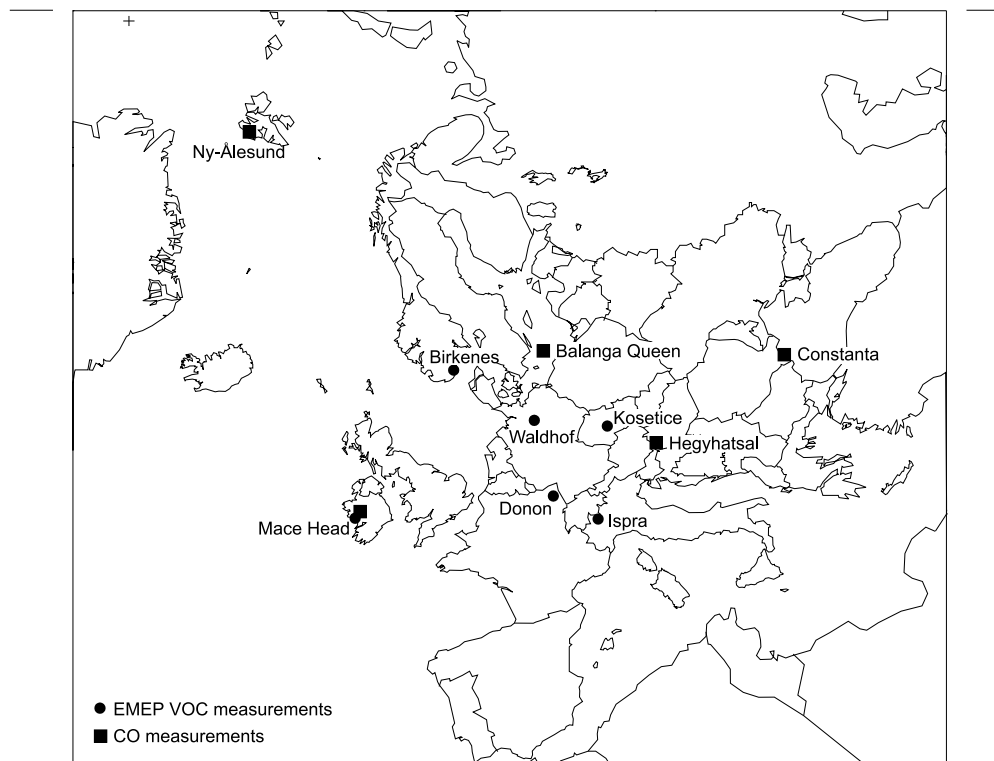


Figure 4.1: Locations of measurement sites for VOC and CO

to the atmospheric chemical condition (OH-concentration, dissociation etc.). VOC in general are also useful for evaluation purposes, particularly for validating VOC emission speciation and OH-concentration (due to the differential removal of individual VOC by OH). A comparison with CO measurements has also been included in the following, as CO is indicative of the models' description of atmospheric dynamic processes.

The EMEP VOC measurements, sampling procedures, etc., have been documented in detail elsewhere (EMEP, 1995, Solberg et al., 1997) and are thus not repeated here. In short, the measurements of carbonyls are 8 hours samples, centered around noon, and the hydrocarbons are grab samples in canisters (filling time 10-20 min) which are taken around noon. All the VOC are measured approximately twice a week. Measurements of CO have been carried out by the Carbon Cycle group at NOAA (National Oceanic and Atmospheric Administration) at a few sites in Europe (Novelli et al., 1998). Flask samples of CO are collected at a frequency of every 3 - 5 days.

The Eulerian and Lagrangian models were run for the whole year of 1996 for the monitoring sites shown in 4.1. Note that whereas carbonyls were measured at all the VOC sites, light hydrocarbons were measured at only three of these sites, Birkenes, Waldhof and Kosetice. For this comparison, the results from the Eulerian model were averaged over an 8 hours period (8-16), whereas the results from the Lagrangian model at 6, 12 and 18 UT were averaged. In the comparison with CO, daily averaged concentrations from the Eulerian model were used.

