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## Historical Aspects of Soil Chemistry

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### **The Origins of Agricultural Chemistry: The Forerunner of Soil Chemistry**

In ancient times Aristotle proposed that plants derive nourishment from their roots that obtain preformed organic matter. This view was held for more than 2000 years, and ultimately resulted in the humus theory of plant nutrition that was discounted by Sprengel and later by Liebig (Browne, 1944; van der Ploeg et al., 1999). Agricultural chemistry in the beginning focused on practical observations and experience, and did not have a real scientific basis until over 1000 years after the fall of the Roman Empire (Browne, 1944). Sir Humphrey Davy (1778–1829) used the title “Elements of Agricultural Chemistry” for a book containing lectures he presented before the British Board of Agriculture in 1802–1812. He noted that “Agricultural chemistry has for its objects all those changes in the arrangements of matter connected with the growth and nourishment of plants—the comparative values of their produce is food; the constitution of soils; and the manner in which lands are enriched by manure, or rendered fertile by the different processes of cultivation.” In his treatise, Davy listed 47 chemical elements with details on their properties. Elements that were named included Na, K, Ca, Si, Ba, and Mg. He also noted the importance of rocks and parent material in soil formation (Browne, 1944).

The Phlogistic period was the time when the humus theory was first proposed by J.G. Wallerius (1709–1785), a Swedish professor of chemistry at the University of Uppsala. This theory stated that plants obtain nutrients from humus-derived extracts (in German Extraktivstoff) that contain water soluble compounds of C, H, O, and N from which the plants could rebuild more complex plant tissue. From these four elements they could also form, using an internal vital source (in German Lebenskraft and in Latin, *vis vitalis*), other vital elements such as Si and K (van der Ploeg et al., 1999). The theory further assumed that while salts and lime

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were important to plants, they primarily served the role of promoting the decomposition of humus and the dissolving or dissolution of organic matter into the soil solution (van der Ploeg et al., 1999).

Contrary to prevalent thinking, the debunking of the humus theory, the formulation of mineral nutrition of plants, and the Law of the Minimum, were first proposed by a German scientist Phillip Carl Sprengel (1787–1859), not the celebrated chemist, Justus von Liebig (Browne, 1944; Wendt, 1950; Böhm, 1987; van der Ploeg et al., 1999). Sprengel was born near Hannover, Germany and earned his Ph.D. degree for the University of Gottingen. He became an instructor in agriculture and agricultural chemistry at Gottingen and gave courses in soil analyses, fertilizers, and crops (Browne, 1944). Sprengel's early experiments focused on the humus theory and the sole role of soil organic matter (SOM) as the source of plant nutrients. He determined the water-soluble components in humus extracts of soils and found salts of alkali nitrates, sulfates, chlorides, and phosphates. He concluded that the soluble salts were plant nutrients, and thus disproved the humus theory. However, the humus theory persisted until 1840 when the great influence and stature of Liebig resulted in its demise. Sprengel also investigated inorganic compounds found in the root zones of soils (Sprengel, 1828). He considered 15 elements as important. These included O, C, H, N, S, P, Cl, K, Na, Ca, Mg, Al, Si, Fe, and Mn. Based on these findings he developed the Law of the Minimum (Sprengel, 1838) which stated that if only one of the elements needed for plant growth is lacking, the plant will suffer, despite the fact that all the other essential elements are present in sufficient quantity. Sprengel also noted that elements such as As, Pb, and Se could be detrimental to plants. He stated: "When a plant needs 12 substances to develop, it will not grow if any one of these is missing."

Liebig in his many writings and experiments made these ideas generally accepted. Browne (1944), in his book on the history of agricultural chemistry, stated that "in Liebig's books he was more a promulgator and defender of truths that had already been announced than a discoverer of new knowledge." Despite these landmark discoveries by Sprengel, Justus von Liebig (1803–1873) was a world class organic chemist and is considered by most to be the patriarch of agricultural chemistry as well as the most important scholar of the Modern Period of soil science (Fig. 1). Liebig was born in Darmstadt, Germany and first studied chemistry at the University of Bonn, later transferring to Erlanger where he received his doctoral degree. He then went to Paris where he studied with Gay-Lussac and Thenard. On the recommendation of Alexander von Humboldt he was appointed as Professor of Chemistry at the University of Giessen in Germany in 1824 (Browne, 1944). He rapidly became a star in organic chemistry and students and scholars from around the world were attracted to his laboratories. His early research resulted in the development of techniques for determining the



