

## COMMENTS & LETTERS TO THE EDITOR

### Letter to the Editor on “From the Earth’s Critical Zone to Mars Exploration: Can Soil Science Enter Its Golden Age?”

Soil science research is undergoing significant changes, driven by new societal priorities, emerging technologies, and a better understanding of natural systems and anthropogenic impacts. Recent publication of a special issue of *Science* on “Soils—The Final Frontier” (11 June 2004) and two other special issues on the remarkable success of Mars Exploratory Rover mission—“*Spirit at Gusev Crater*” (6 Aug. 2004) and “*Opportunity at Meridiani Planum*” (3 Dec. 2004)—were timely and encouraging. However, as Sugden et al. (2004) pointed out—over 500 yr after Leonardo Da Vinci—the ground beneath our feet is still as alien as a distant planet. I therefore wish to express some perspectives on the future of soil science in this letter, and would like to call on the public to embrace soil science in the broadest sense and to urge fellow soil scientists to unite as a community to address “big” science questions.

While best known for its role in providing water and nutrients to sustain agriculture and ecosystems, the soil indeed plays diverse critical roles in sustaining life, the environment, and society. Thus, an inclusive vision for integrative soil science should encompass “7 + 1” roles from the earth’s critical zone to extraterrestrial explorations, as portrayed in Fig. 1. I believe it is time to embrace soil science as a science in the broadest sense and to move beyond current fragmentation. Soil is a natural integrator of the “7 + 1” functions, providing a central link to multiscale interdisciplinary integration for studying the earth’s critical zone.

The earth’s critical zone concept (Nation Research Council [NRC], 2001a) provides an appealing framework for integrated studies of soil with water, air, rock, and biotic resources in the earth’s surface and near-surface environments. Interactions at these interfaces between the solid earth and its fluid envelopes determine the availability of nearly every life-sustaining resource (NRC, 2001a). Hence, the National Research Council has identified the integrated studies of the earth’s critical zone as one of the most compelling research areas in the 21st century. Moreover, I believe knowledge of the soil and its forming processes pose unique contributions to extraterrestrial explorations in search of water and life and for developing advanced life support systems used in space exploration. Although some might argue that Martian soils (and other planetary surface materials) may not be called “soils” because biological processes have not yet been confirmed, early stages of soil formation and subsurface pedogenesis do not always require a biological factor (e.g., Ugolini and Edmonds, 1983). As the amazing *Spirit* and *Opportunity* are continuing the exciting exploration for signs of water on Mars through investigations on soils, rocks, and landforms, answers to the fundamental question of how the weathering engine on Mars has transformed the protolith into various soils would likely shed light on the role of water (and other soil-forming factors such as climate) in the genesis of Martian soils.

Historically, soil science has followed a circuitous path in its evolution from a discipline with roots in geology, to an applied agricultural and environmental discipline, and now to a bio- and geoscience with a focus on the earth’s critical zone (Wilding and Lin, 2005). This closes the loop, but along the way soil science has become more extensive and comprehensive. I

believe soil science can enter its golden age through vigorous integration of its expertise with other bio- and geosciences. Such integration will significantly increase public understanding as well as advance soil science.

For example, synergies can be generated if soil science is adequately integrated into the science and infrastructure initiatives of the Consortium of Universities for the Advancement of Hydrologic Sciences, Inc. (CUAHSI), a NSF-sponsored and community-based organization. A number of recent NRC reports have already highlighted the significance of integrated soil and water studies in the context of agriculture (NRC, 1993a, 1997), groundwater vulnerability (NRC, 1993b), watershed management (NRC, 1999), earth sciences (NRC, 2001a), water resources (NRC, 2001b), and environmental sciences (NRC, 2001c). It is worth mentioning that all of the eight Grand Environmental Challenges identified by the NRC (2001c) are directly or indirectly related to soil and water resources, especially in the areas of land-use dynamics, hydrologic forecasting, biogeochemical cycles, climate variability, and ecosystem functioning.

Another example of synergistic advancement of soil science lies in the interface with biogeochemistry. The recent formation of the Weathering System Science Consortium (WSSC) calls for answers to the fundamental scientific question regarding the earth’s weathering processes under the influence of climatic, tectonic, and anthropogenic forces (Anderson et al., 2004). Pedogenesis is essentially an integrated weathering phenomenon that results from a series of physical, chemical, and biological processes over time. It provides a holistic view and valuable historical record of the processes that occurred, or are occurring, in the earth’s critical zone (or in other planetary surfaces). Biogeochemical cycles are inseparable from the hydrologic cycle and the critical reservoir of the soil, thus indicating the fundamental importance of integrated studies for the fluxes of water, energy, and chemical elements.

Soils have many other significant roles to play in various emerging national and international environmental networks designed to address “big” science questions that are increasingly called for by funding agencies and various scientific consortia. In NSF alone, planning is underway to establish the National Ecological Observatory Network (NEON), the National Hydrologic Observatory (HO) Network, and the Collaborative Large-scale Engineering Assessment Network for Environmental Research (CLENER). At the international level, coordinated efforts such as the Earth System Science Partnership (including IGBP, IHDP, WCRP, and DIVERSITAS), the Global Climate Observing System (GCOS), and the Integrated Global Observing Strategy (IGOS) have attracted considerable interest. It is apparent that there are ample opportunities for soil scientists to contribute in a variety of “7 + 1” functions that are of importance to society.

