Atmos. Chem. Phys. Discuss., 13, 30611–30652, 2013 www.atmos-chem-phys-discuss.net/13/30611/2013/ doi:10.5194/acpd-13-30611-2013 © Author(s) 2013. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# Simulating the integrated Δ<sup>14</sup>CO<sub>2</sub> signature from anthropogenic emissions over Western Europe

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Received: 7 November 2013 – Accepted: 8 November 2013 – Published: 21 November 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.



## Abstract

Radiocarbon dioxide ( ${}^{14}CO_2$ , reported in  $\Delta {}^{14}CO_2$ ) can be used to determine the fossil fuel CO<sub>2</sub> addition to the atmosphere, since fossil fuel CO<sub>2</sub> no longer contains any  ${}^{14}C$ . After release of CO<sub>2</sub> at the source, atmospheric transport causes dilution of strong local

- signals into the background and detectable gradients of  $\Delta^{14}CO_2$  only remain in areas with high fossil fuel emissions. This fossil fuel signal can moreover be partially masked by the enriching effect that anthropogenic emissions of  ${}^{14}CO_2$  from the nuclear industry have on the atmospheric  $\Delta^{14}CO_2$  signature. In this paper, we investigate the regional gradients in  ${}^{14}CO_2$  over the European continent and quantify the effect of the emissions
- from nuclear industry. We simulate the emissions of fossil fuel  $CO_2$  and nuclear  ${}^{14}CO_2$ for Western Europe for a period covering 6 months in 2008 and their transport using the Weather Research and Forecast model (WRF-Chem). We evaluate the expected  $CO_2$  gradients and the resulting  $\Delta^{14}CO_2$  in simulated integrated air samples over this period, as well as in simulated plant samples.
- <sup>15</sup> We find that the average gradients of fossil fuel CO<sub>2</sub> in the lower 1200 m of the atmosphere are close to 15 ppm at a 12 km × 12 km horizontal resolution. The nuclear influence on  $\Delta^{14}$ CO<sub>2</sub> signatures varies considerably over the domain and for large areas in France and UK it can range from 20 % to more than 500 % of the influence of fossil fuel emissions. Our simulations suggest that the resulting gradients in  $\Delta^{14}$ CO<sub>2</sub>
- <sup>20</sup> are well captured in plant samples, but due to their time-varying uptake of CO<sub>2</sub> their signature can be different with over 3 ‰ from the atmospheric samples in some regions. We conclude that the framework presented will be well-suited for the interpretation of actual air and plant <sup>14</sup>CO<sub>2</sub> samples.

## 1 Introduction

<sup>25</sup> The magnitude of anthropogenic fossil fuel CO<sub>2</sub> emissions is relatively well known on the global scale (Raupach et al., 2007; Friedlingstein et al., 2010) as bottom-up inven-



tories constrain the sum of all emissions to within 6–10% uncertainty (Marland and Rotty, 1984; Turnbull et al., 2006; Marland, 2008). But it is widely acknowledged that confidence in the estimated magnitude of these emissions reduces quickly when we consider the regional and national scale (Olivier and Peters, 2002; Gurney et al., 2009;

- <sup>5</sup> Ciais et al., 2010; Francey et al., 2013). This is partly a disaggregation problem that arises when nationally reported data on economic activity, energy use, and fuel trade statistics must be attributed to smaller geographic areas and more diverse processes. At the same time, there is a challenge to aggregate available bottom-up information on the level of individual roads, or power plants, or industrial complexes to a larger
   <sup>10</sup> scale consistently. In between these two lies an important opportunity for atmospheric
- monitoring, as it can independently verify the reported emission magnitudes at the intermediate scales, uniquely constrained by the integrating capacity of atmospheric transport.
- Several atmospheric monitoring strategies for fossil fuel emissions have been applied in recent years. Most of these use spatiotemporal variations in  $CO_2$  mole fractions (Koffi et al., 2012), often augmented with various other energy related gases such as CO (Levin and Karstens, 2007), NO<sub>x</sub> (Lopez et al., 2013), or SF<sub>6</sub> (Turnbull et al., 2006). The advantage of using these other gases lies first of all in attribution, as each process induces its own typical ratio of these gases to the atmosphere. An example is the much
- <sup>20</sup> higher CO/CO<sub>2</sub> ratio produced by traffic emissions than by power plants. A second advantage of these other gases is that they can be measured continuously and relatively cheaply with commercially available analyzers, of which many have already been deployed. This is in large contrast with the one tracer that is generally considered the "golden standard" for fossil fuel related CO<sub>2</sub> detection: radiocarbon dioxide or <sup>14</sup>CO<sub>2</sub>
- <sup>25</sup> (Kuc et al., 2003; Levin et al., 2003; Levin and Karstens, 2007; Levin and Rödenbeck, 2008; Levin et al., 2008; Turnbull et al., 2006; Djuricin et al., 2010; Miller et al., 2012), reported usually as  $\Delta^{14}$ CO<sub>2</sub> (Stuiver and Polach, 1977; Mook and van der Plicht, 1999).

Radiocarbon derives its strength for fossil fuel monitoring from the absence of any  $^{14}\mathrm{C}$  in carbon that is much older than the typical half-life time of the radiocarbon



 $-5730 \pm 40$  yr (Godwin, 1962). This typically applies only to carbon in fossil reservoirs, as other carbon reservoirs are continuously supplied with fresh <sup>14</sup>C from exchange with the atmosphere where <sup>14</sup>CO<sub>2</sub> is produced in the stratosphere (Libby, 1946; Anderson et al., 1947). In the natural carbon balance this <sup>14</sup>C would cycle through the atmospheric, biospheric, and oceanic reservoir until it decays. But very large anthropogenic 5 disturbances on this natural cycle come specifically from (a) large scale burning of very old and <sup>14</sup>C depleted carbon from fossil reservoirs, the "Suess effect" (Suess, 1955; Levin et al., 1980), and (b) production of highly enriched  ${}^{14}C$  in CO<sub>2</sub> such as from nuclear bomb tests (Nydal, 1968), or some methods of nuclear power production (McCartney and Baxter, 1988a, b). Samples of <sup>14</sup>CO<sub>2</sub> taken from the atmosphere, but 10 also from the oceans and biosphere that exchange with it, consistently show their dominant influence on the <sup>14</sup>CO<sub>2</sub> budget of the past decades (e.g.: Levin et al., 1989; Meijer et al., 1996; Nydal and Gislefoss, 1996; Levin and Hesshaimer, 2000; Randerson et al., 2002; Naegler and Levin, 2006; Levin et al., 2010; Graven et al., 2012a, b).

<sup>15</sup> Monitoring of atmospheric <sup>14</sup>CO<sub>2</sub> is done through several methods. One commonly applied approach is by absorption of gaseous CO<sub>2</sub> into a sodium hydroxide solution from which the carbon content is extracted and converted into a graphite target for <sup>14</sup>C/C analysis either by radioactive decay counters, or accelerator mass spectrometry. The air flowing into the solution typically integrates the sampling time over days, weeks, or even longer time periods. This is different from an air sample collected in a flask, which is filled within less than a minute and thus representative of a much smaller atmospheric time-window. At the other end of the time spectrum is the use of plants to sample <sup>14</sup>C/C ratios in the atmosphere through their photosynthetic fixation of atmospheric CO<sub>2</sub>. Depending on the species these integrate over sampling windows
 <sup>25</sup> of a full growing season (annual crops, fruits – Shibata et al., 2005; Hsueh et al., 2007;

Palstra et al., 2008; Riley et al., 2008; Wang et al., 2013) or longer (trees, tree-rings – Suess, 1955; Stuiver and Quay, 1981; Wang et al., 2012).

