A re-evaluated Canadian ozonesonde record: measurements of the vertical distribution of ozone over Canada from 1966 to 2013

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Abstract. In Canada routine ozone soundings have been carried at Resolute Bay since 1966, making this record the longest in the world. Similar measurements started in the 1970s at three other sites, and the network was expanded in stages to 10 sites by 2003. This important record for understanding long-term changes in tropospheric and stratospheric ozone has been re-evaluated as part of the SPARC/IO_3C/IGACO-O_3/NDACC (SI^2N) initiative. The Brewer-Mast sonde, used in the Canadian network until 1980, is different in construction from the ECC sonde, and the ECC sonde itself has also undergone a variety of minor design changes over the period 1980-2013. Corrections have been made for the estimated effects of these changes, to produce a more homogeneous dataset.

The effect of the corrections is generally modest~~, and so should not invalidate past analyses that have used Canadian network data~~. However, the overall result is entirely positive: the comparison with co-located total ozone spectrometers is improved, in terms of both bias and standard deviation, and trends in the bias have been reduced or eliminated. An uncertainty analysis (including the additional uncertainty from the corrections, where appropriate) has also been conducted, and the altitude-dependent estimated uncertainty is included with each revised profile.

The resulting time series show negative trends in the lower stratosphere of up to 5% per decade for the period 1966-2013. Most of this decline occurred before 1997, and linear trends for the more recent period are generally not significant. The time series also show large variations from year to year. Some of these anomalies can be related to cold winters (in the Arctic stratosphere), or changes in the Brewer-Dobson circulation, which may thereby be influencing trends.

In the troposphere trends for the 48-year period are small, and for the most part not significant. This suggests that ozone levels in the free troposphere over Canada have not changed significantly in nearly 50 years.

1 Introduction

Ozone plays a major role in the chemical and thermal balance of the atmosphere~~,~~. It controls~~ling~~ the oxidizing capacity of the lower atmosphere via its photochemical link to the OH radical, and also ~~acting~~ acts as an important short-lived climate forcer~~,~~. ~~while o~~Ozone changes in the stratosphere, as well as strongly affecting surface UV radiation, may also affect future climate (*IPCC*, 2013, and references therein). In addition to the information ozone soundings ~~they~~ provide on the vertical distribution of ozone in the lower stratosphere, ~~ozone soundings~~ they are the major source, worldwide, of information on ozone amounts in the free troposphere.

Vertical distribution information is particularly important for ozone transport studies, as transport in the atmosphere occurs in thin, quasi-horizontal layers. The global ozonesonde record is therefore increasingly important for understanding long-term changes in both tropospheric and stratospheric ozone, as each may be affected by changes in long-range quasi-horizontal transport, as well as by vertical exchange/mixing between layers. For example, ozonesonde measurements show impact on near-surface ozone concentrations of intrusions of ozone from the lower stratosphere (e.g. *He et al.*, 2011; *Hocking et al.*, 2007), and the inter-continental transport of tropospheric ozone and its precursor species (*Oltmans et al.*, 2006; 2010). Canadian ozonesondes have also provided essential information on the nature of Arctic stratospheric ozone loss (*Manney et al.*, 2011Fioletov et al., 1997; Kerr et al., 1993~~, and references therein~~), of Arctic surface depletion events (*Tarasick and Bottenheim*, 2002; *Bottenheim et al.*, 2002), and of the global circulation of ozone (~~e.g.~~ *Lin et al.*, 2015; *Bönisch et al.*, 2011; *Pan et al.*, 2009), as well as of tropospheric sources and budgets (~~e.g.~~ *Emmons et al.*, 2015; *Parrington et al.*, 2012; *Walker et al.*, 2010; 2012; *Macdonald et al.*, 2011; *Thompson et al.*, 2007; *Tarasick et al.*, 2007).

Station	Location	Altitude (m)	Start of sonde record
Edmonton	53.6°N, 114.1°W	766	Brewer-Mast (1970); ECC (1979)
Goose Bay	53.3°N, 60.3°W	44	Brewer-Mast (1969); ECC (1980)
Churchill	58.8°N, 94.1°W	35	Brewer-Mast (1973); ECC (1979)
Resolute	74.7°N, 95.0°W	64	Brewer-Mast (1966); ECC (1979)
Eureka	80.1°N, 86.4°W	10	ECC (1992)
Alert	82.5°N, 62.3°W	62	ECC (1987)
Kelowna	49.9 °N, 119.4°W	456	ECC (2003)
Bratt's Lake	50.2 °N, 104.7°W	580	ECC (2003-2011)
Egbert	44.2 °N, 79.8°W	251	ECC (2003-2011)
Yarmouth	43.9 °N, 66.1°W	9	ECC (2003)

Table 1: The Canadian ozonesonde network. Soundings are weekly (generally Wednesdays), with extra releases during special campaigns (i.e. MATCH, TOPSE, IONS, BORTAS). Regular ozone soundings have been made at Resolute since January, 1966.

The time series of ozone soundings from Canadian stations comprises some of the longest records of vertical ozone profile measurement that exist, as well as the only time series of measurements in the free troposphere over Canada. Following some initial ozone soundings conducted in cooperation with the US Air Force Cambridge Research Laboratories (AFGL) from 1963-1965 at Goose Bay and Churchill, employing chemiluminescent *(Regener*, 1960) sondes (*Hering*, 1964; *Hering and Borden*, 1964; 1965; 1967), regular ozone soundings using electrochemical Brewer-Mast sondes (*Brewer and Milford*, 1960) began at Resolute in January, 1966. Table 1 describes the locations of Canadian ozonesonde stations and their data records.

Preparation procedures for the Brewer-Mast sondes are described in *Tarasick et al.* (2002), but essentially followed *Mueller* (1976). In 1980 the Canadian network switched to electrochemical concentration cell (ECC) sondes *(Komhyr*, 1969). ECC sonde preparation and launch procedures are as described in *Tarasick et al.* (2005). Although these procedures were not changed at any time in the Canadian record, the change of sonde type, as well as minor changes in the design of the ECC sonde over the past three decades, may have introduced biases in the measurement time series that could affect trends (Table 2). The associated radiosonde has also changed, which could influence the ozone profile by introducing altitude shifts, primarily above 25 hPa (25km), due to temperature or pressure biases.

Year	Change	Possible Effect
1979	ECC 3A introduced	~15% increase in tropospheric response response relative to BM sondes. Sonde T measured via rod thermistor.
1984	ECC 4A introduced	redesigned pump; maximum change <1%, at 50-20 hPa. Sonde "box" T measured; new rod thermistor.
1993	ECC 5A introduced	New pump correction; maximum change ~1%, at 100 hPa.
1993	Vaisala RS-80, RSA-11 introduced	Older VIZ sonde: warm bias in daytime; pressure errors. May introduce altitude shifts in profile; ozone increases of up to ~2% at 20 hPa.
1996	ECC 6A	No differences below about 20-25 km (*Smit et al*., 2000).
2000	ENSCI 1Z design change	High bias with 1% KI solution (*Smit et al*., 2007).
2004	3cc solution (new sites)	Better ozone capture in troposphere
2006	Vaisala RS-92 introduced	RS80s low by ~20m in the troposphere, high by 100m at 10hPa (*Steinbrecht et al.,* 2008)
2007	Thermistor in ECC pump	More accurate measurement of air volume

Table 2: Changes in ozonesondes and associated radiosondes in the Canadian network.

As part of the SPARC/IO_3C/IGACO-O_3/NDACC (SI^2N) initiative, the Ozonesonde Data Quality Assessment (O3S-DQA) was initiated in order to resolve inhomogeneities in the global long-term ozone sounding record. The effects of many of the changes listed in Table 2 have been characterized by recent laboratory and field work and can now be corrected. The uncertainty of ozonesonde profile measurements can now also be described with a degree of confidence that was not available in the past. These developments are described in a recent report (*Smit et al*, 2012), and the re-evaluation of the Canadian record described here follows those recommendations.

2 Corrections to the sounding data

The operating principle of ozonesondes is the well-known reaction of potassium iodide with ozone:

$$2KI + O_3 + H_2O \longrightarrow 2KOH + I_2 + O_2 \qquad (1)$$

followed by

$$I_2 + 2e^- \longrightarrow 2I^- \qquad (2)$$

Thus for each molecule of ozone two electrons are produced and an equivalent amount of current flows through the external circuit. The measurement is therefore, in principle, absolute; however there may be losses of ozone and/or of iodine, and there may be side reactions that also convert iodide to iodine. Ozone partial pressure is calculated using the ideal gas law, noting from (R2) that the number of moles per second of ozone passing through the sonde is equal to half the current divided by the Faraday constant. This gives (e.g. *Komhyr*, 1986),

$$P_{O_3} = k(i - i_B)Tt \qquad (3)$$

where i is the measured cell current ~~in microamperes~~, i_B is the background current, T is the temperature of the air in the pump in kelvins (often approximated by the sonde box temperature) and t is the measured time in seconds for the sonde to pump 100 ml of air. k is a constant, equal to 0.0004307 for current in microamperes and ozone partial pressures in mPa. Errors or bias changes in the temperature or background current measurement or the pump rate (or its change with ambient pressure during flight) can therefore affect the ozonesonde measurement.

2.1 Total ozone normalization

In practice ECC ozonesondes have a precision of 3-5% and a total uncertainty of about 10% (*Smit et al.*, 2007; *Kerr et al*, 1994; *Deshler et al.*, 2008a; *Liu, G., et al.*, 2009). The precision of the older Brewer-Mast sonde is somewhat poorer, at about 5–10% (*Kerr et al.*, 1994; *Smit et al.*, 1996). The Brewer-Mast soundings required normalizing, or “correcting”, by linearly scaling the entire ozone profile (plus an estimate of the residual above the balloon burst altitude) to a total ozone measurement. This was because they showed a typical response equivalent to about 80% of the actual ozone amount when prepared according to the manufacturer's instructions (the Canadian practice), and so needed to be scaled, by what is traditionally referred to as the "correction factor", to give a more accurate result. Although the ECC sonde response is much closer to 100%, normalizing to a coincident Brewer or Dobson spectrophotometer measurement has continued to be the Canadian practice because it demonstrably reduces uncertainties in ozonesonde data (e.g., *Kerr et al.*, 1994; *Smit et al.*, 1996; *Beekmann et al.*, 1994, 1995). Uncertainties are 7–10% for non-normalized data and 5–7% for normalized data (*Fioletov et al.*, 2007). This improvement is because of the greater accuracy of total ozone measurements~~:~~. ~~for~~ For well-calibrated total ozone instruments the standard uncertainty of direct sun measurements is less than 3% (*Basher*, 1982).

The Canadian total ozone record has been extensively revised, but the corresponding revisions to normalization factors in the sonde record had not, until now, been made. We found occasional cases of surprisingly large differences (~35%). In some cases, particularly in the older Dobson record, a total ozone value for the previous day appears to have been used. In addition, historical practice in Canada for estimating the residual ozone amount above the profile top has been to simply assume constant ozone mixing ratio above the balloon burst altitude. Much better knowledge now exists for the distribution of ozone at higher altitudes, and so the use of a climatological estimate is preferred. We have used the climatology of *McPeters and Labow* (2012) to renormalize the Canadian data. The total ozone normalization is applied only after all other corrections have been applied (to the non-normalized data; that is, any previous normalization is first removed). Normalization is not applied to flights that fail to reach 32 hPa. This is also a change from previous practice, which required flights to reach 17 hPa for total ozone normalization to be applied.

There are arguments against normalization of ECC sonde profiles: the process introduces a degree of uncertainty because the amount of ozone above the balloon burst height can only be estimated. It is also not clear that a scaling factor that is constant with altitude is appropriate in all cases. This is of particular concern for the tropospheric part of the profile; whether normalization, which is necessarily weighted to the much larger stratospheric part of the profile, improves tropospheric measurements is an open question. Normalization also renders the sonde record no longer independent of the total ozone record, which is an important issue for trend studies (although to some extent alleviated if there is no trend in scaling factors), and evidently can introduce a serious bias if the total ozone instrument calibration is in error. Fortunately, since the scaling is linear in measured ozone, it can be applied, and as easily removed, in post-processing or by the data user.

The normalization factor is unquestionably of value as a data quality control indicator, and we will use it as such in the analysis to follow. We present here normalized data, for consistency between the Brewer-Mast and ECC records, and with past trend analyses (e.g. *Tarasick et al*, 2005).

2.2 Correction for Brewer-Mast tropospheric response

Laboratory work (*Tarasick et al.,* 2002) suggests that the response of Brewer-Mast sondes in the Canadian program was biased low in the troposphere. We have applied a correction based on simple quadratic fit to the data shown in Figure 7 of *Tarasick et al.* (2002). The correction is consistent with that implied by the WMO-II intercomparison of 1978 (*Attmannspacher and Dütsch*, 1981; see also Figure 10 of *Liu et al.*, 2013) and also similar to, but somewhat more modest than that suggested by the WMO-I and BOIC sonde intercomparison campaigns (*Attmannspacher and Dütsch*, 1981; *Hilsenrath et al.,* 1986) and the analysis by *Lehmann* (2005) of Brewer-Mast data from the Australian program. The Australian program used similar procedures to those in Canada.

2.3 Pump corrections

The efficiency of the ozonesonde pump decreases at low pressures, and a correction for this is part of normal data reduction. Pump corrections from *Komhyr et al.* (1968) were used for Canadian Brewer-Mast sonde data (*Mateer,* 1977). We have now applied the more commonly used *Komhyr and Harris* (1965) pump corrections, recommended by WMO (*Claude et al.,* 1987), which are larger than the *Komhyr et al.* (1968) corrections. Significantly larger pump corrections have been recommended by *Steinbrecht et al.,* (1998), but these may not apply to older Brewer-Mast sondes (*Lehmann and Easson,* 2003).

For ECC model 3A sondes, flown in Canada between 1979 and 1982, no change to the pump correction has been made, but the pump correction table has been added to the file. The correction is that supplied by the manufacturer, but also similar to that found by *Torres* (1981).

