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Spatial distribution of $^{14}\Delta CO_2$ across Eurasia: measurements from the TROICA-8 expedition

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Abstract. Because fossil fuel derived CO$_2$ is the only source of atmospheric CO$_2$ that is devoid of $^{14}$C, atmospheric measurements of $^{14}\Delta CO_2$ can be used to constrain fossil fuel emission estimates at local and regional scales. However, at the continental scale, uncertainties in atmospheric transport and other sources of variability in $^{14}\Delta CO_2$ may influence the fossil fuel detection capability. We present a set of $^{14}\Delta CO_2$ observations from the train-based TROICA-8 expedition across Eurasia in March–April 2004. Local perturbations in $^{14}\Delta CO_2$ are caused by easily identifiable sources from nuclear reactors and localized pollution events. The remaining data show an increase in $^{14}\Delta CO_2$ from Western Russia ($40^\circ$E) to Eastern Siberia ($120^\circ$E), consistent with depletion in $^{14}CO_2$ caused by fossil fuel CO$_2$ emissions in heavily populated Europe, and gradual dispersion of the fossil fuel plume across Northern Asia.

Other trace gas species which may be correlated with fossil fuel CO$_2$ emissions, including carbon monoxide, sulphur hexafluoride, and perchloroethylene, were also measured and the results compared with the $^{14}\Delta CO_2$ measurements. The sulphur hexafluoride longitudinal gradient is not significant relative to the measurement uncertainty. Carbon monoxide and perchloroethylene show large-scale trends of enriched values in Western Russia and decreasing values in Eastern Siberia, consistent with fossil fuel emissions, but exhibit significant spatial variability, especially near their primary sources in Western Russia.

The clean air $^{14}\Delta CO_2$ observations are compared with simulated spatial gradients from the TM5 atmospheric transport model. We show that the change in $^{14}\Delta CO_2$ across the TROICA transect is due almost entirely to emissions of fossil fuel CO$_2$, but that the magnitude of this $^{14}\Delta CO_2$ gradient is relatively insensitive to modest uncertainties in the fossil fuel flux. In contrast, the $^{14}\Delta CO_2$ gradient is more sensitive to the modeled representation of vertical mixing, suggesting that $^{14}\Delta CO_2$ may be a useful tracer for training mixing in atmospheric transport models.

1 Introduction

Fossil fuel derived carbon dioxide (CO$_2$) is entirely devoid of radiocarbon ($^{14}$C) as a result of radioactive decay (mean lifetime=8267 yr (Godwin, 1962)) whereas other sources of CO$_2$ to the atmosphere contain $^{14}$C at near ambient atmospheric concentrations. Thus, precise measurements of the radiocarbon content of atmospheric CO$_2$ ($^{14}\Delta CO_2$) provide an excellent tracer for recently added fossil fuel CO$_2$. The expected signal, expressed as a deviation from a globally well-mixed background value, is $-2.8$ permil ($\delta$) in $^{14}\Delta CO_2$ for each part per million (ppm) of fossil fuel CO$_2$ added (Turnbull et al., 2006). $^{14}CO_2$ has been applied successfully as a fossil fuel CO$_2$ tracer at the local and regional scales where fossil fuel contributions are relatively large and uncertainties associated with atmospheric transport can be ignored (Turnbull et al., 2006; Levin et al., 2003; Meijer et al., 1996; Zondervan and Meijer, 1996). However, if the approach is to be successfully applied at larger spatial scales, all potential
sources of \( \Delta^{14}\text{CO}_2 \) variability and their transport must be considered.

Previous studies of the time evolution of \( \Delta^{14}\text{CO}_2 \) (Levin and Kromer, 1997, 2004; Manning et al, 1990; Nydal et al., 1983) have shown that production of \( ^{14}\text{C} \) from atmospheric nuclear weapons testing (“bomb \( ^{14}\text{C} \)) led to a near doubling of atmospheric \( ^{14}\text{CO}_2 \) in the early 1960s (Levin et al., 1985), an increase of 900‰ in \( \Delta^{14}\text{CO}_2 \). Following the cessation of most atmospheric nuclear weapons testing in 1963 ongoing isotopic exchange with the oceans and terrestrial biosphere has reduced \( \Delta^{14}\text{CO}_2 \) of the atmosphere to near pre-bomb values. However, because of the relatively short residence time of carbon in the biosphere (about 10 years), the biosphere is now believed to be slightly enriching the atmosphere in \( ^{14}\text{CO}_2 \) (Randerson et al., 2002).

Initial decreases in \( \Delta^{14}\text{CO}_2 \) in the mid-1960s of 80‰ yr\(^{-1} \) were dominated by the very large disequilibrium between the atmosphere and the oceans (and to a lesser extent, the terrestrial biosphere). More recently, equilibration between the atmosphere and surface reservoirs has reduced the secular trend to just \( \sim 5\%e \text{yr}^{-1} \) (Turnbull et al., 2007; Randerson et al., 2002). Fossil fuel \( ^{14}\text{CO}_2 \) emissions, which are currently about 7.5 GtC yr\(^{-1} \) globally (Marland et al., 2006) and are entirely devoid of \( ^{13}\text{C} \), would alone cause a globally averaged decrease in \( \Delta^{14}\text{CO}_2 \) of about 10‰e yr\(^{-1} \). Thus, fossil fuel emissions now dominate the observed secular change, but contributions to \( \Delta^{14}\text{CO}_2 \) from other sources may complicate the interpretation of the spatial distribution.

