

Review of Federal Reference Method for Ozone: Nitric Oxide-Chemiluminescence

Supplemental Material for CASAC AMMS

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AMMS	Air Monitoring and Methods Subcommittee
CASAC	Clean Air Science Advisory Committee
EPA	Environmental Protection Agency
FRM	Federal reference Method
MDA8	Maximum Daily Eight Hour Average
NO	Nitric Oxide
NO-CL	Nitric Oxide-Chemiluminescence Method
O₃	Ozone
ORD	Office of Research and Development
UV	Ultraviolet Absorption Method
UV-Drier	Ultraviolet Absorption Method with Sample Drier
UV-SL	Scrubberless Ultraviolet Absorption Method



Further Analysis of Ambient Ozone Research Data

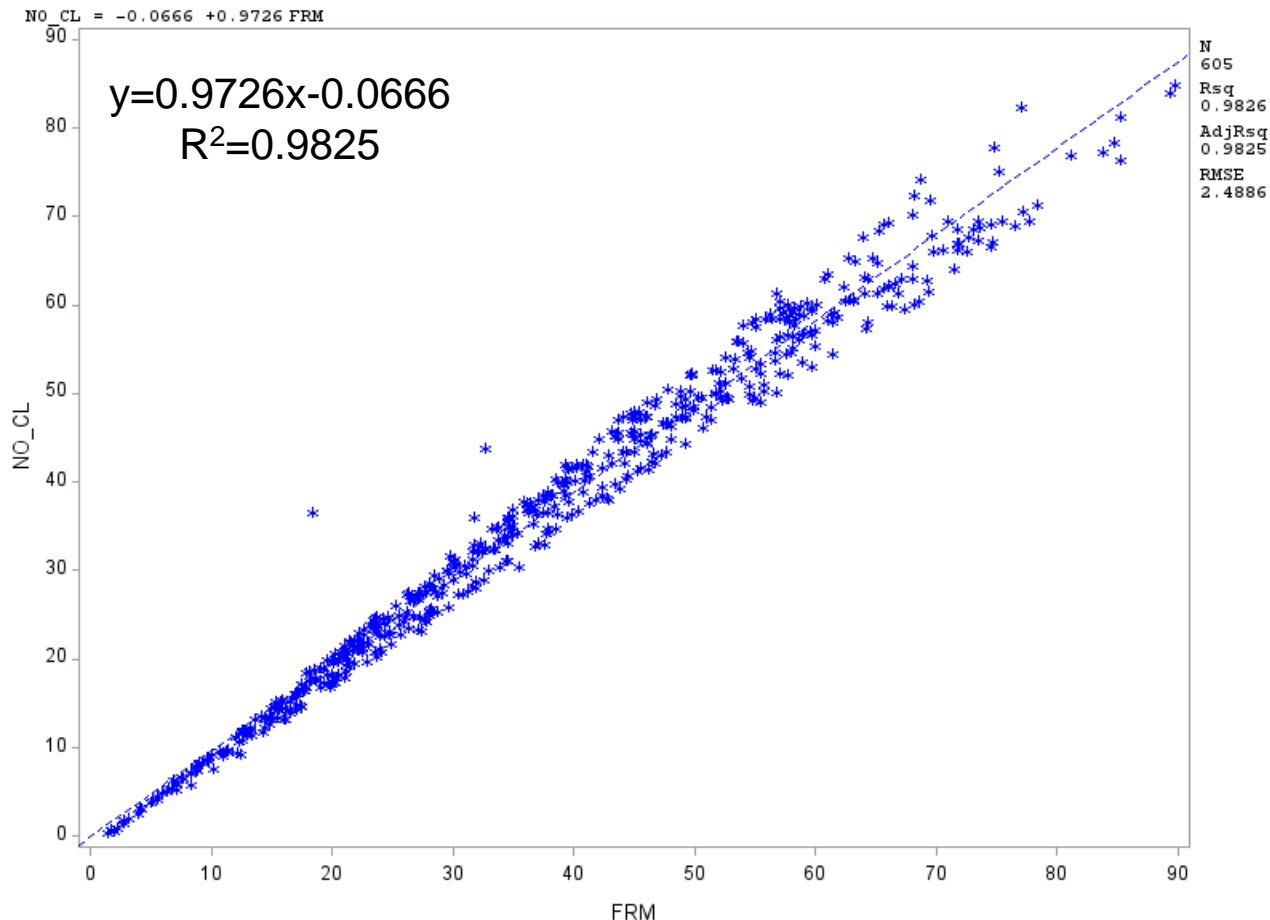
Approach

- Per suggestion made by CASAC AMMS members during the April 3, 2014 conference call on the Review of Federal Reference Method for Ozone: Nitric Oxide-Chemiluminescence, ORD has performed additional data analysis activities to explain and mitigate scatter observed in the comparisons of the FRM vs. NO-CL methods.
- In April 2014, an additional research study began at the EPA/AIRS sampling site in Research Triangle Park, NC comparing ambient ozone results obtained from the current FRM and potential FRM candidates including the NO-CL and the SL-UV methods.
- The attached figures give the results from the further data analysis performed by ORD and also early results from the Spring 2014 study.

Conclusion

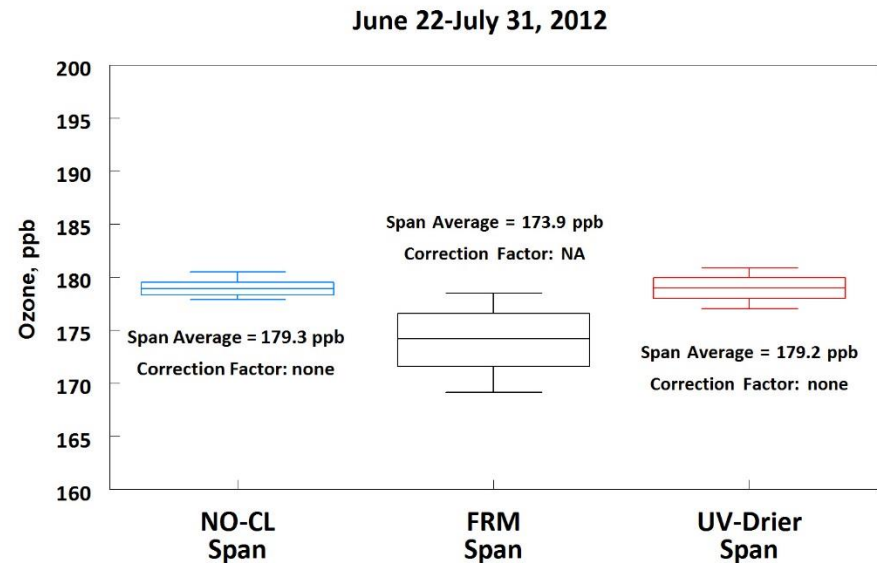
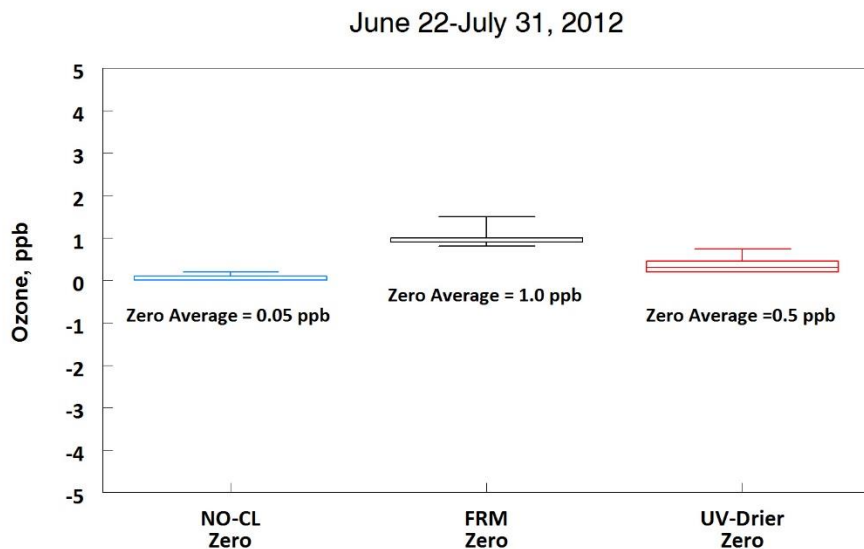
- Based upon the work that has been done to date and this subsequent data analysis. ORD is confident that the NO-CL method meets and exceeds all requirements for proposal of a new FRM for ozone.

22 June – 22 July 2012 – RTP/AIRS (1 hour) FRM vs. NO-CL



- The above figure was presented during April 3, 2014 call. Scatter in the comparison of FRM and NO-CL data was observed and commented on by AMMS members during the call.
- ORD acknowledges the presence of the scatter and as a result performed further analysis of the data set used to generate the above figure.

