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CORRIGENDUM

Corrigendum: Low NO_X and high organic compound emissions from oilfield pumpjack engines

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1. Introduction

After the publication of the article, we discovered two errors in our work. The first involved problems with the calculation of air–fuel equivalence ratios, and the second involved an error in the determination of carbonyl concentrations from analytical results.

2. Error in calculation of air—fuel equivalence ratios

When using the Brettschneider equation to calculate air–fuel equivalence ratios (Section 2.10 of the publication), we introduced an error in our code that effectively set hydrocarbon concentrations in the exhaust gas to near zero. This led to an overestimation of the equivalence ratio, and the amount of overestimation increased for higher equivalence ratios. **Figure C1** shows a comparison of the original and corrected Brettschneider-based equivalence ratios.

Air–fuel equivalence ratios are a measure of the amount of oxygen taken in by the engine relative to the minimum amount needed for complete combustion of the fuel. The Brettschneider equation, correctly applied, calculates the equivalence ratio by determining the ratio of oxygen atoms to carbon atoms in the exhaust, regardless of the nature of the carbon-containing molecules. Thus, even though it uses data from engine exhaust, it attempts to provide a representation of the chemical conditions at the engine intake.

An alternative, simplified means of calculating equivalence ratios that is commonly used is to divide the percent oxygen in ambient air by the difference between ambient oxygen and oxygen in the exhaust. **Figure C2** shows that our original, incorrect equivalence ratios compare well to equivalence ratios calculated by this method. This method would accurately determine the equivalence ratio only in cases of complete combustion since it fails to account for fuel that is introduced to the engine, but that isn't fully combusted. For typical engines, uncombusted fuel is a small enough percentage of total exhausted carbon. The

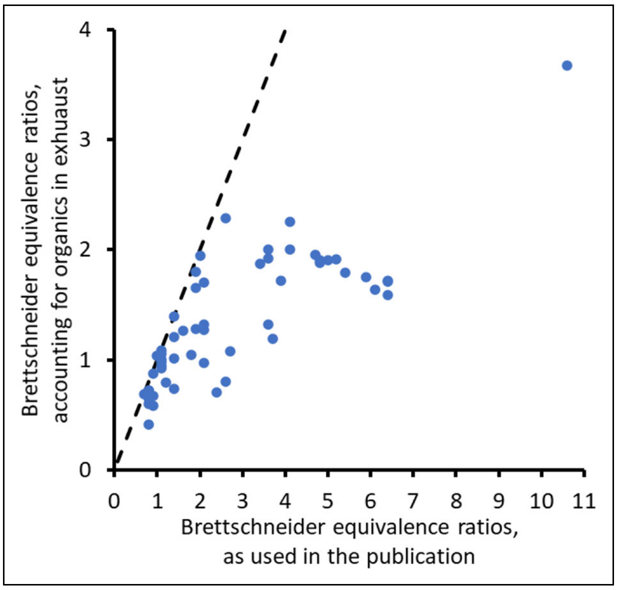

Figure C1. Corrected equivalence ratios calculated from the Brettschneider equation, compared the original values in the publication.

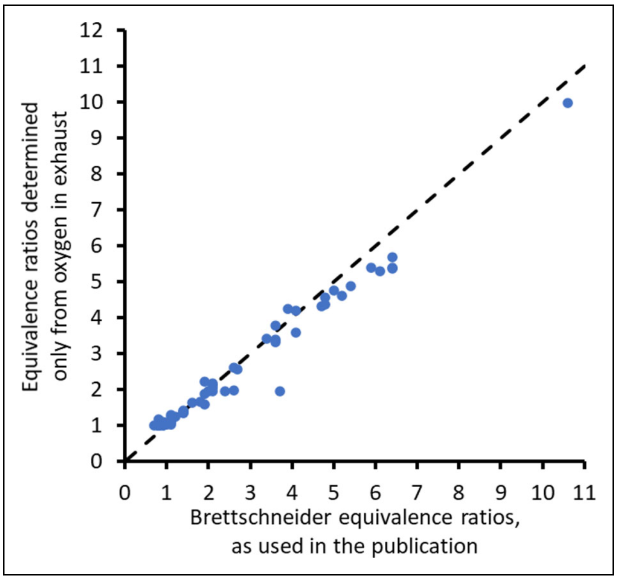

Figure C2. Equivalence ratios calculated only from O_2 in exhaust versus the original equivalence ratios used in the publication.