The gross disequilibrium flux of \( ^{14}\text{C} \)-depleted \( ^{14}\text{CO}_2 \) from the ocean and the analogous \( ^{14}\text{C} \)-enriched flux from the biosphere to the atmosphere are each about half the magnitude of the flux of \( ^{14}\text{C} \)-free \( ^{14}\text{CO}_2 \) from fossil fuel burning and are thus expected to have some influence on global \( \Delta^{14}\text{CO}_2 \) (see Sect. 2.3). For ocean disequilibrium fluxes, the impact on fossil fuel \( ^{14}\text{CO}_2 \) detection using \( \Delta^{14}\text{CO}_2 \) over land is likely to be small because the fossil fuel and \( ^{14}\text{C} \)-depleted ocean sources are geographically separated, with the fossil fuel source almost entirely confined to the Northern Hemisphere land regions and the ocean contribution predominantly in the Southern Hemisphere (Randerson et al., 2002). In contrast, the flux from the biosphere, while small (Turnbull et al., 2006), must be accounted for. Natural cosmogenic production and radioactive decay of \( ^{14}\text{C} \) in the troposphere are also unlikely to deplete the \( \Delta^{14}\text{CO}_2 \) fossil fuel detection capability significantly, since production has a nearly uniform zonal distribution, and decay in the troposphere decreases \( \Delta^{14}\text{CO}_2 \) by only about 0.1‰e yr\(^{-1} \). Exchange with the \( ^{14}\text{C} \)-enriched stratosphere may produce \( \Delta^{14}\text{CO}_2 \) anomalies in the upper troposphere, but the impact of this is likely small within the continental boundary layer (hereafter, CBL), due to the vertical distance from the tropopause to the CBL and the relatively slow vertical mixing of the CBL with the free troposphere. The nuclear reactor \( ^{14}\text{C} \) source also affects the CBL and thus needs to be accounted for (see Sect. 2.3).

While there have been numerous studies of the temporal change in \( \Delta^{14}\text{CO}_2 \), only a few observations of the synoptic spatial distribution have been made (Hsueh et al., 2007; Rozanski et al., 1995). Here we present \( \Delta^{14}\text{CO}_2 \) results from a transect across Russia from Moscow (55° 44’ N, 37° 33’ E) to Khabarovsk (48° 33’ N, 135° 6’ E) as part of the Trans-Siberian Observations Into the Chemistry of the Atmosphere 8 (TROICA-8) expedition from 19 March–1 April 2004. These observations represent a transect through a large expected longitudinal \( \Delta^{14}\text{CO}_2 \) gradient as European fossil fuel \( ^{14}\text{CO}_2 \) emissions are dispersed by the westerly air stream across Eurasia. We examine the spatial distribution of \( \Delta^{14}\text{CO}_2 \) for this region, and the impact of the various sources on it, showing that fossil fuel \( ^{14}\text{CO}_2 \) emissions must be the dominant control on the observed spatial gradient.

Several trace gas species have been used or proposed as fossil fuel \( ^{14}\text{CO}_2 \) tracers, based on estimates of the ratio of tracer to \( ^{14}\text{CO}_2 \) emissions (which may vary in space and time) and assuming co-location of the tracer and fossil fuel \( ^{14}\text{CO}_2 \) sources. Such tracers have the advantage over \( \Delta^{14}\text{CO}_2 \) in ease and lower cost of measurement, although their empirical correlation with fossil fuel \( ^{14}\text{CO}_2 \) emissions appears to be weaker than for \( \Delta^{14}\text{CO}_2 \) (Turnbull et al., 2006). We therefore compare measurements of the prospective tracers carbon monoxide (CO), sulphur hexafluoride (SF\(_6\)), perchloroethylene (PCE) and chloroform with the \( \Delta^{14}\text{CO}_2 \) observations in order to evaluate their performance on the continental scale.

We also compare our observations to atmospheric \( \Delta^{14}\text{CO}_2 \) simulated by the TM5 atmospheric transport model (Krol et al., 2005). This allows us to test the consistency of model transport and emissions with our observations. As large-scale fossil fuel emissions are believed to be known within 10–15% (Marland et al., 2006), differences between simulated and observed \( \Delta^{14}\text{CO}_2 \) are more likely to result from model representation of atmospheric transport. In particular, the parameterization of vertical mixing is a major uncertainty in atmospheric transport models (Yang et al., 2007; Stephens et al., 2007; Peters et al., 2004; Denning et al., 1999) and we therefore evaluate the impact of changing vertical diffusion on the modeled \( \Delta^{14}\text{CO}_2 \) horizontal gradient. We also test the sensitivity of the simulated east-west gradient to the magnitude of European fossil fuel emissions.