An effective monitoring strategy for fossil fuel emissions is likely to take advantage of all methods available to collect <sup>14</sup>C samples, and combine these with high resolution



monitoring of related gases (e.g. CO,  $SF_6$ ). Levin and Karstens (2007), van der Laan et al. (2010) and Vogel et al. (2010) already demonstrated the viability of a monitoring method in which observed CO/CO<sub>2</sub> ratios are periodically calibrated with  $^{14}CO_2$  to estimate fossil fuel emissions at high temporal resolutions. More recently, this strategy was also employed by Lopez et al. (2013), where additionally the  $CO_2/NO_{\nu}$  ratios were used to estimate fossil fuel derived CO<sub>2</sub> from continuous CO and NO<sub>x</sub> observations in Paris. Turnbull et al. (2011) showed for the city of Sacramento, that using a combination of  $\Delta^{14}$ CO<sub>2</sub> and CO observations can reveal structural detail in CO<sub>2</sub> from fossil fuel and biospheric sources that cannot be obtained by CO<sub>2</sub> measurements alone. van der Laan et al. (2010) and recently Vogel et al. (2013) showed that the agreement between fossil 10 fuel CO<sub>2</sub> modeled estimates with observations of <sup>14</sup>C-corrected CO can be further improved by including <sup>222</sup>Rn as a tracer for the vertical mixing. Finally, Hsueh et al. (2007) and Riley et al. (2008) used <sup>14</sup>C/C ratios in corn leaves and C3 grasses to reveal fossil fuel emission patterns on city, state, and national scales. Given so many different methods to use <sup>14</sup>C in monitoring strategies, its increasing accuracy, reduction 15 in required sample size, and decreasing costs, it is likely that this tracer will play a more important role in the future of the carbon observing network.

Obviously, the quantitative estimation of fossil fuel emissions from all of the <sup>14</sup>Cbased monitoring strategies above requires different methods and emphasizes different terms in the <sup>14</sup>CO<sub>2</sub> budget. For example, interpretation of <sup>14</sup>C in air samples from aircraft requires detailed dispersion modeling of surface emissions into a highly dynamic atmosphere. Conversely, interpretation of monthly integrated air samples from tall towers requires the inclusion of stratospheric sources and re-emergence of old <sup>14</sup>C signals after longer turn-over in the oceans and biosphere. In a recent publication (Bozhinova

et al., 2013), we showed that the interpretation of growing season integrated plant samples additionally requires simulation of location and weather dependent photosynthetic uptake and plant development patterns. A successful <sup>14</sup>C monitoring strategy will thus depend strongly on our ability to capture these diverse processes on diverse scales.



In this work, we present a newly-built framework designed to interpret  ${}^{14}CO_2$  from different types of samples and from different monitoring strategies. The framework includes atmospheric transport of surface emissions of total  $CO_2$  and  ${}^{14}CO_2$  on hourly scales on a model grid of a few kilometers, but integrates signals up to seasonal time

- <sup>5</sup> scales and even down into the leaves of growing crops (maize and wheat). Both regional transport and plant growth are based on meteorological drivers that are kept consistent with large-scale weather reanalyses. In addition to fossil fuel signals in the atmosphere and in plants, we simulate the spread of nuclear derived <sup>14</sup>C release from major reprocessing plants and from operational nuclear power production plants across
- <sup>10</sup> Europe based on work of Graven and Gruber (2011). We applied our framework to the European domain for the summer of 2008. After explaining the components of the framework (Sect. 2) we will demonstrate its application (Sect. 3.1), assess the fossil and nuclear derived <sup>14</sup>C gradients across Europe (Sect. 3.2), and simulate the signal that will be recorded into annual crops growing across the domain (Sect. 3.3). We
- will evaluate its potential benefits compared to simpler but less realistic fossil fuel estimation methods from integrated samples alone (Sect. 3.4). We will conclude with a discussion (Sect. 4) of the application of this framework to actual measurements and recommendations for future studies.

#### 2 Methods

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## <sup>20</sup> 2.1 The regional atmospheric CO<sub>2</sub> and $\Delta^{14}$ CO<sub>2</sub> budget

The regional CO<sub>2</sub> mole fractions and  $\Delta^{14}$ CO<sub>2</sub> signature of the atmosphere observed at a particular location are described in Eqs. (1) and (2), following the methodology used by Levin et al. (2003), Turnbull et al. (2006), Hsueh et al. (2007), Palstra et al. (2008) and described thoroughly in Turnbull et al. (2009b). Here the  $\Delta_x$  and CO<sub>2x</sub> (or <sup>14</sup>CO<sub>2x</sub>) indicate the  $\Delta^{14}$ CO<sub>2</sub> signature of CO<sub>2</sub> (or <sup>14</sup>CO<sub>2</sub>) mole fractions of particular origin, expressed in the index as follows: obs – observed at location, bg – background,



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nant effect of the fossil fuels and are consequently omitted (Levin and Karstens, Hsueh et al., 2007; Palstra et al., 2008; Turnbull et al., 2009b; Naegler and 2009a, b; Levin et al., 2010). The intrusion of <sup>14</sup>CO<sub>2</sub>-enriched stratospheric air c 25 of importance for observations in the upper troposphere or higher, however in our this term can be considered as part of the background, as the stratospheric <sup>14</sup>C already well mixed by the time it reaches the lower troposphere.

of the globe. For our domain both terms are of much smaller influence than the

We set  $\Delta_p = \Delta_{bq}$  similar to the approach in Turnbull et al. (2006) as the calculat  $\Delta^{14}$ CO<sub>2</sub> accounts for changes in the signature of the photosynthesized CO<sub>2</sub> flu 10 to fractionation. The atmosphere-ocean exchange in the northern Atlantic make region generally a sink of carbon (Watson et al., 2009), but we assume that its port to our domain is uniform and captured by the inflow of background air and also carries the signature  $\Delta_{bq}$ . For the ecosystem respiration and ocean exchange

- terms  $\Delta_r$  and  $\Delta_o$  can be also written as  $\Delta_{bg} + \Delta_{bio}^{dis}$  and  $\Delta_{bg} + \Delta_{ocean}^{dis}$ , where the dis 15 librium terms ( $\Delta^{dis}$ ) describe the difference between the signature of the carbon particular reservoir and the current atmospheric background. These differences from the past enrichment of the atmosphere with  $^{14}CO_2$  from the atmospheric nu bomb tests since the 1960s. In the following decades this enrichment was incorpo

 $\Delta_{\rm obs} \rm CO_{2obs} = \Delta_{\rm bg} \rm CO_{2bg} + \Delta_{\rm ff} \rm CO_{2ff} + \Delta_{\rm p} \rm CO_{2p}$  $+\Delta_r CO_{2r} + \Delta_o CO_{2o} + \Delta_n^{14} CO_{2n} + \Delta_s CO_{2s}$ Several of the terms in both equations can be ommited or transformed in our studescribed next.

