The O_3–N_2O relation from balloon-borne observations as a measure of Arctic ozone loss in 1991/92

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SUMMARY

We analyse balloon-borne measurements of ozone (O_3) and nitrous oxide (N_2O) in the Arctic, obtained during the European Arctic Stratospheric Ozone Experiment campaign in winter and early spring 1991/92. Using N_2O as a long-lived tracer, we identify chemical ozone depletion in the Arctic vortex in the presence of ozone variations caused by dynamical effects. Substantial chemical ozone loss of about 25% locally over the height range of 15–21 km, corresponding to the potential-temperature range of 400–550 K, is deduced for late winter. Mixing processes can be ruled out as the major cause of the observed anomaly in the O_3–N_2O relation by considering the concurrently measured chlorofluorocarbon-11–N_2O relation. The chemical ozone loss derived from the balloon-borne measurements is in agreement with the loss derived, following the same methodology, from satellite (Halogen Occultation Experiment) vortex observations. Consistent with the dynamical development of the polar vortex and with the observed chlorine activation, the major fraction of the ozone decline occurred before February 1992. The reduced ozone levels persisted over the lifetime of the polar vortex until late March 1992.

KEYWORDS: Arctic Chemical ozone destruction Mixing across vortex edge Ozone loss Stratosphere Tracer relations

1. INTRODUCTION

A series of experiments in the Arctic winter during the late 1980s (e.g. Hofmann *et al.* 1989; Turco *et al.* 1990; Pommereau and Schmidt 1991) demonstrated that the potential exists for substantial chemical ozone destruction in the Arctic during late winter and early spring. It was discovered that the chlorine chemistry in the Arctic vortex in 1988/89 and 1989/90 was highly perturbed (e.g. Brune *et al.* 1990, 1991; Schiller *et al.* 1990; Adrian *et al.* 1991; Perner *et al.* 1991; Toon *et al.* 1992b), in a similar way as earlier observed for the Antarctic (de Zafra *et al.* 1987; Anderson *et al.* 1991). Furthermore, theoretical studies predicted large ozone loss rates (e.g. McKenna *et al.* 1990; Salawitch *et al.* 1990; Brune *et al.* 1991) and aircraft measurements indicated that chemical ozone loss had indeed occurred (Browell *et al.* 1990; Proffitt *et al.* 1990).

Further experiments focused on the problem of Arctic ozone loss, in particular, in the Arctic winter 1991/92 two extensive measurement campaigns were conducted: the Airborne Arctic Stratospheric Expedition II (AASE-II) (Anderson and Toon 1993) and the European Arctic Stratospheric Ozone Experiment (EASOE) (Pyle *et al.* 1994). Moreover, for the 1991/92 winter, the first results from the Upper Atmosphere Research Satellite (UARS), which was launched in September 1991, are available.

In 1991/92, strong chlorine activation—a prerequisite for ozone destruction—was observed inside the Arctic vortex until the end of January by a variety of instruments (e.g. Toon *et al.* 1992a; Toohey *et al.* 1993; Waters *et al.* 1993; Oelhaf *et al.* 1994; Pommereau and Piquard 1994; Traub *et al.* 1994). Furthermore, both observations from the Microwave Limb Sounder (MLS) and from the Halogen Occultation Experiment

(HALOE) (Russell *et al.* 1993) aboard UARS (e.g. Waters *et al.* 1993; Müller *et al.* 1996), as well as the results from EASOE and AASE II (e.g. Browell *et al.* 1993; Proffitt *et al.* 1993; Salawitch *et al.* 1993; Braathen *et al.* 1994; Traub *et al.* 1994; von der Gathen *et al.* 1995; Rex *et al.* 1998; Lucic *et al.* 1999), indicate substantial ozone loss in the Arctic vortex in early 1992. For subsequent winters, the occurrence of significant ozone depletion in the Arctic stratospheric vortex has been confirmed and corroborated through numerous studies (e.g. Manney *et al.* 1994, 1997; Müller *et al.* 1996, 1997a,b; Newman *et al.* 1997; Rex *et al.* 1997; Goutail *et al.* 1999; Hansen and Chipperfield 1999; Woyke *et al.* 1999, and references therein).

Here, we focus on the winter of 1991/92. We analyse a series of co-ordinated ozone sonde (Pyle *et al.* 1994) and balloon-borne tracer measurements (Bauer *et al.* 1994; Schmidt *et al.* 1994) in the Arctic vortex up to about 28 km altitude or 750 K potential temperature, performed regularly throughout the winter in the framework of EASOE (see Table 1 for an overview). We consider the relation between ozone (O_3) and the long-lived tracer nitrous oxide (N_2O) to deduce chemical ozone loss and compare the results with estimates of ozone loss deduced for the same winter from airborne (Proffitt *et al.* 1993) and HALOE measurements (Müller *et al.* 1996).

The mixing ratios of trace species in the stratosphere are influenced both by chemical or physical transformation and by transport processes. Under certain circumstances (see section 2) the relation between two species will not be influenced by the mixing processes that occur during transport. Then, by considering the relation between active species and long-lived tracers, e.g. N_2O or methane (CH_4), large dynamical variations can be eliminated from the analysis so that chemical or physical change can be identified (e.g. Proffitt *et al.* 1989, 1990, 1992; Strahan *et al.* 1989, 1993; Fahey *et al.* 1990; Borrmann *et al.* 1993; Müller *et al.* 1996; Rex *et al.* 1999). Examples of such active species are hydrochloric acid (HCl) or ozone which are subject to chemical change, or total reactive nitrogen (NO_y) that is removed from the stratosphere because it is sequestered in polar stratospheric cloud (PSC) particles. Specific questions regarding the applicability of relations between long-lived tracers and ozone in the stratosphere to deduce chemical ozone loss in the high latitudes in winter and spring were discussed by Proffitt *et al.* (1992), Michelsen *et al.* (1998), Müller *et al.* (1999), and Plumb *et al.* (2000). The behaviour of ozone–tracer relations in the lower stratosphere over all seasons has been recently reviewed (Proffitt *et al.* submitted to *J. Geophys. Res.*).

All these studies in which ozone–tracer relations in the polar region were considered, are in some way restricted by the characteristics of the employed observations. More precisely, the data either have a good horizontal resolution, but are limited in their vertical extent (owing to the restrictions of the flight altitude of the high-altitude research aircraft, ER-2) or have a good vertical coverage, but are restricted to certain latitudes (owing to the orbit geometry of solar occultation instruments) leading to an incomplete coverage of the vortex over the winter. For both the aircraft and the space-borne measurements, the temporal coverage of the vortex area over the winter is imperfect. The latter restriction is particularly severe for the ATMOS experiment aboard the space shuttle that provides accurate data for a large number of species, but only where occultations are possible and only for a relatively short time period (of about two weeks).

The advantage of the EASOE balloon dataset considered here is that regular measurements were performed inside the vortex from the tropopause up to altitudes of about 28 km and extending over the whole winter (30 November 1991 to 20 March 1992). Furthermore, the availability of several independent tracer measurements (N_2O, and the chlorofluorocarbons CFC-113, CFC-11, and CFC-12) allows the question of how far the

relation between two tracers inside the polar vortex will be affected by mixing processes to be addressed; a question not considered in earlier studies where chemical ozone loss has been deduced from ozone–tracer relations (e.g. Müller *et al.* 1997a,b).

The EASOE measurements indicate a substantial chemical loss of ozone (about 25% locally in the lower stratosphere) in the Arctic in 1991/92 in agreement with both independent observations (Proffitt *et al.* 1993; von der Gathen *et al.* 1995; Müller *et al.* 1996; Rex *et al.* 1998; Lucic *et al.* 1999) and model results (Salawitch *et al.* 1993; Lefèvre *et al.* 1994; Lutman *et al.* 1994; Müller *et al.* 1994; Becker *et al.* 1998). Further, the measurements show that the major fraction of the chemical ozone depletion occurred during January 1992 and that the depletion had ceased by early March 1992. This observation for early 1992 is in accordance with both measurements of the temporal development of chlorine monoxide (ClO) (Waters *et al.* 1993) and estimates of the ozone loss rate derived from an analysis of the measurements from the EASOE ozone sonde network (von der Gathen *et al.* 1995; Rex *et al.* 1998). Finally, the observed tracer–tracer relations in the Arctic vortex in 1991/92 are not compatible with the picture that continuous mixing across the vortex edge has substantially altered compact ozone–tracer relations in a way that could lead to an overestimate of deduced chemical ozone loss.