To stimulate discussions on how best to embrace soil science in the broadest sense, to debate how to unite ourselves to address “big” science questions, and to instill in the public an appreciation of the soil as a precious gift from nature, I would like to highlight three actions that could help propel soil science into its golden age:

- *Get involved:* An inclusive and integrative soil science requires that our door be opened to non-traditional clientele and that we enter through the doors of other com-

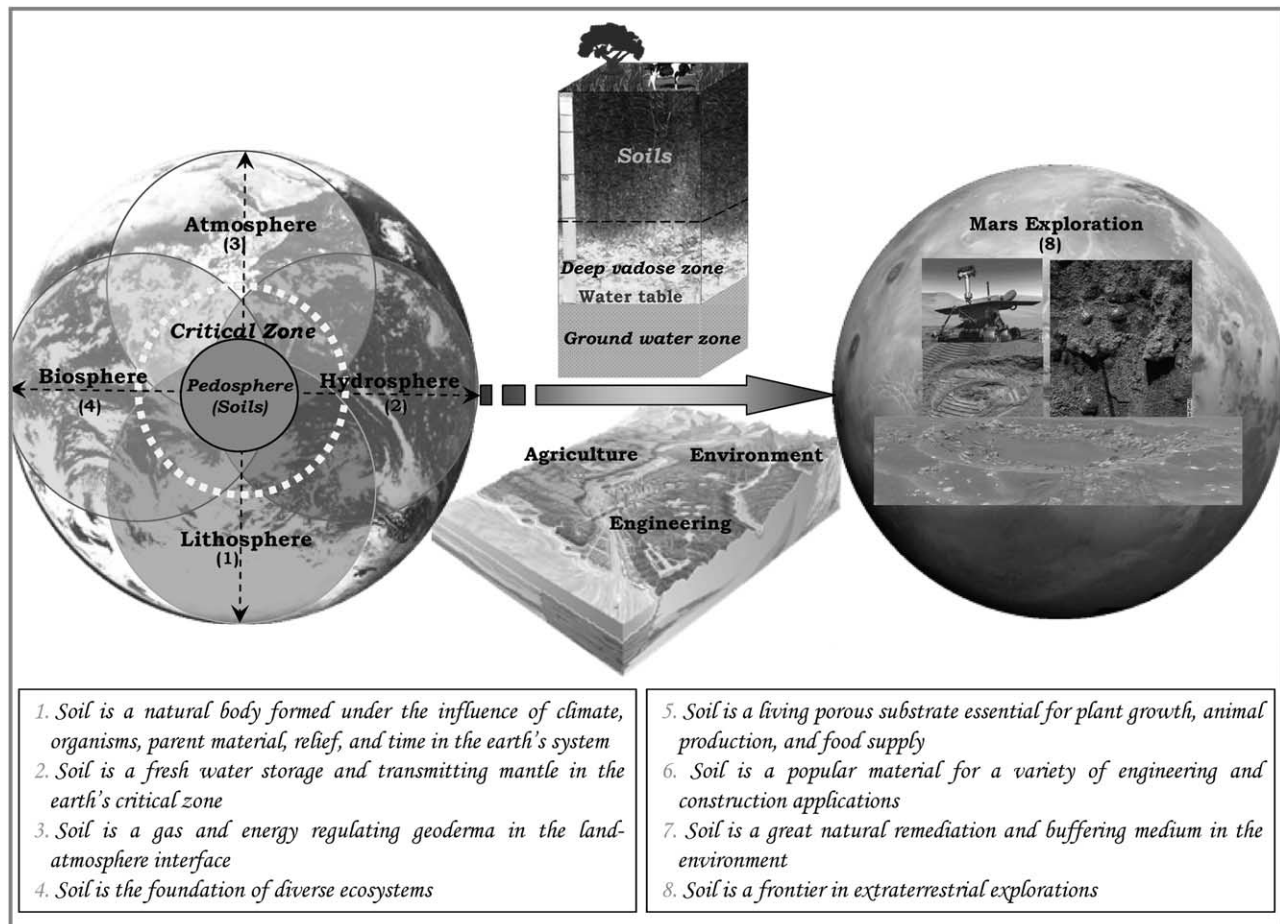


Fig. 1. 7 + 1 Roles of the Soil: An Inclusive Vision for Integrative Soil Science.

munities. Soil science community should promote further interactions and collaborations with all relevant scientific societies (including social and economic sciences). This will only strengthen our profession, and help gain sustainable future growth and legitimate support. To this end, an independent and neutral status of our soil science society will be more attractive to non-agricultural professionals. The definition of “soil” may also be broadened to reflect soil scientists’ sphere of interest that includes the whole regolith and the earth’s critical zone. But, regardless of how we broaden the domain of our interest, our unique aspects remain (such as pedogenesis and soil-forming theory). To create true cooperation and interchange in the interdisciplinary arena, we also need to adopt a joint learning trajectory and the salesman principle to effectively help formulate environmental regulations and policies (Bouma, 2005). Scientists playing such a role should be prepared to invest time, creativity, and energy to establish such communication.

- *Come together:* Subdisciplines of soil science need to be integrated to address “big” science questions. Soil scientists, however, tend to use entities for research that are less well defined and procedures that are less integrated, based often on the ability or feasibility to measure, rather than on fundamental differences in integrated physical, chemical, and biological processes (e.g., Lin et al., 2005). We should strive to unite ourselves on several fronts, including: (1) Formulating “big” science questions that can lead to major breakthroughs. As an example, a fundamental question in unsaturated zone flow and transport is:

“How to predict flow paths and patterns in heterogeneous and structured *in situ* soils across spatial and temporal scales”? (2) Developing integrated databases and models that are consistent and interoperable. For instance, there is currently no concerted effort for a national database that addresses the spatial distribution and temporal dynamics of soil hydraulic properties, geochemical elements, and biotic communities; (3) Coordinating shared facilities and tools to provide an infrastructure for long-term systematic data collections and synthesis using distributed field observatories and sensor networks. It is amazing that, while large-scale observing networks have been or are being established for atmosphere, biosphere, lithosphere, and hydrosphere, such a network for the pedosphere (or the earth’s critical zone as a whole) is lacking.