 $CO_{2obs} = CO_{2bg} + CO_{2ff} + CO_{2p} + CO_{2r} + CO_{2o}$ 

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ff – fossil fuels, p – photosynthetic uptake, r – ecosystem respiration, o – ocean, n – nuclear and s - stratospheric.

nuclear and s – stratospheric.  

$$CQ_{2obs} = CQ_{2bg} + CQ_{2ff} + CQ_{2p} + CQ_{2r} + CQ_{2o}$$
 (1)  
 $\Delta_{obs}CQ_{2obs} = \Delta_{bg}CQ_{2bg} + \Delta_{ff}CQ_{2ff} + \Delta_{p}CQ_{2p}$  (2)  
Several of the terms in both equations can be ommited or transformed in our study, as  
described next.  
We set  $\Delta_{p} = \Delta_{bg}$  similar to the approach in Turnbull et al. (2006) as the calculation of  
 $\Lambda^{14}CQ_{2}$  accounts for changes in the signature of the photosynthesized CQ<sub>2</sub> flux due  
to fractionation. The atmosphere-ocean exchange in the northern Atlantic makes the  
region generally a sink of carbon (Watson et al., 2009), but we assume that its trans-  
port to our domain is uniform and captured by the inflow of background air and thus  
also carries the signature  $\Delta_{bg}$ . For the ecosystem respiration and ocean exchange the  
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particular reservoir and the current atmosphere between the signature of the carbon in the  
globe. For our domain both terms are of much smaller influence than the domi-  
nant effect of the fossil fuels and are consequently omitted (Levin and Kastens, 2007;  
Hsueh et al., 2007; Palstra et al., 2008; Turnbull et al., 2009; Naegler and Levin,  
2009a, b; Levin et al., 2010). The intrusion of <sup>14</sup>CQ<sub>2</sub> enriched stratospheric air can be  
of importance for observations in the upper troposphere or higher, however in our case  
this term can be considered as part of the background, as the stratospheric air can be  
of importance for observations in the upper troposphere.  
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Most studies neglect the effects of anthropogenic nuclear production of <sup>14</sup>CO<sub>2</sub> on the atmospheric  $\Delta^{14}$ CO<sub>2</sub> since on the global scale this production averages to the smallest contribution, compared to the other terms (Turnbull et al., 2009a). However, Graven and Gruber (2011) showed that on a regional scale for a domain with a dense nuclear power plant network its influence can not be neglected. They estimated the potential bias in 5 the recalculation of fossil fuel CO<sub>2</sub> due to nuclear power plant production is on average between 0.5 and 1 ppm for Europe, but the horizontal resolution of their transport model  $(1.8^{\circ} \times 1.8^{\circ})$  limits the analysis for the regions close to the sources. We note that two of the three existing worldwide Spent Fuel Reprocessing Plants are located in Western Europe (SFRP, in La Hague, France and Sellafield, UK), which generally have higher 10 than average emissions of  ${}^{14}CO_2$ . Particularly the site of La Hague is estimated to be

- the largest point-source of <sup>14</sup>CO<sub>2</sub> emissions in the world, in recent years accounting for more than 10% of the global budget of nuclear produced <sup>14</sup>CO<sub>2</sub> (Graven and Gruber, 2011). The magnitude of this source and its spatial location close to the major fossil fuel emitters in Europe pose a challenge in estimating the uncertainty with which the 15
- method of recalculating fossil fuel  $CO_2$  can be applied in the region.

All these considerations allow us to simplify Eqs. (1) and (2) to Eqs. (3) and (4).

$$CO_{2obs} = CO_{2bg} + CO_{2ff} + CO_{2p} + CO_{2r}$$
(3)  
$$\Delta_{obs}CO_{2obs} = \Delta_{bg}(CO_{2bg} + CO_{2p} + CO_{2r}) + \Delta_{ff}CO_{2ff} + \Delta_{n}^{14}CO_{2n}$$
(4)

20

The instantaneous  $\Delta^{14}$ CO<sub>2</sub> signature of the atmosphere is calculated using Eq. (4), using the specific signatures for various sources of  $CO_2$  (various  $\Delta$  terms) as listed below:

- 1. Fossil fuels are entirely devoid of  $^{14}CO_2$  and their  $\Delta_{\rm ff} = -1000$  ‰.
- 2. The nuclear emissions are of pure  ${}^{14}CO_2$  and in this formulation  $\Delta_n$  is the  $\Delta^{14}CO_2$ 25 signature that a pure <sup>14</sup>CO<sub>2</sub> sample would have. We calculate it using the activity



(4)

of pure  $^{14}\text{CO}_2$  sample in the fomulation of  $\Delta^{14}\text{CO}_2$  as follows:

 $A_{\rm s} = \lambda \cdot N_{\rm a}/m_{^{14}\rm C}$ 

5

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where  $N_a = 6.022 \times 10^{23} \text{ mol}^{-1}$  is the Avogadro constant,  $\lambda = 3.8332 \times 10^{-12}$  Bq is the decay rate of <sup>14</sup>C and  $m_{^{14}C} = 14.0 \text{ gmol}^{-1}$  is the molar mass of the isotope. In a sample of a pure <sup>14</sup>CO<sub>2</sub> there is no fractionation and the calculation of  $\Delta^{^{14}CO_2}$ (Stuiver and Polach, 1977; Mook and van der Plicht, 1999) can be simplified to the ratio between the activity of the sample and activity of the referenced standard  $A_{\text{ABS}} = 0.226 \text{ BqgC}^{-1}$  (Mook and van der Plicht, 1999):

10  $\Delta_n = A_s / A_{ABS} \cdot 1000 [\%]$ 

The resulting  $\Delta_n \approx 0.7 \times 10^{15}$  [‰] is much higher than any of the other  $\Delta$  signatures, but this is balanced by the concentrations of the <sup>14</sup>CO<sub>2</sub>, which are only a very small fraction (~ 10<sup>-12</sup>) of the observed CO<sub>2</sub> concentrations.

<sup>15</sup> 3. Finally, we use  $\Delta_{bg}$  from monthly observed  $\Delta^{14}CO_2$  at the high alpine station Jungfraujoch (3580 m a.s.l., Switzerland) (Levin et al., 2010), which is considered representative for European  $\Delta^{14}CO_2$  background. These are shown in red on Fig. 2b.

The transport and resulting spatiotemporal gradients in total  $CO_2$  and  ${}^{14}CO_2$  over Eu-<sup>20</sup> rope are simulated with WRF-CHEM model, described next.

#### 2.2 WRF-CHEM

For our simulation with WRF-Chem (version 3.2.1) (Skamarock et al., 2008) we use meteorological fields from the NCEP FNL Operational Model Global Tropospheric Analyses (NCEP, US National Centers for Environmental Prediction, 2013) for lateral meteorological boundary conditions, which are updated every 6 h. We use three domains



(5)

(6)

with horizontal resolution of 36 km, 12 km and 4 km and respectively 60 × 62, 109 × 100 and 91 × 109 grid points, centered over Western Europe and the Netherlands. Our vertical resolution includes 27 pressure levels, 18 of which are in the lower 2 km of the troposphere, and the time step used is 180 s in the outer domain. Important physics schemes used are the MYNN2.5 boundary layer scheme (Nakanishi and Niino, 2006), BBTM long wave radiation (Mlawer et al., 1997), and Dudbia shortwave radiation (Dud-

- RRTM long wave radiation (Mlawer et al., 1997), and Dudhia shortwave radiation (Dudhia, 1989). We use the Unified Noah LSM (Ek et al., 2003) as our surface physics scheme and additionally use time-varying surface conditions, which we update every 6 h.
- We use separate passive tracers for the different CO<sub>2</sub> terms in Eq. (4). We prescribe our initial and lateral boundary conditions for the background CO<sub>2</sub>, while the biospheric uptake, respiration, fossil fuel CO<sub>2</sub> and nuclear <sup>14</sup>CO<sub>2</sub> are implemented with surface fluxes only, which are prescribed and provided to the model every hour. This is partially a consequence of our interest in the recent influence of the biosphere and anthropogenic emissions and once these CO<sub>2</sub> signals leave our outer domain they will not re-enter it again. For this reason we will avoid using direct results from the outer
- domain, and instead use only the nested domains, where boundary conditions for all tracers are provided through their respective mother domain.

