Wine ethanol $^{14}$C as a tracer for fossil fuel CO$_2$ emissions in Europe: Measurements and model comparison

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1. Introduction

$^{[1]}$ $^{14}$C (radiocarbon) in atmospheric CO$_2$ is the most direct tracer for the presence of fossil-fuel-derived CO$_2$ (CO$_2$-ff). We demonstrate the $^{14}$C measurement of wine ethanol as a way to determine the relative regional atmospheric CO$_2$-ff concentration compared to a background site ("regional CO$_2$-ff excess") for specific harvest years. The carbon in wine ethanol is directly back traceable to the atmospheric CO$_2$ that the plants assimilate. An important advantage of using wine is that the atmosphere can be monitored annually back in time. We have analyzed a total of 165 wines, mainly from harvest years 1990–1993 and 2003–2004, among which is a semicontinuous series (1973–2004) of wines from one vineyard in southwest Germany. The results show clear spatial and temporal variations in the regional CO$_2$-ff excess values. We have compared our measured regional CO$_2$-ff excess values of 2003 and 2004 with those simulated by the REgional MOdel (REMO). The model results show a bias of almost +3 parts per million (ppm) CO$_2$-ff compared with those of the observations. The modeled differences between 2003 and 2004, however, which can be used as a measure for the variability in atmospheric mixing and transport processes, show good agreement with those of the observations all over Europe. Correcting for interannual variations using modeled data produces a regional CO$_2$-ff excess signal that is potentially useful for the verification of trends in regional fossil fuel consumption. In this fashion, analyzing $^{14}$C from wine ethanol offers the possibility to observe fossil fuel emissions back in time on many places in Europe and elsewhere.


1. Introduction

$^{[2]}$ CO$_2$ emitted by the combustion of fossil fuels (CO$_2$-ff) is worldwide the largest net carbon flux to the atmosphere. In densely populated and industrialized regions such as Europe, this net source overwhelms the natural net sources and sinks [Levin and Karstens, 2007a]. If under these circumstances one still wants to quantify the net exchange of CO$_2$ by the biosphere and coastal seas, accurate knowledge about the spatial and temporal behavior of CO$_2$-ff is essential. In the case of Europe, both detailed, reliable statistical data about fossil fuel combustion, and atmospheric measurements of the CO$_2$-ff concentration are therefore indispensable. Determination of the amount of CO$_2$-ff is also of crucial importance by itself: emission reductions in the framework of the Kyoto Protocol should be independently verified, and a robust and accurate verification tool is important for policy-makers and -thus- for society.

$^{[3]}$ The atmospheric CO$_2$-ff concentration cannot be deduced directly from atmospheric CO$_2$ measurements, because it cannot be distinguished from CO$_2$ released by other sources (e.g., the biosphere). Other measurements are therefore needed to identify and quantify atmospheric CO$_2$-ff concentrations. The measurement of $^{14}$C in air and plant samples has proven to be a very useful tracer for atmospheric CO$_2$-ff [Suess, 1955; Levin et al., 1989, 2003; Turnbull et al., 2006; Hsieh et al., 2007; Levin and Rödenbeck, 2007]. SF$_6$ and CO have been investigated recently as “surrogate” tracers for CO$_2$-ff [Turnbull et al., 2006; Gamnitzer et al., 2006; Levin and Karstens, 2007b], but $^{14}$C is the only direct tracer available. Since CO$_2$-ff contains no $^{14}$C, the atmospheric $^{14}$CO$_2$ concentration is diluted when CO$_2$-ff is added to the atmosphere. Other (current) CO$_2$ sources do not dilute or concentrate the regional/local atmospheric $^{14}$CO$_2$ concentration to such a significant extent as CO$_2$-ff and therefore the rate of dilution compared to a background location can be used as a relative measure for local and/or regional CO$_2$-ff concentrations (mentioned in the text as “regional CO$_2$-ff excess” and in equations as “CO$_2$-ffx”).

$^{[4]}$ $^{14}$CO$_2$ is currently measured on a regular basis in air samples (continuous bi-weekly or monthly integrated) of less than 10 measurement sites in Europe (beside our own measurement site Lutjewad in the Netherlands, the sites mentioned by Levin et al. [2008] and Kuc et al. [2007]). Therefore little data and knowledge is available about...
spatial and temporal differences in the regional CO$_2$-ff excess within Europe and more representative measurement sites of atmospheric $^{14}$CO$_2$ are needed in which long-term trends can be monitored. Since setting up and maintaining an air measurement site is labor and cost intensive, we have started the analysis of $^{14}$C in wine ethanol of different European regions to supplement the monitoring network in Europe in an easy and relatively cheap way. Several studies already showed that $^{14}$C in (annual) plant materials like corn leaves [Hsueh et al., 2007], rice [Shibata et al., 2005], grape wine ethanol [Burchuladze et al., 1989], grass [Quarta et al., 2005], tree leaves [Levin et al., 1980] and tree rings [Tans et al., 1979; Levin and Kromer, 1997], sampled by the plant during the photosynthesis process and until it was harvested, is a reliable tracer of atmospheric $^{14}$CO$_2$ concentrations of the respective growing period. Although the use of $^{14}$C from plant material as a proxy for atmospheric $^{14}$CO$_2$ is not ideal (as we discuss in section 4 of this paper) and each plant material has its own advantages and disadvantages, we choose wine ethanol as sample material because, (1) wines are easy to obtain (in a local wine store or supermarket), (2) the wine grapes grow at many different locations in Europe, (3) contrary to air samples and most annual plant materials, previous sampling years can still be measured: trends in atmospheric $^{14}$CO$_2$ and in the regional CO$_2$-ff excess (if $^{14}$CO$_2$ data of a background site are available) can be monitored back in time and (4) we already had an archive of 128 $^{14}$C-measured wine ethanol samples. The measured $^{14}$C in wine ethanol represents the atmospheric $\Delta^{14}$C value, because atmospheric CO$_2$ has been transformed into sugars in the grape leaves, which are almost immediately transported to the grape berries [Hale and Weaver, 1962; Koblet, 1975; Alleweldt, 1977; Alleweldt et al., 1975; Coombe, 1992]. The sugars in the grape berries have been transformed into ethanol in the wine making process.

[5] In this paper we first show that our measurements of $^{14}$C in wine ethanol samples agree well with air measurements in Europe. Secondly, we demonstrate the spatial and temporal variations in the regional CO$_2$-ff excess (relative to background site Vermunt, Austria in the period until 1985 and Jungfraujoch, Switzerland in the period 1985–2004) of the different investigated European wine regions based on our wine results. Thirdly, we present a comparison between the measured regional CO$_2$-ff excess of the different wine regions and the regional CO$_2$-ff excess as simulated for 2003 and 2004 with regional atmospheric transport model REMO using different CO$_2$-ff emission inventories. From this comparison we conclude how to use the model-corrected measurements for trend analysis in fossil fuel consumption.