2. OZONE–TRACER RELATIONS AS A QUANTITATIVE MEASURE OF CHEMICAL OZONE LOSS IN THE POLAR VORTEX

(a)   Relations between long-lived tracers in the polar vortex

Plumb and Ko (1992) have demonstrated that throughout the stratosphere compact relations are expected between tracers for which quasi-horizontal mixing along isentropes is fast compared with their local chemical lifetimes. The relation is, furthermore, linear if the local chemical lifetimes of the two tracers in question are long compared with the time-scale of vertical advection (Plumb and Ko 1992). Compact, and over the course of the winter constant, relations between long-lived tracers are also expected for the special case of the air mass inside a polar vortex that is, to a large degree, isolated from its surroundings. Plumb and Ko (1992) have expressed this fact as: ' . . . we expect these relationships for long-lived species to remain valid inside the polar vortex, (. . .). Since the vortex is in place only for a few months during winter, the correlations will be maintained through the winter, though the mixing ratio isopleths may become severely distorted at the vortex edge . . . '. Indeed, such a behaviour is found in HALOE observations in the Arctic vortex in 1995/96 which showed that the relation between the long-lived compounds hydrogen fluoride (HF) and CH_4 was conserved over the course of the winter (Müller *et al.* 1999).

However, if the compact relation between two long-lived tracers is nonlinear, any individual mixing event between two air masses separated in tracer–tracer space (that always leads to a straight line in correlation diagrams) will produce points that fall off the compact relation (dotted line in Fig. 1(a)). In particular, this is the case when air is mixed across the vortex edge. Then, owing to the strong diabatic descent inside the polar vortex compared with its surroundings, air masses with substantially different tracer mixing ratios are mixed and, thus, air masses become separated significantly in tracer–tracer space. For nonlinear tracer–tracer relations, such mixing events will, therefore, cause a deviation from the original tracer–tracer relation; although they will not be evident in scatter plots of tracers with linear relations (e.g. Waugh *et al.* 1997; Michelsen *et al.* 1998; Kondo *et al.* 1999; Rex *et al.* 1999; Plumb *et al.* 2000). Such mixing lines have been clearly observed in fragments of polar vortex air following its breakup (e.g. Waugh
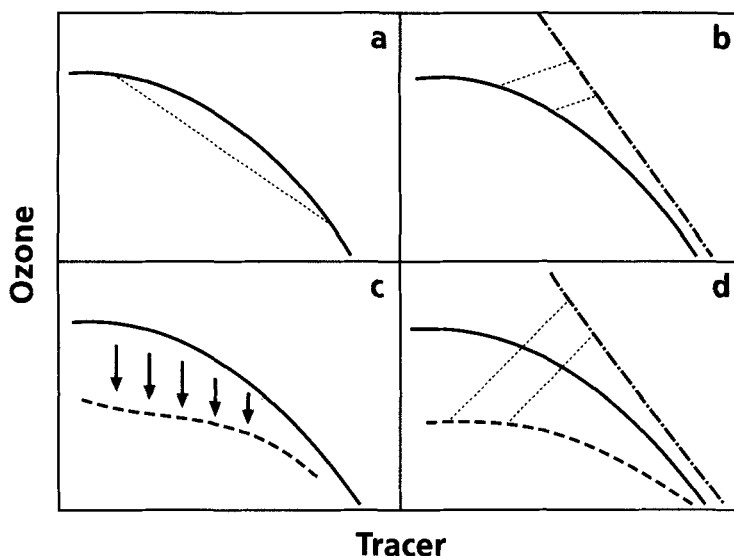
Figure 1. Schematic view of the impact of mixing and chemical ozone loss on the ozone–tracer relation inside the vortex. Thick lines indicate ozone–tracer relations, thin dotted lines 'mixing lines' showing the result (in tracer–tracer space) of mixing of two distinct air masses on a given potential-temperature surface. The solid line (all panels) indicates the 'early vortex' ozone–tracer relation, the dashed line (panels (c) and (d)) an ozone–tracer relation showing the impact of chemical ozone loss, and the dash–dot line (panels (b) and (d)) an 'outside vortex' ozone–tracer relation. Panel (a) shows the impact of mixing of two air masses possessing the same initial tracer–tracer relation, panel (b) the impact of mixing (with outside-vortex air) on a chemically unperturbed vortex ozone–tracer relation, panel (c) the impact of chemical ozone loss on a vortex ozone–tracer relation, panel (d) the impact of both mixing and chemical ozone loss concurrently on the ozone–tracer relation in the vortex.

et al. 1997; Herman et al. 1998; Rex et al. 1999; Rinsland et al. 1999). Further, the NO_y–N_2O relation shows a strong nonlinearity between 5 and 50 parts per billion (10^9) by volume (p.p.b.v.) of N_2O and mixing processes have been shown to impact on the NO_y–N_2O relation substantially in this N_2O range (e.g. Michelsen et al. 1998; Kondo et al. 1999; Manney et al. 1999; Rinsland et al. 1999; Rex et al. 2000).

(b)   The impact of chemical ozone change and mixing on O_3–tracer relations

Ozone in the stratosphere generally can not be considered long-lived enough for compact relations of ozone to tracers to be expected there (Plumb and Ko 1992; Hall and Prather 1995). Indeed, stratospheric ozone in the low latitudes and in the summer hemisphere is under local photochemical control (e.g. WMO 1990), a fact that inhibits the formation of compact ozone–tracer relations.

However, Proffitt et al. (1992) have shown that the lifetime of ozone in the winter high latitudes—in the absence of a perturbed chlorine chemistry and halogen-catalyzed ozone loss—is long enough, larger than 100 days (e.g. WMO 1990), so that ozone can be considered long-lived with respect to the time-scales (several weeks) in question here. Thus, the relation between O_3 and N_2O is expected to remain unaltered (i.e. 'maintained through the winter' in the sense of Plumb and Ko (1992)) inside the polar vortex.

However, if chemical ozone loss due to halogen-catalyzed reactions is occurring, it will lead to a reduction of the ozone value at constant tracer mixing ratios (see Fig. 1(c)) and thus to a deviation from the 'early vortex' relation. Deviations of the—slightly concave—'early vortex' ozone–tracer relation may further be caused by mixing of air separated in ozone–tracer space, in particular by mixing processes across the vortex
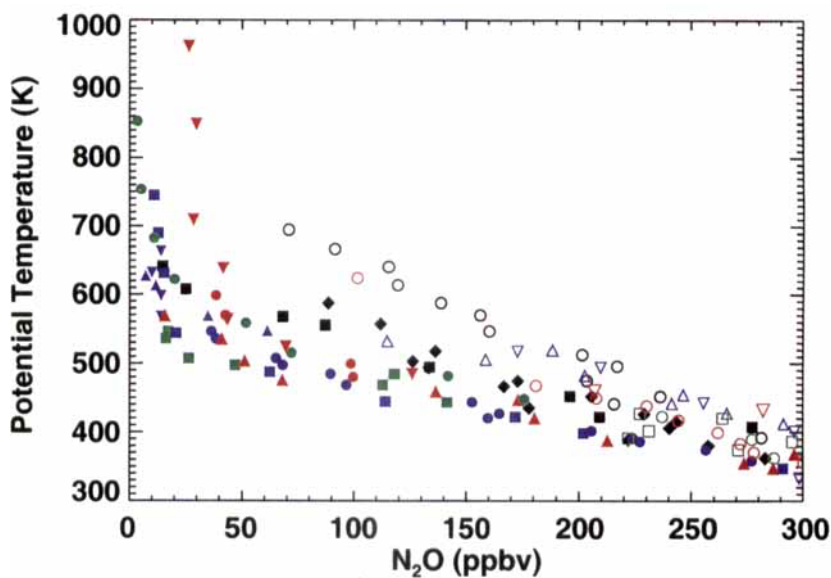
Figure 2. Vertical profiles of nitrous oxide (N_2O) mixing ratio (in parts per billion (10^9) by volume (p.p.b.v.)) against potential temperature as the vertical coordinate. Measurements are shown for November/December 1991 (black symbols), January 1992 (blue symbols), February 1992 (green symbols) and March 1992 (red symbols). The different symbols denote the individual flights (see Table 1); open symbols indicate measurements outside the vortex, filled symbols measurements inside the vortex.
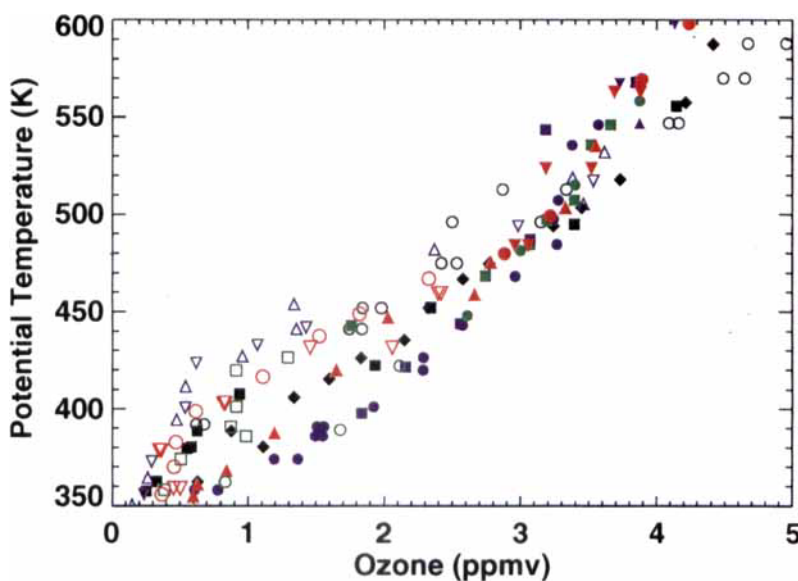