4.3.1 Carbonyls

The calculated formaldehyde and acetaldehyde are presented in Figure 4.2 and Figure 4.3 for each of the two models together with the measured values. Only results for the days with measurements are given. Compared to the results presented one year ago (Solberg et al., 1999) this comparison is much more encouraging for the Eulerian model and clearly shows that the recent model development has been successful. Still, the general concentration levels are higher in the Eulerian model than compared with the Lagrangian model and also the linear correlation with the measurements is somewhat higher for the Lagrangian model. However, the large differences found in the previous comparison is not seen in the present results. Compared to the measurements, the general concentration level of formaldehyde and acetaldehyde are

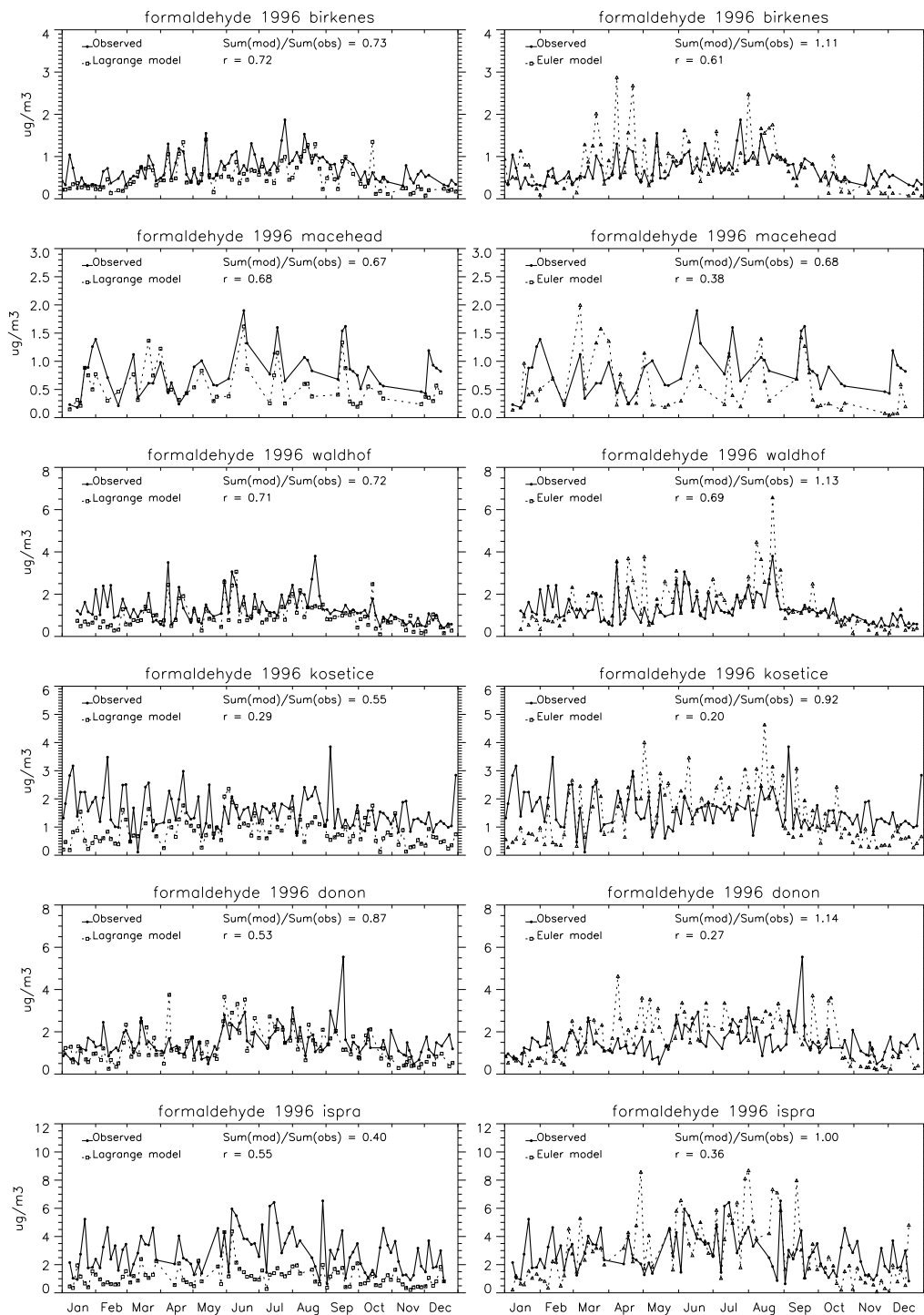


Figure 4.2: Concentrations of formaldehyde at six EMEP VOC sites in 1996 as calculated by the Lagrangian model (left) and the Eulerian model (right) together with the measurements. All values are in $\mu\text{g m}^{-3}$. The linear correlation coefficients (r) and the ratio of the average modelled concentrations relative to the average measured concentrations are also given.

better modelled by the Eulerian model compared to the Lagrangian model (which gives a general underestimation of the concentrations). As pointed out previously, it is natural that the Eulerian model, with a finer vertical resolution, calculates somewhat higher concentrations at ground than the one-layered Lagrangian model which assumes complete mixing in the boundary layer.

The day-to-day variation, as indicated by the correlation coefficients, are slightly higher for the Lagrangian model; however, as seen from Figures 4.2 and 4.3, there are large variations in

