

Abstract

We present a global dataset of CO₂ emissions and O₂ uptake associated with the combustion of different fossil fuel types. To derive spatial and temporal patterns of oxygen uptake, we combined high-resolution CO₂ emissions from the EDGAR (Emission Database for Global Atmospheric Research) inventory with country level information on oxidative ratios, based on fossil fuel consumption data from the UN energy statistics database. The results are hourly global maps with a spatial resolution of 1° × 1° for the years 1996–2008. The potential influence of spatial patterns and temporal trends in the resulting O₂/CO₂ emission ratios on the atmospheric oxygen signal is examined for different stations in the global measurement network, using model simulations from the global TM3 and the regional REMO transport model. For the station Hateruma Island (Japan, 24°03′ N, 123°48′ E), the simulated results are also compared to observations. In addition, the possibility of signals caused by variations in fuel use to be mistaken for oceanic signals is investigated using a global APO inversion.

1 Introduction

High-precision measurements of atmospheric oxygen play an increasingly important role in our understanding of the global carbon cycle (see e.g. Keeling et al., 1993; Battle et al., 2000; Bender et al., 1998; Manning and Keeling, 2006). The close coupling between oxygen and carbon cycle results in anti-correlated changes in the atmospheric CO₂ and O₂ mixing ratios for almost all major exchange mechanisms: Photosynthesis of the terrestrial biosphere produces oxygen and consumes CO₂ whereas fossil fuel combustion consumes O₂ and produces CO₂. Only ocean related changes are decoupled in the carbon-oxygen system, allowing to use measurements of atmospheric oxygen for the separation of oceanic and terrestrial carbon sinks (Keeling and Shertz, 1992). Additional information can be gained from the fact that the terrestrial processes can be distinguished by their oxidative ratios. The oxidative ratio of a process is defined

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



OR_{ff} for the different countries calculated from CDIAC national CO₂ emission inventory (Boden et al., 2009).

To investigate whether – and where – information on the local fuel mix can be helpful for interpreting atmospheric CO₂ and O₂ signals, we have created time-dependent high-resolution global maps for the oxygen uptake associated with fossil fuel burning that can be used as input for global and regional models. These maps show where significant deviations from the global average α_F exist and need to be taken into account. In the following, Sect. 2 describes the methodology of creating the dataset for these uptake maps; Sect. 3 shows spatial patterns and temporal trends in the resulting O₂/CO₂ ratios, including the influence of their variation on the calculation of global land and ocean carbon budgets. In Sect. 4, the potential influence of the variations in fossil fuel mix on the atmospheric oxygen signal is investigated for different stations in the global measurement network, using a global and regional atmospheric transport model. The simulated results are compared to observations from a selected station, Hateruma Island. In Sect. 5, we investigate the possibility of mistaking variations in fossil fuel use for ocean signals when calculating APO fluxes with inverse methods. Section 6 concludes the paper.

2 The COFFEE dataset: data and methodology

To estimate spatial and temporal patterns in O₂/CO₂ emission ratios, high-resolution CO₂ emissions were combined with oxidative ratios at national level derived from fuel consumption statistics. CO₂ emissions are taken from the Emission Database for Global Atmospheric Research (EDGAR, Olivier and Berdowski, 2001). We use EDGAR version 3.2, containing annual CO₂ emissions on a 1° × 1° grid, that are split into 16 categories (e.g. power generation, transport). These emissions were available until the year 2001, with the extension 1996–2001 (calculated using process-specific scaling factors given by J. Olivier) provided by S. Houweling (personal communication, 2004). To allow comparison with recent atmospheric observations, the dataset

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



was further extended until the year 2008 by keeping the spatial distribution and relative contributions of the different categories from the year 2001 and extrapolating the amount of emissions using fuel consumption and cement production data at national level (coal, oil and gas consumption data assembled by BP (BP, 2009), biofuel consumption from the UN Energy statistics (UN, 2009) and cement production data from CDIA

Fuel-mix specific oxidative ratios for each country, year and category were determined using worldwide energy statistics compiled by the United Nations Statistics Division (UN, 2009). This dataset, currently available for the years 1991–2007, contains data on fuel production, import, export, consumption and conversion for 44 fuel types and over 200 countries. Fuel types include different sorts of coal, liquid and gaseous fuels as well as biofuels (e.g. fuelwood, biodiesel and various waste types). This dataset was chosen because the information on fuel consumption and conversion is not only given as national totals, but also split into different categories. These categories were merged to match the EDGAR categories, resulting in combined fuel consumption information at a resolution higher than country level.

To calculate the fuel-mix specific oxidative ratios from these consumption data, CO₂ emissions and oxygen uptake are at first derived for each fuel, country, category and year separately. CO₂ emissions are estimated from the carbon content of the consumed fuels, following the procedure and using the fuel-specific conversion factors from the 2007 statistics report by the International Energy Agency (IEA, 2007): Fuel consumption is first converted to a common energy unit (Terajoules) and then multiplied with carbon emission factors (CEF, given in tons of carbon per Terajoule). Full combustion of fuels is assumed, therefore the resulting carbon emissions are not corrected for unoxidized carbon, which is also consistent with the EDGAR methodology. Instead of applying a general correction (in terms of a percentage) for carbon stored in non-energy products, only the categories that actually produce CO₂ emissions were chosen.

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



For calculating the corresponding O₂ uptake, CO₂ emissions for each entry in the dataset were multiplied with their specific oxidative ratio. Different oxidative ratios were used for the four main fuel types: coal, oil, gas and biofuels. Note that variations within these fuel groups are rather small compared to the differences between the different fuel types, e.g. the ratio for different types of coal ranges from 1.09 to 1.18 (Keeling, 1988). For coal, oil and gas the above mentioned ratios are used. For biofuels a weighted average of 1.07 was taken, derived by calculating the oxidative ratios of the biofuels present in the dataset from Eq. (1) and taking into account their relative contribution.

CO₂ emissions and O₂ uptake for the different fuel types were added up for each country, category and year. The total O₂ uptake divided by the total CO₂ emissions gives the specific oxidative ratio for this set. After the calculation of oxidative ratios, the dataset was checked for missing values. These were replaced by “best estimate” oxidative ratios: If only single years were missing, oxidative ratios were extrapolated from the surrounding years, and where no information existed for the whole category in a certain country, either the category mean (for categories with a special oxidative ratio, e.g. gas flaring) or the country mean was used. Since the fuel consumption data for the early 1990s seemed not very reliable, with unrealistically large variations and many missing values, only data from 1996 onward was used.

To derive the O₂ uptake at gridcell level, the EDGAR CO₂ emissions for each category and year were multiplied with the obtained oxidative ratios for the country to which the respective gridcell belongs. For the allocation of gridcells to countries, information from Brenkert (1996) was used. In case a gridcell belongs to several countries, CO₂ emissions are split up according to the different countries’ population in the gridcell. Temporal factors for seasonal, weekly and daily cycles for the different categories were applied to the resulting annual values of CO₂ emission and O₂ uptake. These temporal factors are based on a set of time profiles for the Netherlands that are provided in the EDGAR database, but were modified to provide a better global representation: Seasonal cycles in fuel use were reversed for Northern and Southern Hemisphere and

**The COFFEE dataset:
effects from varying
oxidative ratios**J. Steinbach et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

suppressed in the lower latitudes for those categories where it seemed reasonable. To avoid discontinuities in the final timeseries, the original step functions for the seasonal cycles were smoothed by applying an exponentially weighted running-mean and using an iterative correction of the results to ensure the conservation of the annual mean.

5 Finally, the sum of emissions and uptake over all categories was calculated for each gridcell. The resulting dataset consists of hourly fluxes of CO₂ emissions and O₂ uptake for the years 1996 to 2008. In the following, it will be referred to as the “CO₂ release and Oxygen uptake from Fossil Fuel Emissions Estimate” (COFFEE) dataset.

