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PURPOSE

• There are numerous compounds in atmosphere that are important for the NO_x and HO_x cycle, O₃ formation, and aerosol growth (e.g., isoprene, α-pinene, oxidants of these compounds); however, there are no commercial gas cylinder standards for these compounds.

• Currently, there are two cited methods to make cylinders: gravimetric [1-2, 5-9] or volumetric [3-4]. Both methods introduce uncertainty in the concentration of the analyte(s) due to the way the analyte(s) are prepared or injected into the cylinder.

• **GOAL:** To develop a new method to prepare a standard (in μmol/mol or ppm range) gas cylinder with at least 0.3% (one standard deviation) uncertainty for the laboratory to use in the future.

METHOD DEVELOPMENT

• Pull an aliquot of CH₂Cl₂ (99.9% Purity) into micro-syringe and weighed on analytical balance.



• Flow ~3 L/min high purity N₂ through glass-T into standard gas cylinder (Figure 1). Inject CH₂Cl₂ into glass-T after ~5 minutes of flow. Re-weigh micro-syringe after injection.

• After ~20 minutes, directly connect N₂ tank to standard gas cylinder (Figure 2). Fill until approximate pressure equilibrium.

• Rolled cylinders to ensure CH₂Cl₂ is well mixed throughout entire cylinder.

• Sampled cylinder with Shimadzu GC-14B with ⁶³Ni Electron Capture Detector (Figure 3).

• Two columns used: between March and July, a Supel-Q PLOT Column (Column 1, 30 m x 0.32 mm) and after August, a Rtx-1701 Column (Column 2, 30 m x 0.53 mm).



FIGURE 2. Direct flow set-up.

• The columns were held isothermally.

• The sample loop was ~0.62-mL.

• A vent between the standard gas cylinder and the 6-port valve was used to ensure build of pressure did not occur in the instrument.



FIGURE 3. GC-ECD Set-up.

RESULTS

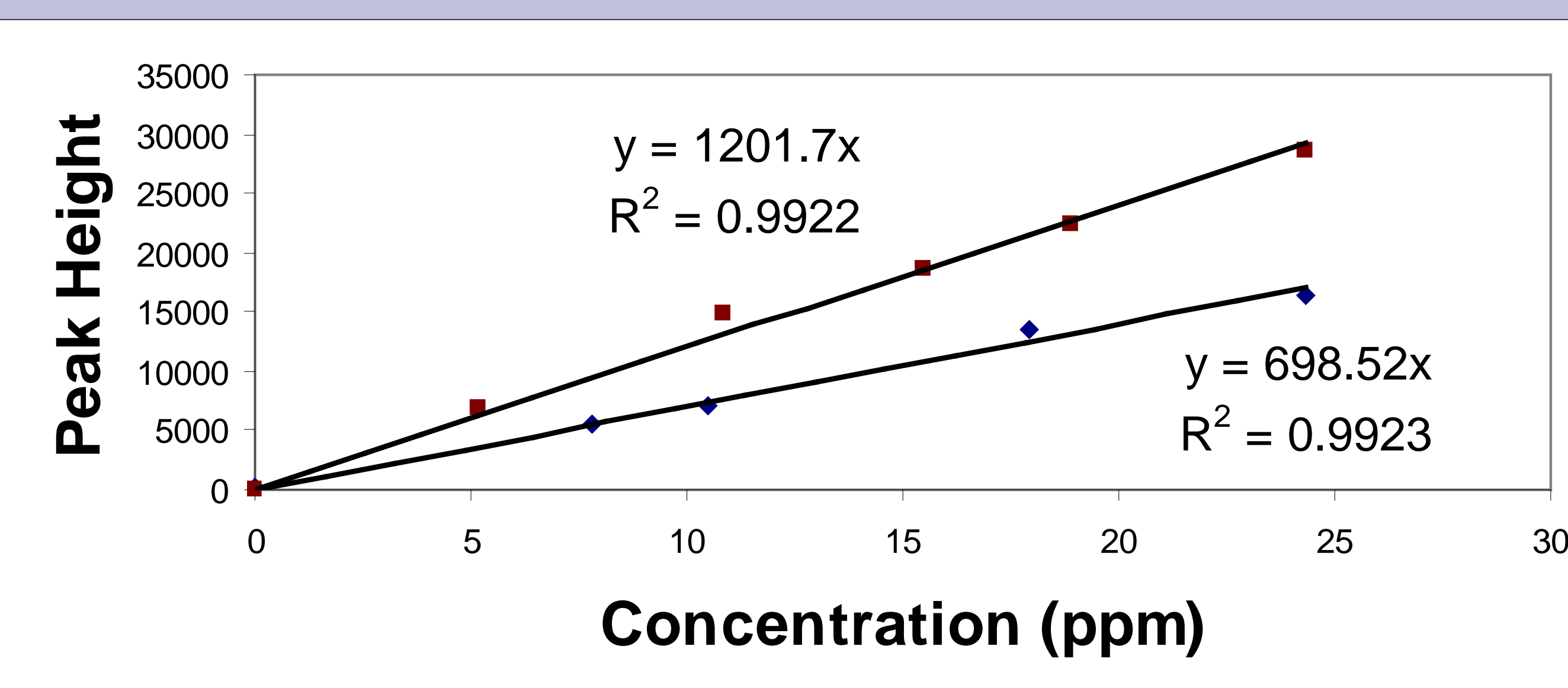


FIGURE 4. Example calibration curves for CH₂Cl₂ on both columns. The top calibration curve is for Column 1 and the bottom calibration curve is for Column 2. Note: error bars are less than ±200 counts peak height.