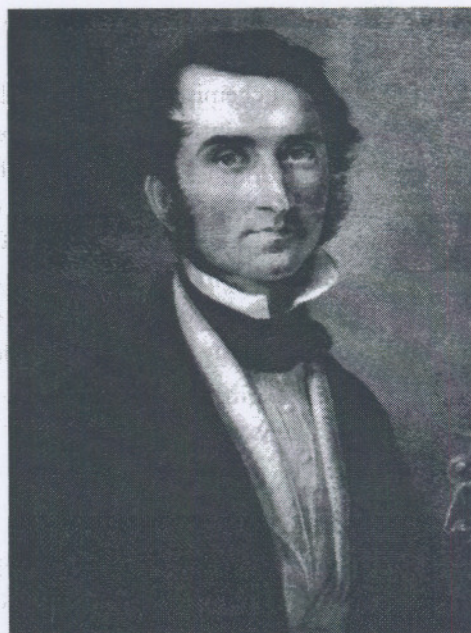


Figure 1. Justus von Liebig (1803–1873).

elementary composition of organic materials such as malic, aspartic, and uric acids and plant alkaloids.

Liebig published the book that rapidly became famous, "Organic Chemistry In Its Applications to Agriculture and Physiology." In this book Liebig mentions three chemical requirements of crops: 1) substances containing C and N that can provide these elements to the plants; 2) water and its elements; and 3) soil that can provide the inorganic matters vital to plant growth. He de-emphasized the role of humus in soil fertility and plant growth and the humus theory by stating: "Humus does not nourish plants, by being taken up and assimilated in its unaltered state, but by presenting a slow and lasting source of carbonic acid, which is being absorbed by the roots and is the principal nutrient of young plants at a time when being destitute of leaves, they are unable to extract food from the atmosphere."

It can arguably be stated that Liebig established the field of agricultural chemistry. One piece of evidence that supports his stature and influence in the field of agricultural chemistry was that by 1880, there were nine professorial chairs in agricultural chemistry in Germany that were primarily held by Liebig's students (Yaalon, 1997). An example of the influence of Liebig's ideas in the work initiated by Lawes and Gilbert at Rothamsted, England. This is discussed in the chapter by Addiscott in this volume.



## Major Themes in Soil Chemistry

As soil became the focus of agricultural chemistry, the term soil chemistry became a more accepted term. There is a vast amount of literature about various historical developments in soil chemistry. I have chosen to focus on a few topics that have profoundly affected the research directions and leitmotifs in soil chemistry, and at the same time have been characterized by lively debates and scientific excitement. I have also chosen to discuss what I believe are some of the frontiers in the field over the next decade. I apologize ahead of time to those soil chemists whom I do not cite or topics that are not included. There is certainly no intention to deliberately slight any piece of work.

### Ion Exchange

Soil chemistry, as a subdiscipline of soil science, had its roots in the early 1800s in the observations of two Italian scientists, Giuseppe GAZZERI (1828) and Lambruschini (1830) (see Boulaine, 1994), as well as the German pharmacist Johann Bronner (1837), who noted the importance of the ability of soils to exchange elements. As early as 1819 GAZZERI showed that clay decolorized and deodorized liquid manure and retained soluble substances that were available to plants. In 1845, a British farmer, H.S. Thompson (Thomas, 1977), began among the first detailed studies documenting the ability of soils to exchange ions. Thompson, knowing that soils might absorb gaseous ammonia conducted a series of experiments to ascertain: 1) if ammonia, absorbed to soil, could be leached out by rainfall, 2) if soils differed in their ability to absorb ammonia, and 3) if soils can absorb ammonia in the form of  $\text{NH}_4\text{SO}_4$ , which was being used at the time as a N fertilizer. Some of his major findings were that Ca and  $\text{SO}_4$  appeared in the leachates examined after rainfall, suggesting that  $\text{NH}_4$  was exchanged by Ca and  $\text{SO}_4$ , and was not retained. Thompson told a consulting chemist to the Royal Agricultural Society, J. Thomas Way, about his discoveries but did not publish his work until 1850, at which time Way had already conducted more in-depth studies (Thomas, 1977).

Way conducted what is now recognized as pioneering research on ion exchange, which has for the most part stood the test of time. He can be considered a patriarch of soil chemistry. Way conducted a remarkable group of experiments and discovered that soils can exchange Ca and Mg and to a lesser extent  $\text{NH}_4$  and K. The term base exchange was used to describe this process. At the time it was not known that H, in most cases resulting from hydrolysis of Al, could also be exchangeable. Even after exchangeable H was recognized, the term base exchange was used for many years. It also should be noted that the base exchange process was referred to as absorption



