

Prediction of pH Errors in Soil-water Extractors Due to Degassing¹

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ABSTRACT

Moisture samples taken from the unsaturated zone with soil water extractors undergo degassing and an upward shift in pH. The measured pH values from commercially available extractors are usually sufficiently in error that they cannot be used in a quantitative manner. A model has been developed that predicts the extent of CO₂ degassing and the resulting pH error. Using this model measured pH values can be corrected back to in situ soil water pH provided that precipitation has not occurred in the extractor. Extractors are classified into two groups—single chamber and multichambered. The extractors are evaluated for both operation under constant vacuum (open to the source) and decreasing vacuum (evacuated and then sealed). Analysis of the data and model predictions indicates that the major factor controlling the pH error is the ratio of liquid volume to total extractor volume. Additional factors exerting major influence are the initial extractor gas composition and the total pressure in the extractor when sampled. Variations in soil solution composition and differences in soil CO₂ concentrations in carbonate buffered systems had a major effect on pH values but a negligible effect on the extractor induced pH error. Under typical field conditions the multichambered extractor is predicted to give the most satisfactory results; the pH errors were sufficiently small that no corrections for degassing were necessary.

Additional Index Words: suction lysimeter, tension lysimeter, ceramic cup, soil moisture, unsaturated zone, carbon dioxide, sampler.

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VACUUM EXTRACTORS are commonly used to obtain soil solution samples from the unsaturated zone. They are easy to use and mostly sample water

in the larger pores. Thus the solution samples obtained relate better to solute fluxes than solution extracts taken from soil cores. However, vacuum extractors can extract water only under relatively wet conditions and do not represent average soil water compositions. From the study by Hansen and Harris (1975) it can be concluded that a constant vacuum is preferable in order to minimize the variation in pore sizes sampled. Errors caused by the ion exchange capacity of the extractor are well documented for ceramic (Grover and Lamborn, 1970) and can be minimized by the use of teflon. Available extractors with teflon tips, however, have low bubbling pressures and thus cannot be evacuated to low pressures.

An additional problem is that soil solutions buffered by carbonate chemistry undergo an upward shift in pH when collected by extractors. This pH shift is due to CO₂ loss from solution during sample collection. When vacuum is applied to an extractor, the partial pressure of CO₂ in the extractor is reduced proportionately to the reduction in total pressure. As soil water enters the extractor, the solution degasses and CO₂ is released. The loss of dissolved H₂CO₃ causes an increase in pH as well as potential precipitation of carbonates, phosphates, and oxides in the extractor. Accurate pH measurements are especially necessary when the data are used to determine potential mineralogical controls on solution compositions or when trace species such as heavy metals or phosphate are being measured. Suarez (1986) described the design of a multichambered extractor that reduces the pH error by flushing the sampling chamber with solution and minimizing the relative air volume in the extractor.

This study contains an evaluation of the factors contributing to the discrepancy between the pH inside extractors and the pH of the soil water. Additionally, the predicted pH effects are compared with measure-

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ments taken with a multichambered extractor under controlled conditions.

DESCRIPTION OF THE MODEL AND EXPERIMENTAL PROCEDURES

A computer program was written to predict the pH shift due to degassing of CO₂ from solution. The program uses the gas law ($PV = nRT$), k_{Hj} values for O₂, N₂ (Handbook of Chemistry and Physics, 1957), and CO₂ (Harned and Davis, 1943) and a solution chemistry subroutine containing the carbonic acid dissociation constants and ion pairs given in Suarez (1977). The model inputs are soil P_{CO₂}, soil solution composition, initial P_{CO₂} in the extractor, extractor configuration, and initial vacuum applied. The model simulates an extractor by allowing discrete increments of liquid to enter the extractor.

