Aalysis of the ozone uncertainties for the the McMurdo measurements, but these results are probably more universal than that.

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Overall uncertainties for ozonesonde measurements from “O3S-DQA-Guidelines Homogenization-V2-19November2012.doc”.

[Eq.3] $$\frac{\Delta \mathbf{P_{O3}}}{\mathbf{P_{O3}}} = \sqrt{\frac{(\Delta \mathbf{I_M})^2 + (\Delta \mathbf{I_B})^2}{(\mathbf{I_M} - \mathbf{I_B})^2} + \left(\frac{\Delta \eta_C}{\eta_C}\right)^2 + \left(\frac{\Delta \Phi_P}{\Phi_P}\right)^2 + \left(\frac{\Delta \mathbf{T_P}}{\mathbf{T_P}}\right)^2}$$

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1. ΔI_B and ΔI_m

From the McMurdo measurements the results for average and standard deviation are:

Science Pump :
I_{b0}(225 sondes) = 0.058 ± 0.018 μA - Ib0
I_{b1}(225 sondes) = 0.099 ± 0.060 μA - Ib1
I_{b2}(380 sondes) = 0.057 ± 0.046 μA - Ib2

ENSCI :
I_{b0}(520sondes) = 0.045 ± 0.020 μA - Ib0
I_{b1}(520 sondes) = 0.057 ± 0.032 μA - Ib1
I_{b2}(520 sondes) = 0.028 ± 0.033 μA - Ib2

From this I assume
ΔI_B(Science Pump) = 0.05 μA and ΔI_B(Ensci) = 0.03 μA

Assume ΔI_M = 0.1 μA – resolution of digital interface board (Herman Smit, personal communication).

With these values
$\frac{(\Delta \mathbf{I_M})^2 + (\Delta \mathbf{I_B})^2}{(\mathbf{I_M} - \mathbf{I_B})^2}$ contributes over half of the uncertainty for **I_m < 3.0 μA (< 1.4 μA – with a transfer function).**

2.0 Conversion Efficiency η_C -- O3s-DQA pp 13 (section **8.1)**

$$\frac{\Delta \eta_{C,}}{\eta_C} = \sqrt{\left(\frac{\Delta \alpha_{O3}}{\alpha_{O3}}\right)^2 + \left(\frac{\Delta \mathbf{S}_{O3/I2}}{\mathbf{S}_{O3/I2}}\right)^2}$$

$\Delta\alpha_{O3} = 0.02$, $\alpha_{O3} = 1.0$, $\Delta S_{O3/I2} = 0.03$, $S_{O3/I2} = 1.0$,

→ **$(\Delta\eta_c/\eta_c)^2 = 0.0013$ with no transfer function.**
This is biggest contributor to uncertainty for $I_m > 3.0$ µA.

With a transfer function

$\Delta S_{O3/I2} = 0.03+0.05$ (O3S-DQA, pp 16), $S_{O3/I2} = 1.0$

→ **$(\Delta\eta_c/\eta_c)^2 = 0.0068$ with a transfer function**

This is biggest contributor to uncertainty for $I_m >1.4$ µA with a transfer cuntion.

3.0 Pump Temperature Measurement -- O3s-DQA pp 29 (section **8.3)**

$$\left(\frac{\Delta \mathbf{T_P}}{\mathbf{T_P}}\right)^2 = \left(\frac{\Delta \mathbf{T_{P,Measured}}}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PC}})}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PPI}})}{\mathbf{T_{P,Measured}}}\right)^2$$

For the modern (digital) sounding systems $\Delta \mathbf{T_{P,Measured}}$ **~ ±0.5 K.**

$\Delta T_{PPI}(P_{Air})$ is the correction to obtain the "truest" pump piston housing temperature from the internal pump base temperature as given by [Eq.12], whereby uncertainty contribution **$\delta(\Delta T_{PPI})$=±0.5K.**

