# Seasonal, synoptic, and diurnal-scale variability of biogeochemical trace gases and $O_2$ from a 300-m tall tower in central Siberia

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Received 27 February 2008; revised 19 August 2008; accepted 16 September 2008; published 23 December 2008.

[1] We present first results from 19 months of semicontinuous concentration measurements of biogeochemical trace gases ($CO_2$, CO, and $CH_4$) and $O_2$, measured at the Zotino Tall Tower Observatory (ZOTTO) in the boreal forest of central Siberia. We estimated $CO_2$ and $O_2$ seasonal cycle amplitudes of 26.6 ppm and 134 per meg, respectively. An observed west-east gradient of about −7 ppm (in July 2006) between Shetland Islands, Scotland, and ZOTTO reflects summertime continental uptake of $CO_2$ and is consistent with regional modeling studies. We found the oceanic component of the $O_2$ seasonal amplitude (Atmospheric Potential Oxygen, or APO) to be 51 per meg, significantly smaller than the 95 per meg observed at Shetlands, illustrating a strong attenuation of the oceanic $O_2$ signal in the continental interior. Comparison with the Tracer Model 3 (TM3) atmospheric transport model showed good agreement with the observed phasing and seasonal amplitude in $CO_2$; however, the model exhibited greater $O_2$ (43 per meg, 32%) and smaller APO (9 per meg, 18%) amplitudes. This seeming inconsistency in model comparisons between $O_2$ and APO appears to be the result of phasing differences in land and ocean signals observed at ZOTTO, where ocean signals have a significant lag. In the first 2 months of measurements on the fully constructed tower (November and December 2006), we observed several events with clear vertical concentration gradients in all measured species except CO. During "cold events" (below −30°C) in November 2006, we observed large vertical gradients in $CO_2$ (up to 22 ppm), suggesting a strong local source. The same pattern was observed in $CH_4$ concentrations for the same events. Diurnal vertical $CO_2$ gradients in April to May 2007 gave estimates for average nighttime respiration fluxes of 0.04 ± 0.02 mol C $m^{-2}$ $d^{-1}$, consistent with earlier eddy covariance measurements in 1999–2000 in the vicinity of the tower.

**Citation:** Kozlova, E. A., A. C. Manning, Y. Kisilyakhov, T. Seifert, and M. Heimann (2008), Seasonal, synoptic, and diurnal-scale variability of biogeochemical trace gases and $O_2$ from a 300-m tall tower in central Siberia, *Global Biogeochem. Cycles*, *22*, GB4020, doi:10.1029/2008GB003209.

## 1. Introduction

[2] Scientific research worldwide provides more and more evidence that recent climatic changes on Earth are the consequences of human-induced fossil fuel burning and land use change. In addition to already existing alterations in atmospheric composition, scenarios for the 21st century envisage even more rapid and abrupt changes [*Denman et al.*, 2007; *Prentice et al.*, 2001]. The major driver of these changes is the increasing concentrations of infrared-active gases (so-called greenhouse gases (GHGs), $CO_2$, $CH_4$, $N_2O$, and others), which have been rising since the beginning of the Industrial Era, though at different rates and impacts on the environment. Since the second half of the 20th century a large number of scientific studies have been dedicated to acquiring more knowledge about the accumulation rates of different GHGs in the atmosphere and their interannual and seasonal patterns and variability in order to identify and quantify their anthropogenic and natural sources and sinks. Particularly concerning is the possibility of modifications to sources and sinks induced by a changing climate, thus constituting positive (or negative) feedbacks in the Earth system. Nevertheless, owing to a lack of long-term observations in continental interiors the understanding of such feedbacks and their underlying processes is limited. Thus, model predictions of the future fate of terrestrial carbon in response to global warming show a variety of responses and need further improvement [*Friedlingstein et al.*, 2006].

[3] The continental boreal zone in Siberia represents one of the world's most vulnerable ecosystems. It contains large amounts of carbon stored in forests, wetlands and soils, with a sizable fraction dominated by permafrost. The climate is characterized by an extreme seasonal temperature cycle (up

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0886-6236/08/2008GB003209$12.00

to 70°C range) and large interannual variability. Therefore, the consequences of globally increasing GHG concentrations, further exacerbated by rising temperatures in positive feedback mechanisms, are expected to be particularly significant in Siberia [*Chapin et al.*, 2005; *Yoshikawa et al.*, 2008], with strong and potentially irreversible impacts on local ecosystems. The very large region and large-scale nature of these changes, however, might have a global impact on the carbon cycle.

[4] To learn more about the carbon cycle and its evolution in a midcontinental boreal ecosystem under changing climate, a 300-m tall tower (Zotino Tall Tower Observatory (ZOTTO)) equipped with semicontinuous measurements of $CO_2$, $CH_4$, CO, $N_2O$, and $O_2$ was erected in central Siberia (60.80°N, 89.35°E; 114 m asl). We analyze air from five heights on the tower (4, 52, 92, 227, and 300 m) allowing vertical profiles of these gases to be observed. Measurements are made in situ on a semicontinuous basis, cycling through the five tower heights. We use a paramagnetic technique previously described by *Kocache* [1986] and *Manning et al.* [1999] for high-precision $O_2$ measurements. $CO_2$ is measured by a commercially available NDIR analyzer (Siemens AG, Ultramat 6F), and a gas chromatographic system (6890A, Agilent Technologies) is used for $CH_4$, CO and $N_2O$ measurements. The analytical methodology used to collect and measure all gas species is described in detail by *Kozlova et al.* [2008].

[5] The approach of using preexisting tall towers for continuous atmospheric measurements is relatively recent. Two tall towers in North Carolina and Wisconsin, USA, were equipped (in 1992 and 1994, respectively) for $CO_2$ measurements [*Bakwin et al.*, 1998a] and later (1994–1996) for periods of a few years for measurements of $CH_4$, CO, hydrogen ($H_2$), $N_2O$, chlorofluorocarbons (CFCs), other halocarbons, and $SF_6$ [*Bakwin et al.*, 1997; *Hurst et al.*, 1997] and in 2000 for $O_2$ [*Stephens et al.*, 2007]. Prior to tall tower measurements most long-term atmospheric observations were made from coastal or mountain sites where local source/sink influences are relatively small, leaving terrestrial ecosystems underrepresented in the global carbon observational network [*Tans*, 1993]. Thus, the goal of establishing the midcontinental tall tower stations in Wisconsin and North Carolina was to address this geographic "gap" in the observations. In addition to GHG measurements, surface fluxes of $CO_2$, $H_2O$ and sensible heat were estimated using the eddy covariance method at the Wisconsin tower [*Davis et al.*, 2003]. Flask samples were also collected for measurements of $CO_2$, $CH_4$, $H_2$, CO, $N_2O$, and $SF_6$ [*Bakwin et al.*, 1998a]. The isotopic composition of $CO_2$ was studied using $^{13}C/^{12}C$ measurements to discriminate between different source processes controlling carbon exchange between the land biota and atmosphere [*Bakwin et al.*, 1998b]. In addition, a suite of CFCs, other halocarbons and $SF_6$, owing to their almost purely anthropogenic origin, was used as a tracer for polluted air masses to distinguish between the anthropogenic and natural $CO_2$ emissions [*Bakwin et al.*, 1997].

[6] In Europe, tall tower measurements (for $CO_2$) were first initiated in 1994 in Hegyhatsal, Hungary [*Haszpra*, 1995], and recently, in parallel to our ZOTTO project, GHG observations have been established at eight preexisting tall towers as part of the European Commission–funded Continuous High Precision Tall Tower Observations of greenhouse gases (CHIOTTO) project (described by *Vermeulen et al.* [2004]). The advantage of tall tower measurements is an opportunity to probe (during daytime, mainly in summer) a well mixed part of the atmosphere (the mixed layer), where the influence of local sources/sinks is dampened, thus allowing us to observe the smaller regional and long-term "background" changes in atmospheric composition. The height of the mixed layer varies diurnally and seasonally (with maxima in the daytime and summertime, respectively), and additionally, depends on latitude. The mixed layer is also much more pronounced over the continents, for example, in Siberia, extending from ~200 m up to 2000 m in summer [*Styles et al.*, 2002]. In addition, the homogeneity of the surrounding landscape and topography around ZOTTO will potentially allow for large "footprints" of the tower [*Gloor et al.*, 2001]. In contrast to other tall tower sites, the area around ZOTTO is characterized by low anthropogenic pollution influences, which makes it an excellent location for a midcontinental background station. A brief overview of the role of each of the species measured at ZOTTO in global climate change and our motivations for establishing their long-term continuous monitoring in Siberia is given below.

[7] Precise continuous measurements of $CO_2$, the most important anthropogenic GHG, were initiated 50 years ago at the remote location of Mauna Loa, Hawaii [*Keeling*, 1960]. According to data from the WMO-GAW global greenhouse gas network [*World Meteorological Organization*, 2007], the atmospheric burden of $CO_2$ has increased from 280 ppm in 1800 to 381.2 ppm in 2006, mainly owing to the combustion of fossil fuels and intensive land use changes. Enhanced $CO_2$ uptake by land biota and its dissolution in the oceans, however, slows down the incremental increase of atmospheric $CO_2$ concentrations compared to that predicted on the basis of the amount of fossil fuel emissions alone [*Keeling*, 1995]. In light of the ratified Kyoto Protocol and future international agreements, atmospheric $CO_2$ measurements along with regional source and sink estimates, will become crucial, not only for the scientific community, but also for the general public and policy makers. Our ZOTTO site is situated in the middle of the world's largest continental boreal zone with large amounts of carbon stored in wood, soils (including permafrost) and wetlands [*Shvidenko and Nilsson*, 2003]. The ZOTTO site is also close to the southern border of the permafrost zone, thus continuous measurements of $CO_2$ would allow us to monitor changes in future carbon emissions caused by thawing permafrost, which might occur with the increasing temperature [*Zimov et al.*, 2006]. Carbon emissions from biomass burning in Siberia are another important process, particularly in light of a warming and possibly drying climate. According to *van der Werf et al.* [2006], fire-caused carbon emissions in Siberia average 188 ± 133 Tg C $a^{-1}$, but with large interannual variability making it difficult to identify trends, and thus to predict the magnitude of future emissions. Additional observations are needed to determine the robustness of such estimates and to understand the processes behind them.