For extractors that are closed to the vacuum source, the partial pressure of each gas is initially increased proportionately to the decrease in gas volume for each added increment of liquid. The concentrations of dissolved O₂, N₂, and CO₂ are recalculated to account for mixing of each new liquid increment with the existing solution in the sampler. After each mixing the gas and liquid are equilibrated using the following relationships

$$P_y = P_{yi} + (Aq_{yi} - P_{yi} \cdot K_{Hy}) \cdot (R \cdot T \cdot VL/VA) / [1 + (R \cdot T \cdot K_{Hy} \cdot VL/VA)]$$

$$Aq_y = Aq_{yi} - (Aq_{yi} - P_{yi} \cdot K_{Hy}) / [1 + (R \cdot T \cdot K_{Hy} \cdot VL/VA)]$$

where P_y is the equilibrium partial pressure of gas y , P_{yi} is the partial pressure of gas y after mixing, Aq_{yi} is the concentration of dissolved gas y in moles L⁻¹ after mixing, K_{Hy} is the Henry's Law constant for gas y , R is the universal gas constant (0.812 L·Pa·mole⁻¹·deg⁻¹), T is the temperature in degrees Kelvin, VL/VA is the ratio of the liquid to gas volume, and Aq_y is the equilibrium concentration of the dissolved gas. For CO₂ the K , and Aq values correspond to the sum of dissolved CO₂ and H₂CO₃. The solution pH is then calculated using the solution composition, calculated P_{CO₂} and an ion speciation subroutine. After accounting for C mass and the recomputed Aq values, the program cycles until P_y , P_y , and pH convergence is achieved.

For extractors open to the vacuum, the total pressure is fixed by the vacuum source. Upon addition of solution, the mixed solution is allowed to degas until gas-liquid equilibrium is attained and the calculated total pressure equals the total pressure specified. The excess gas leaves the sample chamber and flows to the reservoir connected to the vacuum. After the sample chamber fills, any subsequent solution increment is assumed to displace an equal volume of liquid out of the sampler. The simulation does not consider chemical precipitation. The relationship between pH errors (due to degassing) and extractor design, soil solution composition, soil CO₂ partial pressure (P_{CO₂}), and the ratio liquid/total volume in the extractor, were investigated with the model, with all calculations at 25°C.

Extractors can be either single or multichambered and either connected to the vacuum source (constant vacuum) or closed off from the vacuum source (decreasing vacuum). Multichambered extractors were evaluated by placing them in a container filled with Ca²⁺, Na⁺, Cl⁻, HCO₃⁻ solutions at 25°C and bubbling them with a CO₂-air mixture.

The single chamber extractor is similar to a commercially available extractor but smaller. After evacuation, the sampler is isolated from the vacuum source and allowed to partially fill. Samples are taken by pressurizing the unit and collecting solution from the tube extending to the sampler tip.

The new multichambered extractor consists of ceramic which is glued to a 50-mm long PVC tube and connected to a 10-mL closed pyrex container with 1 mm i.d. tubing. Tubing extends from the container cap to a solution reservoir which is in turn connected to a constant vacuum source. Samples are obtained by removing, replacing, and immediately capping the 10-mL sampling container (see Suarez, 1986 for construction details).

RESULTS AND DISCUSSION

Single Chamber Extractors

For a single chamber extractor that has been evacuated and then sealed, the extent of the pH shift depends primarily on the relative quantities of liquid and gas in the extractor. The solid line in Fig. 1 shows the pH error predicted for an extractor initially filled with air, then pumped down to a total pressure of 5.05 kPa (0.05 atm), and sealed. If the soil matric potential, or pressure head, is between 0 and -101 kPa, the extractor fills until the total pressure inside the extractor equals 101 kPa + the pressure head. For this simulation the soil CO₂ pressure is 1.01 kPa (0.01 atm), and the soil water contains 2 mmol_c L⁻¹ alkalinity. The calculated pH error (Δ pH) is the pH of the solution in the extractor minus the pH of the soil solution.

As the extractor fills the pH error follows the solid line in Fig. 1. The extractor should fill with water if the water content of the soil is at saturation and sufficient time is allowed after the vacuum is applied. Under these conditions and assuming that any precipitated material redissolves, the final pH error approaches zero, as shown by the solid line in Fig. 1.