3 Spatial and temporal variations in fossil fuel related oxidative ratios

10 3.1 Spatial distribution

Figure 1 shows the resulting global maps of CO₂ emissions (a), O₂ uptake (b) and oxidative ratios OR_{ff} (c) as determined from the COFFEE dataset. All maps are annual averages for the year 2006. It can be seen that the patterns in oxygen uptake mostly follow the patterns of the CO₂ emissions. As expected, high CO₂ emissions occur
15 mainly in the US, Europe and some parts of Asia, while they are rather low in South America and Africa. The lines between the continents represent ship tracks. The oxidative ratio, determined as the ratio of O₂ uptake to CO₂ emissions, covers the whole range from 0 to 1.95, with a spatial standard deviation of 0.2. For better visibility, the range of OR_{ff} in Fig. 1c is limited from 1 to 2, thus omitting a few gridcells with
20 OR_{ff} = 0 that are caused by dominant cement production. The colors in Fig. 1c are representative for the fuel types the respective oxidative ratio would correspond to: green for biofuels, black for coal, brown for oil and blue for gas. In the US and most of Europe, OR_{ff} is close to the global average, as oil is the main fuel source. This is expectedly also the case for emissions caused by international shipping. Lower OR_{ff}
25 are found in Africa and Eastern Asia, as fuel combustion in Africa is dominated by a mix of biofuels (in this case traditional fuels as fuelwood and animal manure) and oil,

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



whereas in Asian countries like China and India coal is the main fuel source. In China, cement production plays an important role as well, contributing to a further decrease in the ratio. A high contribution of gas can be seen in the oxidative ratios from e.g. Russia, Argentina and Canada. Blue and grey colors in the plot represent oxidative ratios above 1.8, where gas is the main source of fossil fuel burning, while the orange colors (representing ratios higher than 1.6) are a sign of significant contribution of gas to the fuel mix.

3.2 Temporal variations

In addition to these spatial variations, OR_{ff} can also vary temporally on different timescales, depending e.g. on seasonal and short-term variations in fuel use. The variations in CO_2 emissions and OR_{ff} on these timescales are shown in Fig. 2 (again for the year 2006, results for the other years are comparable). Variations are integrated over the three latitudinal bands Northern Hemisphere (NH, $+20^\circ$ to $+90^\circ$, Tropics (TR, -20° to $+20^\circ$) and Southern Hemisphere (SH, -90° to -20°). The upper row (Fig. 2 a and b) shows the variation in CO_2 emissions, given in percent of the mean annual emission in the respective latitudinal band. For better visibility, different timescales are separated, with Fig. 2a showing the seasonal cycle (monthly averages), whereas short-term variations (hourly to weekly) are illustrated in Fig. 2b. The lower row (Fig. 2c and d) shows the respective plots for the variations in OR_{ff} .

Figure 2a shows that CO_2 emissions are always higher during each hemisphere's winter, as more fuel is used for heating purposes. With a range of about 30% of the mean annual emissions, this effect is expectedly more pronounced in the NH and SH than in the Tropics (18%). Seasonal variations in the type of fuel used seem to be smaller, at least on these spatial scales: A clear seasonal cycle in OR_{ff} , however with an amplitude of merely 0.04, can only be seen for the Northern Hemisphere, whereas the timeseries for the SH and the Tropics are rather flat.

Figure 2b and d shows hourly CO_2 emissions and OR_{ff} for one week in January, illustrating the additional short-term variations. For all latitudinal bands, CO_2 emissions

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



exhibit a diurnal cycle: Emissions are higher during daytime than at night, and variations in transport lead to emission peaks in the morning and afternoon. The relative magnitude of the daily variations is slightly lower in the Southern Hemisphere (61% peak-to-peak range) than in the Northern Hemisphere (83%) and the Tropics (78%).

5 In addition, emissions are lower on the weekend, being about 85 % of the emissions during the week for all latitudinal bands.

The oxidative ratio OR_{ff} also exhibits diurnal and weekly variations resembling the patterns in the CO_2 emissions. The fact that OR_{ff} is also highest in the morning and afternoon and lowest at night must not be misinterpreted as higher CO_2 emissions causing higher oxidative ratios. Instead variations in OR_{ff} are due to the temporal factors differing for the different categories, thus the oxidative ratio is dominated by different categories at different times of the day, e.g. by transport in the morning/afternoon.

10 These differences in the temporal patterns are much smaller for the weekly cycle (all categories either have lower emissions on the weekend or no weekly cycle at all). Therefore, the difference between weekdays and weekend is not as pronounced in OR_{ff} as it is in the CO_2 emissions.

Long-term trends in OR_{ff} over the COFFEE-period are shown in Fig. 3. Figure 3a shows the global trend on gridcell level, determined from linear regressions for each pixel. Red colors indicate an increase and blue colors a decrease in OR_{ff} . The plot

20 shows no general positive or negative trend for this time period, rather tendencies in both directions for different regions. Maximal changes range from -0.2 to $+0.3$ per decade. Figure 3b shows timeseries of the global average of OR_{ff} (in analogy to Sect. 1, this average will be referred to as α_F in the following). The global average obtained from the COFFEE dataset, represented by the black line and the circles, is close to the value of 1.4 that is normally used for fossil fuel burning (here shown as dashed line). Over the whole timeperiod, α_F varies between 1.39 and 1.42, with a mean of 1.41 and a standard deviation of 0.01. Deviations from 1.4 are less than $\pm 1.5\%$. Again, no general trend is seen for the complete timeseries. However, starting

25 from the year 2000, α_F is decreasing continuously. As seen in Fig. 3c, this trend can

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

be explained by a strong increase in global CO₂ emissions from coal burning, including also a shift in the largest fuel emission source from oil to coal in the year 2005. Rather than by local changes in fuel use, this increase is caused by the fact that emissions from mainly coal-burning countries like China have been strongly increasing and are becoming globally more significant.

In Fig. 3b, α_F from COFFEE is also compared with results derived from two other datasets, shown in grey. The squares show α_F obtained from fuel consumption data from BP (BP, 2009). The BP dataset contains continental and national level consumption data of coal, oil and natural gas, but no information on biofuels and cement production. The third dataset (represented by the triangles) is the CDIAC dataset (Boden et al., 2009), that – like the oxidative ratios in COFFEE – is primarily based on the UN energy statistics, but also uses additional sources to complete the information. This inventory provides country level CO₂ emissions from the consumption of coal, oil and gas as well from gas flaring and production of cement. The global oxidative ratios from those two datasets are calculated by dividing the total oxygen uptake by the total CO₂ emissions. The oxygen uptake $O_{2\text{ total}}$ was determined by $O_{2\text{ total}} = \Sigma (1.17 \times CO_2(\text{coal}) + 1.44 \times CO_2(\text{oil}) + 1.95 \times CO_2(\text{gas}))$, with CO₂ (fuel) being the CO₂ emissions of that fuel type.

It can be seen from Fig. 3b that α_F shows similar patterns in all three datasets; however the temporal variations are small against the offset between the different inventories (up to 4%). This offset is mainly caused by the different fuel types included in the different inventories; when calculating α_F from the common part of all dataset (coal, oil and natural gas), the maximum offset between the results decreases to below 1%.

The question now arises whether these variations in the global average are significant for the partitioning of global carbon sinks. The most recent sink estimate for the period 1990 to 2006 has given a result of 1.9 ± 0.6 and 1.2 ± 0.8 Pg C yr⁻¹ (uncertainties given here as 1 σ standard deviations) for the total oceanic and land biotic sink, respectively (Manning and Keeling, 2006). The uncertainty in α_F , assumed by Manning

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and Keeling as ± 0.04 , results in a significant contribution of $\pm 0.2 \text{ PgC yr}^{-1}$ to the uncertainty of both sinks. However, Fig. 3b shows that the temporal variations of α_F in any of the datasets are about a factor 6 smaller than the uncertainty value of ± 0.04 (here illustrated by the dotted lines), thus resulting in maximum sink uncertainties of $\pm 0.035 \text{ PgC yr}^{-1}$. Nevertheless, Manning and Keeling (2006) already stated that temporal variations, in their case derived from CDIAC data for the 1990s, are not the major source of uncertainty in α_F . Their uncertainty is rather determined by the uncertainty in the absolute value, since interannual changes in fuel production or consumption are resolvable to a finer degree than the total production in any given year. This uncertainty can not be quantified in the COFFEE dataset; only the remaining offset between the different inventories (after correction for the different fuel types included) could be used as an estimate for this uncertainty. However, this would give only a realistic range if these inventories were based on completely independent sources. This is unfortunately not the case, as both the COFFEE and the CDIAC dataset are based on the UN statistics, and BP uses “governmental sources” for its inventory that might also overlap with the UN statistics.