2 Methods

2.1 Sample collection and tracer concentration measurements

Air samples were obtained from an electric train based platform on the Trans-Siberian railway from Moscow (55° 44’ N, 37° 33’ E) to Khabarovsk (48° 33’ N, 135° 6’ E) between 19 March and 24 March 2004 and the return journey from 27 March to 1 April 2004. The laboratory wagon was coupled directly behind the electric locomotive of a regular passenger train.
train for the entire 8549 km (each way) journey. Outside
air was drawn from the leading top edge of the laboratory
wagon, about four meters above the rails, through 10 m of
six mm OD Synflex tubing to a diaphragm pump. Samples
were collected from this in 3 L electro-polished stainless steel
flasks by flushing for 10 min at 2–4 L min$^{-1}$ (flasks were fit-
ted with inlet and exhaust valves, with the former including
an internal dip tube to allow turbulent flushing of the flask
interior) followed by filling to a pressure of 3 atmospheres
over a fill time of about seven minutes (Crutzen et al., 1998).

These flasks were analyzed for multiple species, including
several halocarbons, and these measurement methods are
described elsewhere (Montzka et al., 1993; Belikov et al.,
2006; Tarasova et al., 2006). $\Delta^{14}$CO$_2$ measurements were
also made from these flasks and are described below.

In situ measurements of 12 different trace gas species,
including CO and SF$_6$, were made using the four chan-
nel Airborne Chromatograph for Atmospheric Trace Species
(ACATS-IV), using electron capture detection (Hurst et al.,
2004; Romashkin et al., 2001). The measurement interval for
the SF$_6$ (and N$_2$O) chromatographic channel was 70 s, while
CO (and CH$_4$, H$_2$) were assayed every 140 s. To compare
with the flask measurements, we identified the in situ mea-
surements made while each flask was filled. Typically, 2–3
in situ measurements of CO and 4–7 in situ measurements
of SF$_6$ were made during each flask-filling period, and these
were averaged to obtain a single data point. Uncertainties
were assigned as the larger of the nominal measurement pre-
cision, or the one-sigma standard deviation of the averaged
results.

2.2 $\Delta^{14}$CO$_2$ sample selection and measurement

In order to characterize the $\Delta^{14}$CO$_2$ signal arising from re-
gional emissions and transport, samples with readily de-
tectable contributions from local city sources must be iden-
tified and avoided. We used in situ CO measurements for
this purpose, setting the local pollution threshold arbitrarily
at 250 parts per billion (ppb) (compared to baseline values
of CO for this transect varying from 227 ppb in the west to
156 ppb in the east). Only flasks corresponding with in situ
CO measurements below 250 ppb were selected for $\Delta^{14}$CO$_2$
analysis (Fig. 1).

Methods for sample preparation, AMS measurement and
uncertainty estimates are described in detail in Turnbull et
al. (2007). Briefly, at the University of Colorado Labora-
tory for AMS Radiocarbon Preparation and Research, CO$_2$
was cryogenically extracted from the air samples and then
split into two aliquots prior to reduction to graphite. Each
graphite sample typically contained 0.6 mg C, and was ana-
yzed for $^{14}$C content at the University of California, Irvine
accelerator mass spectrometry (AMS) facility. Results are
reported as $\Delta^{14}$C, the per mil deviation of the sample $^{14}$C
content from the absolute radiocarbon standard, corrected for
isotopic fractionation and radioactive decay (Stuiver and Po-
lach, 1977). Single sample uncertainties range from 1.8‰ to
2.8‰, and are the larger of the reported AMS counting sta-
tistical uncertainty and the one-sigma standard deviation of
repeated measurements of an in-house CO$_2$-in-air standard.
Of the 23 flasks collected, 20 were replicated; the pair differ-
ences are shown in Fig. 2. The single-sample uncertainties
appear to be consistent with the observed pair differences.
(the normalized chi-squared value is 1.34; note that in the case where the uncertainties vary from sample to sample, the chi-squared test is a better test of the uncertainties than the root mean square). In one case, we measured $^{14}$CO$_2$ in four simultaneously collected flasks, and there is no significant difference between the four results.

Empirical evidence has suggested that undried CO$_2$ measurements from stainless steel flasks may be biased high, on the order of 1 ppm (T. Conway, personal communication). Qualitative comparison with CO$_2$ measurements on glass flasks collected during the same expedition, but not at the same times, suggests that CO$_2$ values in the stainless steel flasks are enriched in CO$_2$ by less than 2 ppm (versus the atmospheric CO$_2$ loading of 383 ppm in spring 2004 at high northern latitudes (Tans and Conway, 2005)). This amount of CO$_2$ is unlikely to alter $^{14}$CO$_2$ by more than 0.5‰ (even assuming a 100‰ $^{14}$CO$_2$ difference between the flask CO$_2$ source and the atmospheric sample), substantially smaller than the measurement uncertainty.