until the studies of Wiegner began in 1912. Based on his comprehensive studies, Way drew the following conclusions (Way, 1850, 1852; Kelley, 1948): 1) The cation of a neutral salt solution is absorbed on the soil with an equivalent displacement of Ca from the soil, but the anion of the salt is not absorbed, remaining in solution, unless an insoluble Ca salt is formed; 2) absorption was not due to sand, organic matter,  $\text{CaCO}_3$  or free alumina, but by the clay fraction of the soil; 3) the ability of the soil to absorb ions was reduced by preheating the sample, but not completely eliminated except at high heating temperatures; 4) absorption was rapid, almost instantaneous; 5)  $(\text{NH}_4)\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  were absorbed by the soil in their entirety, with no exchange of the cation; 6) the ability of soils to exchange bases includes  $\text{NH}_4$ , K, Na, and Mg but if any bases are applied in the OH or  $\text{CO}_3$  forms, the base is absorbed without exchange; 7) Ca, added as sulfate, chloride, or nitrate, passes through the soil without alteration, but  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{HCO}_3)_2$  are absorbed completely, like alkaline compounds of other cations; 8) the ability of soils to absorb ammonium increases with the concentration of the ammonium solution and as the ratio of solution to soil increases; and 9) base absorption is irreversible.

The majority of these conclusions have proven to be correct. However, the conclusions that ion exchange is irreversible and that SOM is not important in ion exchange are clearly incorrect. Additionally, although the soils that Way studied indicated that anions were not absorbed, this was probably due to their relative lack of metal oxides. Of course, we now know that soils contain variable-charge minerals such as metal oxides and clay minerals such as kaolinite. As Sumner (1998) has noted, Way's conclusion that soils did not adsorb anions caused most scientists to dismiss the importance of anion exchange capacity until the work of Gedroiz (1925), and particularly Mattson (1927). In 1852, Way published a second paper in which he determined which soil components were important in cation exchange. He proposed that soil silicates were important exchangers and was among the first to propose an order of replacing power of one cation for another. Assuming Ca was the absorbed cation and the exchanger was reacted with a 0.01 N solution of Cl, he proposed the following replacing power order:  $\text{Na} < \text{K} < \text{Ca} < \text{Mg} < \text{NH}_4$ . Liebig, being the ever critical scientist, said about Way's findings: "Agriculture cannot be advanced by agricultural experiments of this kind."

Following Way's remarkable experiments, a number of studies were carried out that confirmed his results. Henneberg and Stohmann (1858) found that the amount of  $\text{NH}_4$  adsorbed by a soil depended on the concentration of the  $\text{NH}_4$  and the ratio of solution to soil employed. Peters (1860) showed that K could be replaced by Na, Ca, or Mg ions and most easily by  $\text{NH}_4$ . He found the order of Mg,  $\text{NH}_4$  and Na to replace Ca was:  $\text{Mg} > \text{NH}_4 > \text{Na}$ . He also confirmed Way's finding that cation exchange appeared to be a rapid process. Rautenberg (1862)



concluded that organic matter was important in cation exchange. Knop (1872, 1874) hypothesized that certain soil sorbents, such as Al and Fe silicates were important for absorption of  $\text{NH}_4$ , that the process was chemical in nature, and that the degree of  $\text{NH}_4$  absorption was roughly proportional to the quantity of fine-grained soil materials present. Although he did not know it at the time, Knop had correctly pointed out the role of clay minerals and metal oxides in cation exchange and that soil components could have different abilities to retain cations. Pillitz (1875) discovered that soils differed in their abilities to absorb  $\text{NH}_4$ , but that under constant pressure and temperature, every soil has a maximum "absorptive power." He was thus the first scientist to demonstrate that under a given set of conditions, the cation exchange capacity (CEC) of each soil is a definite quantity. van Bemmelen (1878) concluded that the ion exchange process is a true chemical reaction and he and Eichhorn concluded that zeolites or zeolitic materials absorbed cations and were the primary soil component responsible for cation exchange. For the next 50–70 years, most scientists believed that zeolites were the primary soil exchanger material.

### Ion Exchange Studies in the 1900s

For almost 20 years after van Bemmelen's 1888 paper, no important work appeared on ion exchange. In the early 1900s some seminal studies were carried out by the German chemist, G. Wiegner, the Russian scientist, G. Gedroiz, and the Dutch scientist, Hissink. Wiegner and his students studied cation exchange from a colloidal chemistry viewpoint. They concluded that permutite in soils and certain adsorption compounds were important sorbents and that exchangeable ions were held on particle surfaces and in capillaries by an adsorption process and not by chemical attraction. Wiegner also made the perceptive conclusion that the anions form a swarm around the particle and in aqueous medium are more or less hydrated and proposed an order in which ions would be preferred on soil exchangers of  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$  and  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ , which is the Hofmeister lyotropic series. Along with his student, Hans Jenny, they emphasized the importance of ion size and hydration in ion exchange selectivity, concluding that the smaller the ion the greater its selectivity and replacing power.