- *Educate the public:* To effectively communicate the “7 + 1” roles of the soil, education and outreach are needed at all levels, from grade schools to policy forums. This issue is critically linked to many challenges we have been facing, including student enrollment, future workforce, research funding, public perception, and land and water ethic. Ongoing efforts to establish the Smithsonian soils exhibit are expected to have far-reaching impacts, but we need to do much more. The following examples illustrate the point: (1) If elevated attention to aerosols can be effectively linked to climate change, why can’t we attractively convey the “secret and magic” of soil and water in sustaining life and civilization on this blue planet? Soil and water as complex environmental systems are as

worthy of study as the heavens and the oceans; (2) Amidst the vast number and variety of microorganisms in the soil (one heaping tablespoon of soil may contain up to 10 billion microbes—one and a half times the human population on earth) are a host of microbes now valued for their potential to help solve environmental problems as well as supply cures for diseases (including botulism and anthrax) (Singer, 2003); (3) Soil scientists need to proactively involve in land-use decisions and “smart growth” planning. New land-use plans and land development practices should consider the manner in which natural soils vary over the landscape, which offers clues as to “what” can best be done and “where” with the lowest risks and the greatest opportunities.

In closing, the soil is the essence of the earth’s critical zone. It contributes to the origin and development of life on this planet, the rise and decline of human civilizations, and the sustainability or deterioration of global ecosystems. Water flux into and through the soil in the landscape resembles the way blood circulates in a human body. Soil and water combined thus create the foundation that sustains the earth’s ecosystems and human society, bearing direct impacts on a variety of societal and environmental concerns. We need to be constantly reminded that a broken geoderma cannot be left uncured and that “*Our own civilization is now being tested in regard to its management of water as well as soil*” (Hillel, 1991). A call for embracing soil science in the broadest sense and for uniting soil scientists as a viable community will pave the way for soil science to enter its golden age.

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## REFERENCES

- Anderson, S.P., J. Blum, S.L. Brantley, O. Chadwick, J. Chorover, L.A. Derry, J.I. Drever, J.G. Hering, J.W. Kirchner, L.R. Kump, D. Richter, and A.F. White. 2004. Proposed initiative would study Earth’s weathering engine. *EOS* 85:265–269.
- Bouma, J. 2005. *Hydropedology as a powerful tool to environmental policy research*. Geoderma (in press).
- Hillel, D. 1991. *Out of the earth—Civilization and the life of the soil*. The Free Press, New York.
- Lin, H.S., J. Bouma, and Y. Pachepsky. (ed.) 2005. *Hydropedology: Bridging disciplines, scales, and data*. Geoderma special issue, Elsevier. (In press).
- NRC. 1993a. *Soil and water quality: An agenda for agriculture*. National Academy Press, Washington, DC.
- NRC. 1993b. *Ground water vulnerability assessment—Contamination potential under conditions of uncertainty*. National Academy Press, Washington, DC.
- NRC. 1997. *Precision agriculture in the 21st century*. National Academy Press, Washington, DC.
- NRC. 1999. *New strategies for America’s watersheds*. National Academy Press, Washington, DC.
- NRC. 2001a. *Basic research opportunities in earth science*. National Academy Press, Washington, DC.
- NRC. 2001b. *Envisioning the agenda for water resources research in the twenty-first century*. National Academy Press, Washington, DC.
- NRC. 2001c. *Grand challenges in environmental sciences*. National Academy Press, Washington, DC.
- Singer, M. J. 2003. *Soil science*. Geotimes. July 2003.
- Sugden, A., R. Stone, and C. Ash. 2004. *Ecology in the underworld*. Science (Washington, DC) 304:1613.
- Ugolini, F.C., and R.L. Edmonds. 1983. *Soil biology*. p. 193–231. In L. P. Wilding et al. (ed.) *Pedogenesis and soil taxonomy. I. Concepts and interactions*. Elsevier, Amsterdam, The Netherlands.
- Wilding, L.P., and H.S. Lin. 2005. *Advancing the frontiers of soil science towards a geoscience*. Geoderma (in press).

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## Comments on “Amounts, Forms, and Solubility of Phosphorus in Soils Receiving Manure”

Mineral stability plots are a handy tool that is becoming more widely used as computer geochemical models have spread among soil and environment scientists. These plots may indicate possible geochemical processes in various systems and suggest discrete mineral phases that control the activity of various soluble components in soil solutions. But, as is true for many other tools, they may lead to erroneous conclusions as well. Our purpose herein is to note a few pitfalls that should be avoided in using stability plots.