[8] Data on the interannual and seasonal dynamics of $CO_2$ uptake by the land biota and oceans are key to a better understanding and mitigation of anthropogenic carbon

emissions. This is where atmospheric $O_2$ measurements come into play as a method to estimate the magnitudes and partitioning of the land biotic and oceanic $CO_2$ sinks [e.g., *Bender et al.*, 1996; *Keeling and Shertz*, 1992]. The approach [*Keeling*, 1988; *Keeling et al.*, 1993] makes use of the different behavior of $O_2$ and $CO_2$, otherwise coupled through photosynthesis, respiration and combustion, which occurs in seawater. First, the solubility of $O_2$ in seawater is much less than that of $CO_2$, and second, when dissolved, $O_2$ is geochemically inert, while $CO_2$, on the contrary, reacts with seawater forming a range of carbonic acid compounds, and thus allowing further dissolution of atmospheric $CO_2$. It is these differences in the chemical and physical properties of $O_2$ and $CO_2$ which make $O_2$ measurements a powerful tool in constraining various aspects of the global carbon cycle, including global carbon sink estimates of the land biota and oceans [*Bender et al.*, 2005; *Manning and Keeling*, 2006; *Tohjima et al.*, 2008]. With a higher-density measurement network, and improved models of the carbon cycle and atmospheric transport, we hope that in future this methodology can also be used for regional carbon sink estimates.

[9] The atmospheric burden of $CH_4$ has increased from about 715 ppb in preindustrial times to 1782 ppb in 2006 [*World Meteorological Organization*, 2007] caused by changes in both natural (e.g., wetlands) and anthropogenic (e.g., energy production, biomass burning, rice agriculture, ruminant animals, and landfills) sources. The growth rate of $CH_4$ has been variable during the last few decades, showing periods of relatively rapid rise during the late 1980s, and periods of stabilization and even decline in the 1990s and early 2000s which are not well understood [*Dlugokencky et al.*, 2003, 1994, 2001]. Despite the recent slow down of the growth rate, $CH_4$ still remains the second most important anthropogenic GHG, contributing up to 20% of global mean direct radiative forcing [*Ramaswamy et al.*, 2001]. Apart from persistent anthropogenic emissions, the potential changes in natural $CH_4$ emissions from wetlands [*Friborg et al.*, 2003], thawing lakes [*Walter et al.*, 2006], and melting permafrost [*Khvorostyanov et al.*, 2008; *Zimov et al.*, 2006], which may be induced by regional changes in temperature or precipitation patterns, make $CH_4$ measurements particularly pertinent in Siberia, with the world's largest area of wetlands ($\sim$131 million ha [*Sohngen et al.*, 2005]).

[10] CO does not absorb infrared radiation and therefore is not a direct GHG. However, changes in its concentration have an impact on atmospheric chemistry and thus on the lifetimes of other GHGs, such as $CH_4$ and tropospheric $O_3$. CO concentration variations can usually be clearly referred to local anthropogenic sources such as fossil fuel and biomass burning owing to its relatively short lifetime in the atmosphere (from 20 to 50 days) [*Warneck*, 1988]. In boreal regions of the Northern Hemisphere including Siberia, an increasing frequency in natural and human-induced fires has become one of the major sources of CO in summer [*Kasischke et al.*, 2005]. The global trend in CO concentrations has experienced both increases and decreases during the last few decades [*Khalil and Rasmussen*, 1994; *Novelli et al.*, 1998, 2003], which are only partially understood.

[11] In section 2 of this paper we briefly describe the ZOTTO site. Section 3 presents examples of data obtained from our measurement system during the testing phase (November 2005 to September 2006), and from October 2006 to June 2007, which is the time when the tower was fully constructed to 300 m. Section 3 also compares our observations with those from the Shetland Islands, Scotland station, with the TM3 atmospheric tracer transport model, and examines synoptic variations and diurnal cycles.

## 2. ZOTTO Site

[12] The ZOTTO site is situated in a region characterized by a strong continental climate. The average January temperature is $-26$°C with observed minima of $-56$°C; the average July temperature is 22°C with a highest recorded temperature of 36°C; average annual precipitation is between 500 and 600 mm [*Schulze et al.*, 2002]. The tower base (60.80°N, 89.35°E, elevation 114 m asl) is situated about 30 km to the west of the Yenisei River. The nearest village, Zotino, with a population of about 500 people, lies about 25 km northeast of the tower, on the bank of the Yenisei. The nearest city of appreciable size is Krasnoyarsk, population $\sim$1 million, 600 km to the south. The river divides the region into two distinct parts, with *Pinus sylvestris* forests and bogs to the west, and dark coniferous taiga dominated by *Pinus sibirica* to the east. The western region (where the tower is built) consists of a fluvial sand plateau (50–100 m above the river level) and is intercepted by numerous lakes and ponds owing to the presence of clay lenses. The soil type is podzolic characterized by low $pH_{H2O}$ (4.7–5.3), low nitrogen (2–3 tN $ha^{-1}$), and low soil carbon content (<35 tC $ha^{-1}$ in the uppermost 1-m layer) [*Schulze et al.*, 2002].

[13] Several studies were previously conducted close to the ZOTTO site. Eddy covariance flux measurements of $CO_2$, $H_2O$, and energy exchanges were made in a nearby pine forest [*Lloyd et al.*, 2002b; *Shibistova et al.*, 2002b], dark taiga [*Röser et al.*, 2002], and bogs [*Kurbatova et al.*, 2002]. These measurements were accompanied by process studies on soil respiration [*Shibistova et al.*, 2002a] and detailed forest inventories [*Schulze et al.*, 2002; *Wirth et al.*, 1999]. These studies indicated that the local forest and bog ecosystems constitute a moderate carbon sink (typical growing season net ecosystem exchange (NEE) for forests from $-300$ to $-150$ g C $m^{-2}$ and for bogs about $-50$ g C $m^{-2}$) with relatively large interannual variability. Additional measurement programs included several years of monthly atmospheric vertical profile sampling up to 3000 m by light aircraft establishing a seasonal climatology of the major GHGs and their isotopic composition in central Siberia [*Levin et al.*, 2002; *Lloyd et al.*, 2002a]. Atmospheric chemistry measurements of shorter-lived gas species have been performed in neighboring regions along the Trans-Siberian Railroad (TROICA project) [e.g., *Tarasova et al.*, 2006]. The observations have been accompanied by a series of modeling studies on various scales: global atmospheric inversion calculations of $CO_2$ documenting the large interannual variability of Siberian ecosystems, partly attributable to variations in fire emissions [*Rödenbeck et al.*, 2003]; continental-scale forward simulations with mesoscale models investigating the large-scale transport patterns over the area [e.g., *Chevillard et al.*, 2002; *Karstens et al.*, 2006]; and high-resolution model simulations for the determination of

diurnal cycle variations in the ZOTTO area caused by the Yenisei river [*van der Molen and Dolman*, 2007].

[14] The construction of the ZOTTO site and tower itself, and preparation of all scientific equipment and related permissions from the Russian authorities were ongoing for several years. In August 2005 the scientific equipment was shipped to Russia, and the tower was built up to 52-m height; further construction had to be halted owing to the approaching winter. By the end of November 2005 we finished all equipment installations in the laboratory container and installation of temporary sampling lines, which allowed us to start the testing phase of our measuring system, up to 52 m.

[15] By the end of September 2006, the construction of the tower was completed up to 300 m and the end of October 2006 is considered the official start of the measurements (with approval from the Russian Gostech Commission). Since then, both the $O_2$ and $CO_2$, and GC subsystems have been collecting measurements from five heights on the tower.

## 3. First Results

[16] In the particular case of $O_2$, we report measurements as changes in the $O_2/N_2$ ratio in "per meg" units following *Keeling and Shertz* [1992]. Given that $N_2$ changes are typically much smaller than $O_2$ changes, the $O_2/N_2$ ratio can be used to quantify changes in $O_2$ concentration. Our $O_2$ sensor, however, measures $O_2$ mole fraction [see *Kozlova et al.*, 2008]; thus we convert the sensor signal to per meg units using an equation similar to that given by *Stephens et al.* [2003]:

$$\delta(O_2/N_2) = \frac{\delta X_{O_2} + (X_{CO_2} - 363.29)S_{O_2}}{S_{O_2}(1 - S_{O_2})}, \quad (1)$$

where $\delta(O_2/N_2)$ is the $O_2/N_2$ ratio in per meg units and $\delta X_{O_2}$ is the $O_2$ mole fraction of the air sample as determined by the $O_2$ sensor, multiplied by $10^6$, and relative to an arbitrary "zero" defined in the Scripps Institution of Oceanography (SIO) international scale. Changes in $CO_2$ concentration influence the $O_2$ mole fraction but not $O_2/N_2$ ratios, thus we correct for this influence as shown in equation (1), where $X_{CO_2}$ is the $CO_2$ mole fraction of the air sample (in ppm), and 363.29 is an arbitrary $CO_2$ reference value implicit in the definition of the SIO $O_2/N_2$ per meg scale. $S_{O_2}$ is the standard mole fraction of $O_2$ in air, given as 0.20946 [*Machta and Hughes*, 1970].

[17] From equation (1), if one considers a change in $O_2$ mole fraction, keeping $CO_2$ constant, it can be seen that a 1 $\mu$mol mol$^{-1}$ change in $O_2$ mole fraction is equivalent to a 6.04 per meg change in $O_2/N_2$ ratio. This factor should not be confused with the factor of 4.8, which is sometimes mistakenly used as an $O_2$ "conversion factor" from ppm to per meg units. As stated by *Keeling et al.* [1988, p. 3384], "4.8 per meg is equivalent to the same number of molecules as 1 $\mu$mol mole$^{-1}$ in a trace gas abundance" (for example, $CO_2$, but not $O_2$, which is obviously not a trace gas).