2.3 TM5 model description

We compare the TROICA $^{14}$CO$_2$ observations with two model runs of the TM5 atmospheric transport model in which we have specified and transported CO$_2$ and $^{14}$CO$_2$ emissions. Model resolution is 6°×4°, with 25 vertical layers, and the model is sampled at three hourly resolution to allow comparison with observations. Net oceanic CO$_2$ fluxes are derived from $\Delta p$CO$_2$ (Takahashi et al., 2002), using the Wanninkhof (1992) gas exchange formulation and 10 m winds. Net fluxes from the terrestrial biosphere taken from the CASA biogeochemical model (Gurney et al., 2002). Annual global total fossil fuel CO$_2$ emissions are from Marland et al. (2006) until 2003 and linearly extrapolated to 2004. This annual global total flux is spatially distributed by extrapolating the trend in the 1995–2000 spatial distributions of fossil fuel emissions from the 1°×1° EDGAR inventories (http://www.rivm.nl/edgar/; Olivier and Berdowski, 2001). Additionally, a seasonal cycle based on the Blasing et al. (2005) analysis for the United States, which has ~20% higher emissions in winter than in summer, is imposed on the global emissions.

The modeled $^{14}$CO$_2$ budget is defined as

$$^{14}\text{CO}_2(\text{modeled}) = ^{14}\text{CO}_2bg + ^{14}\text{CO}_2ff + ^{14}\text{CO}_2th + ^{14}\text{CO}_2o + ^{14}\text{CO}_2cp$$

(1)

where $^{14}$CO$_2$(modeled) is the modeled $^{14}$CO$_2$ mixing ratio for a given grid point. $^{14}$CO$_2bg$ is the background atmospheric $^{14}$CO$_2$ mixing ratio, which is a single value we estimate at the start of our model run from the Northern Hemisphere $^{14}$CO$_2$ records of Levin and Kromer (2004). $^{14}$CO$_2ff$ is the $^{14}$CO$_2$ mixing ratio at that grid point due to fossil fuel emissions, and is, by definition, zero, as fossil fuels contain no $^{14}$C. $^{14}$CO$_2th$, $^{14}$CO$_2o$ and $^{14}$CO$_2cp$ are the heterotrophic respiration, ocean and cosmogenic production $^{14}$CO$_2$ source mixing ratios and are described in detail below. $^{14}$CO$_2$
mixing ratios are then combined with the separately transported total CO$_2$ mixing ratios to obtain $\Delta^{14}$CO$_2$.

The $\Delta^{14}$CO$_2$ terrestrial disequilibrium-flux term is estimated using pulse-response functions from the CASA biosphere model (Thompson and Randerson, 1999) and the time history of atmospheric $\Delta^{14}$CO$_2$ (Levin and Kromer, 2004). The CASA pulse response functions are generated by allowing uptake of carbon for one year (as NPP) and then following its monthly release as heterotrophic respiration for 200 years. The result is an age distribution of heterotrophic respiration for each 1$^\circ$ x 1$^\circ$ land region, which is then convolved with the atmospheric $\Delta^{14}$CO$_2$ history to give the $\Delta^{14}$CO$_2$ of the respiratory flux. Given the terrestrial residence time of decades, we do not account for radioactive decay, resulting in a slight overestimate in the flux term (of less than 5%). The difference between the $\Delta^{14}$CO$_2$ of the respiratory flux and the current atmosphere is the disequilibrium, which when multiplied by the heterotrophic respiration flux gives the disequilibrium flux, or gross biospheric $\Delta^{14}$CO$_2$ flux.

For 2004, our estimated global total biospheric flux to the atmosphere is 370 mol $\Delta^{14}$CO$_2$ (3.9% yr$^{-1}$ increase in $\Delta^{14}$CO$_2$ if distributed globally), most of which is in the tropics. The gross ocean-to-atmosphere $\Delta^{14}$CO$_2$ flux is estimated using climatological surface ocean $p$CO$_2$ (Takahashi et al., 2002) as an assembly of surface ocean $\Delta^{14}$C of dissolved inorganic carbon (DIC) measurements from the GLODAP project (cdiac.ornl.gov/oceans/glodap/Glodap_home.htm), and the gas transfer formulation of Wanninkhof (1992). The flux is calculated on a monthly basis on a 4$^\circ$ x 5$^\circ$ grid of ice-free ocean areas. Compared to previously published results (e.g. Takahashi et al., 2002), which used the 0.995 sigma level winds ($\sim$40 m above sea level), using 10 m winds results in a less negative global disequilibrium flux, mainly due to lower wind speeds in the Southern Ocean. The calculated disequilibrium flux varies interannually, but only as a result of the changing atmosphere. Given that the GLODAP product is not a climatology, but instead consists of surface ocean measurements taken over more than a decade, there is no easy way of extrapolating the values to 2004. Nonetheless, it is likely that the dominant cause of changing disequilibrium is the atmospheric $\Delta^{14}$CO$_2$ and not the surface ocean values. For 2004, the estimated global total oceanic flux to the atmosphere is $-325$ mol $\Delta^{14}$CO$_2$ ($-3.4%$ yr$^{-1}$ if distributed globally), most of which is in the Southern Ocean.

Cosmogenic production of $^{14}$C occurs in both the stratosphere and troposphere and the total production of 530 mol yr$^{-1}$ is distributed horizontally with maximum production at the magnetic poles and a minimum at the equator as described by Masarik and Beer (1999). Production is scaled vertically to agree with vertical distribution estimates from Masarik and Beer (1999) and Lal (1988) such that there is a maximum near the tropopause with a nearly linear decay to zero production at the surface and 60 km, yielding roughly equal production in the stratosphere and upper troposphere. This vertical distribution of production reflects the balance between cosmic ray flux, which attenuates from the top of the atmosphere, and atmospheric density.