The ECC model 4A sonde differs significantly from the 3A; the major difference is a redesigned pump. In the original data reduction the correction curve supplied in 1983 by the manufacturer was used for all 4A flights. We have now applied the revised *Komhyr* (1986) correction curve. This correction curve was already in use for 5A and all subsequent ECC sonde models. The pump correction table has been added to the WOUDC file for all flights.

2.4 Solution volume correction

Standard practice in Canada has been to charge ECC sensors with 2.5 ml of sensing solution, rather than the 3.0 ml which is now recommended. Laboratory and field investigations have shown that with 2.5 ml of sensing solution only ~96% of the ozone is captured by the sensing solution at ground pressure, but at lower pressures the 4% deficit vanishes, apparently because of faster gas-diffusion rates in solution (*Davies et al.,* 2003). We have made a correction for this effect.

2.5 Use of standard 1% buffered KI solution in En-Sci sondes

Two types of ECC ozonesondes have been in use since about 2000, the 2Z model manufactured by EnSci Corp. and the 6A model manufactured by Science Pump, with ~~minor~~ differences in construction and in recommended concentrations of the potassium iodide sensing solution and of its phosphate buffer (*Smit et al.*, 2007). Since the Canadian network has used standard 1% buffered KI solution at all times, where En-Sci sondes have been used a positive bias of about 4% below 50 hPa and somewhat larger above is expected (*Boyd et al.*, 1998; *Smit et al.*, 2007; *Deshler et al.*, 2008b). We have made a correction for this bias.

2.6 Pump Temperature Measurement

The measurement of pump temperature is required to accurately measure the amount of air passing through the pump into the ECC sensor cell. In the past this has been approximated by a measurement using a rod thermistor at the base of the electronics unit (3A and 4A sondes), and later a thermistor suspended in the sonde box. Field and laboratory experiments suggest that this produced a consistent relationship between the "box" temperature and the pump body temperature (*Komhyr and Harris,* 1971). Measurement of the actual pump temperature only became standard in Canada in about 2008. We have made corrections for temperatures measured by either "rod" or "box" thermistors ~~(~~following *Smit et al.*~~,~~ (2012).

2.7 Background current

The background current of the ECC sonde is not well understood, and may have several sources. It represents a non-equilibrium condition in the cell, possibly from residual tri-iodide in new sensing solution (*Thornton and Niazy,* 1982; 1983), or from previous exposure to ozone (*Johnson et al.*, 2002). Canadian practice has been to treat it as proportional to pressure, but there is no reason now to think that this is correct, and treating it as approximately constant over the duration of a flight may be a better approximation and is in fact recommended (*Smit and ASOPOS panel*, 2011). Unfortunately to properly recalculate ozone assuming a constant background current requires knowledge of the pump temperature profile, and this information has ~~recorded in the WOUDC file~~been preserved only for flights after 1999. We have therefore not attempted to correct the background current, but have instead treated it as an error source (see Section 4), a not entirely satisfactory choice, since although randomly variable in magnitude, it is always a positive bias.

2.8 Radiosonde changes

Errors in radiosonde pressure or temperature will imply corresponding errors in calculated geopotential heights, causing measured ozone concentrations to be assigned to incorrect altitudes and pressures. This is potentially an important issue for the derivation of trends, as radiosonde changes may therefore introduce vertical shifts in the ozone profile, and apparent changes in ozone concentration at a given height.

A number of different radiosonde designs have been used in the Canadian observing network over the last five decades. Temperature differences between the VIZ sonde, used widely in the 1980's and early 1990's, and the Vaisala RS-80 sonde, adopted subsequently ~~Environment~~ in Canada, are well documented. The VIZ sonde showed a warm bias in the daytime by as much as 2C (*Richter and Philips*, 1981; *Luers and Eskridge*, 1995; *Wang and Young*, 2005). From simultaneous measurements made during a WMO intercomparison in 1985, *Schmidlin* (1988) estimates that this bias contributed 17m at 50hPa and 71m at 10hPa to the difference in geopotential height estimates from the two sondes. ~~This corresponds to a shift of ~1% at 10hPa (31km), but less than 0.1% at 50hPa (21km). Nevertheless, S~~Statistical comparisons, however, show that the switch from VIZ to Vaisala RS-80 at U.S. stations introduced a shift of as much as 120m at 50hPa in the daytime (*Elliot et al.*, 2002).

This may be in part due to pPressure errors, which appear to have a much larger effect than temperature errors (e.g. *Morris et al.*, 2012; *Stauffer et al.*, 2014): comparisons with radar measurements of height showed the VIZ high relative to the radar (and the Vaisala) in daytime by ~150m at 20hPa; up to 500m at 10hPa (*Schmidlin*, 1988; *Nash and Schmidlin*, 1987), while at night both VIZ and Vaisala RS80 calculated geopotentials were low by ~100m at 20hPa, and ~150m at 10hPa. The daytime differences correspond to ozone differences of ~2% and ~7% at 20 hPa and 10hPa respectively. The effect of pressure errors is most significant at higher altitudes: a 1hPa offset will introduce a geopotential height error of 63m at 100hPa, 120m at 50hPa, and over 300m at 20hPa; these correspond to ozone differences of 0.25%, 0.5% and ~4% respectively. Pressure errors also seem more variable, as well: local noon flights during the same intercomparison show much smaller height differences between the VIZ and Vaisala.

The Vaisala RS-92 has replaced the RS-80, and has been in use in Canada since 2006. Comparison flights with GPS tracking show that it gives more accurate heights than the RS80; differences from the GPS are small (*Steinbrecht et al.*, 2008; *Nash et al.*, 2006). RS80 sondes, however, were found to be low by ~20m in the troposphere, and high by 100m at 10hPa (*Steinbrecht et al.*, 2008; also *da Silveira et al.*, 2006).

Unfortunately intercomparison experiments do not tell the whole story, as not all manufacturing changes are advertised by a change in model number. For example, *Steinbrecht et al.* note systematic differences between batches of RS-92 sondes produced before July, 2004. Overall, the expected systematic differences in the ozone profile resulting from radiosonde errors are probably small below 50hPa. We do not attempt to correct for radiosonde errors, but do include possible pressure offsets as an error source in the uncertainty estimation (Section 4). Estimated radiosonde errors are largest for the older VIZ sonde, with the manufacturer quoting a 1σ uncertainty in the pressure measurement of 1 hPa.

3 Effects of the corrections

An analysis of the effects of these corrections is shown in Figures 1-4 for the station at Edmonton (Stony Plain). The average change to the ozone profile has been calculated for the corrections described above, both individually and collectively. Figure 1 shows the changes for the 1970s when only Brewer-Mast sondes were flown at Edmonton. The largest change is in the lowermost troposphere, where the response correction raises ozone values by about 15%, although the changes to the normalization make a significant difference as well. In Figure 2, the changes to the ECC record in the 1980s are comparatively minor, although again the largest change is in the lowermost troposphere, where the solution volume correction raises ozone values by as much as 4%. The new normalization also increases ozone values through the entire profile by 1%. In the 1990s (Figure 3) the shifts are larger: up to 2-3% throughout the stratosphere. Most of this appears to be due to the change of temperature measurement, from the rod thermistor at the base of the electronics unit, to the "box" temperature, and in a few cases in 1999, pump temperature measurements. In the 2000s (Figure 4) the "DESHLER" correction for the change to En-Sci sondes seems to almost cancel that for the change of temperature measurement, so that the overall correction is close to zero, except at the top of the profile, and in the lower troposphere.

With the exception of the Brewer-Mast data in the troposphere, ~~The~~ the overall effect of the corrections is generally modest~~, and so should not invalidate past analyses that have used Canadian network data~~. They can be summarized as:

	Mean Ratio (Normalization Factor)	Standard Deviation	Trend in Normalization Factors
BM data (up to 1979)			
Original	1.27	0.303	2.7%/decade
Renormalized	1.20	0.198	
Response correction	1.03	0.179	2.2%/decade
ECC data (1980-2013)			
Original	0.97	0.101	-2.6 +/- 0.6 %/decade
All corrections	0.99	0.087	0.6 +/- 0.5 %/decade

Table 3: Cummulative effects of corrections to ozonesonde data for the record at Edmonton (Stony Plain), as indicated by changes in the comparison of the integrated profile to a coincident spectrophotometric total ozone measurement.

- Tropospheric changes: increases of up to 5% after 1979; up to 20% before 1980 (Brewer-Mast sondes), declining with altitude.
- Stratospheric changes: decreases of up to 4% before 1980 at 25 km, smaller decreases~~less~~ above and below ~~25km~~. Increases of ~1% in the 1980s, ~2-3% in the 1990s, and little change in the 2000s.

An examination of the revised record shows that the removal of these artifacts from it has indeed reduced uncertainty, as measured by the changes in the comparison to the total ozone record. Table 3 describes these differences. The normalization factors are closer to 1, and their variance is reduced, for both Brewer-Mast and ECC sondes. A trend in the normalization factors for the Brewer-Mast sondes is reduced, and that for ECC sondes is effectively removed (no longer statistically significant).

4 Uncertainty analysis

An important goal of the Ozonesonde Data Quality Assessment (O3S-DQA) is to produce an uncertainty analysis for ozonesonde data. There have been only a few published efforts to quantify

Error Source	**Uncertainty** (1σ)				
	BM	3A	4A	5A/6A	2Z
Stoichiometry	±1.0%	±1.0%	±1.0%	±1.0%	±1.0%
T measurement	±3.0%	±0.3%	±0.3%	±0.2%	±0.2%
Pump calibration	±0.5%	±0.5%	±0.5%	±0.5%	±0.5%
Pump cal. RH error	--	±0.5%	±0.5%	±0.5%	±0.5%
En-Sci 1% KI correction error	--	--	--	--	±0.5%
Pump corr. error (100hPa/10hPa)	±2.0%/±6.9%	±0.5%/±2.1%	±1.1%/±2.6%	±1.1%/±2.6%	±1.1%/±2.6%
2.5 ml solution corr. error ($\propto p$)	±4% (sl)	±4% (sl)	±4% (sl)	±4% (sl)	±4% (sl)
Background current	±0.05 mPa	$i_B(1-p/p_0)$	$i_B(1-p/p_0)$	$i_B(1-p/p_0)$	$i_B(1-p/p_0)$
BM response corr. error ($\propto$ *correction*)	±7.0% (sl)	--	--	--	--
Iodine loss ($\propto 1/p$)	±6% (10 hPa)	--	--	--	--
Ascent rate variation	--	±12%* $e^{-\Delta t/\tau}\nabla O_3$	±12%* $e^{-\Delta t/\tau}\nabla O_3$	±12%* $e^{-\Delta t/\tau}\nabla O_3$	±12%* $e^{-\Delta t/\tau}\nabla O_3$
Pressure offset	±1 hPa (VIZ)	±1 hPa (VIZ)	±1 hPa (VIZ)	±0.5 hPa (RS80)	±0.5 hPa (RS80) ±0.15 hPa (RS92)

Table 4: Sources of ozonesonde profile error considered in this analysis and their estimated magnitudes. See text for details.

the uncertainty in ozonesonde profile measurements, either from an analysis of error sources (*Komhyr et al.*, 1995) or empirically, from field or laboratory intercomparisons (*Smit et al.*, 2007; *Kerr et al*, 1994; *Deshler et al.*, 2008; *Barnes et al.*, 1985; *Smit and ASOPOS panel*, 2011) or via statistical data analysis (*Liu et al.*, 2009). Here we attempt a "bottom-up" approach similar to that of *Komhyr et al.*, (1995).

Table 4 lists the error sources considered in this analysis. The first five lines refer to errors that are assumed constant throughout the profile:

1. *Stoichiometry*

Although the stoichiometry of the neutral buffered-KI method for measuring ozone was the subject of some controversy in the 1970s (e.g. *Boyd et al.*, 1970; *Pitts et al.*, 1976) most workers have found a stoichiometry of 1.0 within experimental error (*Hodgeson et al.*, 1971; *Kopczynski and Bufalini*, 1971; *Dietz et al.*, 1973) especially when potassium bromide is added (*Lanting*, 1979; *Bergshoeff et al.*, 1980), as is the case in ozonesondes, and provided that slow side reactions with the phosphate buffer are excluded (*Saltzman and Gilbert*, 1959; *Flamm*, 1977; *Johnson et al.*, 2002). We have allowed a modest (1%) uncertainty for the reaction stoichiometry in both types of ozonesonde.

2. *Temperature measurement*

The Brewer-Mast sonde did not have a measurement of the instrument temperature, and so the processing assumes a constant temperature of 300K. Measurements of the actual temperature made by *Dütsch* (1966) and *Steinbrecht et al.* (1998) suggest that it varies over a range of 10-20K (3-6%) over a flight, with a standard deviation of 1-3%. We have represented this as a 3% uncertainty. For the ECC sondes, the box temperature measurement in the 3A and 4A models was less accurate than the pump measurement used with later models; we have assumed a standard error of 0.5K for the latter and 1.0K for the former.

3. *Pump ~~calibration~~flow measurement*

An examination of pre-flight volumetric pump flow measurement~~calibration~~ data from several sites shows that standard deviations of 0.1-0.3% in this measurement (performed the day before launch) are typical. However, differences between this measurement and the corresponding flow rate determination made at the manufacturer's facility are larger, with standard deviations of about 1%. *Torres* (1981) found a 1σ variation in the speed of individual model 3A pump motors of 0.5%. We have assumed a calibration uncertainty of 0.5% for all types of sonde.

4. *Relative humidity error*

For ECC sondes an additional error source is present, as the during the pump flow measurement~~calibration~~ the pump draws relatively dry air from the room and expels ~~it~~ water-saturated air into the graduated cylinder~~ at close to 100% relative humidity~~. The measured volume is larger than the actual volume pumped by an amount proportional to the ratio of the saturation vapour pressure to the room pressure, times the relative humidity change. Assuming a typical indoor humidity range of 40-70% (1σ) gives an uncertainty of ±0.5%.