2. Experimental
2.1. Wine Samples
[6] We have measured $^{14}$C in wine ethanol of 165 different wines from 32 different regions in 9 different European countries (Figure 1). The wines were bought in supermarkets, wine stores and, in one case, directly from the local producer (Rheinland-Pfalz region, southwest Germany). On the basis of the information on the label of the wine bottle, we selected non-mixed wines (of one region, one harvest year and of one wine-farmer). We have investigated wines from different harvest years and mainly from the periods 1990–1993 and 2000–2004. The different wine regions have not been measured with the same frequency. The investigated German Rheinland-Pfalz wines have harvest years in the period 1965–2004. Many of the Rheinland-Pfalz wines originated from one and the same vineyard near the village Birkweiler (22 different harvest years in period 1973–2004).

2.2. Measurement of $\Delta^{14}$C in Wine Ethanol
[7] In the period 1993–2007, 128 wine ethanol samples have been analyzed on $^{14}$C at the Centre for Isotope Research (CIO) Groningen using a method in which, after complete distillation of wine ethanol form the wine, wine ethanol is first combusted and oxidized to CO$_2$ and then complete distillation of wine ethanol form the wine, wine ethanol is first combusted and oxidized to CO$_2$ and then measured with a low background proportional gas counter [Mook and Streurman, 1983; van der Plicht et al., 1992]. The obtained $\Delta^{14}$C data are given relative to the activity of the international certified oxalic acid calibration material, and are corrected by convention for fractionation ($\delta^{13}$C) and decay [Stuiver and Polach, 1977]. The $\Delta^{14}$C sample data are expressed as $\%$ (per mil) deviation from this calibration.

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Figure 1. Investigated wine regions (big black dots) and current (gray triangles) and former (small black dots) atmospheric measurement sites. The regions/cities and sites mentioned in the text or in other figures are labeled. Ir, Ireland: MH, Mace Head; Po, Portugal: D, Douro; Sp, Spain: P, Penedes, which also labels the city Barcelona; R, Rioja, which also labels the nuclear power plant of Santa Maria de Garona; Fr, France: ML, Maine-et-Loire; A, Alsace; B, Bourgogne; Co, Corbieres; and G, Gironde, which also labels the city Bordeaux; C, Côtes-du-Rhône, which also labels the nuclear power plants of Tricastin and Cruas; NL, Netherlands: L, Lutjewad; and Sm, Smilde; Ger, Germany: SU, Saale-Unstrut; Sa, Sachsen; F, Franken; H, Heidelberg; S, Schauinsland; and Rheinland-Pfalz (RP), which also labels the village Birkweiler; CR, Czech Republic: M, Moravia; Sw, Switzerland: J, Jungfraujoch; Au, Austria: N, Neusiedlersee; T, Thermenregion; and Vermunt (V); Hu, Hungary: E, Eger; and It, Italy: As, Asti; Ve, Verona; To, Toscana; and Le, Lecce, which also labels the city Lecce. The sites of Poland (Pol) and Greece (Gr) have not been mentioned specifically in the text.
material. Samples are analyzed four times to increase the total number of counts and thus decrease the statistical uncertainty (Poission statistics). The combined uncertainty (or accuracy) of the mean $\Delta^{14}$C value of an individual sample is 2–3%.

In 2007, 40 wine ethanol samples have been analyzed on $^{14}$C using the $^{14}$C dedicated Accelerator Mass Spectrometer (AMS) at the CIO, Groningen. After distillation of a few milliliter ethanol from a wine, the ethanol was first combusted and oxidized to CO$_2$ and then graphitized and pressed into targets as described by Aerts-Bijma et al. [1997, 2001]. All sample targets (two targets per wine ethanol sample) have been measured twice in two different batches using the AMS system [van der Plicht et al., 2000]. Background samples (anthracite) and standards (certified oxalic acid) have been measured in every batch as part of the calibration and quality control procedures. The fractionation and decay corrected $\Delta^{14}$C value of a wine ethanol sample is calculated as the weighted average value of the (max. 4) individual measurements. In this way, we can achieve a combined uncertainty that is mostly below 3% [Meijer et al., 2006]. The results of both used analysis methods agree very well (within the measurement uncertainty: ±3%).

2.3. Calculation of the Regional Atmospheric CO$_2$-ff Excess From $^{14}$C in Wine Ethanol

The regional atmospheric CO$_2$-ff excess at a particular measurement site compared to a background site is derived from $^{14}$C measurements by using two mass balance equations, which describe the atmospheric mixing ratios of CO$_2$ (equation (1)) and of $\Delta^{14}$C (equation (2)) at the measurement site. This approach is to some extent the same as described by Zondervan and Meijer [1996], Levin et al. [2003], Turnbull et al. [2006], and Levin and Rödenbeck [2007].

\[
CO_2(\text{site}) = CO_2(\text{bg}) + CO_2(\text{bio}) + CO_2(\text{oc}) + CO_2(\text{x}) + CO_2(\text{ffx})
\]

\[
\Delta^{14}C(\text{site}) = \Delta^{14}C(\text{bg}) \cdot \frac{CO_2(\text{bg})}{CO_2(\text{site})} + \Delta^{14}C(\text{bio}) \cdot \frac{CO_2(\text{bio})}{CO_2(\text{site})} + \Delta^{14}C(\text{oc}) \cdot \frac{CO_2(\text{oc})}{CO_2(\text{site})} + \Delta^{14}C(\text{x}) \cdot \frac{CO_2(\text{x})}{CO_2(\text{site})} + \Delta^{14}C(\text{ffx}) \cdot \frac{CO_2(\text{ffx})}{CO_2(\text{site})}
\]

The CO$_2$ concentration and the $\Delta^{14}$C value measured at a specific site consist of the mixing ratio in the free troposphere (“bg”), background, the regional biosphere components (“bio”), photosynthesis and heterotrophic respiration, the regional ocean component (“oc”), unknown regional components (“x”, for instance $^{14}$CO$_2$ emitted by nuclear power plants or CO$_2$ released by the burning of biomass) and, last but not least, the regional fossil fuel component (“ffx”: regional CO$_2$-ff excess). The relative contribution of each component to the total atmospheric CO$_2$ concentration and $\Delta^{14}$C value at a measurement site is time and location-specific.

The regional CO$_2$-ff excess (in our definition this can also be a negative value: deficit) at a measurement site compared to a background site can be calculated from equation (2). Since we only had data for $\Delta^{14}$C(ffx) (which is always $\leq$1000%), $\Delta^{14}$C (site), $\Delta^{14}$C (bg) and CO$_2$ (bg), we have made a few assumptions about the other parameters mentioned in this equation. With the assumption:

\[
CO_2(\text{site}) \approx CO_2(\text{bg}) + CO_2(\text{ffx})
\]

and the assumption that the regional biosphere, ocean and unknown CO$_2$-sources and sinks have not contributed significantly to the measured $\Delta^{14}$C value at a site, we have calculated the regional CO$_2$-ff excess according to:

\[
CO_2(\text{ffx}) \approx \frac{\Delta^{14}C(\text{fgx})}{\Delta^{14}C(\text{bg}) / \Delta^{14}C(\text{site})}
\]

In our approach a regional CO$_2$-ff excess of 1 ppm at a measurement site corresponds with a difference between the $\Delta^{14}$C values of the measurement site and the background site of $-5.6\%$ in 1965 to $-2.8\%$ in 2004. The difference in time is related to the decreased atmospheric background $\Delta^{14}$C value after the ban treaty for aboveground nuclear bomb tests in 1963, because of oceanic and biosphere carbon exchange and (partly) global CO$_2$-ff emissions [Levin and Hesshaimer, 2000; Randerson et al., 2002].