In their recent paper, Sharpley et al. (2004) aimed to determine the effect of continual long-term (10–25 yr) manure applications on the forms and solubilities of P in soils. Their sequential extraction data indicate that although acidic ( $4.8 \leq \text{pH} \leq 6.8$ ), all of the studied unmanured soils contained Ca-P phases (P extracted by 1 M HCl). Subsequent to long-term manure application the pH increased slightly in all soils to range from 5.7 to 7.6, and the sequential P extraction data suggest that most of the applied P was precipitated as additional Ca-P phases rather than being adsorbed on the surface of other solid particles or precipitating as Fe- or Al-P phases. The Ca-P accumulation is in line with the expectation that at equilibrium hydroxyapatite (HA) and fluorapatite will form instead of the Fe-P mineral strengite and the Al-P mineral variscite in soils with pH higher than approximately 5.5, and as pH increases even the more soluble Ca-P minerals, such as brushite, will be more stable than these Fe- and Al-P phases (Lindsay, 1979). However, oversaturation alone is merely a prerequisite for mineral formation; nonequilibrium is the common state in soils and kinetics of precipitation would be an important factor to dictate whether and to what extent various Ca-, Fe-, or Al-P minerals would accumulate in the soil. To examine which Ca-P mineral phases formed, Sharpley et al. (2004) used geochemical modeling based on extraction concentrations after equilibration for 16 h in 0.01 M CaCl<sub>2</sub>, using a 1:5 soil/solution ratio. Figure 6 in their paper shows a “double function” plot of  $(\log \text{H}_2\text{PO}_4^- - \text{pH})$  vs.  $(\log \text{Ca}^{2+} + 2\text{pH})$  of the soil extracts, and by comparing their data to the stability plots of several Ca-P minerals they attempt to determine which Ca-P minerals are present in the soils studied. Thus, by showing that all the data points for the unmanured soils fall below the HA line, they propose that HA was the main mineral form of Ca-P in these soils. Similarly, based on soil extracts that were oversaturated with respect to HA and undersaturated with respect to dicalcium phosphate dihydrate (DCPD), they propose that tricalcium phosphate (TCP) and octacalcium phosphate (OCP) dominated the Ca-P forms in the manured soils.

We propose that neither statement is adequately established. Using the data presented in their paper, we calculate that for five of the unmanured soils, even if all the HCl (1 M)-extracted inorganic-P is assumed to have originated from Ca-P minerals and to have been dissolved completely by the extractant (1:5 in 0.01 M CaCl<sub>2</sub>) during the short extraction period (16 h), the solutions would have been undersaturated with respect to all Ca-P minerals, and it is not possible to say which form of Ca-P was actually dissolved. Thus, even if equilibrium were to be attained in 16 h, it is not possible to distinguish

which Ca-P mineral is controlling P concentration under field moisture conditions, or which Ca-P mineral dominates the Ca-P phases of the soils. For the manured soils most of the data points plotted in Fig. 6 of Sharpley et al. (2004) were above the HA line and below the TCP line, but Ca and P could have been dissolved from small quantities of any of the Ca-P minerals for which solution is shown to be undersaturated, even if most of the Ca-P phase was in the form of HA. Thus, with a low soil/solution ratio metastable phases present in low concentrations may dissolve completely, even though these phases may control P solubility at field moisture conditions.

The short equilibration time adopted by Sharpley et al. (2004) would have further limited the utility of an equilibrium plot for identifying any Ca-P mineral as a dominant phase. Mackay et al. (1986) found that dissolution of finely ground (<180  $\mu\text{m}$ ) rock phosphate materials approached steady state in various moistened soils only after 30 d, and Pierzynski et al. (1990) found that soil suspensions (1:2 in deionized water) attained steady state relative to OCP or HA only after 42 to 105 d, while shorter extraction times resulted in undersaturation for these minerals.

Geochemical studies, based on solution composition, can provide important information, but must be used with caution in characterizing the mineralogical composition of soils. Toward that end, x-ray diffraction (XRD), electron induced x-ray emission spectroscopy, or other mineralogical tools, should be used. For example, Beauchemin et al. (2003), who similarly found by sequential extraction that Ca-P minerals were the dominant P form in the B horizon of an acidic loamy soil (pH 5.5) amended for >25 yr with animal manure, used x-ray absorption near-edge structure spectroscopy (XANES) to estimate that 11% of the total P content of this soil occurred as HA and 45% as OCP.

Determination of the phase controlling P solubility in field soils can be important in understanding plant P supply over the rather short periods involved in P uptake. Kinetic control by the least stable mineral, regardless of its amount, or adsorbed P, must be considered. Thus, relatively large amounts of HA in a soil may not be able to maintain a P concentration that satisfies plant demand, while an ample supply may result from even small amounts of meta-stable OCP or DCPD. Solution data and geochemical modeling can be used to ascertain which soil phase or phases control the activities of soluble constituents and can also suggest processes such as mineral formation or transformation that take place in a soil; however, conclusions should be based on firm data that indicate near equilibrium with a specific mineral over a wide range of conditions that result in its dissolution or precipitation. For example, Brennan and Lindsay (1998) used geochemical calculations to study transformations of iron hydroxides after altering redox conditions in suspensions of synthetic iron oxides and soil. Their experimental results were collected over a wide pe + pH range of 2 to 14, and since their data fell along distinct lines of  $\text{Fe}(\text{OH})_3$  (amorphous) in the 14 to 11 pe + pH range, and of  $\text{Fe}_3\text{O}_4$  (amorphous) in the pe + pH range of 11 to 4, they could differentiate the range within which each mineral controlled Fe activity. Hence they could suggest that in their experiment, ferric oxides were transformed on reduction to  $\text{Fe}_3\text{O}_4$  (amorphous) rather than  $\text{Fe}_3\text{O}_4$  (magnetite). Their conclusion was indeed supported by XRD examination of the solid phases.