5. *Correction for use of standard 1% buffered KI solution in En-Sci sondes*

A bias correction of about 4% below 50 hPa and somewhat larger above has been made to En-Sci sondes flown with 1% KI solution (*Deshler et al.*, 2008b). We have allowed an additional uncertainty of ±0.5%, representing the standard error of the *Deshler et al.* measurements, where this correction was made.

The latter seven lines refer to errors that vary throughout the profile, either with pressure or ozone gradient. Errors are calculated for each point in the profile:

6. *Pump correction error*

Pump corrections, and their associated uncertainties, have been measured by a small number of authors. For Brewer-Mast sondes we have used the estimates of *Komhyr and Harris* (1965), and for ECC 3A sondes those of *Torres* (1981). For ECC 4A and later models (which have similar pumps), *Johnson et al.* (2002) provide a table summarizing the results of very large number of pump tests, primarily at the University of Wyoming and at the NOAA/CMDL laboratories. Both of these give much larger uncertainties than those quoted by *Komhyr* (1986), for a small number of tests. We have averaged these larger uncertainty values from the Wyoming and NOAA/CMDL tests. *Torres* (1981) also notes that his uncertainty estimates are based on a modest number of sondes from the same manufacturing batch, and so may also be biased low. For each sonde type we have interpolated the measured uncertainties to other pressures to estimate this error for all points in each profile.

7. *Solution volume correction*

As the ozone loss in sensors charged with only 2.5 ml of KI solution appears quite variable, a fairly large error of 4% at 1000 hPa, withinversely proportional to ~~declining with~~ pressure, was assumed.

8. *Background current*

As noted above, Canadian practice has been to treat background current as proportional to pressure, but it is now recommended (*Smit and ASOPOS panel*, 2011) to treat it as constant. Here we have treated the difference between the two values as an uncertainty, although it should be noted that although randomly variable in magnitude, it is always a positive bias. It is largest in relative terms just below the tropopause, where absolute amounts of ozone tend to be lowest. The average magnitude of the difference ~~is shown in Figures 5-8; it~~ is largest in the 1980's, and has a modest effect on calculated trends in the upper troposphere (*Tarasick et al.*, 2005).

9. *Brewer-Mast response correction*

The quadratic fit to the data shown in Figure 7 of *Tarasick et al.* (2002) has a standard deviation of ~7%. We have added this uncertainty, scaled to the absolute magnitude of the correction, which is largest at 1000 hPa. The correction is largest (i.e. 7%) at 1000 hPa and declines quadratically with~~and quadratic in~~ log(pressure).

10. *Iodine loss*

Brewer-Mast sondes show increasing errors at higher altitudes relative to ECC sondes (*Kerr et al.*, 1994; *Fioletov et al.*, 2007). One possibility for this is solution evaporation, and/or iodine ~~evaporation~~ loss from the sensing solution. The Brewer-Mast sensor has a somewhat more open construction that may allow more solution evaporation. Brewer-Mast sondes also use a much weaker (0.1%) KI solution, which may allow significant iodine evaporation (*Brewer and Milford*, 1960; *Tarasick et al.*, 2002). We have included an empirical estimate for this uncertainty of $0.6/p$, where p is pressure in hPa.

11. *Ascent rate variation*

The relatively slow response of ECC sondes causes their response to lag changes in the ozone concentration as the balloon rises. This implies that different balloon rise rates will give somewhat differing ozone amounts, especially in parts of the profile with large ozone gradients. We assumed an e^{-1} response time of $\tau =$20 s (*Smit and Kley*, 1998). The standard deviation of balloon rise rate at Edmonton in the 2000s is ~12%, which yields modest errors (<1%) at the sharp ozone gradients near the tropopause and mostly insignificant errors elsewhere.

12. *Pressure offset*

The error in ozone implied by an a pressure offset equal to the manufacturer's estimated 1σ uncertainty is calculated for every point in the profile by multiplying by the measured ozone gradient with respect to pressure. We have used the values quoted by *Richner and Phillips* (1981) for the VIZ sonde and *Steinbrecht et al.* (2008) for the Vaisala sondes.

The uncertainty profile is calculated for each flight, using the pressure and ozone partial pressure data for that flight. Figure 5 shows the average uncertainty profile for the Brewer-Mast flights at

Edmonton, along with the standard deviation of the response of ECC sondes during the Vanscoy and JOSIE 1996 ozonesonde intercomparison campaigns (*Kerr et al*, 1994; *Smit et al.,* 2007), and the standard deviation of the response of Brewer-Mast sondes during the Vanscoy campaign (*Kerr et al*, 1994). Several of the individual contributions to the overall uncertainty are shown. The total uncertainty without the contribution from radiosonde pressure offsets, labelled "Same balloon", is also shown, to facilitate comparison with the JOSIE 1996 and Vanscoy intercomparison uncertainty estimates, which were referenced to a common pressure measurement. It will be noted that the uncertainty in the VIZ radiosonde pressure measurement dominates the calculated uncertainty above about 32 km.

Figure 6 shows similar calculations for the first decade of ECC soundings (3A and 4A models). The VIZ radiosonde was used throughout. As the other sources of uncertainty are smaller, the uncertainty in the VIZ radiosonde pressure measurement now dominates the calculated uncertainty above about 26 km. Figures 7 and 8 show similar calculations for the 1990s and 2000s respectively. Notable improvements are reductions in background current, and the reduction of pressure offsets with the introduction of the Vaisala radiosondes.

5 Time series and trend analysis

For this analysis each ozone profile was represented by a surface-level measurement (the ozone measurement at sonde release) and 11 layers equally spaced in log pressure (each ~3 km in thickness). Troposphere and stratosphere have been explicitly separated: that is, integration for the 400-250 hPa layer is from 400 hPa to 250 hPa or the tropopause, whichever comes first. Similarly, integration of the 250-158 hPa layer starts either at 250 hPa or at the tropopause, if the latter is found above 250 hPa. (Cases where the tropopause is below the 400 hPa height or above 158 hPa occur rarely but are dealt with similarly). The WMO definition of the tropopause (*WMO*, 1992) is employed.

Partial ozone columns were integrated within these 11 layers and divided by the pressure difference across each layer to find average ozone mixing ratios. These and the ground-level mixing ratio values were deseasonalized by subtracting the average annual cycle as described in *Tarasick et al.* (1995). The deseasonalized time series were also adjusted for the effects of diurnal variation in ozone concentration. Sondes are generally launched at either 12 or 0 GMT, which are early morning and mid-afternoon in Kelowna and Edmonton, and later at other stations. The amount of diurnal shift (a scalar value for each station at each level) was calculated as the average difference between values for the two launch times, where both were available in the same year and month. The effect is significant primarily at Edmonton, where it can be as large as 42% at ground level, and 14% below 700 hPa (*Tarasick et al.*, 2005). However, for consistency all stations were adjusted at all levels.

Figures 9 through 14 show time series of percent deviations in average ozone mixing ratio for three northern midlatitude stations (Edmonton, Goose Bay, and Churchill) and for the three Arctic stations (Resolute, Alert, and Eureka). For ease of visualization, a 4-month running average has been applied to smooth the data.

Figures 9 and 10 show the surface and the three tropospheric layers. The most notable feature in both cases is that there appears to be no long-term trend in the troposphere, over the 45-year (midlatitude) or 48-year (Arctic) record, except at the surface and possibly in the upper troposphere of the Arctic. In the latter cases these trends are negative. The surface trend at the northern midlatitude sites ~~appears~~ may be primarily due to urban development near Edmonton (*Tarasick et al.*, 2005), although Churchill shows a strong decline at the surface in recent decades, for unknown reasons. The surface trend at the Arctic sites may be related to an increase in the frequency of halogen-induced surface ozone depletions, which appear to correlate with negative anomalies in the surface ozone record shown in Figure 10 (*Oltmans et al.*, 2012). The frequency of such events at Resolute has increased by nearly 32% over the 1966-2013 period (*Tarasick et al.*, 2014).

The decadal trends (not shown) are much more variable. In general, however, trends are negative in the 1980s, positive in the 1990s, and small after 2000.

Figures 11 and 12 show the four lower stratospheric layers. Here the long-term trends are all negative (with the exception of Eureka, whose record began in 1993). Notable features are the low values in the early 1990s, and the high values in the early 2000s, the latter possibly caused by small changes in the Brewer-Dobson circulation (*Bönisch et al.*, 2011). These high values cause the lower stratospheric trends for 2000-2013 (which might otherwise be expected to show signs of recovery from stratospheric ozone depletion with declining effective chlorine levels over this period) to be negative, both at midlatitudes and in the Arctic. In the Arctic, particularly above 100 hPa, the springtime negative anomalies in cold vortex years (1996, 1997, 2000, 2005, and 2011) are evident. At these levels the 2011 anomaly (e.g. *Manney et al.*, 2011) is larger than the 1993 anomaly related to the eruption of Mt. Pinatubo.

The four middle stratospheric layers (Figures 13 and 14) show less variability, and the decadal trends more closely follow the long-term trends at each level. These long-term linear trends are shown in Figures 15-17.

Figure 15 shows calculated trends in ozone mixing ratio from ozonesonde data at six Canadian stations from 1966-2013 (for Alert and Eureka from 1987 and 1992 respectively), for the ground level and the 11 layers equally spaced in log pressure. To calculate these trends the deseasonalized station time series were averaged by month, and a simple linear regression (without subtraction of QBO, solar-cycle, or other known influences on ozone) was used to derive trends. Trends are expressed as per cent per decade, relative to the layer mean. The time series of monthly means show in general significant autocorrelation both in the stratosphere and the troposphere. Allowance is made for this in the confidence limits for trends by basing the confidence limit calculation on a (reduced) effective sample size, $n_{eff} = n(1-\rho)/(1+\rho)$, where ρ is the lag-1 autocorrelation coefficient, and the ozone variability is assumed to be an AR(1) process (*Zwiers and von Storch*, 1995; *Thiebaux and Zwiers*, 1984).

Except at the surface, trends in the troposphere are in general non-significant over this very significant period. Trends in the middle stratosphere are also non-significant at the 95% (2σ) level, while those in the lower stratosphere are significant and negative. Trends in the lower stratosphere, however, are as large -5% per decade over the 48-year record. To gauge the uncertainty introduced by the addition of the older Brewer-Mast data, we have also calculated trends using only ECC data (that is, from 1980). The differences are surprisingly modest. We also show trends from 1980 calculated using ECC data before corrections are applied. The largest differences are seen at Alert and Eureka. The increases of 2-5% to the 1990s data (Figure 3) have a larger effect on trends at these sites as they lack data from the early 1980s.

For comparison with other analyses in the SI^{2}N initiative (e.g. *Harris et al.*, 2014) and the WMO *Scientific Assessment of Ozone Depletion: 2014* (*WMO*, 2014), in Figures 16 and 17 we show trends calculated using only data prior to 1997 (Figure 16), and from 1997-2013 (Figure 17). The trends for 1966-1996 show a similar picture to that of Figure 15, although here some of the middle stratospheric layers show positive trends. If the trends are calculated using only data after 1979 (that is, ECC-only data) the trend picture is quite similar. However, trends in the 17-year period from 1997-2013 are almost all non-significant at the 95% (2σ) level, except at the surface, which shows some surprisingly large variations. This is true even in the Arctic lower stratosphere, despite the large negative anomaly in 1997 (Figure 14). Since stratospheric halogen loading has been decreasing during this period (*WMO*, 2014), the lack of evident ozone increases recovery may be due to atmospheric variability (*Kiesewetter et al.*, 2010; *Chehade et al.*, 2014), in particular the high values in the early 2000s, possibly caused by changes in the Brewer-Dobson circulation (*Bönisch et al.*, 2011). However, the standard deviations of the monthly ozone anomalies in the stratosphere at the four long-term stations for the 17 years prior to 1997 average 8-40% greater than those for the 17 year period 1997-2013, which suggests that the stratosphere has in fact been *less* variable in the latter period.

6 Conclusion

As part of the SPARC/IO_3C/IGACO-O3/NDACC (SI^2N) initiative, Canada's important record of ozone sounding data has been re-evaluated, taking into account the estimated effects of changes in the type and design of ozonesondes used in Canada over the last five decades.

The effect of the corrections is generally modest, and so should not invalidate past analyses that have used Canadian network data. However, the overall result is entirely positive: the comparison with co-located total ozone spectrometers is improved, in terms of both bias and standard deviation, and trends in the bias have been reduced or eliminated. An uncertainty analysis (including the additional uncertainty from the corrections, where appropriate) has also been conducted, and the altitude-dependent estimated uncertainty is included with each revised profile.

The resulting time series show negative trends in the lower stratosphere of up to 5% per decade for the period 1966-2013. Most of this decline occurred before 1997, and linear trends for the more recent period are generally not significant. The time series also show large variations from year to year. Some of these anomalies can be related to cold winters (in the Arctic stratosphere), or changes in the Brewer-Dobson circulation, which may thereby be influencing trends.

In the troposphere trends for the 48-year period are small, and for the most part not significant. This suggests that ozone levels in the free troposphere over Canada have not changed significantly in nearly 50 years.