Case IV: <u>*External pump (epoxied/glued thermistors) temperature measurements in digital sounding systems:*</u>

$$\Delta T_C(P_{Air}) = \Delta T_{PIG}(P_{Air}) \text{ [see Eq.11]}$$

Uncertainty **$\delta(\Delta T_{PIG})$ = ±0.5K**

Thus,

$\Delta T_{P,M} = \Delta T_{PC} = \Delta T_{PPI} = 0.5 \rightarrow$

$$\left(\frac{\Delta \mathbf{T_P}}{\mathbf{T_P}}\right)^2 = \left(\frac{\Delta \mathbf{T_{P,Measured}}}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PC}})}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PPI}})}{\mathbf{T_{P,Measured}}}\right)^2 = 3 \bullet 0.5^2 / T_{P,M}^2 = 0.75/ T_{P,M}^2$$

For a typical ozonesonde, $T_{P,M}$ is near 300 K $\rightarrow (\Delta T_P/T_P)^2 = 0.75/300^2$.

Then **$(dTp/Tp)^2$ = 0.000031**

Case V: <u>*Internal pump (thermistors inside pump base) temperature measurements in digital sounding systems*</u>

No correction: ΔT_C=0 K & Uncertainty $\delta(\Delta T_C)$ = 0 K

Thus,

$\Delta T_{P,M} = \Delta T_{PPI} = 0.5$, and $\Delta T_{PC} = 0.0 \rightarrow$

$$\left(\frac{\Delta \mathbf{T_P}}{\mathbf{T_P}}\right)^2 = \left(\frac{\Delta \mathbf{T_{P,Measured}}}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PC}})}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PPI}})}{\mathbf{T_{P,Measured}}}\right)^2 = 2 \bullet 0.5^2 / T_{P,M}^2 = 0.5/ T_{P,M}^2$$

For a typical ozonesonde, $T_{P,M}$ is near 300 K $\rightarrow$ **$(\Delta T_P/T_P)^2$ = 0.50/300^2 =** `3.06573e-005`

Then **$(dTp/Tp)^2$ = 0.000020**

Averaging of the two cases $(dTp/Tp)^2$ = 0.000026

4. **Pump Flow Rate at Ground: Corrections for "Humidification Effect" & "Piston Temperature" --** O3s-DQA pp 32-33 (section 8.4) and **Pump Flow Efficiency at Low Pressures -- --** O3s-DQA pp 34-35 (section 8.5)

To obtain the uncertainty of the corrected pump flowrate determined at ground Consequently the propagation of individual uncertainty contributions can be expressed as: *[Eq.20]*

$$\frac{\Delta\,\Phi_{P,\,Ground}}{\Phi_{P,\,Ground}} = \sqrt{\left(\frac{\Delta\,\Phi_{P,\,Measured}}{\Phi_{P,\,Measured}}\right)^2 + \left(\frac{\Delta\,C_{PL}}{1+C_{PL}-C_{PH}}\right)^2 + \left(\frac{\Delta\,C_{PH}}{1+C_{PL}-C_{PH}}\right)^2}$$

$C_{PL} \ll 1$ and $C_{PH} \ll 1$ such that this simplies into:

[Eq.21]
$$\frac{\Delta\,\Phi_{P,\,Ground}}{\Phi_{P,\,Ground}} = \sqrt{\left(\frac{\Delta\,\Phi_{P,\,Measured}}{\Phi_{P,\,Measured}}\right)^2 + (\Delta\,C_{PL})^2 + (\Delta\,C_{PH})^2}$$

With $\Delta\Phi_{P,Measured}/\Phi_{P,Measured}$ better than ±2% →
$(\Delta\Phi_{P,Measured}/\Phi_{P,Measured})^2 = (0.02)^2 = 0.0004$

$C_{PL} = \frac{T_{Pump} - T_{Lab}}{T_{Lab}}$, usually $(T_{Pump} - T_{Lab})$ is ~ +2 K with an uncertainty of about ±0.5 K

Following the analysis for C_{PH}

$C_{PL,Average} = (C_{PL,High}+C_{PL,Low})/2$ and $\Delta C_{PL} = \pm(C_{PL,High}-C_{PL,Low})/2$