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difference between this method and a correct application of the Brettschneider equation can be expected to be small, but for the inefficient engines measured in this study, the difference is large.

The purpose of the air–fuel equivalence ratio calculation is to provide information about the chemical conditions present during combustion. For the inefficient 2-stroke engines examined in this work, however, the ratio of oxygen to carbon atoms in the exhaust is not likely to be representative of conditions during combustion. As discussed in the publication, fuel may have passed through the engines uncombusted because (1) the combustion temperature was too low for complete combustion, as evidenced by low NO_X in engine exhaust; (2) methane/natural gas fuel that is present in cooler recesses or edges of the combustion chamber can fail to be combusted; and (3) 2-stroke engines are prone to exhaustion of uncombusted fuel because fuel is introduced to the engine during the exhaust step, allowing it to pass through to the exhaust during this step, before any combustion has occurred.

Thus, the assumption in air–fuel equivalence ratio calculations that all fuel introduced to the engine has the potential to be involved in combustion reactions is likely invalid for these engines. A portion of the uncombusted fuel in the exhaust is likely not even present in the engine during the combustion step, and another portion, while it is present in the engine during combustion, is likely uninvolved. Figure 2 in the publication shows an average fuel slip of about 20%, even for the lowest equivalence ratios (i.e., the warmest combustion conditions). This may represent the minimum fuel slip these engines are able to achieve.

Correct application of the Brettschneider equation likely underestimates the effective air–fuel ratio during the combustion reaction in these engines, especially because of fuel that may pass through the engine during the exhaust step. On the other hand, ratios determined from the simplified equation that only takes O_2 measurements into account are probably an overestimate since they implicitly assume complete combustion.

The trends with equivalence ratio shown in the publication become weaker when the corrected Brettschneider results are used. **Figures C3** and **C4** show this by providing comparisons to original figures with figures that utilized corrected Brettschneider results.