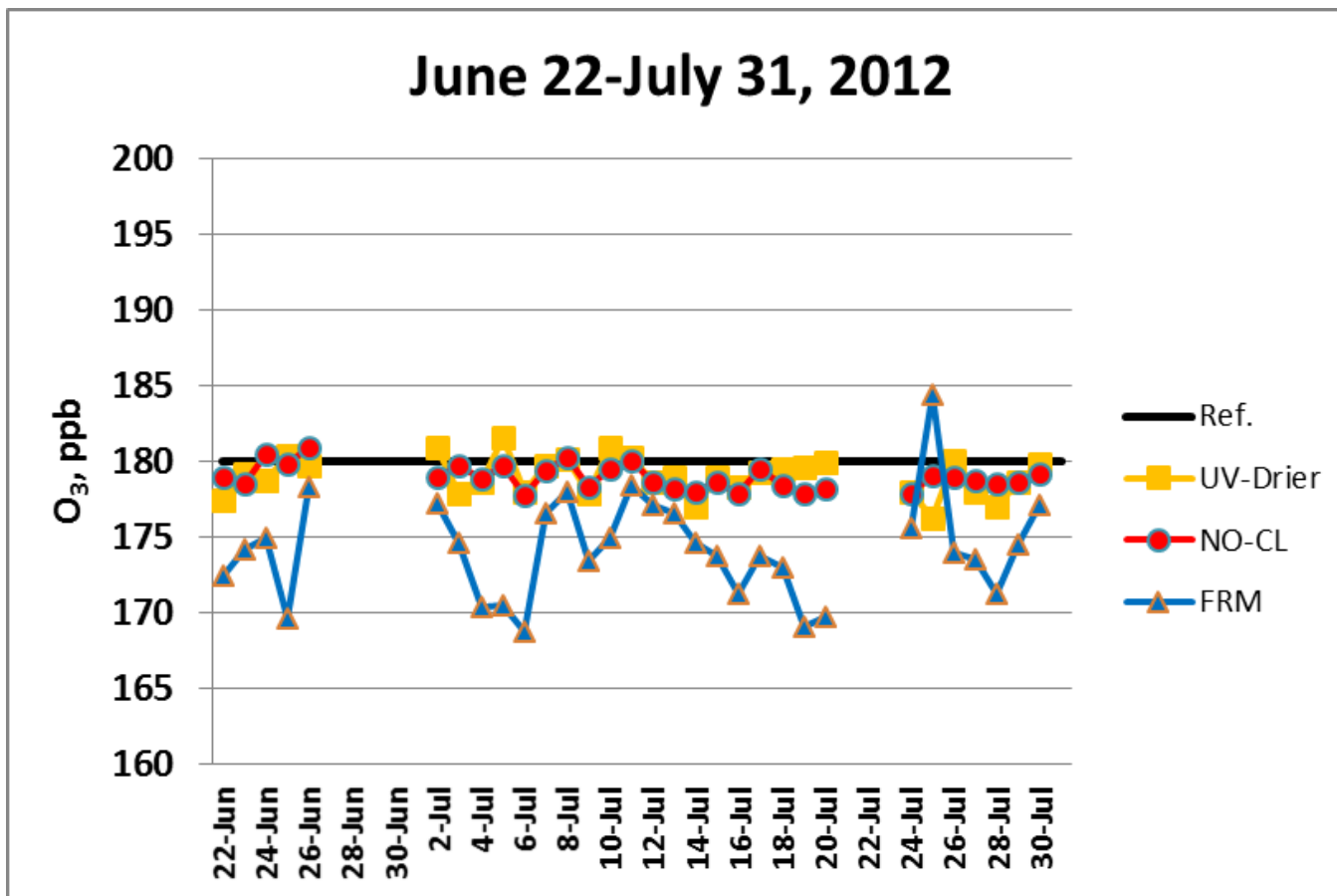
22 June – 31 July 2012 – RTP/AIRS Nightly Span (180 ppb) and Zero Results



During the June-July 2012 study period, automated nightly zero and span (180 ppb) checks were conducted.

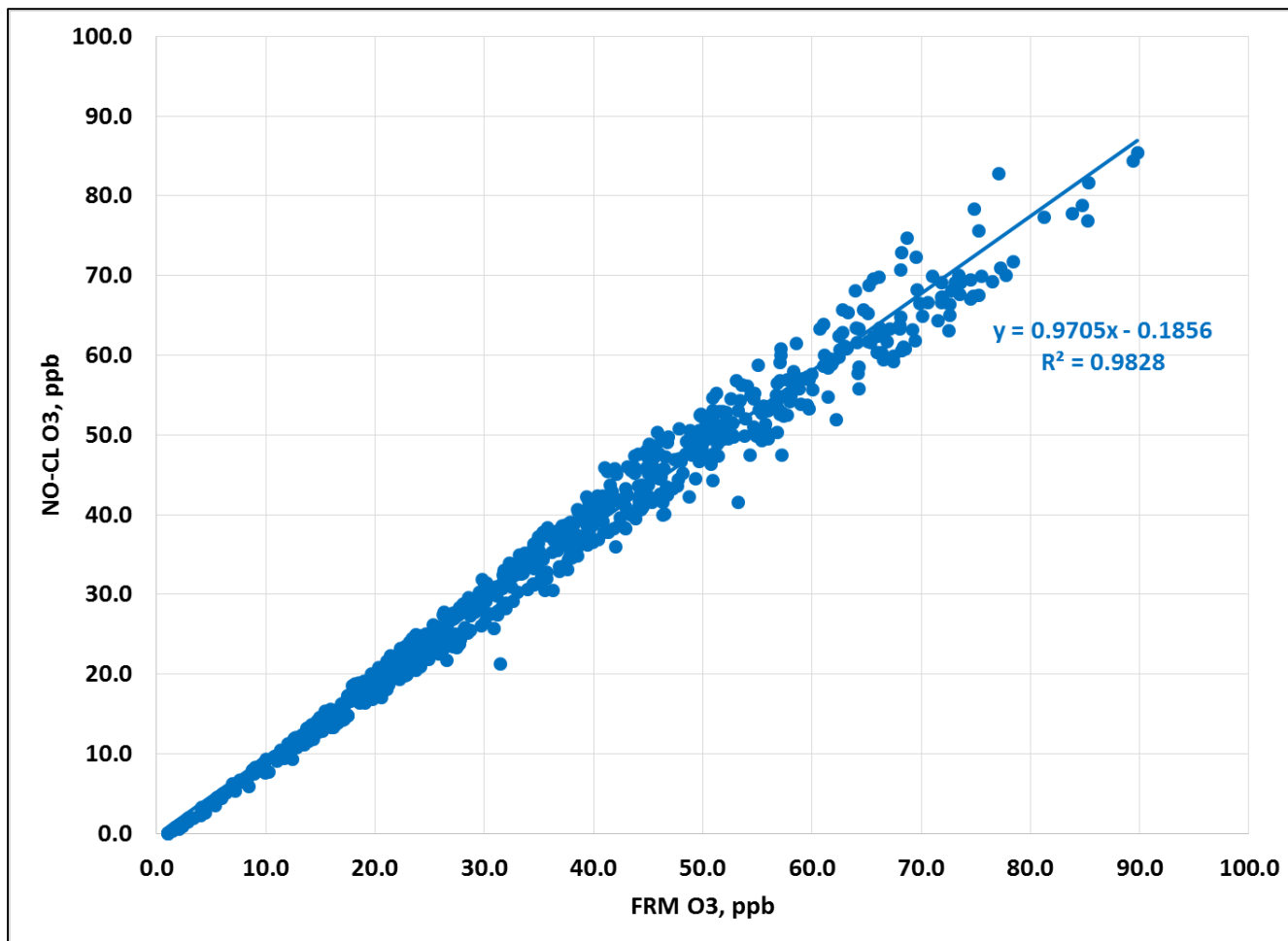
- Ambient data correction factors were obtained from analysis of the zero and span check data results.
- Zero and span results for each method were analyzed independently to generate a correction factor unique to that specific method.
 - A defensible correction factor for FRM data could not be obtained due to highly variable span check results
 - No correction factors required for NO-CL and UV-Drier methods

RTP/AIRS Nightly Span (180 ppb) Results



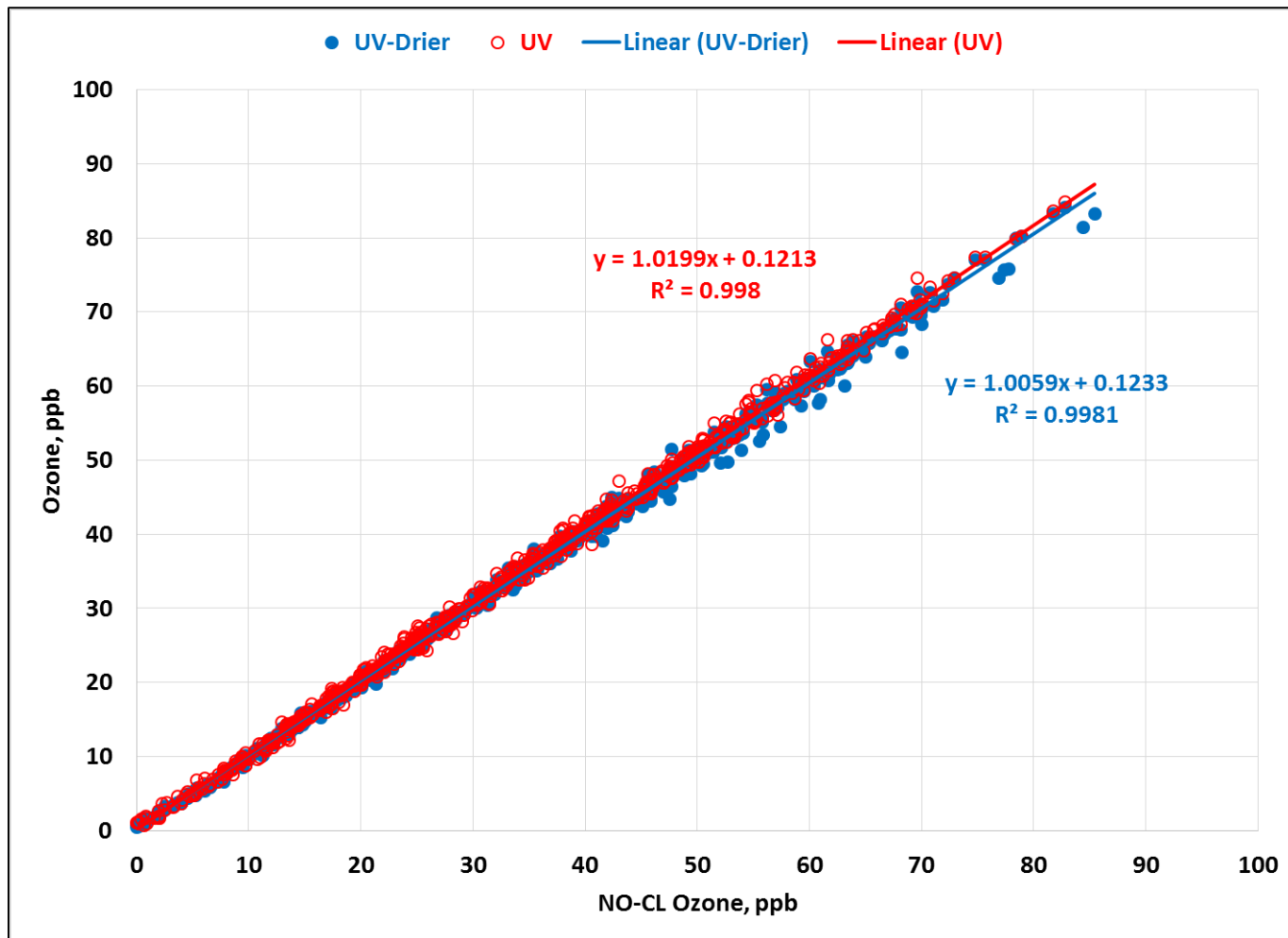
- High variability and lack of identifiable trends in the FRM span check data, result in the inability to generate a correction factor for the FRM data.

