# A

## A HORIZON

See *Horizon, Profile, Horizon Designations*.

## ABIOTIC

Describes soil constituents (for example quartz, kaolinite), processes (hydrolysis, redox reactions), or factors (temperature, relative humidity, salinity for example), that are inorganic in nature, and that are capable of forming or acting in the absence of life. However, since even the most rudimentary of soils contains organisms, organic constituents and processes inevitably interact with and impact upon the inorganic ones. In 1840, Justus von Leibig suggested that a biological population is limited by whichever extensive factor (particularly abiotic ones such as inorganic nutrient concentrations) is in shortest supply (Lomolino et al., 2006, p.79).

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Lomolino, M.V., Riddle, B.R., and Brown, T.H., 2006. *Biogeography*, 3rd edn. Sunderland, MA: Sinauer Associates, 845 pp.

### Cross-reference

Law of the Minimum

## ABRASION

The wearing away by surface friction of solid bodies (minerals and rocks for example) when brought into contact with each other by such agents of erosion as wind, water, ice or animals (including *Homo sapiens*). The reaction of a mineral with water at an abraded surface yields a characteristic pH. A typical range of abrasion pH is 6–7 for clay minerals and quartz, 7–8 for micas, 8 for calcite, 8–11 for silicates other than micas (Porta et al., p 442).

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Porta, J., Lopez, M., and Roquero, C., 1994. *Edafologia para la agricultura y el medio ambiente.* Madrid: Editions Mundi-Prensa, 807 pp.

## ABRUPT TEXTURAL CHANGE

A phrase used in the WRB Classification to mean either a doubling of the clay content within a vertical distance of 7.5 cm if the overlying horizon has less than 20% clay, or an absolute increase in clay of 20% within 7.5 cm if the overlying horizon has 20% or more clay. In this case some part of the lower horizon should have at least twice the clay content of the upper horizon (FAO, 2001, Annex 2).

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FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

## ABSORPTION

The assimilation of one substance by another, or by an organism (water or aqueous solution by plants for example). Absorption of chemical elements by roots may modify the chemistry (pH and redox potential for example) in the immediate soil environment. This has been called the “rhizosphere effect” (McBride, 1994, P. 310).

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McBride, M.B., 1994. *Environmental Chemistry of Soils*. New York: Oxford University Press, 406 pp.

## Cross-reference

Sorption Phenomena

# ACID DEPOSITION EFFECTS ON SOILS

Acid deposition has been implicated as a factor contributing to forest decline and surface water acidification in eastern North America and Europe. Acid deposition increased continuously in North America and Europe during the 1900s reaching peak levels in the 1970–1980s. In contrast, acid deposition in northeast Asia has increased rapidly in the past decade due to industrial development and will probably exceed levels observed previously in the most polluted areas of central and eastern Europe (Grübler, 1998). Increased emissions will severely threaten the sustainable basis of many natural and agricultural ecosystems in the region. Although unequivocal evidence directly linking acidic deposition to ecosystem damage may often be lacking, there is considerable data implicating acid deposition with recent deterioration in the health of terrestrial and aquatic ecosystems.

The mean annual pH of precipitation in eastern North America and Europe is in the range of 3.0 to 4.7; however, individual storm events have been recorded with pH values as low as 2. The deposition of anthropogenic sources of $H^+$ in the most polluted regions of Europe exceeds 7 $kmol_c\ ha^{-1}\ yr^{-1}$ compared to about 1 $kmol_c\ ha^{-1}\ yr^{-1}$ in eastern North America (Pearson and Stewart, 1993; NADP/NTN, 2004). The impact of acid deposition on terrestrial and aquatic ecosystems is mediated primarily through interactions with soil biogeochemical processes. Ecosystems in humid environments experience an internal production of acidity associated with biogeochemical processes that may overshadow the effects of acid deposition. However, for a number of ecosystems, primarily in Europe, the external sources of acidity greatly exceed the contribution from internal sources (van Breemen et al., 1984). Some terrestrial ecosystems are relatively resilient to strong acid loadings due to acid buffering reactions by soils that neutralize the acid ($H^+$) inputs. While a number of intermediate buffering reactions occur, the ultimate acid sink is chemical weathering. If acidic inputs exceed the soil buffering capacity, the soil becomes acidified which can lead to the export of ecologically significant quantities of $H^+$ and aluminum to surface waters. In addition, soil acidification may increase leaching of plant nutrients (e.g., $NO_3^-$, $SO_4^{2-}$), decrease levels of nutrient cations (e.g., $Ca^{2+}$, $Mg^{2+}$, $K^+$), increase concentrations of potentially toxic metals (e.g., $Al^{3+}$, $Cu^{2+}$, $Zn^{2+}$), alter the solubility of organic compounds, and impose changes in populations of soil organisms.

## Forms and quantities of acidic deposition

The principal anthropogenic sources of acid deposition are sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$) and ammonium ($NH_4^+$) derived from sulfur dioxide ($SO_2$), nitrogen oxides ($NO_x$), and ammonia ($NH_3$), respectively. These compounds are emitted primarily by the burning of fossil fuels, industrial activities and agricultural and livestock production. Ammonia interacts in the atmosphere and on the surface of vegetation to form $NH_4^+$, which may subsequently undergo nitrification in the soil to produce nitric acid:

$$NH_4^+ + 2O_2 = 2H^+ + NO_3^- + H_2O$$

Bulk precipitation includes both wet (soluble components) and dry (particulate material and washout of adsorbed/reacted gases captured by vegetation) deposition. Dry deposition appears to be roughly equivalent to wet deposition for sulfate and nitrate (Binkley et al., 1989), while dry deposition appears to be the dominant source of $NH_4^+$ (van Breemen et al., 1982). Cloud water (fog) deposits are especially concentrated having 5 to 30 times more acidic components than the bulk precipitation originating from the same air mass. Thus, those ecosystems receiving frequent inputs of fog may receive significantly greater inputs of acidic components. Total deposition rates for all acidic components are considerably higher in Europe than for eastern North America (Table A1). Emission of $SO_2$ and sulfate deposition have declined 38–82% in Europe and 52% in the United States over the past decade, while emissions of $NO_x$ and nitrogen deposition showed a smaller declined of 17–20% (Prechtel et al., 2001; Wright et al., 2001; U.S.-EPA, 2003).

## Soil processes neutralizing acidic inputs

In many ecosystems, acid consumption may be attributed to the replacement of the normal weak acids, generally carbonic and organic acids, by strong acids (e.g., $H_2SO_4$ and $HNO_3$). In this case, acid deposition does not add to the background acidity of the system, but instead replaces it altogether by suppressing the dissociation of these weak acids. Therefore, there may be no net increase in the rate of soil acidification due to acidic deposition of strong acids.

Both internal and external sources of acidity are largely neutralized within the soil profile by a number of coupled reactions between the soil solution, solid-phase, and biological components (van Breemen et al., 1983). If these reactions fail to completely neutralize the acidity, the excess $H^+$ is exported from the ecosystem in the drainage waters. The dominant proton consuming processes responsible for neutralizing the acidity are shown in Table A2.

### Weathering of primary minerals

The ultimate acid sink in soils is the weathering of primary minerals. The process of hydrolysis results in the transfer of

**Table A1** Total deposition (wet + dry deposition) rates $kmol_c\ ha^{-1}\ yr^{-1}$ of acid and acid forming components in atmospheric deposition

| Acid component | Eastern North America | Highest deposition regions of Europe |
|---|---|---|
| Sulfate | 0.2 – 1.3[†§] | 5.2[‡] |
| Nitrate | 0.13 – 0.43[†§] | 1.1 – 1.2[‡¶] |
| Ammonium | 0.06 – 0.55[†§] | 3.4 – 7.2[¥] |

[†]Binkley et al., 1989; [§]NADP/NTN, 2004; [‡]Ulrich, 1984; [¶]van Breemen and van Dijk, 1988; [¥]Pearson and Stewart, 1993.