Figure 3. As Fig. 2, but for the mixing ratio of ozone (in parts per million by volume (p.p.m.v.)).

edge. It has been suggested (Michelsen *et al.* 1998; Plumb *et al.* 2000) that such mixing processes could be misinterpreted as chemical ozone loss, since both processes could lead to a similar pattern in tracer–tracer relations (see Fig. 1(a) and (c)). Furthermore, Plumb *et al.* (2000) have considered a scenario, where mixing is occurring continuously throughout the winter during the existence of the vortex and while the vortex air

mass is continuously descending. Under such circumstances, the erosion of nonlinear tracer–tracer relations will be stronger and more complex than the simple picture of an individual mixing event (Fig. 1(a)) suggests.

In the line of arguments above, it is implicitly assumed, as in Plumb *et al.* (2000), that the same tracer–tracer relation holds inside and outside of the vortex. This is, however, in general not the case for an ozone–tracer relation. Ozone at high latitudes in fall and winter recovers from summertime ozone loss as the transport of tropical, ozone-rich air poleward is increasing owing to cooling at high latitudes (Proffitt *et al.* submitted to *J. Geophys. Res.*). Ozone inside the polar vortex, however, is largely isolated from this recovery. Therefore, outside-vortex air should be characterized by larger O_3 mixing ratios (for a specific tracer mixing ratio) than inside; an expectation confirmed by in-situ and remote-sensing measurements (e.g. Proffitt *et al.* 1992, 1993, submitted to *J. Geophys. Res.*; Müller *et al.* 1996, 1999).

Thus, mixing between outside- and chemically unperturbed inside-vortex air will lead to an increase in the O_3 values (at given tracer mixing ratios) in the vortex (Fig. 1(b)). After chemical ozone loss has changed the ozone–tracer relation inside the vortex, the effect of mixing still tends to increase ozone mixing ratios relative to tracer mixing ratios (Fig. 1(d)), indeed, even more strongly than for a chemically undisturbed inside-vortex ozone–tracer relation. Thus, if ozone–tracer relations are analysed for chemical ozone loss, any mixing-in of outside-vortex air into the polar vortex should lead to an *underestimate* rather than an overestimate of the chemical ozone loss.

3. OBSERVATIONS IN THE ARCTIC VORTEX IN 1991/92

(a) Vertical profiles

The N_2O vertical profiles (Fig. 2) investigated here were obtained by balloon-borne whole-air samplers (Bauer *et al.* 1994; Fabian *et al.* 1979) launched from Kiruna in northern Sweden (68°N, 21°E). Together with N_2O, mixing ratios of CFC-11, CFC-12 and CFC-113 were determined (Schmidt *et al.* 1994). The N_2O, CFC-11, and CFC-12 data discussed here were reprocessed compared with earlier published values (Bauer *et al.* 1994; Schmidt *et al.* 1994) and (with the exception of the flights on 18 January 1992, 6 February 1992 and 20 March 1992) conform now to the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory standard (Elkins *et al.* 1993). Relative to the earlier publications, the N_2O values change by less than 3%; the CFC values by less than 10%. While today the analytical precision is of the order of 1%, it is typically of the order of 5% for the N_2O and CFC observations presented here.

The N_2O profile measured on 30 November 1991 outside the polar vortex corresponds well with a mid-latitude early winter reference (Schmidt *et al.* 1991; Bauer *et al.* 1994). The N_2O profiles measured inside the vortex in December 1991 already show clear signatures of diabatic subsidence inside the polar vortex (e.g. Schmidt *et al.* 1991; Tuck *et al.* 1992; Bauer *et al.* 1994) compared with the earlier out-of-vortex measurement. The further N_2O measurements in January 1992 indicate continuing subsidence until January; the profiles in February and March are similar to those observed in January (Fig. 2).

Ozone mixing ratios (Fig. 3) were measured by standard electrochemical-concentration-cell sondes (Pyle *et al.* 1994) which were either flown 'piggyback' on the large balloons or were launched independently, but almost simultaneously (usually within an hour, but with a maximum of 10 hours difference between the time of the launch of the main balloon and that of the ozone sonde, see Table 1). On a few occasions, when

TABLE 1. THE BALLOON FLIGHTS

Symbol	Date	Whole-air sampler	Δt (h)	PV (PVU) at		Col. O_3 loss (DU)	
				475 K	550 K	450–550 K	500–650 K
○	30 Nov. 91	cryo	1; 4	25.4	48.3	–	–
◇	5 Dec. 91	grab	2; 10	33.2	72.2	–	–
□	12 Dec. 91	cryo	0	37.0	93.3	3	–
○	9 Jan. 92	grab	1; 5	50.2	112.1	15	–
□	18 Jan. 92	cryo	0	50.1	105.3	21	12
△	22 Jan. 92	grab	3	22.6	63.2	–	–
▽	31 Jan. 92	grab	1	24.5	70.4	–	–
○	6 Feb. 92	cryo	5	44.4	90.0	17	6
□	10 Feb. 92	grab	10	32.1	88.1	–	–
○	5 Mar. 92	grab	1	36.9	83.6	7	6
△	12 Mar. 92	grab	1	43.7	88.1	21	8
▽	20 Mar. 92	cryo	1; 7	40.0	87.9	–	–

Table lists information on the balloon flights; both 'cryo' and 'grab' samplers were employed (Fabian *et al.* 1979; Bauer *et al.* 1994), Δt is the time difference between the launch of the main balloon and the ozone sonde in hours, the potential vorticity (PV) in PV units (1 PVU $= 10^{-6}$ K kg^{-1} m^2 s^{-1}) at the location of the measurement (67.9°N, 21.1°E) is listed on the 475 K and the 550 K isentropic surface. Loss of column ozone (O_3) (in Dobson units, DU) in early 1992 between the isentropic levels 450–550 K and 500–650 K is listed for profiles inside the vortex in the respective altitude regime. The impact of mixing on the 'early vortex' relation leads to a potential overestimate of the column loss of about 2.5 DU at 450–550 K, the altitude range 500–650 K is not affected (see text for details).

two ozone profiles are available for one N_2O profile, both ozone profiles were used to construct two N_2O-O_3 relations for that day. Diabatic subsidence inside the vortex (e.g. Schmidt *et al.* 1991; Tuck *et al.* 1992; Bauer *et al.* 1994) is anticipated to lead to larger ozone mixing ratios inside the vortex, compared with outside observations (on the same potential-temperature surface), as ozone mixing ratios increase with height in the altitude range investigated here. In contrast, chemical ozone destruction, which is expected to occur predominately inside the polar vortex, counterbalances this effect, as it tends to lead to a decrease of ozone mixing ratios inside, relative to outside the vortex. In 1991/92, the former effect seems to dominate below about 475 K as, there, the ozone mixing ratios are clearly larger inside than outside the vortex. Between 475 K and 550 K, the two counteracting effects seem to balance approximately as, there, similar ozone mixing ratios are measured inside and outside the vortex (Fig. 3).