If the soil water pressure head is <0 (unsaturated conditions) the extractor cannot fill completely and at equilibrium a partial vacuum (with pressure equal to 101 kPa + soil water pressure head) remains in the extractor. Within a few days of an irrigation or major rainfall event the soil pressure head will commonly decrease to field capacity or -10 to -30 kPa (-0.1 to -0.3 atm). Under field conditions, extractors commonly fill until they are 10 to 80% water filled. This

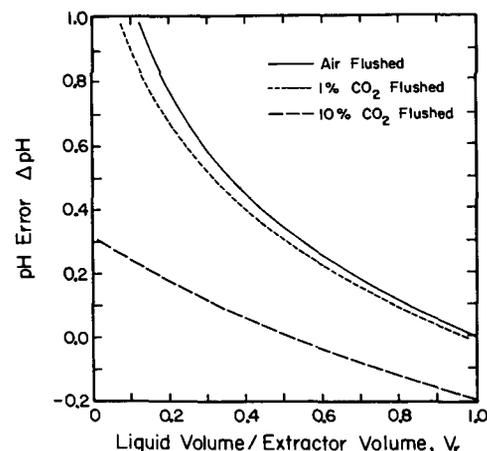


Fig. 1. The pH error (extractor pH-soil moisture pH) as a function of liquid to extractor volume for single chamber extractors which were evacuated and then sealed. The solid line represents an extractor flushed with air and then evacuated. The dotted and dashed lines represent extractors flushed with 1 and 10% CO₂, respectively, then evacuated and sealed.

range corresponds to a large and variable pH error of 1.06 to 0.11 pH units (Fig. 1, solid line). Since the pH error is dependent on the extent to which the extractor fills, the error is greatest when only a small amount of water enters the extractor. The extractor is not likely to fill to the extent expected due to the decreased pressure gradient around the extractor as it fills and the reduced hydraulic conductivity of the adjacent soil as the water content is reduced.

Differences in the initial gas composition in the extractor also affect the magnitude of the pH error. The dashed and dotted lines in Fig. 1 represent extractors initially flushed with a 1.0% and 10.0% CO₂-air mixture respectively, evacuated to total pressures of 5.05 kPa (0.05 atm) and then closed off from the vacuum source. Initial flushing of the extractor with a gas having comparable or higher CO₂ content than the soil air, substantially reduces the pH error. Under these conditions the pH error also changes less with changing liquid volume in the extractor. In these simulations, use of 100% CO₂ gas to flush the extractor results in large decreases in the pH of the water in the extractor. The Δ pH values range from -0.70 to -0.83 as the extractor fills (data not shown).

The disadvantages of flushing extractors with a high CO₂ content gas are that the pH error is now dependent on the initial vacuum applied, in addition to the liquid to gas ratio in the extractor. The pH error of an extractor that initially contains air and is then evacuated is not dependent on the initial total pressure if the same liquid volume to extractor volume ratio is achieved. This result is shown in Fig. 2, where the uppermost line represents the superimposed pH errors for extractors evacuated to total pressures of 2.02, 5.05, 10.1, and 20.2 kPa. While the Δ pH values superimpose on the same line, this result does not mean that the pH error is the same. The pH error is predicted using Fig. 2, but the extractors fill to different liquid volume to total extractor volume ratios. In contrast to these results, an extractor initially filled with an air-CO₂ mixture and then evacuated, has different pH er-

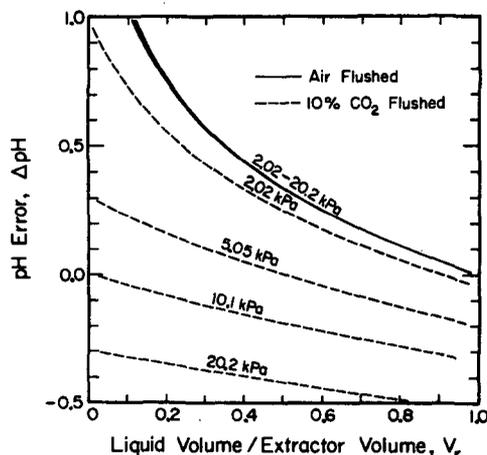


Fig. 2. The pH error as a function of liquid volume to extractor volume for single chamber extractors. The uppermost solid line represents predicted values for an air filled extractor evacuated to 2.02, 5.05, 10.1, and 20.2 kPa and then sealed. The dashed lines represent predictions for an extractor filled with a 10% CO₂-air mixture, evacuated to total pressures of 2.02, 5.05, 10.1, and 20.2 kPa and then sealed.