Beginning in 1912, Gedroiz (1872–1933), a Russian, published an amazing group of papers over the next 13 years (1925) that further advanced our understanding of ion exchange. The following studies were conducted: 1) the influence of a number of exchangeable cations on the physical, chemical, and plant nutritional properties of soils; 2) the kinetics of the exchange reaction and the replacing power of different cations; 3) methods for determining exchangeable cations and determining the CEC of soils; 4) ascertaining the relation of exchangeable



Na to alkali and saline soils; 5) the role of exchangeable cations in Chernozem and Podzol soils; 6) base unsaturation and degradation of soils; and 7) the nature of the exchange materials in soils. He, like Wiegner, felt that ion exchange was not a chemical reaction but rather a physicochemical reaction. Gedroiz also reported the following replacing powers of cations:  $\text{Li} < \text{Na} < \text{K} < \text{Mg} < \text{Rb} < \text{NH}_4 < \text{Co} < \text{Al}$ .

Gedroiz, A. De Dominicis in Italy and J.A. Prescott in Africa (Kelley, 1948) independently proposed that the base exchange principle proposed by Way played a major role in alkali soils. Eugene Woldemar Hilgard (1833–1916), the great soil scientist at Berkeley, who had trained with R.W. Bunsen at the University of Heidelberg in Germany, had identified soils in California as white alkali or salty soils and black alkali soils, and pioneered processes for reclaiming the soils including leaching and adding gypsum. Kelley and coworkers confirmed the role that base exchange played in alkali soils by their finding that Na adsorbed on clay minerals caused the black alkali soils. In Budapest, De' Sigmund (1873–1939) contributed to research on exchange phenomena.

During the 1930s Walter P. Kelley (1878–1965, Fig. 2), a soil chemist trained under Eugene Hilgard at the University of California at Berkeley, and later a faculty member at UC-Riverside and Berkeley, along with his students and colleagues carried out many studies on ion exchange, the cation exchange capacities of soils and seminal research on the chemistry of alkali and saline soils (Kelley and



Figure 2. Walter P. Kelley (1878–1965).



Brown, 1924; Kelley, 1937; Kelley et al., 1939a,b). Much of Kelley's research on cation exchange is summarized in his landmark books, "Cation Exchange in Soils" in 1948, and "Alkaline Soils: Their Formation, Properties and Reclamation," in 1951.

Beginning in 1929, a Swedish soil chemist, Sante Mattson (1886–1980), published a series of papers that at the time were not well accepted, in the journal "Soil Science" with a lead title of "Laws of Soil Colloidal Behavior." In these landmark papers, Mattson (Fig. 3) explained cation exchange on the basis of ionization. He also correctly proposed the idea that soil components have an isoelectric point (IEP) in which equivalent quantities of cations and anions are dissociated, while below the isoelectric point, the dissociation of OH anions exceeds that of cations and in this pH range, anion adsorption can take place. At pHs above the isoelectric point, cation dissociation predominates and cation adsorption predominates. Mattson had pioneered the idea of variable or pH-dependent charge and correctly noted that CEC could vary in soils with pH changes and that pH should be stated when the CEC is reported (Mattson, 1927, 1931, 1932). In fact, he beautifully illustrated that soils from the Southeastern USA contained variable charge colloids that carried a positive charge at acid pHs. Important studies conducted by Schofield and Samson (1953) and Mehlich (1952) also appeared on pH-dependent or variable charge soils.



Figure 3. S.E. Mattson (1886–1980).



Unfortunately, the perceptive observations of Mattson were largely ignored until the late 1950s and 1960s when Coleman and Rich and coworkers rediscovered the importance of Mattson's seminal studies (Coleman et al., 1959; Rich, 1968). However, because much of the soil chemistry research was being conducted in areas where constant (permanent) charge soil minerals dominated, the chemistry of variable charge soils did not receive the attention it deserved (Sumner, 1998). This resulted in practices such as liming and soil analyses methodologies being transferred to parts of the world such as Africa, Asia, and South America where they were not appropriate. For example, the idea of measuring the CEC at pH 7 by extracting with 1 M ammonium acetate solution (a standard and widely used procedure), while appropriate for soils dominated by constant charge minerals such as montmorillonite and vermiculite, is not proper for CEC measurements on highly weathered soils high in kaolinite and Al- and Fe-oxides.

In the first few decades of the 20th century many attempts were also made to derive an equilibrium constant for a binary exchange reaction and numerous ion exchange equations were developed to explain and predict binary reactions (reactions involving two ions) on clay minerals and soils. These were named after the scientists who developed them and included the Kerr, Vanselow, Gapon, Schofield, Krishnamoorthy and Overstreet, Donnan, and Gaines and Thomas equations. However, from a thermodynamic standpoint, it was Albert Vanselow (Vanselow, 1932) who correctly established that a true exchange equilibrium constant should express the activity on the solid phase as the product of the mole fraction and the adsorbed phase activity coefficient. In the early 1950s two seminal papers appeared (Argersinger et al., 1950; Gaines and Thomas, 1953) that provided a theoretical framework for determining a thermodynamic exchange constant,  $K_{ex}$ , for a binary process. All of the aforementioned landmark research laid the groundwork for numerous studies throughout the world on ion exchange processes in soils (Sparks, 1995, 2002) and truly established ion exchange as one of the hallmarks of soil chemistry. The reader is further referred to a number of reviews and books dealing with ion exchange history and developments in soil chemistry (Kelley, 1948; Thomas, 1977; Sposito, 1981a,b, 2000; Sparks, 1995, 2002).