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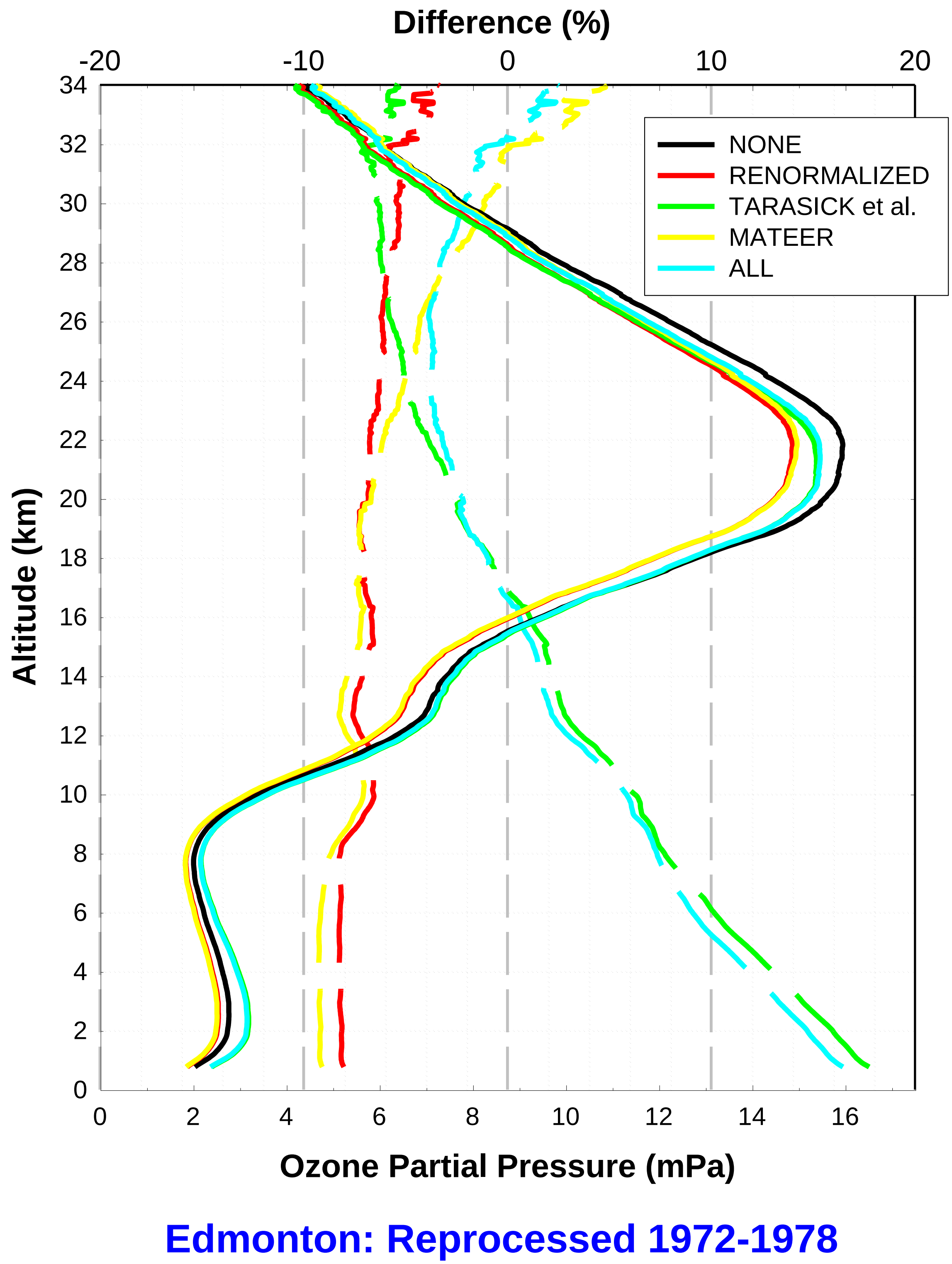


Figure 1: Average ozone profile at Edmonton before (NONE) and after corrections to the Brewer-Mast record. The largest change is in the lowermost troposphere, where the response correction raises ozone values by about 15%.

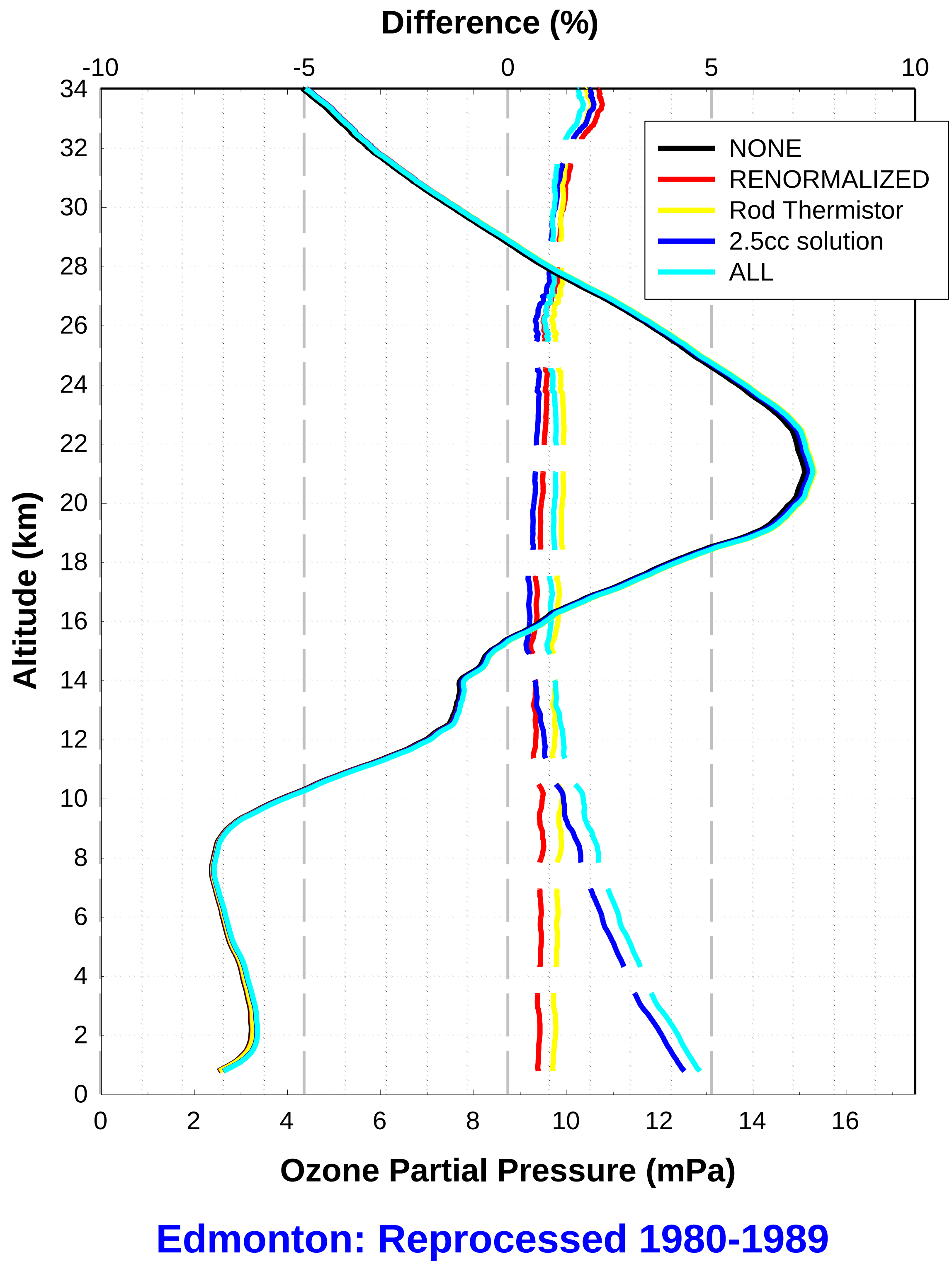


Figure 2: As Figure 1, but for the first decade of ECC soundings. The changes to the ECC record in the 1980s are comparatively minor.

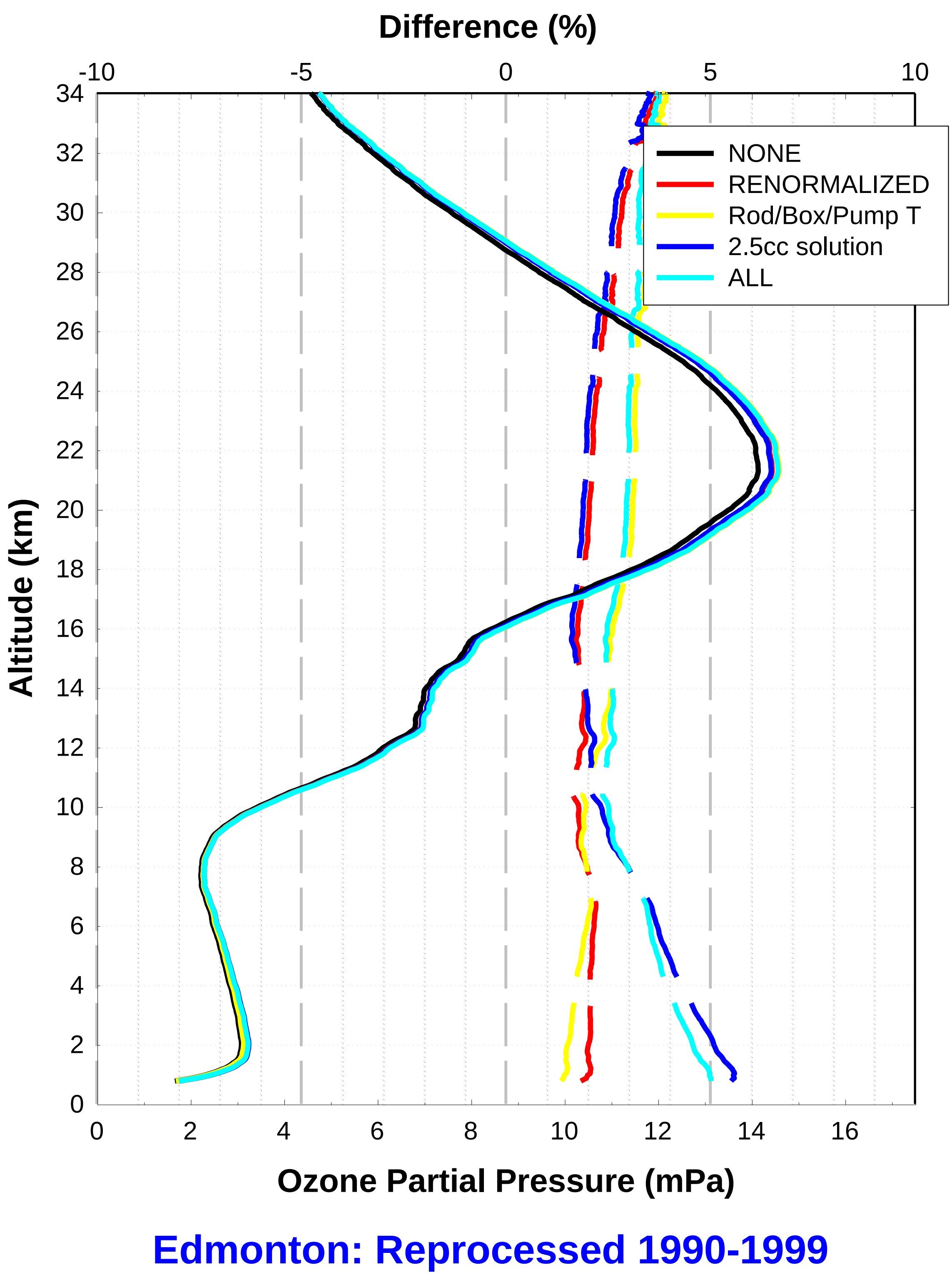


Figure 3: As Figure 1, but for the 1990s.

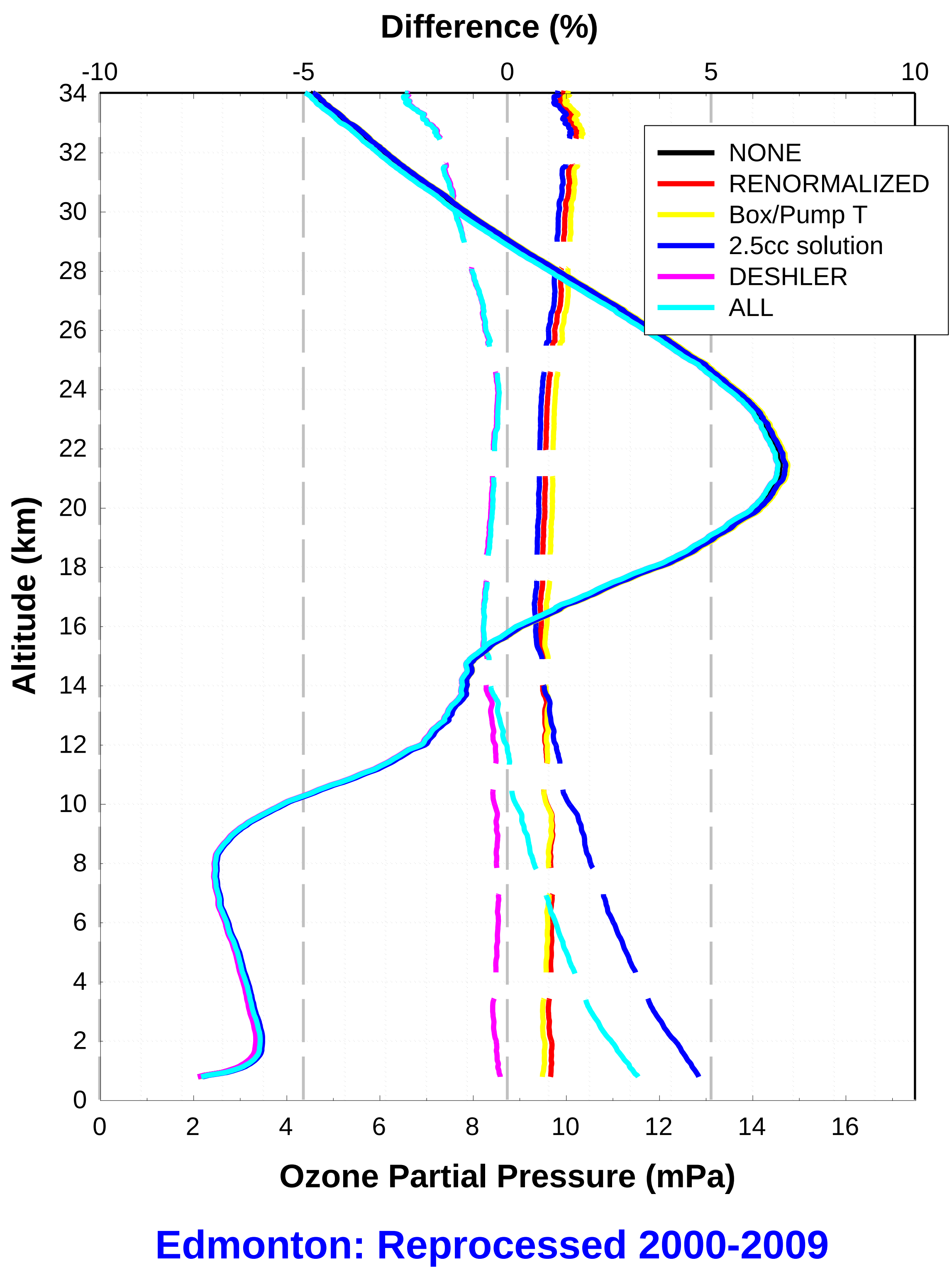


Figure 4: As Figure 1, but for the 2000s. Overall changes to the record are minor.