4 Influence of fuel mix on atmospheric O_2 mixing ratio

4.1 Global and regional model simulations

The spatial and temporal variations in OR_{ff} shown above leave a signature in atmospheric oxygen that can potentially be seen in the network of oxygen measurements. For investigating this influence, CO_2 emissions and O_2 uptake from the COFFEE dataset were used as input for atmospheric transport models. Fossil fuel related changes in the atmospheric CO_2 and O_2 mixing ratios – hereafter called $\text{CO}_{2\text{ff}}$ and $\text{O}_{2\text{ff}}$ – were extracted from the simulations for a number of monitoring stations. Two different transport models were used: the global model TM3 (Heimann and Körner, 2003) and the regional model REMO (Langmann, 2000; Chevillard et al., 2002). TM3 provides worldwide coverage and therefore can give a complete overview of fossil fuel related

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



effects. The advantage of REMO is its higher temporal and spatial resolution, which allows for better capturing of synoptic variations in fossil fuel use. REMO provides hourly output on a $0.5^\circ \times 0.5^\circ$ grid covering the area north of 30° N, whereas TM3 output is 6-hourly, and its finest resolution is $1.8^\circ \times 1.8^\circ$. Comparison of the $\text{CO}_{2\text{ff}}$ and $\text{O}_{2\text{ff}}$ results for stations that are within the domain of both models shows similar patterns in TM3 and REMO. An example is given in Fig. 4, containing simulations for the year 2006 at the station Ochsenkopf in Germany ($50^\circ 01' 49''$ N, $11^\circ 48' 39''$ E, 1022 m a.s.l, see Thompson et al. (2009)). The simulated $\text{CO}_{2\text{ff}}$ and $\text{O}_{2\text{ff}}$ signals, shown in Fig. 4a and b, are dominated by synoptic scale pollution events rather than by seasonal or other periodic variations. As expected, the signals from the regional model show higher variability, resulting in sharper and taller peaks with increases in CO_2 and decreases in O_2 . Figure 4c presents the perceived atmospheric oxidative ratio OR_{ffp} at the station location, derived from a running regression of $\text{O}_{2\text{ff}}$ versus $\text{CO}_{2\text{ff}}$. As this perceived oxidative ratio is subject to atmospheric transport and mixing, it is not the same as the O_2/CO_2 ratio from the uptake/emissions of the respective gridcell. To get a signal representative for the synoptic time scale that dominates the atmospheric fossil fuel signal, a timeframe of 5 days was chosen for the regression. The negative slope of the $\text{O}_{2\text{ff}}$ versus $\text{CO}_{2\text{ff}}$ regression for a given 5-day-period corresponds to the perceived oxidative ratio OR_{ffp} at the middle of the time interval. The OR_{ffp} resulting from the two models do not show significant systematic differences. Both are varying between 1.35 and 1.56, with an average value slightly higher than α_{F} . In Fig. 4d the difference $\Delta\text{O}_{2\text{ff}} = \text{O}_{2\text{ff}}(\text{OR}_{\text{ff COFFEE}}) - \text{O}_{2\text{ff}}(\text{OR}_{\text{ff}} = 1.4)$ is shown, i.e. the difference in the fossil fuel related O_2 signal calculated using the variable oxidative ratios from COFFEE instead of a constant oxidative ratio of 1.4. As $\Delta\text{O}_{2\text{ff}}$ depends both on the size of fossil fuel signals and the deviation of the local fuel mix from the global average, it is significantly higher in the simulations from the regional model. In the example here, differences up to -3 ppm in the fossil fuel related O_2 signal are caused. Taking into account the typical measurement precision of 1 ppm for atmospheric oxygen measurements, this deviation is quite small, but probably still detectable.

**The COFFEE dataset:
effects from varying
oxidative ratios**

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.2 Comparison with observations from Hateruma Island

When interpreting fossil fuel related oxidative ratios, as shown in Fig. 4c, one needs to keep in mind that the total oxidative ratio observable at a monitoring station is not only determined by fossil fuel related signals, but also by contributions from biospheric and oceanic processes. Whether a specific fuel signature can be seen in measured oxidative ratios at a given station depends on the size of fossil fuel signals compared to the atmospheric signals caused by other processes. This section examines oxidative ratios derived from CO₂ and O₂ observations at the monitoring station Hateruma Island and investigates whether it is possible to detect specific fuel signatures in these observations. The reason for choosing this station is the above mentioned variation in OR_{ffp} that has been observed at this station. As explained in Sect. 1, these variations are caused by air masses originating from different Asian countries with different fuel mix signatures.

The Hateruma monitoring station, operated by the National Institute of Environmental Studies (NIES), Japan, is situated on the eastern edge of Hateruma Island (24°03' N, 123°48' E, 10 m a.s.l.). Air is sampled from a small observation tower at a height of 36 m a.g.l. Air masses arriving at Hateruma are mostly influenced by the Asian continent during winter time and from the Pacific Ocean in summer (Tohjima, 2000; Tohjima et al., 2010). As in-situ O₂ measurements started in October 2006, we investigate here the time period from October 2006 to December 2006. For this time period, the fossil fuel contribution to the atmospheric CO₂ signal is expected to be significant: Mostly continental air is measured, and biospheric activities are lower during wintertime.

Figure 5a and b show CO₂ and O₂ observations from Hateruma (represented by brown dots), together with TM3 simulations for CO_{2ff} and O_{2ff} (black lines). Here it can be seen that indeed most of the synoptic variability in the observations is caused by fossil fuel events: Most peaks in CO₂ (and corresponding dips in O₂) correlate with peaks/dips in the fossil fuel simulations. (As already seen in Fig. 4, the peak heights tend to be underestimated by TM3). Figure 5c shows the perceived oxidative

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ratios, determined from the observations (brown) and the simulated values (black), using a 5-day regression as in Fig. 4c. Shaded error bars indicate the respective errors of the linear fit. For oxidative ratios with an error larger than 0.05 (marked in orange), the O_2/CO_2 correlation is considered not to be sufficient for interpretation.

The results indicate that a significant part of the observed variations in the oxidative ratios can be captured using the fossil fuel component simulated by even a coarse global model like TM3. This also suggests that the information about the local fuel mix is important for interpreting atmospheric measurements at this station: On the one hand, the assumption of $OR_{ff} = 1.4$ is generally an overestimation here. On the other hand, the information on the diverse fuel mix of the surrounding Asian countries in combination with measured variations in the oxidative ratios can be used for detecting the origin of air masses and thus for testing and evaluation of transport models.

4.3 Potential effects of variable OR_{ff} at other monitoring stations

With Hateruma Island we have presented an example where the effects of variable oxidative ratios need to be taken into account when interpreting atmospheric oxygen measurements. The question is whether these effects also play a significant role for other stations in the global monitoring network. Figure 6 illustrates results from REMO and TM3 simulations for all oxygen monitoring stations where output from one or both of the models exist. Figure 6a shows OR_{ffp} , determined from the 5-day running regression of O_{2ff} versus CO_{2ff} , and Fig. 6b the difference ΔO_{2ff} caused by the variable OR_{ff} as defined in Sect. 4.1. Stations locations are shown in Fig. 6c, also indicating the range of the REMO domain. Since both models show similar results for oxidative ratios on the synoptic timescale investigated here (see Fig. 4), both of them can be used for the respective set of stations, depending on their availability. For the difference ΔO_{2ff} results from the regional model are used where available, since they presumably capture the fossil fuel related variations better. As this needs to be taken into account

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



when comparing the magnitude of signals at different stations, the letter “R” or “T” next to each station’s results indicates whether output from REMO or TM3 is used.