[18] We also present results of Atmospheric Potential Oxygen (APO), which reflect the weighted sum of $O_2$ and $CO_2$ concentrations, where the weighting is adjusted so that APO is essentially invariant with respect to $O_2$ and $CO_2$ exchanges in land biota [*Manning and Keeling*, 2006; *Stephens et al.*, 1998]. We define APO in per meg units as

$$APO = \delta(O_2/N_2) + \frac{\alpha_L}{S_{O_2}}(X_{CO_2} - 350), \quad (2)$$

where $\alpha_L$ corresponds to a typical $O_2$:$CO_2$ molar exchange ratio for land biotic photosynthesis and respiration in units of moles of $O_2$ produced per mole of $CO_2$ consumed (taken as 1.10 [*Severinghaus*, 1995]), and 350 is an arbitrary reference $CO_2$ concentration used in the SIO definition of APO.

### 3.1. Seasonal Cycles of $CO_2$, $O_2$, and APO

[19] Figure 1 shows the seasonal cycles of $CO_2$, $O_2$, and APO as observed at the ZOTTO site. We present data only from the 52-m level, since they are available for a longer period (including before the tower was fully constructed). A quantitative comparison with "background" observations elsewhere can be obtained by means of a data selection procedure where we selected only daytime values between 1100 and 1700 (local standard time, which is UTC + 7 h), and averaged these excluding the 25% highest and lowest values to obtain trimmed daily averages (black dots in Figure 1). This minimizes the impact of incomplete vertical mixing during stable atmospheric conditions, in particular during the night. Finally, we fitted a three-harmonic function to a base period of 1 year plus a linear trend to the trimmed daily averages (red lines in Figure 1). The fitting procedure was iteratively repeated, removing daily averages lying outside three standard deviations from the fit functions. This procedure removed outliers that we consider to be caused by local effects and which despite being relatively sparse, do not represent the large-scale seasonal variation that the fitting function should capture. The yellow bands represent ±1 standard deviation of the residuals of the daily averages from the fit functions. Since for $O_2$ and APO the data records are not long enough to reliably determine a long-term trend, we used the linear trends of $-18.6$ per meg a$^{-1}$ ($O_2$) and $-7.2$ per meg a$^{-1}$ (APO) determined from observations during a similar time period at the Shetland Islands, Scotland station (60.28°N, 1.28°W), run by the Max Planck Institute for Biogeochemistry (MPI-BGC), which is at the same latitude as ZOTTO.

[20] For comparison purposes, we also display the fit functions (blue lines in Figure 1) obtained by a similar data selection procedure from weekly flask measurements collected at the Shetland Islands station (with ±1 standard deviation of the residuals shown as light blue bands). For further comparison, in the case of $CO_2$, we plot the "marine boundary layer reference" at 60°N as defined and given by the GLOBALVIEW-$CO_2$ database [*National Oceanic and Atmospheric Administration*, 2007] (black dashed line in Figure 1).

[21] The $CO_2$ daytime data shown in Figure 1 exhibit the expected seasonal cycle, with the spring/summer drawdown caused by net land biotic photosynthesis and the autumn/winter release caused by net respiration. Clearly, the presently available short record does not permit a rigorous determination of the amplitude of the $CO_2$ seasonal cycle in the planetary boundary layer in central Siberia. Nevertheless, from the fitting function we estimated an amplitude

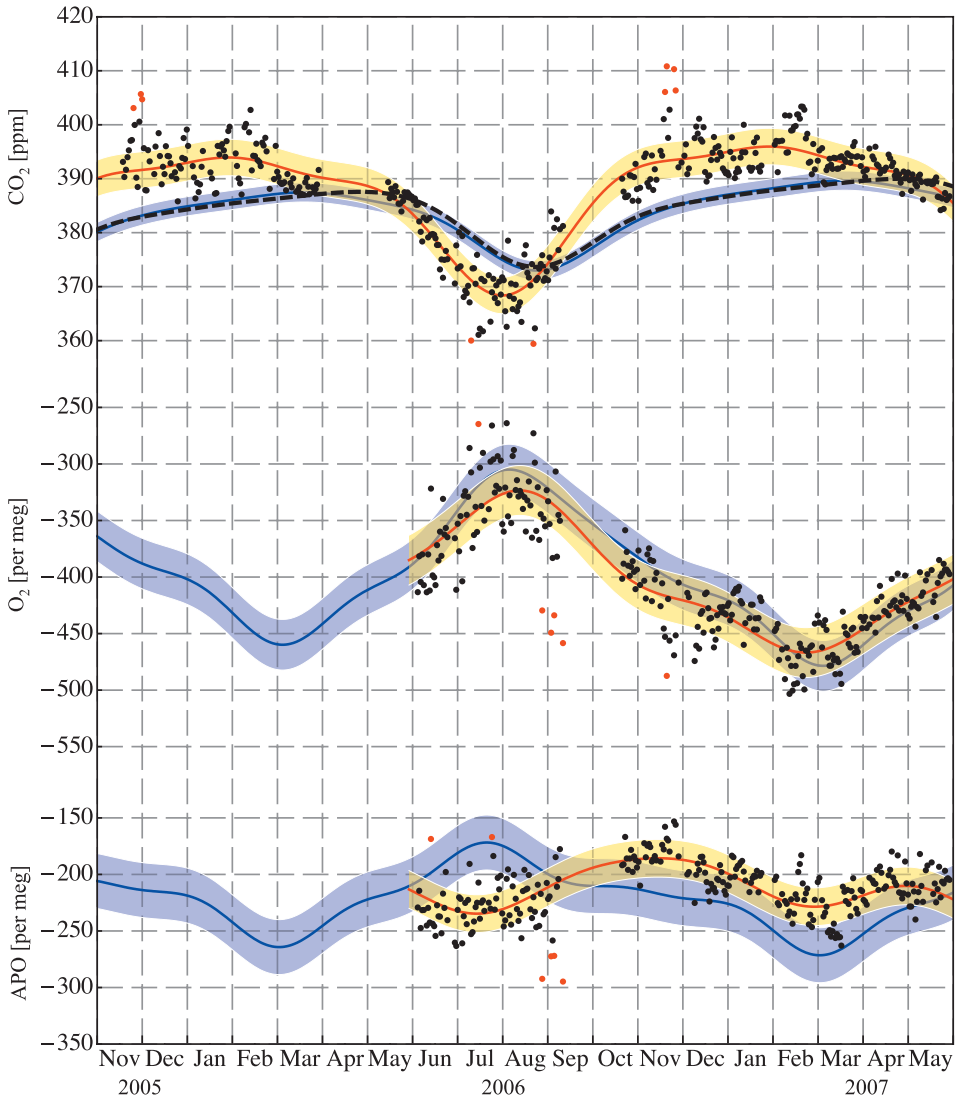


**Figure 1.** Seasonal cycles of $CO_2$, $O_2$, and Atmospheric Potential Oxygen (APO) from the 52-m height of the Zotino Tall Tower (ZOTTO). The *y*-axis scales of all three plots have been adjusted so that visually, changes in $CO_2$ (shown in ppm) and $O_2$ and APO (shown in per meg) are directly comparable on a mole-to-mole basis. Black and red dots on all three plots show trimmed daytime averages of measurements between 1100 and 1700 (local standard time: UTC + 7 h). The fit functions (red lines, described in the text) were computed iteratively from the trimmed daytime averages. Convergence was achieved after four ($CO_2$ and APO) and three ($O_2$) iterations, identifying a total of nine ($CO_2$) and six ($O_2$ and APO) outliers (red dots). Yellow bands on all plots denote ±1 standard deviation of the residuals of the trimmed daytime averages from the fit functions. For comparison, the blue lines and bands show similar fit functions and ±1 standard deviation of the residuals determined from flask measurements (approximately weekly frequency) from the Shetland Islands station (60.28°N, 1.28°W). The black dashed line on the $CO_2$ plot shows the "marine boundary layer reference" concentration at a latitude of 60°N as given in the GLOBALVIEW-$CO_2$ database [*National Oceanic and Atmospheric Administration*, 2007] (linearly extrapolated after 1 January 2007). $CO_2$ data are reported on the National Oceanic and Atmospheric Administration (NOAA)/World Meteorological Organization (WMO) X2005 scale, and $O_2$ and APO data are reported on the Scripps Institution of Oceanography (SIO) scale (both scales were transferred to the site via reference to the Max Planck Institute for Biogeochemistry, or MPI-BGC, primary standards). The $O_2$ (and thus APO) record began 6 months later than $CO_2$, owing to pressure control problems that could not be fixed until the second visit to the site in October 2006. There are a few gaps in the data, caused by tower construction work and by equipment installations and upgrades.

of about 26.6 ppm, which is consistent with previous results from aircraft observations averaged over the planetary boundary layer (about 22 ppm), performed a few kilometers away from ZOTTO [*Lloyd et al.*, 2002a]. Comparing Shetlands and ZOTTO data, we observed a seasonal amplitude of 15.4 ppm at Shetlands, 11.2 ppm smaller than at ZOTTO. In July, between these two stations we observed a west-east gradient of about −7 ppm, most likely reflecting the summertime continental uptake of $CO_2$. This gradient is consistent with results from regional model simulations for this time of year [*Chevillard et al.*, 2002; *Karstens et al.*, 2006]. The $CO_2$ minimum at ZOTTO occurred at the end of July, which was also found by *Lloyd et al.* [2002a]. At Shetlands the minimum occurred at the end of August with a much more gradual autumn increase, as expected owing to the more maritime character of this station. At ZOTTO, $CO_2$ increased rapidly until the end of October, then continued to increase relatively slowly, reaching a maximum in late January, compared to the later maximum at Shetlands in late March. The Shetlands maximum is about 7 ppm lower than that observed at ZOTTO, most likely reflecting both anthropogenic and land biotic $CO_2$ sources from the European continent in the ZOTTO signal. The linear trend in the ZOTTO $CO_2$ record determined in the fitting procedure yielded an increase rate of 2.02 ppm $a^{-1}$, which is similar to the trend observed at Shetlands (2.17 ppm $a^{-1}$) and from the marine boundary layer reference (2.0 ppm $a^{-1}$).