The assumptions leading from equations (1) and (2) to equations (3) and (4), but also some other assumptions we have made to calculate the regional CO$_2$-ff excess, are not at all as crude as they seem to be at first sight. Still, some of the assumptions may have a significant effect on our final results, especially in regions with relatively small regional CO$_2$-ff excess (<1 ppm) and therefore we will discuss and estimate (if possible) the effects.

In our approach we do not have data for “CO$_2$ (site)”, which is needed to calculate the regional CO$_2$-ff excess using equation (2) and is also used in other studies in which the regional CO$_2$-ff excess has been calculated [Levin et al., 2003; Turnbull et al., 2006]. We have therefore approximated this CO$_2$ concentration according to equation (3). The average contribution of “oc” and “bio” to the total CO$_2$ concentration that the wine plants experience during daytime in the growing season (the time they assimilate CO$_2$) is relatively low: thanks to the well-mixed atmosphere under these circumstances the conditions the wine plants experience are relatively close to background [Levin et al., 1995]. As CO$_2$ background concentrations for the period 1965–2004 we used the weighted monthly mean CO$_2$ concentrations measured at Mauna Loa (Hawaii, 19$^\circ$32’N, 155$^\circ$34’W, 3397 m asl) and published by Keeling and Whorf [2005], because no other available data sets of background sites representing the free continental troposphere of Europe were found for this specific time period. Mauna Loa is an elevated marine site, which will not fully represent the background of all our continental measurement sites, where different continental sources and sinks (mainly biosphere and fossil fuel emissions) affect the free troposphere CO$_2$ concentrations. On the basis of studies about spatial and temporal differences in CO$_2$ concentration by Levin et al. [1995], Chevillard et al. [2002b], and Schmidt et al. [2003],
we have estimated the effect of our approach, in which we neglect regional biosphere and ocean contributions to the CO$_2$ background concentration and use Mauna Loa as background site, on the calculated regional CO$_2$-ff excess. If “CO$_2$ (site)” in our assumption (equation (3)) is over- or underestimated by maximal ±20 ppm, a calculated regional CO$_2$-ff excess of 10 ppm will deviate maximal ±0.65 ppm (“+” when overestimated) and a regional CO$_2$-ff excess of 1 ppm maximal ±0.06 ppm.

[13] The second main assumption we have made in the calculation of the regional CO$_2$-ff excess is that the regional biosphere, ocean and unknown CO$_2$-sources and sinks have not contributed significantly to the measured difference between the $^{14}$C value at a site and a background site, because the $^{14}$C values of these regional sources and sinks are (in general) relatively close to the background value (which is, as example: +71% in May–October 2003, Swiss High Alpine Research station Jungfraujoch [Levin and Kromer, 2004]). The $^{14}$C-ff value (−1000%), however, is far more different from the background value and therefore the contribution of the regional CO$_2$-ff excess to the total $^{14}$C value at a measurement site (equation (2)) is relatively large.

[14] The effect of our assumption on the calculated regional CO$_2$-ff excess can (partly) be estimated based on model calculations of other researchers. Turnbull et al. [2006] observed, based on the use of simulated heterotrophic respiration data a deviation of maximal +0.5 ppm CO$_2$-ff when no correction was made for this respiration ($^{14}$C value used for 2003 data: 166 ± 100% [Turnbull et al., 2006]). Levin and Rödenbeck [2007] also correct for this anomaly based on model simulations. The ocean exchange has a minor influence on the atmospheric $^{14}$C value, especially at continental sites, based on the work of Hsueh et al. [2007] who simulated this for North America (data of 2004). Only at coastal sites a “regional CO$_2$ (oc) excess” of maximal 1% was found and for these sites we calculated the regional CO$_2$-ff excess according to our approach would be over-estimated approximately by 0.35 ppm (based on CO$_2$ (site) ≈ 380 ppm and $^{14}$C value of the background CO$_2$ concentration at the background site itself). We have assumed that both these measurement locations represent the free troposphere for all our measurement sites and are not significantly influenced by variable local/regional CO$_2$ sources and sinks. However, the background sites represent mainly “continental” sites where the effect of the $^{14}$CO$_2$ from the ocean is relatively small [Levin and Hesshaimer, 2000], and mountain venting at sites like Jungfraujoch [Henne et al., 2005] adds a variable regional CO$_2$ excess to the free tropospheric background CO$_2$ concentration at the background site itself. These effects, which are difficult to determine but could influence (part of) our results, will be taken into consideration in the discussion of our results (section 2.5).

[17] We have calculated the regional CO$_2$-ff excess for the period in which the wine grapes of all our investigated wines will in general have sampled atmospheric CO$_2$. This is annually a period of approximately 6 weeks between July and the end of October. When exactly depends on the wine region, the grape sorts and the weather conditions [Alleweldt, 1977; van Leeuwen et al., 2004], but for the majority of our wines this period is in August and September. To approach this sampling time period of the grapes for the used background CO$_2$ concentration and background $^{14}$C value for every investigated harvest year, we have chosen to use the averages of the (monthly) mean values over the period July–October with extra (three-fold) weight for August and September. The relative standard deviation of these average monthly mean values was for the period 1965–2004, 0.4% for the average CO$_2$ concentrations of Mauna Loa (319–375 ppm), unknown for the mean summer $^{14}$C values of Vermont (780–190%) and 1.4% for the average $^{14}$C values of Jungfraujoch (192–59%). The uncertainties in the used average background values (the standard deviation can be used as a measure for that), especially in the $^{14}$C values, introduce an uncertainty in the calculated regional CO$_2$-ff excess of a measurement site. Because the calculation of the regional CO$_2$-ff excess is based on the absolute difference in the $^{14}$C value between the measurement site and the background site (equation (4)), the absolute uncertainty in the background $^{14}$C is a main factor of influence. We have calculated the uncertainty in the regional CO$_2$-ff excess of 1965, 1986 and 2004 based on the relative standard deviation in the average $^{14}$C values at Jungfraujoch (also used for Vermont). The uncertainty (1 sigma) in the calculated regional CO$_2$-ff excess (1–10 ppm) is ≈2 ppm in 1965, ≈1.2 ppm in 1986 and ≈0.75 ppm in 2004.