Stations located on the Southern Hemisphere and on tropical islands usually receive a well-mixed background fossil-fuel signal instead of being influenced by local sources.

Hence, their perceived oxidative ratio shows only small variations and its median does not differ significantly from the global average. For European, Asian and North American stations, variations in OR_{ffp} are larger. Besides, deviations of their median OR_{ffp} from the global average are in accordance with the results for the O_2/CO_2 emission ratios in Fig. 1c: the median is slightly higher for Europe and North America, significantly higher for the Russian station (Zotino Tall Tower Observatory (ZOT), located in Siberia) and lower for the two Eastern Asian Stations (one of them being Hateruma (HAT)). As expected, variations in OR_{ff} and deviations from the global average are larger for continental stations or stations with dominant continental influence (recognizable by the black symbols) than for remote stations (marked by green symbols). Nevertheless also some of the remote stations, e.g. Alert (ALT, Canada) or Barrow (BRW, Alaska), exhibit larger variations in OR_{ffp} . However, as seen from Fig. 6b, large variations in the oxidative ratios do not necessarily lead to detectable changes in the atmospheric signal at the station. If the fossil fuel related CO_2 and O_2 signals are small, as it is the case for the remote stations, variations in OR_{ffp} do not cause any significant difference ΔO_{2ff} . In contrast, differences range between -8 and $+4$ ppm for continental stations, being largest for stations located in the vicinity of fossil fuel sources with a non-standard fuel mix, e.g. Hateruma in Asia or Lutjewad in the Netherlands.

The use of a global average OR_{ff} of 1.4 can therefore be regarded as sufficient when only interpreting data from remote stations. For continental stations, however, the influence of local fuel sources, especially those with a non-standard fuel mix, can lead to detectable changes in the atmospheric O_2 signals. For the stations where model output from TM3 is used, the fossil fuel related atmospheric signals are presumably larger than in the simulations as the global model tends to underestimate the magnitude of the synoptic scale signals. In addition, variations in fossil fuel emissions occurring on

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



scales smaller than the $1^\circ \times 1^\circ$ resolution of the COFFEE dataset (e.g. emissions from point sources as power plants) are not taken into account, but might have an additional impact on the synoptic scale OR_{ffp} .

Whether the contribution of OR_{ffp} to the total atmospheric oxidative ratio is significant, depends on the relative strengths of fossil fuel signals compared to the influence of other processes, e.g. related to biospheric activity. Hence the possibility to use fossil fuel related oxidative ratios for identification of emission sources or improvement of atmospheric transport is also subject to the strengths of these other sources and sinks at a given station.

5 Impact of variable oxidative ratios on APO fluxes

Spatial and temporal variations in fuel use are also likely to influence the calculation of oceanic and biospheric fluxes derived from atmospheric O_2 and CO_2 measurements. To isolate the oceanic component from measured oxygen signals, usually the tracer $APO = \Delta O_2 + 1.1 \Delta CO_2$ (Stephens et al., 1998) is used. Whereas APO is by definition not changed by biospheric processes (at least to the extent where OR_b agrees with the global average of $\alpha_B = 1.1$), the influence from fossil fuel burning is reduced, but still present in the signal. This is usually accounted for by using fossil fuel statistics to calculate a fuel-corrected APO signal (assuming a constant value for OR_{ff}). A well-established method to interpret measured APO signals in terms of surface fluxes is the atmospheric transport inversion (Enting et al., 1995), applied to APO by Rödenbeck et al. (2008). For this method, spatial and temporal variations in the atmospheric tracer concentration at measurement locations are simulated using a transport model. By minimizing the differences between observed and model-derived concentrations, the contributing surface fluxes are estimated using inverse techniques.

Here we investigate whether it is necessary to include variable OR_{ff} in APO inversions to avoid mistaking fossil fuel related variations for signals caused by ocean processes. For this, we performed an APO inversion following that of Rödenbeck et

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al. (2008). We used the ‘standard setup’ described in that paper (Sect. 2.4) with TM3 as a transport model. As observational input, atmospheric CO₂ and O₂ data from 16 measurement sites (in the following referred to as “inversion stations”) were used. These data result from the measurement programs of the Scripps Institute of Oceanography (Manning and Keeling, 2006; Keeling and Shertz, 1992), the University of Princeton (Bender et al., 1996; Battle et al., 2006) and the Japanese National Institute for Environmental Studies (Tohjima et al., 2003). Sampling at these stations started at different times between 1991 and 1999. To avoid spurious flux variations in the inversion calculations caused by the sudden appearance of a new station in the observational dataset, we only used the time period from 1999 to 2005 where records from all 16 sites contain reliable data. Fluxes were calculated from the year 1996 on to allow for sufficient spin-up time of the model, but only results from 1999 on are considered for further analysis. For testing the effects of variable oxidative ratios, a synthetic dataset was created, containing the simulated difference $\Delta APO_{\text{ff}} = APO_{\text{ff}}(\text{OR}_{\text{ff}} = \text{OR}_{\text{COFFEE}}) - APO_{\text{ff}}(\text{OR}_{\text{ff}} = 1.4)$ at the monitoring stations. These APO differences were inverted, resulting in a set of flux differences $\Delta F_{APO_{\text{ff}}}$. Since the inversion can only adjust the ocean fluxes, differences caused by non-constant oxidative ratios are attributed to ocean fluxes. To quantify the fossil fuel effects on different timescales, we applied two sets of filters to the results: In Sect. 5.1, we are focusing on long-term biases and interannual variability, in Sect. 5.2 we investigate effects on the seasonal cycle.

5.1 Long-term mean and interannual variability

For characterizing the influence of variable oxidative ratios on APO fluxes on multi-year and interannual timescales, the mean seasonal cycle and most variations faster than one year were subtracted from the results (using the filter “Filt0.5gd”, described by Rödenbeck, 2005). Figure 7 shows global maps of the filtered $\Delta F_{APO_{\text{ff}}}$ fluxes, with Fig. 7a depicting the long-term mean of $\Delta F_{APO_{\text{ff}}}$ (indicating systematic offsets in the APO fluxes) and Fig. 7b the temporal standard deviation of the filtered fluxes as a

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measure for the interannual variability. A dominant feature in both plots is seen around the Hateruma monitoring station, consistent with the results from Sect. 4.2 and 4.3. Since the fossil fuel related oxidative ratio influencing the atmospheric signal at this station is significantly lower than the global average, the assumption of $OR_{ff} = 1.4$ leads to an overestimation of the oceanic APO fluxes in that region (and thus a positive ΔF_{APOff} offset in the long-term mean). The same effect also causes an increase in the interannual variability in the Hateruma region. Besides, most of the other features in Fig. 7a and b, e.g. the negative offset and higher variability in the Northern Pacific, can be attributed to far-field effects of the overestimation of OR_{ff} at Hateruma. This was tested by running another inversion without the Hateruma station.

To access if these effects are significant, we compare the resulting differences to the magnitude of the APO ocean fluxes F_{APO} (as determined from the standard inversion) and their uncertainties. Figure 7c shows timeseries of F_{APO} calculated with constant (black) and variable (orange) OR_{ff} for the Hateruma region (i.e. the area enclosed by the box in Fig. 7 a and b). For characterizing the uncertainties of F_{APO} , we compare the “standard run” with an ensemble of runs where specific setup details were varied. To cover the range of uncertainties realistically, we have varied the inversion parameters to which the resulting fluxes are most sensitive (according to Rödenbeck et al. (2008)): tightness of the a priori constraint relative to the data constraint (“ $\mu = 4$ ”), scales of the spatial and temporal smoothing (“long” – increased a priori correlation length, “fast2x” – decreased a priori correlation time) and resolution of the transport model (“fg” – fine grid ($4^\circ \times 5^\circ \times 19$ vertical levels) instead of coarse grid ($\approx 8^\circ \times 10^\circ \times 9$ vertical levels)). The fluxes F_{APO} resulting from these different scenarios are shown in different shades of blue in Fig. 7c. The plot reveals that the fossil fuel related differences ΔF_{APOff} in the Hateruma area are in the same order of magnitude as the uncertainty given by the ensemble range. It is therefore recommended to include the information on variable OR_{ff} when using data from such a station. When removing the Hateruma station from the stationset for the inversion, the resulting ΔF_{APOff} become negligible. This is due to the fact that apart from the second Japanese station Cape Ochi-Ishi (COI), the

**The COFFEE dataset:
effects from varying
oxidative ratios**J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



remaining “inversion stations” are typical remote stations, most of them located on the Southern Hemisphere. As already seen in Sect. 4.3, the influence of local fuel sources is insignificant at these locations.