[22] The seasonal cycle of $O_2$ is roughly anticorrelated with the cycle of $CO_2$ as expected from the coupling of the two gases in land biotic photosynthesis and respiration. In July, assuming simplistically that the observed 7 ppm $CO_2$ west-east drawdown is entirely due to land biotic uptake, we would expect to see ZOTTO $O_2$ concentrations elevated by ~37 per meg compared to Shetlands. Instead, we observed ZOTTO $O_2$ in July to be ~20 per meg lower than Shetlands. The main reason for this can be attributed to the larger oceanic component in the Shetlands $O_2$ seasonal cycle. In addition, it is possible that the west-east land biotic $CO_2$ sink is even greater than implied by the −7 ppm July concentration gradient, because it may be partially offset by fossil fuel emissions in Europe and Russia. If so, such fossil fuel emissions would result in a corresponding $O_2$ uptake at a greater $O_2$:$CO_2$ ratio than that released from land biotic exchanges, thus also contributing to a lower $O_2$ signal at ZOTTO. However, the airflow over the Eurasian continent is not completely zonal, which complicates this interpretation, with possibly different source and sink patterns influencing ZOTTO compared to Shetlands. In section 3.2 we investigate this assumption further by using a three-dimensional atmospheric transport model.

[23] We calculated an approximate seasonal $O_2$ amplitude of 134 per meg, corresponding to 28.1 ppm of $CO_2$ (on the basis that mole for mole, a 1 ppm change in $CO_2$ corresponds to a 4.77 per meg change in $O_2$; see beginning of section 3). The $O_2$ maximum at ZOTTO almost coincided with the $CO_2$ minimum, in early August. In the winter months, ZOTTO $O_2$ and $CO_2$ are not as well anticorrelated, as $O_2$ continued to decrease relatively steadily to a minimum in February, in contrast to the comparatively stable $CO_2$ from November onward. An atmospheric $O_2$ marine reference does not exist; thus we used Shetlands $O_2$ data as a proxy reference and observed a seasonal amplitude of 163 per meg, about 29 per meg greater than at ZOTTO. In summertime, in contrast to ZOTTO, Shetlands $O_2$ and $CO_2$ cycles are slightly out of phase: The $O_2$ maximum occurred in the beginning of August while the $CO_2$ minimum occurred 1 month later. In the winter months, Shetlands $O_2$ and $CO_2$ show stronger anticorrelation than at ZOTTO, although with $CO_2$ still lagging $O_2$ by 1 month.

[24] We interpret these observations as follows: in summertime at ZOTTO, $CO_2$ and $O_2$ changes are dominated by strong, anticorrelated land biotic exchanges, whereas at Shetlands, changes in $O_2$ are influenced by both land and ocean exchanges, with different phasing, and only the former influencing $CO_2$ changes. In the winter months, at Shetlands the situation is much the same as in summer (but reversed), whereas at ZOTTO, with little activity from the land biosphere, there is a greater influence from the (attenuated) $O_2$ seasonal signal derived from the distant oceans. In the very cold, snow covered environment at ZOTTO, land biotic respiration is minimal during the winter months, as shown by the very broad $CO_2$ maximum.

[25] The seasonal amplitude of APO at ZOTTO, shown in the bottom plot of Figure 1, is about 51 per meg, compared to a much larger amplitude of 95 per meg at Shetlands, reflecting a strong attenuation of the oceanic signal in the continental interior. What is surprising, however, is the lag of 4 months in the ZOTTO APO minimum and maximum in comparison to Shetlands. A lag is to be expected as the oceanic signal propagates into the continental interior, but not of such a long duration. This finding is not very robust, however, with only 1 year of data and because of the large gap in observations during the tower construction in September and October 2006, which very plausibly may have masked a significantly earlier APO maximum. In addition, the "signal-to-noise ratio" is low when considering the APO amplitude, and as a result the fitted curve exhibits double maxima/minima (which are unlikely to be real), and with the seasonal minimum in particular not very distinct. Clearly, additional years of data collection are required in order to define a more robust APO seasonal cycle.

### 3.2. Comparison of the Observed Seasonal Cycles With TM3 Model Simulations

[26] By definition, the APO seasonal cycle should be primarily driven by seasonal air-sea fluxes of $O_2$ (plus a small component from air-sea fluxes of $N_2$). Thus the dilution of the APO seasonal amplitude over the continents by atmospheric mixing provides a convenient way to evaluate models of atmospheric transport [*Blaine*, 2005; *Heimann*, 2001]. Simulations of the global distribution of atmospheric $CO_2$, $O_2$ and $N_2$ (from which APO can be derived) were performed in the TRANSCOM atmospheric transport model intercomparison activity [*Blaine*, 2005; *Gurney et al.*, 2000]. Here, we compare the simulation results of the TM3 model [*Heimann and Koerner*, 2003] with our observations as an illustrative example. The $CO_2$ concentration was obtained as a composite from simulations using three surface flux fields: (1) fossil fuel emissions [*Andres et al.*, 1996], (2) seasonal land biosphere exchange fluxes from a steady state run of the CASA model [*Randerson et al.*, 1999], and (3) air-sea $CO_2$ fluxes from $pCO_2$ observations [*Takahashi et al.*, 1999]. The

corresponding $O_2$ composite was derived from (1) the fossil fuel $CO_2$ simulation using an $O_2$:$CO_2$ molar ratio of 1.4, (2) the land biosphere $CO_2$ simulation using an $O_2$:$CO_2$ molar ratio of 1.1, and (3) a simulation with the air-sea fluxes of $O_2$ from the compilation of *García and Keeling* [2001]. The $N_2$ simulation included only the air-sea fluxes of $N_2$ calculated from air-sea heat fluxes [*Gibson et al.*, 1997] and the $N_2$ solubility temperature dependence [*Weiss*, 1970]. Modeled APO concentrations were then computed according to equation (2) given above. In most respects our model simulation protocol corresponds to that given by *Battle et al.* [2006] except that we neglect any annual mean uptake or release by the land biosphere (of $O_2$ and $CO_2$) or oceans (of $O_2$ and $N_2$). These annual mean flux components are not well constrained and are relatively small compared to the seasonal exchanges.

[27] Figure 2 compares modeled and observed seasonal cycles of $CO_2$, $O_2$, and APO at ZOTTO and Shetlands. Both Shetlands (model: blue dashed line; observations: blue solid line and blue band) and ZOTTO (model: red dashed line; observations: red solid line and yellow band) show good agreement for amplitude and phasing of $CO_2$. For the $O_2$ seasonal amplitude, the model underestimated Shetlands by 43 per meg but overestimated ZOTTO by 43 per meg. The $O_2$ phasing was in good agreement at both stations between model and observations. For APO, the model underestimated the seasonal amplitudes by 36 per meg and 9 per meg at Shetlands and ZOTTO, respectively. Observations and model results for APO from both stations do not show distinct annual minimums, therefore for phasing analysis, we examined only annual maximums. Shetlands gave good agreement, whereas at ZOTTO the observations annual maximum lagged the model maximum by 2 months.

[28] The model/observations discrepancy in the APO seasonal amplitude at Shetlands can be explained as a result of the discrepancy in $O_2$. Although *Battle et al.* [2006] generally found TM3 modeled APO results in the Northern Hemisphere to underestimate the APO seasonal amplitude by about 10–20%, the exception was Cold Bay, Alaska (55.20°N, 162.72°W), where the modeled amplitude was about 25 per meg greater than observations. *Battle et al.* [2006] explained this discrepancy on the basis of the existence of a large seasonal oceanic $O_2$ outgassing in the vicinity of Cold Bay [*García and Keeling*, 2001], and previous evidence of the TM3 model overestimating tracer concentrations near source regions [*Denning et al.*, 1999]. Shetlands is also in close proximity to regions of large air-sea $O_2$ fluxes [*García and Keeling*, 2001, Plate 3], therefore our model result of a large underestimation of the Shetlands APO seasonal amplitude is possibly inconsistent with *Battle et al.* [2006] and *Denning et al.* [1999].

[29] The ZOTTO model/observations seasonal amplitude discrepancies appear at first inconsistent, with opposite discrepancies between $O_2$ and APO. Closer analysis of Figure 2, however, reveals that the $O_2$ seasonal amplitude discrepancy resulted in the large phasing discrepancy in APO, giving large model/observation differences from June to August, in the time of the $O_2$ maximum. These differences appear to be the result of phasing differences in land and ocean signals as observed at ZOTTO where ocean signals have a significant lag. None of the stations used by *Battle et al.* [2006] are midcontinental stations, precluding comparisons with ZOTTO. *Blaine* [2005] and *Stephens et al.* [1998] modeled APO simulations at Niwot Ridge, Colorado (40.05°N, 105.63°W), a midcontinental site in the USA, and both found the model to give a small underestimation in the APO seasonal amplitude, similar to our findings at ZOTTO, and with an annual maximum about 1 month earlier than the observations. The APO phasing discrepancy at ZOTTO, while larger, is consistent with these results. But such a comparison is further convoluted because Niwot Ridge is a high-altitude station (3749 m asl), which will affect both the phasing of the observed seasonal cycle and the performance of the transport model.

[30] The reasons for the model/observation differences at ZOTTO are likely to be related to the more complex source/sink patterns of $O_2$, which contain a significant contribution from the distant oceans, resulting in $O_2$ (and APO) concentrations at ZOTTO being more sensitive to errors in model transport, in contrast to the $CO_2$ signal which is dominated by continental sources closer to ZOTTO. Alternatively, the $O_2$ air-sea flux fields that are input to the model could contain errors, and either these, or seasonal changes in vertical transport, are more likely to explain the $O_2$ and APO amplitude discrepancies observed at Shetlands. Since the land biotic $O_2$:$CO_2$ molar ratio is not well constrained, we also examined the sensitivity of our results by using values ranging from 0.9 to 1.2 rather than 1.1 typically used ($\alpha_L$ in equation (2)). Choosing ratios of less than 1.1 (in both model and observation calculations) reduces the observed APO seasonal amplitude at ZOTTO and results in an earlier maximum, which consequently improves the model/observations comparison. At Shetlands, however, the APO seasonal amplitude and phasing is relatively insensitive to changes in the ratio. These findings can be explained by a much larger land biotic component in the ZOTTO $O_2$ signal, whereas at Shetlands the $O_2$ signal is predominantly driven by oceanic fluxes. As discussed above, however, an important caveat in our findings with respect to APO is the untimely 2-month gap in the ZOTTO data record and the low signal-to-noise ratio in the APO seasonality.