Input meteorological driver data for TM5 is derived from the ECMWF model (www.ecmwf.int; Gibson et al., 1999), and for the simulations here, meteorology for March and April 2004 is used. TM5 transport is described more fully by Krol et al. (2005).

Production of $\Delta^{14}$CO$_2$ from the nuclear power industry is estimated to be 45–80 mol $^{14}$C yr$^{-1}$ (equating to less than 1% e yr$^{-1}$ in $\Delta^{14}$CO$_2$ if distributed globally) (UNSCEAR, 2000) and is ignored in the model, as it is small and there is considerable uncertainty in both the magnitude and temporal distribution. Ignoring this term introduces a small bias, especially in the temporal evolution of the modeled $\Delta^{14}$CO$_2$, and also means that we cannot expect our model simulation to reproduce observations influenced by nuclear reactor emissions near the TROICA route.

Gross $\Delta^{14}$CO$_2$ fluxes into the biosphere and ocean are not included because $\Delta^{14}$CO$_2$ accounts for natural mass-dependent fractionation (Stuiver and Polach, 1977) and these fluxes are therefore necessarily zero. Autotrophic respiration is also assumed to have a zero effect, since the short residence time (of a few months) results in $\Delta^{14}$CO$_2$ values almost identical to that of the atmosphere.

For any given emissions at the surface, the model representation of trace gas concentration within the CBL is expected to be sensitive to the strength of simulated or specified vertical mixing (i.e., ventilation of the CBL). Comparison of observed mixing ratios of both SF$_6$ (Peters et al., 2004; Denning et al., 1999) and CO$_2$ (Yang et al., 2007; Stephens et al., 2007) with their simulated values suggest that vertical mixing may be underestimated in some atmospheric transport models, including TM5. To examine this further, we use two different model constructions: (a) the standard TM5 vertical mixing scheme (TM5std), which includes parameterization of convection and vertical diffusion (Krol et al., 2005); and (b) a “fast mixing” scheme (TM5fast), where surface emissions are nearly instantaneously mixed up to the height of the model boundary layer. In the latter, vertical diffusion below the height of the model boundary layer is set to 1000 m$^2$ s$^{-1}$, compared to typical values of order 50 m$^2$ s$^{-1}$ (mid-day, summer) and $<1$ m$^2$ s$^{-1}$ (night). This fast mixing scheme is not intended to present a realistic mixing scheme, but rather is a simple implementation of mixing to test for differences (Peters et al., 2004).

## 3 Results and discussion

### 3.1 $\Delta^{14}$CO$_2$ results

The $\Delta^{14}$CO$_2$ results are shown in Fig. 3 and are available for digital download at ftp://ftp.cmdl.noaa.gov/ccg/co2c14. Of the 22 sampling locations between 37° E and 124° E (including one location where two pairs of flasks were collected
In order to screen for such local enrichments we used the values 250‰ above background (Magnusson et al., 2004). The Russian RBMK reactor is elevated by up to 20 000‰, with typical enrichments may occur close to nuclear power plants, and highly-efficient fossil fuel pollution sources that emit 14C-free CO2, but very little CO.

While global production of 14C in nuclear power plants is small compared to other 14C sources (increasing the global mean 14CO2 by less than 1‰ yr−1), substantial local 14CO2 enrichments may occur close to nuclear power plants. The magnitude of the 14CO2 source is dependent on the reactor type. Pressurized water reactors (PWR) predominantly produce 14C as 14CH4, which is well-mixed in the atmosphere by the time it oxidizes to 14CO2. Other reactor types, including boiling water reactors (BWR) and the Russian RBMK light-water cooled, graphite-modernated reactors produce 14C mostly as 14CO2 (UNSCEAR, 2000). 14CO2 values 50–300‰ over background have been measured within 2 km of two German BWR reactors (Levin et al., 1988) and plant material around the Ignalina, Lithuania RBMK reactor is elevated by up to 20 000‰, with typical values 250‰ above background (Magnusson et al., 2004). In order to screen for such local enrichments we used the HYPLIT back-trajectory model (Draxler and Rolph, 2003), obtaining back-trajectories for each sampling location and time (Fig. 4). From this, we identified three samples that received air that may have been influenced by local nuclear reactor effluent (within 200 km of the HYPLIT 48-h back trajectory line, and excluding PWR reactors which should not affect 14CO2 measurements). These flagged samples are excluded from further analysis.

Incursions of stratospheric air, which is enriched in 14C by about 100‰ relative to the troposphere (Nakamura et al., 1994), may also produce anomalously high 14CO2 values. Such incursions would also be expected to cause depletion in nitrous oxide (N2O), methane (CH4) and CO, which are all produced in the troposphere and destroyed in the stratosphere. In situ measurements of these three species do not indicate any significant depletions. We also examined the vertical component of the HYPLIT back-trajectories, which do not indicate stratospheric incursions. We conclude that this process has not significantly influenced our dataset.