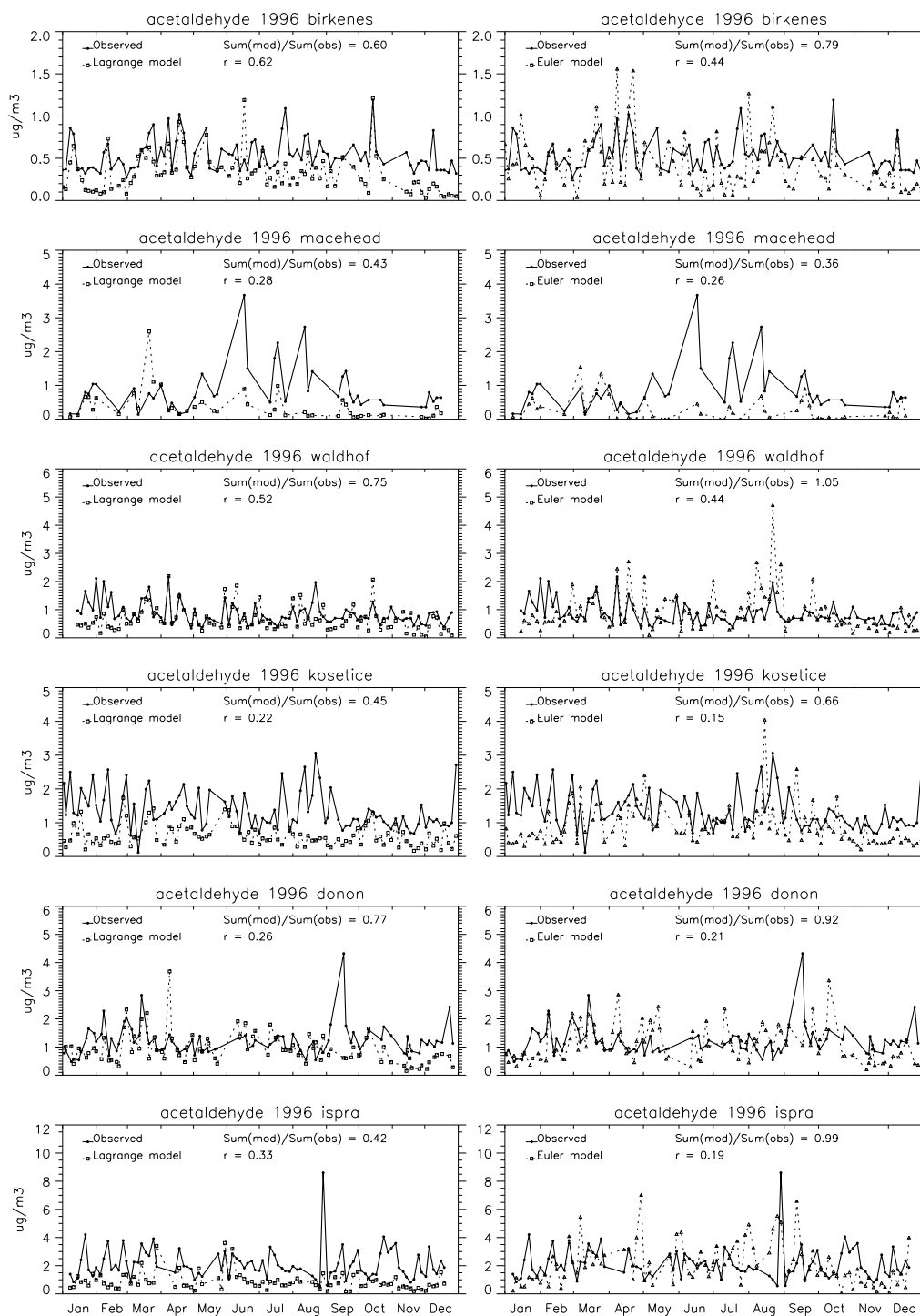


Figure 4.3: Concentrations of acetaldehyde at six EMEP VOC sites in 1996 as calculated by the Lagrangian model (left) and the Eulerian model (right) together with the measurements. All values are in $\mu\text{g m}^{-3}$. The linear correlation coefficients (r) and the ratio of the average modelled concentrations relative to the average measured concentrations are also given.

the performance during the year. Both models underestimate the formaldehyde concentrations in mid-winter (December-January) whereas for e.g. Birkenes and Waldhof both models perform very well in the period May-September, although the Eulerian model predicts a few high spikes which are not measured.

Differences in the modelled aldehyde concentrations and the correlations could have several causes. First of all, as the chemical reaction scheme are somewhat different in the two models, the calculated formaldehyde will also differ. As shown by Solberg et al. (2000), isoprene has

a large effect on the formaldehyde concentration calculated in the Lagrangian model, and the different parameterisations of isoprene emissions and degradation in the two models may explain parts of the differences seen in Figure 4.2. Secondly, the vertical resolution in the Eulerian model compared to the one-layered Lagrangian model may also have a pronounced effect on a short-lived species such as formaldehyde.

4.3.2 Hydrocarbons

Whereas measurements of formaldehyde and acetaldehyde are directly comparable to the model calculations, such a comparison is not straightforward for the hydrocarbons. As the models use chemical reaction schemes with lumping of the VOC, individual primary VOC in the models are not directly comparable to the observed concentrations. The sum of primary hydrocarbons was used for comparison instead. For the Eulerian model the sum of ethane, ethene, propene, butane, hexane and aromatics were calculated and for the Lagrangian model the sum of ethane, ethene, propene, butane and o-xylene. This captures the main part of the primary, emitted anthropogenic VOC in both the models. For comparison with the measurements, the sum of observed ethane, ethene, propane, propene, n-butane, i-butane, n-pentane, i-pentane, benzene and toluene was calculated. This sum of measured species makes out approximately one third of the mass of emitted VOC, according to a VOC emission inventory for the UK (PORG, 1997).

In the comparisons with the model results, the sum of measured hydrocarbons was thus multiplied with a factor of 3. However, due to the differential reactivity this factor of 3 may be less relevant when the air mass has experienced some oxidation if the average reactivity of all VOC differs from the average reactivity of the 10 components used in this study.