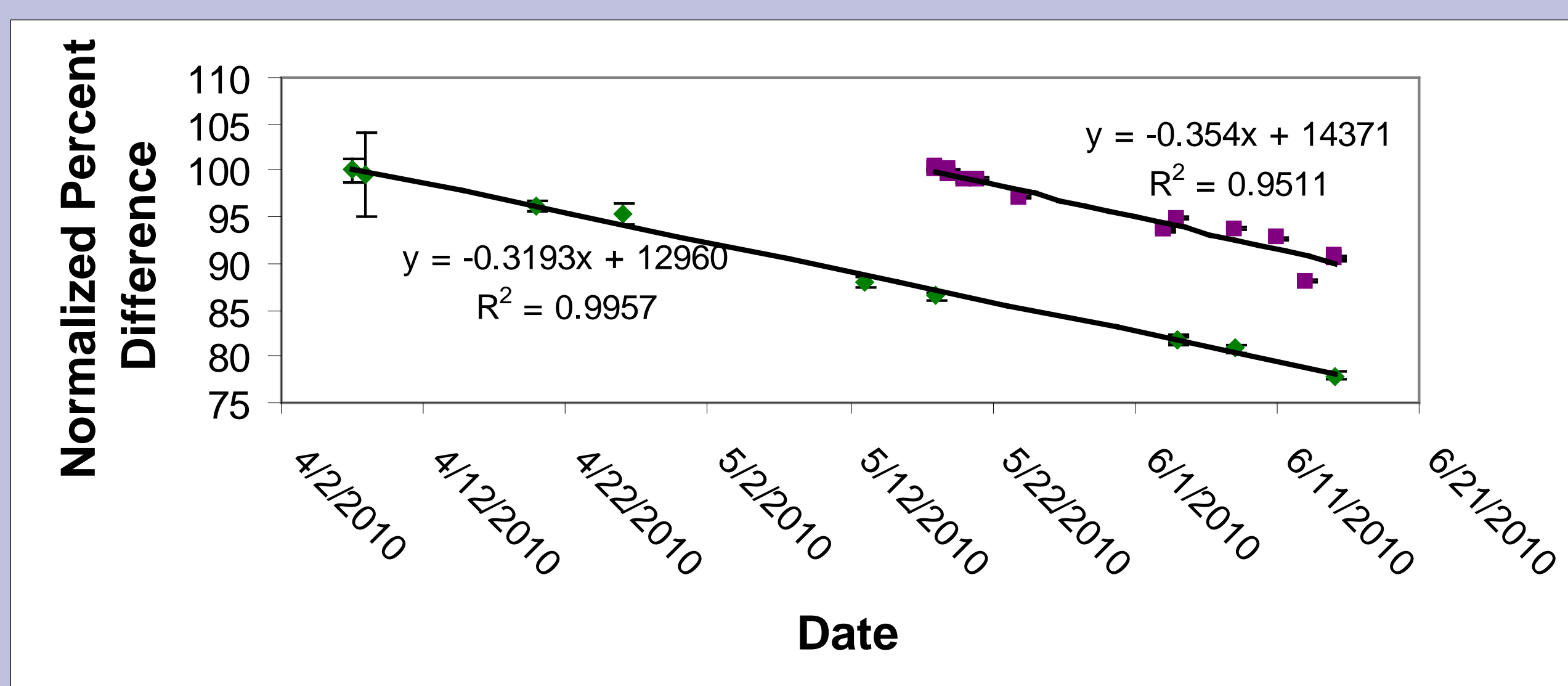


FIGURE 5. Change in analyte concentration from cylinder fill to September. Cylinder 2 is green and Cylinder 1 is purple. Error bars are at 95% confidence interval.