### 3.3. Synoptic Variations

[31] In Figures 3a and 3b, the concentration records of $CO_2$, $O_2$, $CH_4$, and CO from all five measurement heights on the tower are shown for the months of November and December 2006, the first 2 months of measurements from the fully constructed tower to 300 m. Also shown are temperature data from four meteorological stations within a perimeter of about 100 km around ZOTTO (since no meteorological equipment was installed at ZOTTO).

[32] In November there were three events which display clear vertical concentration gradients in $CO_2$, $O_2$ and $CH_4$ (4, 17–22, and 24–27 November), where each event corresponds to a period of very low and decreasing temperatures to −30°C or less. High ambient pressure and low wind speeds were also observed during these periods. Radiosonde data from the meteorological station at Bor (61.60°N, 90.00°E, ~95 km from ZOTTO) for this time period show the development of a strongly stratified temperature inversion layer that extended up to about 700 m. During these so-called "cold events" (shown in greater detail for $CO_2$ in Figure 4) the $CO_2$ concentrations from the three lower levels increased while at the top levels (227 and

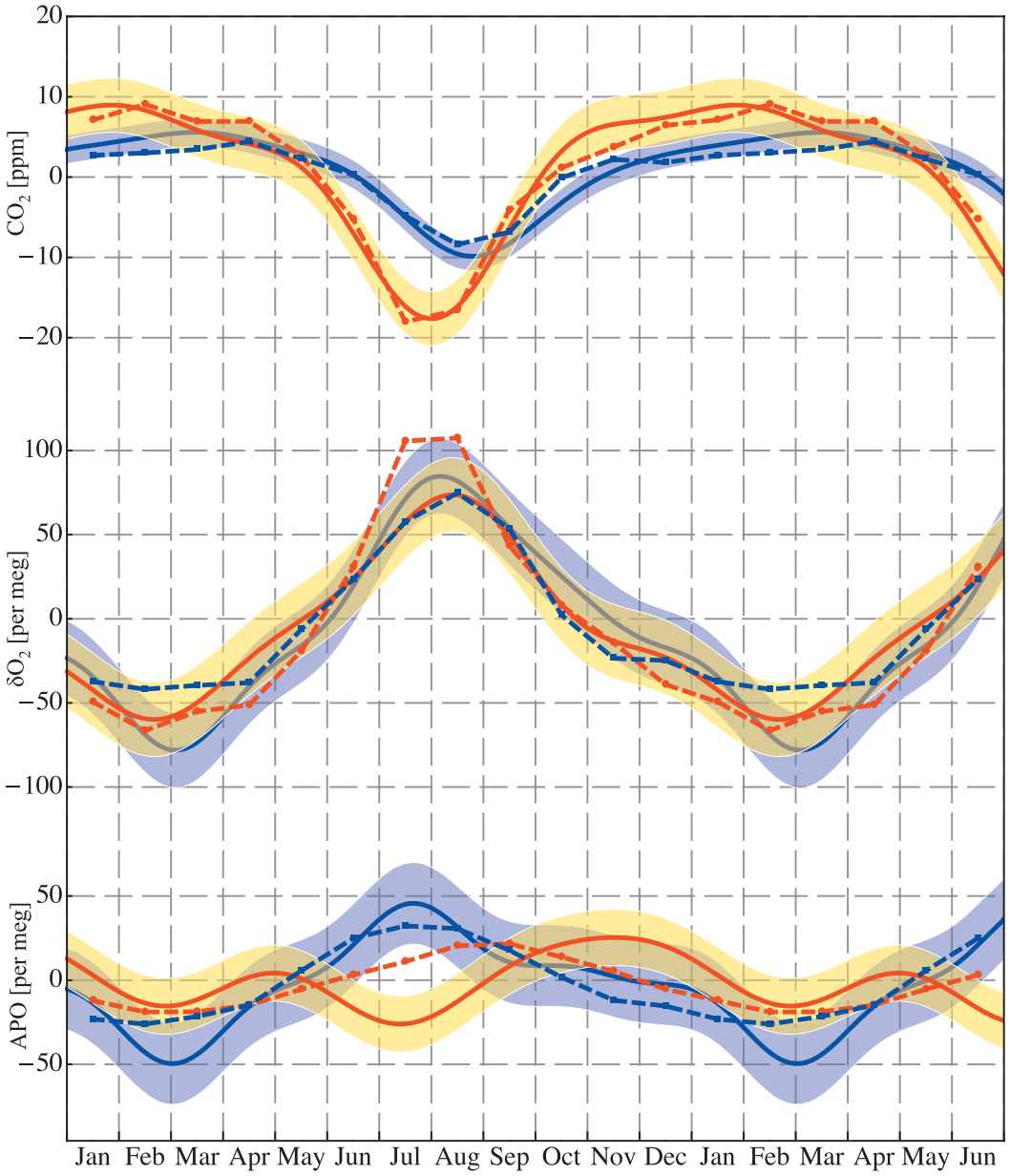


**Figure 2.** Seasonal cycles of $CO_2$, $O_2$, and APO from model results (dashed lines) and fit functions to the observations (solid lines) at ZOTTO (red lines) and Shetland Islands (blue lines). Seasonal cycles were obtained by subtracting the linear trends and annual means from the fit functions of the observations and the model results. The yellow (ZOTTO) and light blue (Shetlands) bands denote ±1 standard deviation of the residuals of the daytime averages from the fit functions (as for Figure 1). For visual clarity, the first 6 months are repeated, and as for Figure 1, all species can be compared visually on a mole-to-mole basis.

300 m) a concurrent slight decrease in $CO_2$ concentration was observed. On 20–21 November, the highly stratified air column appeared to break down and we observed a decrease in $CO_2$ concentrations at the lower heights (52 and 92 m) toward the values observed at the top. $CH_4$ vertical gradients on 18–21 November (Figure 3a) exhibited a similar pattern: $CH_4$ concentrations at 227 and 300 m decreased while a concurrent increase occurred at 4, 52 and 92 m, however, with a 1–2 day lag relatively to $CO_2$.

[33] In Figure 4 no $CO_2$ gradient can be seen on 23 November, when temperature increased, followed again by a second cold period, which resulted in a similar gradient. $O_2$ data for both cold events almost exactly mirror $CO_2$. During the following winter months (not shown), under similar conditions (very low temperature, high pres-

sure, and low wind speed), we also found increasing $CO_2$ concentrations in the lower 100 m and decreasing concentrations at and above 227 m. To a lesser extent, this tendency was also observed in the vertical gradients of $CH_4$. In the second half of November some variability can be seen in the 300-m $O_2$ data (which are not correlated with $CO_2$), which we believe are technical artifacts (discussed by *Kozlova et al.* [2008]).

[34] The $CO_2$ buildup at the lower levels cannot be explained by local anthropogenic emissions (diesel generators and wood burning) since concurrent CO measurements did not show any increase. Previous workers have observed haze formation under very low wind and cold conditions during winter at ZOTTO (E.-D. Schulze, personal communication, 2007). During these events, the air column from the bottom to the top of the tower may be divided into two separate layers, each with independent air circulation patterns. While $CO_2$ at the lower levels could increase as the result of local respiration, which can occur even under very cold conditions [*Zimov et al.*, 1993], and/or diffusion of $CO_2$ through the soil after frost, the upper levels of the tower could show a concurrent decrease since mixing with the higher $CO_2$ concentration air at the bottom is restricted. Unfortunately, we did not have in situ soil temperature measurements during the winter of 2006–2007, however, at the nearby flux tower site (60.73°N, 89.15°E) the soil temperature at 10-cm depth never decreased to less than −10°C during 6 years (1998–2004) of measurements [*Shibistova et al.*, 2002a], which could confirm the potential contribution of soil respiration to the $CO_2$ buildup near the ground. Figure 4 shows that the $CO_2$ concentrations increased at the lower levels faster than they decreased at 227 and 300 m. The vertical integral of $CO_2$ concentration over the height of the tower showed an increase of about 3000 ppm meters during the 3–4 day buildup phase of both cold events. If we assume that this increase is entirely due to a local ground source, then this corresponds to a source flux of about 0.36–0.48 $\mu$mol C $m^{-2}$ $s^{-1}$ (0.03–0.04 mol C $m^{-2}$ $d^{-1}$). Early wintertime $CO_2$ respiration fluxes of similar magnitude were observed at the nearby flux tower site in 1999 [*Shibistova et al.*, 2002b] and soil respiration flux measurements in northeastern Siberia [*Zimov et al.*, 1993].

[35] An initial buildup of $CH_4$ occurred similarly at all heights on November 17–18, with the development of a concentration gradient beginning only on 19 November. This contrasting behavior between $CO_2$ and $CH_4$ demonstrates that the two gases do not have identical local source patterns, with $CH_4$ likely having a more heterogeneous source distribution. This would be expected if the observed $CH_4$ concentration increases resulted primarily from $CH_4$ outgassing from the waterlogged bogs surrounding the ZOTTO site.

[36] In December there were some periods with concentration variations in all gas species but, with the exception of $CO_2$ and $O_2$ during another cold event from 10 to 13 December, essentially no separation between heights, showing that the horizontal movement of air was dominant over vertical mixing. A short event suspected to be the result of localized pollution on 7 December caused a vertical gradient in $CH_4$ and CO, and also "spikes" in $CO_2$ and $O_2$ although not with clear vertical gradients. $CH_4$ demonstrated the greatest change, with a peak up to 2300 ppb at 4, 52, and 92 m and concentrations of about 2030–2050 ppb at 227 and 300 m. A back trajectory analysis using the NOAA HYSPLIT model [*Draxler and Hess*, 1998] revealed that this event was most likely pollution coming from the settlement Sym-Faktoriya, located about 75 km southwest of ZOTTO.