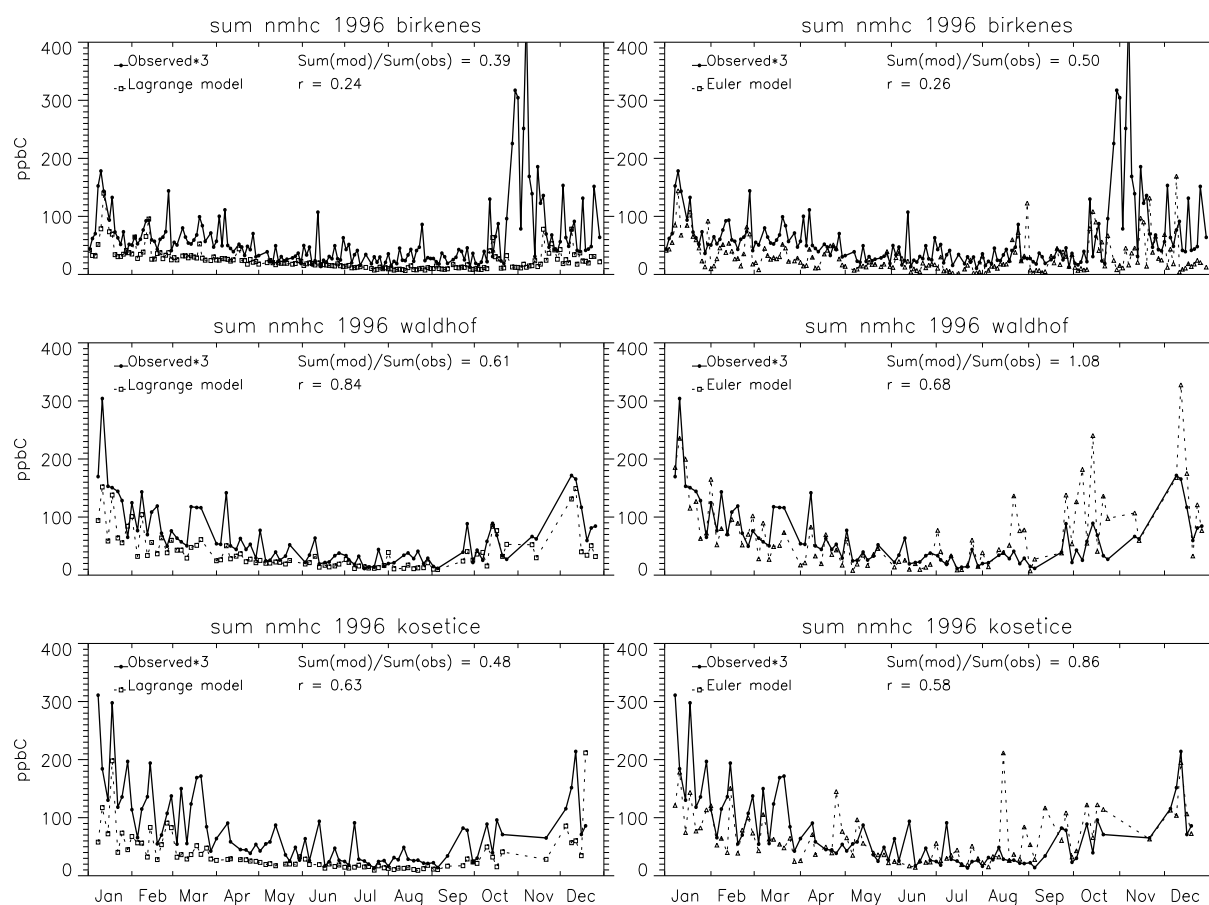


Figure 4.4: Sum of primary hydrocarbons at three EMEP VOC sites in 1996 as calculated by the Lagrangian model (left) and the Eulerian model (right) together with the measurements (multiplied with 3). All values are in ppbC. The linear correlation coefficients (r) and the ratio of the average modelled concentrations relative to the average measured concentrations are also given.