The potential vorticity (PV) on the 475 K and 550 K isentropic surfaces (Table 1) at the location of the measurements (68°N, 21°E) indicates that all observations in 1992, except those on 22 and 31 January, were taken inside the polar vortex. Here, we employ the average PV at the location of the wind-speed maximum (i.e. about 31 potential vorticity units (PVU) at 475 K and 67 PVU at 550 K) as the criterion for the location of the vortex edge (Rummukainen *et al.* 1994). This is not a very conservative measure of the vortex edge; therefore, not all measurements discussed here are taken deep inside the vortex.

(b)   The observed change in the relations between long-lived tracers

The relation between the two long-lived tracers N_2O and CFC-12 remains compact over the winter 1991/92 for the balloon dataset discussed here (Fig. 4). (Note that precise measurements of N_2O and CFC-12 are necessary to establish the conservation of such a tracer–tracer relation.) This behaviour is indeed expected from the arguments given in section 2(*a*). The observed CFC-12–N_2O relation is linear and in agreement with ER-2 (Kawa *et al.* 1993) and Cryogenic Limb Array Etalon Spectrometer (CLAES) observations (Nightingale *et al.* 1996) in this and other winters.
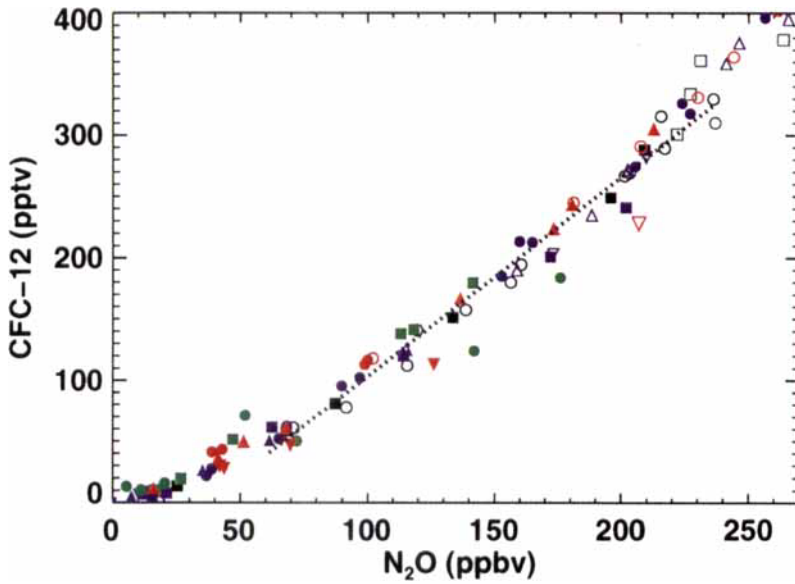
Figure 4.   The relation between nitrous oxide (N_2O) in parts per billion (10^9) by volume (p.p.b.v.) and chloroflurocarbon 12 (CFC-12) in parts per trillion (10^{12}) by volume (p.p.t.v.) from the balloon-borne measurements (Schmidt *et al.* 1994) in December 1991 (black) and January, February, and March 1992 (blue, green, and red, respectively; symbols as in Figs. 2 and 9). A linear fit through the data (dotted black lines) yields CFC-12 (p.p.t.v.) = 1.62 × N_2O (p.p.b.v.)−59.2, (for 60 p.p.b.v. < N_2O < 240 p.p.b.v.).

Figure 5.   The relation between nitrous oxide (N_2O) in parts per billion (10^9) by volume (p.p.b.v.) and chloroflurocarbon 11 (CFC-11) in parts per trillion (10^{12}) by volume (p.p.t.v.) from the balloon-borne measurements (Schmidt *et al.* 1994) in December 1991 (black) and January, February, and March 1992 (blue, green, and red, respectively; symbols as in Figs. 2 and 9). A linear fit through the data (dotted black line) yields CFC-11 (p.p.t.v.) = 1.45× N_2O (p.p.b.v.) −208.8, (for 160 p.p.b.v. < N_2O < 260 p.p.b.v.). The solid magenta line indicates a possible mixing line between subsided vortex air masses and outside-vortex air (see text for details).
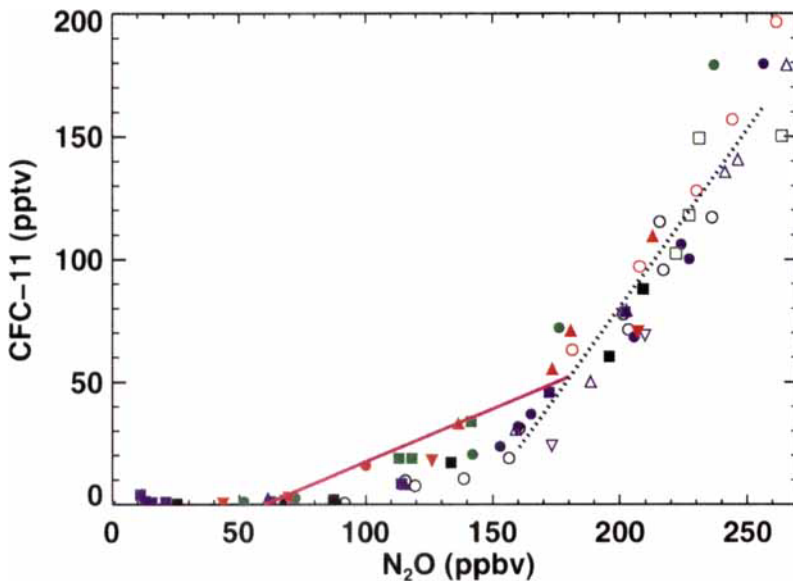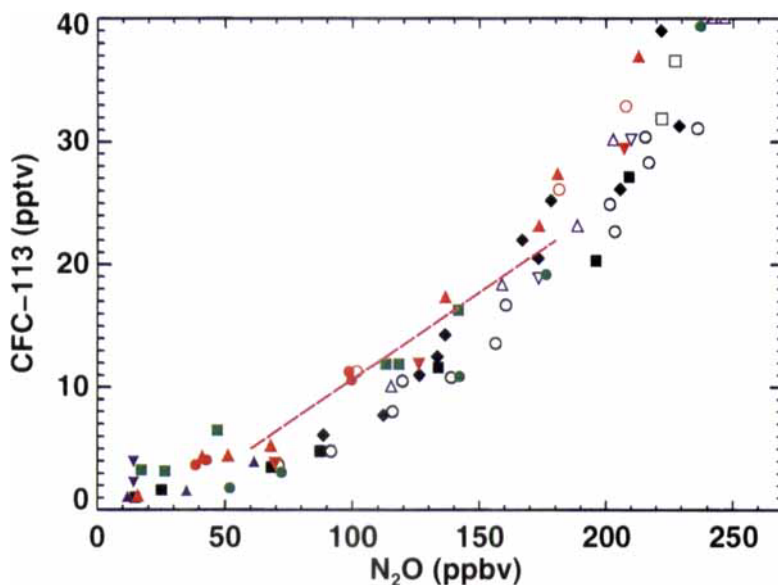
Figure 6. The relation between nitrous oxide (N_2O) in parts per billion (10^9) by volume (p.p.b.v.) and chlorofluorocarbon 113 (CFC-113) in parts per trillion (10^{12}) by volume (p.p.t.v.) from the balloon-borne measurements (Schmidt *et al.* 1994) in December 1991 (black) and January, February, and March 1992 (blue, green, and red, respectively; symbols as in Figs. 2 and 9). The dashed magenta line indicates a possible mixing line between subsided vortex air masses and outside-vortex air (see text for details).

The relation of CFC-11 to N_2O measured in the winter 1991/92 by the balloon-borne whole-air samplers (Fig. 5) shows a nonlinear behaviour in the N_2O range ≈ 100–180 p.p.b.v. It is in accordance with earlier ER-2 observations (Kawa *et al.* 1993). While no substantial deviation from the early winter CFC-11–N_2O relation (black symbols) over the course of the winter is apparent (Fig. 5), measurements in February and March (green and red symbols) nevertheless show somewhat enhanced mixing ratios of CFC-11 (for 100 p.p.b.v. $< N_2O < 150$ p.p.b.v.) that could be due to mixing of vortex air with outside-vortex air, the latter being characterized by greater mixing ratios of CFC-11 and N_2O. Again, precise measurements are required for the validity of such conclusions.