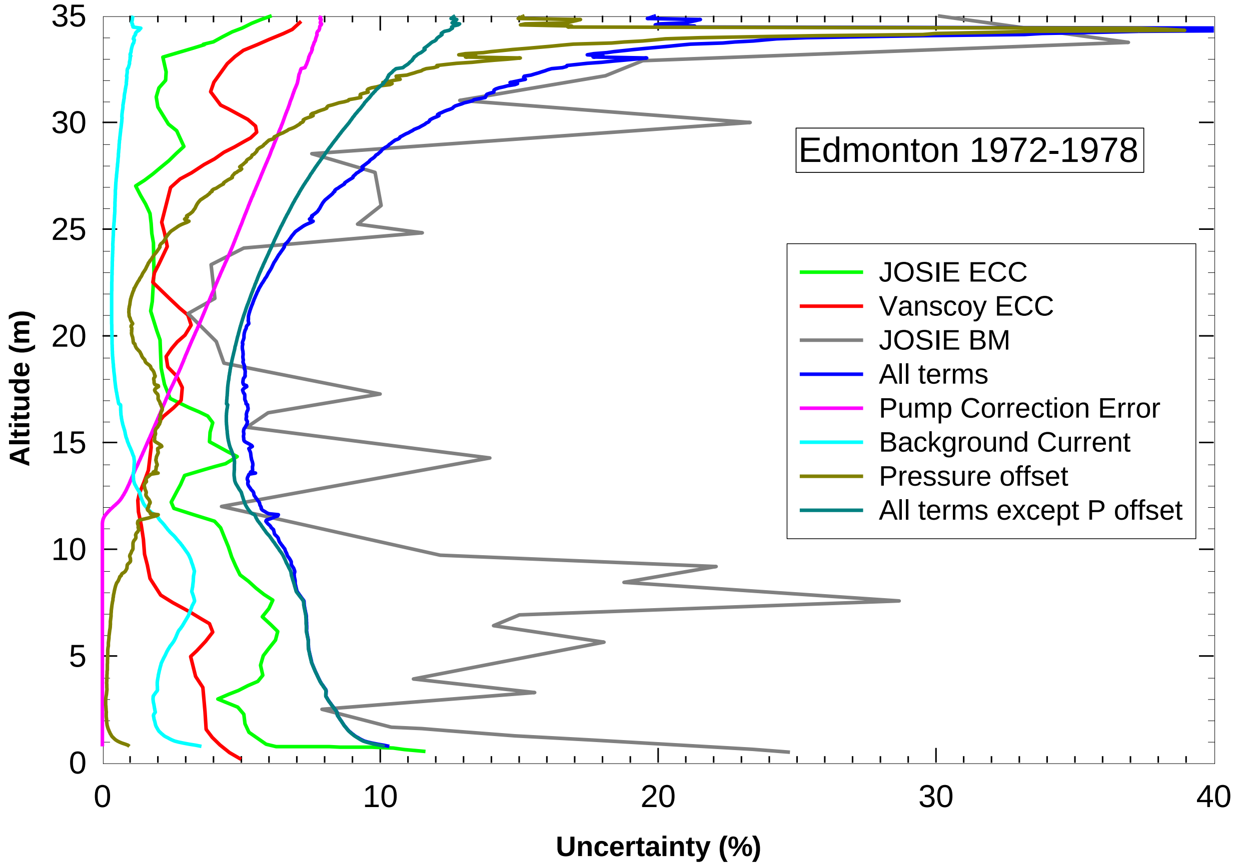


Figure 5: Average estimated uncertainty of Brewer-Mast soundings at Edmonton, showing contributions from selected sources. "Same balloon" indicates the total uncertainty without the contribution from radiosonde pressure offsets, to facilitate comparison with the JOSIE and Vanscoy intercomparison uncertainty estimates, which were referenced to a common pressure measurement. The uncertainty in the VIZ radiosonde pressure measurement dominates the calculated uncertainty above about 32 km.

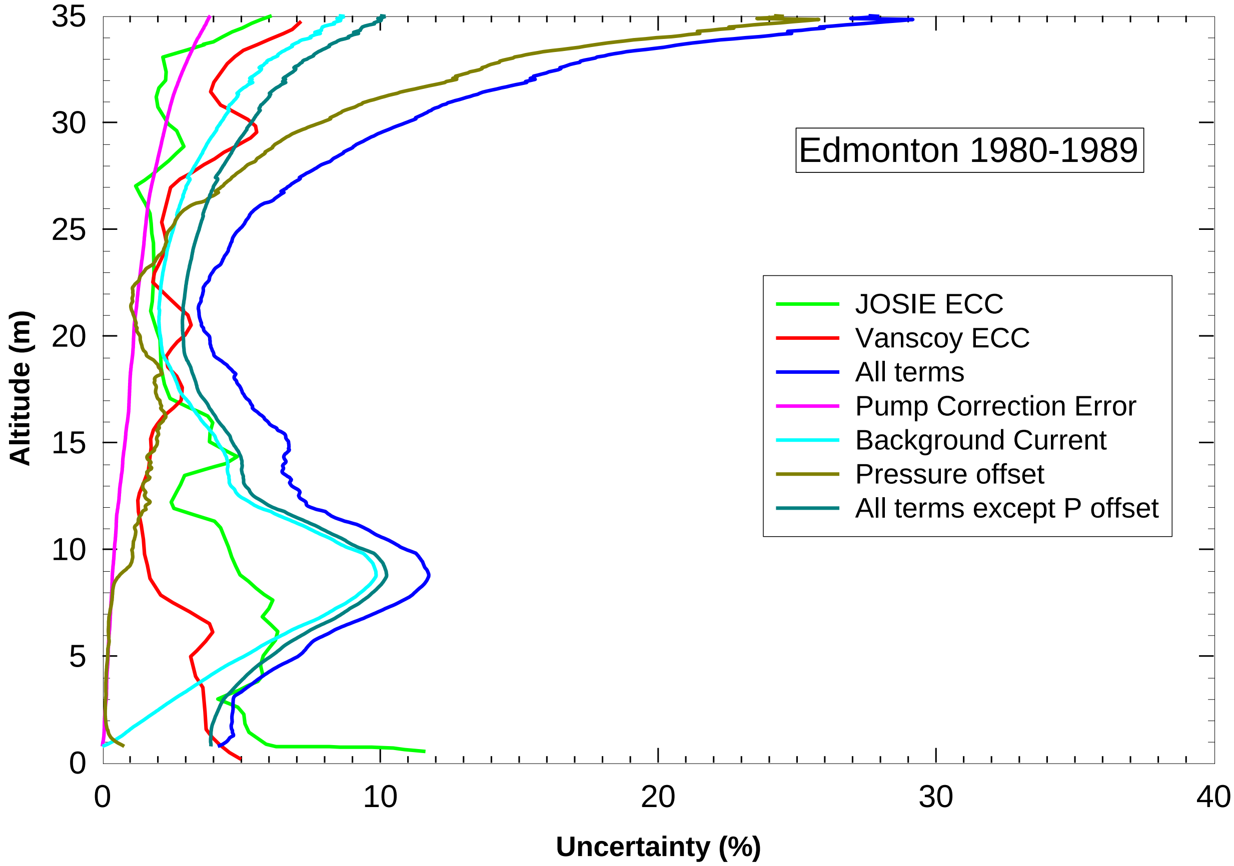


Figure 6: Average estimated uncertainty of ECC (3A and 4A) soundings in the 1980s at Edmonton, showing contributions from selected sources. "Same balloon" indicates the total uncertainty without the contribution from radiosonde pressure offsets, to facilitate comparison with the JOSIE and Vanscoy intercomparison uncertainty estimates, which were referenced to a common pressure measurement. As the overall uncertainty is smaller, the uncertainty in the VIZ radiosonde pressure measurement now dominates the calculated uncertainty above about 26 km.

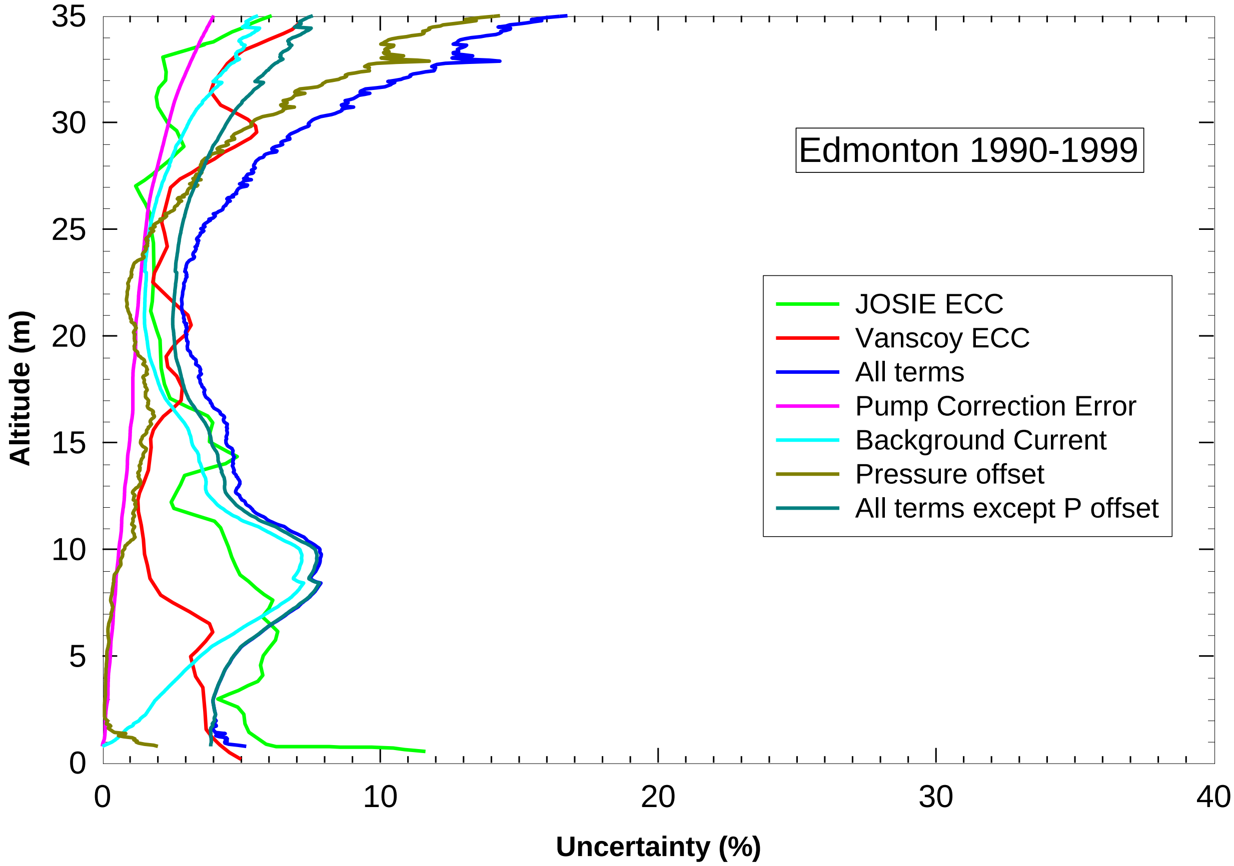


Figure 7: Average estimated uncertainty of ECC (4A and 5A) soundings in the 1990s at Edmonton, showing contributions from selected sources. The uncertainty in the VIZ or (from 1994) RS-80 radiosonde pressure measurement dominates the calculated uncertainty above about 28 km.

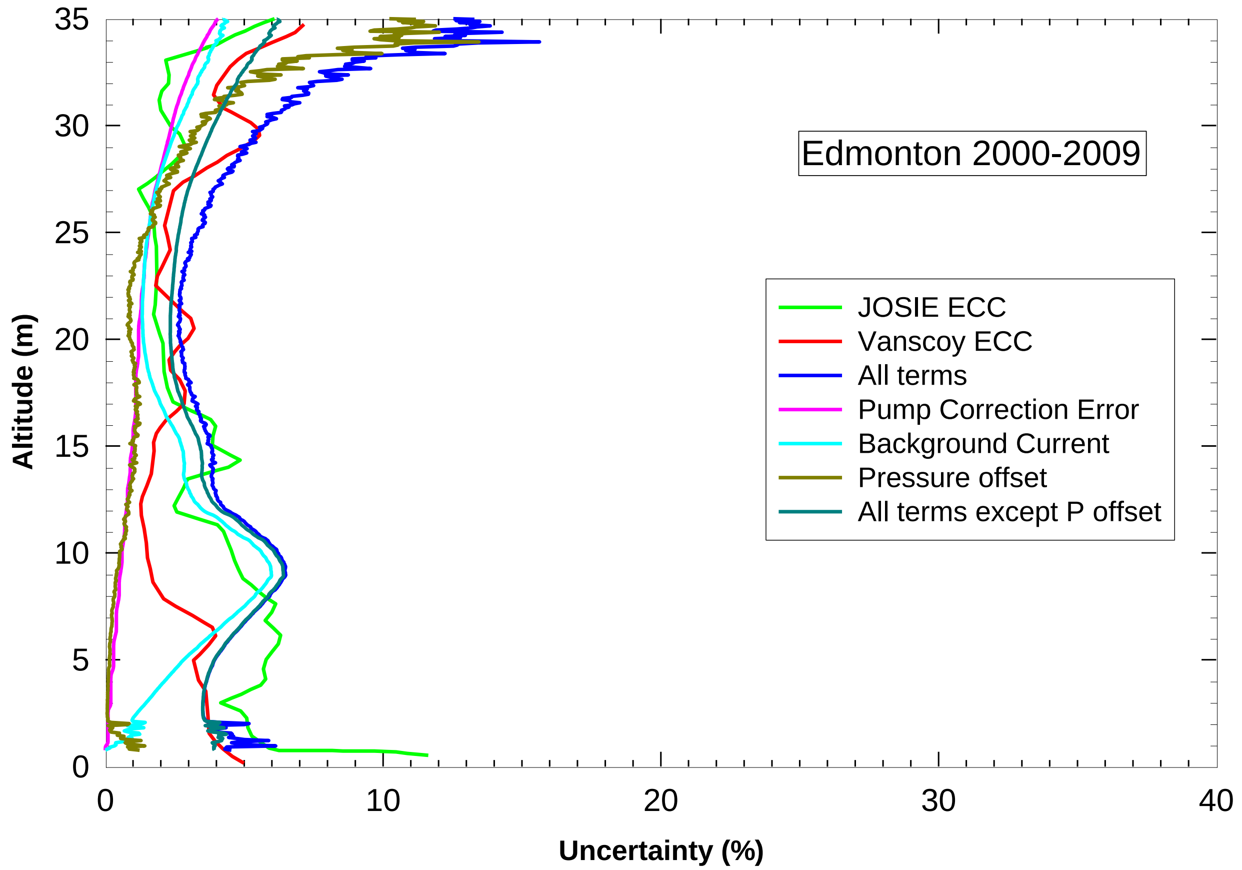


Figure 8: Average estimated uncertainty of ECC (5A and En-Sci) soundings in the 2000s at Edmonton, showing contributions from selected sources. The uncertainty in the RS-80 or (from 2006) RS-92 radiosonde pressure measurement now dominates the calculated uncertainty only above about 31 km.