rors even at the same liquid to extractor volume ratio, depending on the vacuum applied. The dashed lines in Fig. 2 represent the pH errors of an extractor flushed with a 10% CO₂-air mixture and then evacuated to total pressures of 2.02, 5.05, 10.1, and 20.2 kPa respectively. Note that the pH error cannot be estimated by merely measuring the extent to which the extractor filled. One must now also know the initial gas composition and the initial pressure (i.e., vacuum applied). In addition, an air-filled extractor evacuated to high vacuum can fill and produce essentially no pH error, if the soil pressure head is near zero. This is not true for extractors flushed with CO₂ and then evacuated. The dashed lines in Fig. 2 indicate that the maximum potential liquid volume in the extractor increases with increasing vacuum.

The pH errors for solutions of different soil CO₂ concentrations and/or different solution compositions are nearly identical to those shown in Fig. 1 (data not shown). Although solutions of high pH and alkalinity are better buffered and undergo less change in proton activity, the Δ pH values are comparable to those for lower pH and alkalinity. From these calculations, it is concluded that the pH error of a single chamber extractor initially filled with air, then evacuated (to any pressure) and sealed, can be determined by using the solid line in Fig. 1. We need only know the ratio of solution volume to total extractor volume. If the extractor is flushed with a CO₂-air mixture, the total pressure in the extractor when it is sealed must also be known. This information is rarely available.

The pH errors associated with a single chamber extractor operated at constant vacuum are the same as those for multichambered extractors having liquid/sampling chamber volumes ≤ 1.0 , as discussed below.

Multichambered Extractors

Multichambered extractors are also subject to degassing and pH errors. It was assumed that a small amount of air (5% of the sampling chamber volume) remains trapped in the sampler after it fills and liquid is spilled into the larger reservoir.

Figure 3 shows the calculated pH errors (solid lines) for a multichambered extractor flushed with air (0.033% CO₂) and then connected to a vacuum source operated at various pressures. The lines represent extractor pH errors associated with a soil P_{CO₂} of 1.01 kPa (0.01 atm) and a soil solution containing 2 mmol_c L⁻¹ alkalinity. Liquid to total volume ratios >0.95 indicate that water is flowing out of the sampling chamber and into the reservoir. Large pH errors are evident as the extractor initially fills. After several volumes of liquid have flushed through the sample chamber, the Δ pH stabilizes at 0.01 for an extractor operated at 50.5 kPa. The entrapped air of the sample chamber becomes enriched in CO₂ because of the greater total quantity of dissolved CO₂ as compared to O₂ and N₂. Most of the pressure loss is thus N₂ and O₂. After five volumes have flushed the sample chamber, the pH errors for 2.02 kPa (0.02 atm), 10.1 kPa (0.1 atm), and 20.2 kPa (0.2 atm) are 0.35, 0.17 and 0.04 pH units, respectively (Fig. 3).