2.4. Experimental Results

[18] Figure 2 shows the temporal trend of the annual average $^{14}$C values in the period July–October (weighted as described in the previous section) in air samples of different measurement sites in Europe [Levin and Kromer,
2004; Levin et al., 2008; Meijer et al., 1994] and our Δ14C values of wine ethanol samples from the Rheinland-Pfalz region in Germany. The decreasing trend in our wine results shows good agreement with the atmospheric Δ14C measurements and confirms the conclusion of other wine ethanol studies [Burchuladze et al., 1989; Martin et al., 1995] that wine ethanol is a good indicator of the atmospheric Δ14C content at a specific measurement site.

As explained before we assume that the measured lower Δ14C values in the Rheinland-Pfalz region, Smilde and Schauinsland compared to the background sites Vermunt and Jungfraujoch (free troposphere) are entirely due to the dilution of atmospheric 14CO2 by regional CO2-ff emissions. This difference in Δ14C of a measurement site with the background, which is clearly visible in Figure 2, is our signal, leading to the regional CO2-ff excess at a measurement site according to equation (4). The difference in Δ14C between the Rheinland-Pfalz and the background sites has increased since 1965 and is on average -10%o since 1985. Levin et al. [2003] observed a deficit of 10–30%o in air samples from the city of Heidelberg during summer periods compared to Jungfraujoch. Heidelberg is relatively close to the investigated Rheinland-Pfalz wines areas (distance <100 km). The observed lower Δ14C values (higher regional CO2-ff excess) at Heidelberg compared to the Rheinland-Pfalz wine area are expected due to differences in the sampling location (city of Heidelberg versus rural wine area: differences in local CO2-ff emission rates) and in the daily sampling period (sampling at night in Heidelberg and by day in wine area: differences in atmospheric mixing rates).

Wines that originate from vineyards in the vicinity of nuclear power plants cannot be used for our purpose. We can conclude this from the regional CO2 excess values we calculated for a part of our investigated wines from the Côtes-du-Rhône region in France. The values are very negative (a CO2-ff deficit): -1.61 ppm (1993), -38.31 ppm (2001) and -3.96 ppm (2004). We assume that this is due to 14C emissions by nuclear power plants in the vicinity of the investigated wine sites (we do not know the location of the wine sites exactly, but estimate that the distance to nuclear power plants Cruas or Tricastin has been <20 km). The 2001-value is extreme corresponding with a measured Δ14C value of 195%o, while the Δ14C value of Jungfraujoch (bg) in 2001 was 83%o. Martin et al. [1995] also observed such large Δ14C values in wine ethanol of the same region. Levin et al. [2003] showed an approach to correct for this anomaly in Heidelberg. We could not adopt this approach for our investigated wine regions near nuclear power plants, in France (Côtes-du-Rhône) and Spain (Rioja: Santa Maria de Garona), because we do not have 14C emission and dispersion data in time from the nuclear power plants in these regions. In our research we have investigated for every wine site, whether it was located >50 km from an active nuclear power plant in Europe. We have chosen this distance because we wanted to be sure that our measurement results would not be biased, while we did not know the exact locations of the wine sites and also did not know the exact impact area of a nuclear power plant. The chosen distance might therefore be too large [Roussel-Debet et al., 2006].

2.5. Regional Atmospheric CO2-ff Excess Values Derived From Wine Measurements

The regional CO2-ff excess values calculated from our wine measurements give insight in both spatial and annual variations of different sites in Europe within the period July–October. In Figures 3a and 3b the regional CO2-ff excess (in ppm) derived from the wine ethanol samples of 2003 and 2004 are shown in maps of Europe. The measurement uncertainty in the numbers is about 1 ppm. Different parts of Germany and also the Northern...
part of Italy are characterized by a combination of a high-density population, large mobility and intensive industrialization. On the basis of the regional CO₂-ff excess values for both 2003 and 2004 we can distinguish these regions with relatively large values from other regions where the regional CO₂-ff excess values are not significantly different from zero. The differences in regional CO₂-ff excess between regions indeed show a strong relation with the intensity of CO₂-ff emissions in the (vicinity of) specific wine regions. Hsueh et al. [2007], who investigated the spatial pattern of ¹⁴C in corn leaves in North America during the summer of 2004, also observed this relation. On the basis of our results we can distinguish wine areas in the vicinity of airports and cities (like Barcelona, Lecce and Bordeaux) from more remote regions.

[22] The calculated regional CO₂-ff excess in a specific region varies between successive years. This interannual variation is even better visible in Figure 4, in which the regional CO₂-ff excess for different years is shown for a selection of investigated wine regions. This variation can be due to several factors, like (1) variations in atmospheric mixing and transport at the measurement site and/or the background site, (2) variation in regional CO₂-ff emissions, (3) interannual changes in the CO₂-sampling period of grapes, (4) the measurement of different wine locations within the same wine region (different local CO₂-ff emissions) and (5) interannual differences in Δ¹⁴C due to other anomalies than regional CO₂-ff emissions at the measurement site and/or the background site that have not been taken into account in the calculation of the regional CO₂-ff excess (as discussed in section 2.3). An example of the latter are probably the negative regional CO₂-ff excess values (Δ¹⁴Cwine site > Δ¹⁴Cbg; see equation (4)) we derived from Portuguese wines, which indicate that the tropospheric oceanic atmosphere influencing these measurement sites, has higher Δ¹⁴C values then the free but more continental troposphere at Jungfraujoch and should have been taken into account in the calculation of the regional CO₂-ff excess. This oceanic atmosphere influence is confirmed by measurements at the (elevated) marine site Izaña, Canary Islands [Levin and Hesshaimer, 2000]. The negative regional CO₂-ff excess values we derived for several continental European sites in 2004 might also have been due to influences of the oceanic atmosphere or other regional Δ¹⁴C anomalies, introducing a difference between the wine site and the background site (for instance: mountain venting at Jungfraujoch, as mentioned in section 2.3 [Henne et al., 2005]). Correction for these anomalies or using a more representative background site in order to investigate long-term trends in the regional CO₂-ff excess will be subject for further research.