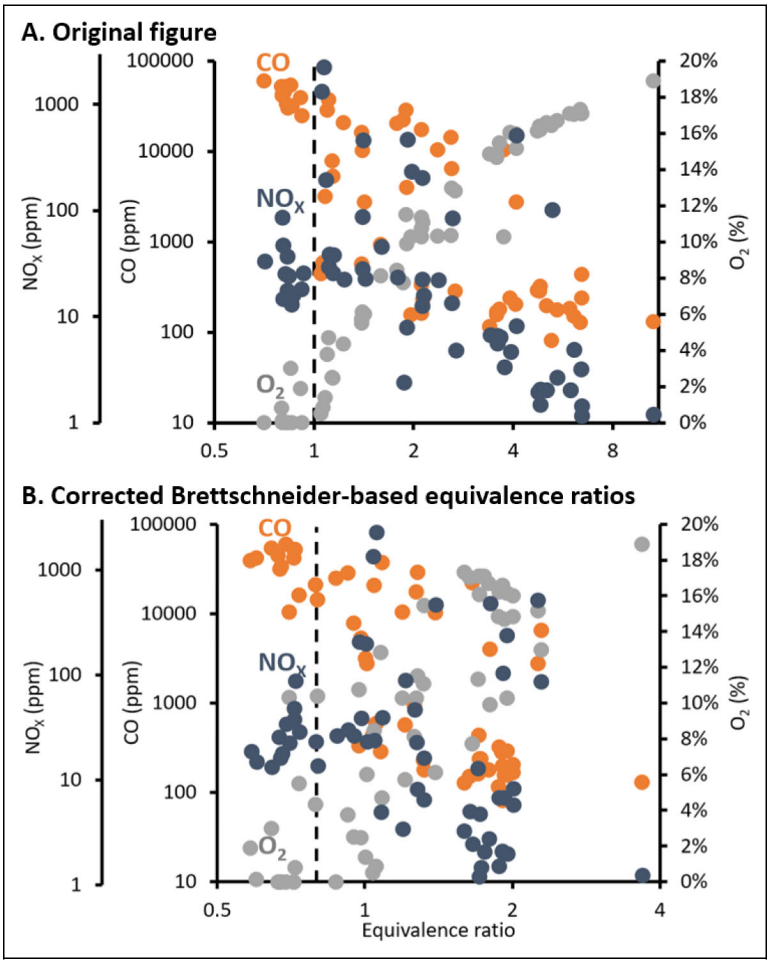

Figure C3. NO_X, CO, and O_2 versus equivalence ratio. The *x*-axis and *y*-axis for NO_X and CO are in log scale. The dashed line indicates an equivalence ratio of 1. Orange circles are CO, blue circles are NO_X, and gray circles are O_2. Panel A is the original Figure 1 from the publication. Panel B uses air–fuel equivalence ratios derived from a correct application of the Brettschneider equation.

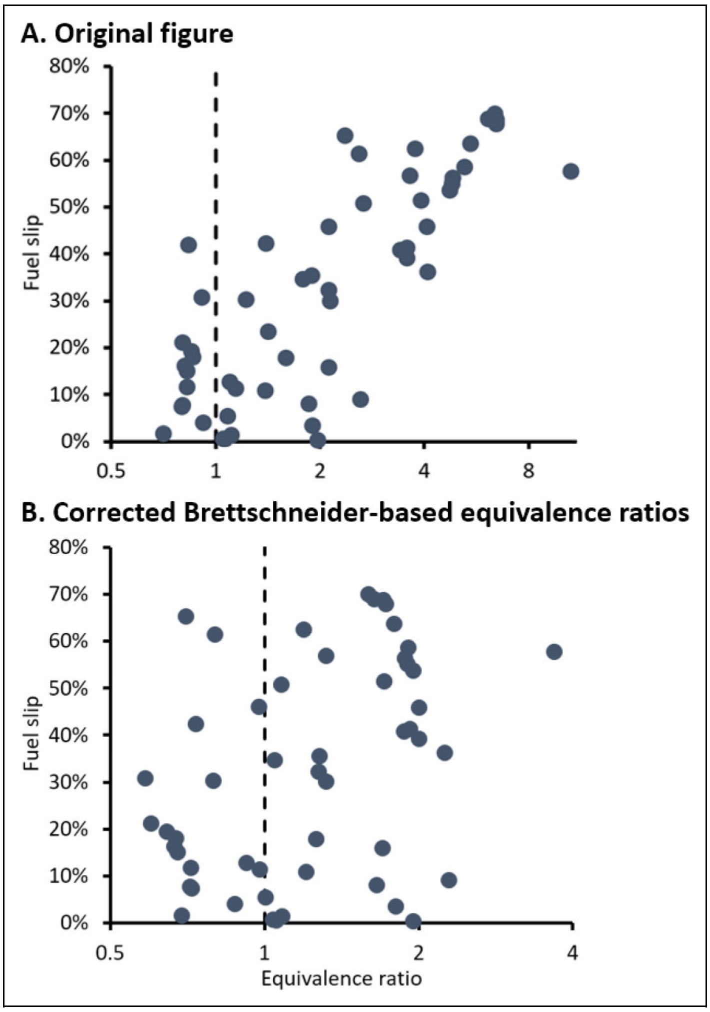

Figure C4. Fuel slip versus equivalence ratio. The *x*-axis is in log scale. The dashed line indicates an equivalence ratio of 1. Panel A is the original Figure 2 from the publication. Panel B uses air–fuel equivalence ratios derived from a correct application of the Brettschneider equation.