### 3.4. Diurnal Variations

[37] Figure 5 shows diurnal variations of $CO_2$ and $O_2$ concentrations from 21 to 31 May 2007. The data exhibit clear though not large diurnal anticorrelated changes in $CO_2$ and $O_2$. The highest $CO_2$ concentrations (lowest $O_2$) were observed from 4 m, as expected. The vertical gradients were most pronounced when stable atmospheric conditions (low wind speed) prevailed, which was the case for the entire time period shown except 26–27 May when higher wind speeds resulted in air mixing up to the top of the tower. The gradients were rather small probably because of relatively cold weather conditions, with ambient temperatures often below freezing in the first half of May. Only after 16 May did the air temperature begin to rise and stabilize at above zero values in the night. As seen in Figure 5, $CO_2$ concentrations gradually increased during the night, reaching a maximum between 0300 and 0600. Sunrise (about 0400) caused ground-level warming and hence mixing of the stratified air column, usually becoming well mixed by 1200. Changes in $O_2$ concentration almost always mirrored $CO_2$ with maxima shortly after midday and minima in the night (from 0000 to 0300).

**Figure 3.** $CO_2$, $O_2$, $CH_4$, and CO concentrations during (a) November 2006 and (b) December 2006, the first 2 months of data from the completed tower. As for $CO_2$, $CH_4$ and CO data are reported on the NOAA/WMO scales ($CH_4$: NOAA04; CO: NOAA-Global Monitoring Division (GMD)/WMO 2000), transferred to the site via MPI-BGC. $N_2O$ data were not available, because of a sampling valve failure. Temperature data (given in the bottom plot) are also shown from four localities within 100 km of ZOTTO: Bor, Sym-Faktoriya, Vorogovo, and Yartsevo. The legends shown in the bottom two plots of Figure 3a apply for all plots. In the $CO_2$ and $O_2$ plots, each data point represents an average of two consecutive measurements from a given height. Each measurement is a 4-min average, and consecutive measurements are 16 min apart; thus each data point represents a 32-min average. In the $CH_4$ and CO plots, each data point represents an average of three consecutive measurements from a given height, where consecutive measurements are 12 min apart; thus each data point represents a 36-min average. For $CO_2$, all data are shown for both months: For $O_2$, 92% of November data and 90% of December data are shown, and for $CH_4$ and CO, 84% of November data and 95% of December data are shown. The main reasons for discarding data were problems of insufficient inlet pressure for the gas chromatographic (GC) measurements and a problem with the $O_2$ analyzer reading off scale, owing to baseline drift at the end of November and the beginning of December.

[38] Typical nighttime vertical profiles of $CO_2$ and $CH_4$ concentrations are shown in Figures 6a and 6b, respectively (circles), shown for 7–8 May 2007. The concentrations at the top two levels were nearly constant, and steadily increased from 92 m down to 4 m, suggesting that the measurements from both 227 and 300 m were representative of the mixed boundary layer. We also show typical afternoon profiles (Figure 6, triangles), when the air column was well mixed, from the same time period. We estimated nighttime $CO_2$ respiration flux by examining several events in April and May 2007 which exhibited clear nighttime vertical gradients and stable $CO_2$ concentrations at the top level of the tower throughout the day. Fluxes were calculated by integrating between the $CO_2$ concentration before the nighttime buildup (afternoon values) and the maximum nighttime concentration (before vertical mixing the following day eroded the vertical concentration gradient). On the basis of several profiles, we estimated an average flux of $0.04 \pm 0.02$ mol C $m^{-2}$ $d^{-1}$, which is consistent with eddy covariance measurements made in the vicinity of the tower in May 1999–2000 [*Shibistova et al.*, 2002b]. Unfortunately, we do not have any summer data for the fully constructed