[23] The difference in regional CO₂-ff excess in a specific region over a number of years can be due to a trend in regional CO₂-ff emissions. The Verona wines suggest that this is the case in that region (the 2003 and 2004 results are significantly higher than the 1991 and 1993 ones), but a longer time series is necessary to confirm this. The current investigated time series are for most wine regions too short to observe those long-term trends. The only long-term time series we have at the moment are the wines from the German Rheinland-Pfalz region. Figure 5 shows the regional CO₂-ff excess we derived from wines of 1970–2004, which originated all from the same small area of vineyards (a few hectares) nearby the village Birkweiler (8°07'E, 49°12'W, 230 m asl). Relatively large differences between successive years, up to 5 ppm, can be observed, that complicate the identification of long-term regional CO₂-ff emission trends. Levin and Rödenbeck [2007] also observed relatively large interannual variations in the derived regional CO₂-ff excess values from atmospheric ¹⁴CO₂ measurements at Heidelberg and Schauinsland and concluded, based on model simulations, that at least half of this variation can be related to the variation in atmospheric mixing processes. Nevertheless, in spite of the interannual scatter, a clear increasing trend is visible in Figure 5: the average annual regional CO₂-ff excess (with standard error) is 1.38 ± 0.75 (n = 7), 2.45 ± 0.36 (n = 8) and 3.14 ± 0.69 (n = 9) for the periods 1973–1985, 1985–1995 and 1995–2004 respectively. Still, the increase in the regional CO₂-ff excess in the Rheinland-Pfalz area over the decades is no proof that the CO₂-ff emissions in the specific region (or neighboring regions) have increased, at least not at the same rate. Long-term changes in atmospheric mixing and transport processes or in the different regional Δ¹⁴C components, in the specific
region or at the background site may also contribute to such a trend. Levin and Rödenbeck observed in both observations and modeled simulations of the regional CO₂-ff excess in the period 1998–2006, an increase of almost 1 ppm at Schauinsland (Germany) related to changes in atmospheric mixing. In determining a long-term trend in the regional CO₂-ff excess based on ¹⁴C measurements of plant material (like wine ethanol in our case), we should also be aware of the relatively large absolute uncertainties in the calculated regional CO₂-ff excess (up to 1–2 ppm), especially in the period 1965–1990, due to uncertainty in the used average Δ¹⁴C background values, because the period in which the plants have sampled CO₂ is not exactly known (as discussed and estimated in section 2.3). The measurement of plant material from the period 1965–1990 might therefore be less suitable to determine long-term trends.

[24] In spite of the above, the trend in the decadal averages of the German Birkweiler wine makes an increase in fossil fuel consumption in the region likely. The increasing trend, however, does not correspond to the trend in estimated CO₂-ff emissions in the Rheinland-Pfalz area 1990–2004, which shows an increase of CO₂-ff emissions in the period 1990–1995 and then a decrease in the period 1995–2004 [Statistisches Landesamt Rheinland-Pfalz, 2008]. For the time periods 1985–1995 and 1995–2004, this would imply that there should not be a large difference (<5%) in the average estimated CO₂-ff emissions between these periods, while our wine measurements show an average increase of 30% (0.7 ppm). Possible explanations for this difference include the influence from neighboring regions (France, other German regions), which have not been taken into account in the particular emission estimates, and the difference in compared time period (average esti-

![Figure 4. Regional CO₂-ff excess (in ppm) derived from wine ethanol samples, relative to the Swiss High Alpine station Jungfraujoch. The investigated wines of a specific region originate all within a 50 km distance. The measurement uncertainty in the calculated value is typically 1 ppm.](image-url)
transferred emissions of a whole year vs. measured concentrations in summer/autumn period.

[25] The above shows that, in order to determine the long-term trend in CO$_2$-ff emission fluxes at a specific measurement site to verify the effects of reduction efforts (Kyoto protocol) and to verify emissions inventories, it is essential to (1) perform long-term annual $^{14}$C measurements at more European sites, (2) know and quantify all the different factors of the used method that might have influence on this trend, (3) know the area for which a measurement site represents the measured regional CO$_2$-ff excess and (4) know and quantify all the different factors that influence the $\Delta^{14}$C value at a measurement site or the background site, like atmospheric mixing and transport processes. A method should be developed to correct the regional CO$_2$-ff excess for annual and long-term changes in the atmospheric mixing and transport processes. Methods to correct for these kinds of processes include the use of the atmospheric transport tracer $^{222}$Rn [Schmidt et al., 2003; Levin et al., 2003]. Unlike wines, there is no way of performing $^{222}$Rn measurements back in time, so in our case the use of atmospheric radon measurements is not possible. Another way of correcting is the use of regional (high resolution) atmospheric transport models that simulate the atmospheric mixing and transport of tracers like CO$_2$ in Europe. These model simulations can be performed, at least in principal, for a long period (1970-current). We have chosen to use the REMO model [Chevillard et al., 2002a, 2002b], and show the comparison between the simulations and our measurements, for the years 2003 and 2004, below.

3. Model—Observation Comparison

3.1. Model Description and Data Selection

[26] The regional atmospheric transport model REMO is based on the regional weather forecast model “Europa-modell” of the German Weather Service [Majewski, 1991] and additionally includes the physical parameterizations of the global circulation model ECHAM-4 [Roeckner et al., 1996], which are used for this study. REMO (version 5.0) has been extended to an on-line atmospheric chemistry model by implementing modules for the transport of tracers and tropospheric chemical processes [Langmann, 2000]. The tracer transport is represented by horizontal and vertical advection, vertical diffusion and convective transport. REMO divides the atmosphere into 20 layers in a hybrid-coordinated system with six layers below 1500 m. The horizontal resolution is 0.5° in a rotated spherical coordinate system, with grid cells of approximately 55 x 55 km$^2$. The domain of REMO covers the area north of 30°N. In this study we focused mainly on model results for Western Europe and on the lowest atmospheric layer above ground level (0–60 m). The used boundary conditions for the three years have been derived from the global coarse-grid TM3-model [Heimann and Körner, 2003]. REMO simulates its own meteorology inside the domain, but in order to stay close to “reality” it is restarted from ECMWF analyses (European Centre for Medium-Range Weather Forecasts) every day (“forecast mode”), whereas tracer transport is computed continuously [Chevillard et al., 2002b]. The ECMWF analyses contain many surface, upper air and satellite observations and give a representative description of the atmospheric state. For the sake of completeness, we mention that the terrestrial biosphere inside REMO is described using fluxes provided by the Biome-BGC terrestrial ecosystem model [Churkina et al., 2003], and oceanic fluxes are prescribed according to Takahashi et al. [1999]. Other studies in which REMO model simulations of atmospheric tracers have been compared with atmospheric observations at different European sites are described by Chevillard et al. [2002a] who evaluated the performance of the tracer transport parameterization using $^{222}$Rn as a tracer and by Chevillard et al. [2002b] who investigated the spatial distribution and temporal variability of atmospheric CO$_2$ over Europe and western Siberia.

[27] We have used the hourly-simulated CO$_2$-ff concentrations (this is the total CO$_2$-ff concentration, not the regional excess) of 2002, 2003 and 2004 from data sets generated by REMO, based on four different emission

![Figure 5](image_url)  
**Figure 5.** Regional CO$_2$-ff excess (in ppm) derived from wines from the village of Birkweiler, Germany.