In another study, by using geochemical modeling Shenker et al. (2005) showed that on soil reduction and release of adsorbed P from dissolution of ferric hydroxides, TCP and HA controlled P activities in two rewetted calcareous wetland soils but not in two other gypsum-rich peat soils from the same wetland. Their conclusion was based on an experimental data set that reflected a long equilibration period (120 d) with

wide ranges in pe + pH values (2–12) and P concentrations (2–40  $\mu\text{M}$ ), such that TCP and HA were identified as having been formed in two of the soils because P solubility data fell along phase lines for these minerals.

No such tendency is apparent in the paper by Sharpley et al. (2004), nor indeed would be expected considering the short equilibration period and the low soil/solution ratios employed, which would have completely dissolved metastable DCPD, OCT, and TCP phases. Consequently, no conclusions can be reached as to which Ca-P minerals actually precipitated in the soils studied, or to what extent. The retained P could have precipitated as any of the Ca-P minerals when oversaturation occurred. The extent of such precipitation will be affected by kinetic considerations and various factors that control it. Thus, HA precipitation might be inhibited by the presence of soluble organic substances, even if solutions were oversaturated with respect to this mineral, as was shown by Inskeep and Silvertooth (1998). On the other hand, the undersaturation found by Sharpley et al. (2004) for extracted solutions might be related to dilution, if dissolution proceeded so slowly as to prevent re-establishment of a semi-equilibrium state within the 16-h extraction period.

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## REFERENCES

- Beauchemin, S., D. Hesterberg, J. Chou, M. Beauchemin, R.R. Simard, and D.E. Sayers. 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-edge structure spectroscopy and chemical fractionation. *J. Environ. Qual.* 32:1809–1819.
- Brennan, E.W., and W.L. Lindsay. 1998. Reduction and oxidation effect on the solubility and transformation of iron oxides. *Soil Sci. Soc. Am. J.* 62:930–937.
- Inskeep, W.P., and J.C. Silvertooth. 1998. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic, and tannic acids. *Soil Sci. Soc. Am. J.* 52:941–946.
- Lindsay, W.L. 1979. *Chemical equilibrium in soils*. John Wiley & Sons, New York.
- Mackay, A.D., J.K. Syers, R.W. Tillman, and P.E.H. Gregg. 1986. A simple model to describe the dissolution of phosphorus rock in soils. *Soil Sci. Soc. Am. J.* 50:291–296.
- Pierzynski, G.M., T.J. Logan, and S.J. Traina. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: Solubility equilibria. *Soil Sci. Soc. Am. J.* 54:1589–1595.
- Sharpley, A.N., R.W. McDowell, and P.J.A. Kleinman. 2004. Amounts, forms, and solubility of phosphorus in soils receiving manure. *Soil Sci. Soc. Am. J.* 68:2048–2057.
- Shenker, M., S. Seitelbach, S. Brand, and A. Haim. and M. I. Litaor. 2005. Redox reactions and phosphorus release in re-flooded soils of an altered wetland. *Eur. J. Soil Sci.* doi:10.1111/j.1365-2389.2004.00692.x.

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### Response to “Comments on ‘Amounts, Forms, and Solubility of Phosphorus in Soils Receiving Manure’”

We thank Drs. Moshe Shenker and Paul Bloom for their letter and for giving us the opportunity to focus the reader on the objectives of our paper; namely to identify P forms and solubilities in manured soils, to explain their behavior and potential for P loss in runoff.

The true nature of Ca-associated P remains an elusive subject. Even so, the main point of our manuscript was to show that acid-based soil test P extractants, such as Mehlich-3, can overestimate the amount of P that is potentially released to water from soils that have received large amounts of manure over several years. This point holds true regardless of inferred speciation of Ca-P compounds.

Shenker and Bloom repeatedly make two points, (i) that ion solubility products should be combined with other data to support conclusions, and (ii) that the equilibration period was insufficient to determine a “true controlling phase.”

By reading the literature (e.g., Pierzynski et al., 1990), a common theme is evident: studies using solubility equilibrium data should include supporting data, and double-function plots, such as Fig. 6 in our paper, can only infer solubility. We support this view and only use the double-function plot to show differences between manured and unmanured soils. At no stage do we conclude by these plots alone, that different or distinct Ca-P minerals are present. Moreover, we only *infer* that increasingly soluble Ca-P minerals have formed with the application of manure for up to 25 yr in some cases. These Ca-P forms are likely to represent amorphous phases forming via heterogeneous precipitation and as such are not “pure.” The use of sequential fractionation data supports increased formation of HCl-P, commonly thought to represent apatite. Shenker and Bloom also make the point that if HCl-P was used as the sole indicator of Ca-P extracted into the equilibration solution, then they would be undersaturated vis-a-vis Ca-P minerals. We would like to point out that Ca-P is also found in bicarbonate- and resin-extractable P fractions (Tiessen and Moir, 1993).

The second point Shenker and Bloom make is that the equilibration period is insufficient to indicate the “true controlling phase.” They also point out that kinetics are important. We completely agree that kinetics are important and pose the following question. Considering the aim of our research presented in Sharpley et al. (2004) was to show the forms and solubility of P in soil receiving manure with respect to P release and transport in runoff, what time frame should be considered? In essence, the equilibration of a soil with a solution at any one time effectively gives an indication of the phase dissolved at that time. As we used the same time for both manured and unmanured soils, the comparison between these soils is valid. We noted in the paper, “as more P and Ca are introduced into the system, P is increasingly precipitated into more soluble P forms.” We would also like to refer readers to previous studies of ours that used double-function plots in combination with solid-state nuclear magnetic resonance spectroscopic techniques to show that increasingly soluble Ca-P phases do occur with increasing P and pH (McDowell et al., 2003).