Table C1. Correction factor for each measured carbonyl (i.e., the fraction of total carbonyl-DNPH mass that was due to the carbonyl compound alone); we multiplied original carbonyl concentrations by these values to obtain corrected concentration results

Compound	**Correction Factor**
Formaldehyde	0.143
Acetaldehyde	0.197
Acetone	0.244
Acrolein	0.237
Propionaldehyde	0.244
Crotonaldehyde	0.280
2-Butanone	0.286
Methacrolein	0.280
N-Butyraldehyde	0.286
Benzaldehyde	0.371
Valeraldehyde	0.323
M-Tolualdehyde	0.400
Hexaldehyde	0.357

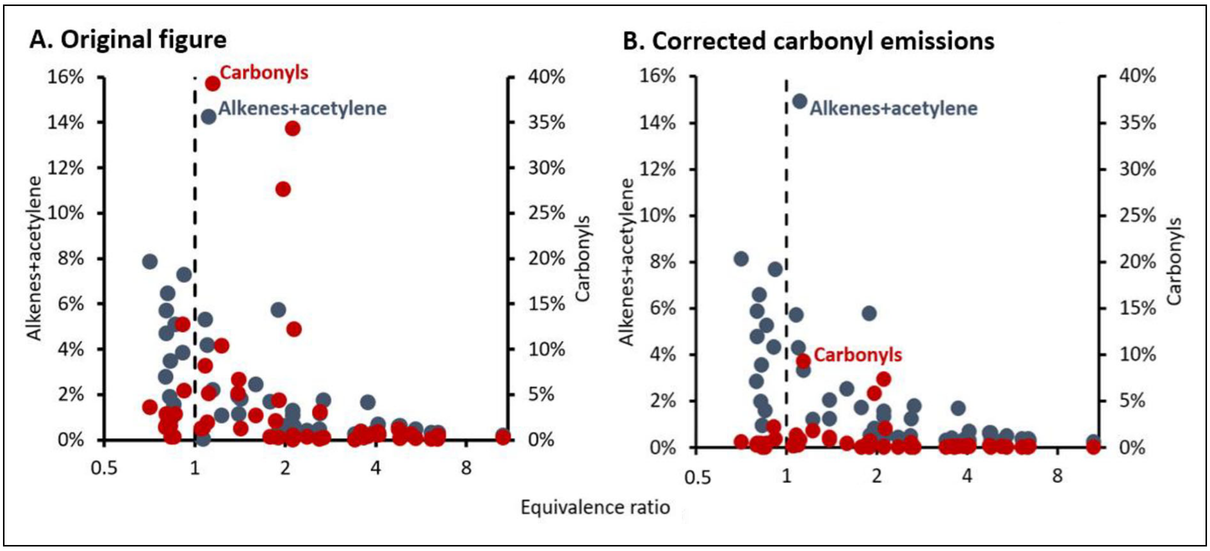

Figure C5. Percent by volume of alkenes + acetylene and carbonyls in total organic compounds in exhaust gas versus equivalence ratio. The *x*-axis is in log scale. The dashed line indicates an equivalence ratio of 1. Panel A is the original Figure 3 from the publication. Panel B is the same figure with corrected carbonyl emissions data.