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Table 1. CO$_2$-ff Emission Inventories Used to Simulate Atmospheric CO$_2$-ff Concentrations

<table>
<thead>
<tr>
<th>Emission Inventory (yr)</th>
<th>Used Abbreviation</th>
<th>Region</th>
<th>Temporal Resolution</th>
<th>Horizontal Resolution</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDGAR 32FT2000 (2000)</td>
<td>Edg-yr</td>
<td>Global</td>
<td>Yearly</td>
<td>$1^\circ \times 1^\circ$</td>
<td>Olivier et al. [2005]</td>
</tr>
<tr>
<td>EDGAR 32FT2000 (2000)</td>
<td>Edg-hr</td>
<td>Europe</td>
<td>Hourly</td>
<td>$1^\circ \times 1^\circ$</td>
<td>Olivier et al. [2005], M. Krol (personal communication, 2007)</td>
</tr>
<tr>
<td>IER2000 (2000)</td>
<td>Ier-hr</td>
<td>Europe</td>
<td>Hourly</td>
<td>$10 \times 10$ km</td>
<td>Pregger et al. [2007]</td>
</tr>
<tr>
<td>Transcom (1998)</td>
<td>Tec-yr</td>
<td>Global</td>
<td>Yearly</td>
<td>$1^\circ \times 1^\circ$</td>
<td>On the basis of CDIAC NDP-058A, gridded data were obtained for the Transcom Continuous Experiment [Law et al., 2008]</td>
</tr>
</tbody>
</table>

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8 of 14
inventories (Table 1) and the meteorological conditions of 2002, 2003 and 2004. Only the results of 2003 and 2004 have been used for the comparison with the regional CO₂-ff excess values derived from our wine measurements.

In analogy to the observational approach, we have calculated the regional CO₂-ff excess compared to background site Jungfraujoch. The simulated regional CO₂-ff excess is obtained by subtracting the model simulated CO₂-ff concentration at the grid cell corresponding to Jungfraujoch, from the model simulated CO₂-ff concentration of the grid cell corresponding to a specific measurement site. Since the model topography of Jungfraujoch is lower than the site altitude, simulation results from the sixth level above ground level are extracted. The center of the air layer (3182 m asl) is approximately 250 meters below the altitude of the measurement station. This air layer is considered to represent the same air as sampled at atmospheric monitoring station Jungfraujoch.

In order to compare the simulated regional CO₂-ff excess by REMO with those calculated from wine samples, we have made some assumptions about the average sampling period of the grape vines (partly) based on research about the uptake and transport of atmospheric CO₂ and of sugars by grape vines [Hale and Weaver, 1962; Koblet, 1975; Alleweldt et al., 1975; Alleweldt, 1977; Coombe, 1992; van Leeuwen et al., 2004]. In analogy to the used measured background values (section 2.3), we have calculated the average simulated regional CO₂-ff excess for the period July–October, with three-fold weight for August and September. The diurnal time periods and moments of CO₂ assimilation by the grapes of our investigated wines are influenced by several variable (climate) factors like light-

Figure 6. Average regional CO₂-ff excess (ppm) in different European regions (one grid cell per region; day and month averages as explained in the text; error bars show the standard error from these averages) modeled by REMO for 2003 based on four different emission inventories. The regional CO₂-ff excess values simulated for 2002 and 2004 are not shown. These values differ in average −11% and −23% with 2003 but give the same relative differences between the emission inventories.
of atmospheric mixing, the atmospheric CO₂ concentration has been based on the diurnal period when, because regional CO₂-ff excess of the diurnal time periods 06:00–20:00 h has been high enough for the grapevines to assimilate CO₂ in the respective growing period. The period 12:00–20:00 h has been based on the period in which the (sun)light intensity (a main factor in the photosynthesis process) might be compared with the measurement results. We have calculated the average simulated regional CO₂-ff excess values of the two diurnal periods give an indication of how critical the precise choice of the time period is for the model results. Typically, the average simulated regional CO₂-ff excess for the period 06:00–20:00 h has been based on the period in which the (sun)light intensity (a main factor in the photosynthesis process) might have been high enough for the grapevines to assimilate CO₂ in the respective growing period. The period 12:00–20:00 h has been based on the diurnal period when, because of atmospheric mixing, the atmospheric CO₂ concentration is in general the lowest [Chevillard et al., 2002b]. The differences between the monthly average regional CO₂-ff excess values of the two diurnal periods give an indication of how critical the precise choice of the time period is for the model results. Typically, the average simulated regional CO₂-ff excess for the period 06:00 h–20:00 h is 25% higher than for the period 12:00 h–14:00 h.

We have calculated the average simulated regional CO₂-ff excess for all the grid cells in which the investigated wine areas of 2003 and 2004 are located. The uncertainty in the values has been based on the uncertainty (standard error) in the average diurnal and annual sampling period (obtained as described above). In the simulations the fossil-fuel emissions have been chosen identical for all years. Any interannual variability is therefore caused solely by variability in atmospheric mixing and transport.

3.2. Simulated Regional CO₂-ff Excess by REMO

Figure 6 shows the average regional CO₂-ff excess in 2003 simulated by REMO using the four different emission inventories (see Table 1) for the different investigated European wine regions. In comparison with the average results of REMO using emission inventory “edg-hr” for the different measurement sites, the results obtained with “ier-hr” are in average 11% higher, “tcc-yr” +19% and “edg-yr” +25%. The simulated CO₂-ff concentrations for emission inventories “edg-hr” and “ier-hr” are in general the lowest, because in these emission inventories the seasonal (summer/winter) and diurnal variations in CO₂-ff emissions have been taken into account, while the CO₂-ff emissions in “tcc-yr” and “edg-yr” are constant in time. Since we measure in the summer period when the regional CO₂-ff emissions are usually relatively low, “tcc-yr” and “edg-yr” yield too high regional CO₂-ff excess values. The differences between the emission inventories can also be due to several other factors, like differences in the estimated emissions of a country or differences in the spatial patterns of the emission inventories. In the latter case, the results of different emission inventories, are based on (slightly) different areas with more or less CO₂-ff emission sources (like a city, or the sea). In the regions Moravia (Czech Republic) and Lecce (Italy) the relatively large differences between the results of “edg-hr” and “ier-hr” (+43% and −54% for “ier-hr” respectively), might be an indication for one of the just mentioned factors.

3.3. Results and Discussion of Model—Observation Comparison

In Figure 7 we have plotted the regional CO₂-ff excess simulated by REMO (Edg-hr) against the regional CO₂-ff excess derived from our wine-measurements. The black line shows the ideal 1:1 relation. Even though there is considerable scatter, there is a clear systematic difference between model and observations. The REMO simulations show an average bias of almost +3 ppm.

The observed differences between the model and observations can be due to many different factors in both the method to derive the regional CO₂-ff excess from ¹⁴C wine ethanol measurements as in the model simulation. Although we used emission inventories of 1998 and 2000, which might not have been representative for 2003 and 2004, it cannot explain the difference of +3 ppm we observed. It would imply a decrease of a few 100% in the CO₂-ff emissions within a few years in some regions. On the basis of the statistics of the German Rheinland-Pfalz region (mentioned in section 2.5 [Statistisches Landesamt Rheinland-Pfalz, 2008], we think that is not realistic. A few probable factors that can cause such a systematic deviation between the measurement and model results are related to the chosen background site Jungfraujoch. Firstly, (part of) the systematic deviation might be due to the use of too low simulated CO₂-ff concentrations of Jungfraujoch, caused by difficulties in the REMO model to simulate the atmosphere processes at elevated mountain sites, like mountain venting [Henne et al., 2005]. Chevillard et al. [2002a] observed in the comparison of measured and REMO-simulated ²²²Rn concentrations that the atmospheric ²²²Rn concentrations at elevated (mountain) sites were difficult to simulate. Secondly, the background Δ¹⁴C values of Jungfraujoch we have used for 2003 and 2004, might have been too low because of regional ¹⁴CO₂ influences at the background site. In that case, Jungfraujoch has not been representative for the free
have assimilated (‘‘sampled’’) CO2. Average time period (monthly and diurnal) in which grapes and also mentioned in section 2.5) and (3) the estimated other regional 14CO2 sources (as described in section 2.3 values.