Continental – and therefore likely more polluted – monitoring stations are currently not included in the set of stations used for the inversion. Since atmospheric measurements at an increasing number of continental stations have become available in the recent decade, future inversions will probably include also data from this kind of stations. It is thus worth investigating whether fossil fuel related effects from these stations can be as significant as the effects caused by the Hateruma station. Therefore a further synthetic experiment was performed, using a new set of pseudo-data for all monitoring stations that currently measure O_2/N_2 and CO_2 . To avoid artifacts due to different sampling frequencies or differences in the start of the measurements, weekly sampling at every station was assumed over the whole time period. The resulting ΔF_{APOff} fluxes are shown in Fig. 7d and e. In analogy to the results for the inversion stations, Fig. 7d shows the long-term mean and Fig. 7e the standard deviation of ΔF_{APOff} . Station locations are included in both maps. It can be seen that the addition of continental stations does not change the global picture completely. As most of the additional stations are located in Europe or North America, main differences occur in the Northern Atlantic, the Mediterranean Sea and the North Sea. Here the negative offset in the long-term mean becomes stronger, reaching up to $\sim 50\%$ of the F_{APO} signals in this region. This negative bias is in accordance with OR_{ff} being slightly higher than 1.4 for Europe and North America and thus becoming underestimated in the standard inversion. This also causes a higher interannual variability of ΔF_{APOff} in the mentioned regions.

On the other hand, both the negative offset and the amplitude of the interannual variability are reduced in the Pacific Area; the interannual variability is also lower in the Arctic Ocean. From the inversion with the smaller stationset, ΔF_{APOff} fluxes in these areas were already identified as far-field effects from the Hateruma station. With the inclusion of the additional European and North American stations, fluxes in the North Atlantic and North Pacific are now better constrained. Therefore, the inversion

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

algorithm has less freedom to distribute the excess fluxes globally. These fluxes are now more localized in the Hateruma region; in this area both offset and interannual variability are slightly higher in the inversion setup with the continental stations.

5.2 Seasonality

To investigate the effect of seasonal variations in fuel use on the seasonal cycles of F_{APO} , we extracted the mean seasonal cycle from the inversion results (using the triangular filter “Filt6.0Tm” from Rödenbeck (2005)). As only annual averages for fossil fuel CO_2 emissions are used in global APO inversions, the seasonal component of ΔF_{APOff} can be influenced by seasonal variations in both $\text{CO}_{2\text{ff}}$ and OR_{ff} , i.e. by variations in the amount and the type of fuel used, respectively. To separate these two effects, we performed an additional inversion of APO pseudodata containing the CO_2 seasonality as in COFFEE, but only using $\text{OR}_{\text{ff}} = 1.4$.

The range of the resulting seasonal variations is shown in Fig. 8, with Fig. 8a showing the effects due to variations in the oxidative ratios and Fig. 8b the influence of seasonal variations in the CO_2 emissions. Differences in the seasonal cycle occur mainly in the Northern Hemisphere, being highest in the North Atlantic and in the area around Hateruma. In general, the effect of variability in OR_{ff} is stronger than that of the seasonality in CO_2 emissions. However, the seasonal ΔF_{APOff} fluxes are small against the seasonal amplitudes of F_{APO} and their uncertainties. This is seen in Fig. 8c, illustrated by a timeseries for the region with the highest ΔF_{APOff} fluxes (indicated by the black box in Fig. 8a and b). In analogy to Fig. 7c, the black line shows the seasonal F_{APO} fluxes and the blue lines the ensemble of runs characterizing their uncertainty. The results represented by the orange line take into account the total ΔF_{APOff} , i.e. the sum of the effects caused by CO_2 seasonality and variable OR_{ff} . Here only the results from the “inversion stations” are shown, as the results for all monitoring stations do not show any significant differences.

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



6 Conclusions

We have presented a global dataset of CO₂ emissions and O₂ uptake associated with fossil fuel burning, created from emission inventories and fuel consumption data. We have used this dataset to characterize the range of spatial and temporal variations of oxidative ratios OR_{ff} from fossil fuel combustion, and to investigate the influence of these variations on atmospheric oxygen signals. The “CO₂ release and Oxygen uptake from Fossil Fuel Emission Estimate” (COFFEE) dataset contains hourly resolved anthropogenic CO₂ emissions and the corresponding O₂ uptake for the years 1996 to 2008 on a 1° × 1° grid. It is available for download at <ftp://ftp.bgc-jena.mpg.de/pub/outgoing/coffee>.

Spatial variations in the O₂/CO₂ emission ratios resulting from COFFEE show clear differences in the fuel mix of different regions, with OR_{ff} covering the whole range from 0 to 1.95 and having a spatial standard deviation of 0.2. Temporal variations in OR_{ff} occur on different timescales: Long-term changes show differences ranging from -0.2 to 0.3 per decade on gridcell level, with no predominant trend in one direction. In addition, OR_{ff} is varying due to seasonal and short-term variations in fuel use, with variations on daily level dominating, especially in the Southern Hemisphere and the Tropics. In general, however, the range of temporal variations is rather small compared to that of the spatial differences.

On the global scale, the average OR_{ff} calculated from COFFEE varies between 1.39 and 1.42 and thus does not differ significantly from the commonly used value of $\alpha_F = 1.4$. It is also in good agreement with the results derived from other datasets, namely the BP and CDIAC data (after correcting for the different types of fuels considered in the different datasets). All datasets show a downward trend in α_F starting from the year 2000 on, related to increasing CO₂ emissions from coal burning. This shift in fuel use is attributed to a growing contribution of CO₂ emissions from China and other countries where coal is the main fuel source. Despite this recent trend, temporal variations in α_F are too small to have significant influence on the partitioning of global carbon sinks.

The influence of variable OR_{ff} on the atmospheric oxygen signals at ground-based

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The COFFEE dataset:
effects from varying
oxidative ratios**J. Steinbach et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

monitoring stations was investigated using model simulations from the TM3 and REMO models with the COFFEE dataset as input. Fossil fuel related O_2 and CO_2 signals at the stations are mainly influenced by synoptic scale events. Expectedly, the perceived OR_{ff} on synoptic time scales shows larger variations and deviations of its mean from the global average for continental monitoring stations than for the classical remote stations. Depending on the magnitude of fossil fuel related CO_2 fluxes at the measurement location, the influence of the local fuel mix can change the atmospheric O_2 mixing ratio by several ppm. Whether these effects can be detected in atmospheric CO_2 and O_2 observations has been examined for the case of the Hateruma monitoring station. As this station often receives polluted air from several Asian countries with differing OR_{ff} , the information on the local fuel mix is crucial for interpreting observations there and can potentially be used for identifying the origin of airmasses. Whether this information is required to interpret data for other stations as well or can even be used to identify specific emission sources, needs to be investigated for the individual station and investigated time period (e.g. summer/winter), as also the size of the fossil fuel signal in comparison to signals from other processes (e.g. biospheric) plays a role. For these investigations, the use of regional models with a higher resolution is recommended, as the global model used here tends to underestimate the magnitude of synoptic events that dominate the variation in OR_{FF} . In the case of remote monitoring stations, however, fossil fuel signals and thus the influences of variable OR_{ff} are mostly negligible. In addition, most of the existing continental stations that are influenced by local fossil fuel sources are located in Europe or North America, where the average OR_{ff} does not differ much from 1.4. An exception here is the station Lutjewad in the Netherlands, where the high usage of natural gas makes it necessary to use a higher OR_{ff} . Here the COFFEE dataset has already been used successfully for the separation of the fossil fuel part from APO signals (van der Laan-Luijkx et al., 2010).