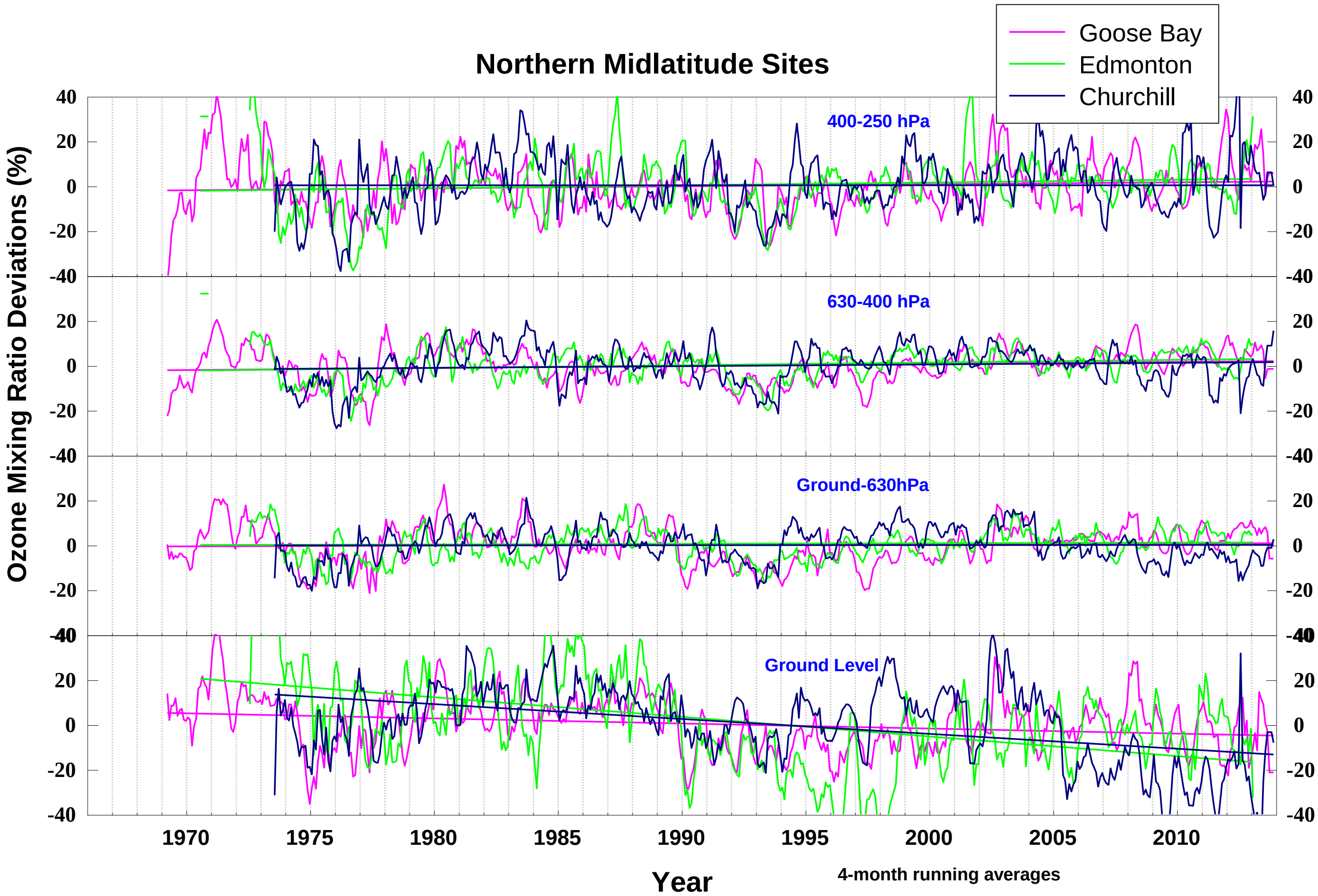


Figure 9: Percent deviations in average ozone mixing ratio for the surface and three tropospheric layers, for three midlatitude stations. Monthly anomalies have been smoothed with a four-month running average. The overall station trend lines (up to 45 years in the case of Goose Bay) are shown. The troposphere and stratosphere have been explicitly separated: that is, integration for the 400-250 hPa layer is from 400 hPa to 250 hPa or the tropopause, whichever comes first.

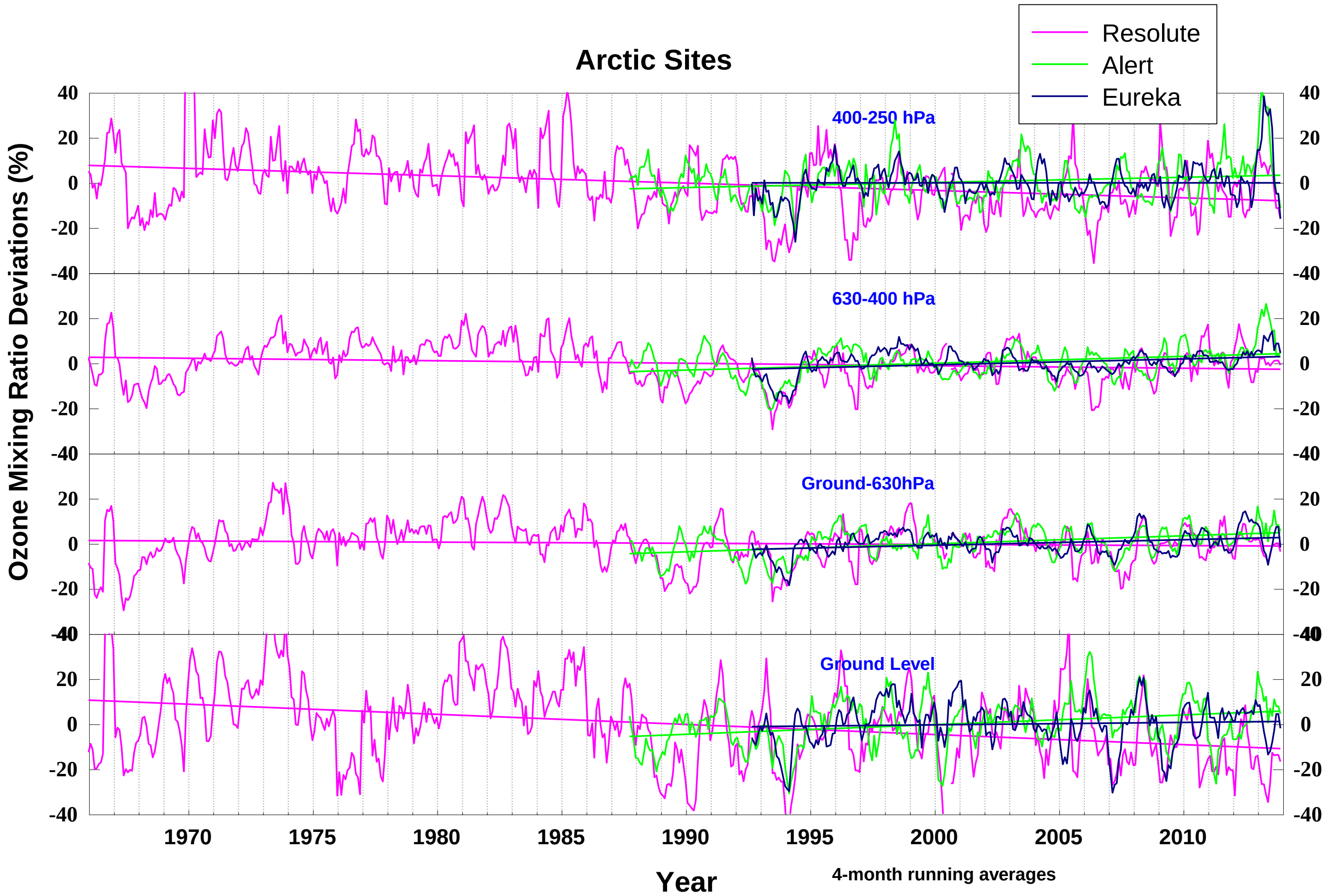


Figure 10: As Figure 9, for the three Arctic stations. The overall station trend lines (up to 48 years in the case of Resolute) are shown.

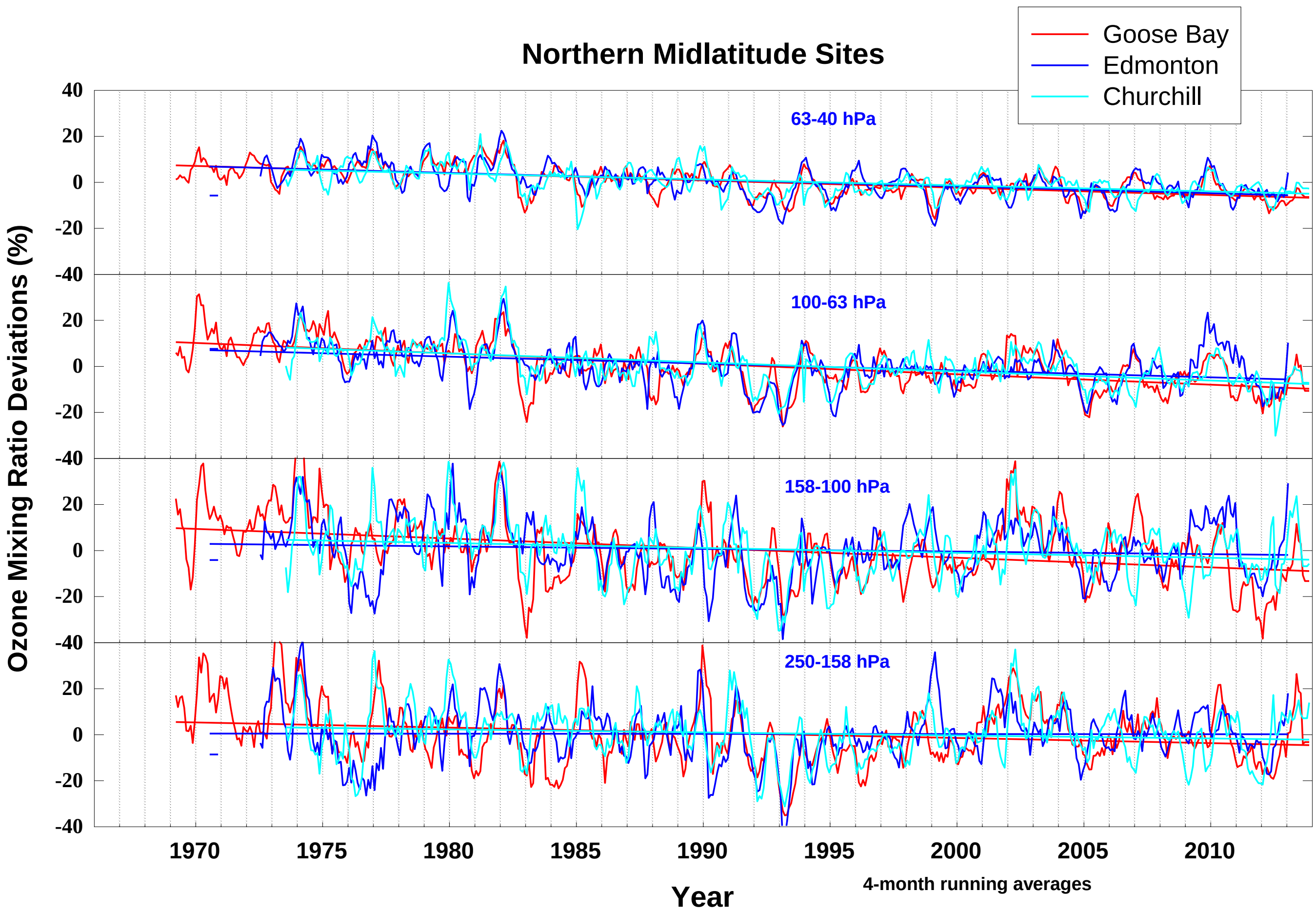


Figure 11: Percent deviations in average ozone mixing ratio for four lower stratospheric layers, using data from three midlatitude stations. Monthly anomalies have been smoothed with a four-month running average. The overall station trend lines are shown. The troposphere and stratosphere have been explicitly separated: that is, integration of the 250-158 hPa layer starts either at 250 hPa or at the tropopause, if the latter is found above 250 hPa.