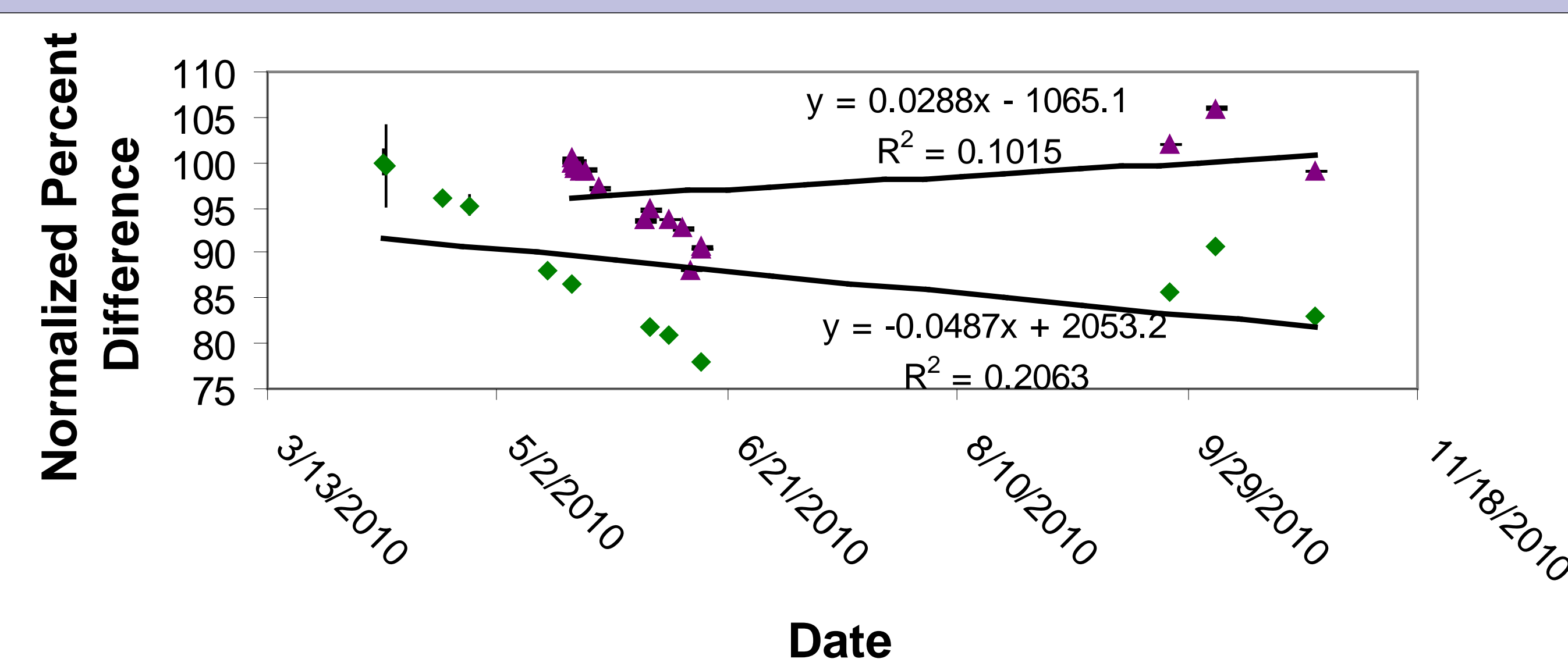


FIGURE 5. Change of concentration from initially making cylinders to present. Error bars are at 95% confidence interval.

TABLE 1. Calculated and measured concentrations. Numbers in parentheses are one standard deviation.

	Calculated Concentration	Measured Concentration	% Difference
Small Concentration Cylinder (Cylinder 1)	6.17 (±0.04) μmol/mol	7.5 (±0.3) μmol/mol	22%
Large Concentration Cylinder (Cylinder 2)	11.5 (±0.0) μmol/mol	22.4 (±1.9) μmol/mol	95%

DISCUSSION

• Both slopes in Figures 5 and 6 are statistically different from 0.

• Before September, the decrease of concentration was nearly linear. After September, cylinder 2 is at approximately 87% of its original value and cylinder 1 is at approximately 102% of its original value.

• The decrease in concentration is not fully understood. It is possible that the cylinders are not well-mixed; however, this would then yield results that are low. Similarly, losses of the analyte during the injection process, or during sampling from the cylinder would yield results that are low.

• There was a larger change of concentration over time and percent difference in calculated versus measured than literature [1-9]; however, in those references, most of the analytes are hydrocarbons instead of halogenated organic compound. Also, the cylinders were analyzed over longer time periods (~2 years minimum), which could result in a more stable average (Figure 4 versus Figure 5).

• The percent difference between calculated and measured concentrations is unclear. Contamination from the glass-T and transfer lines were tested and found to be negligible. Also, the analytical balances were carefully calibrated.

• There is a 4% and 8% (1 standard deviation) uncertainty with cylinders 1 and 2, respectively. This corresponds well with G. C. Rhoderick's [7] results; however, lower than the theoretical percent uncertainty from propagation of error from balances (~0.3%).

FUTURE WORK

• We are working to understand the difference in the calculated and observed concentrations. Future tests will include trying multiple approaches in parallel and trying different polarity compounds.

• This work is necessary in order to accurately calibrate instruments to measure low concentrations species in the atmosphere. The drifts currently observed would cause an over estimation of the gases.

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