### Clay Mineralogy

One of the major landmarks in soil chemistry and the identity of soil mineral components was the discovery by Hendricks and Fry (1930) and Kelley et al. (1931) that the major portion of the inorganic fraction of soils was crystalline (Cady and Flach, 1997). In the paper of Hendricks and Fry (1930) they presented results of total chemical analyses, optical studies, and X-ray diffraction on geological specimens of



montmorillonite, bentonite, halloysite, kaolinite, and dickite and related them to data on 23 samples of colloids from soils. They indicated that the diffraction patterns showed "the presence of only one crystalline component in each soil" and that "none of the primary soil minerals such as micas, feldspars, and quartz are shown as crystalline components of the colloid fraction." Over the next 12 years, Hendricks and his associates published many papers on clay mineral structures and their physical properties (e.g., Hendricks and Alexander, 1939; Ross and Hendricks, 1945). Kelley et al. (1931), Hoffman et al. (1933), Marshall (1935), Kelley and co-workers (1939 a,b) and M.L. Jackson and his students and colleagues (Coleman and Jackson, 1945) also made significant contributions in delineating the crystal structures of clay minerals and the types of clay minerals found in USA soils. M.L. Jackson and his coworkers also developed many standard procedures for soil particle fractionation and separation and phyllosilicate identification (Jackson, 1956). Jacob et al. (1935) analyzed the clay minerals found in soils around the world and Nagelschmidt et al. (1940) determined the clay minerals in soils of India. From these investigations, it was found that in most soils more than two clay minerals were found with kaolinite, montmorillonite, and mica being common. These researchers and others, based on clay mineralogical analyses, concluded that weathered soils were dominated by kaolinite while grassland soils were dominated by montmorillonite.

Clay mineralogy of soils was later developed with more detailed methods of identification of the minerals and their significance in soil chemistry.

### Soil Acidity

Another significant leitmotif in soil chemistry in the 20th century was the merry-go-round on soil acidity (Jenny, 1961). Perhaps the first person to lime soils for the correct reason was Edmund Ruffin (1794–1865). His paper "An Essay on Calcareous Manures" greatly influenced soil science in the USA. Ruffin (Fig. 4), as Grant Thomas in his outstanding paper "Historical Developments in Soil Chemistry: Ion Exchange" (1977) so eloquently and eruditely noted, Ruffin was a gentleman farmer, an amateur chemist, politician, philosopher, and rebel who was trying to making a living farming near Petersburg, Virginia, USA. Ruffin fired the first Confederate shot at Fort Sumter, South Carolina, which began the U.S. Civil War, and committed suicide after Appomattox because he did not wish to live under the "perfidious Yankee race." Ruffin added oyster shells to his soils to correct the acidity problem and also accurately described zinc deficiencies in his journals (Thomas, 1977). He concluded that all calcareous soils are naturally fertile and durable and all soils that are naturally poor are devoid of calcareous materials. He speculated that soils on the Eastern US coast were low in  $\text{CaCO}_3$ , which was correct (Jenny, 1961). Ruffin can be considered the father of soil chemistry in the USA.



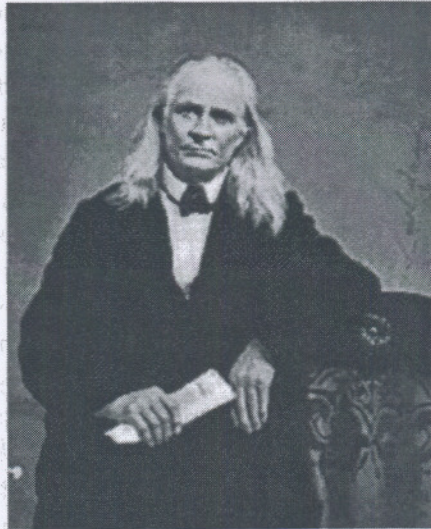


Figure 4. Edmund Ruffin (1794–1865).