The relation between CFC-113 and N_2O shows a similar pattern to CFC-11 and N_2O (Fig. 6), although the relation is curved less strongly since the lifetimes of CFC-113 and N_2O are more similar than those of CFC-11 and N_2O. Nonetheless, the mixing behaviour apparent in the CFC-113–N_2O relation is consistent with the one derived from the CFC-11–N_2O relation (see the mixing line in Fig. 6). The potential impact of such mixing events on estimates of chemical ozone loss will be discussed below.

(c)   The observed change in the O_3–N_2O relation

The change in the N_2O–O_3 relation over the winter 1991/92 will be analysed below to deduce chemical ozone loss; here the balloon-borne observations will be compared with ER-2 and HALOE measurements of the same winter and the reference relations necessary for the deduction of ozone loss will be established. These relations are given as empirical polynomial functions deduced from the measurements (Table 2). They were compared with the observed N_2O–O_3 relation over a wide range of latitudes and seasons (Proffitt *et al.* submitted to *J. Geophys. Res.*).

TABLE 2.   TRACER RELATIONS

Relation	(y)	(x)	Valid range of (x)	a_0	a_1	a_2	a_3	a_4	Reference
R1	O_3	N_2O	100–290	8.71	-2.83×10^{-2}	—	—	—	This work
R2	O_3	N_2O	160–275	8.434	-2.788×10^{-2}	–	–	–	Proffitt *et al.* (1990)
R3	O_3	N_2O	50–290	8.56	-2.72×10^{-2}	–	–	–	Proffitt *et al.* (1990)
R4	O_3	N_2O	135–275	7.172	-2.306×10^{-2}	–	–	–	Proffitt *et al.* (1993)
R5	O_3	N_2O	90–270	5.93	-1.86×10^{-2}	–	–	–	This work
R6	O_3	N_2O	10–260	3.94	4.84×10^{-3}	-6.40×10^{-5}	–	–	This work
R7	O_3	N_2O	135–275	1.682	1.862×10^{-2}	-7.98×10^{-5}	–	–	Proffitt *et al.* (1993)
R8	O_3	N_2O	20–255	4.51	-2.31×10^{-2}	3.53×10^{-4}	-2.29×10^{-6}	4.16×10^{-9}	This work
R9	O_3	CH_4	0.5–1.5	21.38	-75.43	119.84	-81.63	19.52	Müller *et al.* (1999)
R10	N_2O	CH_4	0.5–1.7	-136.1	261.8	–	–	–	Engel *et al.* (1996)

Polynomial functions of the form: $(y) = \sum_{i=0}^{n} a_i \cdot (x)^i$ with $n \leqslant 4$. O_3 = ozone in parts per million by volume (p.p.m.v.), N_2O = nitrous oxide in parts per billion (10^9) by volume (p.p.b.v.) and CH_4 = methane in p.p.m.v.
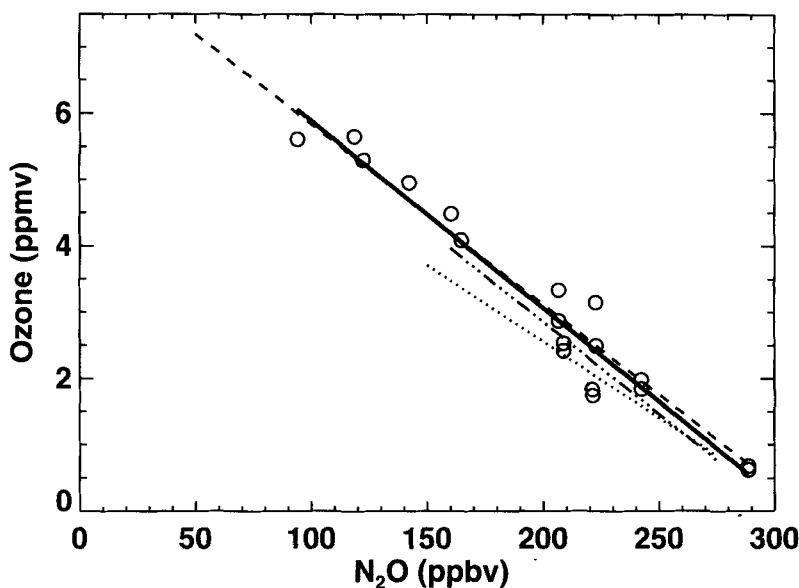

Figure 7.   The relation between nitrous oxide (N_2O) in parts per billion (10^9) by volume (p.p.b.v.) and ozone (O_3) in parts per million by volume (p.p.m.v.) outside the vortex from balloon-borne N_2O and O_3 measurements (circles) from Kiruna on 30 November 1991. The solid line shows a fit through the data (R1 in Table 2). The dashed–dot-dot-dot line indicates the mid-latitude reference from ER-2 measurements in February 1989 at 37°–39°N (Proffitt *et al.* 1990), the dotted line the 'outside vortex' reference from ER-2 measurements December 1991 through March 1992 (Proffitt *et al.* 1993), and the dashed line a linear fit to the observations by the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument in May 1985 at 28°N and 48°S (Proffitt *et al.* 1990). The relations are listed in Table 2.

The first balloon-borne measurement of the N_2O–O_3 relation in the Arctic winter 1991/92 (Fig. 7) was obtained on 30 November 1991 outside the polar vortex. Over the observed N_2O range, the relation is approximately linear (solid line in Fig. 7, R1 in Table 2). This is the only profile of the balloon dataset discussed here that represents out-of-vortex conditions at all altitudes. This N_2O–O_3 relation corresponds to the general 'outside vortex' relation denoted by a dash–dot line in Fig. 1. It is in accordance with the mid-latitude relation obtained in February 1989 by the ER-2 (dashed–dot-dot-dot line in Fig. 7, R2 in Table 2), (Proffitt *et al.* 1990) and the observations by the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument in May 1985 at 28°N and 48°S

(dashed line in Fig. 7, R3 in Table 2), (Proffitt *et al.* 1990). However, the N_2O–O_3 'outside vortex' relation obtained for December 1991 through March 1992 by the ER-2 in high northern latitudes (dotted line in Fig. 7, R4 in Table 2), (Proffitt *et al.* 1993):

$$O_3 \text{ (p.p.m.v.)} = 7.172 - (2.306 \times 10^{-2}) \cdot N_2O \text{ (p.p.b.v.)} \tag{1}$$

where p.p.m.v. is parts per million by volume, shows somewhat lower ozone mixing ratios, possibly because of the export of processed, low-ozone (and high N_2O) air out of the vortex.

The first balloon-borne vortex measurements were obtained on 5 and 12 December 1991. As the minimum temperatures in the vortex did not drop significantly below the equilibrium existence point of nitric acid trihydrate (NAT) before mid December 1991 (O'Neill *et al.* 1994; Pawson *et al.* 1995), the N_2O–O_3 relation observed inside the vortex in early December 1991 (Fig. 8) should not be influenced by ozone loss due to heterogeneous chlorine activation and subsequent halogen-catalyzed chemical ozone loss. The balloon observations of 5 and 12 December may thus serve as a reference for chemically undisturbed vortex conditions. A linear fit through the balloon-borne observations can be obtained for $N_2O > 90$ p.p.b.v. (R5 in Table 2), while the empirical relation for these data can be extended to lower N_2O mixing ratios (10 p.p.b.v. $< N_2O < 260$ p.p.b.v.) and thus higher altitudes for a quadratic fit (R6 in Table 2)

$$O_3 = 3.94 + (4.84 \times 10^{-3}) \cdot N_2O - (6.40 \times 10^{-5}) \cdot (N_2O)^2 \tag{2}$$

(O_3 in p.p.m.v. and N_2O in p.p.b.v.). In the following we will always employ Eq. (2) as the reference state for chemically unperturbed conditions in the early vortex. This relation corresponds to the general 'early vortex' relation depicted as a solid line in Fig. 1.