**Table A2** Examples of important reactions active in the consumption and production of $H^+$ in soils

| $H^+$-consuming reaction | | $H^+$-producing reaction |
|---|---|---|
| Weathering | $M^+(AlSi_3O_8) + 7H_2O + H^+ = M^+ + Al(OH)_3 + 3H_4SiO_4$ | Reverse weathering |
| $H^+/M^{n+}$ exchange | $M^{n+}\text{-exch} + nH^+ = nH^+\text{-exch} + M^{n+}$ | $M^{n+}/H^+$ exchange |
| Anion Adsorption | $\text{Ads-}(OH)_2 + A^{n-} + nH^+ = \text{Ads-A} + nH_2O$ | Anion desorption |
| Assimilation of anions | $n\text{R-OH} + A^{n-}(aq) + nH^+(aq) = nH_2O + n\text{R-A}$ | Mineralization of anions |
| Al dissolution | $Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$ | Al precipitation |

*M* = cation; *A* = anion; *exch* = cation exchange site; *Ads* = adsorption site; *R* = organic molecule.

acid ($H^+$) to $CO_3^{2-}$ and $HCO_3^-$ to form $HCO_3^-$ and $H_2CO_3$, respectively, in the weathering of carbonate minerals and to $H_3SiO_4^-$ to form $H_4SiO_4$ in the weathering of silicate minerals. Associated with this $H^+$ transfer is the release of base cations (e.g., $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$) from the primary minerals. Weathering of carbonates and silicates proceeds simultaneously in the soil environment; however, carbonate weathering reactions are kinetically much more rapid. Carbonate minerals are present in some sedimentary rocks and their metamorphic equivalents, in the scarce igneous rock carbonatite, and in soils found in arid and semi-arid environments. When carbonate minerals are present, the soil is capable of neutralizing acidic deposition rapidly and totally, maintaining the solution pH near a value of 8. As the carbonates become depleted, the pH of the soil will drop and dissolution of silicates becomes the dominant weathering reaction.

Silicate minerals comprise greater than 90% of the minerals present in the Earth's crust and represent an almost unlimited sink for neutralization of acidic deposition. Hydrolysis of silicate minerals results in the release of base cations from the silicate lattice with the consumption of protons equal to the equivalents of base cations released. The amount and rate of acid neutralization depend on the base cation concentration of the mineral, the structure (stability) of the mineral, amount of surface area exposed to weathering, temperature, and the $H^+$ concentration of the soil solution. When comparing basalt versus granite, basalt will have a greater acid neutralization capacity due to higher concentrations of base cations and a mineralogical assemblage that is less stable with respect to chemical weathering (e.g., olivine and pyroxene in basalt versus quartz and K-feldspar in granite). Deeper soils with finer particle-sized parent material (e.g., glacial till versus bedrock) provide a greater surface area for chemical weathering to act upon. Weathering rates show an exponential increase with increasing temperature resulting in greater acid neutralizing capacity in warmer regions (White and Blum, 1995). Weathering rates increase with increasing $H^+$ concentrations below a pH value of 5; the $H^+$ dependence of weathering rates is equal to about $[H^+]^{0.5}$.

While weathering of silicate minerals theoretically has a high capacity to neutralize acid, silicate weathering is a non-equilibrium process limited by reaction kinetics. In reviews of weathering rates based on watershed mass balance studies, Sverdrup and Warfvinge (1988) and Sverdrup (1990) found that most watersheds have a proton consumption rate between 0.1 and 1.5 kmol $H^+$ $ha^{-1}$ $yr^{-1}$. These rates compare with acid deposition rates of up to 7 kmol $H^+$ $ha^{-1}$ $yr^{-1}$. Therefore, silicate-weathering reactions do not keep pace with the higher loadings of acid deposition, especially when considering that internal proton sources add to the total amount of proton loading in an ecosystem.

## Cation exchange reactions

Cation exchange reactions are similar to weathering reactions in their effect on acid/base chemistry. The negatively charged exchange sites are electrically balanced by base cations ($Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$) and acidic cations ($Al^{3+}$ and $H^+$). Exchange reactions neutralize acidity by exchanging base cations for $H^+$ leading to a decrease in the base saturation. In contrast to weathering reactions, exchange reactions are reversible and very rapid. Thus, the soil solution rapidly equilibrates with exchangeable cations, and the equilibrium between the soil solution and exchangeable cations controls the soil solution composition in the short-term. Base cations liberated by mineral weathering are redistributed between the soil solution and exchange sites to attain a new equilibrium. The pool of exchangeable base cations available for pH buffering is the product of the base saturation times the cation exchange capacity (CEC). As long as the base saturation remains above about 10–20%, the acid load in the soil solution will be effectively buffered by exchange reactions. When the base saturation is depleted below levels of 10–20%, those remaining base cations are more tightly held and are less available for pH buffering (Reuss and Johnson, 1986). The base cations released from the exchange sites can be leached from the soil profile with mobile anions (e.g., $SO_4^{2-}$ and $NO_3^-$) originating from strong acid inputs. Some acid neutralization also occurs as pH dependent exchange sites become protonated leading to a loss of CEC as the pH is lowered.

## Anion retention

The retention of anions by sorption or biological uptake consumes protons by removing mobile anions that would otherwise induce the leaching of base cations from the soil profile (Figure A1). Sulfate has a moderate capacity for sorption while $NO_3^-$ has essentially no affinity for sorption to the solid-phase. Sulfate sorption is a concentration dependent process, which means that the capacity to sorb $SO_4^{2-}$ increases as the soil solution $SO_4^{2-}$ concentrations increase. As the $SO_4^{2-}$ retention capacity of soils is exceeded, $SO_4^{2-}$ is leached to deeper soil layers and ultimately to surface waters. Because $SO_4^{2-}$ leaching is always accompanied by cation leaching, leaching of $SO_4^{2-}$ will cause soil acidification (depletion of base cation pools). Sulfate sorption occurs primarily on the surfaces of Al/Fe oxides and hydroxides through a combination of specific and non-specific sorption mechanisms. Thus, soils containing high concentrations of these minerals will have a greater affinity for anion sorption. Anion sorption capacity also increases as the solution pH drops reaching a maximum at approximately pH 4. The $SO_4^{2-}$ sorption reaction is rapid and it appears that the process is not completely reversible leading to an irreversibly adsorbed $SO_4^{2-}$ fraction.

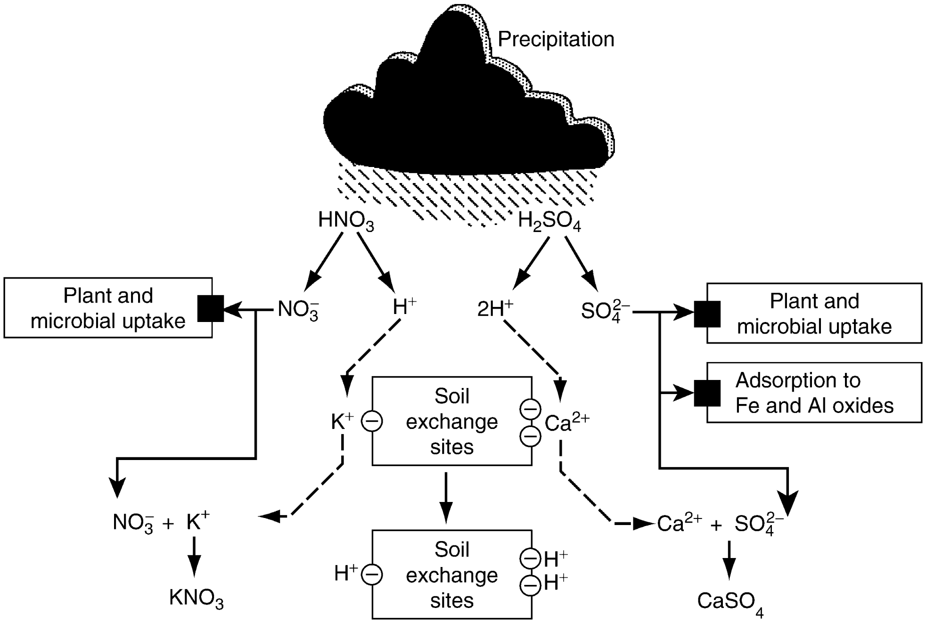

**Figure A1** Atmospheric deposition of nitric and sulfuric acids acidify the soil through replacement of exchangeable base cations with $H^+$ and the subsequent leaching of base cations from the soil with the strong acid anions.