For McMurdo C_{PL} ranges from:
```
For 1986-1992: AvCpl =  0.006882 dCpl=  0.000059 dCpl^2 =  0.000000004
For 1993-2010: AvCpl =  0.006765 dCpl=  0.000057 dCpl^2 =  0.000000003
For 1986-2010: AvCpl =  0.006823 dCpl=  0.000058 dCpl^2 =  0.000000003
```

$$C_{PH} = \left[1 - \frac{RH_{In}}{100}\right] \bullet \frac{P_{H_2O,Sat}(T_{Lab})}{P_{Lab}},$$

$C_{PH,Average} = (C_{PH,High}+C_{PH,Low})/2$ and $\Delta C_{PH} = \pm(C_{PH,High}-C_{PH,Low})/2$

For McMurdo C_{PH} ranges from:
```
For 1986-1992: AvCph =  0.017214 dCph=  0.005182 dCph^2 =  0.000026855
For 1993-2010: AvCph =  0.019054 dCph=  0.004909 dCph^2 =  0.000024096
For 1986-2010: AvCph =  0.018134 dCph=  0.005045 dCph^2 =  0.000025476
```

This leads to an overall $(\Delta\Phi_{P,ground}/\Phi_{P,ground})^2$ = 0.000425

4.1 Pump efficiency at low pressures

Then we must add the pump efficiency factor for the Wyoming pump corrections. These are given by the SD of 794 Oz Pump CF measurements

University of Wyoming Ozone pump flow efficiency measurements,
See c:\prog\OZPUMPS\AvSdozpumps.cf

```
Prs-hPa NoMeas. Ave    SD   CubicFitSD    Stoic
 100.0     793  1.024  0.010  0.011       1.007
  50.0     788  1.038  0.013  0.010       1.021
  30.0     794  1.052  0.016  0.015       1.029
  20.0     788  1.070  0.020  0.022       1.038
  10.0     794  1.124  0.030  0.034       1.067
   7.0     794  1.168  0.038  0.039       1.091
   5.0     794  1.225  0.050  0.043       1.122
   3.0     197  1.289  0.042  0.044       1.188

Cubic fit to sd = C(i)*(natural log(prs-hPa))^i,
where C(i) =  0.023159  0.039282 -0.021000  0.002583

Then
Prs   PCF    sdPCF   sdCalc   sd/PCf    (sd/PCF)^2    (dF/F)^2
 100 1.024 0.0100 0.0110    0.01071    0.00011     0.00054
  50 1.038 0.0130 0.0101    0.00972    0.00009     0.00052
  30 1.052 0.0160 0.0155    0.01470    0.00022     0.00064
  20 1.070 0.0200 0.0218    0.02039    0.00042     0.00084
  10 1.124 0.0300 0.0338    0.03007    0.00090     0.00133
   7 1.168 0.0380 0.0391    0.03349    0.00112     0.00155
   5 1.225 0.0500 0.0428    0.03490    0.00122     0.00164
   3 1.289 0.0420 0.0444    0.03444    0.00119     0.00161
```

This leads to an overall $(dFR/FR)^2$ = 0.000425 - 0.001612

$(\Delta\Phi_P/\Phi_P)^2$ = f(P) = 0.00164 (P=5 hPa) – 0.00043 (P>100 hPa).

These results are summarized in the following table and figure.

	$\frac{\Delta P_{O3}}{P_{O3}}$	$\frac{(\Delta I_M)^2 + (\Delta I_B)^2}{(I_M - I_B)^2}$	$(\Delta\eta_c/\eta_c)^2$	$(\Delta\Phi_P/\Phi_P)^2$	$(\Delta T_P/T_P)^2$
I > 0.4 μA					
Best	0.04	0.004	0.0013	0.000425	0.000020
Worst	0.30	0. 1		0.001612	0.000031
I < 0.4 μA					
Best	0.30	0.10	0.0013	0.000425	0.000020
Worst	3.0	3.0		0.001612	0.000031
With	a	transfer	funtion		
I > 0.4 μA					
Best	0.10	0.004	0.0068	0.000425	0.000020
Worst	0.30	0. 1		0.001612	0.000031
I < 0.4 μA					
Best	0.30	0.10	0.0068	0.000425	0.000020
Worst	3.0	3.0		0.001612	0.000031