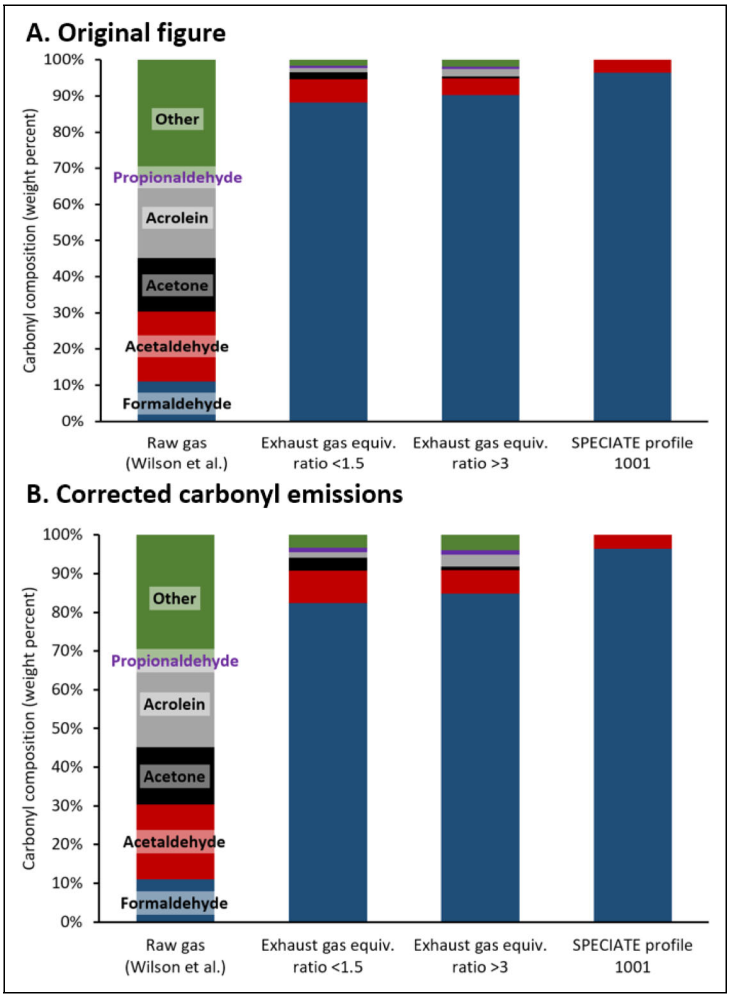

Figure C6. Average carbonyl composition of fuel and exhaust gases. SPECIATE profile 1001 is a composition profile for natural gas-fueled pumpjack engines in the EPA's SPECIATE database (EPA, 2020). Only measurements from 2-stroke engines are included. The leftmost bar shows carbonyls in raw natural gas in the Uinta Basin as determined by Wilson et al. (2020). Panel A is the original Figure S9 from the publication. Panel B is the same figure with corrected carbonyl emissions data. The two middle bars show the data collected in the current study.

In **Figure C4**, the relationship between equivalence ratio and fuel slip entirely disappears when corrected values are used. This may indicate that the equivalence ratios used in the publication provide a better indicator of combustion conditions than corrected Brettschneider results.

In summary, while we acknowledge our error, the corrected Brettschneider equivalence ratios are not an apparent better indicator than our original equivalence ratios of the actual oxygen-to-fuel ratio experienced by the engines during combustion. While uncertainty remains about how to properly determine equivalence ratios for these engines, we hope this discussion at least allows readers to better contextualize our results.

We changed the final dataset (https://doi.org/10.26078/H62D-3F89) to include equivalence ratios correctly calculated via Brettschneider. The corrected dataset also retains the original ratios, for which we have coined the term "effective equivalence ratio," meaning an equivalence ratio that ignores uncombusted fuel. We also added O_2-based equivalence ratios to the final dataset.

3. Error in determination of carbonyl emissions

We erroneously included the dinitrophenylhydrazine mass with carbonyl mass in our HPLC calibration curves, leading to overestimates of carbonyl concentrations and emission rates.

We corrected carbonyl values in the final dataset (https://doi.org/10.26078/H62D-3F89). **Table C1** shows the correction factors we used for each compound.

This error led to an approximate 2.5–7 times overestimate of the emissions of carbonyl compounds in the publication. To show the difference between original and corrected carbonyl data, original and revised versions of Figure 3 from the publication are shown as **Figure C5**.

