CO_2 Flux Measurement Using Soda Lime: Correction for Water Formed during CO_2 Adsorption

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CO$_2$ FLUX MEASUREMENT USING SODA LIME: CORRECTION FOR WATER FORMED DURING CO$_2$ ADSORPTION

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Abstract. Terrestrial carbon budgets and models of ecosystem carbon cycling rely on accurate field measurements of CO$_2$ release from soils. Despite limitations of accuracy that require the use of a calibration curve, the soda-lime technique has distinct advantages that have resulted in its continued use for in situ measurements of soil respiration. In this note I report an error in the correction factor used to account for water formed during chemical adsorption of CO$_2$ by soda lime. The appropriate correction factor (1.69 in place of 1.41) implies that all previously reported CO$_2$ fluxes using the soda-lime method should by increased by 20%. Recent global estimates of soil CO$_2$ release have relied largely on soda-lime data and will require reevaluation in the light of this correction.

Key words: CO$_2$ flux measurements; soda lime; soil respiration.

Carbon dioxide release from soil is an indicator of microbial and root activity and as such is an essential component of terrestrial carbon budgets and models of ecosystem carbon cycling. The soda-lime technique has been used extensively for >30 yr to measure CO$_2$ fluxes from soil under field conditions (e.g., Monteith et al. 1964). Inaccuracies with the method arise because the CO$_2$ adsorption rate of soda lime is rarely in equilibrium with the efflux rates being measured. The use of a calibration curve (see below) is necessary to compensate for this error. Despite this limitation, soda lime has distinct advantages for making field estimates of CO$_2$ fluxes: (1) it can readily provide single integrated measures over a daily time scale and thus incorporate the effects of diurnal fluctuations in abiotic variables that control CO$_2$ release; (2) it is robust and economical, making it more appropriate for the large numbers of replicate field measurements necessary to account for the enormous spatial heterogeneity associated with soil surface CO$_2$ effluxes (Cropper et al. 1985, Raich et al. 1990, Rochette et al. 1991). For these reasons, the soda-lime technique is likely to continue to have applications for in situ field measurements of soil respiration. Protocols for its use are described in most major soils methods texts (e.g., Soil Science Society of America: Anderson 1982, Zibilske 1994). Furthermore, the technique has been used to report soil respiration fluxes in at least 12 studies in major ecological journals since 1988.

Soda lime is a variable mixture of sodium and calcium hydroxides that reacts with CO$_2$ to form carbonates. The amount of CO$_2$ adsorbed by soda lime exposed beneath

an inverted chamber placed over the soil surface is proportional to the increase in soda-lime dry mass during the sampling period. In recent years, many researchers have preferred to use a "dynamic" method in which the rate of change in CO$_2$ concentration of air circulated through an inverted chamber is measured using an infrared gas analyzer (IRGA). Laboratory studies with known fluxes and simulated soil surfaces (e.g., Nay et al. 1994) have demonstrated that better accuracy is achieved with the dynamic approach because the soda-lime adsorption rate is rarely at equilibrium with the flux being measured. At flux rates reported as $\leq$1.6 g CO$_2$-C·m^{-2}·d^{-1}, Nay et al. demonstrated that soda lime overestimated fluxes. Under such conditions, adsorption of CO$_2$ by soda lime lowered headspace concentrations below ambient thus enhancing the flux diffusion gradient. By contrast, underestimation occurred at a flux rate of 5.0 g CO$_2$-C·m^{-2}·d^{-1}. At this value, CO$_2$ concentrations in the headspace greatly exceeded ambient levels, suggesting that soda-lime adsorption efficiency became progressively more limiting as flux rates increased. In the field, an extensive field comparison of soda lime and IRGA methods (Ewel et al. 1987) found that underestimation occurred at values >1.4 g CO$_2$-C·m^{-2}·d^{-1} (see Fig. 1). Almost identical logarithmic regression equations relating results from the two techniques have now been derived independently (Ewel et al. 1987, Haynes and Gower 1995) that allow correction for underestimation by soda lime at high fluxes. The following discussion outlines an inherent error in the method used to calculate soda-lime fluxes that modifies the slope of the soda lime/IRGA relationship.