In order to obtain the regionally representative background signal, we avoid samples taken very close to localized fossil fuel sources. In selecting samples for measurement, we screened for high CO values to avoid obviously polluted samples. However, high efficiency combustion can produce fossil fuel CO2 with very little accompanying CO emission (e.g. in the United States, power plants have very low CO emissions of 0.1 ppb CO/ppm CO2 (USEPA, 2004)). Three samples were collected within 20 km of large population centers (Novosibirsk, population 1 200 000; Irkutsk, population 750 000; and Ulan-Ude, population 400 000) and these were flagged as potentially influenced by local pollution sources.

During the winter at 50–60° N latitude, biospheric respiration is small, but we estimate its impact as follows: the respiration 14C value was assumed to be 120‰ (from a 10 year mean soil turnover time (Trumbore, 1997) and the atmospheric 14CO2 history (Levin and Kromer, 2004)), with a CO2 flux of 0.5 µmol m−2 s−1 which was allowed to build up over several days within a boundary layer 1000 m deep. This results in an increase in 14CO2 in the boundary layer of less than 0.2‰. This estimate is in agreement with results from both of our model runs using the CASA biosphere model input (Randerson et al., 1997, described in Sect. 2.3), which indicate that respiration contributes less than 0.2‰ to the modeled 14CO2 gradient, which is not significant relative to the 14C measurement uncertainties.

Biomass and biofuel combustion could also contribute to changes 14CO2. Biomass combustion is usually less efficient than fossil fuel combustion, with emission ratios of 60–250 ppb CO/ppm CO2 (Andreae and Merlet, 2001) so that we would expect to see high CO values if biomass combustion was contributing to CO2 and hence to 14CO2. We screened for CO values higher than 250 ppb, so that the maximum elevation in CO is 80 ppb above the lowest CO value of 170 ppb observed during times when flasks were being filled for 14CO2. Assuming a 14C value of 120‰ for biomass combustion, and the most efficient combustion ratio of 60 ppb CO/ppm CO2, the contribution from biomass burning to the 14CO2 value is at most 0.2‰.
We noted earlier that the impact of ocean exchange on $\Delta^{14}$CO$_2$ over Eurasia is expected to be small and that cosmogenic $^{14}$C production is distributed evenly by longitude. It follows then that since the local influences of nuclear reactor effluent can be easily identified, the remaining $\Delta^{14}$CO$_2$ observations must predominantly reflect the influence of fossil fuel emissions.

Figure 5 shows the “clean air” dataset (solid points, each point is the average of the two measurements from that flask) along with the samples flagged as influenced by either nuclear reactor effluent or by local city pollution sources. We note two anomalously high values amongst the retained data, at 38° E and 106° E. These values may be simply due to statistical uncertainty, or may be due to real (but otherwise unidentified in our screening protocols) atmospheric variability in $\Delta^{14}$CO$_2$ values; in either case, these points are valid and must be considered in the remainder of our analysis.

$\Delta^{14}$CO$_2$ increases by 5.0±1.0‰ across the transect from 40° E to 120° E (Fig. 5) and this difference is significant at the 99% confidence level. This is consistent with a $(^{14}$C-free) fossil fuel CO$_2$ source in the western part of the transect, which is gradually dispersed by atmospheric transport across Eurasia. The observed isotopic change implies a gradient of 1.8 ppm of fossil fuel derived CO$_2$ (assuming a −2.8‰ change in $\Delta^{14}$CO$_2$ per ppm of fossil fuel CO$_2$ added). $\Delta^{14}$CO$_2$ measurements from Niwot Ridge, Colorado, USA (NWR, 40.05° N, 105.58° W, 3475 m a.s.l.) are believed to represent relatively clean free tropospheric air over North America and, likely, the Northern Hemisphere mid-latitudes in general. NWR observations for 3 sampling dates during the time of the TROICA-8 campaign give a mean $\Delta^{14}$CO$_2$ value of 66.8±1.3‰ (grey bar in Fig. 5) (Turnbull et al., 2007). The Eastern Siberian part of the TROICA transect shows values (62.8±0.5‰) most similar to the NWR value, consistent with an easterly dilution of the fossil fuel content in boundary layer air away from the primary source, but suggesting that some influence from the European fossil fuel CO$_2$ source remains in the Eastern Siberian air mass.

3.2 Comparison with correlate tracer species

CO is co-emitted with CO$_2$ during fossil fuel combustion, and if the emission ratio of CO to CO$_2$ ($R_{CO}$) is known, it can be used to estimate fossil fuel emissions (Levin and Karstens, 2007; Turnbull et al., 2006; Potosnak et al., 1999; Bakwin et al., 1997; Wofsy et al., 1994). In order to examine the potential correlation of measured CO with fossil fuel emissions, the CO observations made during the TROICA transect were compared with the $\Delta^{14}$CO$_2$ observations, using only those CO observations corresponding to the time periods of samples in the cleaned $\Delta^{14}$CO$_2$ dataset (Fig. 6).