The background  $(CO_{2bg})$  initial and boundary conditions are implemented using 3-D mole fraction output from Carbon Tracker (Peters et al., 2010) for 2008 at 1° × 1° resolution and interpolated vertically from 34 to 27 levels using the pressure fields. The CO<sub>2</sub> lateral boundary conditions are added to the standard meteorological boundary

conditions and also updated every 6 h.

Our biospheric fluxes (CO<sub>2r</sub> and CO<sub>2p</sub>) are generated using the SiBCASA model (Schaefer et al., 2008), which used meteo fields from the European Centre for Medium-Range Weather Forecasts (ECMWF). It provides us with monthly averaged gross photosynthetic production (GPP) and terrestrial ecosystem respiration (TER) at 1° × 1° resolution. Due to the coarse resolution of the SiBCASA model, we find land-use categories in the higher resolution map of WRF that are not in the natural land-use map of



SiBCASA. To address this issue, we ran 9 simulations with SiBCASA prescribing a single vegetation category, alternating through all the vegetation categories to produce biospheric fluxes for the different land-use categories within the resolution of WRF. For temporal interpolation of the monthly fluxes, we scale the GPP and TER with the in-

<sup>5</sup> stantaneous WRF meteorological variables (temperature at 2 m and shortwave solar radiation) following the method described in Olsen and Randerson (2004). We first scale the SiBCASA output using the monthly mean averaged radiation (for GPP) and a  $Q_{10}$  relation towards the monthly averaged temperature (for TER). These scaled down fluxes are then prescribed in the WRF model on an hourly basis and multiplied with the WRF calculated shortwave radiation and  $Q_{10}$  at every time step.

Anthropogenic (fossil fuel)  $CO_2$  emissions ( $CO_{2ff}$ ) are provided by the CarboEurope project (IER, Stuttgart, Pregger et al., 2007) at 5 (geographical) minutes horizontal resolution over Europe in the form of annual emission at the location and temporal profiles to add variability during different months, weekdays and hours during the day. These are then aggregated to every WRF domain horizontal resolution and updated

<sup>15</sup> These are then aggregated to every WRF domain horizontal resolution and updated every hour for the duration of our simulation. The emissions are introduced only at the lowest (surface) level of the model.

Anthropogenic (nuclear)  $^{14}CO_2$  emissions ( $^{14}CO_{2n}$ ) are obtained by applying the method described in Graven and Gruber (2011) for the year of 2008. We used informa-

- tion from the International Atomic Energy Agency Power Reactor Information System (IAEA PRIS, available online at http://www.iaea.org/pris) for the energy production of the nuclear reactors in our domain and reported <sup>14</sup>CO<sub>2</sub> discharges for the spent fuel reprocessing sites (van der Stricht and Janssens, 2010). These were scaled down directly from annual to hourly emissions, assuming that these emissions are continuous
- <sup>25</sup> and constant during the year. We will further comment on these assumptions in our Discussion (Sect. 4).



## 2.3 Integrated $\Delta^{14}CO_2$ air and plant samples

Integrated  $\Delta^{14}CO_2$  samples ( $\Delta_{absorption}$ ), where the sampling rate is usually constant (e.g. in various  $CO_2$  absorption setups), are represented with the concentration-weighed time-average  $\Delta^{14}CO_2$  signature for the period and height of sampling, as seen in Eq. (7):

$$\Delta_{\text{absorption}} = \sum_{t} \Delta_{\text{obs}}^{t} \frac{\text{CO}_{2\text{obs}}^{t}}{\sum_{t} \text{CO}_{2\text{obs}}^{t}}$$

5

Plant samples (Δ<sub>plant</sub>) integrate the atmospheric Δ<sup>14</sup>CO<sub>2</sub> signature with CO<sub>2</sub> assimilation rate which varies depending on various meteorological and phenological factors.
Photosynthetic uptake and the allocation of the assimilated CO<sub>2</sub> in the different plant parts strongly depend on the weather conditions and plant development. To simulate such samples we use WRF meteorological fields in the crop growth model SUCROS2 (van Laar et al., 1997) and use the modeled daily growth increment as a weighting function (averaging kernel) on the daytime atmospheric Δ<sup>14</sup>CO<sub>2</sub> signatures (Bozhi-15 nova et al., 2013). For each location we use the same sowing date and the model simulates the crop development until it reaches flowering, when we calculate Δ<sub>plant</sub>.

More explicitly these integrated sample signatures are calculated as:

$$\Delta_{\text{plant}} = \sum_{t} \Delta_{\text{obs}}^{t} \frac{X_{t}}{\sum_{t} X_{t}},$$

where  $X_t$  is the growth increment at time t, which in the case of SUCROS2 simulation is the dry matter weight increment at day t.

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(7)

(8)

#### 3 Results

## 3.1 Model evaluation – how realistic are our $CO_2$ and $\Delta^{14}CO_2$ simulations?

The meteorological conditions for 2008 that were simulated by WRF and used for the plant growth simulation in SUCROS2 were previously assessed in Bozhinova  $_{5}$  et al. (2013). Here we assess the model performance compared to observed CO<sub>2</sub> fluxes, CO<sub>2</sub> mole fractions, and boundary layer heights. Figure 1 shows this comparison at the observational tower of Cabauw, the Netherlands (data available at http://www.cesar-observatory.nl). The simulated net CO<sub>2</sub> flux (NEE) compares well to observations with a root-mean squared deviation (RMSD) of  $0.26 \text{ mg} \text{CO}_2 \text{ m}^{-1} \text{ s}^{-1}$  and correlation coefficient (r) for the entire period of 0.70, which is even higher in clear 10 days. Overestimates of NEE occur during cloudy conditions, which are notoriously difficult to represent in many mesoscale models. The CO<sub>2</sub> mole fractions compare well to observations (Vermeulen et al., 2011) and overall model performance is similar to other studies for the region (Tolk et al., 2009; Meesters et al., 2012). Similar to Steeneveld et al. (2008), Tolk et al. (2009), Ahmadov et al. (2009) the night-time stable boundary 15 layer poses a challenge to the model. Note that the skill at modeling the boundary layer height can be of a particular importance for the correct simulation of the  $CO_2$  budget, as it controls the diurnal evolution of the CO<sub>2</sub> mole fractions (Vilà-Guerau de Arellano et al., 2004; Pino et al., 2012). Thus, we have included this comparison in the last panel of Fig. 1. More detailed statistics for this and other stations and observations are 20 listed in Table 1. We show the mean difference between the predicted and observed time series, with the according RMSD, and calculated correlation coefficient and coefficient of determination (Willmott, 1982) for each location. While in Table 1 we show the statistics for the daily time-series, we also evaluated their hourly and daytime-only counterparts and the differences between each. Overall, our comparison shows that 25

although the model overestimates the night-time  $CO_2$  concentrations, it captures the observed daytime  $CO_2$  mole fractions features and their variability on scales of hours to days satisfactorily over the full period simulated for Cabauw.