22 June – 31 July 2012 – RTP/AIRS (1 hour) FRM vs. NO-CL



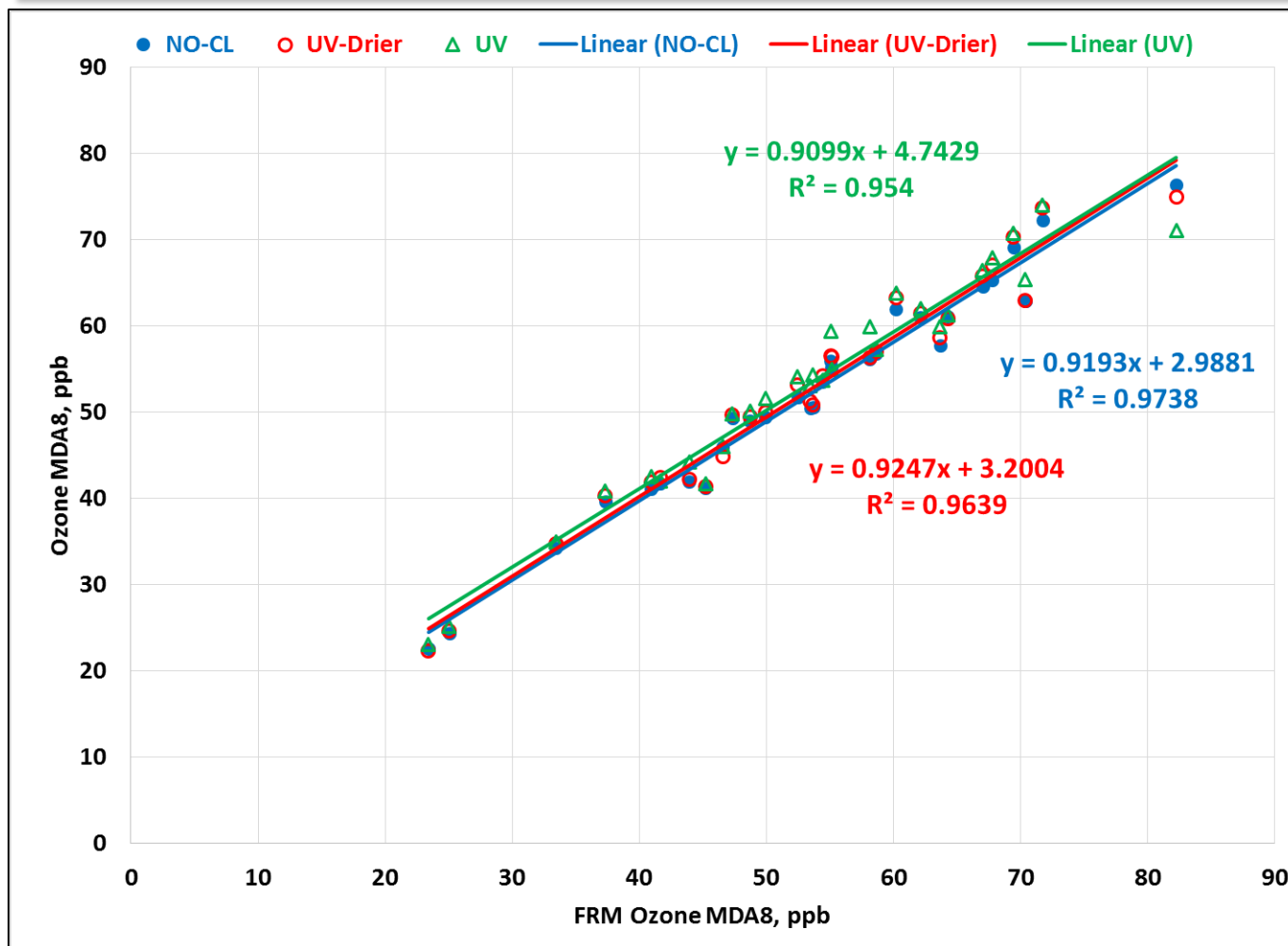
- Scatter observed in FRM vs NO-CL comparison is contributed to the FRM data.
- FRM analyzer was rebuilt and returned to service just prior to study start date after a prolonged period of inactivity.

22 June – 31 July 2012 – RTP/AIRS (1 hour) NO-CL vs. UV Methods



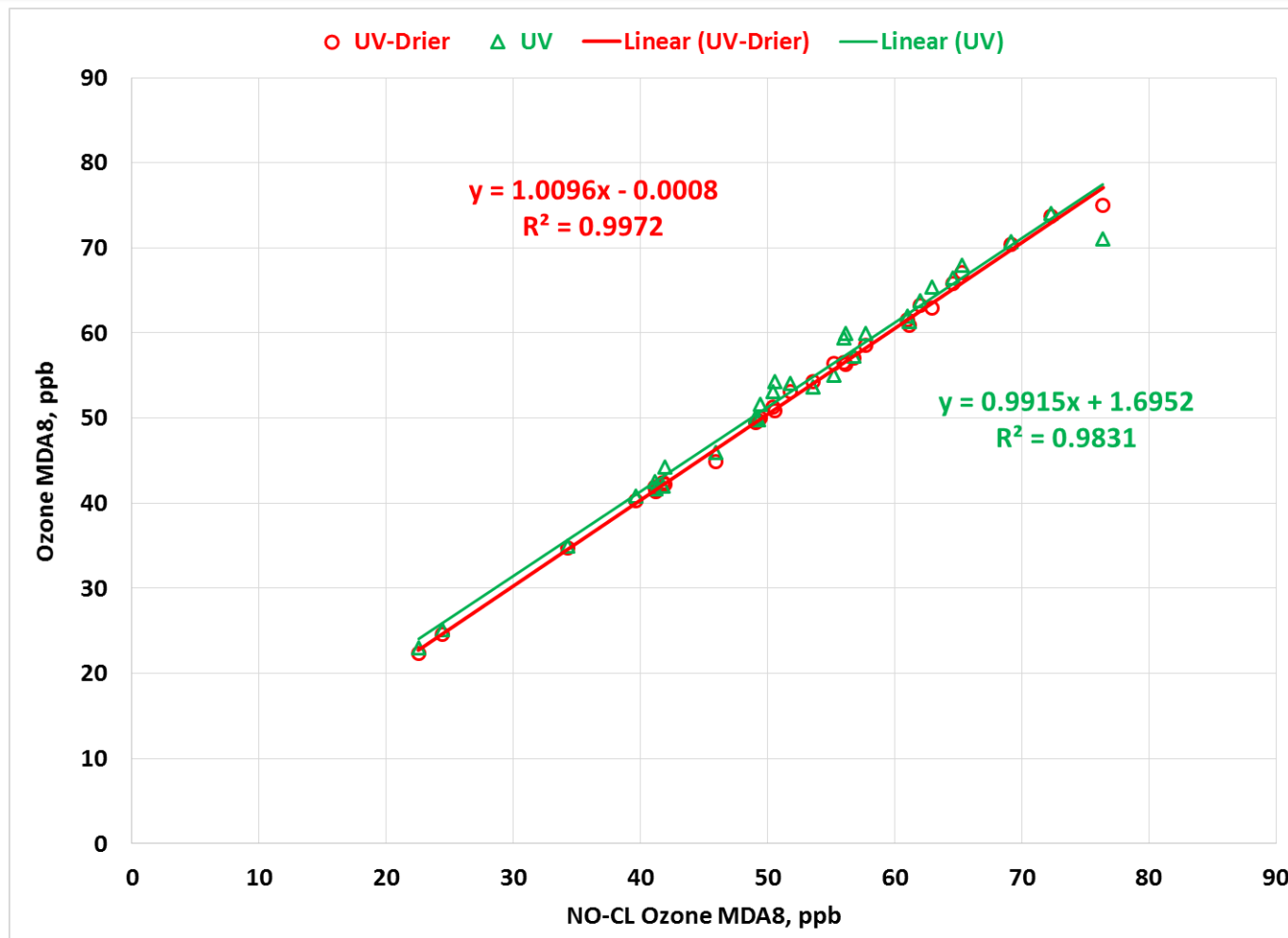
- A more robust comparison (less scatter) was observed between NO-CL and UV methods.
- Data correction factors were not required for these data through out the study period.