The CO observations show a decline in value from west to east, consistent with a CO source in the west being gradually diluted by mixing and CO destruction as the air mass moves eastwards. The longitudinal dependence of the CO observations is roughly the opposite of that for $\Delta^{14}$CO$_2$, and the slope of the relationship is $-7.9±1.9$ ppb/%, implying an $R_{CO}$ value of 22.3±5.3 ppb CO/ppm CO$_2$ (given $-2.8%/ppm$ of fossil fuel CO$_2$). This is consistent with inventory-based estimates of $R_{CO}$ for this region (Olivier and Berdowski, 2001). However, the correlation between the two species is not particularly strong ($r^2=0.44$, $p=0.005$). This may be due in part to difficulties in matching the sometimes
rapidly varying CO measurements (made every 140 s) with the $\Delta^{14}$CO$_2$ measurements from flasks (collected over about seven minutes). The strongest variability in the CO values occurs in the west, suggesting that CO measurements can provide a reasonable estimate of fossil fuel emissions far from the source region, where atmospheric transport and mixing has resulted in a regionally representative emissions ratio. Close to the source region other sources of CO and/or variability in $R_{CO}$ appear to confound the relationship between CO and fossil fuel CO$_2$. We also note that the usefulness of CO as a tracer for fossil fuel CO$_2$ in Siberia is likely to be limited to winter and spring when destruction of CO by OH and production by biomass burning and biogenic hydrocarbon oxidation is low.

SF$_6$, which is entirely anthropogenic and emitted to the atmosphere via leaks from electrical switching equipment, has also been used as a fossil fuel CO$_2$ tracer (Hurst et al., 2006; Bakwin et al., 1997). On regional scales, SF$_6$ does not appear to perform well as a fossil fuel CO$_2$ tracer, probably because SF$_6$ and fossil fuel CO$_2$ emissions are not well correlated in space (Turnbull et al., 2006; Rivier et al., 2006) (on larger scales, the assumption of co-location of SF$_6$ and fossil fuel CO$_2$ sources may have greater validity). There is no statistically significant east-west difference in the observations (Fig. 6c). The variation amongst the observations, which is $\pm0.03$ ppt at one-sigma, lies within measurement uncertainty of 0.06–0.09 ppt for this experiment. This also holds for the entire set of in situ SF$_6$ observations made during this transect (mean 5.59$\pm0.07$ ppt), excluding 23 measurements in the vicinity of the city of Perm, where SF$_6$ is apparently produced. This is consistent with results from SF$_6$ observations during a previous TROICA transect in 1996 (Crutzen et al., 1998), but is in contrast to continental scale observations for North America for 2003, where much larger variability in SF$_6$ mixing ratios was observed (Hurst et al., 2006).

Perchloroethylene (1,1,2,2-tetrachloroethene, C$_2$Cl$_4$, “PCE”) is widely used as a dry cleaning solvent, and has been used as a tracer for polluted air masses (Barnes et al., 2003; Gloor et al., 2001). It has been proposed as a tracer for fossil fuel CO$_2$, (Rivier et al., 2006; Wofsy et al., 1994), but has not been well evaluated for this purpose. Concentrations of PCE were measured in the same flask samples as the $\Delta^{14}$CO$_2$ measurements. The overall correlation between PCE and $\Delta^{14}$CO$_2$ is weak for this dataset ($r^2=0.16$, $p=0.13$, Fig. 6d). The observed spatial pattern of PCE is nonetheless similar to that for CO, with very little variability and generally lower mixing ratios in the eastern part of the transect versus larger mixing ratios and variability in the west, near probable source areas. The two flasks with highest PCE values (13.1 and 13.5 ppt) also contain elevated levels of
Fig. 6. Comparison of $\Delta^{14}$CO$_2$ measurements (panel (a)) with: (b) ACATS CO measurements from the same time period as flask filling; (c) ACATS SF$_6$ measurements; (d) PCE measured in the same flasks. Uncertainties shown are either the measurement uncertainty (PCE and $\Delta^{14}$CO$_2$) or the 1-sigma standard deviation of the individual measurements made during the flask filling time (CO and SF$_6$). The error bars for PCE are smaller than the symbol size. Only the sampling locations considered in the cleaned $\Delta^{14}$CO$_2$ dataset are included.

many other anthropogenic trace gases, including HCFC-22, HFC-134a, benzene and toluene (data not shown), implying that much of the variability in the western part of the transect may be due to local anthropogenic trace gas sources unrelated to fossil fuel sources.

Numerous halocarbon species were also measured in the same flasks. Since most of these species are anthropogenic, they may be useful as fossil fuel CO$_2$ tracers. Of the 27 species analyzed, only chloroform (trichloromethane, CHCl$_3$) shows any correlation consistent with a co-location with fossil fuel sources, at least in this data from Russia (data not shown). A larger dataset would be required to evaluate the chloroform source, and whether its atmospheric signature could be widely applied as a fossil fuel tracer.

3.3 Comparison with atmospheric transport model

Simulated $\Delta^{14}$CO$_2$ values were extracted from the two TM5 model runs for grid cells and times corresponding to the TROICA samples, as well as those corresponding to NWR sampling times. The simulated NWR values are 67.0‰ and 67.4‰ for TM5std and TM5fast, respectively, in agreement with the observed NWR value of 66.8±1.3‰ for the same time period.