We next analyze the results for the  $\Delta^{14}CO_2$  signature corresponding to these  $CO_2$  mole fractions to evaluate our skill at modeling the large scale  ${}^{14}CO_2$  over Europe. Figure 2 shows the comparison between monthly and bi-weekly integrated samples and their modeled counterparts for three measurement sites – Jungfraujoch and Schauins-

- Iand (Institut für Umweltphysik, University of Heidelberg, Germany, Levin et al., 2013) and Lutjewad (Centre for Isotope Research, University of Groningen, the Netherlands, unpublished data). Complementary statistics are included in Table 1. Note that solid statistics are prevented by the low amount of samples. The comparison shows we capture well the seasonal trend for the first two sites, suggesting that our choice of
- <sup>10</sup> background  $\Delta^{14}CO_2$  location (Jungfraujoch, for which the comparison is not independent as the observed monthly fit is used as  $\Delta_{bg}$  in our Eq. 4) is indeed representative for the region. However, at Lutjewad the typical seasonal cycle that our model gives seems almost completely reversed, with a correlation coefficient of -0.87 compared to the monthly integrated samples. Since we have other independent observations that <sup>15</sup> could give more insight into this mismatch, we will take a more detailed look at the
- results for this location.

Figure 3 shows the 6 month hourly results for Lutjewad. The first two panels of the figure show the comparison between the observed (van der Laan et al., 2009) and modeled total  $CO_2$  and only fossil fuel  $CO_2$ . The latter has been compared to esti-

- <sup>20</sup> mates derived from <sup>14</sup>C-corrected high-resolution CO observations (van der Laan et al., 2010). See Table 1 for details. The fossil fuel signal dominates over any variability in the background, clearly defining periods with enhanced transport of fossil fuel CO<sub>2</sub> to the location (late April, start of May, start of July, start of August) as compared to less polluted air transported from the North sea (mid-May, mid-June). In the last panels we see this influence on the resulting  $\Delta^{14}CO_2$  signature and especially its high temporal variability that is not captured in the integrated samples shown in Fig. 2. The large
- mismatch between the observed and modeled  $\Delta^{14}CO_2$  monthly integrated samples could have been caused by an underestimation of the fossil fuel component reaching Lutjewad. However, the complementary independent observations of CO<sub>2</sub> and the CO-



derived fossil fuel CO<sub>2</sub> estimates show good agreement with our model results in that period and this could indicate a possible issue with the  $\Delta^{14}CO_2$  observations by themselves. Note that even though station Lutjewad is distant to nuclear emission sources, the signal from nuclear activity (shown in the last pannel) can be occasionally of the same order of magnitude as the fossil fuel signal. This shows how important it is to evaluate the nuclear infuence at every measurement site, as it will contribute to the uncertainty in the recalculation of fossil fuel CO<sub>2</sub>.

# 3.2 Fossil fuel vs. nuclear emissions influence on $\Delta^{14}CO_2$

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The lowest  $\Delta^{14}CO_2$  values in the domain are modeled in the regions with high fossil fuel emission in west Germany (the Ruhrgebiet), and the highest  $\Delta^{14}CO_2$  is near the large emitting sites in Western France and UK. This pattern can be clearly seen in Fig. 4a–c where results for average situation in the lower 1200 m of the atmosphere over the 6 months are shown. Note that the nuclear enrichment reaches much higher amplitude than the opposite effect by the fossil  $CO_2$ , but its influence on the atmospheric  $\Delta^{14}CO_2$ 

- is usually on the local scale around the average nuclear power plant reactors. The influence is more pronounced in the west part of our domain, where it captures the influence from the SFRP in La Hague (France) and several newer generation nuclear reactors in the UK. Even then, the influence of the nuclear enrichment averaged over 6 months is mostly about 1 to 6‰ in areas that are not in direct vicinity of the sources.
- As a comparison, the fossil fuel infuence in our domain on the same temporal and spatial scale is mostly between -3 and -15% outside the very polluted area of the Ruhrgebiet, Germany.

As the nuclear enrichment will (partially) mask the effect of fossil fuel  $CO_2$  on the atmospheric  $\Delta^{14}CO_2$ , we show in Fig. 4d the average 6 month ratio of the influences due

to nuclear and fossil fuel sources in our domain. Again, in most of the east and central parts of our domain the nuclear infuence is less than 10% the fossil fuel influence. This differs from the west part of our domain, where the ratio varies between 3 times smaller



to about the same magnitude as the fossil fuel contribution and even to a more than 5 times larger influence in the area around the nuclear sources. These findings are consistent with Graven and Gruber (2011) and the improvement in the horizontal resolution of the transport model results in a much larger nuclear enrichment in the grid box
<sup>5</sup> containing a nuclear source. The magnitude and size of the influenced area are highly variable and strongly dependent on the atmospheric transport. As a result, in months with dominant easterly winds the nuclear enrichment has a minimum effect in our do-

- main, as most of the nuclear emissions are transported towards the Atlantic ocean and out of our area of interest. However, in months with dominant westerly winds, which is the more often the observed case, the nuclear <sup>14</sup>CO<sub>2</sub> spreads widely over the domain.
  - For sites located in Northern and Central France, Southern Germany and the UK the nuclear enrichment means that corrections are needed that account for the nuclear influence in the observed  $\Delta^{14}CO_2$  before estimating the fossil fuel influence. As an illustration, we show the influence of the different anthropogenic emissions for three lo-
- cations with different characteristics in our domain, in Fig. 5: Cambridge (UK), Cabauw (the Netherlands) and Kosetice (Czech Republic). The locations were chosen to be in rural or agricultural areas, without large local CO<sub>2</sub> emissions. As seen in Fig. 5, the west part of our domain (represented by Cambridge) has an equal influence from fossil fuel and nuclear emissions; the center (represented by Cabauw) does see some events
- with relatively high nuclear emissions influence, but is defined mostly by the very high fossil fuel emissions in this region, which are on average about 3 times higher than in Cambridge. In the east (represented by Kosetice) there is no significant signal of nuclear emissions, but the fossil fuel emissions influence is also considerably lower.

# 3.3 $\Delta^{14}CO_2$ plant vs. atmospheric samples

<sup>25</sup> In our previous work (Bozhinova et al., 2013) we described a method to model the  $\Delta^{14}CO_2$  in plant samples as the first step in quantifying the differences between such samples and integrated atmospheric samples. Here we build on this work by calculating the plant signature resulting from uptake of spatially and temporally variable atmo-



spheric  $\Delta^{14}CO_2$ . The results for modeled samples from maize leaves at flowering, are shown in Fig. 6. Clearly, spatial gradients in  $\Delta^{14}CO_2$  in plants are sizeable compared to the measurement precision of approximately 2‰. The regions with high influence from anthropogenic emissions from Fig. 4, namely the Ruhrgebiet in West Germany and

- the Benelux are also visible in the modeled plant signature, and so are some hotspots around larger european cities, like Frankfurt, Paris, London and others. It is important to point out that in addition to fossil fuel and nuclear gradients, plants develop at different rates in different parts of the domain, and even the different parts of a plant (roots, stems, leaves, fruits) grow during different time periods.
- <sup>10</sup> The plant-sampled  $\Delta^{14}CO_2$  includes the effect of the covariance between the atmospheric  $\Delta^{14}CO_2$  variability and the variability in the assimilation of  $CO_2$  in the plant during growth, which is absent in traditional integrated samples where the absorption of  $CO_2$  is based on constant flow rate through an alkaline solution and thus only varies with the  $CO_2$  concentration present in the flow (Hsueh et al., 2007). In Fig. 7 we
- <sup>15</sup> show this effect of the plant growth on the resulting plant  $\Delta^{14}CO_2$  signature. We should stress, that this is the magnitude of the error one should expect if the plant sampled  $\Delta^{14}CO_2$  is assumed equal to the atmospheric mean  $\Delta^{14}CO_2$  for the growing period of the plant. For many parts of Europe in our simulated period this error is approaching the measurement precision of the  $\Delta^{14}CO_2$  analysis (of approximately ±2%). In the region
- <sup>20</sup> located between the areas with high fossil fuel and large nuclear emitters, however, the magnitude of the error can be several times larger. This is likely due to the absorption of some very high signature values on a few specific days when the wind direction is directly from the nuclear source. Actual plant samples, taken during different period than the one investigated here (namely 2010–2012), will be used to further investigate these signatures in a fellow up publication.
- these signatures in a follow-up publication.