Correction of carbonyl data resulted in a small change to carbonyl speciation in emissions. **Figure C6** illustrates this by showing the original and corrected versions of Figure S9 from the Supplemental Material.

Correction of carbonyl data also led to less of a difference between measured and inventoried carbonyls, as shown in **Figure C7**.

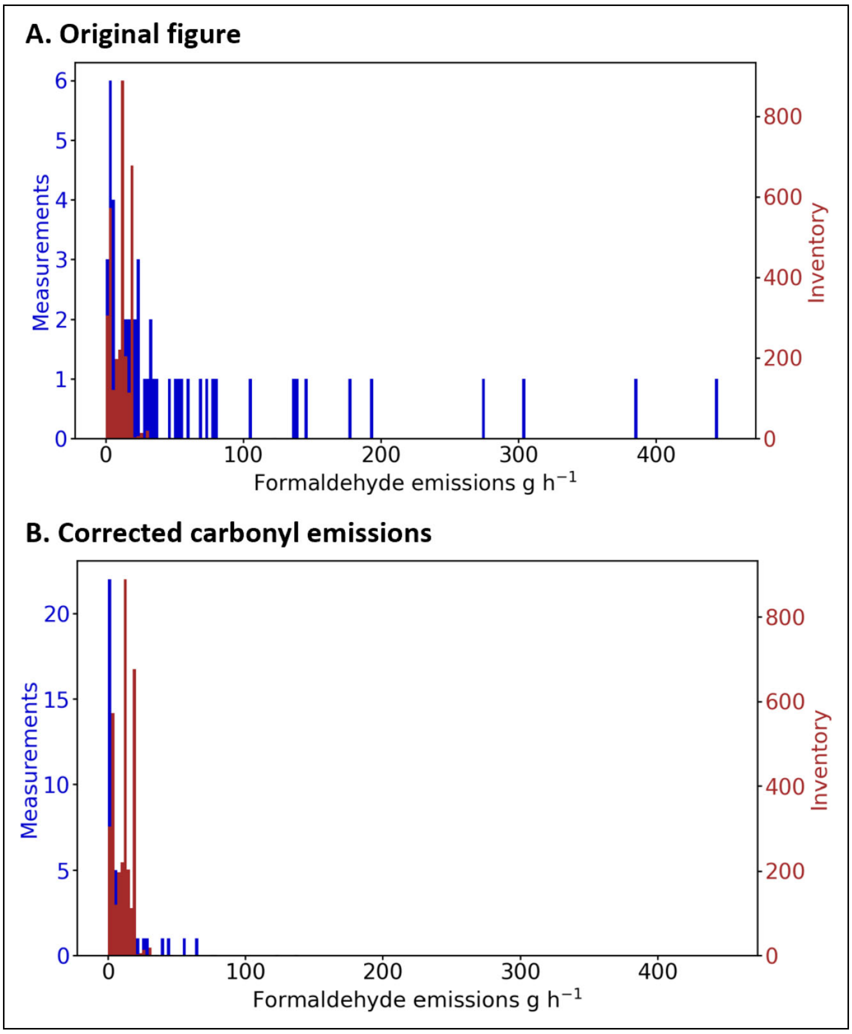

Figure C7. Histogram of measured and inventoried formaldehyde emissions from natural gas-fueled engines. *Y*-axes show the frequency of occurrence for each emission rate bin. Panel A is the original Figure S12 from the publication. Panel B is the same figure with corrected carbonyl emissions data.

The error in carbonyl emissions did not impact our quality assurance tests of carbonyl recovery since the tests were a comparison of carbonyl recovery through our sampling system against recovery directly from the calibration source, so the error would have applied equally to both measurements.

The error impacted total nonmethane organics emissions as reported in the published paper. The average percent of total nonmethane organics comprised of carbonyls changed from 15% to 4%, reducing the average total nonmethane organics emissions from engines in the study from 784 g h^{-1} to 708 g h^{-1}.