Variations in OR_{ff} might also still play a significant role for other European and North American stations, when airmasses are influenced by local fuel sources that deviate from the average mix of the country (e.g. power plants, cement production). However, it

remains to be investigated whether the $1^\circ \times 1^\circ$ resolution of the COFFEE dataset is sufficient to account for this. Otherwise the oxidative ratios on category/country level could also be easily combined with a higher resolved fossil fuel inventory, e.g. by including point sources with the information on their categories. For potential future monitoring stations in regions such as South America, Africa or Asia, at least the information on the average local OR_{ff} and thus the spatial component of COFFEE is useful.

As one of the main applications of atmospheric oxygen measurements is the calculation of oceanic carbon sinks, we have investigated the possibility of variations in OR_{ff} to be mistaken for oceanic signals. For that we calculated long-term, interannual and seasonal oceanic fluxes for constant and variable OR_{ff} , using a global APO inversion. Whereas the resulting differences in the seasonal cycle are in general negligible, long-term biases and differences in the interannual variability can be significant. This is strongly depending on the stationset chosen for the observational input: When using only remote stations, fossil fuel effects are expectedly negligible, but as soon as data from the Hateruma monitoring station is included, the local overestimation of OR_{ff} leads to – both local and far-field – differences in the fluxes. The addition of data from existing non-remote monitoring stations in North America and Europe to the inversion partly counteracts the effects caused by the overestimation of OR_{ff} at Hateruma, but also causes an additional bias in the North Atlantic due to the slight underestimation of the OR_{ff} in European and North America. The resulting effects can be as large as the uncertainties of the inversion, thus it is recommended to take into account the spatially variable oxidative ratios such as those provided by the COFFEE dataset. For regional inversions, the influence is likely to be larger, making the use of variable oxidative ratios more important.

Altogether the COFFEE dataset has proven to be a useful tool for quantifying the effects of variable oxidative ratios from fuel combustion. We have shown that while for interpretation of observations from remote stations and many global implementations the use of a constant global average is sufficient, there are applications where more precise information on fossil fuel related oxidative ratios is needed.

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The COFFEE dataset:
effects from varying
oxidative ratios**

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The COFFEE dataset:
effects from varying
oxidative ratios**

J. Steinbach et al.

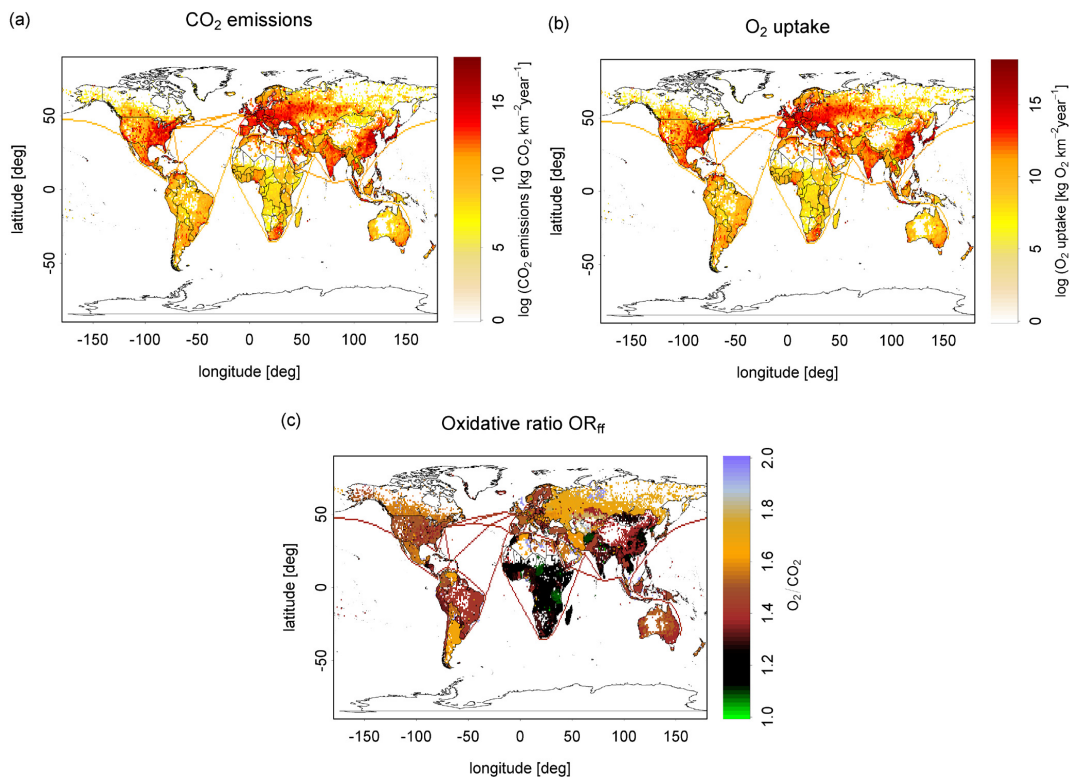


Fig. 1. Global maps of fossil fuel related CO₂ emissions **(a)**, oxygen uptake **(b)** and fossil fuel related oxidative ratios **(c)** for the year 2006 as calculated from the COFFEE dataset.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



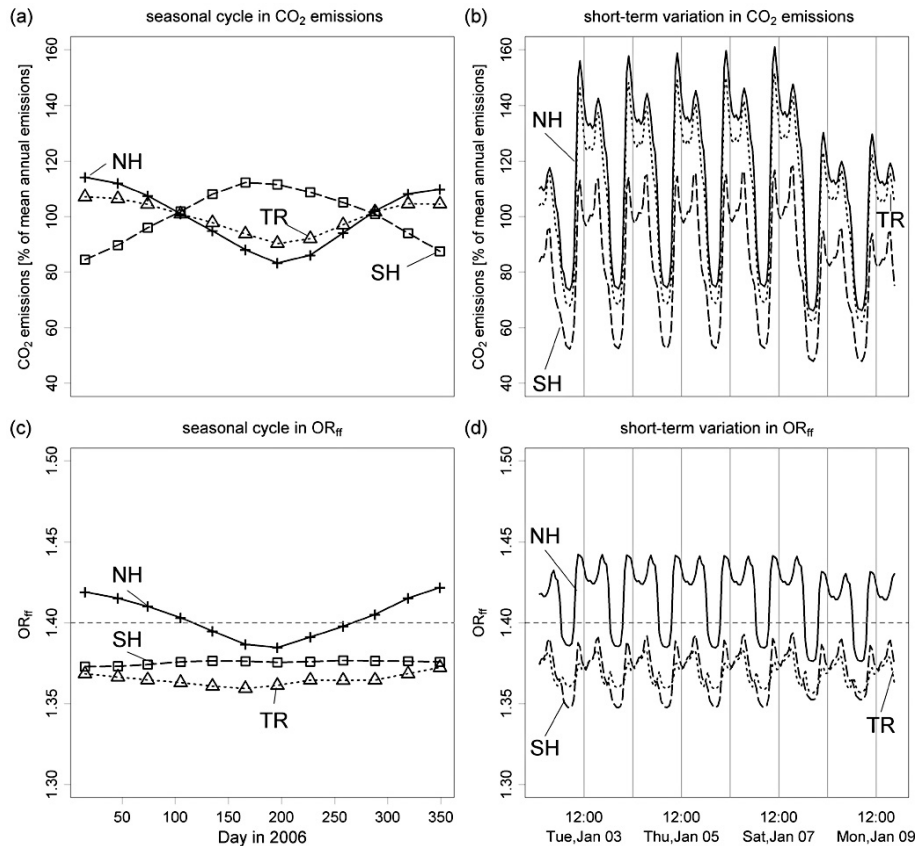


Fig. 2. Seasonal and short-term variations in CO₂ emissions (upper row, **a** and **b**) and OR_{ff} (lower row, **c** and **d**) for the year 2006, integrated over the three latitudinal bands NH, SH and Tropics (TR). The left column shows monthly averages for the whole year, illustrating the seasonal cycle; the right column short-term variations for the first week in January. Grey vertical lines in plots **(b)** and **(d)** indicate the local noon.