In an earlier study of the ozone loss in the Arctic winter 1991/92, Proffitt *et al.* (1993) used ER-2 measurements of the O_3–N_2O relation in high latitudes in October 1991 as the reference for conditions not affected by chemical ozone loss due to heterogeneous chlorine activation (R7 in Table 2):

$$O_3 = 1.682 + (1.862 \times 10^{-2}) \cdot N_2O - (7.98 \times 10^{-5}) \cdot (N_2O)^2 \tag{3}$$

(O_3 in p.p.m.v. and N_2O in p.p.b.v.). The two relations derived from the ER-2 measurements (Eq. (3)) and the EASOE balloon data (Eq. (2)) are consistent at lower altitudes, below about 200 p.p.b.v. N_2O, but the October reference shows lower ozone values above (Fig. 8). These low ozone values may be explained as a remainder of summertime low ozone concentrations in high latitudes, which are observed in the middle and lower stratosphere owing to catalytic ozone destruction by nitric oxide (NO) and nitrogen dioxide (NO_2) (e.g. Farman *et al.* 1985; Proffitt *et al.* 1992; Brühl and Crutzen 2000).

The 'early vortex' reference (Eq. (2)) may be further compared with the tracer–O_3 relation for December 1991 derived from HALOE (version 18) observations (Fig. 8, plus signs in panel (a), R8 in Table 2). This N_2O–O_3 relation is derived from the original CH_4–O_3 relation (R9 in Table 2) (Müller *et al.* 1999), using an observed N_2O–CH_4 relation (R10 in Table 2), (Engel *et al.* 1996). The relation derived from the balloon-borne measurements for the 'early vortex' is in good agreement with the HALOE observations.

Thus, the 'early vortex' data measured by the balloon instruments during EASOE and by HALOE in December 1991 present a baseline for calculating the ozone loss in the course of winter and early spring. Such information was not available in the earlier study based on ER-2 data (Proffitt *et al.* 1993), where it was assumed that the correct reference
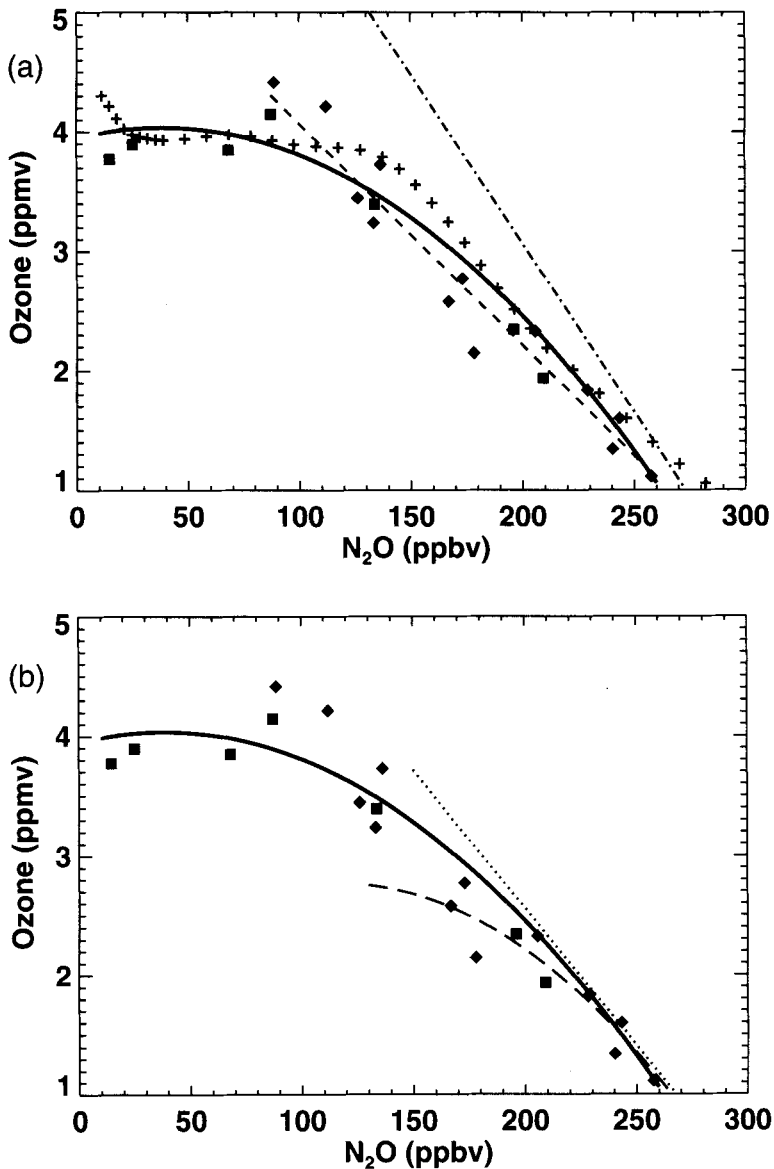
Figure 8. The relation between nitrous oxide (N_2O) in parts per billion (10^9) by volume (p.p.b.v.) and ozone (O_3) in parts per million by volume (p.p.m.v.) for 'early vortex' conditions. In both panels, diamonds indicate the balloon-borne data from 5 December 1991; squares data from 12 December 1991. The thick solid line shows an empirical fit (for 10 p.p.b.v. < N_2O < 260 p.p.b.v.) through those data, Eq. (2). (a) Dashed line shows a linear fit through the balloon-borne data (R5 in Table 2). The dash–dot line shows the 'outside' reference (R1 in Table 2, see also Fig. 7); overplotted (plus signs) is the N_2O–O_3 relation (R8 in Table 2) derived from Halogen Occultation Experiment ozone and methane (CH_4) measurements in the Arctic vortex on 4 December 1991 at 49°N, 92°W (Müller *et al.* 1996) using the N_2O–CH_4 relation R10 in Table 2 (Engel *et al.* 1996). (b) The dotted line shows the vortex exterior, Eq. (1) and the long-dashed line the 'early vortex' reference, Eq. (3), both from ER-2 measurements in October 1991 (Proffitt *et al.* 1993).

state lies between the 'October', (Eq. (3)), and the 'exterior', (Eq. (1)), reference. This conjecture is in accordance with the December 'early vortex' reference derived from the EASOE balloon data and the HALOE measurements (Fig. 8(b)). The latter two relations further extend the validity of the reference to lower mixing ratios of N_2O compared with the ER-2 relation and thus to higher altitudes.

The 'outside vortex', (R1 in Table 2) and the 'early vortex' reference (Eq. (2)), are juxtaposed in Fig. 9 with all N_2O–O_3 relations obtained from the January, February, and March measurements. Clearly, practically all observations inside the vortex in January, February, and March 1992 show substantially lower ozone mixing ratios (for equal values of N_2O) than the 'early vortex' reference from December 1991.

(d)   The impact of chemical ozone change and mixing on the O_3–N_2O relation

Any deviation of measurements in late winter and early spring from the 'early vortex' ozone–tracer relation as in Fig. 9, may be either interpreted as an indication of chemical ozone loss (e.g. Proffitt et al. 1990; Müller et al. 1996) or possible mixing with air with a different O_3–N_2O relation from outside the vortex (see section 2(b)). Such mixing processes should show up in the temporal development of tracer–tracer relations of compounds that possess a nonlinear relation; the more strongly nonlinear the relation is in the region affected by mixing, the more substantially is the tracer–tracer relation changed. For example, the NO_y–N_2O relation shows a strong nonlinearity between 5 and 50 p.p.b.v. N_2O and mixing processes have been shown to impact on the NO_y–N_2O relation substantially in this N_2O range (e.g. Kondo et al. 1999). Mixing in this N_2O regime, in contrast, will hardly affect the O_3–N_2O relation in the early vortex of 1991/92 (Eq. (2)), because of lack of nonlinearity (Fig. 8). This relation is more susceptible to mixing in the N_2O range ≈ 100–180 p.p.b.v., where it shows some nonlinearity.

Therefore, we investigate the CFC-11–N_2O relation that shows a nonlinear behaviour in this N_2O range (Fig. 5). The measurements in February and March show indications of mixing processes (magenta line in Fig. 5, see also section 2(b)). Such mixing processes would also impact on the O_3–N_2O relation and could in principle lead to a change in the 'early vortex' O_3–N_2O relation due to mixing processes that might be misinterpreted as chemical ozone loss (e.g. Michelsen et al. 1998; Plumb et al. 2000). The mixing line in the O_3–N_2O scatterplot corresponding to the possible CFC-11–N_2O mixing line (Fig. 5) is shown as a magenta line in Fig. 9. The maximum possible over-estimate of chemical ozone loss occurs at $N_2O \approx 120$–140 parts per trillion (10^{12}) by volume (p.p.t.v.) (about 480 K) and amounts to 0.2 p.p.m.v. of ozone. The difference in terms of total ozone between the reference curve as in Eq. (2) and the one including the mixing line in Fig. 9 amounts to about 5 Dobson units (DU).