22 June – 31 July 2012 – RTP/AIRS (MDA8) FRM vs NO-CL and UV Methods



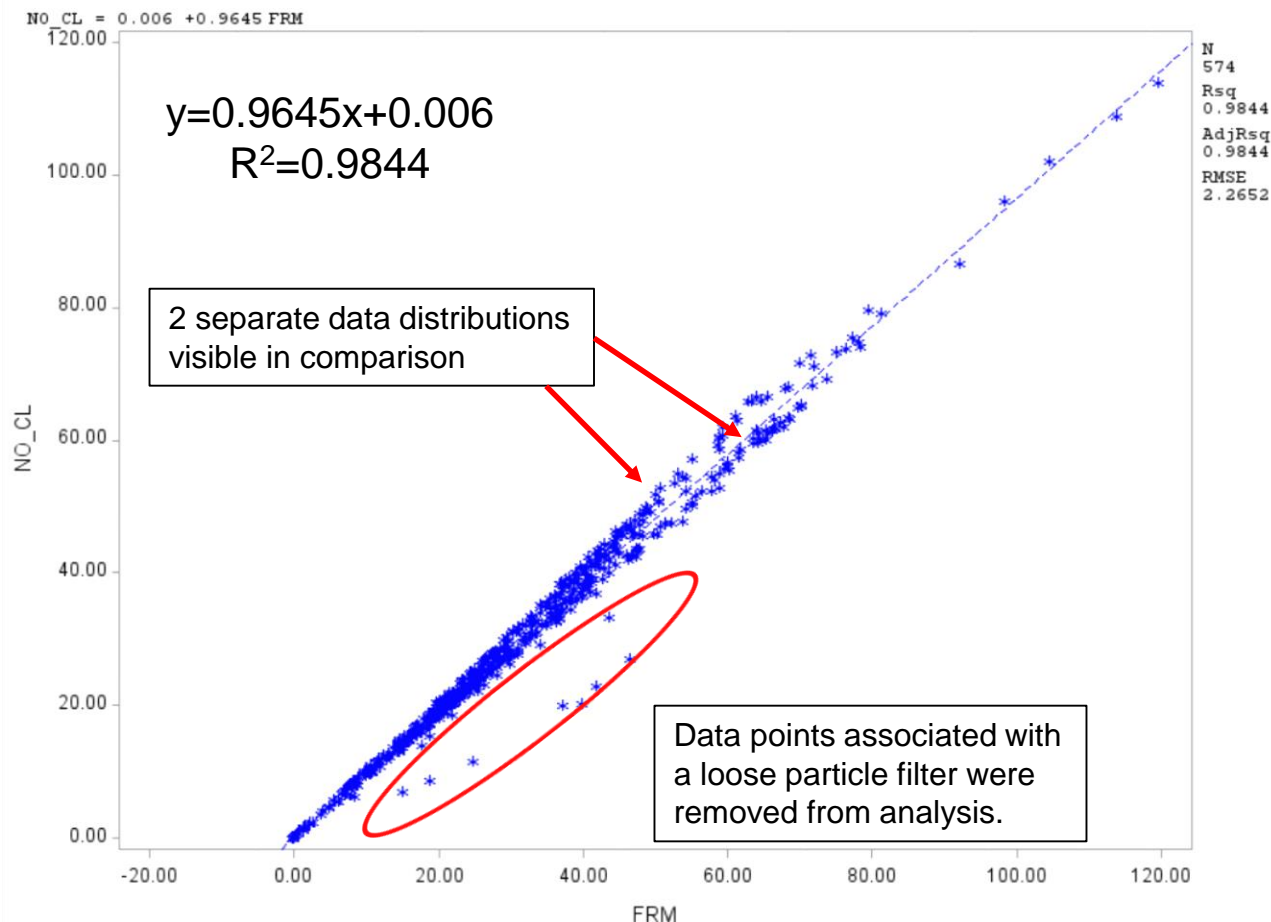
- Comparison of the maximum daily eight hour ozone averages (MDA8) for the Summer 2012 study period show ~10% decrease (from unity) in slope a large offset, and significant scatter for all method types when compared to the FRM.

22 June – 31 July 2012 – RTP/AIRS (MDA8) NO-CL vs UV Methods



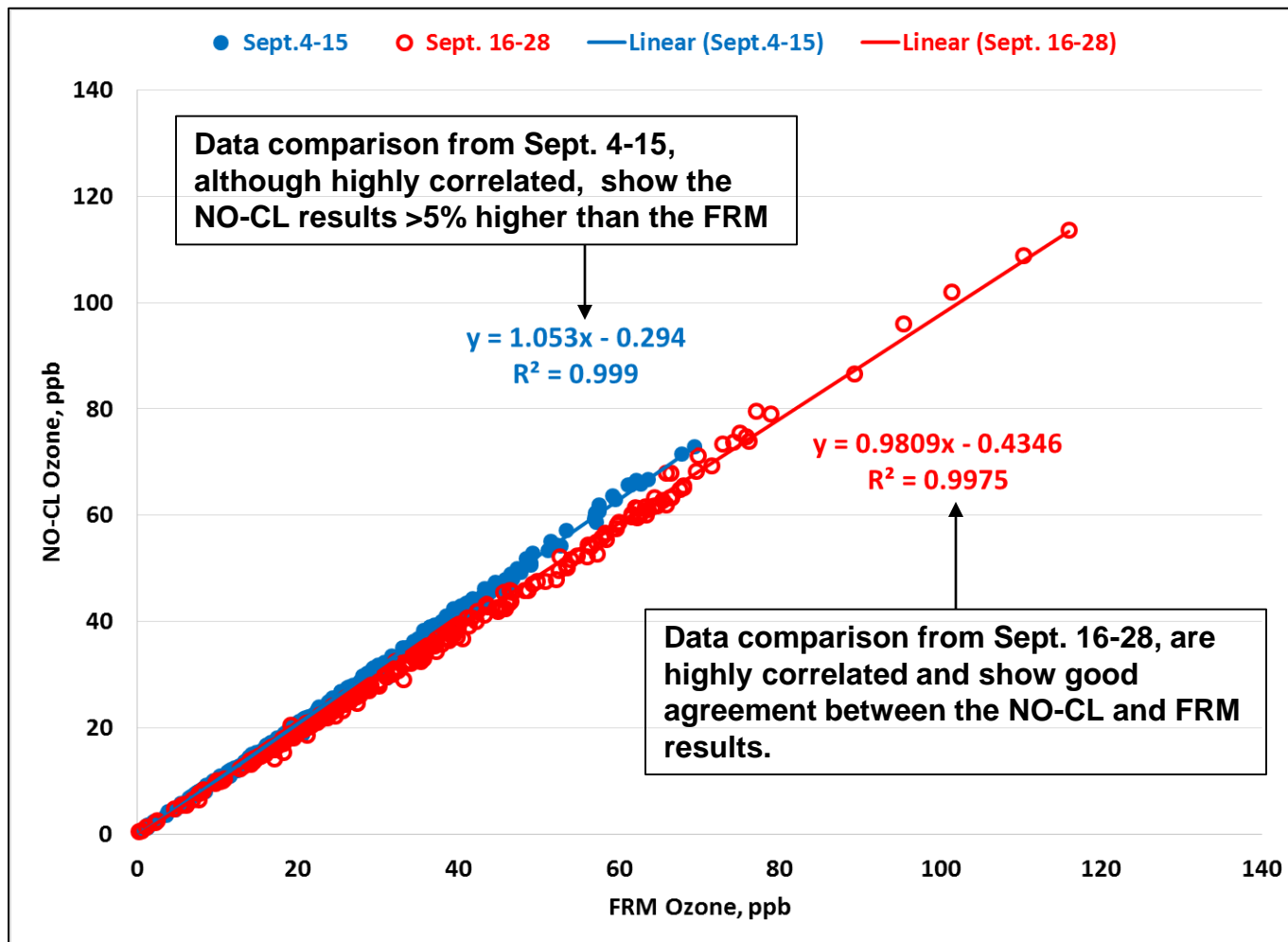
- Comparison of the maximum daily eight hour ozone averages (MDA8) for the Summer 2012 study period show very good agreement in the absence of the FRM data.
- >95% of the MDA8 values for each individual method coincided during the same hour of the corresponding day

04 – 28 Sept 2013 – LaPorte/Houston (1 hour): FRM vs. NO-CL



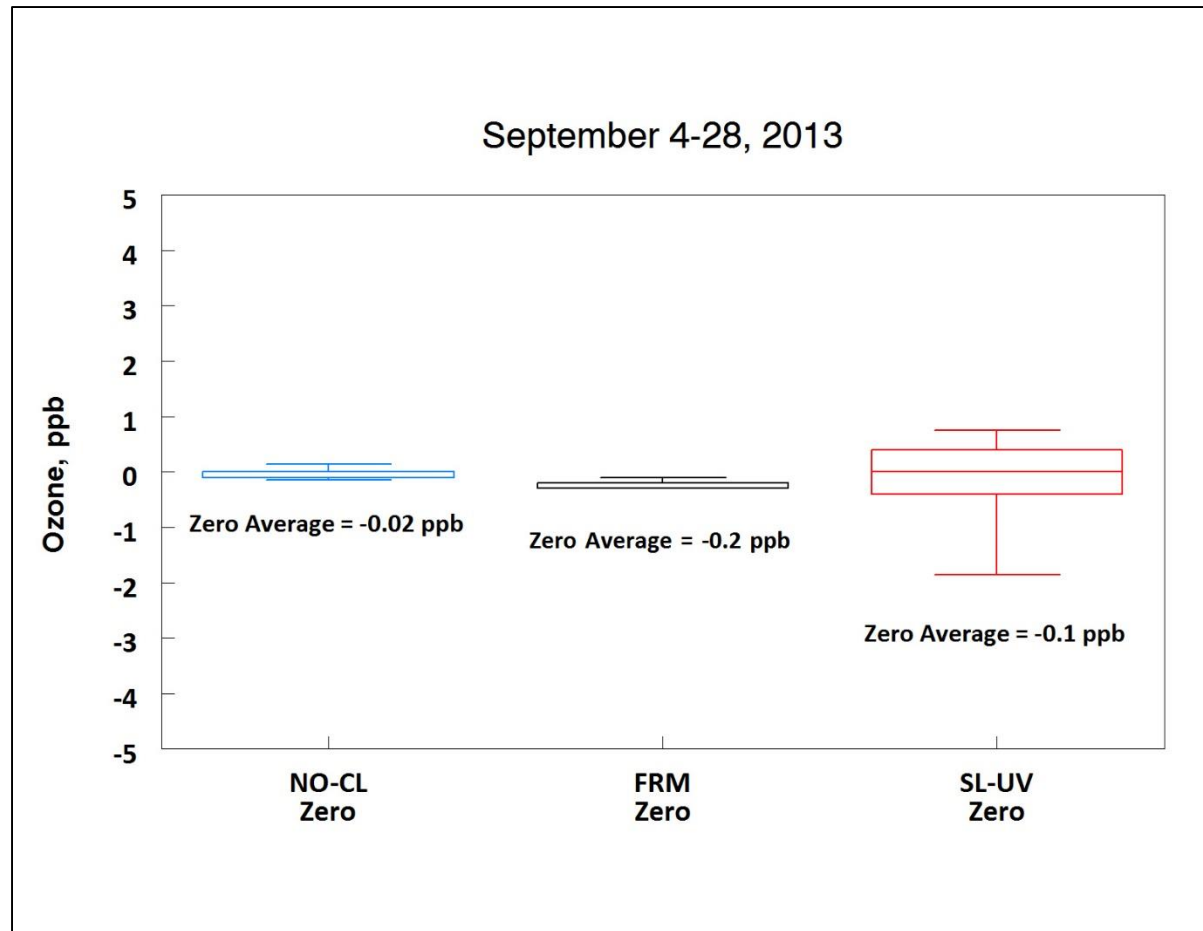
- The above figure was presented during April 3, 2014 call. Scatter in the comparison of FRM and NO-CL data was observed and commented on by AMMS members during the call.
- ORD acknowledges the presence of the scatter and as a result performed further analysis of the data set used to generate the above figure.