Biological uptake of $SO_4^{2-}$ and $NO_3^-$, originating as strong acid inputs, ameliorates soil acidification by removing mobile anions that could otherwise induce the leaching of base cations. The assimilation of anions is a $H^+$ consuming reaction while the uptake of cations is a $H^+$ liberating reaction (Table A2). When plants assimilate more anions than cations, there is a net consumption of protons and vice versa. With regard to S, the nutritional requirement for most forests is low ($<5$ kg ha$^{-1}$ yr$^{-1}$) and is greatly exceeded by the sulfur deposition rate of many acid impacted ecosystems. There appears to be some increase in the sulfur content of forests in response to increased S deposition, but the increased S accumulation in biomass represents only a small part of the total ecosystem capacity to accumulate sulfur; the majority being adsorbed to soil surfaces.

Nitrogen may be taken up either as a cation ($NH_4^+$) or anion ($NO_3^-$). Uptake of one mole of $NH_4^+$ results in the transfer of one mole of $H^+$ to the soil solution and thus soil acidification. The same magnitude of acidification occurs if $NH_4^+$ is first oxidized to $NO_3^-$ producing $2H^+$, followed by the uptake of $NO_3^-$ which consumes one $H^+$; the net effect being the production of one $H^+$. If however, nitrogen deposition occurs as $HNO_3$ and the $NO_3^-$ is biologically assimilated, there is no acidification because the accompanying $H^+$ is neutralized by the uptake process. The net nitrogen retention capacity of aggrading coniferous forest is generally in the range 5–30 kg N ha$^{-1}$ yr$^{-1}$ (Johnson, 1992). In addition to plant uptake, there is appreciable N immobilization by microbial and abiotic soil processes resulting in increased N storage in soil organic matter pools (Johnson et al., 2000). Therefore, in nitrogen-limited ecosystems, $NO_3^-$ uptake may substantially neutralize the acidity added from atmospheric sources. However, there is evidence that N deposition rates may exceed the forest requirement in some parts of Europe and North America leading to a state of “nitrogen saturation” (Aber et al., 1989; Fenn et al., 1998). Any nitrogen in excess of the nutritional requirement is subject to leaching as $NO_3^-$ from the soil profile resulting in acidification through retention of $H^+$ by the soil and the release and leaching of base cations in the drainage waters. In Europe, sites with deposition less than 10 kg N ha$^{-1}$ yr$^{-1}$ have low $NO_3^-$ concentrations in stream water, whereas all sites receiving $>25$ kg N ha$^{-1}$ yr$^{-1}$ have elevated concentrations (Wright et al., 2001).

## Aluminum dissolution

If all of the above mentioned acid neutralizing processes fail to maintain the soil pH above 5, Al dissolution becomes an important acid neutralizing reaction. The dissolution reaction consumes three moles of $H^+$ for each mole of $Al^{3+}$ released: $Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O$. Neutralization of $H^+$ by dissolution of Al results in potentially high concentrations of soluble $Al^{3+}$ (up to 370 µmol l$^{-1}$ at Solling, FRG, Cronan et al., 1989). The dissolved Al originates from a number of solid-phase pools including exchangeable, organically complexed, hydroxy-Al interlayer material, clay mineral lattices, and primary minerals (Dahlgren and Walker, 1993). The kinetics of Al dissolution are rapid for exchangeable and organically complexed forms, but are very slow for clay and primary mineral dissolution (Dahlgren et al., 1989; Dahlgren and Walker, 1993). Therefore, acid neutralization by Al dissolution depends on the kinetics and quantity of the Al-phase being dissolved. The solid-phase pools of Al represent a very large acid neutralizing capacity and prevent most mineral soils from becoming acidified below a pH range of approximately 4.2–4.5. The major problem with $H^+$ neutralization by Al dissolution is that $Al^{3+}$ is toxic when present at elevated levels. Concentrations of aquo $Al^{3+}$ in excess of 10 µmol l$^{-1}$ have been shown to be toxic to aquatic organisms including fish (Baker and Schofield, 1982), while conifers grown in solution and soil cultures show significant detrimental effects at Al concentrations of approximately 200–250 μmol $l^{-1}$ (Cronan et al., 1989). Some agricultural crops show Al toxicity symptoms at levels as low as 0.4 μmol $l^{-1}$ (Adams and Moore, 1983).

## Example of acidification and recovery of a soil horizon

Results from a laboratory study examining soil chemical processes active during acidification and recovery from sulfuric acid inputs are shown in Figure A2 (Dahlgren et al., 1990). With the onset of acidification, acid neutralization was dominated by sulfate sorption and base cation release. As the exchangeable cations were depleted and sulfate sorption reached equilibrium between the input concentration and the solid-phase, Al dissolution became the dominant proton neutralizing reaction. The recovery stage was characterized by the release of previously sorbed $SO_4^{2-}$. Thus, $SO_4^{2-}$ desorption reactions were a source of acidity that continued to be neutralized by Al dissolution even during the recovery stage. The retention of base cations by the solid-phase during the recovery stage also contributed a small amount of acidity as the exchangeable cation composition equilibrated to a new equilibrium having a greater base saturation. There is a considerable lag in both the acidification and recovery stages due to proton buffering by sulfate sorption/desorption, base cation retention/release, and Al dissolution. The contribution of chemical weathering reactions was too slow to exhibit an influence in this study.

Similar processes have been demonstrated for acid neutralization in impacted ecosystems. Measurable changes in soil acidification in heavily impacted regions of Europe are only observed in the upper 30 cm of the soil profile. The observed changes include decreased pH, depletion of exchangeable base cations and solid-phase aluminum pools, decreased C/N ratios and increased concentrations of adsorbed $SO_4^{2-}$. Soil acidification proceeds progressively downward in the soil as the buffering capacity of the upper soil horizons is exhausted.

Decreases in sulfur (38–82%) and nitrogen (20%) deposition in Europe over the past decade have allowed a preliminary analysis of the recovery stage (Prechtel et al., 2001; Wright et al., 2001). Sulfate concentrations in stream waters have decreased significantly; however, acidification reversal was delayed (Prechtel et al., 2001). Release of adsorbed sulfate leads to the delay of acidification reversal (Figure A2). Sulfate fluxes in catchments with deeply weathered soils and high sulfate storage capacity responded more slowly to decreased deposition than catchments with thin soils and relatively small sulfate storage capacity. Compared to the sulfur response, there was an overall lack of significant trends in nitrate leaching in stream waters of Europe following a 20% reduction in nitrogen deposition over the past decade (Wright et al., 2001). This analysis suggests that recovery from nitrogen saturation is a slow process that requires many decades, at least at levels of N deposition typical for Europe. In contrast, field experiments with roofs to exclude acid deposition all show immediate and large decreases in $NO_3^-$ leaching following large reductions in N deposition. These experiments showed that terrestrial ecosystems exhibit extreme hysteresis in $NO_3^-$ leaching in response to N deposition; increased $NO_3^-$ leaching occurs first after many decades of high N deposition, but decreased $NO_3^-$ leaching occurs immediately following decreases in deposition. Reductions in particulate emission throughout Europe and North America have further delayed recovery from acidification due to the decrease in base cation deposition associated with particulate matter (Driscoll et al., 1989).