Finally, we ask the readers to consider the following point. McDowell et al. (2001) showed using  $^{33}\text{P}$ , that P in runoff was best related to P released from soil to solution in up to 24 h and that the pool of P released beyond this and up to 90 d was a poor indicator of P in runoff. If in fact we used the equilibration time proposed by Shenker et al. (2005) of 120 d, how well would this relate to P in runoff?

We support the view of Shenker and Bloom that any methodology, whether it be analytical, field, or modeling must be used under the conditions for which it was developed. Our research covers the long-term field equilibration of soil and manure (10–25 yr) and the rapid release (1 min to several hours) of soil P to runoff water during a rainfall-induced flow event. Inasmuch, we believe the equilibration times we used relate to reaction times that exist during the release of soil P to rainfall/runoff water. The limitations of using P solubility or double-function plots to infer mineral stability were clearly defined by Sharpley et al. (2004). Inferences from them were made only in support of chemical extraction data (both individual and sequential). We believe the overall conclusion of our research, that the acid extractability (Mehlich-3) of soil P increased to a greater extent than water extractability in heavily manured soils, is still valid, and that these findings have important implications to environmental soil P test procedures and recommendations.

We appreciate the opportunity to have this dialog with other researchers and that it has clarified the appropriateness of using various methods to elucidate the extractability and solubility of soil P in terms of its estimation with regard to ever expanding agronomic and environmental contexts.

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### REFERENCES

- McDowell, R.W., N. Mahieu, P.C. Brookes, and P.R. Poulton. 2003. Mechanisms of phosphorus solubilisation in a limed soil as a function of pH. *Chemosphere* 51:685–692.
- McDowell, R.W., S. Sinaj, A.N. Sharpley, and E. Frossard. 2001. The use of isotopic exchange kinetics to determine phosphorus availability in overland flow and subsurface drainage waters. *Soil Sci.* 166:365–373.
- Pierzynski, G.M., T.J. Logan, and S.J. Triana. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: Solubility equilibrium. *Soil Sci. Soc. Am. J.* 54:1589–1595.
- Sharpley, A.N., R.W. McDowell, and P.J.A. Kleinman. 2004. Amounts, forms, and solubility of phosphorus in soils receiving manure. *Soil Sci. Soc. Am. J.* 68:2048–2057.
- Shenker, M., S. Seitelbach, S. Brand, A. Haim, and M.I. Litaor. 2005. Redox reactions and phosphorus release in re-flooded soils of an altered wetland. *Eur. J. Soil Sci.* (in press).
- Tiessen, H., and J.O. Moir. 1993. Characterization of available P by sequential extraction. p. 75–86. *In* M.E. Carter (ed.) *Soil sampling and methods of analysis*. Can. Soc. Soil Sci. Lewis Publishers, Boca Raton, FL.

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### Comments on “Field Calibration of Water Content Reflectometers”

Chandler et al. (2004) tried to evaluate and improve the performance of the commercial soil moisture sensor CS-615 (Campbell Scientific Inc., Logan, UT). The authors should be complimented for their devoted efforts to provide growers with an accurate yet inexpensive tool for monitoring water content (WC), a critical parameter in agricultural production. Practically the authors propose a three-phase campaign:

1. Extensive use of low cost but problematic sensors;
2. An upgrade, by one way or another, of the factory-supplied sensor calibration; and
3. Use of time domain reflectometry (TDR) technology to intermittently verify water content reflectometer (WCR) calibration stability under field conditions.

My following comments intend to show that: (i) the calibration strategy offered and discussed by the authors may be problematic, (ii) the measurement frequency gap is unbridgeable, (iii) the selected experimental site is not a typical agricultural example, and (iv) it is worth checking if a simple and cheap electrical resistance measurement could not bring the same benefit for a fraction of the price.

The authors assume that “TDR is a reliable, most widely accepted electrical technique for measuring soil WC”; it is desirable to identify a substitute for the TDR technique due to its high price; and Campbell Scientific’s Water Content Reflectometer (WCR, CS-615) is a suitable candidate because, similarly to the TDR it measures soil dielectric properties, differing only in the measurement frequency (15–45 MHz, compared with the 1000–1450 MHz of TDR).

Contrary to the superlatives used for describing TDR, the characteristics of the WCR presented in the article include (verbatim): “WCR-determined volumetric WC (VWC) is more sensitive to soil type, because the effects of EC are strongly temperature dependent ... WCR data are also temperature (T) dependent for high EC soils.” For three of the four soils tested, the authors report, “there were substantial deviations from the factory calibration and substantial T effects.” The authors also stated, “at present there are insufficient data to know, a priori, how much the calibration for a given WCR application might deviate from the factory calibration, however it appears that the calibration will vary with soil properties, with deviation tending to increase with clay content, and that it may vary with each individual sensor, and in addition, it is difficult to account for individual sensor variability, which may vary with site characteristics.” Sensors’ production seems also to have contributed to the error, as was indicated by the trends between individual sensor pairs (TDR-WCR), and the error in the overall relationship is primarily due to variability in the offset constant among the individual WCR sensors whose response may vary with production season or field installation or both.

The site-specific regressions show a difference in accuracy of WCR between the two sites, attributed by the authors to the difference in clay content. However, the 8% difference in clay content between the soils in both sites would not have made this difference with a true TDR. The authors note, “Much of the data for both sites fell near or outside the 3% error bounds. Assuming this range of error, the total measurement error of 6% WC is approximately 1/4 of the annual range in volumetric WC for these soils.” Their Fig. 2, reporting

$WC_{TDR} - WC_{WCR}$  relations, conveniently demonstrates several types of disparity: partly or fully biased, systematically shifted, and a wide range of scatter, all relative to factory calibration.