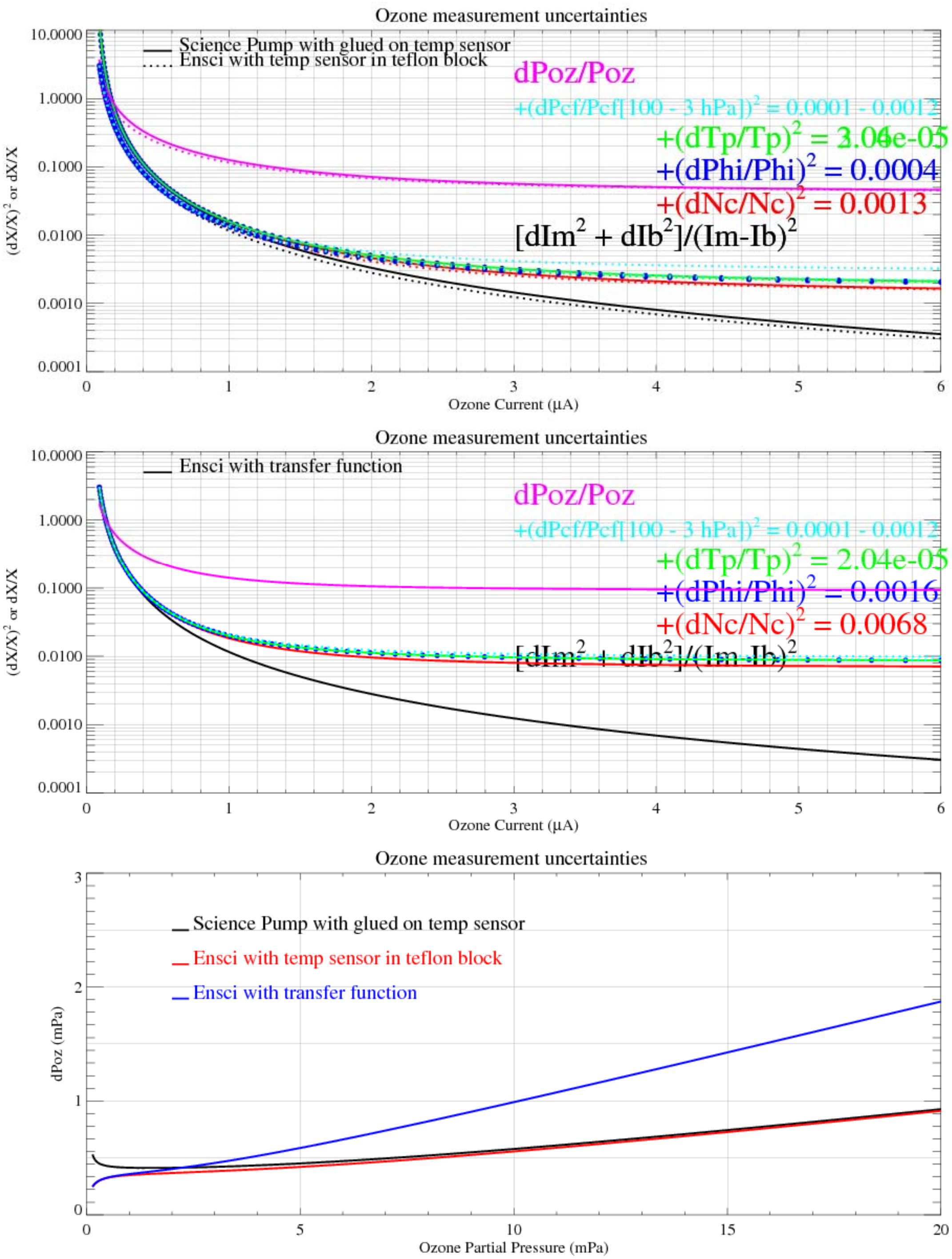
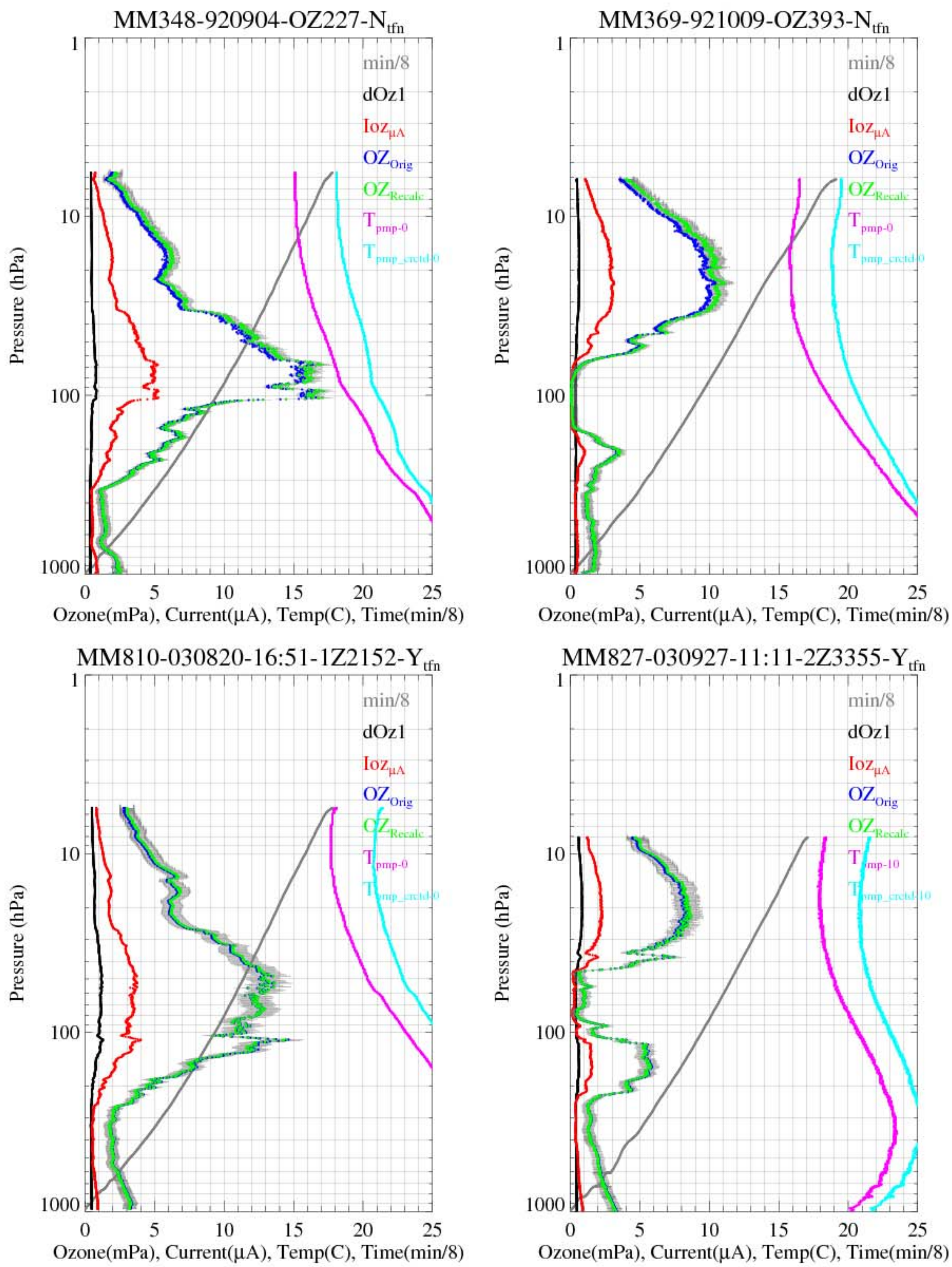


Figure: Top, middle the quantities $(dX/X)^2$ for each contributor to the uncertainty, adding each element to the preceding quantities. The cayan dashed lines show the contribution from the unvertainty associated with the low pressure pump flow correction. Bottom, the unvertainty in absolute value of partial pressure using the dPoz/Poz in the first two graphs oaver a range of partial pressures.



Examples of corrections and uncertainties applied to McMurdo Science Pump ozone data in 1992 with no transfer function and to ENSCI sondes in 2003 with a 1.0 to 0.5% transfer function applied.