## Acid deposition stresses on ecosystems

The direct impact of acid deposition on biological processes is often difficult to determine. High $H^+$ concentrations lead to elevated levels of soluble $Al^{3+}$, which have been shown to produce severe ramifications on terrestrial and aquatic species. High $Al^{3+}$ concentrations can be directly toxic to plants resulting in a death of fine roots and mycorrhizae symbionts and can interfere with the acquisition of base cations and other nutrients from the soil solution inducing nutrient deficiencies and imbalances in plants. Not only the $Al^{3+}$ concentrations,

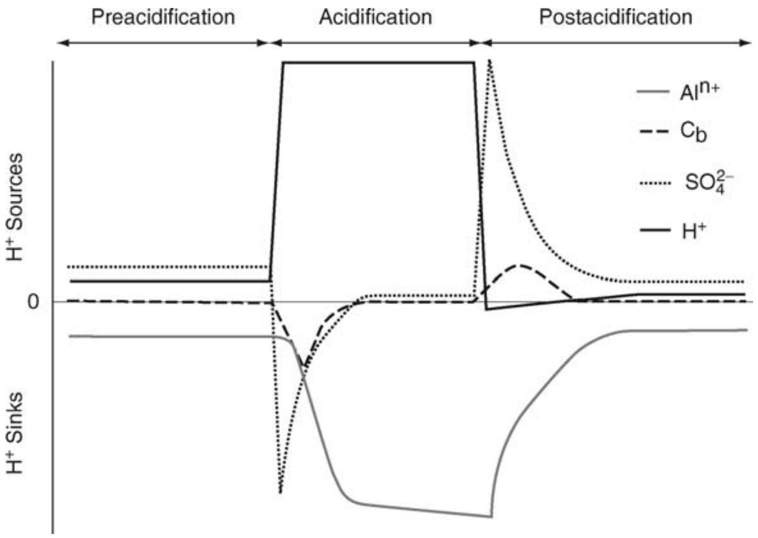

**Figure A2** Proton-producing and -consuming reactions regulating acid/base chemistry during acidification and recovery of a soil horizon from sulfuric acid inputs (*$Al^{n+}$*: Al precipitation/dissolution; *$C_b$*: base cation retention/displacement from cation exchange sites; *$SO_4^{2-}$*: sulfate adsorption/desorption; *$H^+$*: strong acid input/release of protons).

but also the Al/Ca ratio of the soil solution appears to be an important factor regulating nutrient acquisition (Cronan and Grigal, 1995). Base cation ($Ca^{2+}$, $Mg^{2+}$ and $K^{+}$) deficiencies develop as the base saturation is depleted due to displacement of base cations by acidic cations and the base cations are subsequently leached from the rooting zone with associated mobile anions (e.g., $SO_4^{2-}$ and $NO_3^{-}$). A loss of membrane-bound calcium makes some tree species more susceptible to freezing damage, while calcium and magnesium deficiencies make some trees more susceptible to insect infestations and drought stress. Increased acidity also affects adsorption, mobility and chelation capacity of metal-complexing organics and mobility and bioavailability of heavy metals, such as Pb, Zn, Cu, Mn and Cd.

In nitrogen limited ecosystems, the deposition of additional N may initially increase plant growth inducing deficiencies of other nutrients, such as base cations or phosphorous. As ecosystems become nitrogen saturated, nitrate leaching can lead to elevated nitrate concentrations in surface and ground waters. Higher soil nitrate concentration leads to increased denitrification resulting in production of $N_2O$, a powerful greenhouse gas. Nitrogen deposition lowers the C/N ratio of organic matter potentially leading to an initial increase in the decomposition rate. However, as the soils become more strongly acidified, there appears to be a change in the composition of microbial populations, which may ultimately lead to decreased decomposition (Greszta et al., 1992). The effect of acidification on microbial processes appears to be highly variable depending on several characteristics of the ecosystem. Increased availability of nitrogen in terrestrial ecosystems also affects species diversity, often promoting an increase of invasive species (Tillman, 1987).

Deposition of nitrogen on lakes and their watersheds leads to increased algal biomass and a loss of water clarity (Tarnay et al., 2001). Severe lake acidification (low pH and elevated $Al^{3+}$) has been shown to adversely impact lower food-web transfers (i.e., phytoplankton-zooplankton) that ultimately impact the higher components of the food web (i.e., fish). Aquatic species diversity is progressively changed as aquatic ecosystems become acidified. Effects of acidification include long-term increases in mortality, emigration, and reproductive failure of fish, as well as short-term acute effects (Driscoll et al., 2003). Acidification of lakes and streams can increase the amount of methyl mercury available in aquatic systems (Driscoll et al., 1994). Coastal eutrophication is becoming common in regions with elevated nitrogen deposition leading to excessive production of algal biomass, blooms of toxic algal species, hypoxia, fish kills, and loss of important plant and animal diversity (Jaworski et al., 1997).

**Table A3** Characteristics of soils and ecosystems most susceptible to acidification

| Soil/ecosystem characteristic |
|---|
| Naturally acidic soil – reduced acid neutralizing capacity |
| Shallow soil – low soil water residence time |
| Coarse texture – low surface area and residence time |
| Few easily weatherable minerals – low acid neutralization by chemical weathering |
| Parent materials with low base cation content – few bases released upon weathering |
| High precipitation – low soil water residence time |
| Soils with restrictive layer that reduces water permeability – low soil water residence time |
| Low CEC and base saturation – low buffering capacity |
| Low content of Al and Fe oxides/hydroxides – low anion sorption |
| High fertility status – low capacity to retain additional nutrients |
| Low vegetation coverage – low uptake of strong acid anions |

## Characteristics of acid sensitive soils

Characteristics of soils most susceptible to the adverse effects from acid deposition are shown in Table A3. Shallow, coarse-textured soils with acid pH values, low base saturation and base-poor parent material are the most susceptible to severe acidification by acid deposition. The greater the pool of easily weathering minerals, exchangeable base cations, and Al// hydroxides, the greater the potential for neutralization by mineral weathering, exchange reactions, and anion sorption, respectively. Ecosystems with abundant vegetation have a greater potential for acid neutralization by uptake of strong acid anions ($SO_4^{2-}$, $NO_3^{-}$).

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## Cross-references

Acid Soils
Acidity
Nitrogen Cycle
Podzols
Sorption Phenomena
Sulfur Transformations and Fluxes
Thionic Soils

# ACID SOILS

Acid soils are defined in terms of redox-pH master variables in Figure A3. In the WRB system of classification, the relevant reference soil groups with widest distribution are Acrisols, Ferralsols and Podzols, which are the main focus of this article (Table A4). Acid soils also occur in Andosols, Arenosols, Alisols, Albeluvisols, Cambisols, Histosols, Leptosols, Plinthosols, Planosols, Fluvisols, Regosols and Umbrisols. In those Fluvisols and mine soils (Espoli-Anthropic Regosols) containing pyrite, extreme acidity develops on oxidation.

In the three groups of wide distribution, acidity ranges from a pH between 3.5 and 4 in the A horizons of Podzols to about 6 as an upper limit in Ferralsols. The values are set (see Figure A4) by the dissociation of $H^+$ from the carboxyl groups of humic materials ($pK_a$ from 3.5 to 6), and by the system $H_2O$–$CO_2$, which enters the soil via atmospheric precipitation at a pH of 5.7. It may acquire a $CO_2$ concentration two orders of magnitude greater than the atmospheric value within the upper part of the solum, as a consequence of the metabolic activities of roots and of microorganisms (in breaking down organic matter). Gleyed varieties of all three soils are found in regions of high water-table lows such as river valleys for example.