04 – 28 Sept 2013 – LaPorte/Houston (1 hour) FRM vs. NO-CL



- The combination of the above two data distributions into one comparison plot resulted in the scatter observed in the previous figure.

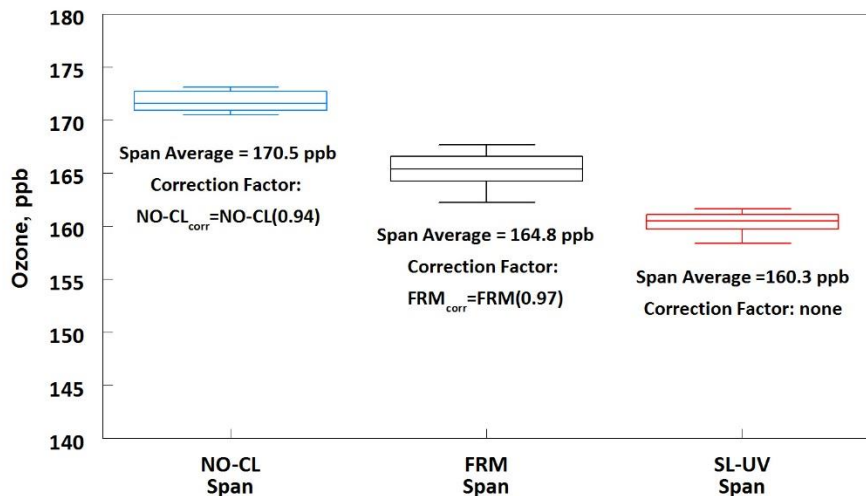
04 – 28 Sept 2013 – LaPorte/Houston Nightly Zeroes



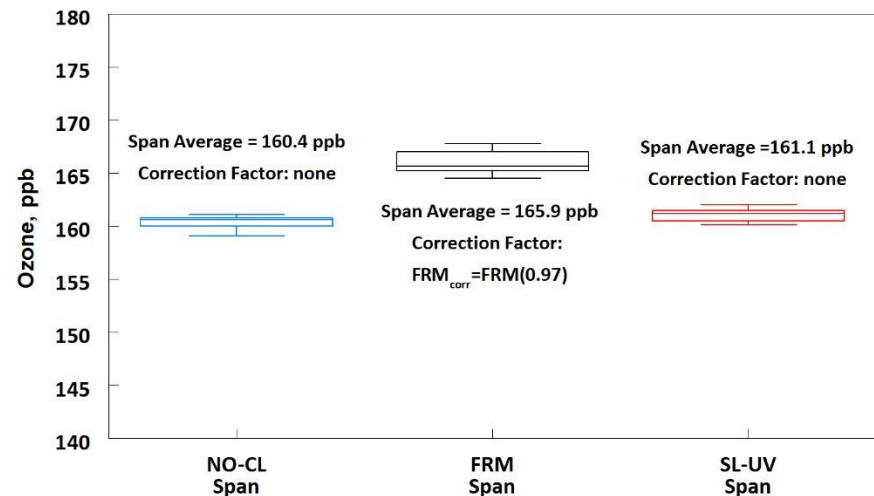
- No zero corrections required during the September 2013 study period.

04 – 28 Sept 2013 – LaPorte/Houston Nightly Spans (160 ppb)

September 4-15, 2013

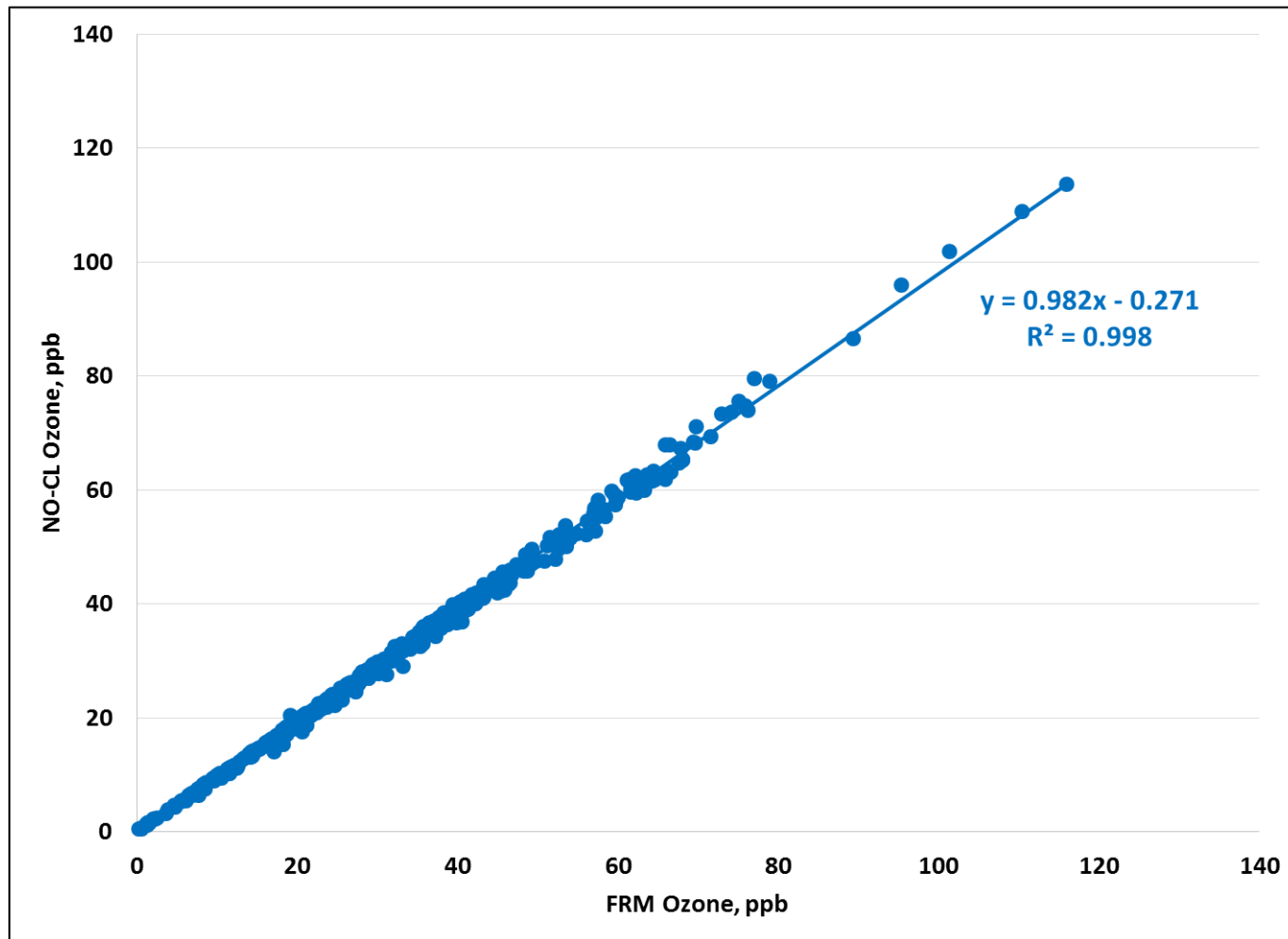


September 16-28, 2013



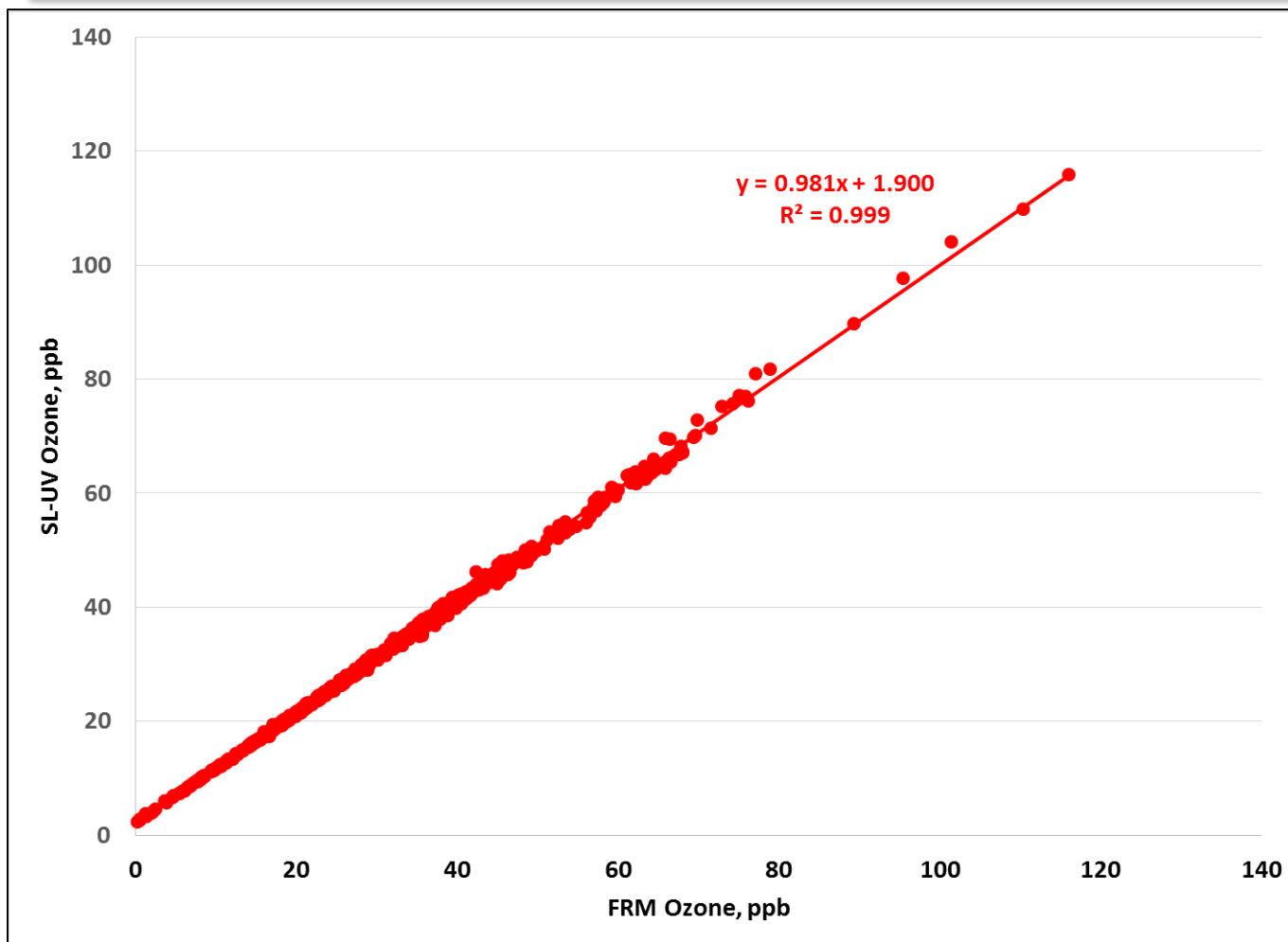
- During the Sept. 4-15 time period, data corrections made to both the NO-CL and FRM based upon results of nightly span checks. Very little variability observed in span check data resulting in the ability to generate a defensible correction factor.
- NO-CL analyzer was re-spanned on Sept 16, 2013
- During the Sept. 16-28 time period, data corrections made to only the FRM based upon results of nightly span checks. Again, very little variability observed in span check data resulting in the ability to generate a defensible correction factor.