The multichambered extractor design with a small sampling chamber and operating at 20 kPa total pres-

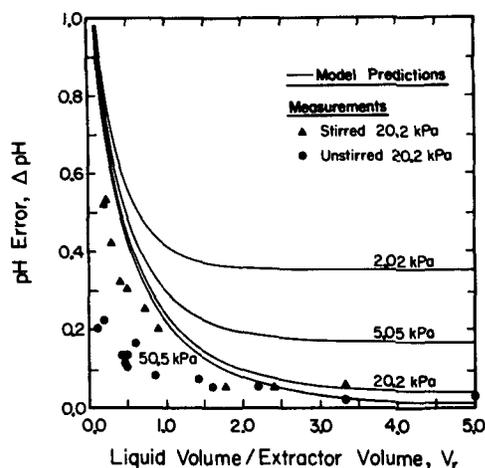


Fig. 3. Relationship between pH error and liquid volume to extractor volume for multichambered extractors connected to a vacuum source with a total pressure of 2.02, 5.05, 20.2, and 50.5 kPa. The triangles represent measurements made on a stirred sampling chamber; the closed circles represent measurements from an unstirred sampling chamber. Volume ratios >0.95 indicate overflow of the extractor solution into a solution reservoir.

sure or greater, provides an accurate soil solution pH and composition while minimizing the potential for precipitation. The calculations for Fig. 3 and 4 assume a well mixed solution in equilibrium with the gas in the chamber. This assumption is not correct when the extractor fills rapidly. Measured ΔpH values from an extractor filling rapidly (10 mL/h), operated at 20.2 kPa and unstirred are shown in Fig. 3 (closed circles). The pH errors measured are smaller than those predicted by the model. The triangles represent ΔpH values measured under the same conditions except that the sampling chamber was placed on a temperature-controlled magnetic stirrer. Values from stirred chambers fall considerably closer to the predicted curve than do the values from the unstirred system. It is likely that a moisture sampler placed in the soil will extract water sufficiently slowly for conditions to resemble those of the well-mixed system.

The portion of the curves shown in Fig. 3 where the liquid volume to extractor volume ratio is <1 can also be used to predict the pH errors of a single chamber extractor under constant vacuum. Under these conditions the pH errors are quite variable, and depend on the extent of filling of the extractor or sampling chamber. More importantly, the pH errors for the single chamber extractor are much larger when the extractor is left connected to the vacuum than when it is evacuated and then sealed. This result can be observed by comparing the solid line in Fig. 1 with any of the lines in Fig. 3 (for liquid volume to extractor volume ratios <1).

The initial gas composition in the multichambered extractor has a large effect on the initial pH error. After several volumes of water pass the sampling chamber the effect is negligible. The ΔpH values for

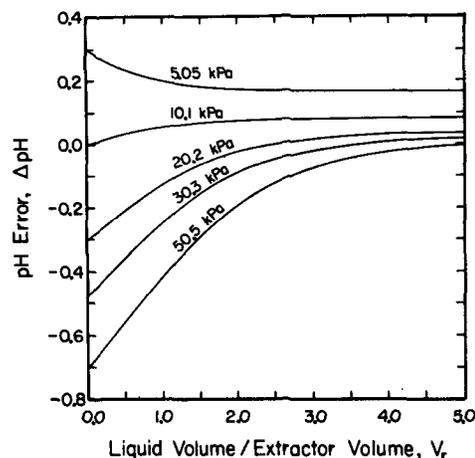


Fig. 4. The pH errors associated with a multichambered extractor initially filled with a 10% CO_2 -air mixture and then operated at a total pressure of 5.05, 10.1, 20.2, 30.3, and 50.5 kPa.

different volumes of water and an initial gas composition of 10% CO_2 and total extractor pressures of 5.05 kPa to 50.5 kPa are shown in Fig. 4. The final pH errors are comparable to those shown in Fig. 3 for the same total operating pressure. Changes in soil CO_2 pressure and alkalinity have only minor effects on pH errors.

Additional calculations using different volumes of entrapped air indicate that even an air volume of 10 to 20% in the sample chamber does not substantially affect ΔpH values after several volumes of liquid pass through the chamber.

The results given for the predicted pH errors for multichambered extractors can be considered as "worst case" conditions. Assuming a piston flow model, which may be reasonable for a narrow sampling container, the ΔpH values approach the equilibrium values at smaller liquid volume to extractor volume ratios. Final pH errors can also be reduced by closing off the reservoir chamber from the vacuum pump. This produces lower final pressures which are desirable, but it also causes water to be extracted from different pore sizes as the extractor fills.

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