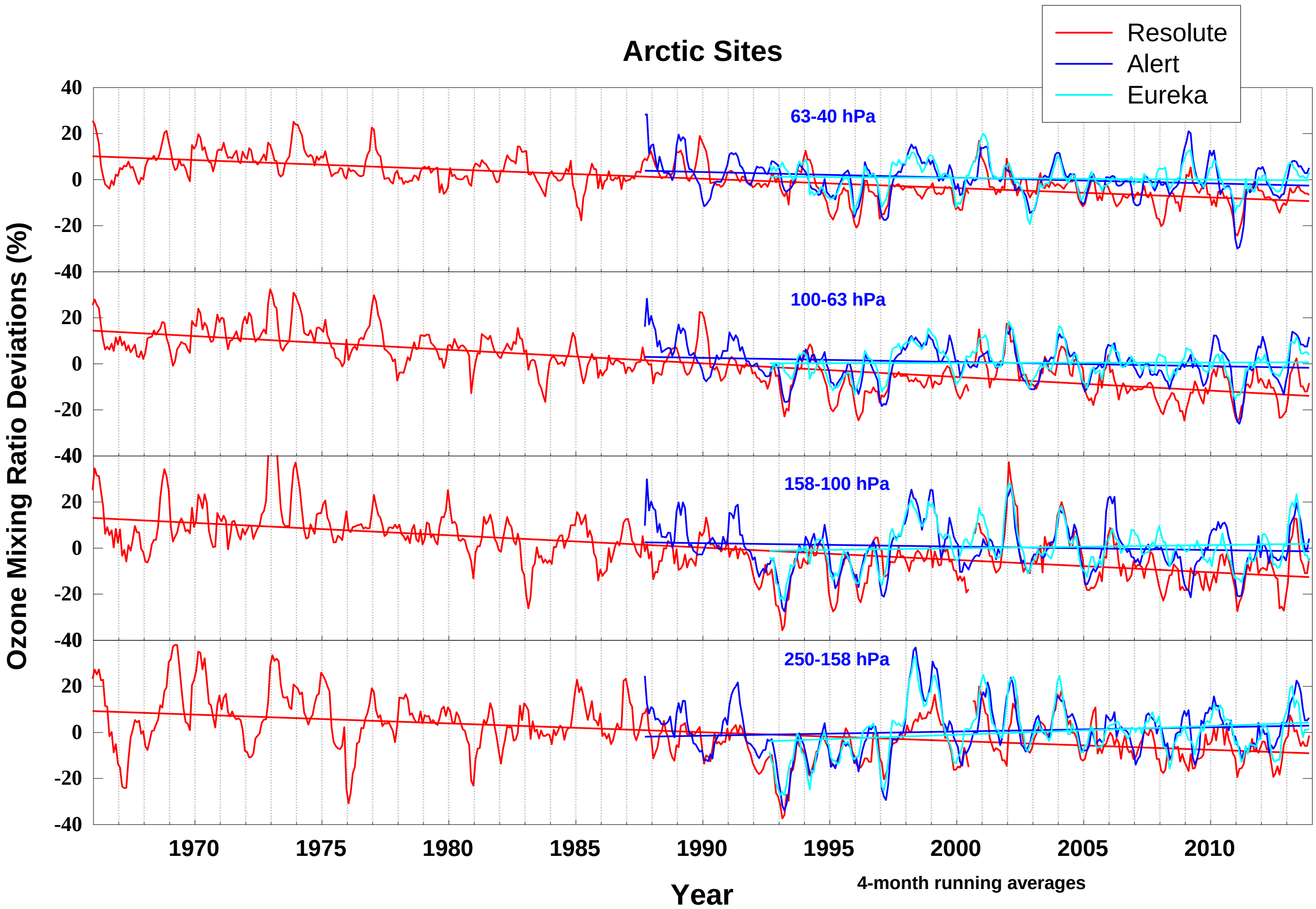


Figure 12: As Figure 11, for the three Arctic stations. The overall station trend lines are shown.

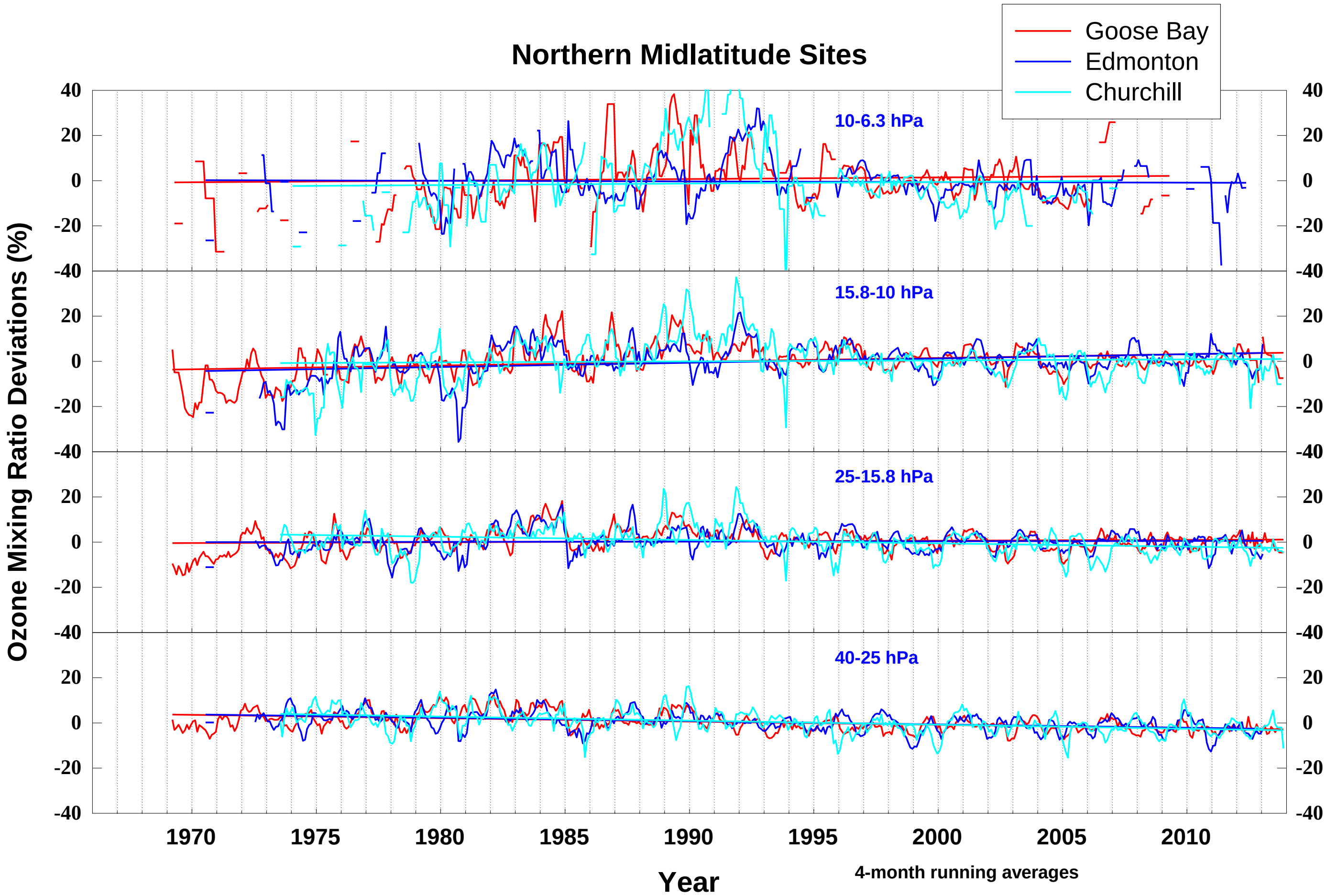


Figure 13: Percent deviations in average ozone mixing ratio for four middle stratospheric layers, using data from three midlatitude stations. Monthly anomalies have been smoothed with a four-month running average. The overall station trend lines are shown.

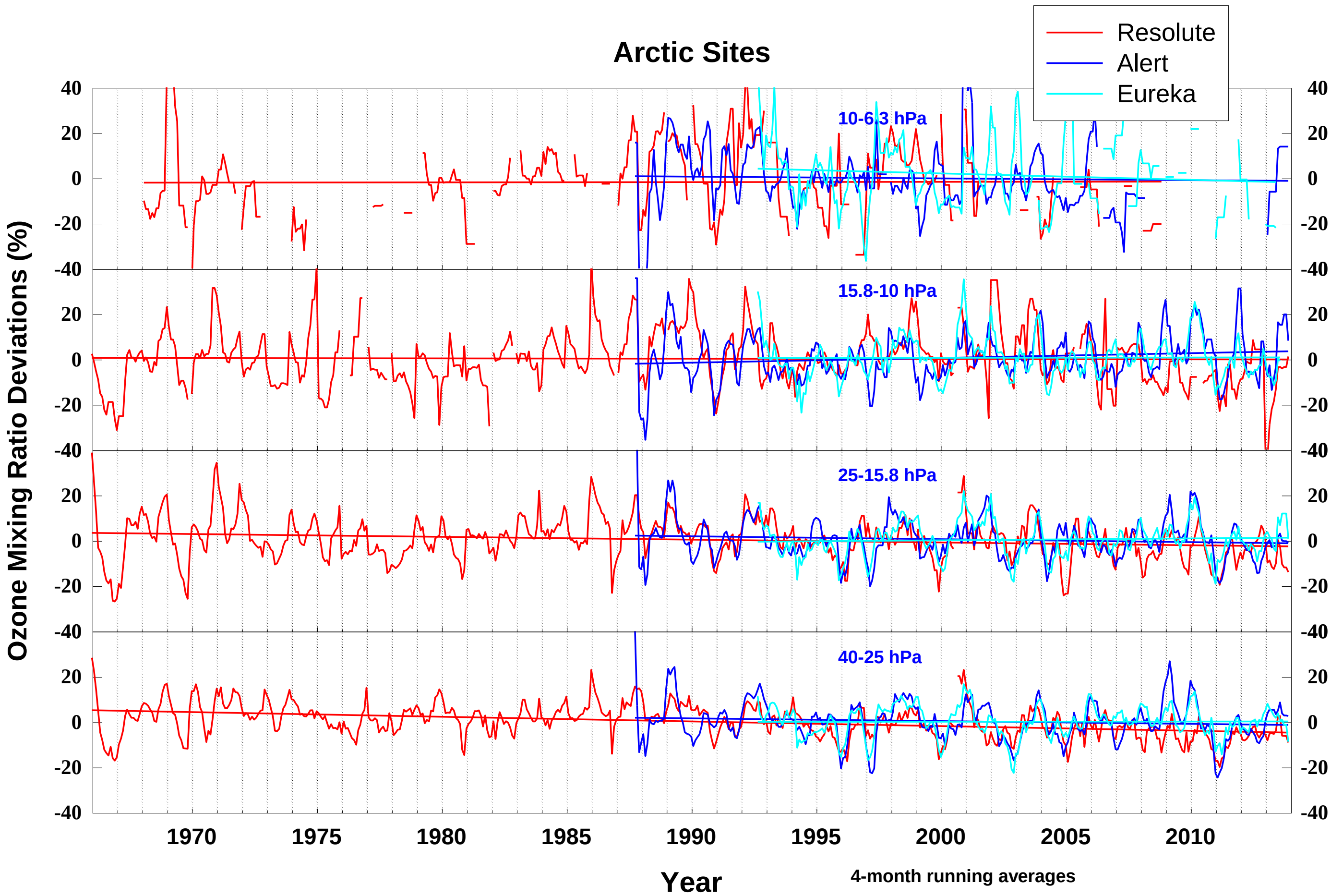
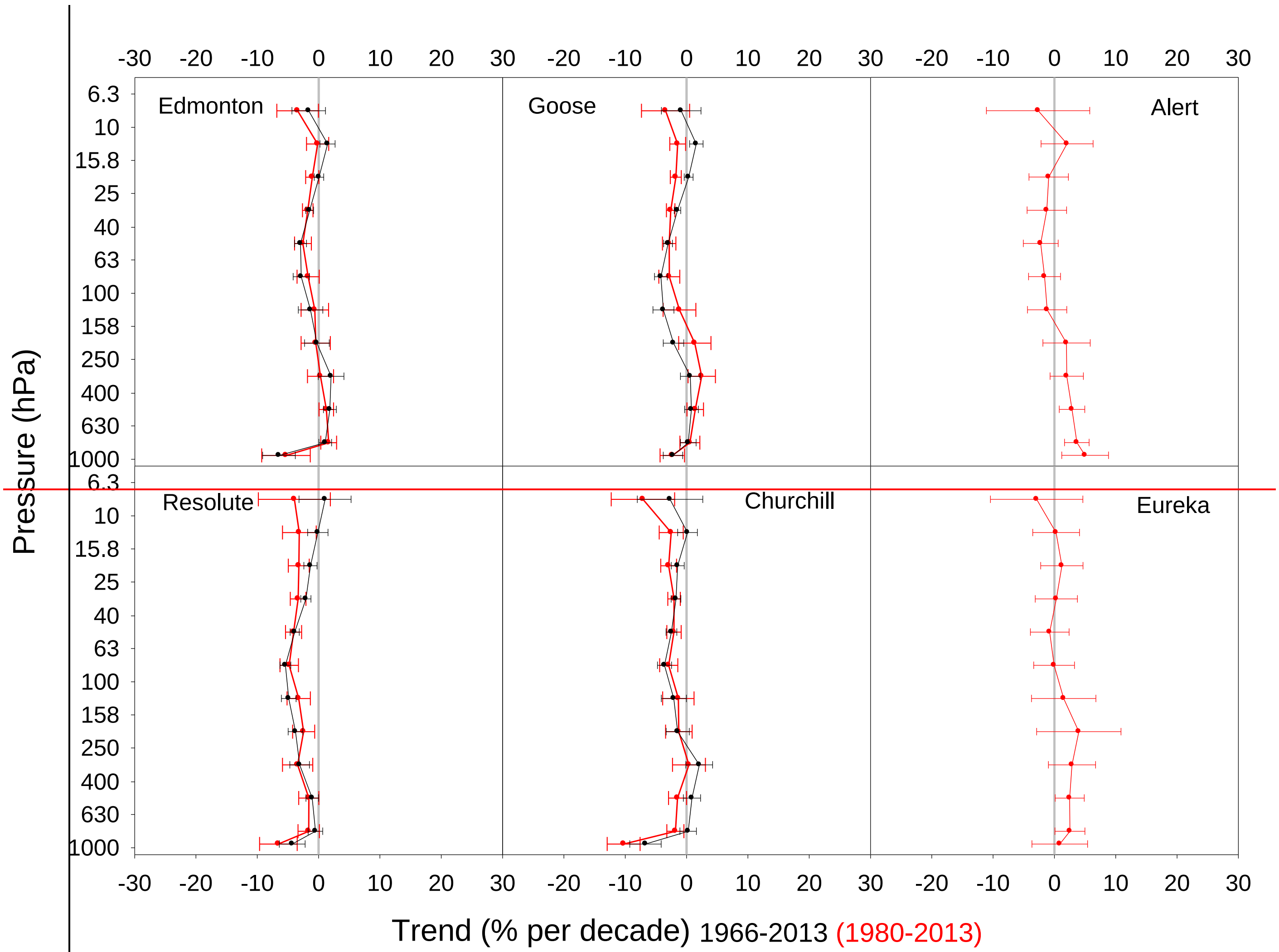


Figure 14: As Figure 13, for the three Arctic stations. The overall station trend lines are shown.