The worldwide distribution of Acrisols, Ferralsols and Podzols is shown in Table A4. Acrisols and Ferralsols are predominantly soils of the humid tropics and subtropics, while Podzols, although common in areas with precipitation much greater than evapotranspiration, occur mainly in cold to temperate zones. An important consequence is that components from organic sources play a more important role in the genesis of Podzols, than in Acrisols and Ferralsols, simply because organic matter tends to have a much longer half-life in colder than in warmer climates. Another important consequence is the poor weathering displayed by the materials on which Podzols develop, which contrasts with Acrisols and Ferralsols. In this case, however, parent material and time also play a role.

## Acrisols and Ferralsols

As well as tropical and subtropical occurrences, Acrisols and Ferralsols are also found to a lesser degree in the warmer parts of humid temperate regions. Their characteristic occurrence however is in cratonic regions (of S. America and Africa especially) on surfaces peneplained in Tertiary and Pleistocene times. Elsewhere, they are found on easily weathered basic igneous rocks, particularly pyroclastics, where leaching is facilitated by the porous, fragmental nature of the parent material.

Acrisols and Ferralsols are deep, highly weathered and leached soils that are stripped down to simple assemblages in the four-component system $SiO_2$–$Al_2O_3$–$Fe_2O_3$–$H_2O$. Except in gleyed varieties Fe is in the ferric state in the minerals goethite or hematite. As a result the solum is commonly yellow or red in color. Prolonged hydrolysis and leaching destroys all primary alumino-silicates, so that kaolinite (monosiallitization) and/or gibbsite (allitization) tend to dominate the clay fraction and account for the low CEC (Figure A5).

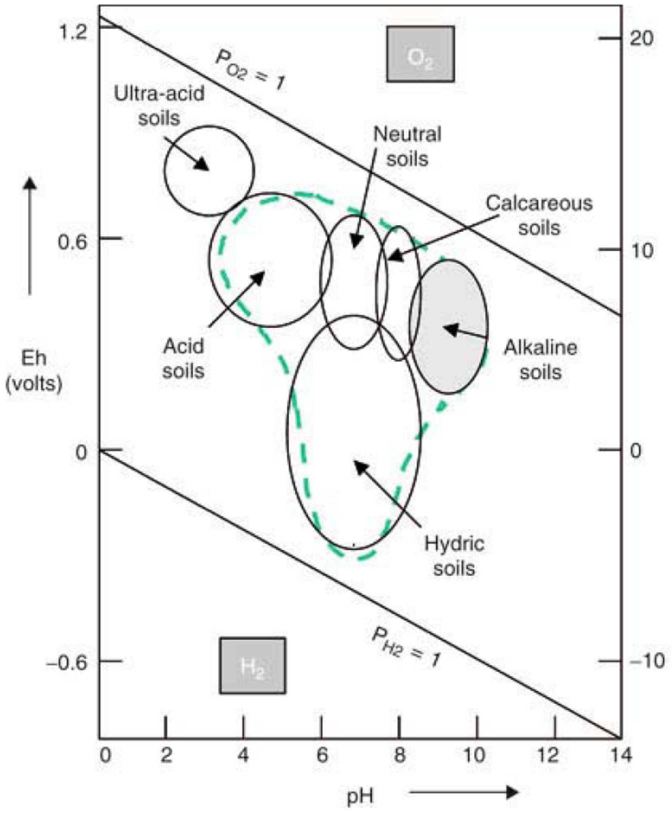
## Podzols

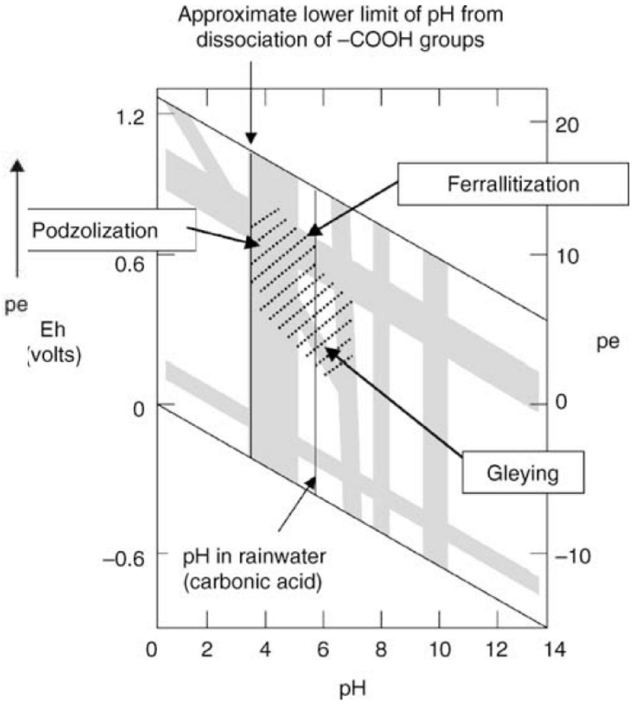
In essence, Podzols form by the titration of a material with a low capacity for buffering acid, against an excess of organic acids. The net release of acid breakdown products from organic debris is influenced by environmental conditions (favored when microbial activity is impaired) and type of vegetation. The acid buffering capacity of the parent material is determined by lithology and/or climate. As temperature decreases, lithology becomes less determinant in Podzol formation. Thus, whereas in tropical environments, Podzols form on sandy materials, which are almost exclusively quartzitic, in colder environments, parent material is more variable. The shifting point of this titration, which depends on both the total organic acid loading and the total base supplied, determines the depth at which the new phases form. That is, organic complexants percolating through the soil profile remove (a process called chelluviation) Fe and Al until the latter become saturated and precipitate, forming the B spodic horizon (a process called illuviation). The eluviated horizon takes on a bleached appearance, as only resistant minerals, such as quartz, remain, and is called the albic horizon. Root growth is promoted in the B spodic horizon – because of its greater water and nutrient availability and less acidity compared with the E eluviated horizon – further enhancing organic matter accumulation at depth.

The pedogenesis of other soils with incipient weathering and an acid trend, developed under similar environmental conditions to Podzols, (Haplic Umbrisols or any Umbric or Fulvic Andosols for example) could be described in a similar way. However, as in these soils the acid buffering capacity of the parent material is greater than in Podzols, the distance traveled by the organic ligands is less (in Umbrisols) or nil (in Andosols).

The clay fraction of a mature Podzol resembles that of an Acrisol or Ferralsol in tending to be enriched in the components $SiO_2$–$Al_2O_3$–$Fe_2O_3$–$H_2O$. However, the process is incipient, since unlike the tropical soils, Podzols, Umbrisols and Umbric or Fulvic Andosols tend to be on young (commonly postglacial) landscapes. Consequently amorphous or short-range order phases commonly occur. On older landscapes the amorphous and short-range order phases will age to progressively more stable minerals by the process known as (Ostwald) ripening. The specific ripening sequence will depend upon the activity of silica in the system (see Figure A6).

Podzols are found in Boreal regions of the cratons of the Northern hemisphere, as well as in temperate, wet zones such as the western Cordilleras of Canada, Chili and Alaska, and along sandy coasts of Western Europe (the Landes of Atlantic France for example). Out of nearly half a billion hectares worldwide, all except some 30 million are in temperate to cool regions. The balance is in the tropics, particularly on alluvial quartz sands. Found along the Rio Negro and in the Guyanas of South America, in SE Asia (Kalimantan, Sumatra, Papua) and in northern Australia.