It was 70 years after Ruffin's work before research on soil acidity was initiated again. Questions about whether acidity was primarily attributed to hydrogen or aluminum were the basis for many of the studies. Fierce arguments ensued in the early 1900s and continued for over five decades. As Jenny (1961, Fig. 5) astutely

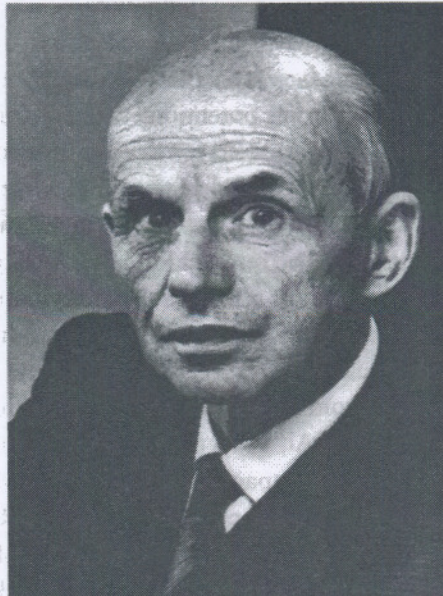


Figure 5. Hans Jenny (1899–1992).



noted the debates were like a merry-go-around, and as Thomas (1977) has so wonderfully and entertainingly noted, some of the giants of soil chemistry were caught up in the often pointed arguments. F.P. Veitch (1902) found that titration of soils that had been equilibrated with  $\text{Ca}(\text{OH})_2$  to a pink endpoint with phenolphthalein was a good test for predicting whether lime (e.g.,  $\text{CaCO}_3$ ) was needed to neutralize acidity, that would be detrimental to crop growth (Thomas, 1977). Hopkins et al. (1903) developed a lime requirement test based on the titration of a soil equilibrated with 1 N NaCl. Veitch (1904) showed that a 1 N NaCl extract, while not replacing all the soil's acidity, was a good lime requirement test. A very important finding by Veitch (1904), that was not recognized at the time, was that the acidity replaced by 1 N NaCl was  $\text{AlCl}_3$ , not HCl.

After Veitch's work a number of soil chemists started to study soil acidity and to debate whether acidity was caused by Al or H. Bradfield (1923, 1925) titrated clays and observed that their  $\text{pK}_a$  values were similar to those found for weak acids. Kelley and Brown (1926) and Page (1926) hypothesized that "exchangeable Al" was dissolved by exchangeable  $\text{H}^+$  during the extraction with salt. Paver and Marshall (1934) believed that the exchangeable  $\text{H}^+$  dissolved the clay structure, releasing Al which in turn became a counterion on the exchange complex. This was indeed an important discovery that was not definitively proved and accepted until the 1950s and early 1960s, as we shall see.

Chernov (1947) had shown that electrodyalized clays and naturally acid clays were primarily Al-saturated. Shortly thereafter, Coleman and Harward (1953) found that H resin-treated clays or clays leached rapidly with 1 M HCl had quite different properties from clays that were slowly leached, leached with dilute acid solutions, or electrodyalized. They concluded, based on their studies, that hydrogen clays were strongly acid. Low (1955), employing potentiometric and conductometric titration analyses, proved that an electrodyalized clay was Al-saturated. Coleman and Craig (1961) confirmed the earlier finding of Coleman and Harward (1953) that H clays are unstable and rapidly convert to Al clay, with temperature having a dramatic effect on the transformation rate. The research on H vs Al clays was very important in that it showed that Al is more important in soil acidity than H.

Also in the 1950s and 1960s there were some important discoveries made about the types of Al found in soils. Rich (Fig. 6) and Obenshain (1955) showed that in some Virginia soils, formed from mica schist, there was not only exchangeable  $\text{Al}^{3+}$ , but also nonexchangeable Al, with the latter blocking exchange sites and thus lowering the cation exchange capacity (CEC) of the soils. The nonexchangeable Al also kept vermiculite from collapsing (Rich, 1964; Rich and Black, 1964) and was referred to as interlayer hydroxy-Al. It was thus Coleman and coworkers (Coleman and Thomas, 1967) and Rich and co-workers (Rich and Obenshain, 1955; Hsu and Rich, 1960) who, based on landmark studies, concluded that





Figure 6. C.I. Rich (1918–1975).

aluminum, including trivalent, monomeric, and polymeric hydroxy Al, was the primary culprit in soil acidity.

During the period of the 1950s and 1960s H. Jenny, P.F. Low, N.T. Coleman, C.E. Marshall, M. Peech, and others also vociferously argued over the cause of the suspension effect (the often observed phenomenon that the pH of a soil suspension was lower than the pH of the overlying solution) and in the end, most agreed that a junction potential, due to differences in ion mobility on soil particle surfaces, was the primary reason for the suspension effect.

Studies on the chemistry of Al and soil acidity reached their zenith in the 1950s and 1960s. In the 1970s and 1980s, as concerns about acid rain escalated, fundamental experiments employing NMR spectroscopy and other analytical techniques and methods were conducted to explore the speciation of Al in solution and soils (Barnhisel and Bertsch, 1982).