04 – 28 Sept 2013 – LaPorte/Houston (1 hour) FRM vs. NO-CL



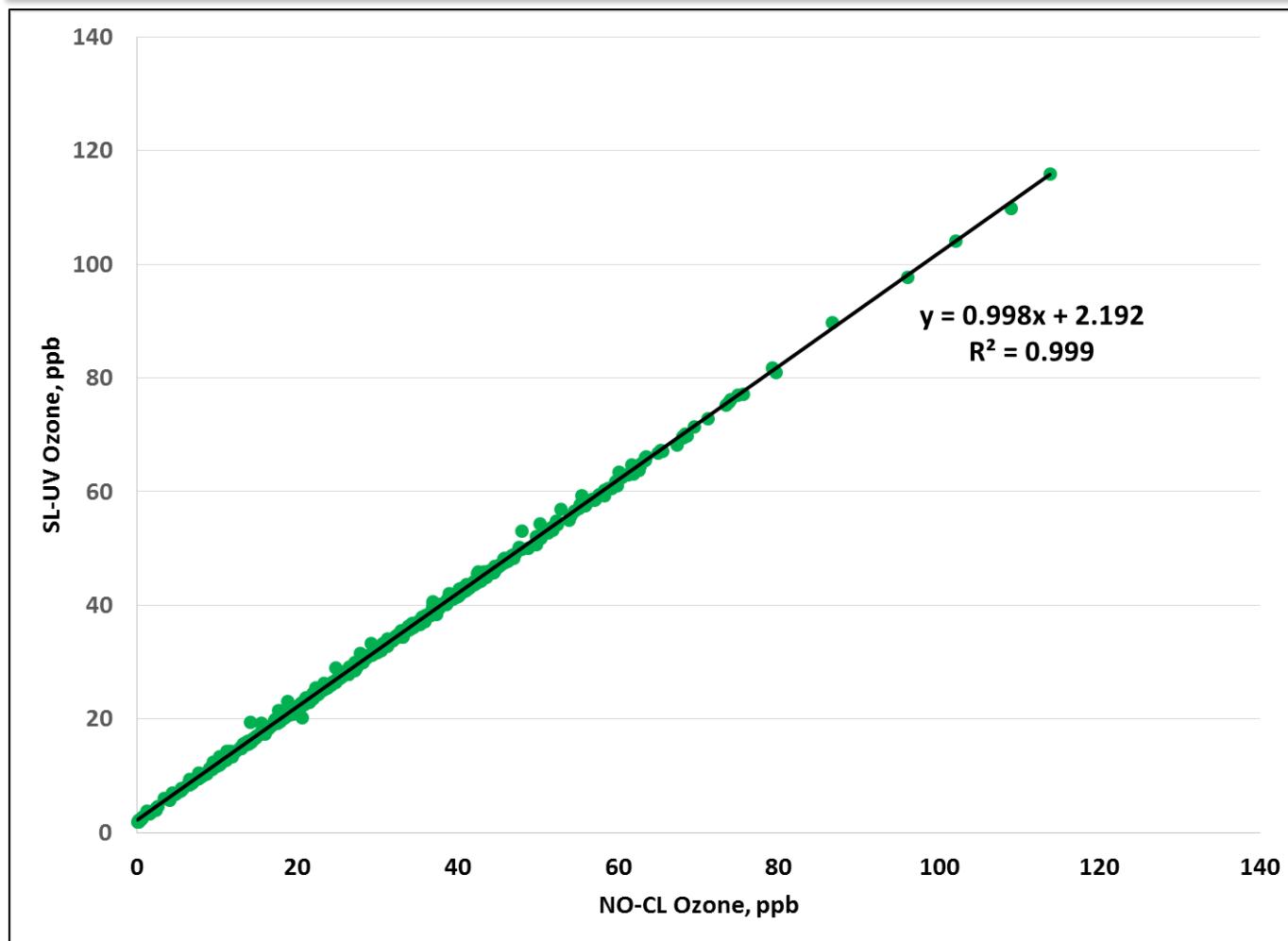
- Nightly Span check based data corrections to FRM (Sept. 4-28) and NO-CL (Sept. 4-15) data result in excellent agreement and correlation between the FRM and the NO-CL results.

04 – 28 Sept 2013 – LaPorte/Houston (1 hour) FRM vs. SL-UV



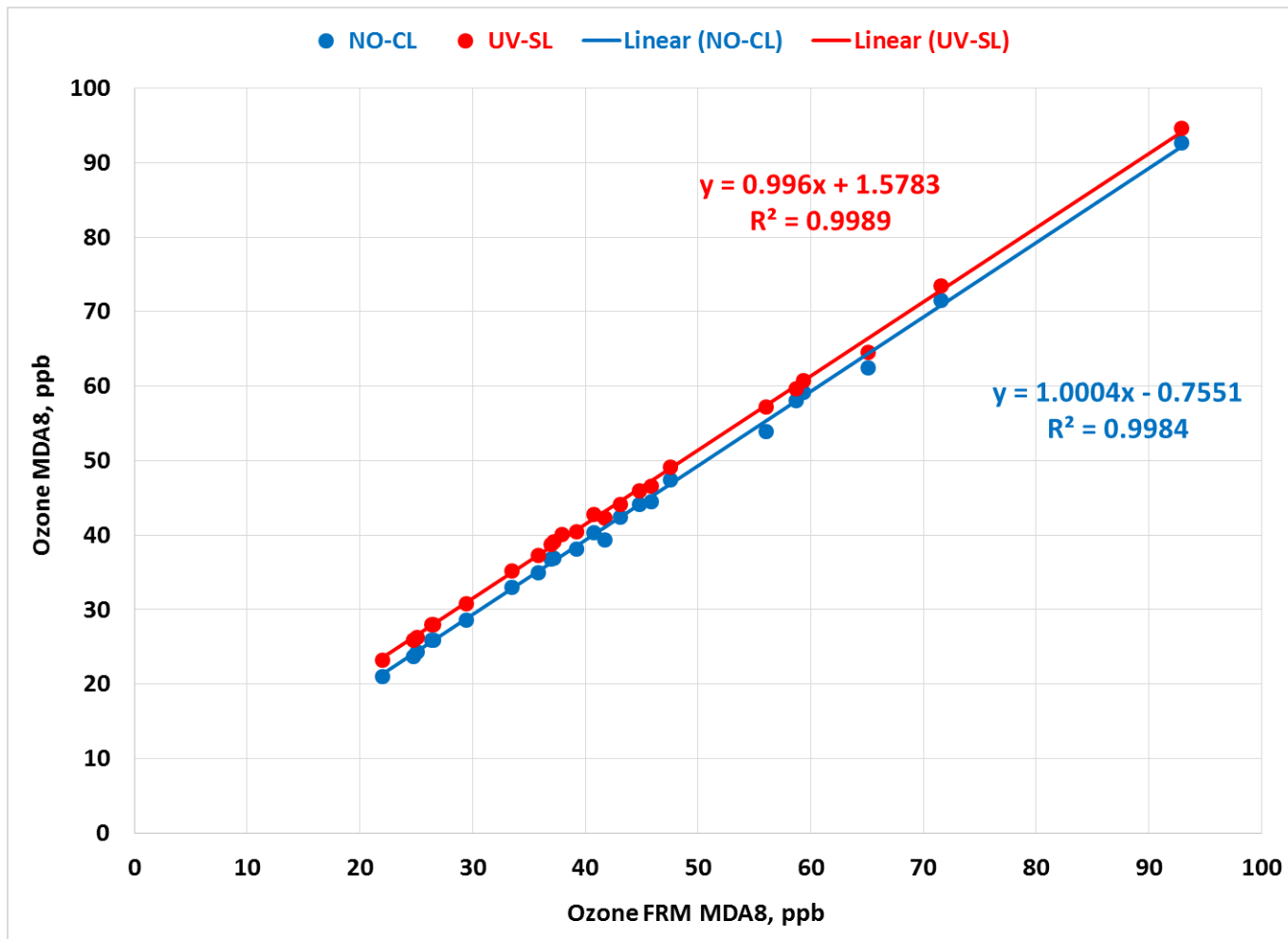
- Nightly Span check based data corrections to FRM (Sept. 4-28) and SL-UV data result in excellent agreement and correlation between the FRM and the SL-UV results.
- ~2 ppb offset observed in comparison of FRM and SL-UV. Offset cannot be explained by nightly zero and span check data (see slides 11-12).