**ıre A4** Soil forming processes found among acid soils, displayed on the pedogenic grid.

**Table A4** Distribution of the three major groups of acid soils (in thousands of hectares)

| | Africa | Australasia | Europe | North America | North and C. Asia | South and C. America | South and SE Asia | Total |
|---|---|---|---|---|---|---|---|---|
| Acrisols | 92 728 | 32 482 | 4 170 | 114 813 | 148 241 | 341 161 | 263 005 | 996 600 |
| Ferralsols | 319 247 | 0 | 0 | 0 | 0 | 423 353 | 0 | 742 600 |
| Podzols | 11 331 | 8 459 | 213 624 | 220 770 | 21 825 | 5 522 | 5 982 | 487 513 |

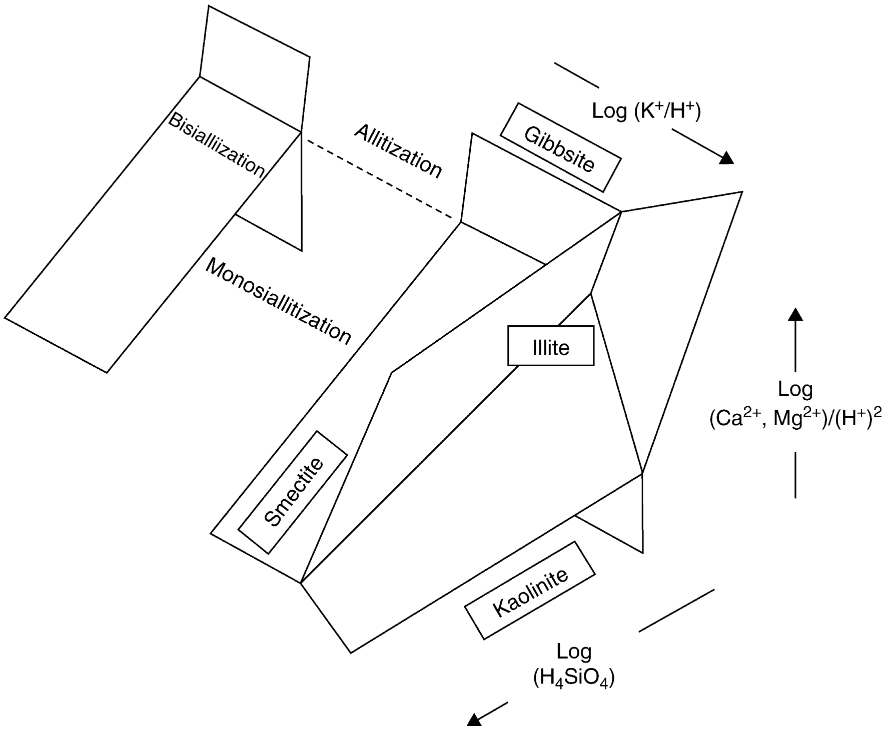


**Figure A5** Mineral formation in acid pedogenesis tends to lead to kaolinitic or gibbsitic assemblages in Acrisols and Ferralsols. The chemical evolution of the soil is towards the bottom right hand corner of the schematic diagram (modified from Chesworth, 1980).

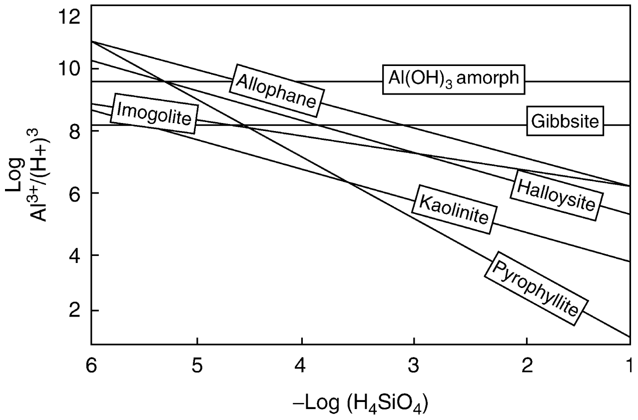


**Figure A6** Diagram to illustrate Ostwald ripening. In the system $SiO_2$–$Al_2O_3$–$H_2O$ the sequence of minerals that form at –log($H_4SiO_4$) = 4, for example, might be allophane, halloysite, kaolinite.

## Agricultural problems of acid soils

High acidity is accompanied by a low cation-exchange capacity and a low base saturation, both of which lead to problems when these soils are utilized in agriculture. Nutrient deficiency and high levels of exchangeable aluminum are the main problems. Al toxicity is a particular management problem. Al toxicity occurs mainly when $pH(H_2O) < 5$, and CEC is >60% Al. The deleterious effect of this so-called alic character is greater in those acid soils poor in organic matter in which 2 : 1 clay minerals are abundant. High levels of exchangeable and soluble Al also promote P fixation and slow down nitrification and $N_{20}$ fixation, leading to deficiency of these nutrients. All this impairs plant growth, leaf functionality (because of yellowing and defoliation), and root development, which, in turn, increases plant susceptibility to other stresses and plant diseases, thereby further decreasing crop yields.

Acid soils require liming and constant fertilization when used in agricultural production. Macronutrients and, in some cases, micronutrients (e.g., molybdenum) have to be added.

In Acrisols and Ferralsols, the exchange capacity of the organic matter is very important because the clay fraction is made up of minerals of low cation-exchange capacity. However the organic matter of these soils is rapidly mineralized under tropical climates, with labile organic C only present at the surface as a consequence of recent deposition of plant and animal residues. In some cases, there can be a fraction of recalcitrant organic C stabilized by sorption processes on to Al and Fe oxihydroxides (such as in some Umbric Acrisols and Ferralsols).

In addition to problems already noted, most Podzols have additional problems. They form generally on sandy materials and may therefore be droughty by reason of excessive drainage. Furthermore, the leaching out of iron and its subsequent accumulation in lower horizons may lead to a thin, impervious iron pan. Drainage may then be restricted so that the soil develops hydromorphic properties. Drainage may be improved by breaking up the iron pan.

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## Cross-references

Acrisols
Andosols
Clay Mineral Alteration in Soils
Clay Mineral Formation
Ferralsols
Podzols
Weathering Systems in Soil Science

# ACID SULFATE SOILS

See *Thionic or Sulfidic soils*.

# ACIDITY

Soil acidity is a term used to describe acid soils; i.e., soils with a pH value <7.0 (Gregorich, 2001). When used as a quantitative term, soil acidity is considered a capacity factor and refers to the total acidity contained in a given soil or soil horizon. Soil pH, a measure of the negative logarithm of the hydrogen ion activity in the soil solution, is used as an indicator of the degree of acidity or alkalinity in soil (Table A5). Another term that is sometimes associated with the degree of acidity of a soil as a function of soil pH is soil reaction.

When used in a qualitative manner, the term soil acidity refers to a variety of possible chemical processes, which are known to occur in acid soils (Thomas and Hargrove, 1984; Sumner et al., 1991; Rengel, 2003). The combined interaction of these processes influences the amount and speciation of nutrient ions in the soil solution and thus their availability for plant growth. In general, an increase in soil acidity is associated with a decrease in the availability of nutrient ions (particularly calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), phosphorus, and molybdenum) and an increase in the presence of acidic cations (hydrogen ($H^+$), manganese ($Mn^{2+}$), aluminum ($Al^{3+}$), and iron ($Fe^{3+}$)) which are known to be toxic to most plants and soil microorganisms (Ritchie, 1989; Robson and Abbott, 1989). The exact mechanisms that result in the deleterious effects observed with an increase in soil acidity have been reviewed elsewhere (Clark, 1984; Foy, 1984). However, toxicity due to the increased activity of $Mn^{2+}$, $H^+$, and especially $Al^{3+}$ ions in the soil solution is recognized as the most common cause of reduced yields. For most agronomic crops, it is the dominance of $Al^{3+}$ on the ion-exchange complex in acid soils that directly affects plant growth (Kamprath, 1970). Because of this, the term soil acidity is sometimes assumed to be synonymous to the presence and subsequent chemical reactions of $Al^{3+}$ ions in acid soils. This is not always true, especially in organic soils, and the use of the term soil acidity in this context should be avoided.