### Sorption Processes

As mentioned earlier, most of the early research on ion sorption focused on cation sorption and exchange on permanent-charge minerals. This can be ascribed to research being conducted on relatively young soils that were dominated by



permanent charge minerals that were negatively charged over a wide pH range. During the 1960s and 1970s, increasing attention was given to chemistry of variable charge systems and anion sorption on variable charge minerals and soils (Sumner, 1963a,b; van Raij and Peech, 1972; Gillman, 1974, 1979; Fey and le Roux, 1976; Thomas, 1977). These studies contributed to our understanding of the effects of pH and ionic strength on the chemistry of variable charge soils and the importance of anion adsorption. The first textbook devoted to the chemistry and physics of variable charge soils appeared in 1981 (Uehara and Gillman, 1981).

In the last 25 years, major advances have been made in modeling sorption reactions at the mineral/water interface and elucidating the kinetics and mechanisms of sorption/desorption phenomena in soils. In the past, soil chemists had employed classical adsorption models such as the Freundlich and Langmuir equations to describe an array of reactions on soils and soil components. While these models often describe experimental data quite well and can be useful in making comparisons about sorption behavior among soils, they provide no mechanistic information. Many investigators, based on parameters calculated from these equations, made conclusions about binding sites and strengths and types of sorption mechanisms (e.g., adsorption, precipitation).

However, in the 1970s and early 1980s, a number of investigators began to question whether the original assumptions of the Langmuir equation were valid for heterogeneous soil materials and the wisdom in making conclusions about sorption mechanisms (Harter and Baker, 1977; Veith and Sposito, 1977; Sposito, 1981b; Harter and Smith, 1981). In a landmark paper, Veith and Sposito (1977) showed that the Langmuir equation could equally well describe both adsorption (accumulation of a substance or material at an interface between the solid surface and the bathing solution) and precipitation (formation of three-dimensional products). Thus, one cannot differentiate between adsorption and other sorption processes, such as surface precipitation, using an "adsorption" isotherm, and clearly mechanistic information cannot be derived from macroscopic models (Sposito, 1986; Scheidegger and Sparks, 1996).

To provide some molecular description to sorption processes at the soil mineral/water interface, a series of surface complexation models (SCM) were developed in the 1970s by Stumm and Schindler and their coworkers, and others, and included the constant capacitance (Schindler and Gamsjager, 1972; Hohl and Stumm, 1976; Schindler et al., 1976; Stumm et al., 1976, 1980), and triple-layer (Davis and Leckie, 1978, 1980) models. Especially detailed reviews on the applications and theoretical aspects of other surface complexation models such as the Stern variable surface charge-variable surface potential (Bowden et al., 1977, 1980; Barrow et al., 1980, 1981), general two-layer model (Dzombak and Morel, 1990) and the one-pK and MUSIC models (Bolt and van Riemsdijk, 1982;



Hiemstra et al., 1987) can be found in Davis and Kent (1990) and Goldberg (1992). Goldberg and Sposito (1984a,b) were among the first soil chemists to apply a SCM (i.e., constant capacitance model) to study the sorption of phosphate on goethite. Since that time, SCM have been widely used by soil chemists and other scientists to describe an array of chemical reactions including proton dissociation, metal cation and anion adsorption reactions on oxides, clay minerals, and soils, organic ligand adsorption on oxides, and competitive adsorption reactions on oxides. Many of these studies are described and alluded to by Goldberg (1992).

While surface complexation models have proved useful in soil chemical investigations, the limitations of the models must be appreciated. One of the major problems with many of them is that multiple adjustable parameters are often used to fit the experimental data. Consequently, it may not be surprising that equilibrium data will fit a number of the models equally well as was beautifully illustrated by Westall and Hohl (1980). Additionally, it has been shown that surface precipitation of metals can occur on soil minerals in addition to purely adsorption phenomena. Most of the SCM do not consider surface precipitation as a possible sorption mechanism, although some attempts have been made to include precipitation processes (Farley et al., 1985; Katz and Hayes, 1995a,b).

Over the past 15 years, major advances have occurred in elucidating sorption mechanisms at the mineral/water interface. Based on pioneering studies by Stumm and Schindler and their coworkers it was assumed that major adsorption complexes were outer-sphere (a water molecule is present between the surface functional group and the bound ion or molecule) and inner-sphere (no water molecule is present between the ion or molecule and the surface functional group to which it is bound). However, until molecular scale studies were performed, conclusions about sorption mechanisms were purely speculative. With the advent of in-situ molecular scale techniques such as Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), and x-ray absorption (XAS) spectroscopies and scanning probe microscopy (SPM), definitive information on sorption products and mechanisms have been gleaned (Sparks, 2002).