04 – 28 Sept 2013 – LaPorte/Houston (1 hour): NO-CL vs. SL-UV



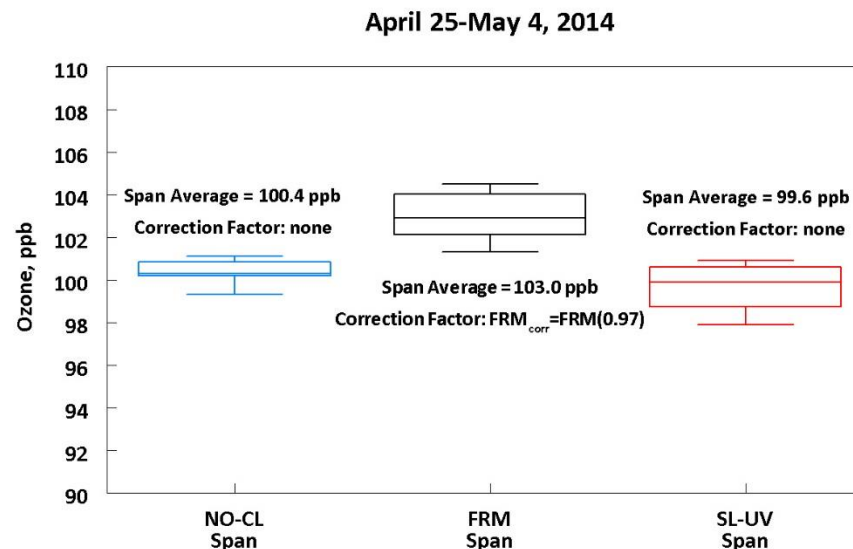
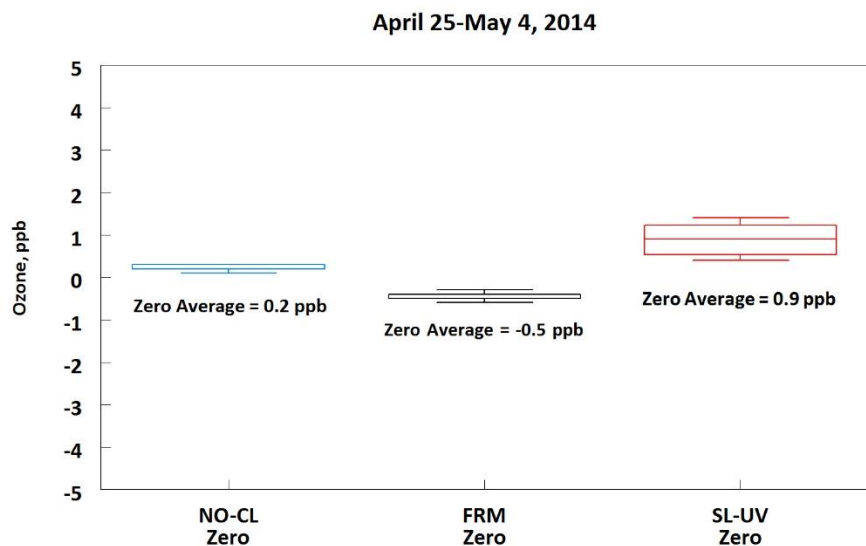
- Excellent agreement and correlation between the NO-CL(Span corrected Sept. 4-15) and the SL-UV results.
- As with the FRM vs. SL-UV comparison, the ~ 2 ppb offset is associated with the SL-UV results

4-28 September 2013 – LaPorte/Houston (MDA8) FRM vs. NO-CL and SL-UV



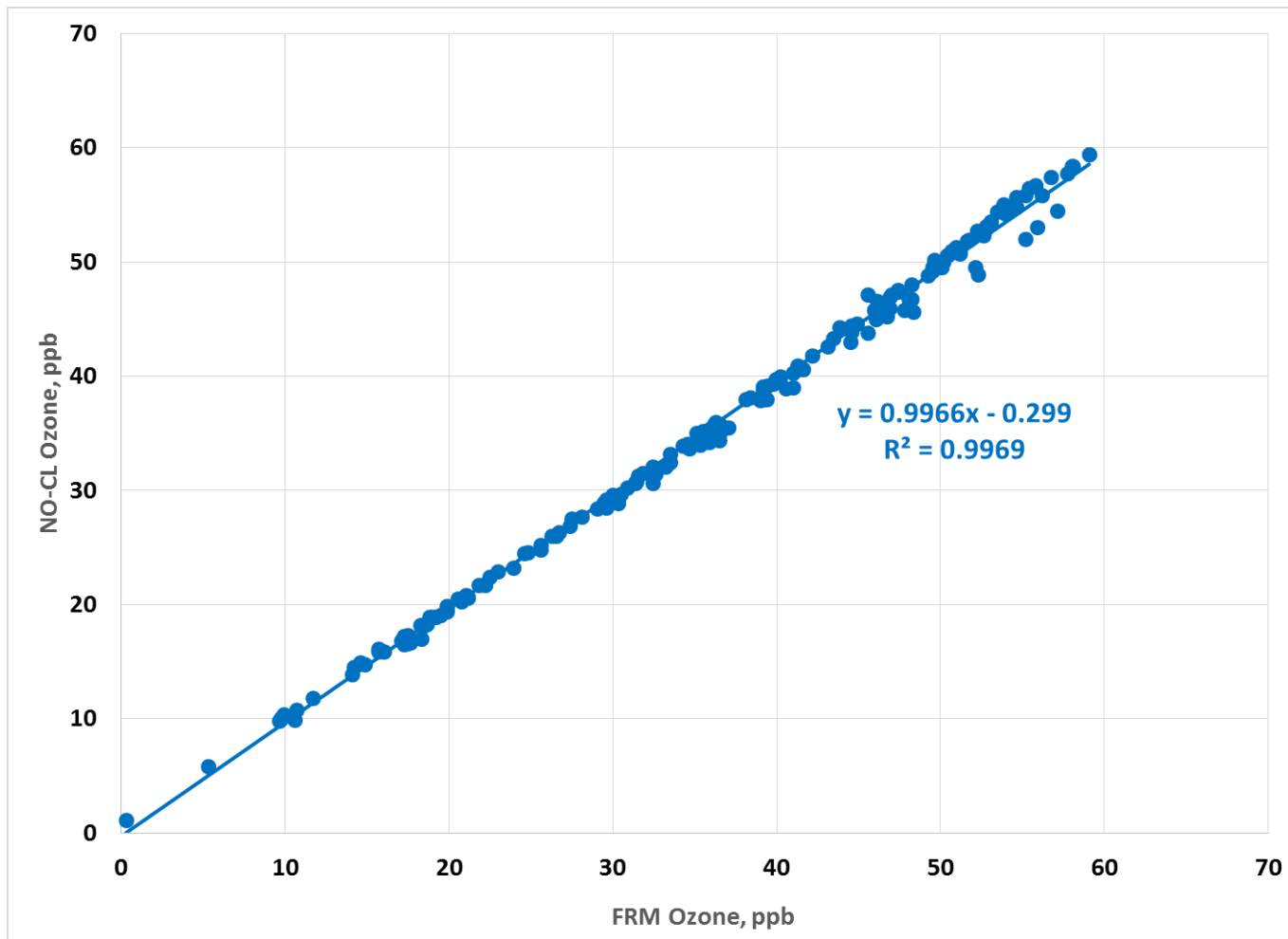
- Comparison of the maximum daily eight hour ozone averages (MDA8) for the September 2013 study period show excellent agreement.
- >95% of the MDA8 values for each individual method coincided during the same hour of the corresponding day

25 April – 4 May 2014 – RTP/AIRS Nightly Span (100 ppb) and Zero Results



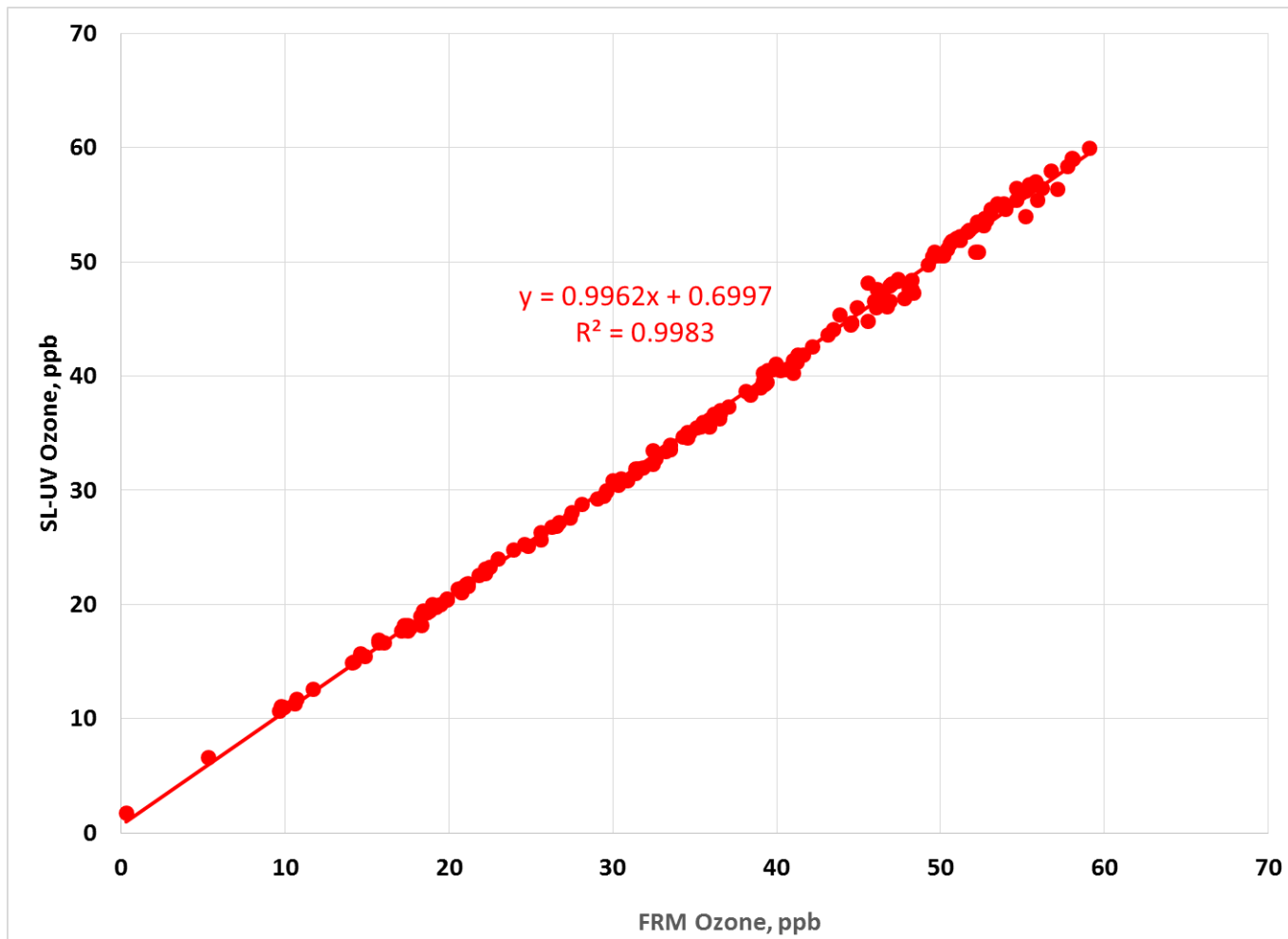
- No zero corrections required during the April 25-May 4, 2014 study period.
- During the April 25-May 4, 2014 study period, data corrections made to only the FRM based upon results of nightly span checks. Very little variability observed in span check data resulting in the ability to generate a defensible correction factor.