Edmonton
Goose
Alert
Resolute
Churchill
Eureka
Pressure (hPa)
6.3
10
15.8
25
40
63
100
158
250
400
630
1000
-30
-20
-10
0
10
20
30
Trend (% per decade) 1966-2013 (1980-2013)

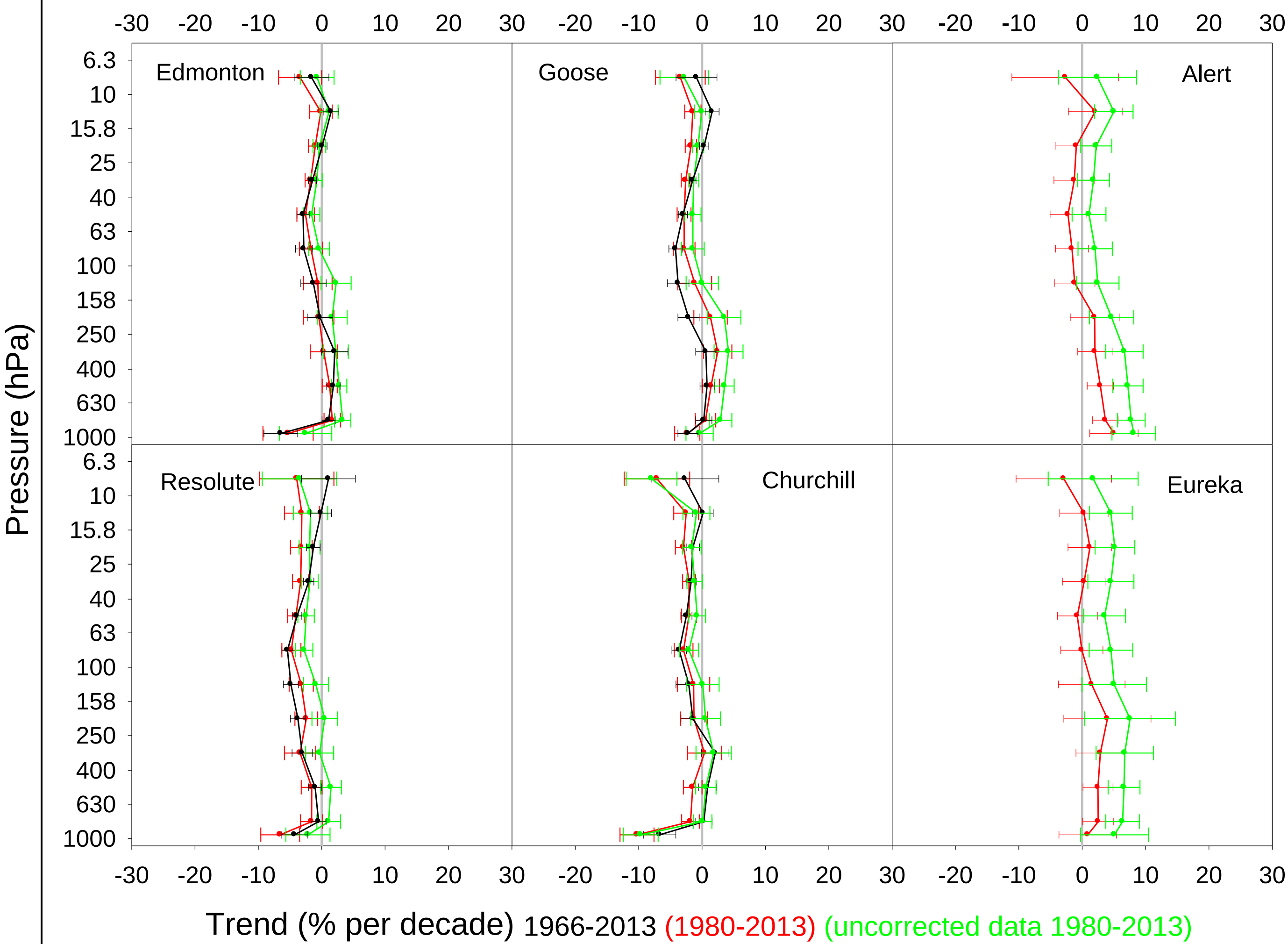


Figure 15: Linear trends in ozone mixing ratio for the overall (48-year) period at the six Canadian sites with long-term ozonesonde records, for the surface and 11 layers equally spaced in log pressure (~3 km). Error bars show 95% (2σ) confidence limits. The troposphere and stratosphere have been explicitly separated: that is, integration of the 250-158 hPa layer starts either at 250 hPa or at the tropopause, if the latter is found above 250 hPa. Similarly, integration of the 250-158 hPa layer starts either at 250 hPa or at the tropopause, if the latter is found above 250 hPa. Trends using only ECC data (from 1980) are shown in red. Trends from 1980 using ECC data before corrections are applied are shown in green.

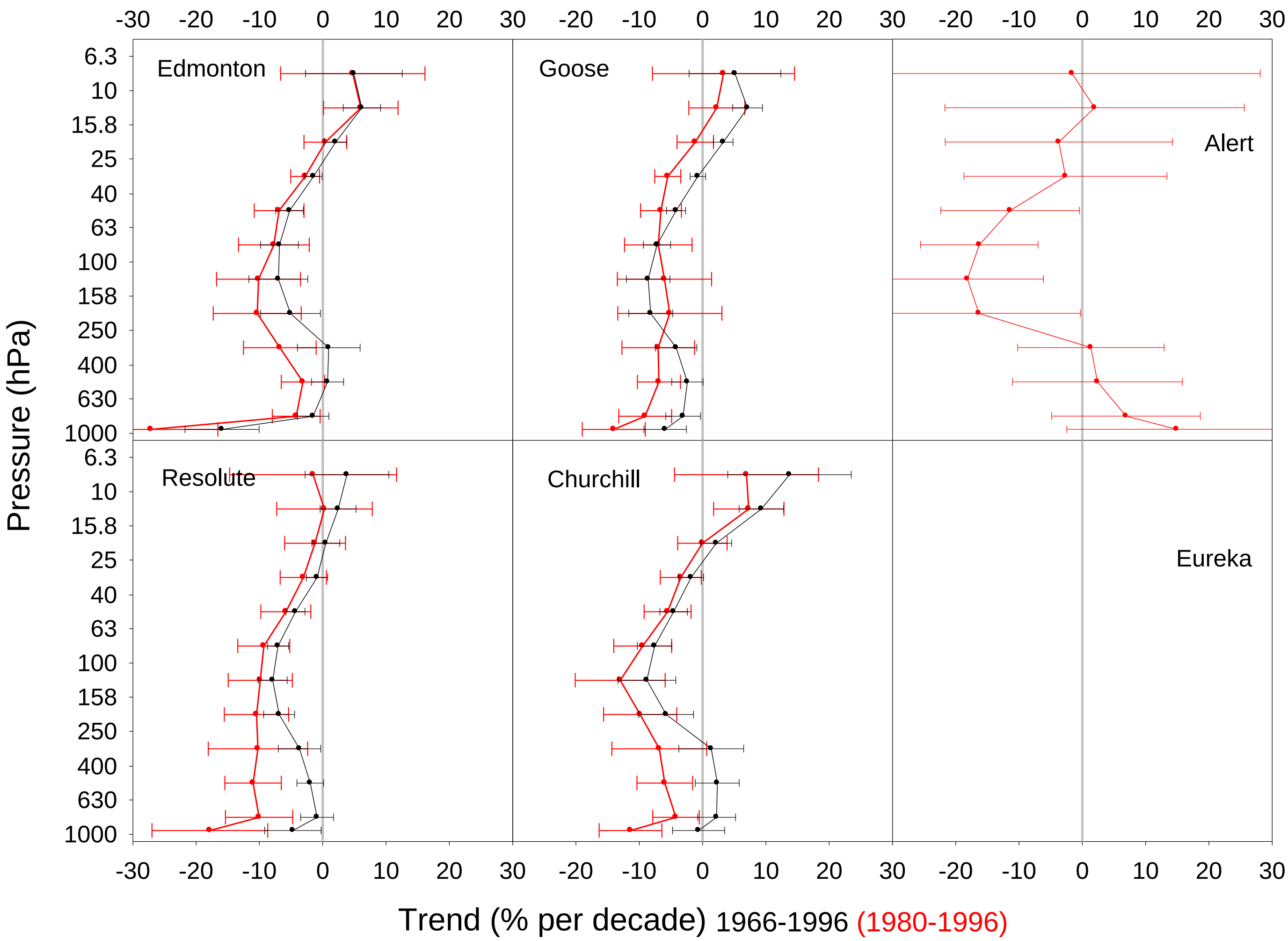


Figure 16: As Figure 17, but for 1966-1996. Trends using only ECC data (from 1980) are shown in red.

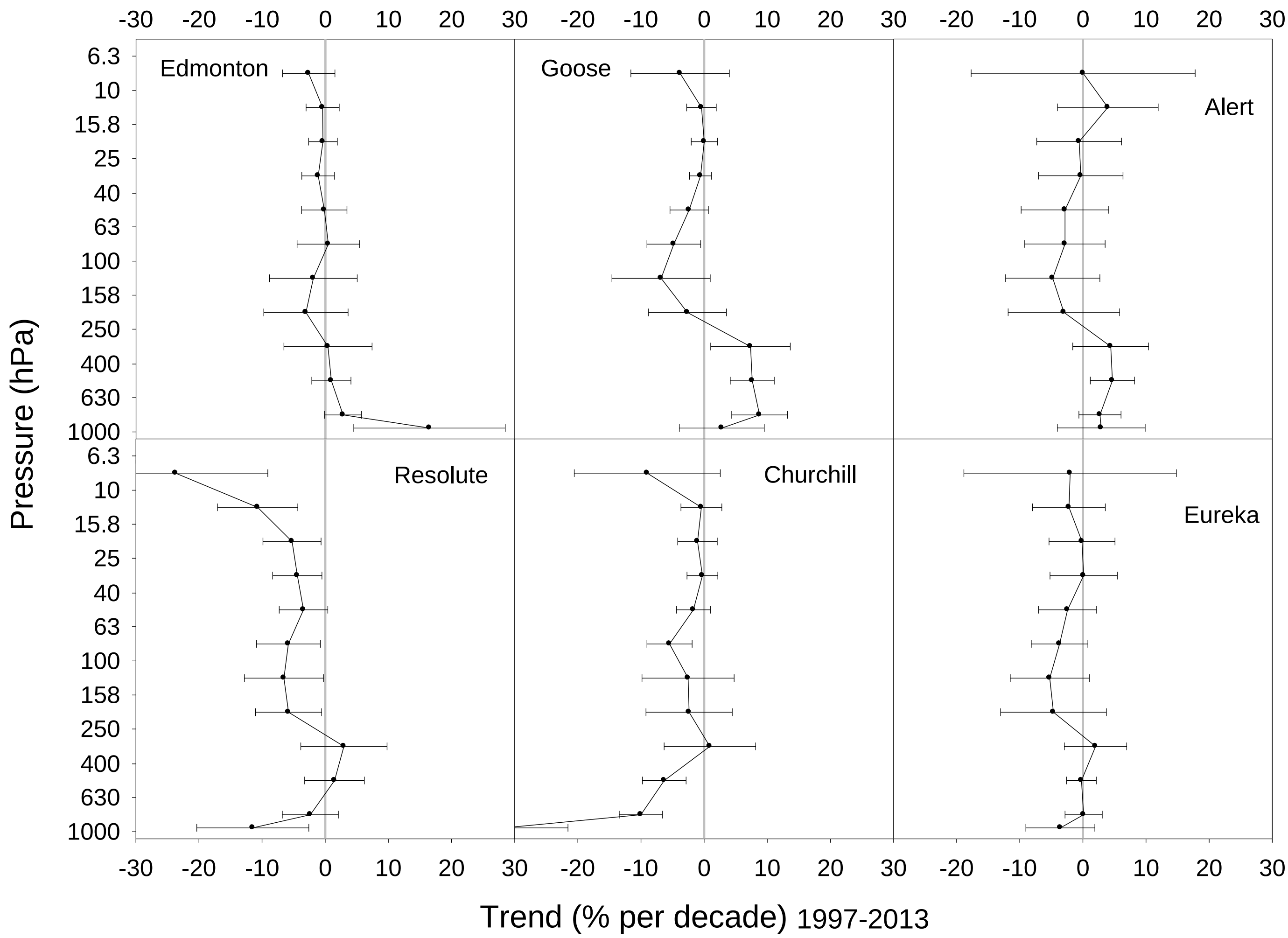


Figure 17: As Figure 17, but for 1997-2013.