The difference between the model results of 2003 and 2004 (Edg-hr). Differences in regional CO2-ff excess (in ppm) between 2004 and 2003 for the wine results and the REMO results (Edg-hr).

(continental) troposphere. These are clearly disadvantages of using the Jungfraujoch site as background site for the determination of the regional CO2-ff excess. The ideal background site would therefore be a lowland site with no local and regional CO2-ff emissions. The use of other background sites in Europe is an important topic for further research in order to identify trends in regional CO2-ff excess values.

Since the regional CO2-ff excess at a wine measurement site is not necessarily representative for the average regional CO2-ff excess of a region of 55 × 55 km^2 as is simulated by REMO, this might also have contributed to the observed deviation between the measurement and model results. The usual rural wine sites might well be systematically ‘‘cleaner’’ than the average of the region. Chevillard et al. [2002a] observed that site-specific effects, such as local emission sources and local topography, biased simulated regional CO2-ff excess values because these factors were difficult to capture in the used resolution of models (same resolution as we used: 55 × 55 km^2). Atmospheric transport models and emission inventories with a higher resolution are therefore needed.

Other factors that might have contributed to the observed systematic deviation between the modeled and observed results of a measurement site are (1) wrong estimations of the emissions for a certain grid cell which influence the simulated regional CO2-ff excess, (2) assumptions we have made in the calculation of the regional CO2-ff excess about the used background CO2 concentration and other regional 14CO2 sources (as described in section 2.3 and also mentioned in section 2.5) and (3) the estimated average time period (monthly and diurnal) in which grapes have assimilated (‘‘sampled’’) CO2.

We have compared the differences in regional CO2-ff excess between 2003 and 2004 for the observations and the model for different regions, to investigate the simulation of interannual variations by REMO. This is shown in Figure 8. The difference between the model results of 2003 and 2004 (calculated as ‘‘2004’’ – ‘‘2003’’) is (in our case) only due to differences in the atmospheric mixing between both years. The simulated regional CO2-ff excess values of 2004 are in most regions approximately 1 ppm lower compared with 2003, while the differences between 2003 and 2004 in the observations in these same regions are approximately 2 ppm lower compared to 2003. When we consider that the differences between 2003 and 2004 in the observations are not only due to changes in atmospheric mixing alone, but also to other factors (see section 2.5: interannual variation in CO2-ff emissions, the sampling period of the grapes, the regional sampling location and differences in ∆14C due to other anomalies than regional CO2-ff emissions at the measurement site and/or the background site) and we assume that the REMO simulations of atmospheric mixing are correct, then we may conclude that a considerable part (in this case approximately 50%) of the total interannual variation in the regional CO2-ff excess can be corrected for using REMO simulations. This is a fortunate fact, since it enables us to use REMO to interpret our observations through the years (Figure 5) in view of the effects of atmospheric transport and mixing and eventually correct for this. After this kind of correction, our observations are a more direct measure for the regional fossil fuel emissions and its trends within Europe. Recently, Levin and Rödenbeck [2007] demonstrated the use of model-simulated data in this fashion, using TM3 as atmospheric transport model. This model, however, has a much lower resolution than REMO. Since REMO simulations are at the moment only available for a few years, we cannot yet compare a long-term trend.

4. Discussion: 14C in Wine Ethanol and Other Plant Materials as Proxy for Atmospheric 14CO2

As we described in the introduction, several studies already showed the use of 14C measurements in annual plant material as a proxy for atmospheric 14CO2. In this paper we also show the good comparison of the ∆14C values of our wine ethanol samples of German wines from the Rheinland-Pfalz region with air measurements from different other regions in Europe in the period 1965–2004 (Figure 2). Beside the main advantage of (annual) plant material that it is widely available and can be obtained from many different areas, several differences with atmospheric measurements appear, which can be considered as disadvantages and need to be taken into account when using the 14C as a proxy for atmospheric 14CO2. Hsueh et al. [2007] discuss this as well in their study about 14C measurements in corn leaves. An important difference with atmospheric sampling is that the period in which 14CO2 has to be sampled (assimilated) by the plants is not adjustable. The sampling period is therefore not known and it is also limited to only a part of a day (daylight) and part of the year (mainly spring and summer). Another disadvantage is that other carbon components (than freshly assimilated CO2) may contain assimilated atmospheric 14C from earlier sampling periods (previous years), can ‘‘pollute’’ the sample (plant) material. This is only the case when plants (or the investigated parts) also take up carbon via other ways than photosynthesis.

Several advantages and disadvantages can be identified as well in a comparison of different plant materials that can be used as a proxy for atmospheric 14CO2. As explained
in the introduction we choose wine ethanol as sample material, partly for practical reasons but also because wine ethanol of previous years can be measured, giving the opportunity to investigate historic trends in the regional CO₂-ff excess (as long as suitable background data is available). The main disadvantage of using wine ethanol we have observed, is the lack of sample information about the content and the origin of the grapes (exact locations) when only the label on the wine bottle is available. This was the case for all our investigated wines, except the German Rheinland-Pfalz wines of the village Birkweiler (Figure 5). These latter wines were directly obtained from the specific wine-farmer and the wine-areas are exactly known. For these wines we also know that they are not from mixed harvest years and no sugar was added in the wine-making process. For all the other wines, we do not know whether the wines were, legally or not, mixed or contained alcohol from other sugar (and atmosphere) sources, what might have biased our calculated regional CO₂-ff values. We have not identified vintage fraud: in which the harvest year mentioned on the bottle of the wine is not the true harvest year. This can be identified based on differences in atmospheric ¹⁴C concentrations between different harvest years due to the decreasing atmospheric ¹⁴C concentration after the nuclear bomb tests in the 1960s. Because the decrease rate has decreased since the mid-1960s and approaches since the mid-1990s the measurement uncertainty of the ¹⁴C measurements, it is not a very suitable tool anymore to identify vintage fraud [Martin et al., 1995]. On the basis of the lack of information about the wine content and origin that we had in our approach, we conclude that it is more fruitful to select a single vineyard locally and obtain information about the wine making process and the location of the vineyard from the specific wine farmer, than to simply purchase wine from a certain region in local shops.