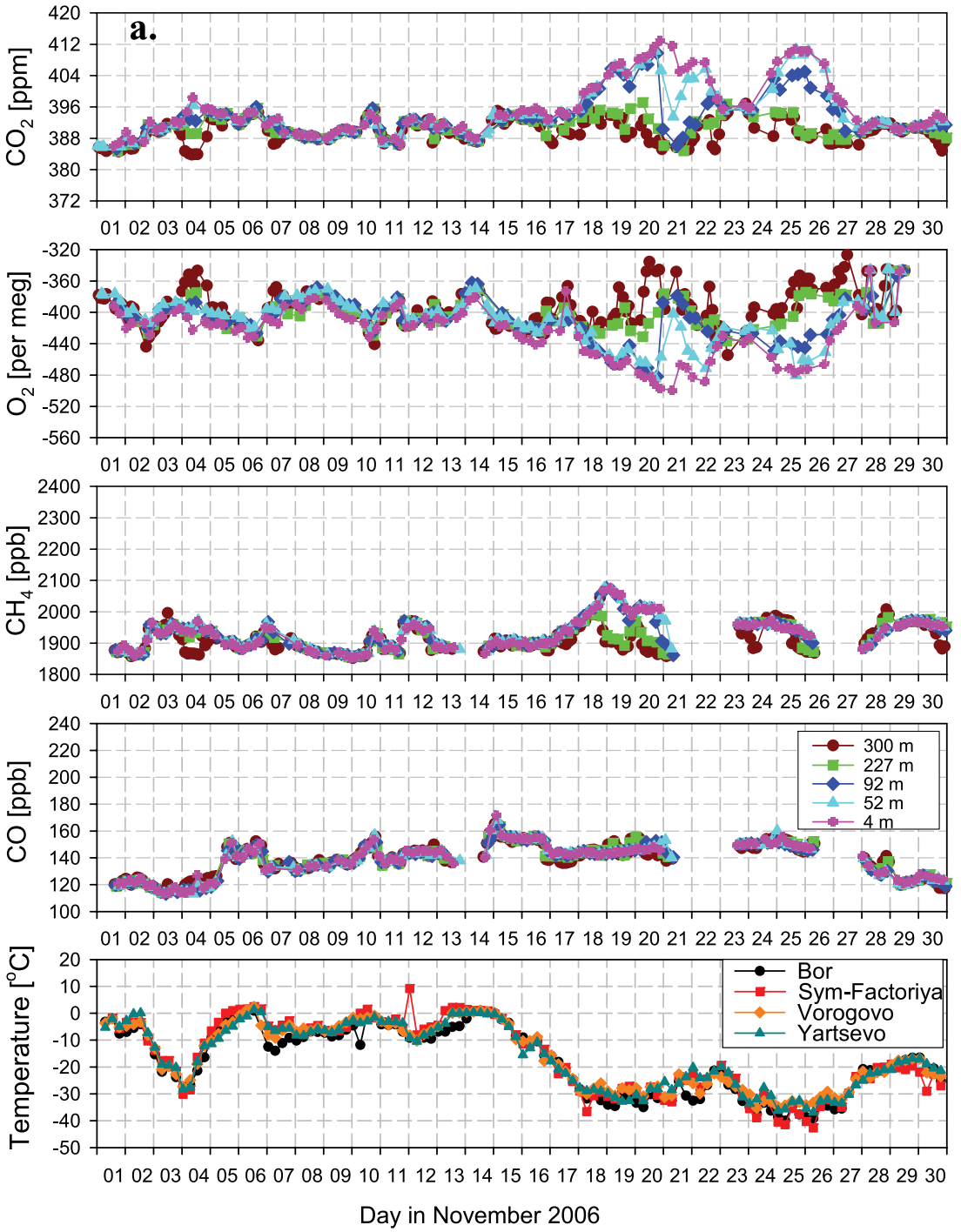


**Figure 3**

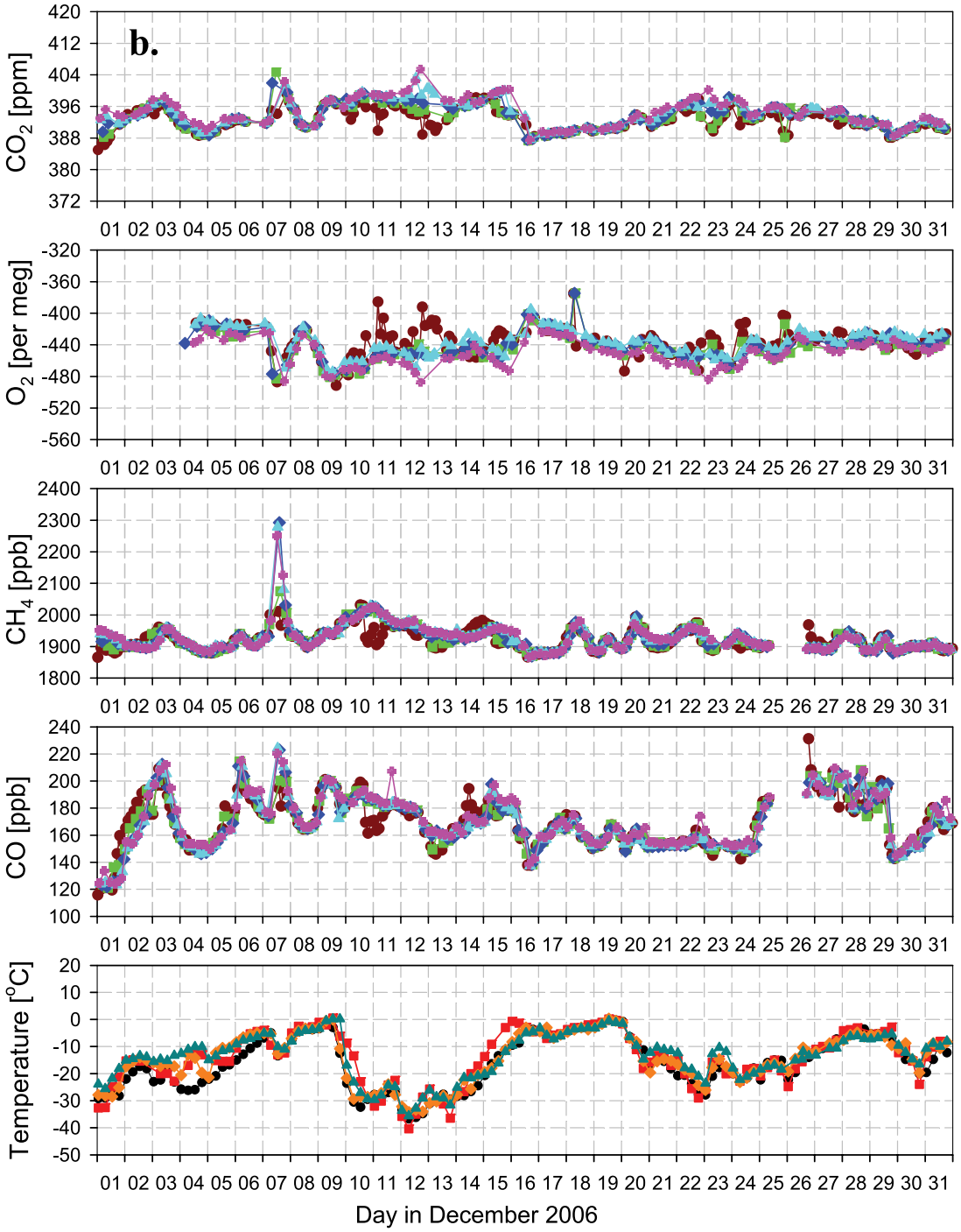


**Figure 3.** (continued)

tower when fluxes would have been much larger. From summer 2006 data, with measurements up to 52 m, we observed significant diurnal gradients (up to 40 ppm at the 4-m height, compared to a maximum observed value of only 15 ppm in May 2007), but it is not possible to estimate the summer respiration flux since we lack $CO_2$ concentration data in the mixed boundary layer.

[39] For $CH_4$, in spring 2007, we did not observe as many events with diurnal gradients as for $CO_2$. For the particular profile shown in Figure 6b we estimated a flux of $7.5 \times 10^{-4}$ mol $CH_4$ $m^{-2}$ $d^{-1}$; a second event with a clear vertical $CH_4$ gradient on 23–24 May gave a similar result. We did not observe any diurnal variations or clear vertical profiles in CO concentrations.

## 4. Discussion and Summary

[40] We have presented first results of semicontinuous trace gas and $O_2$ concentrations measured from the new Zotino Tall Tower Observatory (ZOTTO) in central Siberia. Because of the unpolluted and relatively homogeneous

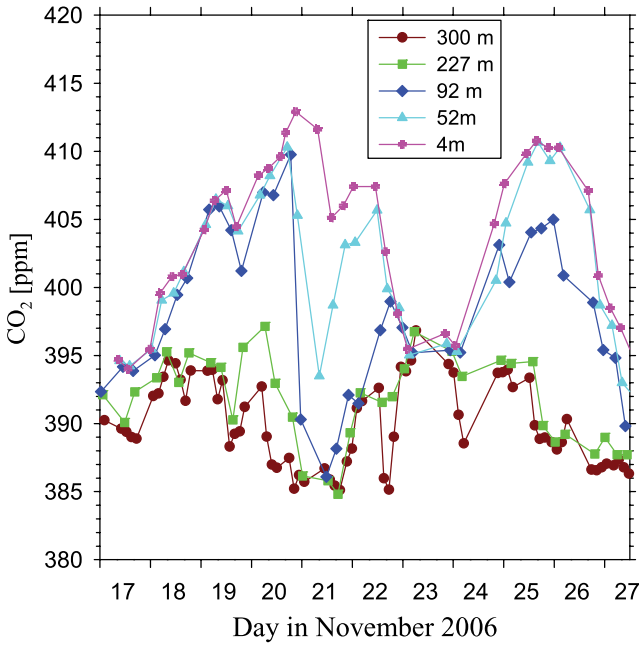


**Figure 4.** $CO_2$ concentrations observed from different heights of the tower between 17 and 27 November 2006. This period was characterized by very cold temperatures, low wind, and high-pressure conditions. The symbols and color codes for the different heights are the same as those for Figures 3a and 3b.

nature of most of Siberia these results are relevant to a large continental, boreal region. From the longer record we have available at the 52-m height on the tower, an examination of the observed variability in $CO_2$ concentrations revealed consistent results with earlier observations from aircraft profiles as well as with regional modeling studies. The seasonal cycle of $CO_2$ was anticorrelated with the cycle of $O_2$ as expected from the tight coupling of the two gases during land biotic photosynthesis and respiration. We estimated seasonal cycle amplitudes for $CO_2$ and $O_2$ of 26.6 ppm and 134 per meg (equivalent to 28.1 ppm in $CO_2$), respectively. We found the oceanic component of the $O_2$ seasonal amplitude (APO) to be 51 per meg, significantly smaller than, for example, the amplitude of 95 per meg observed at Shetland Islands, Scotland, illustrating the strong attenuation of the oceanic signal in the continental interior. When comparing $CO_2$ concentrations in July 2006 between Shetlands and ZOTTO, we found a west-east gradient of about −7 ppm, which we suspect reflects summertime continental uptake of $CO_2$. Conversely, in winter, the $CO_2$ maximum at Shetlands was about 7 ppm lower than at ZOTTO, suggesting that anthropogenic and land biotic sources were contributing to the ZOTTO signal.

[41] The phasing of the minima and maxima of $CO_2$ and $O_2$ were almost the same at ZOTTO but different at Shetlands, reflecting the significant contribution (and different phasing) of the oceanic component in the Shetlands $O_2$ cycle. Evidently, the simplistic view of contrasting the maritime conditions at Shetlands with central Siberia is only illustrative, since it ignores the more complex atmospheric transport patterns over northern Eurasia. Furthermore, with only 1 year of data, and with these particular comparisons based on measurements at a relatively low height owing to the ongoing tower construction, the representativeness of our results cannot presently be ascertained.

[42] A comparison with the TM3 atmospheric transport model at both ZOTTO and Shetlands found good agreement with the observed seasonal amplitudes in $CO_2$, but the model exhibited significantly greater (32% at ZOTTO) and smaller (26% at Shetlands) $O_2$ amplitudes. For APO, the model underestimated the seasonal amplitudes by 18% and 38% at ZOTTO and Shetlands, respectively. Comparisons with other studies are limited, since this is the first study to compare seasonal cycles of atmospheric $O_2$ between observations and a transport model (previous similar studies examined only APO), and the first study to compare model/observations from a midcontinental site, with the exception of a short record at Niwot Ridge, Colorado [*Blaine*, 2005; *Stephens et al.*, 1998], where comparisons with ZOTTO are problematic owing to Niwot Ridge being 3749 m asl. Comparisons were further convoluted by an untimely 2-month gap in the observations owing to the construction of the tower, which most probably masked an earlier APO maximum, and likely contributed to model/observation discrepancies in APO. In addition, we cannot exclude the possibility of interannual variability in the observations having an impact on the model comparisons.

[43] The model underestimation of APO at Shetlands is surprising in light of the work of *Battle et al.* [2006], which showed a large overestimation of APO seasonal amplitude at a site (Cold Bay, Alaska) close to large seasonal air-sea $O_2$ fluxes, similar to that experienced at Shetlands. Further study is needed to explore possible reasons for such model/observation discrepancies, examining model transport uncertainties, input flux fields, as well as the observations themselves. Our analyses, while apparently complicated by data limitations in the observations, have nevertheless shown that additional insight can be gained from comparing model/observations results for both $O_2$ and APO, in contrast to APO alone, particularly at midcontinental stations. We also investigated the influence on APO signals of choosing land biotic $O_2/CO_2$ photosynthesis and respiration exchange ratios different from 1.1 and found better model/observations comparisons at ZOTTO with smaller ratios, owing to a large land biotic component of the midcontinental $O_2$ cycle and the interplay of phasing differences of land and ocean $O_2$ signals as observed in the continental interior. This, however, was not the case for the Shetlands APO signal, which on the contrary showed a slight (but not significant) increase in the seasonal amplitude when lower ratios were applied. In conclusion, we have found that it is important to consider the influence of land biotic $O_2/CO_2$ ratios when examining APO variations from midcontinental stations, while coastal stations are relatively insensitive to choosing different ratios. Our study has illustrated the potential and versatility of APO data from the interior of a continent being used as a tracer to evaluate global atmospheric transport model simulations, and suggest that further studies from other midcontinental stations and longer data sets could result in improved model characterizations.

[44] In the first 2 months of measurements on the completed tower (November and December 2006, to 300 m), we observed several events with clear vertical concentration gradients in all species except CO. Higher $CO_2$ and corre-