25 April – 4 May 2014 – RTP/AIRS (1 hour) FRM vs. NO-CL



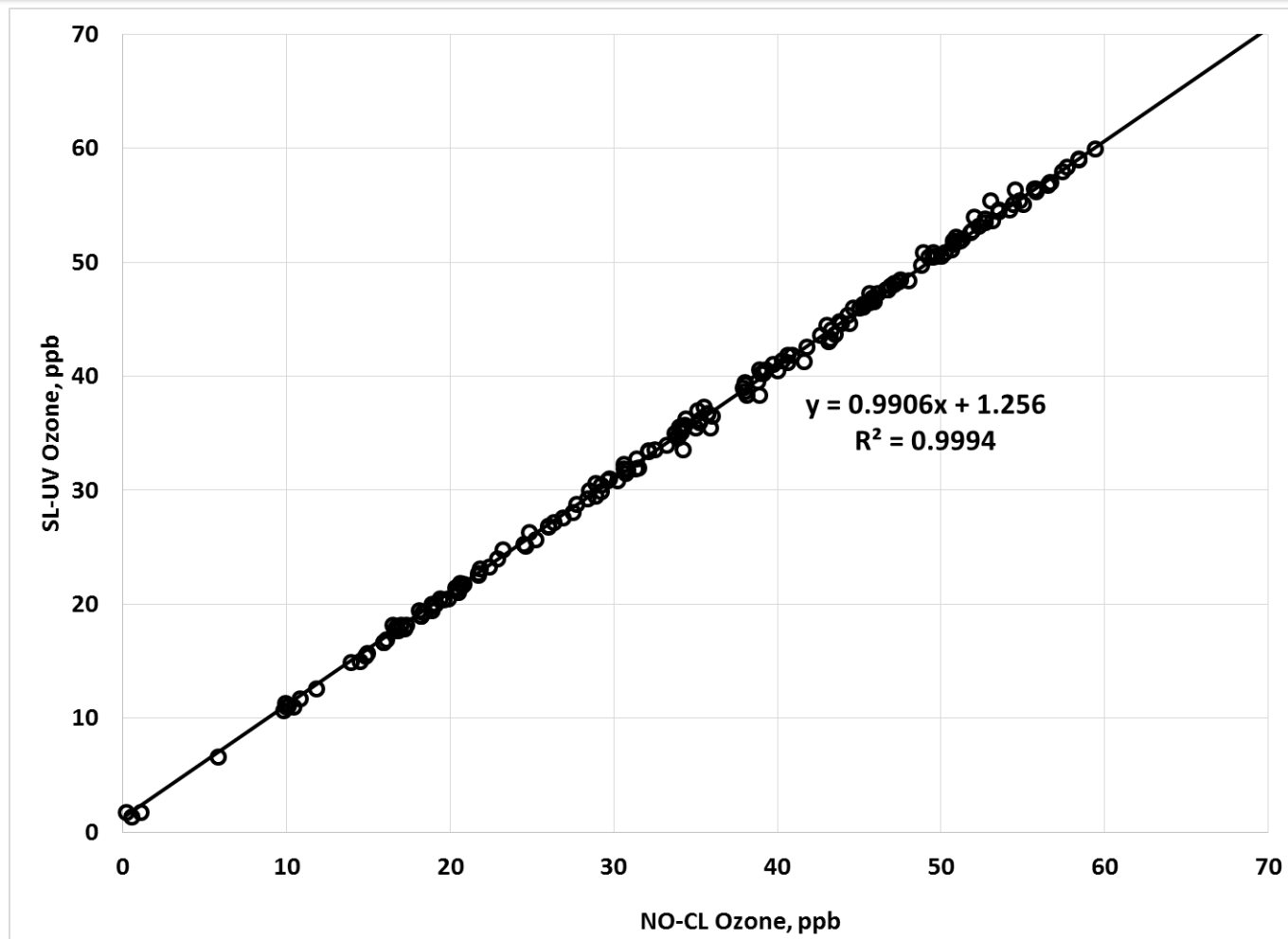
- Nightly Span check based data corrections to FRM (April 25-May 4) data result in excellent agreement and correlation between the FRM and the NO-CL results.

25 April – 4 May 2014 – RTP/AIRS (1 hour) FRM vs. SL-UV



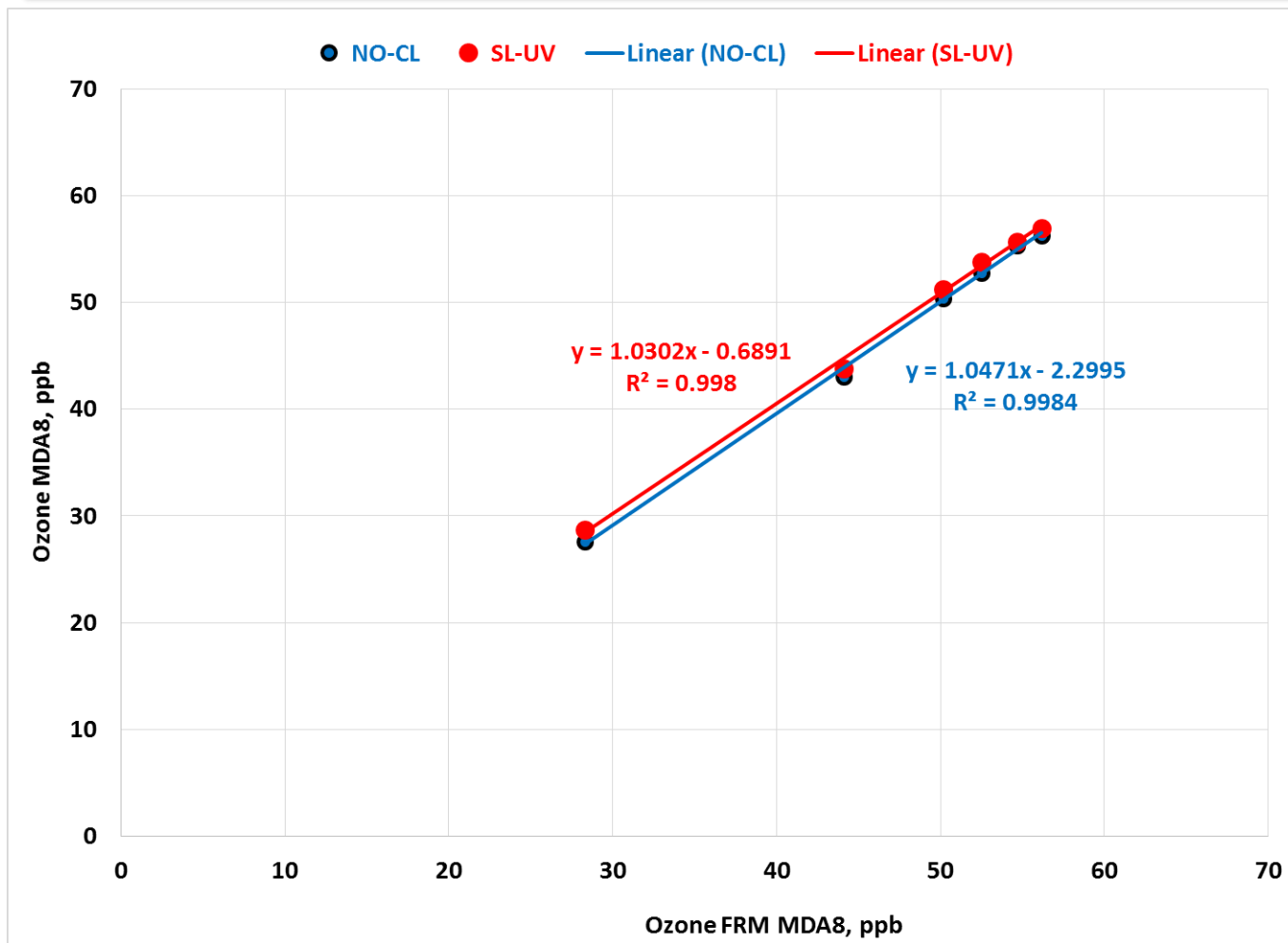
- Nightly Span check based data corrections to FRM (April 25-May 4) data result in excellent agreement and correlation between the FRM and the SL-UV results.

25 April – 4 May 2014 – RTP/AIRS (1 hour) NO-CL vs. SL-UV



- As with the LaPorte/Houston data set, excellent agreement and correlation observed between the NO-CL and the SL-UV results for the April 25-May 4 study period.

25 April – 4 May 2014 – RTP/AIRS (MDA8) FRM vs. NO-CL and SL-UV



- Comparison of the maximum daily eight hour ozone averages (MDA8) for the April 25-May 4, 2014 study period show excellent agreement.
- All of the MDA8 values for each individual method coincided during the same hour of the corresponding day

Implications and Conclusions

- Based upon the work that has been done to date and this subsequent data analysis, ORD is confident that the NO-CL method meets and exceeds all requirements for proposal of a new FRM for ozone.
- Due to judgment on recent litigation, the proposed rulemaking date for the ozone NAAQS review is now under the court ordered deadline of 1 December, 2014
- ORD plans to continue methods evaluation during the Denver 2014 field intensive study with emphasis being placed on both the NO-CL and SL-UV method per AMMS suggestions.
 - However, deadlines associated with the now court ordered proposal date for the ozone NAAQS review will not permit inclusion of the results of the Denver 2014 field evaluation campaign in the proposed rulemaking package.

Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.