[39] We have measured the ¹⁴C content of wine ethanol instead of the wine to assure that we almost only measured carbon from the grape sugars, which we consider as proxy for atmospheric ¹⁴CO₂ of the respective growing period of the grapes (this only holds if no sugar is added in the wine-making process). Since, based on the measured density of our distilled wine ethanol samples, the contribution of other distilled carbon-containing components was not measurable, we think that we have safely assumed that the ¹⁴C contribution of these components has also been negligible. In the case of measuring other plant materials it might be more difficult to be assure that no other carbon-sources than recent assimilated atmospheric ¹⁴CO₂ have contributed to the measured ¹⁴C content of the sample. This might, for instance, be the case if ¹⁴C in tree-rings are used as a proxy for atmospheric ¹⁴CO₂. Tree-rings are, like wine ethanol samples, potentially useful to obtain long-term measurement series of ¹⁴C from previous years. A comparison by Levin and Kromer [1997] of ¹⁴C measurements of tree-rings and air samples at the German site Schauinsland in the period 1974–1986 showed good comparison if the average value of the air samples over the months May–August was taken. However, in comparison with the carbon from wine ethanol, which origins almost completely from wine grapes that assimilated CO₂ during one year (as is very well known from many research studies, among others: Hale and Weaver (1962) and Koblet (1975)), the carbon content of a one-year tree-ring shows intra-annual variation, which is probable not only related to variation in CO₂ uptake by photosynthesis, but also to for instance the input of starch (form earlier years) [Rocha et al., 2006]. More research is therefore needed to identify the contribution of different carbon-sources to the total ¹⁴C-content of tree-rings. Main advantages of using ¹⁴C measurements of tree-rings in comparison to wine ethanol samples, are the ability to investigate many more different sites in whole Europe and, in those cases a annual tree-ring consists of seasonal sequences, it might give more information about seasonal differences in the atmospheric ¹⁴CO₂ content (as long as the contribution and seasonal-variation from other carbon sources is also well-known). Since both wine ethanol and tree-rings have their specific disadvantages, it might be interesting to investigate the long-term ¹⁴C-content of tree-rings and wine ethanol samples from the same measurement site (a tree near a vineyard) and (if possible) compare these results with atmospheric ¹⁴CO₂ measurements from the same location.

5. Conclusions

[40] The measurement of ¹⁴C in wine ethanol of different European regions and different harvest years gives insight into the temporal and spatial distribution of atmospheric ¹⁴CO₂ concentrations in Europe that can be directly related to regional and/or local CO₂-ff emissions. An important advantage of the measurement of wines is that the atmosphere and also its changes can be monitored annually back in time. This can be very helpful in the investigations of long-term trends in regional atmospheric CO₂-ff excess at different sites in Europe. The measurement of ¹⁴C in wines of a known location is a relatively easy way to supplement atmospheric measurement sites where CO₂-ff concentrations can be determined. The main disadvantage of using Δ¹⁴C measurements of wine ethanol as a proxy for atmospheric ¹⁴CO₂ is the unknown diurnal and monthly sampling period. This also holds for other annual plant samples. In the calculation of the regional CO₂-ff excess this unknown sampling period introduces an uncertainty in the used average background Δ¹⁴C values, which adds, especially in the period 1965–1990, significantly to the total uncertainty in the calculated regional CO₂ excess value. Our approach might therefore not be very useful for long-term investigations before 1990.

[41] The interannual variation and the long-term trend in the atmospheric regional CO₂-ff excess derived from the ¹⁴C measurement in wine ethanol at a particular site or area are mainly dependent on the interannual variation and trends in the following factors: (1) the meteorology: atmospheric mixing and transport processes, (2) the Δ¹⁴C value of the background location, (3) the relative regional contribution of the ocean and biosphere CO₂ sources to the ¹⁴C of a site and finally (4) local/regional CO₂-ff emissions.

[42] Obviously, (4) is the signal we are looking for and we have to design a proper procedure to address the other points. As a first attempt toward such a procedure, we compared our CO₂-ff observations to simulations by the regional atmospheric transport model REMO to address point (1). Although the model results show an average bias of almost +3 ppm compared to the observations, both model
and observation results show a decrease in CO₂-fossil fuel emissions between 2003 and 2004. On the basis of our first results we can conclude that by using REMO at least part of the interannual variation in the observed regional CO₂-fossil fuel emissions can be corrected for a non-CO₂-fossil fuel emission related factor: atmospheric mixing and transport. The net result from this exercise then gives a CO₂-fossil fuel signal that is potentially useful for the verification of trends in regional fossil fuel emissions. Further research to address points (1), (2) and (3) for a long-term period is, however, necessary. For REMO, too few years of output are available at present to completely perform this exercise. Long-term results are available from the world-wide grid model TM3 [Levin and Rödenbeck, 2007], but in order to use them for our observations the model output has to be adapted for the average sampling pattern of our wine grapes first (sufficient time and spatial resolution is necessary).

[43] To investigate long-term trends in regional CO₂-fossil fuel emissions more long-term annual ^14C measurements should be performed in different regions, in Europe and elsewhere. On the basis of our experiences using wine ethanol, it is more fruitful to select a single vineyard locally and obtain information about the wine content from the specific wine farmer, than to simply purchase wine from a certain region in local shops with no information about the exact content of the wine and origin of the wine grapes. In the first case, information about the wine content and the exact origin of the vineyard locations can be obtained and secondly locations can be selected with care, in order to avoid large local CO₂-fossil fuel sources (motorways, factories, conventional power plants) and nuclear power plants in the vicinity. Doing so, one eliminates the uncertainties about the content of the wines (added sugars, mixing of different harvest years) and one avoids scatter in (interannual) data because of different local conditions in the same region. Since wine regions do not cover all European countries, it is recommended to use other plants as atmospheric ^14CO₂ samplers as well (like tree rings as investigated by Levin and Kromer [1997] or corn leaves, as investigated by Keeling, C. D., and T. P. Whorf [2005], Atmospheric CO₂ records from 1958 to 1994, Lawrence Berkeley National Laboratory, University of California). To address the atmospheric regional CO₂-fossil fuel excess in different periods of the year, and not only in the period of July–October as with wines, it should be investigated which plants might be useful atmospheric samplers for this purpose.

[44] Acknowledgments. We thank the technical staff of the CIO, Dicky van Zonneveld, Fisaha Gebru, Treav Dijkstra, Henk Jansen, Henk Been, and Stef Wijma for the sample preparation and the ^13C and ^14C measurements. Special thanks to “Wienzerfamilie” Gies, Birkweiler, for providing us with a long series of their wines from the “Kastanienbusch” for providing TM3 simulation results. Special thanks to “Winzerfamilie” Gies, Birkweiler, for providing us with a long series of their wines from the “Kastanienbusch” for providing TM3 simulation results. Special thanks to “Winzerfamilie” Gies, Birkweiler, for providing us with a long series of their wines from the “Kastanienbusch” for providing TM3 simulation results. Special thanks to “Winzerfamilie” Gies, Birkweiler, for providing us with a long series of their wines from the “Kastanienbusch” for providing TM3 simulation results.

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