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

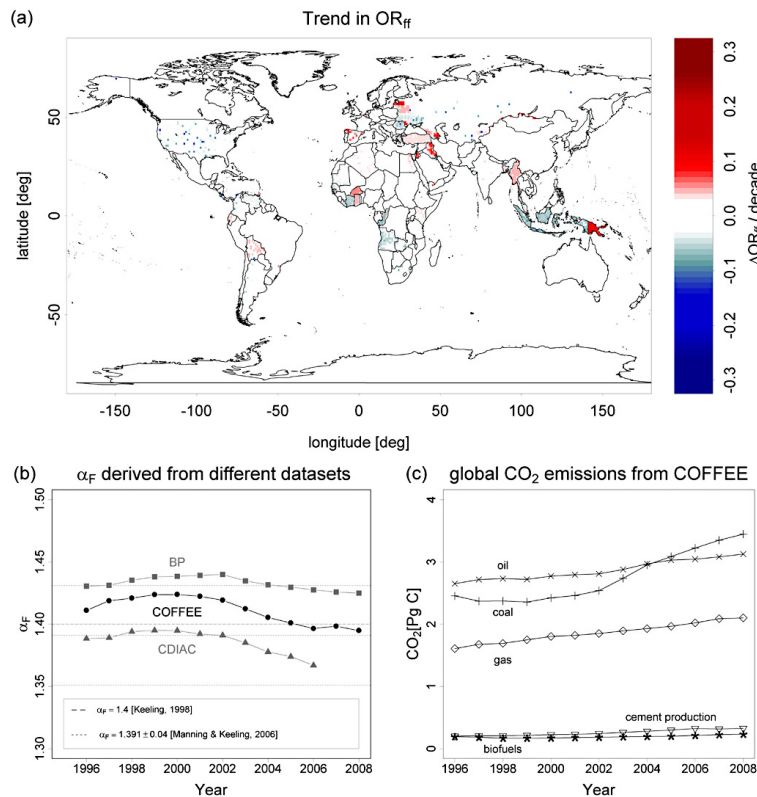


Fig. 3. (a) Trend in fossil fuel related oxidative ratio over the time period covered by the COFFEE dataset, calculated as the slope of a linear fit for each pixel. Red colors indicate an increase and blue colors a decrease in OR_{ff} . (b) Timeseries of global average oxidative ratio α_F , derived from different fossil fuel inventories. The dashed grey line shows the value of 1.4 that is normally used for α_F , the dotted lines show the mean value and uncertainty of α_F for the 1990 as used by Manning and Keeling for the most recent calculation of global carbon sinks (see text for details). (c) Global CO_2 emissions from different fuel types, as derived from COFFEE.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

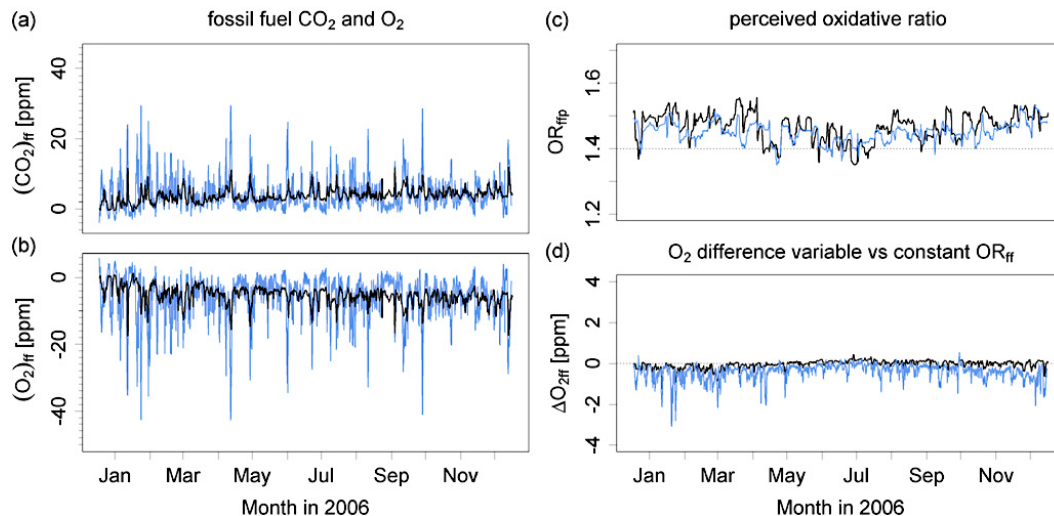


Fig. 4. Comparison of results from the global model TM3 (black) and the regional model REMO (blue) for the station Ochsenskopf (Germany). Fossil fuel related changes in the atmospheric mixing ratios of CO₂ **(a)** and O₂ **(b)** are shown on the left side. On the right side, **(c)** shows the perceived fossil fuel related oxidative ratio OR_{ffp}, and **(d)** the difference in the fossil fuel related O₂ signal calculated using the variable oxidative ratios from COFFEE instead of a constant oxidative ratio of 1.4.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

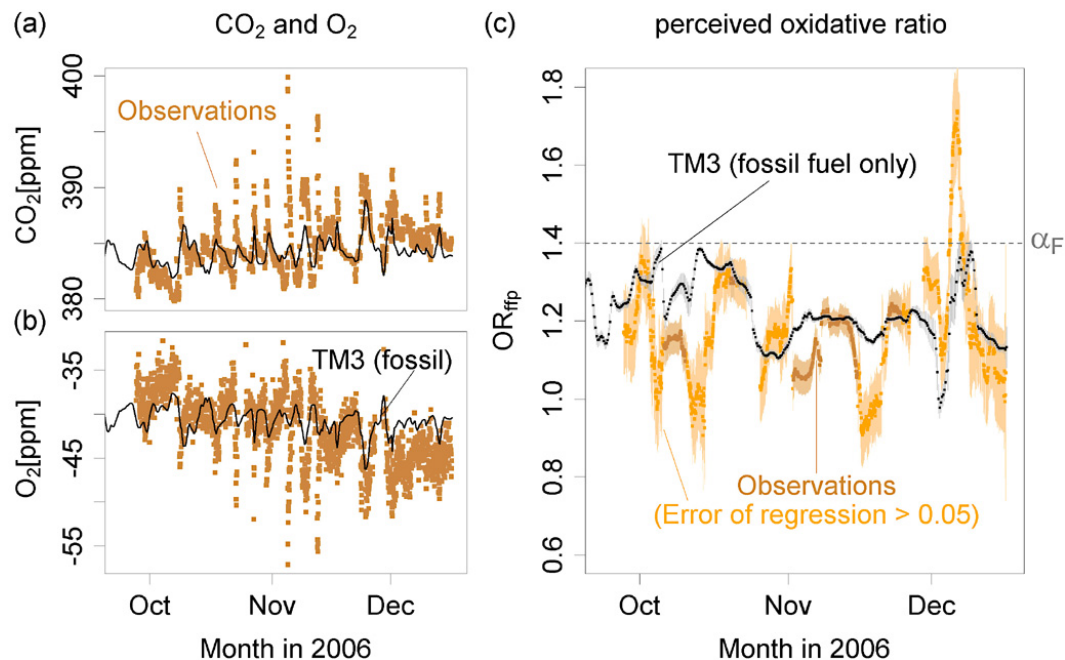


Fig. 5. Left: CO₂ **(a)** and O₂ **(b)** observations from Hateruma Island (brown dots), compared to CO_{2ff} and O_{2ff} simulations from the TM3 model (black lines). Right **(c)**: Oxidative ratios (corresponding color scheme) derived from linear regression of observed and simulated O₂ vs. CO₂. Shaded error bars show errors of the linear regression. Regressions with an error > 0.05 are considered as not sufficiently correlated and marked in orange.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