The use of such a 'mixing line' argument has been criticized by Plumb et al. (2000) if tracer relations with significantly different curvature are considered. They further argue that multiple (shallow) mixing events should cause deviations from a single mixing line if the mixed-air parcel continues to descend after the first mixing event. By considering tracer relations with similar curvature (namely CFC-11–N_2O and O_3–N_2O, see above), we obviate the former problem. Regarding the latter problem, we note that in the winter 1991/92 the major fraction of descent has occurred by January (Fig. 2) when no signs of mixing are noticeable in the CFC-11–N_2O relation (Fig. 5). In February and March 1992, when mixing may have impacted on tracer relations (Fig. 5), no substantial further descent is evident in tracer profiles (Fig. 2). Thus, intermittent (shallow) mixing events in February and March 1992 should produce air parcels lying on a rather narrow mixing line.

Moreover, by transferring the magenta mixing line in the CFC-11–N_2O relation (Fig. 5) in the way outlined above to the O_3–N_2O relation (Fig. 9) one tacitly assumes that the same tracer–tracer relation holds inside and outside of the vortex. While this assumption is defensible in the case of, for example, CFC-11–N_2O, it is generally not applicable to O_3–tracer relations. As discussed above (section 2(*b*)), outside-vortex air has greater O_3 mixing ratios (on constant tracer mixing-ratio isopleths) than inside-vortex air. Thus, if mixing between outside and inside air is occurring this should lead to an *underestimate* of the chemical ozone loss deduced from O_3–tracer relations (Fig. 1).

Therefore, we conclude that under the meteorological conditions of the Arctic vortex in 1991/92, mixing processes can not explain the substantial deviations of the late winter O_3–N_2O relations from the 'early vortex' reference. Without a detailed analysis, it is difficult to say how far these conclusions for 1991/92 can be transferred to other Arctic winters. However, one would expect to find a comparable picture in winters with a similar extent of mixing across the vortex edge, that is, in winters with a similarly strong and stable vortex. Indeed, similar conclusions, namely a rather small impact of mixing processes on deduced ozone losses in mid winter, were reached in a recent study where chemical ozone loss and mixing processes in the Arctic in February 1995 were investigated based on CH_4, N_2O, and O_3 observations (Woyke *et al.* 1999).

4. RESULTS

(*a*) *The deduced chemical ozone loss*

The substantial reduction in ozone for a given value of N_2O between January and March 1992 is thus interpreted as an irreversible, chemically caused ozone loss, as in earlier studies (Proffitt *et al.* 1989, 1990, 1993; Müller *et al.* 1996, 1997a,b). The local ozone loss derived here for the Arctic vortex in the winter of 1991/92 amounts to about 25% in the lower stratosphere (Fig. 9), in approximate agreement with the conclusions drawn from lidar (Browell *et al.* 1993) and in situ (Proffitt *et al.* 1993) ozone measurements during AASE II, as well as with the results of an analysis of HALOE observations in the same winter (Müller *et al.* 1996). On some occasions the balloon air samples were taken outside the vortex in the lower part of the profile (Bauer *et al.* 1994). These data are shown as open symbols in Fig. 9 and, as expected, show much higher ozone mixing ratios for equal values of N_2O than measurements inside the vortex. The same ozone deficit is deduced using the HALOE measurements, relation R8 in Table 2, as the early vortex reference.

Comparing January, February and March observations against the 'early' vortex reference (Fig. 9) furthermore indicates that the ozone loss took place mainly during January 1992 with little ozone destruction thereafter. This observation is consistent with satellite measurements, which indicate a strong decline of the ClO concentrations in the vortex in 1992 from mid January to mid February (Waters *et al.* 1993) brought about by the rise in vortex temperatures at this time (Farman *et al.* 1994; O'Neill *et al.* 1994). The conclusions derived from the balloon data are further consistent with ER-2 measurements of the evolution of the O_3–N_2O relation in early 1992 (Proffitt *et al.* 1990) and with an analysis of the ozone loss rates in the vortex in 1992 (von der Gathen *et al.* 1995; Rex *et al.* 1998) that shows a severe decline of ozone loss in early February 1992. Large ozone loss rates early in the winter are also in accordance with the observation that the vortex in early and mid January was strongly shifted off the pole (e.g. Farman *et al.* 1994; O'Neill *et al.* 1994), that is, into regions with a considerable exposure to solar radiation. The observations presented here are furthermore in agreement with the O_3–N_2O relation for late February 1992 inside the vortex obtained by Emmons *et al.*

(1994) and with their conclusion that no significant ozone depletion occurred in the vortex during this period.

Therefore, the relation of ozone to a long-lived tracer in the Arctic in late 1991 derived from observations by the ER-2 (Proffitt *et al.* 1993), from HALOE satellite measurements (Müller *et al.* 1996) and from the balloon dataset discussed here consistently indicates lower ozone mixing ratios for a given tracer mixing ratio inside the polar vortex than outside, indicative of substantial chemical ozone depletion of about 25% locally in the lower stratosphere.

(b)   Loss of column ozone

Simultaneous measurements of a long-lived tracer (such as CH_4, HF) and ozone over winter and spring in the Arctic vortex were used in the past to deduce a proxy for the ozone mixing ratio $(\widehat{O}_3)$ expected in the absence of chemical loss of ozone. Then, calculating the difference between the integral with respect to altitude of the observed ozone profile and the proxy-ozone profile, one obtains an estimate of the chemical reduction of the ozone column in the lower stratosphere (Müller *et al.* 1996, 1997a,b). Here, we employ the balloon-borne N_2O measurements in early 1992 in the Arctic vortex together with the 'early vortex' $N_2O–O_3$ relation for December 1991 (Eq. 2), to compute $\widehat{O}_3$ and then determine the chemical reduction of column ozone. Since part of the balloon profile at lower altitudes was taken outside of the vortex on several occasions (Bauer *et al.* 1994), an integration over the full altitude range is not always meaningful. Furthermore, $\widehat{O}_3$ can only be computed for the valid range (in N_2O) of the 'early vortex' $N_2O–O_3$ relation (Eq. 2). However, a large fraction of the ozone in the Arctic winter and early spring resides in the altitude range 14–21 km (corresponding to potential temperature $\Theta = 400–550$ K) which is also the altitude regime most vulnerable to halogen-catalyzed ozone destruction: observations indicate substantially enhanced total inorganic chlorine (Cl_y) down to about 400 K due to diabatic subsidence (Schmidt *et al.* 1994), extremely low chlorine nitrate ($ClONO_2$) at about 22 km and below (Oelhaf *et al.* 1994), strongly reduced hydrochloric acid (HCl) between 400 and 475 K (Müller *et al.* 1996), and enhanced chlorine dioxide (OClO) between 15 and 20 km (Pommereau and Piquard 1994).

Therefore, the ozone loss at 400–550 K will constitute a substantial fraction of the depletion in the total ozone column. Significant chemical ozone depletion is deduced from the balloon observations in the vortex in January, February, and March 1992 (Table 1).