Edwards (1982) conducted a review of the soda-lime method in which guidelines for determining the appropriate exposed surface area and quantity of soda lime were
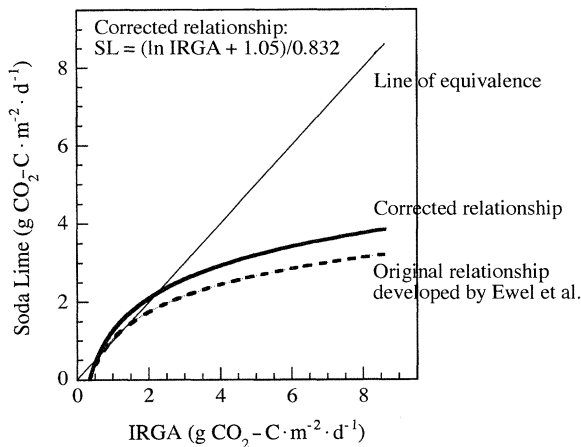
FIG. 1. Relationship between CO_2 efflux rates as measured by infrared gas analyzer (IRGA) and soda-lime methods. (Adapted from Ewel et al. 1987:327: Fig. 3.)

described. Soda-lime adsorption efficiency was tested over extended exposures and shown to decline once the initial mass had increased by 7%. Attention was also drawn to the fact that a correction factor is required to account for water that is formed when soda lime reacts with CO_2:

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$
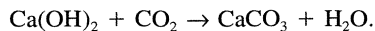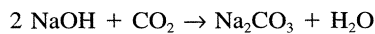
For every mole of CO_2 that is chemically bound to soda lime, a mole of water is formed that is subsequently evaporated during drying. Thus, the increase in dry mass measured before and after exposure underestimates CO_2 absorbed by a factor of 18/44 or 40.9%. Edwards (1982) proposed that a correction factor of 1.41 should be applied to the measured mass difference in order to calculate the actual mass of CO_2 absorbed. In fact, Tesarova and Gloser (1976) had previously reached the same conclusion. However, this conclusion is in error because underestimation by 40.9% implies that the measured mass difference is 59.1% (100 − 40.9) of the true mass of CO_2 absorbed. The appropriate correction factor to be applied to the measured mass difference in order to calculate the true mass of CO_2 absorbed is 1.69 (i.e., 100/59.1).

For example, 1 mole of CO_2 (44 g) reacts with 74 g of $Ca(OH)_2$ to form 100 g $CaCO_3$ and 18 g H_2O in a balanced $CaCO_3$ reaction. The measured increase in soda-lime mass after oven-drying is 26 g (i.e., 100 − 74). Thus a correction factor of 44/26 (i.e., 1.69) should be applied to the measured mass difference to calculate the true mass of CO_2 absorbed. Edwards' 1982 paper includes empirical data on known additions of CO_2 to soda lime that support his conclusion. However, he did not include blanks to control for CO_2 adsorption during the final oven-drying phase in his experiment. CO_2 uptake during drying can

be substantial, and accounts for 5–40% of the total sample mass increase (P. Grogan, *unpublished data*). In the absence of adjustment for blanks, overestimation of CO_2 adsorbed most likely occurred. This omission would have resulted in artificially low computed values for the correction factor due to water formation.

To my knowledge, Edwards' review guidelines have been adopted by all subsequent studies using soda lime. The appropriate correction factor of 1.69 (in place of 1.41) implies that reported fluxes using the soda-lime method and Edwards (1982) protocol are in error and should be increased by 20%. Interpretation of past data sets that used soda lime will obviously be influenced by this correction. Furthermore, this correction modifies the regression equation derived by Ewel et al. (1987) to adjust soda-lime data to equivalent IRGA values (Fig. 1). Finally, integration of data sets using both techniques to generate global patterns of CO_2 emission for modeling purposes (Raich and Potter 1995, Raich and Nadelhoffer 1989) is likely to be significantly affected by this correction.

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