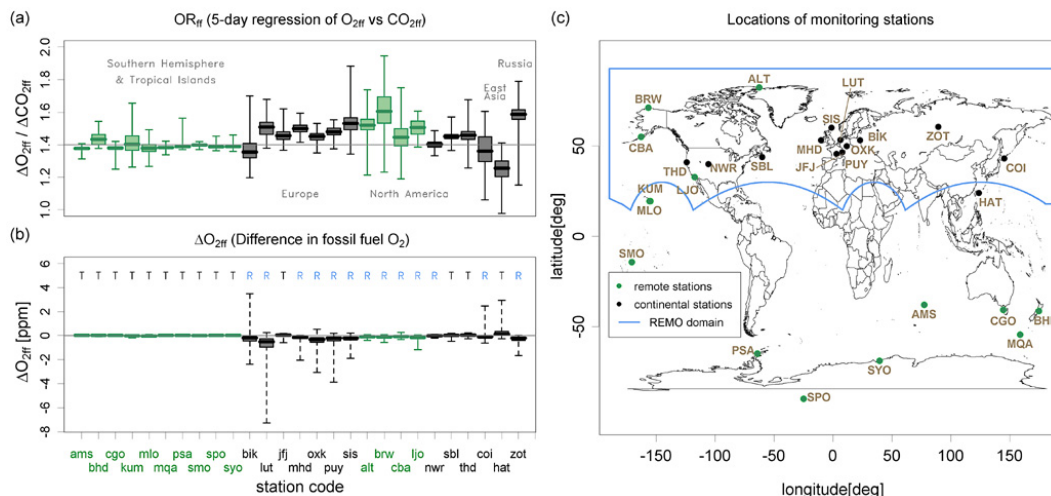



Fig. 6. Perceived fossil fuel related oxidative ratio **(a)** and difference in O₂ signal **(b)** from TM3 and REMO model simulations for all available monitoring stations. The box-and-whisker plot shows minimum, maximum, and quartile scores for the year 2006. Labels denote the station code, station locations are shown in the map **(c)**. To facilitate the recognition of continental and remote stations in this plot, labels of remote stations are green, whereas labels of stations on the continent or on islands mainly influenced by continental air masses are black. Simulation output from REMO is used preferably when available, as TM3 tends to underestimate the magnitude of the fossil fuel signals. The letters “R” and “T” indicate whether results from REMO or TM3 are shown for the respective station.

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

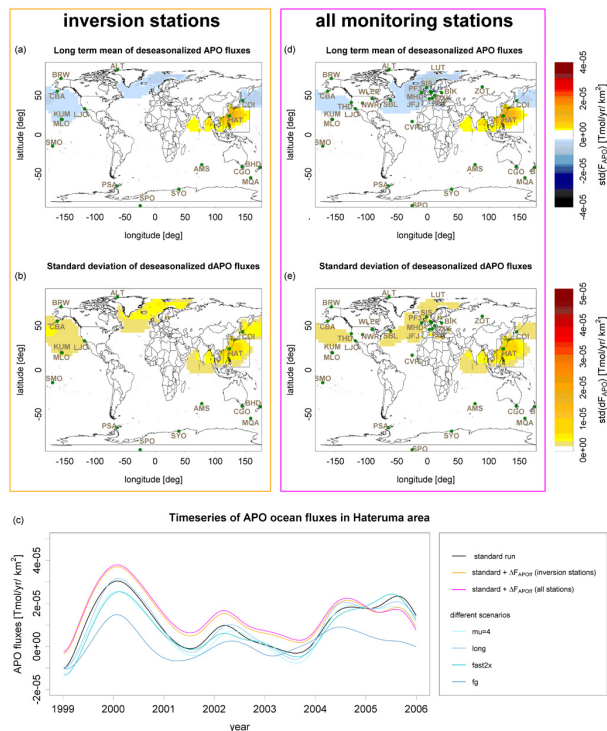


Fig. 7. Influence of variable oxidative ratios on APO fluxes on multi-year and interannual timescales, derived from global APO inversion. Shown are the fossil fuel related fluxes ΔF_{APOff} that are mistaken for ocean signals when ignoring variation in OR_{ff} . The upper row (**a**, **d**) shows the long-term mean of ΔF_{APOff} as indicator for systematic biases, the middle row (**b**, **e**) the deseasonalized temporal standard deviation as measure for temporal variability. The left column shows inversion results using the stationsset from Rödenbeck et al. (2008), the right column the results using all monitoring stations currently measuring atmospheric O_2 and CO_2 . For the area around Hateruma (black box), ΔF_{APOff} for both scenarios is compared to the size of the real ocean fluxes F_{APO} (black) and their uncertainty (blue).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

The COFFEE dataset: effects from varying oxidative ratios

J. Steinbach et al.

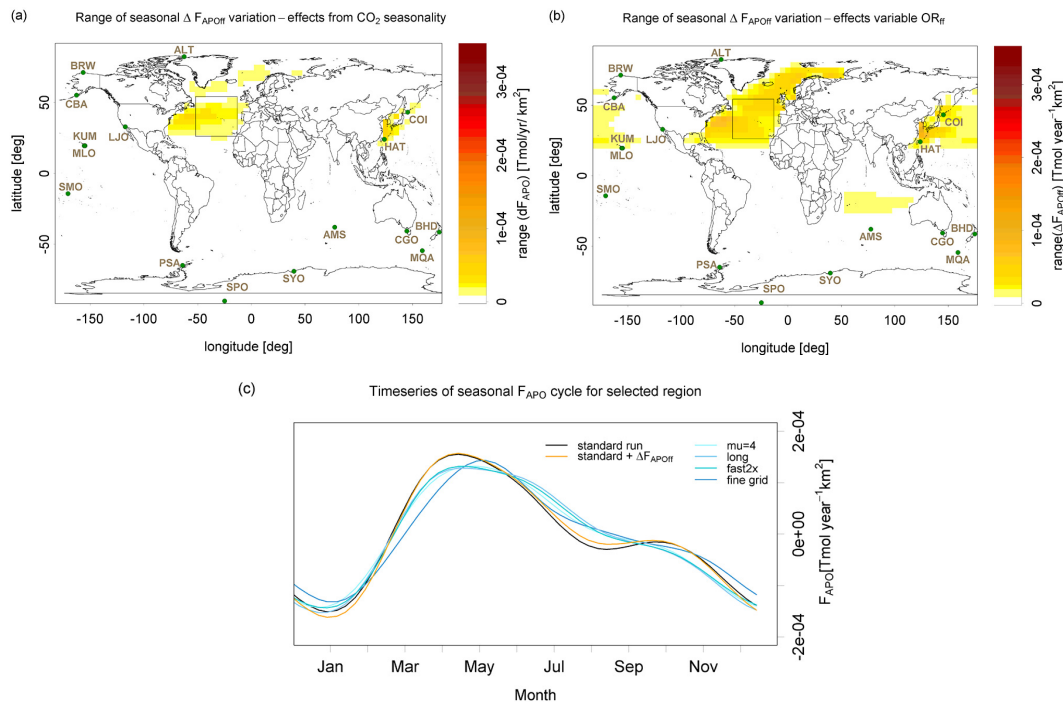


Fig. 8. Influence of variable oxidative ratios on APO fluxes on seasonal timescales. The maps show the amplitude of the seasonal component of the ΔF_{APOff} , split into the part that is caused by seasonal variations in CO_2 (a) and the part that is caused by variations in OR_{ff} (b). For the area with the largest ΔF_{APOff} fluxes (indicated by the black box), the total resulting flux ΔF_{APOff} is compared to the size of the real ocean fluxes F_{APO} (black) and their uncertainty (blue).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