To improve the correspondence between WCR and TDR the authors have applied different forms of averaging, apparently without considering whether the dual TDR-WCR installation can change the inherent properties of the WCR by calibration manipulations.

More specifically, it is given that the CS-615 is sensitive to T, EC, and the soil WC, which are continuously changing during the season, and that undistinguishable interactions exist between them. Thus the user is left with a problem of three unknowns and only one equation.

Experimental results show that the WCR response is predominantly determined by its sensitivity to the resistance of the medium it is imbedded in, including indirectly the complicated, nonlinear, multi-interdependence on T, texture, and salinity. Field measurements obtained by the growers may yield doubtful results, for only the texture can be expected to remain constant, whereas soluble salts and T may vary considerably during periods when TDR measurements are not taken. Consequently, if one adds up the individual sensor production variability and the random offset, or the unavoidable sensitivity to field parameters other than water content, it must be concluded that the CS-615 is no better than two bare metallic rods of a rigid configuration.

Based on the above comments, I would appreciate the authors addressing the following:

- A. Is it reasonable to expect that potential users would be able to internalize the meaning of the recalibration of the factory calibration, to distinguish between a real TDR and its imitation, or will the authors maintain that their WCR-reported data are as reliable as those of a true TDR? Would the average user (ranch manager, extension person, research technician, or engineer) be able to understand, perform, analyze, apply, and supervise the recalibration procedure? And from where could a TDR be “occasionally” borrowed?
- B. An inner contradiction arises, in that the authors praise the TDR as the most widely accepted technique for measuring soil WC that is also reliable and robust, while they also attribute a limitation in their suggested calibration method to the TDR’s poor performance in highly saline or fine-textured soils.
- C. The authors’ rationale for avoiding the use of TDR may indicate a lack of experience. Recent articles (Persson and Haridy, 2003; Jones and Or, 2004; Kelleners et al., 2004; Zhang et al., 2004) have reported successful  $WC_{TDR}$  measurements in high salinity media. If necessary, sensor rods can be shortened to solve the problem.
- D. The authors’ long list of parameters to which the WCR is sensitive, hints that the soil’s galvanic component affects measured WC far more than does the soil’s dielectric properties, namely that WCR measurements reflect changes in bulk soil EC rather than water content changes, as stated. This hypothesis is based on the following reasoning: Bulk EC (ECa) of a medium depends on the product of its ionic concentrations (C) and the effective sampled water volume (WC). The effective soil water volume is that soil fraction of water-filled pores, relative to the larger, geometrically fixed bulk volume. This simple hypothesis should have been tested if the authors suspected that the WCR was responding mostly to the medium’s changes in resistance.

The experimental WC values obtained by the authors do not agree with the above hypothesis, and this may stem from their use of experimental conditions that are not representative of an agricultural field. The experimental site chosen by the authors is characterized by biasing conditions: a single sensor installed in a single location, a narrow range of water salinity, the absence of plants, and a rain fed field. The reader should note that such conditions do not reflect realistic agricultural situations where roots preferentially remove water but not salts, thus enhancing the EC effect.

As to the latter issue, it is surprising that temperature measurements were not reported by the authors. Moreover, if the authors suspect that a significantly different background EC was contributed by 8% clay content (difference between the two experimental sites), why did they not monitor the soil EC profile?

My comments cannot be complete without some mention of the article's humoristic aspect. The authors have concluded from their WCR data that the soil and inter-sensor variability can be effectively field-calibrated with TDR, resulting in WC measurements that approximate the accuracy of the TDR. They further conclude, "The ultimate limitation of the method is tied to the limitations of the TDR."

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## REFERENCES

- Chandler, D.G., M. Seyfried, M. Murdock, and J.P. McNamara. 2004. Field calibration of water content reflectometers. *Soil Sci. Soc. Am. J.* 68:1501–1507.
- Jones, B.J., and D. Or. 2004. Frequency domain analysis for extending time domain reflectometry water content measurement in highly saline soil. *Soil Sci. Soc. Am. J.* 68:1568–1577.
- Kelleners, T.J., R.W.O. Soppe, J.E. Ayars, and T.H. Skaggs. 2004. Calibration of capacitance probe sensors in a saline silty clay soil. *Soil Sci. Soc. Am. J.* 68:770–778.
- Persson, M., and S. Haridy. 2003. Estimating water content from electrical conductivity measurements with short time domain reflectometry probes. *Soil Sci. Soc. Am. J.* 63:478–482.
- Zhang, N., G. Fan, K.H. Lee, G.J. Kluitenberg, and T.M. Loughin. 2004. Simultaneous measurement of soil water content and salinity using frequency response method. *Soil Sci. Soc. Am. J.* 68:1515–1525.

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## Response to "Comments on 'Field Calibration of Water Content Reflectometers'"

In Dr. Nadler's critique of our paper (Chandler et al., 2004), he makes several points critical of the research approach. It seems that his concerns are founded in a misunderstanding of the intent of the paper, which on review, could be open to interpretation. To clarify, the paper was intended for the measurement needs of the plant-soil-water and hydrologic research community, many of whom have purchased and installed this popular sensor for long-term monitoring purposes in nonagricultural settings. Its intent was to demonstrate that improvements in water content (WC) measurements made by water content reflectometers (WCRs) are possible through field calibration. We used data collected at an experimental rangeland watershed in Idaho for this purpose. Our paper is not an endorsement of this particular sensor, which is indeed

influenced by both WC and electrical conductivity (EC), as are all electromagnetic WC measurement methods, albeit to varying extent.