The simulated $\Delta^{14}$CO$_2$ values for the TROICA transect are shown in Fig. 5. The westernmost sample, taken at 56.1° N, 37.9° E, 40 km from central Moscow, appears to be influenced by model representation error, due to the very strong emissions from Moscow (population 8,000,000) which are injected into the same model gridbox. With a horizontal model resolution of 6°×4°, errors of this size near sources are not surprising. The modeled results are otherwise broadly consistent with the observed increase in $\Delta^{14}$CO$_2$ from west to east. The shape of the observed gradient is also well captured by the model, with the areas of steep gradient between 40–60° E and again from about 85–100° E, and flattening in the middle and far eastern regions of the transect. This is reflected in the good correlation between the observations and the modeled $\Delta^{14}$CO$_2$ values ($r$=0.80 and 0.82 for TM5std and TM5fast, respectively).

It is apparent from Fig. 7, where the contribution of each $^{14}$CO$_2$ source to the spatial gradient is shown individually, that the modeled spatial gradient is due almost entirely (90%) to fossil fuel CO$_2$ emissions. The oceans and cosmogenic production, as discussed earlier, contribute very little to the longitudinal gradient. There is greater variability in the terrestrial biospheric contribution, but overall it contributes only 0.1‰ to the gradient.
Despite the overwhelming influence of fossil fuel CO₂ emissions, the magnitude of the modeled gradient is only weakly sensitive to the modest uncertainties in the fossil fuel emissions flux. Increasing the global fossil fuel CO₂ emissions by 10% increased the modeled west-east gradient by only 0.6‰ in TM5std, and 0.4‰ in TM5fast. Similarly, when the model runs were repeated with seasonally flat fossil fuel emissions (but with the same annual emission total), there was only a negligible difference in the modeled results. This is most likely due to the fact that in March and April the seasonally adjusted fossil fuel flux is very close to the annual mean values.

The magnitude of the west-east gradient is slightly overestimated in TM5std compared to the observations, by a factor of 1.2±0.2. This is consistent with a comparison of SF₆ observations from an earlier TROICA expedition (in 1996) with the TransCom suite of models, which indicated that most models, including the precursor of TM5 (TM3), overestimated the observed SF₆ longitudinal gradient, implying that the modeled vertical mixing was too slow (Denning et al., 1999). When unrealistically fast vertical mixing is applied, in the TM5fast simulation, the Δ¹⁴CO₂ values in the west, near the fossil fuel source, are about 2‰ lower than in TM5std, leading to a reduction in the simulated gradient of 35%, and slightly underestimating the observed gradient by a factor of 0.8±0.1.

These findings suggest that with sufficient observations, it may be possible to improve constraints on model vertical mixing parameterizations using Δ¹⁴CO₂ observations, providing a complementary diagnostic to SF₆, which has previously been used for this purpose. While a much larger suite of SF₆ observations is available, Δ¹⁴CO₂ has the advantage of better-constrained source strength, with fossil fuel emissions being known to within 10–15% at the continental scale (Marland et al., 2006). In contrast, the SF₆ source distribution and strength is much less well constrained, especially for Russia, with uncertainties estimated to be 50% (Olivier et al., 2001).

4 Conclusions
We obtained a spatial distribution of Δ¹⁴CO₂ across Eurasia for March–April 2004. Local pollution sources of ¹⁴C-free fossil fuel CO₂ and nuclear reactor produced ¹⁴CO₂ produce locally lower or higher Δ¹⁴CO₂ values, respectively. Use of back-trajectories allowed us to identify these locally influenced samples, and obtain a background continental boundary layer dataset for this region. The magnitude of the Δ¹⁴CO₂ gradient is consistent with the dispersion of fossil fuel CO₂ emissions produced in Europe, and atmospheric transport across northern Asia dispersing and diluting the fossil fuel plume.

Comparison of the Δ¹⁴CO₂ measurements with potential fossil fuel correlate tracer species shows that while several species may be useful fossil fuel tracers on large scales, they exhibit considerable variability in regions close to significant sources. This is likely because, in contrast to Δ¹⁴CO₂ which is directly related to the fossil fuel emissions, correlate tracer emissions may not be entirely co-located with the fossil fuel source. This variability must be accounted for if these correlate tracer species are to be used as fossil fuel tracers.

The Δ¹⁴CO₂ distribution simulated using TMS shows gradients across the TROICA transect similar to that determined from the observations, and indicate that the Δ¹⁴CO₂ gradient is almost entirely due to fossil fuel CO₂. While the gradient is weakly sensitive to the (modest) uncertainty in fossil fuel emissions, ad hoc changes in the model mixing parameterization result in much larger changes in the gradient, demonstrating the potential for Δ¹⁴CO₂ observations over the continents to constrain vertical mixing in atmospheric transport models.

For this dataset, the model uncertainties are larger than the fossil fuel emission uncertainties, but this may not be true for all regions, especially when sampling is closer to loci of fossil fuel emissions and where fossil fuel emissions are changing rapidly and are more uncertain. Our results do suggest that accurate quantification of fossil fuel emissions using ¹⁴C observations and model inversion techniques will be difficult in more remote regions until model transport is better constrained. Methods to constrain fossil fuel emissions from atmospheric measurements of ¹⁴CO₂ (or other tracers) that are less dependent on model transport (e.g. Levin and Rödenbeck, 2007) are likely to be more useful in the short term.

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