The modelled sum of hydrocarbons is shown in Figure 4.4 together with the measurements. For Waldhof and Kosetice the average level of the modelled sum of hydrocarbons in the Eulerian model is fairly close to the measured sum (scaled with the factor 3) although a number of high spikes in the model are seen in the last half of the year, whereas the modelled level for Birkenes is lower than the scaled measurements. The Lagrangian modelled sum of hydrocarbons is lower than the scaled measurements for all three sites.

4.3.3 CO

In Figure 4.5 the calculated concentrations of CO are compared to the measurements. In the comparison it turned out that the fixed initial concentration of 200 ppb CO used in the Lagrangian model was obviously too high in summer and was thus modified to a seasonal cycle with maximum of 200 ppb in late winter and minimum of 100 ppb in summer. Due to the long chemical lifetime this will not influence the rest of the calculated compounds in the model significantly. At the three continental sites (apart from Zeppelin Mountain and Mace Head) the CO general levels are under-predicted by the models at all three sites, particular in winter at Constanta and Hegyhatsal, which is representative of continental air masses. Compared with the measurements at Balanga Queen both the models perform fairly good. The 1996 winter had a continental circulation with low temperatures and winds generally from the east in north and central Europe. The underestimation in the models may be caused by a combination of too low emissions and advection from outside the model domain. Furthermore, with a winter circulation CO can be trapped in a very shallow inversion layer not fully reproduced in the model. The decrease in measured CO at around day 100 at Hegyhatsal, Constanta, and the Balanga Queen coincides with a change in the weather pattern. Interestingly, the performance of the two models with regard to the CO measurements are surprisingly similar, both for the concentration level and the correlation with the observations. One possible explanation for this is that CO have a chemical lifetime much longer than the time scale of transport episodes in Europe (typically 3-5 days) and also that there are no surface deposition processes.

4.4 Sector calculations.

To study differences between the model calculations and measurements as a function of transport, the data were sorted into different transport sectors based on the Lagrangian trajectories. Figure 4.6 shows the spread of data for four 90 degrees wide transport sectors (E, S, W, N) as well as the weighted (by the measurement values) linear correlation coefficients for the two models and the measurements, using the days with measurements only.

In general the Eulerian model gives larger spread in concentrations than compared with both the measurements and the Lagrangian model. Interestingly, the marked underestimation in sector E for Waldhof and sector E and S for Kosetice by the Lagrangian model is less pronounced in the Eulerian model. This type of transport is often associated with anticyclonal flow or wind shear situations preceding approaching low pressure systems. The difference in model performance by the two models could reflect that the one-layered Lagrangian model is less able than the Eulerian model to simulate that kind of transport situations. However, the amount of data within each sector is really too small to draw firm conclusions.

The difference between the transport sectors is fairly well reproduced by both models, whereas the correlation coefficients (with the measurements) are mostly slightly higher in the Lagrangian model than the Eulerian model. The background concentrations, indicated by the W sector at Mace Head, show, on the other hand much higher correlation with the Eulerian model although the concentration level is too low in the model. This could indicate a good representation of the situations with W transport into Europe, but too low initial concentrations for formaldehyde or VOC in general in the Eulerian model.

4.5 Model comparison.

The agreement between the two models were further examined by calculating the linear correlation coefficients and ratios of average concentrations for all calculations in 1996. Figure 4.6 shows the result based on 30 days running data (and using all days of the year) for the sum of hydrocarbons as defined above. This comparison shows that the best agreement between