### Kinetics of Soil Chemical Processes

During the late 1970s, and particularly in the 1980s, soil chemists increasingly realized that while the study of equilibrium processes and reactions in soils were important, most field reactions were seldom at equilibrium. It became apparent that one needed to understand the rates of soil chemical processes to accurately predict the fate and transport of ions and organic compounds in soil and water environments, including the development of predictive models.



Perhaps there are two reasons why equilibrium approaches dominated soil chemistry for so long. J. Thomas Way had conducted some kinetic studies during his classic ion exchange research and concluded that the rate of exchange was almost instantaneous. This was later verified by Hissink and Gedroiz. However, Kelley (1948), in his beautiful book, *Cation Exchange in Soils*, had clearly raised the point that perhaps ion exchange and sorption processes would not be so rapid on soil minerals like mica and vermiculite where ion diffusion could occur, resulting in slow reaction rates. However, few soil chemists appeared to have paid attention to Kelley's perceptive observations.

It was left to the classic study of Boyd et al. (1947) and later the seminal studies of Helfferich (1962) and coworkers who demonstrated that diffusion was the rate-limiting process for ion exchange. Later, Scott and coworkers (Scott and Reed, 1962; Scott and Smith, 1966, 1967) and Mortland and coworkers (Mortland, 1958; Mortland and Ellis, 1959) clearly showed that K release from soil minerals was diffusion-controlled. I recall quite vividly that during my Ph.D. research, a number of scientists questioned my findings that K sorption on soils was quite slow, which I attributed to interparticle diffusion into micropores of soil clay minerals. With time, my results were accepted, and many other soil chemists began to study the kinetics of soil chemical reactions.

Another major impediment in promotion of kinetics as a major area in soil chemistry was the complexity of the topic, particularly as kinetics is applied to heterogeneous soil systems, and the lack of good methods to measure both rapid and slow soil chemical reactions. Over the past two decades, soil chemists have developed and employed an array of batch and flow methods to measure reactions over time scales of minutes and longer, and have used chemical relaxation methods, such as pressure-jump and concentration-jump, to study reaction rates on millisecond time scales. These methods are discussed in a number of books and reviews (Sparks, 1989; Amacher, 1991; Sparks and Zhang, 1991; Sparks et al., 1996). Without question, in the last two decades, kinetics has become a major theme in soil chemistry. There is not space to discuss all the significant contributions that soil chemists have made in the area of kinetics, however, the reader can consult a number of references authored by soil chemists (Sparks, 1989; Sparks and Suarez, 1991; Sposito, 1994; Sparks, 1999, 2000, 2002).

## **The Road in Soil Chemistry, Summary**

It is fair to say that the primary impetus in soil chemistry over the first 120 years was to better understand the reactions and processes of plant nutrients in soils with a major emphasis on ion exchange, clay mineralogy, and soil acidity. In the 1970s, major



societal concerns centered around the environment, including air, soil, and water quality as impacted by greenhouse gases, trace metals, radionuclides, pesticides and other organic chemicals, and nutrients such as nitrogen. As a result, the emphasis in soil chemistry has shifted to studies on environmental soil chemistry/geochemistry. Over the past 25 years, major studies have been conducted on: acid rain effects on soils and waters; effects of trace metals/metalloids in land applied sludge materials and from other sources on metal/metalloid retention/release in soils, plant uptake and bioavailability; speciation of contaminants in soils using chemical extractions and molecular scale techniques; nitrate and phosphate, organic chemical, and radionuclide fate/transport in surface and groundwaters; facilitated colloid transport of metals and organic chemicals; elucidation of humic substances structure and C sequestration; residence time effects on contaminant sequestration; redox transformations and mechanisms of inorganic and organic contaminants in soils; development of surface complexation models, based on classical double layer theory, to describe metal and ligand sorption on soils and soil components; soil remediation using chemical and phytoremediation approaches and microbially-mediated transformations of contaminants.

In the past 25 years, advanced analytical techniques became available for the study of reactions at the soil mineral/water interface. Of particular importance was the advent of molecular scale in-situ techniques in which soil chemical reactions can be monitored in aqueous environments. In fact, a new multidisciplinary field of soil and environmental sciences, which often employs the aforementioned techniques, has been created—molecular environmental science. Molecular environmental science can be defined as the study of the physical and chemical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level. Without question, the employment of in-situ molecular scale techniques, along with macroscopic, equilibrium and kinetic studies has created a revolution in soil and environmental chemistry research. Along with rapid developments in analytical tools, soil chemistry research is becoming highly multi- and inter-disciplinary. Soil chemists are collaborating with chemists, physicists, biologists, geochemists, engineers, material scientists and marine scientists like never before. These interactions and the breathtaking advances and developments in analytical techniques, information technology, and biotechnology will forever change the field of soil chemistry.

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