**Table A5** Descriptive terms commonly used to describe the degree of acidity or alkalinity of a soil[a]

| Descriptive terms | pH range |
|---|---|
| Extremely acid | <4.5 |
| Very strongly acid | 4.5 – 5.0 |
| Strongly acid | 5.1 – 5.5 |
| Moderately acid | 5.6 – 6.0 |
| Slightly acid | 6.1 – 6.5 |
| Neutral | 6.6 – 7.3 |
| Slightly alkaline | 7.4 – 7.8 |
| Moderately alkaline | 7.9 – 8.4 |
| Strongly alkaline | 8.5 – 9.0 |
| Very strongly alkaline | >9.1 |

[a] Source: Soil Science Society of America (1987).

The amelioration of an acid soil with lime to remove the deleterious effects of soil acidity on plant growth requires knowledge of the relationship between the acidity present and soil pH. This is necessary in order to avoid over-liming which also can have a negative impact on plant growth (Kamprath, 1971). Titration of an acid soil with a strong base is one way to obtain the desired relationship between acidity and soil pH. Sources of acidity that react with base include exchangeable acidity and residual acidity. Exchangeable acidity, or salt-replaceable acidity, refers to the acidic cations (primarily $Al^{3+}$ and $Fe^{3+}$) that can be replaced from the ion-exchange complex by an unbuffered salt solution, such as potassium or sodium chloride (Gregorich, 2001). Measurable amounts of exchangeable $H^+$ may also be present due to the acid functional groups associated with soil organic matter (SOM) (Stevenson, 1982).

The remaining soil acidity that cannot be replaced by an unbuffered salt solution is called the residual acidity. Quantification of the residual acidity in an acid soil is difficult because the rate of reaction with base is generally slower than with exchangeable acidity. Sources of residual acidity include $Al^{3+}$ and $Fe^{3+}$ tightly bound by SOM and the acid-functional groups located on the edges of layer silicate minerals and the surfaces of Fe and Al oxides and oxyhydroxides (Thomas and Hargrove, 1984; Sumner et al., 1991). Liming criteria based on exchangeable acidity alone usually requires a multiplication factor to account for the presence of residual acidity. This factor ranges between 1.5 and 3.3 for most acid soils (van Lierop, 1990), demonstrating that residual acidity is not an insignificant fraction of the total acidity. Additional sources of acidity that release $H^+$ to the soil solution include oxidation-reduction or redox reactions, addition of soluble salts (fertilizers), and base cation (Ca, Mg, K) removal during plant uptake (acidification of the rhizosphere) (Thomas and Hargrove, 1984). These sources are more transient in nature and are not included in most quantitative laboratory procedures used to determine the amount of acidity in a soil. The acidity generated from these transient sources, however, must be accounted for in any successful management scheme to optimize crop yields.

## Methodology

Methods to determine soil acidity can be divided into two groups: (1) methods that are designed to give quantitative estimates of the total or some fraction of soil acidity in a given soil, and (2) soil test (quick) methods designed to determine the lime requirement of a large number of different types of acid soils (see Sparks, 1996).

## Exchangeable acidity

The most common quantitative procedure for determining exchangeable acidity (exchangeable $H^+$ and $Al^{3+}$) is extraction with a neutral solution of potassium chloride (1 kmol $m^{-3}$ KCl; Thomas, 1996). The basic procedure employs the titration of an aliquot of the extracting solution to the phenolphthalein endpoint with standardized base. The equivalents of base added corrected to the volume of the extracting solution is the estimate of total exchangeable acidity. This is followed with addition of sodium fluoride (1 kmol $m^{-3}$ NaF) to release the hydroxyl ions ($OH^-$) added with base that are bound to the $Al^{3+}$ in the original extract. Back titration with standardized acid yields the quantitative estimate of exchangeable $Al^{3+}$. A positive difference between the estimates of total exchangeable acidity and exchangeable $Al^{3+}$ is a measure of the exchangeable $H^+$ present in the soil. Modifications to the basic procedure generally consist of direct determination of the $Al^{3+}$ in the extract either by atomic absorption spectroscopy or using one of several different colorimetric procedures (Barnhisel and Bertsch, 1982; Bloom and Erich, 1989). Direct determination of $Al^{3+}$ avoids a positive bias in the procedure due to titration to the phenolphthalein endpoint.

Single extractions of exchangeable acidity ($H^+$ and $Al^{3+}$) using unbuffered salt solutions is quantitative for pure layer silicate minerals (Thomas, 1982), but not for most soils (Oates and Kamprath, 1983). Successive extractions of soils, especially soils containing measurable amounts of SOM, results in the continued release of Al to the extracting solution. The source of this residual extractable Al is assumed to be $Al^{3+}$ tightly bound to SOM. Other extracting salt solutions that have been used in an attempt to include this residual extractable Al fraction in the estimate of exchangeable acidity include lanthanum chloride (1 kmol $m^{-3}$ $LaCl_3$) and copper chloride (1 kmol $m^{-3}$ $CuCl_2$) (Bloom et al., 1979; Juo and Kamprath, 1979). At pH values $<7$, lanthanum is a trivalent ion ($La^{3+}$) and its use is meant to promote ion exchange with $Al^{3+}$ bound to SOM. The cupric ion ($Cu^{2+}$) is known to have a high affinity for the functional groups contained in SOM (Bloom, 1981), and it is reasoned that it should replace $Al^{3+}$ ions not readily displayed by mono- or divalent base cations. Both extracting solutions are quantitative when dealing with SOM extracts or peat, but still continue to release Al with successive extractions of soil samples. One source of this additional release of Al may be dissolution of layer silicate minerals or hydroxy-Al-interlayered 2 : 1 layer silicate minerals (HIM) as a result of the acidity (pH $< 4$) of the equilibrated soil-extracting solution suspensions (Oates and Kamprath, 1983). The terms extractable acidity or extractable Al are often used instead of exchangeable acidity or exchangeable Al because of the inability of unbuffered salt solutions to distinguish between different sources of acidity in whole soils (Barnhisel and Bertsch, 1982).

Total potential acidity is determined in acid soils using the barium chloride (1 kmol $m^{-3}$ $BaCl_2$) – triethanolamine (0.2 kmol $m^{-3}$ TEA) procedure (Thomas, 1982). The term potential acidity refers to the exchangeable plus residual acidity contained in a soil as referenced to a given pH value. A $BaCl_2$ solution, containing TEA (pH 8.2) as a buffer, is allowed to equilibrate with a soil sample. After filtration, the filtrate is titrated with standardized acid to the methyl red – bromocresol green end point. The equivalents of acid required are taken as the measure of the total potential acidity present in the soil. The pH of 8.2 selected for the TEA buffer solution corresponds to the $H^+$ activity maintained in solution by calcium carbonate ($CaCO_3$) in equilibrium with the partial pressure of carbon dioxide ($CO_2$) in the atmosphere. The basic premise of the procedure is that a soil in equilibrium with free calcium carbonate (lime) will have a pH = 8.2, and by definition, contain no exchangeable or residual acidity. Variations to the original $BaCl_2$-TEA procedure include leaching with a neutral salt solution prior to addition of the $BaCl_2$-TEA solution. This modification provides an estimate of both the exchangeable and residual acidity in a soil.

Potentiometric titrations of acid soils with strong base (e.g., sodium, potassium, or calcium hydroxide) to a fixed endpoint provides not only a measure of the exchangeable and residual acidity present, but also an indication of how the amount of acidity varies with solution pH. The slope of the relationship between the equivalents of base added and suspension pH provides an estimate of the buffer capacity of a soil in a given pH range. Buffer capacity refers to the ability of the soil to resist changes in pH. The primary limitation of this procedure, however, is the slowness of the neutralization reaction near the end-point (Thomas and Hargrove, 1984). The shape of the relationship between equivalents of base added and suspension pH is also a function of the concentration and charge of the neutral salt cation used during the titration. The time required to complete the titration prohibits its use as a routine method for a large number of soil samples.