For comparison, the column ozone losses deduced for the same potential-temperature range from HALOE observations in the Arctic vortex in early 1992 are listed in Table 3. Comparing the two datasets it should be noted that the HALOE data constitute averages along the line of sight, that is, over several hundred kilometres, whereas the balloon data are local samples. Further, early in the winter (up to mid February), when large ozone loss rates occur inside a vortex that is very inhomogeneously exposed to sunlight, one likewise would expect an inhomogeneously distributed ozone loss inside the vortex. This is indeed borne out by the HALOE observations (Table 3). In late March and early April, however, HALOE observes a rather homogeneous ozone loss between 450 and 550 K of ≈ 23 DU. Such a value is also in accordance with the balloon data, with the exception of the profile on 5 March, which is influenced by vortex-edge air (Bauer *et al.* 1994). The HALOE observations furthermore indicate, in agreement with the observed chlorine activation (see above), that the largest ozone column change by February and into March and April 1992 occurs between about 400 and 450 K.
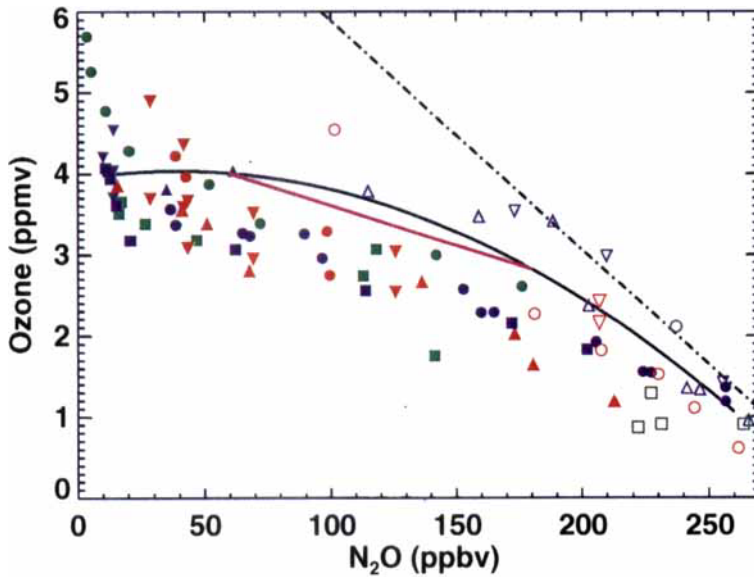
Figure 9. The relation between nitrous oxide (N_2O) in parts per billion (10^9) by volume (p.p.b.v.) and ozone (O_3) in parts per million by volume (p.p.m.v.) from balloon-borne measurements in January 1992 (blue symbols), February 1992 (green symbols) and March 1992 (red symbols). Symbols denote the individual flights (see Table 1); open symbols indicate measurements outside the vortex, filled symbols measurements inside the vortex. The solid black line shows the 'early vortex' reference, Eq. (2); (see also Fig. 8), the dash–dot line the 'outside vortex' reference (R1 in Table 2). The solid magenta line indicates a possible mixing line between subsided vortex air masses and outside-vortex air (compare with Fig. 5 and see text for further details).

Figure 10. Vertical profile of ozone (O_3) mixing ratio in parts per million by volume (p.p.m.v.) measured inside the vortex on 18 January 1992 (red line). Also shown is the proxy ozone ($\widehat{O}_3$), (green line), expected in the absence of chemical processing as derived from the concurrent nitrous oxide (N_2O) measurements (see text for details). The integrated chemical ozone loss between 370 K and 700 K amounts to 57 Dobson units.

TABLE 3.   HALOE OBSERVATIONS IN THE VORTEX IN 1991/92

Date	UARS day	Lat. (°N)	Long. (°E)	PV (PVU) at 475 K	PV (PVU) at 550 K	O₃ col. loss (DU) for 400–550 K	O₃ col. loss (DU) for 450–550 K
4 Dec. 1991	84	48.57	−92.37	31.2	65.0	–	–
14 Jan. 1992	125	49.27	48.55	38.9	75.8	31	19
16 Jan. 1992	127	49.14	46.29	31.8	79.4	41	33
18 Jan. 1992	129	48.29	19.12	32.4	90.4	13	13
8 Feb. 1992	150	51.10	45.47	43.8	87.2	54	18
9 Feb. 1992	151	52.30	44.10	36.4	84.6	42	21
11 Feb. 1992	153	53.82	66.11	44.8	89.8	72	22
12 Feb. 1992	154	54.23	65.39	35.5	78.7	82	39
13 Feb. 1992	155	54.39	88.90	36.7	72.7	48	34
29 Mar. 1992	200	66.36	−255.66	39.9	74.4	78	25
29 Mar. 1992	200	66.27	−231.50	42.2	82.5	74	20
29 Mar. 1992	200	66.18	−207.34	39.3	75.7	61	15
30 Mar. 1992	201	67.68	−258.17	42.3	79.7	70	20
30 Mar. 1992	201	67.60	−234.00	40.0	80.4	76	23
30 Mar. 1992	201	67.51	−209.83	39.9	81.6	78	29
31 Mar. 1992	202	68.93	−260.83	38.3	72.4	74	23
31 Mar. 1992	202	68.85	−236.65	39.4	78.7	78	25
1 Apr. 1992	203	70.10	−263.67	41.0	74.1	75	26
1 Apr. 1992	203	70.02	−239.47	41.0	77.7	78	22
1 Apr. 1992	203	69.94	−215.27	41.4	78.2	72	23
2 Apr. 1992	204	71.19	−266.68	42.1	79.6	61	22
2 Apr. 1992	204	71.12	−242.47	40.7	74.9	69	24
2 Apr. 1992	204	71.04	−218.26	41.4	73.2	69	24

Loss in column ozone (O_3) in Dobson units (DU) between the isentropic levels 400–550 K and 450–550 K for Halogen Occultation Experiment (HALOE) observations inside the vortex in early 1992. UARS day is the number of days since the launch of the Upper Atmosphere Research Satellite on 12 September 1991. Also listed is potential vorticity (PV) in PV units (1 PVU = 10^{-6} K kg^{-1} m^2 s^{-1}) at 475 and 550 K potential temperature at the location of the measurement. HALOE version 18 data are used (in contrast to Müller *et al.* (1996)).

TABLE 4.   VERTICALLY RESOLVED OZONE LOSS

Altitude range (K)	18 Jan. 1992 obs. (DU)	18 Jan. 1992 proxy (DU)	18 Jan. 1992 loss (DU)
370–400	34	46	12
400–450	55	74	19
450–500	35	47	12
500–550	22	31	9
550–700	39	44	5
370–700	185	242	57

Column ozone in Dobson units (DU) in several potential-temperature ranges on 18 January 1992: listed is the observed ozone (obs.), the proxy ozone calculated from the observed nitrous oxide (N_2O) and Eq. (2), and the deduced chemical ozone loss.

The balloon observations on 18 January 1992 (Fig. 10) were taken well inside the vortex throughout almost the complete altitude range, i.e. between 370 and 700 K (Bauer *et al.* 1994). The height-resolved chemical loss for this profile is shown in Table 4. On 18 January 1992, clearly lower observed ozone mixing ratios than calculated $\widehat{O_3}$ are found, with a maximum local deduced ozone loss of ≈ 1.1 p.p.m.v. at 450 K (Fig. 10); consistent with the findings during AASE II (Proffitt *et al.* 1993). The calculated loss in column ozone for this profile between 370 and 700 K is 57 DU, the major fraction

(31 DU, see Table 4) occurring below the isentropic level 450 K in accordance with the conclusion derived above from the HALOE measurements.

5. CONCLUSIONS

An ozone deficit in the Arctic vortex of about 25% in the lower stratosphere is identified in the mid-winter O_3–N_2O relation in 1992 and is observed to persist until March. Analysis of the concurrently measured CFC-11–N_2O relation rules out mixing processes as the major cause for this observation—precise tracer measurements are required for these assertions. Therefore, we conclude that chemical loss is the reason for the observed deficit. The major fraction of the column ozone change occurs below 450 K. No further chemical ozone loss is observed between early February and late March 1992 in accordance with both satellite-borne measurements of the temporal development of ClO over this winter (Waters *et al.* 1993), the ozone loss rate deduced from ozone-sonde observations (von der Gathen *et al.* 1995; Rex *et al.* 1998), and with an analysis of ozone loss based on aircraft data (Proffitt *et al.* 1993) in the Arctic vortex in 1991/92. For the observations inside the vortex discussed here, no recovery from the ozone loss in January 1992 is observed over February and March 1992 in agreement with HALOE measurements in the vortex in the same year (Müller *et al.* 1996).

The observations presented here thus confirm earlier findings about ozone loss in the Arctic vortex in the winter of 1991/92. They further corroborate and refine assumptions in earlier work on the reference relation for unperturbed conditions in the early vortex. Moreover, they extend the validity of these earlier findings to greater altitudes and provide information on the development of the ozone concentrations over the period from January 1992 to early March 1992. Finally, the balloon data discussed here allow the conclusion that mixing across the vortex edge in 1991/92 did not alter tracer–tracer relations in a way which would lead to an overestimate of chemical ozone loss.

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