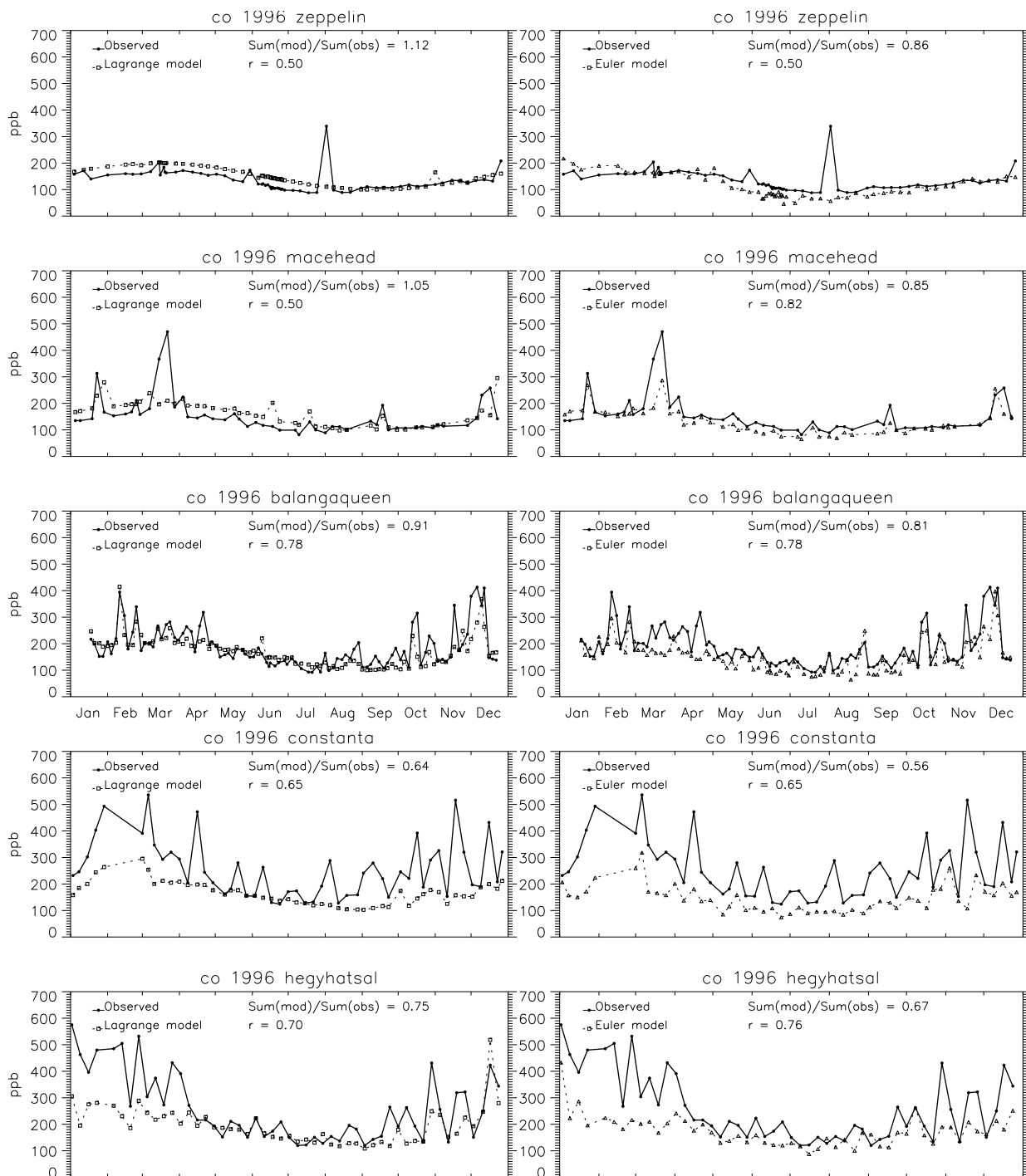


Figure 4.5: Concentrations of CO at five sites in 1996 as calculated by the Lagrangian model (left) and the Eulerian model (right) together with the measurements. All values are in ppb. The linear correlation coefficients (r) and the ratio of the average modelled concentrations relative to the average measured concentrations are also given.

the two models are found for Mace Head, Waldhof, and Donon, which is interesting as these sites also show a generally good agreement with the measurements. For Birkenes, Kosetice and Ispra there are large periods in spring and summer with a linear correlation not significantly different from zero. The concentration ratios show large differences both for the individual days and for the 30 days periods. The Eulerian model results are particularly high compared to the Lagrangian model in the autumn (August/September/October). The reason for this is not clear, but could reflect the vertical stability and layering in that season.