## 3.4 Direct estimation of the fossil fuel CO<sub>2</sub> emissions

As an alternative to modeling of the  $^{14}\text{CO}_2$  budget as presented here, we searched for a possible direct relationship between the prescribed regional emissions and the resulting  $\Delta^{14}\text{CO}_2$  signal that would be observed in air samples or plants. While the

- <sup>5</sup> entire emission map of Europe might be difficult to verify, most of the fossil fuel CO<sub>2</sub> emissions are produced at only a number of sites. This provides an opportunity where only the chosen sites are object of a sampling campaign or study, but these can still provide a better estimate for the highest emitting regions in Europe. As an illustration, 10% of all emissions in our domain are emitted from only 30 grid cells and more than helf of these can share the leasted in classes.
- half of these are already located in densely populated cities or urban conglomerations. We focused our following analysis on the top 25 populated cities and top 30 emitting grids in our domain with 12 km horizontal resolution.

We looked into the relationship between the  $\Delta^{14}$ CO<sub>2</sub> signatures modeled at the surface for each of the locations and the emissions we prescribe in our model. Regard-

ing the Δ<sup>14</sup>CO<sub>2</sub> signatures we used for this analysis, we compared the set of modeled daytime integrated samples, 24 h integrated samples, and samples modeled for maize leaves. Regarding the fossil fuel emissions, we compared each set of modeled Δ<sup>14</sup>CO<sub>2</sub> samples with its according prescribed emissions at the exact grid cell where the Δ<sup>14</sup>CO<sub>2</sub> sample was modeled, and additionally to the prescribed emissions, but averaged over a 5 × 5 grid around it (area-averaged). In all cases, the comparison for the emissions prescribed at the exact location showed some, but quite low correlation, which was considerably higher when comparing to the area-averaged emissions.

After constructing the linear fit to each of these relationships, we used it to recalculate the fossil fuel emissions we would estimate if using only the linear relation and the simulated  $A^{14}CO$  at each location, and evaluated the DMCD between the prescribed

<sup>25</sup> simulated  $\Delta^{14}CO_2$  at each location, and evaluated the RMSD between the prescribed emissions and those estimated afterwards. The best relation we found (i.e., the one that gave the smallest RMSD of the linear fit) was when considering the  $\Delta^{14}CO_2$  signatures for the top 25 cities modeled in maize leaves and compared to the area-averaged emis-



sions (see Fig. 8). Here we also differentiate the case in which we build the relationship only based on the information from our fossil fuel  $CO_2$  tracer, and the one in which the masking effect of the nuclear <sup>14</sup>CO<sub>2</sub> is also included. For most cities the effects are within a few permil, however for Birmingham (UK) the model results differed with close to 10‰, which approximates to 4 ppm of CO<sub>2ff</sub> difference.

The linear relationship shown in Fig. 8 has a slope of approximately 4.5% per 10 000 mol km<sup>-2</sup> h<sup>-1</sup> of the area-averaged emissions. Even in our "best" case, the coefficient of determination ( $R^2$ ) is just over 0.7, meaning that close to 30% of the variance in emissions across Western Europe will not be captured when using this relationship. The resulting RMSD is about 9000 mol km<sup>-2</sup> h<sup>-1</sup>, or 15% of the range of the area-average emissions (on 60 km × 60 km area) that we see in our entire domain, which includes one of the highest emitting regions in Europe. Accounting for the influence of the <sup>14</sup>CO<sub>2</sub> with nuclear origin lowers this number by about 10% or about 8100 mol km<sup>-2</sup> h<sup>-1</sup>. Additionally, we used the relationship to estimate the uncertainty that will be introduced in the recalculation of emissions from the  $\Delta^{14}CO_2$  single measurement precision of about  $\pm 2\%$  given the slope of the linear relation. This number corresponds to 3000 mol km<sup>-2</sup> h<sup>-1</sup> of area-average emissions based on the presented fit or crudely another 5% of our total range. This suggests that the uncertainty of direct fossil fuel CO<sub>2</sub> emission estimates will be high even if a tighter relation between

<sup>20</sup> emissions and observations is found. Together with the large nuclear corrections, this simple exercise suggest that the successful interpretation of  $\Delta^{14}CO_2$  monitoring will benefit from a modeling framework that can capture the specific characteristics of the regional atmospheric transport, like the one presented here.

#### 4 Discussion

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<sup>25</sup> Our modeling results show that over a significant part of our domain the nuclear influence on the atmospheric  $\Delta^{14}CO_2$  signature will be more than 10% (ratio = 0.1 on Fig. 4d) of the estimated fossil fuel influence, introducing considerable uncertainty to



the method of using  $\Delta^{14}CO_2$  to calculate the fossil fuel  $CO_2$  addition to the regional atmosphere. The strongest gradients of  $\Delta^{14}CO_2$  in Western Europe are found in the relatively polluted region in Western Germany and the Netherlands due to the high population density and large industry sector there, and hence high  $CO_2$  emissions.

- <sup>5</sup> More detailed <sup>14</sup>CO<sub>2</sub> observations in this region can possibly prove useful in lowering the uncertainty of the regional fossil fuel emission estimates as also investigated for California by Riley et al. (2008). Furthermore, the high fossil-to-nuclear ratio ensures that uncertainties arising from nuclear emissions will be at their minimum.
- This result relies partly on the underlying emission maps for the anthropogenic (fos-<sup>10</sup> sil fuel)  $CO_2$  and (nuclear) <sup>14</sup> $CO_2$  emissions. We should consider various factors that are uncertain or unknown at this point for these emissions (Peylin et al., 2011; Graven and Gruber, 2011) – such as temporal characters, vertical resolution and even small irregularities in the spatial allocation of the emission sources. All our anthropogenic emissions are located in the lowest (surface) layer of our model, however the vertical
- discretisation is possibly up for improvement. Most of the industrial emission stacks are located at 100 to 300 m height and applying this information, where available, in our input data will likely result in the emissions being transported further away faster and result in less local enrichment. For the fossil fuel CO<sub>2</sub> emissions we apply temporal profiles that disaggregate monthly, weekly and diurnal signals from the provided annual
- emissions. For the nuclear emissions such profiles are unknown and information on their temporal heterogeneity is not publically available. In this study we consider them as continuous and constant throughout the year. This is a relatively safe assumption for the emissions from nuclear power plants as their <sup>14</sup>CO<sub>2</sub> is a by-product of the normal operation of the reactor. This might not be the case for reprocessing sites, where the emissions will depend also on the type and amount of fuel being reprocessed. Addition-
- ally, there is uncertainty if these emissions are released continuously or in few timed or instantaneous big venting events, and the venting procedures are likely reactor-type dependent.