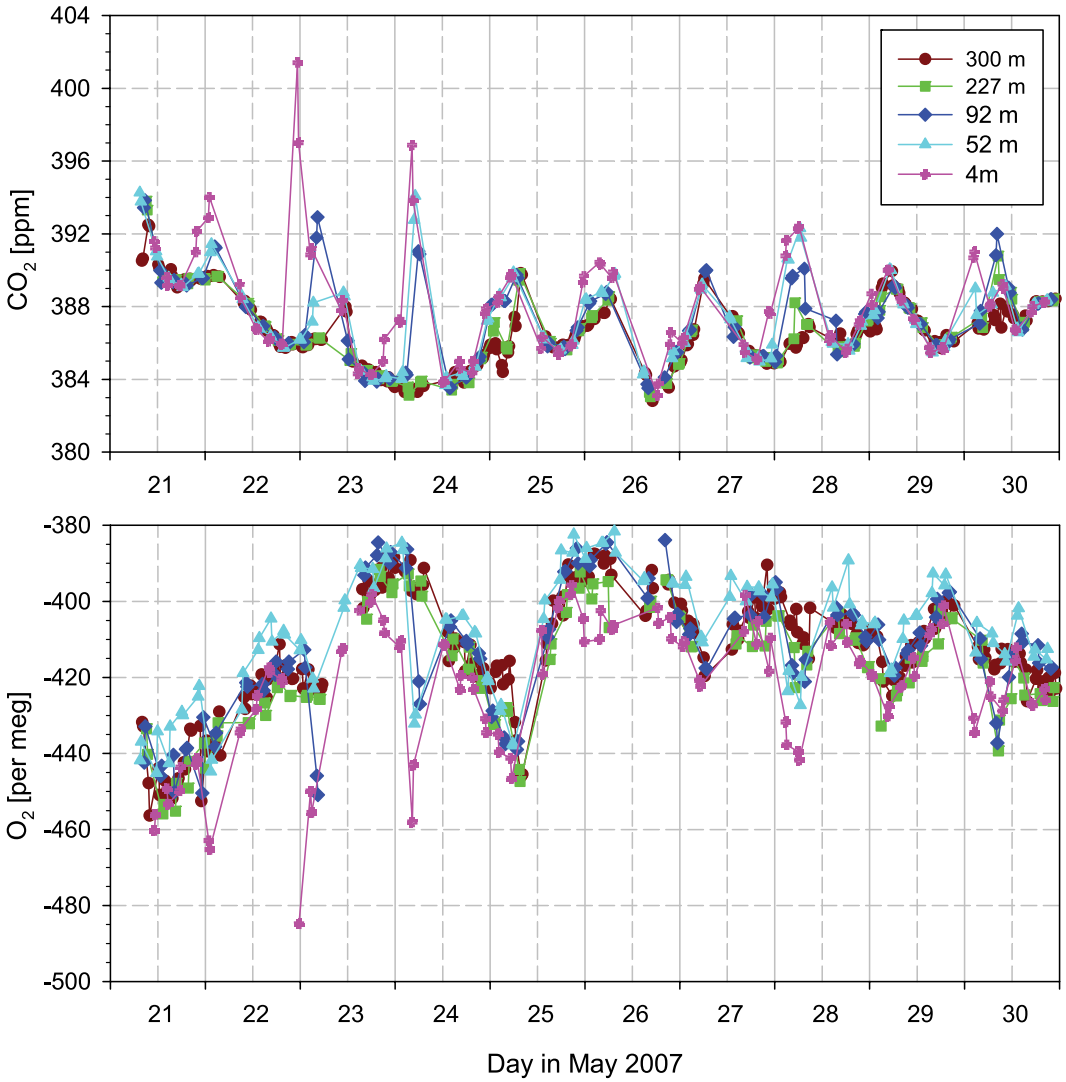


**Figure 5.** Diurnal variations of $CO_2$ and $O_2$ concentrations shown from 21 to 31 May 2007. The *y*-axis scales have been adjusted so that visually, changes in $CO_2$ (ppm) and $O_2$ (per meg) are directly comparable on a mole-to-mole basis. Each data point represents a 4-min average, 16 min apart. Dashed vertical grid lines correspond to 1200 (local standard time) of each day; solid vertical grid lines correspond to 0000.

spondingly lower $O_2$ concentrations were observed from the lower heights (4, 52, and 92 m) as expected owing to ground level $CO_2$ sources (and $O_2$ sinks) from terrestrial respiration and anthropogenic emissions, and the very stable air column caused by low ambient temperature and high-pressure conditions. During "cold events" in November 2006 (ambient temperature below −30°C), large (up to 22 ppm $CO_2$) vertical gradients were observed between the 4-m level and the top of the tower suggesting a source of $CO_2$ in the vicinity of the tower. CO measurements during these events did not exhibit any concurrent increase, therefore the observed $CO_2$ buildup could not be the result of wood burning or power generators. There has been evidence of haze formation under such low wind and cold conditions in Siberia, which could result in the separation of the vertical air column with independent circulation patterns between the top and bottom of the tower. Respired $CO_2$ could thus be responsible for the near-ground $CO_2$ accumulation while upper levels showed small decreases in $CO_2$ concentration because of being isolated from the ground-level sources. This pattern (also seen in $CH_4$ concentrations) was repeated at other times during the winter, particularly in February 2007. We also observed periodic spikes in $CH_4$ concentrations normally occurring at all heights, but sometimes detected only at the lowest levels which indicated local sources that were traced to the surrounding villages from back trajectory analyses.

[45] Unfortunately, summer data exist only for 2006 when the tower was built only up to 52 m, therefore a full analysis of summertime vertical gradients could not be made. In the last month of available measurements, May 2007, we observed vertical gradients and diurnal cycles in $CO_2$, $O_2$ and $CH_4$ but they were relatively small owing to the persistence of relatively cold weather conditions in the first half of May and thus a late start to spring. We estimated average nighttime respiration fluxes in April–May of 0.04 ±

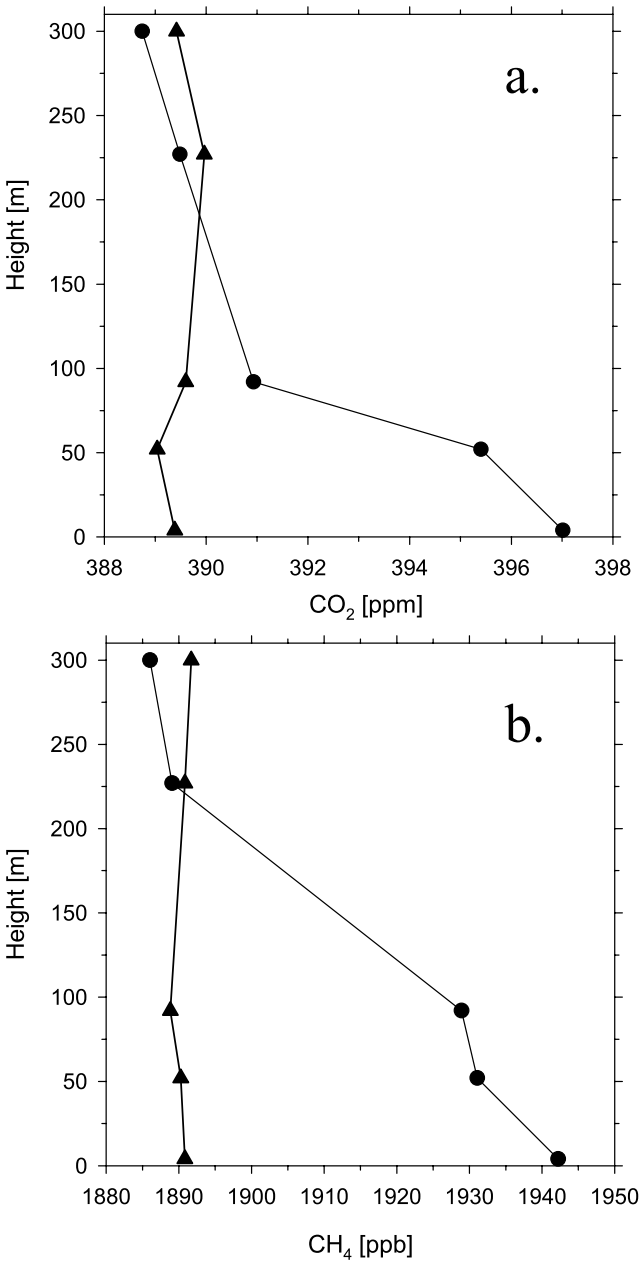


**Figure 6.** Vertical concentration gradients of (a) $CO_2$ and (b) $CH_4$, up to 300 m observed on 7–8 May 2007. The circles show early morning concentrations when the air column was stratified, where each data point is an average over the time period 0500–0700. The triangles represent afternoon averages from the previous day (1400–1600 for $CO_2$ and 1800–2000 for $CH_4$) when the air column was well mixed. The accumulation periods were 15 and 11 h for $CO_2$ and $CH_4$, respectively.

0.02 mol C $m^{-2}$ $d^{-1}$, calculated from $CO_2$ vertical concentration gradients during calm and high-pressure conditions. This result is roughly in agreement with eddy covariance measurements in May made from a nearby location in 1999 and 2000 [*Shibistova et al.*, 2002a]. The same study found respiration fluxes up to ten times greater in July and August, suggesting that observed $CO_2$ concentration gradients at ZOTTO would be much greater later in the summer.

[46] Obviously, longer records of all measured species (especially with the addition of summertime observations) would allow a much more detailed and quantitative analysis of the regional Siberian carbon cycle, as well as tracking long-term trends and interannual variability. With this analysis of the first measurements collected at the ZOTTO tower, this paper demonstrates the potential insight and constraints that multispecies, semicontinuous measurements of trace gases and $O_2$ can provide on the magnitudes and variability of regional land carbon sinks and related processes, and their responses under future climate change.

[47] **Acknowledgments.** We thank A. Jordan (MPI-BGC) and D. Worthy (Environment Canada) for their invaluable advice and contribution in establishing GC measurements at ZOTTO, and we thank R. Keeling and his group (SIO) for their help and advice with the $O_2$ measurements, including the loan of a Servomex $O_2$ sensor. We are very grateful to E.-D. Schulze (MPI-BGC) for many years of work toward the establishment of ZOTTO station. Many thanks to A. Jordan, W. Brand, F. Hänsel, and M. Hielscher (MPI-BGC) for calibration cylinder preparations and to K. Kübler, R. Leppert, S. Schmidt, F. Voigt, B. Schlöffel, R. Schwalbe, and U. Schultz (MPI-BGC) for general advice, instrument design and functioning, and logistical and technical support. We thank all employees of the Sukachev Institute of Forest, SB RAS, in Krasnoyarsk, who participated in the site construction, logistics, and maintenance of the measurement system. We also thank all workers from the Russian construction company "Stroitechinvest." E. A. K. thanks her supervisor, A. Watson (UEA), for general support and advice. The ZOTTO project is funded by the Max Planck Society through International Science and Technology Center (ISTC) partner project 2757p within the framework of the proposal "Observing and Understanding Biogeochemical Responses to Rapid Climate Changes in Eurasia." We are very grateful to Ronnie Robertson from Shetland Islands for the flask samples collection. E. A. K. is supported by a UEA Zuckerman Studentship, and A. C. M. is supported by a U.K. NERC/QUEST Advanced Fellowship (Ref. NE/C002504/1). We also thank three anonymous reviewers for their comments that helped to improve this paper.

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