Below we respond to the points made by Dr. Nadler, beginning with his interpretation of the paper (Points 1–3), followed by some comments (i–iv). Finally, we address four specific issues, identified by Dr. Nadler as A–D, as he requested in his letter.

1. Correct, we acknowledge that the tradeoff between measurement precision and instrumentation expense has resulted in widespread use of sensors such as the WCR. In the end, reliable and standardized distributed WC measurements may be of more utility to field investigations than a few very precise measurements.
2. Nearly correct. We propose using collocated time domain reflectometry (TDR) measurements as standards to develop field calibrations of these sensors. This is the main point of the paper.
3. A good idea, but not mentioned in the paper.

In response to Dr. Nadler's four comments we offer the following.

- i. The calibration strategy is straightforward. To remove the individual sensor bias and improve the slope of the sensor response as affected by soil properties, calibrations were derived from simple regression analysis between measurements made by 22 WCRs and corresponding TDR waveguides.
- ii. Our intent was not to bridge the frequency gap between TDR and the WCR. In Fig. 2 of Chandler et al. (2004), it is shown that *even for low salinity soils*, WC values obtained by factory calibrations of WCR period vary considerably from those obtained from standard TDR measurements.
- iii. Although these calibrations did not include all the factors that may influence the WCR response in an agricultural setting, they were made in two soils, over a range of temperatures typical of a (vegetated) mountain rangeland site in the western USA.
- iv. After listing his intended points, Dr. Nadler uses excerpts from two related papers that share common authors, Chandler et al. (2004) and Seyfried and Murdock (2001), as the basis of an argument that, due to the sensitivity of the CS-615 to EC and the dynamic nature of soil EC in the field, "the CS-615 is no better than two bare metallic rods of rigid configuration." Based on this premise he proposes testing electrical resistance measurement as a means to measure water content for these soils. We are not inclined to do so, but encourage his efforts along these lines.

As to the specific issues raised by Dr. Nadler, we respond as follows.

- A. The linear regressions are simple to use. We clarify that the WCR does not operate at the same frequency as real TDR and identify this as a limitation for the sensor. However, it should also be noted that once calibrated, sensors with the electronics adjacent to the waveguides, such as the WCR avoid the signal transmission loss and noise encountered with TDR systems multiplexed to long cable lengths and deployed in field conditions with widely variable surface temperature and moisture conditions. As clarified above, our paper is not an "effort to provide growers with an accurate yet inexpensive tool for monitoring ... WC," nor did the intended audience

consist mainly of ranch managers, extension agents, or technicians. Considering the availability of TDR in many research institutions, we do not view equipment access as an insurmountable obstacle.

- B. We see no contradiction here. We use TDR as a standard technique and merely state the accepted limitations of TDR.
- C. We do not avoid the use of TDR. We identify the cost of TDR as a limiting constraint for many field studies. It was hoped that the WCR would suffice in our medium-textured soils with low EC. The papers cited describe important advances in the use of TDR for highly saline soils, but do not address the issue of cost.
- D. We do not follow the logic in this point. As in (iv), we invite Dr. Nadler to test his own hypotheses. We reiterate: The main purpose of our paper was to demonstrate that improvements in WC measurements made by WCRs are possible through field calibration to TDR, which is widely accepted as a standard technique. In fact, including soil temperature in the calibration did not improve the calibration of WCR period to TDR WC in this case and as such, soil temperature was not presented.

In conclusion, the proposed calibration approach has been demonstrated only for low-EC soils, where WC can be expected to dominate the sensor response.

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## REFERENCES

- Chandler, D.G., M. Seyfried, M. Murdock, and J.P. McNamara. 2004. Field calibration of water content reflectometers. *Soil Sci. Soc. Am. J.* 68:1501–1507.
- Seyfried, M.S., and M.D. Murdock. 2001. Response of a new soil water sensor to variable soil, water content, and temperature. *Soil Sci. Soc. Am. J.* 65:28–34.

doi:10.2136/sssaj2005.0086le

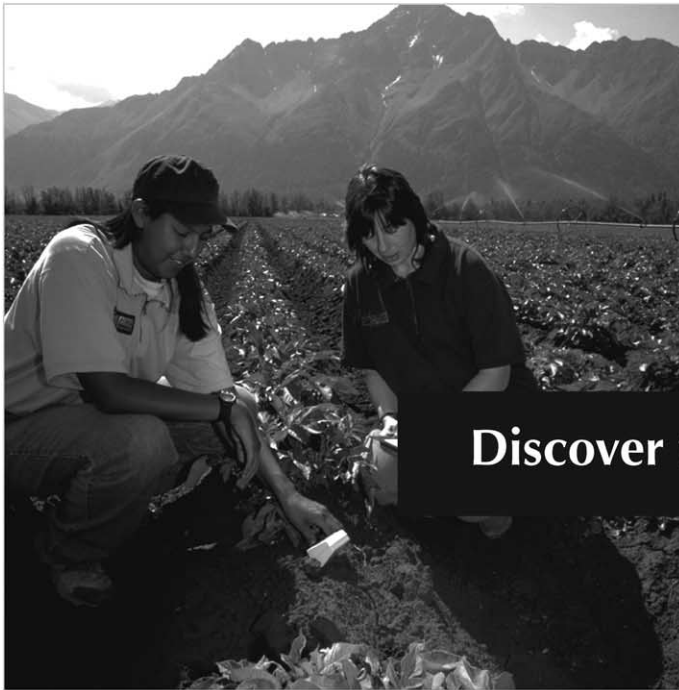


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