When using flask samples for <sup>14</sup>CO<sub>2</sub> measurement nuclear enrichment can relatively easily be recognized. However, in integrated air and plant samples this signal will be averaged over the total sampling period. These latter samples will record the enrichment in  $\Delta^{14}CO_2$ , but depending on the weather variability, local fossil fuel CO<sub>2</sub> addition and the proximity to the nuclear sources, these signals can be within the measurement

- precision (of approximately  $\pm 2\%$ ). Integrated samples are thus likely of too low timeresolution to attribute nuclear emissions, and areas where this influence is high would profit from flask sampling of  $\Delta^{14}CO_2$  in addition to integrated sampling. If the nuclear emissions occur in less frequent but larger events as speculated above, the integrated
- samples are likely to be influenced less, and the flask samples are less likely to capture such events. Overall, we deem a better characterization of the temporal structure of the nuclear emissions a prerequisite for any <sup>14</sup>CO<sub>2</sub>-based monitoring effort in Europe. We should note that our study is also subject to known uncertainties in atmospheric
- transport of current mesoscale models. An inaccurate simulation of wind speed and direction (Lin and Gerbig, 2005; Gerbig et al., 2008; Ahmadov et al., 2009) or boundary layer height development (Vilà-Guerau de Arellano et al., 2004; Steeneveld et al., 2008; Pino et al., 2012) will all affect the transport of emission plumes and resulting mole fractions. Resolving more meso-scale circulations, and improved representation of topography can be particularly advantageous, as they can cause large gradients in
- <sup>20</sup> CO<sub>2</sub> (de Wekker et al., 2005; van der Molen and Dolman, 2007). While WRF-Chem is used for a variety of atmospheric transport studies (among others: Tie et al., 2009; de Foy et al., 2011; Lee et al., 2011; Stuefer et al., 2013), more general air quality studies have shown that an ensemble model can forecast air pollution situations more accurately than a single separate model (Galmarini et al., 2004, 2013). While in our re-<sup>25</sup> search we focused on the passive transport of CO<sub>2</sub> and <sup>14</sup>CO<sub>2</sub>, other chemical species
- <sup>25</sup> search we focused on the passive transport of CO<sub>2</sub> and <sup>14</sup>CO<sub>2</sub>, other chemical species are already available in the core of WRF-Chem. Another step further could be the addition of such chemically active tracers (e.g. CO, NO<sub>x</sub>, and many others) that are regularly measured with regards to air pollution and health safety and connected with anthropogenic emissions that are the ultimate interest of our study. Including <sup>222</sup>Rn as



additional tracer can be very beneficial for lowering the uncertainty associated with the vertical mixing in the model and provide correction factors to be applied to the other passive tracers, as shown in van der Laan et al. (2010), Vogel et al. (2013).

- Considering future uses of  $\Delta^{14}CO_2$  observations as additional constraint on the carbon cycle by the atmospheric modeling community, we should note that atmospheric inversions can use only afternoon observational data. In that case, plant-sampled  $\Delta^{14}CO_2$  observations may provide a better representation of the afternoon atmospheric  $\Delta^{14}CO_2$  signals than conventional integrated samples that also absorb  $CO_2$  during the night.
- <sup>10</sup> We explored the possibility that a relatively simple relationship can be used to calculate the emissions directly from  $\Delta^{14}CO_2$  observations. While the method seems promising, its inability to capture bigger part of the variability in the modeled  $\Delta^{14}CO_2$  signals condemns it to high inherent uncertainty for the reconstructed emissions. While a portion of this uncertainty can be lowered with a better fitting relationship, another is a di-<sup>15</sup> rect consequence by the  $\Delta^{14}CO_2$  measurement precision and will provide a lower limit to the reconstructed emissions.

Our results suggest that a combination of the available sampling methods should be used when planning a  $^{14}CO_2$  observational network for the purpose of fossil fuel emissions investigations. Integrated air and plant samples alone can provide a longer

- <sup>20</sup> period observations at a lower cost, but this feature makes them less useful for evaluation of large nuclear influences in shorter periods. Flask samples are much better suited for this exact task, however their continuous analysis is too costly in the long run. A possible compromise could be obtaining flask samples for a limited period alongside integrated samples for new sampling locations. This would already provide information
- <sup>25</sup> about the possible nuclear enrichment and the wind directions from which it usually occurs. Additionally, while integrated air samples are the current standard for quasi-continuous observations of <sup>14</sup>CO<sub>2</sub> and the uncertainties in their CO<sub>2</sub> assimilation are lower, plant samples can be obtained at a much higher spatial resolution without additional infrastructure investment. Their use is constrained to the sunlit part of the day,



and time and locations where the chosen crop grows, but that should not limit their use to help us verify spatial patterns and gradients.

#### 5 Conclusions

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- In this work, we demonstrated the ability of our modeling framework to simulate the atmospheric transport of CO<sub>2</sub> and consequently the atmospheric Δ<sup>14</sup>CO<sub>2</sub> signature in integrated air and plant samples in Western Europe. Based on our investigation and results we reach the following conclusions.
  - 1. Simulated spatial gradients of  $\Delta^{14}CO_2$  are of measurable size and the 6 month average  $CO_{2ff}$  concentrations in the lower 1 km of the atmosphere across Western Europe are between 1 to 18 ppm.
  - 2. Enrichment by <sup>14</sup>CO<sub>2</sub> from nuclear sources can, at least partly, mask the Suess effect nearby the sources of nuclear emissions, particularly in large parts of UK and North-Western France. This is consistent with previous studies (Graven and Gruber, 2011) and we show that in these regions the strength of the nuclear influence can be comparable and even larger than the influence from fossil fuel emissions.
  - 3. The simulated plant  $\Delta^{14}$ CO<sub>2</sub> signatures show spatial gradients consistent with the simulated atmospheric gradients and many emission hotspots are clearly visible in the modeled plant samples. Plant growth variability induces differences between the simulated plant and the atmospheric mean of magnitude which are mostly within the measurement precision of  $\pm 2\%$ , but of up to  $\pm 7\%$  in some areas.
  - 4. Integrated  $\Delta^{14}CO_2$  from areas outside the immediate enrichment area of nuclear emission sources are not sensitive to occasional advection of enriched air due to their long absorption period. However, to properly account for the nuclear enrich-



ment term on smaller time scales, improvements in temporal profiles of nuclear emissions are needed.

5. New  $\Delta^{14}CO_2$  sampling strategies should take advantage of all the different sampling methods, as their combined use will provide a much more comprehensive picture of the atmospheric  $\Delta^{14}CO_2$  temporal and spatial distribution.

Acknowledgements. This work is part of project (818.01.019), which is financed by the Netherlands Organisation for Scientific Research (NWO). Further partial support was available by NWO VIDI grant (864.08.012). We acknowledge IER Stuttgart for providing the anthropogenic  $CO_2$  emissions maps, IAEA PRIS for the nuclear reactor information and NCEP and ECMWF

- for the meteorological data. We thank I. Levin (University of Heidelberg), A. Vermeulen (ECN), S. Palstra and R. Neubert (CIO), E. Moors (Alterra), M. Fröhlich (EAA, Austria), K. Uhse (UBA, Germany) and F. C. Bosveld (KNMI) for providing the observational data used in this study. We further want to thank H. Graven (Scripps Institute of Oceanography, USA), N. Gruber (Swiss Federal Institute of Technology, Switzerland), and I. van der Laan-Luijkx and M. Combe (Wa-
- <sup>15</sup> geningen University, the Netherlands) for the scientific support and useful comments provided for this manuscript.

