Reply to "Basis for Comparisons of Soil CO$_2$ Respiration Test Procedures"

Jason Warren,* Hailin Zhang, Shiping Deng, Eric McGowen, and Sumit Sharma

THIS LETTER is provided in response to a letter (Brinton and Vallotton, 2018) regarding our recent publication (McGowen et al., 2018). We welcome the constructive discussion to advance laboratory methods for assessing soil health indicators. This is why we shared soil samples from our work with Dr. Brinton's team in hopes of extending efforts to better understand the relationships between CO$_2$ burst methods and the experimental conditions that influence the observed differences. It is expected that different laboratory methods seldom yield the same absolute values but are often correlated with one another. Our goal was to contribute to the science and in-depth understanding for method standardization in soil health assessment.

Our conclusion of lower labor requirement for the GC method was based mainly on the time required washing dishes for the methods. For each analysis, the GC method uses a gas vial with a crimp top closure and gray butyl septa. The closure and septa are discarded, leaving only the vial to be washed. The components needed for one analysis using the Solvita (Woods End Laboratories) method include a jar, a rubber gasket, a lid, and a plastic beaker. The washing of these components combined with manual reading of the Solvita paddle contributes to considerable labor requirement. We agree with Dr. Brinton that the Solvita method could run >60 samples per day as permitted by the GC setup, providing that labor and incubation chambers are not limited. However, the XYZ sampler could be programmed to inject water into the vials, allowing the GC to run continuously with precise incubation times after water introduction.

Regarding the correlation between the two methods, the slope between the two methods presented in McGowen et al. (2018) was low, but the r^2 was 0.90 for the linear range of the Solvita method. Additionally, the r^2 for the curvilinear relationship between the Solvita color number and the GC CO$_2$ burst was 0.92 when all data were used. We agree with Dr. Brinton's team that the low slope is probably the result of differences in headspace volumes and soil sample sizes used in the measurements. We believe that sensitivity analysis is needed to better understand how these two experimental conditions affect emissions per gram of soil. However, in McGowen et al. (2018), we did not attempt to dilute the headspace in the Solvita method as our preliminary experiments using soils within the linear range of the Solvita method did not result in values that were proportional to the Solvita values generated without dilution. In other words, we could not simply use a dilution factor of two when we used half the soil of the original method and arrive at the same value. Therefore, we are currently evaluating the impact of sample size and chamber volume for both the GC method as well as the hydroxide trap method to further understanding.

The data provided by Dr. Brinton and his team show clearly that the paddles used for the Solvita method are accurate in providing a measurement of headspace CO$_2$ concentrations based on the relationships between the other CO$_2$ analytical methods presented in their letter. The data also show the discrepancy between the Solvita values as measured in our laboratory and the current method they used. In fact, the data provided in Brinton and Vallotton (2018) comparing the OKSU-SOL (Oklahoma State University data, Solvita)

J. Warren, J. Zhang, S. Deng, and E. McGowen, Dep. of Plant and Soil Sciences, Oklahoma State Univ., 368 Agricultural Hall, Stillwater, OK 74078; S. Sharma, Oklahoma Panhandle Research and Extension Center, Rt. 1, Box 8-6M, Oklahoma State Univ., Goodwell, OK-73939.

*Corresponding author (jason.warren@okstate.edu).

Abbreviations: GC, gas chromatography.

Table 1. The average CO_2 burst measured from tilled and no-tilled soils at four drying temperatures with the Solvita and gas chromatography (GC) methods.

	Solvita CO_2–C				GC CO_2–C			
	25°C	45°C	65°C	105°C	25°C	45°C	65°C	105°C
	—————————————————————— mg kg^{-1} ——————————————————————							
Till	53	84	119	21	7	12	24	2
No-till	125	150	162	39	22	36	50	10

and WE-SOL (Woods End Laboratory data, Solvita) analysis with linear regression has a slope of 2.29. Similarly, the slope between the OKSU-SOL and WE-CZ (Woods End Laboratory data, COZIR infrared cell) was 1.99. These slopes indicate that when we used the smaller 200-mL jar sold by Woods End Laboratory, we generated values that were approximately twice those generated in the 475-mL jar now used for the Solvita method. This discrepancy warrants the need, as mentioned earlier, to conduct a comprehensive sensitivity analysis of CO_2 burst methods with respect to chamber size but does not discount the potential of using micro-chambers as used in the GC method.

Regarding the calibration of the GC, we reviewed the raw CO_2 data prior to conversion to the CO_2 burst values and found that 5 out of the 72 samples analyzed were above the 40,000 μL L^{-1} standard. This would be a limitation to the methodology described in McGowen et al. (2018).

We agree that a sensitivity analysis with respect to the headspace volume of 0.015 L is warranted. We measured the volume of the samples after they were placed into the vials and found that the average density was 0.96 g cm^{-3} and ranged from 0.8 to 1.14 g cm^{-3}. As a result, the average water-filled pore space was approximately 40%. We did not vary the water applied based on bulk density but agree that a sensitivity analysis would ensure reproducible data for meaningful interpretation.

Dr. Brinton and his team correctly point out that we used paired samples from nine locations of cultivated and their native grass or no-till counterparts across Oklahoma. Comparison of the two field conditions was not presented in McGowen et al. (2018) due to space limitation. However, the data do allow for the assessment of soil management differences. As shown in Table 1, the absolute values of CO_2 burst from the GC method is well below those measured by the Solvita method. The relative differences between the soil management practices were detected by both methods. On average (excluding data obtained at 105°C), we found that the CO_2 burst in the no-till soils were 1.7 times higher than those of tilled soils by the Solvita method. The CO_2 burst for the no-till soils was 2.5 times the cultivated soils based on data obtained by the GC method. These results suggest that GC method, although it yielded lower values of CO_2 burst, was more sensitive than the Solvita method in detecting differences resulting from management practices

Method comparison and validation are crucial initial steps in advancing soil health assessments. We appreciate Dr. Brinton and his team for their interest in our research. I agree that we must work toward sound methodologies for soil health indicators that are highly reproducible and robust to differentiate treatment differences in soil management for meaningful comparison and interpretation. Although the GC method produced values that are lower than Solvita method, the GC method did generate data that differentiate soil management history, and with a greater linear range than the original Solvita method as provided to us at purchase. We will continue the effort to better understand the impact of chamber size, soil mass, incubation temperature, and timing on the GC method as it lends itself to automation. Again, we appreciate Dr. Brinton and Mr. Vallotton's insightful comments and suggestions.

References

Brinton, W.F., and J. Vallotton. 2018. Basis for comparisons of soil CO_2 respiration test procedures. Agric. Environ. Lett. doi:10.2134/ael2018.11.0064

McGowen, E.B., S. Sharma, S. Deng, H. Zhang, and J.G. Warren. 2018. An automated laboratory method for measuring CO_2 emissions from soils. Agric. Environ. Lett. 3:180008. doi:10.2134/ael2018.02.0008