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Table 1. The observational sites with data used in this study and statistics for the daily concentrations of CO<sub>2</sub> and CO<sub>2ff</sub> estimated from CO observations, hourly flux CO<sub>2</sub> and monthly integrated  $\Delta^{14}CO_2$  observations as compared with modeled results. Here  $\overline{Pi - Oi}$  represents the mean model-data difference,  $\sigma_{Pi-Oi}$  – the spread of the difference, both of which carry the units described in the header of each section, while r – the Pearson's coefficient of correlation and d – the coefficient of determination (Willmott, 1982) are dimensionless measures and n – number of members for the statistical analysis.

Site	Latitude [° N]	Longitude [° E]	Elevation [m]	Altitude [m]	Owner	Provider	Pi – Oi	$\sigma_{\rm Pi-Oi}$	r	d	п
CO <sub>2</sub> concentration [ppm]											
Cabauw, NL	51.97	4.93	0.7	20	ECN, NL <sup>a</sup>	CarboEurope IP <sup>b</sup>	5.58	8.19	0.64	0.72	185
Cabauw, NL	51.97	4.93	0.7	60	ECN, NL	CarboEurope IP	3.69	6.37	0.65	0.74	185
Cabauw, NL	51.97	4.93	0.7	120	ECN, NL	CarboEurope IP	2.76	5.48	0.67	0.77	185
Cabauw, NL	51.97	4.93	0.7	200	ECN, NL	CarboEurope IP	1.40	4.50	0.74	0.84	185
Heidelberg, DE	49.42	8.67	116	30	IUP-UHEI, DE <sup>c</sup>	CarboEurope IP	4.29	7.31	0.69	0.77	185
Loobos, NL	52.17	5.74		24.5	Alterra-WUR, NL <sup>d</sup>	CarboEurope IP	3.82	6.90	0.59	0.71	185
Lutjewad, NL	53.40	6.36	3	60	CIO-RUG, NL <sup>e</sup>	CIO-RUG, NL	-0.60	7.43	0.53	0.73	167
Lutjewad, NL – CO <sub>2ff</sub>	53.40	6.36	3	60	CIO-RUG, NL	CIO-RUG, NL	-3.29	3.64	0.66	0.69	166
Neuglobsow, DE	53.17	13.03	65		UBA, DE <sup>f</sup>	WDCGG <sup>g</sup>	-2.31	8.62	0.58	0.74	185
Schauinsland, DE - 5 min	47.92	7.92	1200	7	UBA, DE	WDCGG	0.20	4.13	0.81	0.89	153
Schauinsland, DE – conti	47.92	7.92	1200	7	UBA, DE	WDCGG	0.17	3.59	0.85	0.92	177
Sonnblick, AT	47.05	12.95	3106		EEA, AT <sup>h</sup>	WDCGG	1.57	2.74	0.86	0.88	185
Zugspitze, DE	47.42	10.98	2656		UBA, DE	WDCGG	0.79	3.07	0.82	0.88	161
CO <sub>2</sub> surface flux [mg CO <sub>2</sub> m <sup>-2</sup> s <sup>-1</sup> ]											
Cabauw, NL	51.97	4.93	0.7	1	KNMI, NL <sup>i</sup>	CESAR <sup>j</sup>	-0.01	0.26	0.70	0.83	2662
$\Delta^{14}$ CO <sub>2</sub> integrated sample [‰]											
Jungfraujoch, CH	46.55	8.00	3450	5	IUP-UHEI, DE	IUP-UHEI, DE	1.05	1.61	0.71	0.74	6
Lutjewad, NL	53.40	6.36	3	60	CIO-RUG, NL	CIO-RUG, NL	8.82	5.16	-0.87	0.12	6
Schauinsland, DE	47.92	7.92	1200	7	IUP-UHEI, DE	IUP-UHEI, DE	-1.89	1.83	0.74	0.75	6

<sup>a</sup> ECN – Energy Research Center of the Netherlands, the Netherlands; contact person – Alex Vermeulen, a.vermeulen@ecn.nl

<sup>b</sup> CarboEuropeIP - CarboEurope Integrated Project; http://www.carboeurope.org

<sup>c</sup> IUP-UHEI – Institute of Environmental Physics, University of Heidelberg, Germany; contact person – Dr. Ingeborg Levin, Ingeborg Levin@iup.uni-heidelberg.de

<sup>d</sup> Alterra-WUR – Alterra, Wageningen University, the Netherlands; contact person – Dr. ir. Eddy Moors, eddy.moors@wur.nl

e CIO-RUG - Center for Isotope Research, University of Groningen, the Netherlands; contact person - Prof.dr. Harro Meijer, H.A.J.Meijer@rug.nl

<sup>f</sup> UBA, DE – Federal Environmental Agency, Germany; contact person – Karin Uhse, karin.uhse@uba.de <sup>g</sup> WDCGG – World Data Center for Greenhouse Gases; http://ds.data.jma.go.jp/gmd/wdcgg/

<sup>h</sup> EEA, AT – Environmental Agency Austria, Austria; contact person – Marina Fröhlich, marina.froehlich@umweltbundesamt.at

<sup>1</sup> KNMI – Royal Netherlands Meteorological Institute, the Netherlands; contact person – Dr. Fred Bosveld, Fred.Bosveld@knmi.nl

<sup>j</sup> CESAR - Cabauw Experimental Site for Atmospheric Research, the Netherlands; http://www.cesar-observatory.nl



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**Fig. 1.** Comparison between modeled and observed  $CO_2$  fluxes, concentrations and boundary layer height for the location of Cabauw for one month in the simulated season. Performance is usually better on clear days as compared to cloudy ones, indicated in the graph with the gray background.













**Fig. 3.** 6 months of hourly results for Lutjewad at 60 m height. Comparison between observed and modeled (a)  $CO_2$  concentrations, (b)  $CO_{2ff}$  concentrations (c) atmospheric  $\Delta^{14}CO_2$  and (d) the contrubution of different compounds for the resulting  $\Delta^{14}CO_2$ . The variations in the  $\Delta^{14}CO_2$  signal are directly connected with the transport of fossil fuel  $CO_2$  enriched air at the location, but are not captured by current observations due to their low temporal resolution.



**Fig. 4.** Spatial distribution for the 6 month averaged (a) fossil fuel  $CO_2$  emissions influence, (b) nuclear <sup>14</sup>CO<sub>2</sub> emissions influence, (c) resulting  $\Delta^{14}CO_2$  signature in the atmosphere and (d) the ratio between the nuclear and fossil fuel influences on the atmospheric signature, all averaged over the lower 1200 m of the atmosphere. While the biggest influence over Europe for changes in the  $\Delta^{14}CO_2$  in the atmosphere is of fossil fuel  $CO_2$ , the effect of the nuclear emissions of <sup>14</sup>CO<sub>2</sub> can be of comparable magnitude for large areas in France and UK.











**Fig. 6.** Modeled absolute  $\Delta^{14}CO_2$  signature of maize leaves at flowering. Both the highly industrialized areas in Germany, where the atmospheric  $\Delta^{14}CO_2$  is lower than the background, and the enriched areas near the big nuclear sources in France and UK are visible also in the plants. Even on this resolution we see in the plant signature the hotspots around Paris, London, Frankfurt, and many other big cities.

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shows the covariance between the plant growth and the variability in the atmospheric  $\Delta^{14}CO_2$ , which in essense is the error that should be expected if the plant growth is not taken into account and the plant signature is assumed to be equal to the atmospheric average.