## Lime requirement

Soil test methods designed to determine the lime requirement of a soil are generally based on the assumption that there is an optimum soil pH for the growth of a given crop on a given soil type. The amount of lime required is the amount needed to change the initial soil pH to the optimum soil pH. However, the methods selected for determining the lime requirement of a soil must also be applicable to a wide range of different soil types and be capable of processing relatively large numbers of soil samples in a short period of time. The most common approach used today that meets these criteria is to equilibrate the soil with a buffer solution (Table A6). The buffer solution itself is usually a mixture of two or more buffers such that there is a linear change in pH with incremental additions of acid ($H^+$) over a range of several pH units (e.g., pH 7 to pH 4). This linear change in pH with incremental addition of acid is in turn calibrated to the lime requirement for a particular soil group; the later being determined from lime incubation studies or titration with base. Allowances are also made for the crop to be grown, depth of rooting volume, composition and particle size of liming material and method of incorporation (van Lierop, 1990). Using this approach, the lime requirement for a soil is essentially equal to the change in the pH of the buffer solution after equilibration with the acidic soil.

The basic limitation of this approach is the accuracy and precision possible when the procedure is used on a routine basis with large numbers of soil samples. A change of $+0.1$ pH units can represent a difference in lime requirement of between 400 to 600 kg of lime $ha^{-1}$. Interlaboratory comparisons have suggested differences in pH measurements of as much as $+0.4$ pH units may occur for the same soil samples (van Lierop, 1990). Differences of this order of magnitude represent substantial errors in the estimation of the lime requirement for a soil. Buffer solutions also tend to be less sensitive in predicting lime requirement for soils with pH values $>6$. Offsetting these potential errors is the reality that most lime requirement recommendations are not strict quantitative

**Table A6** Common names and composition of buffer solutions used to determine lime requirements[a]

| Name | Buffer reagents | Comments single buffer procedures |
|---|---|---|
| Shoemaker, McLean, and Pratt (SMP) | *p*-nitrophenol, potassium chromate, triethanolamine | curvilinear calibration, best for high lime requirement soils, over-liming possible for low lime requirement soils |
| Mehlich | triethanolamine, acetic acid | designed to neutralize exchangeable acidity, no optimum pH assumed |
| Woodruff | *p*-nitrophenol, magnesium oxide, calcium acetate | curvilinear calibration, best for low lime requirement soils |
| Adams and Evans | *p*-nitroprenol, boric acid | designed for low lime requirement soils (ultisols) |
| Nômmik | imidazole, malic acid, sodium or potassium acetate | calibrated to pH 7.0, limited calibration data available |
| Yuan | imidazole, pyridine, tris[b], potassium chromate | requires two soil-buffer pH readings, May underestimate lime requirement |
| SMP-Double Buffer | *p*-nitrophenol potassium chromate, triethanolamine | requires two soil-buffer pH readings, improves prediction for low lime requirement soils |

[a] Sources: Yuan, 1974; McLean, 1978; Adams, 1984; van Lierop, 1990.

[b] tris (hydroxymethyl)-aminomethane.

estimates and that the potential error associated with the pH measurement is not likely to cause major problems compared to the advantages of the buffer procedures.

Alternative methods for determining the lime requirement of a soil include estimating lime requirement from soil properties without directly measuring soil acidity, and calculating lime application rates necessary to only neutralize exchangeable $Al^{3+}$ (van Lierop, 1990). Indirect lime requirement determinations are based on statistical correlations between the lime requirement and soil properties (usually exchangeable $Al^{3+}$, SOM, and clay content) and the desired change in soil pH. The approach is accurate but does require calibration with different soil types before use. Liming to neutralize exchangeable $Al^{3+}$ is based on the fact that crop yield responses to liming are inversely correlated with exchangeable $Al^{3+}$ (Kamprath, 1970). If the cost of liming is a factor for successful crop production, lime application rates based on exchangeable $Al^{3+}$ provides a way to increase yields with limited economic resources. This may, however, require more frequent addition of lime in order to maintain the desired soil pH (van Lierop, 1990).

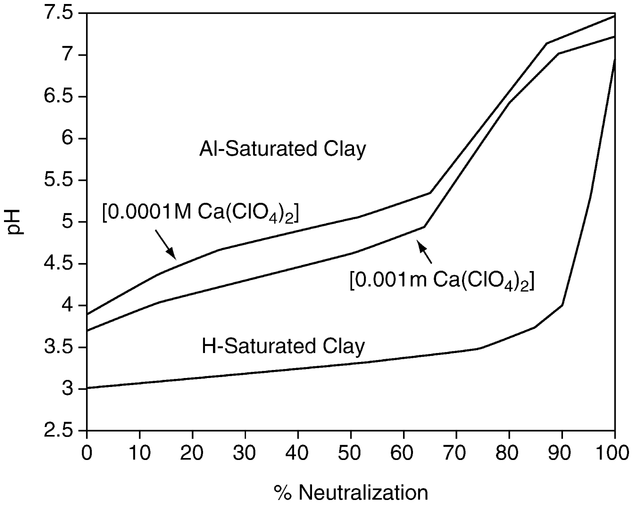

**Figure A7** Theoretical titration curve for an Al-saturated and a H-saturated layer silicate mineral.

## Applications

### Exchangeable acidity

Acid attack of primary and secondary aluminosilicate minerals during chemical weathering is the primary source of exchangeable $Al^{3+}$ in acid soils. Attempts to generate $H^+$-saturated layer silicate minerals have demonstrated that such preparations are unstable. The presence of $H^+$ ions to balance the net negative charge of the layer silicate minerals accelerates their dissolution with release of $Al^{3+}$ and silicic acid ($H_4SiO_4$) to solution. The $Al^{3+}$ ions, in turn, replace the neutralized $H^+$ ions in balancing the net negative charge of the layer silicate mineral. If allowed to go to completion, the dissolution reaction will continue until the clay is essentially 100% saturated with $Al^{3+}$ ions (no exchangeable $H^+$ remains). Potentiometric titrations of montmorillonite suspensions, which are freshly prepared and truly $H^+$-saturated, yield titration curves, which resemble those of a strong mineral acid (Figure A7). Such behavior is consistent with the observation that little or no exchangeable $H^+$ remains associated with aged layer silicate mineral suspensions. These results also explain why appreciable amounts of exchangeable $H^+$ are not associated with clay minerals in acid mineral soils.

During the conversion to an $Al^{3+}$-saturated clay, there is essentially no net change in the equivalents of acidity originally added to form the $H^+$-saturated clay. This is because of the ability of $Al^{3+}$ ions to undergo hydrolysis in aqueous systems. Hydrolysis can be described as a series of consecutive proton transfer reactions between hydrated metal ions and water molecules that result in the release of $H^+$ ions and the formation of monomeric hydrolytic Al species (Baes and Mesmer, 1976). The only difference between $H^+$ produced by Al hydrolysis as opposed to being present as exchangeable $H^+$ is that the extent of the hydrolysis reaction is a function of the activity of $H^+$ ions in solution; i.e., hydrolysis of an acidic cation resembles the behavior of a weak acid rather than a strong acid.

Once an $Al^{3+}$ ion is displaced from a layer silicate mineral by ion exchange, it will begin the step-wise release of $H^+$ as represented by the following equations:

$$Al(H_2O)_6^{3+} + H_2O = Al(OH)(H_2O)_5^{2+} + H_3O^+(K_1) \quad (1)$$

$$Al(H_2O)_6^{3+} + 2H_2O \rightleftharpoons Al(OH)_2(H_2O)_4^{+} + 2H_3O^+\ (K_2) \quad (2)$$

$$Al(H_2O)_6^{3+} + 3H_2O \rightleftharpoons Al(OH)_3(H_2O)_3^{0} + 3H_2O^+\ (K_3) \quad (3)$$

where $K_1$, $K_2$, and $K_3$ are the respective dissociation constants.

Because of its small ionic radius, the $Al^{3+}$ ion assumes a six-fold coordination with the surrounding water molecules. The subsequent hydrolysis is similar in reaction to a polyprotic weak acid with the respective p$K$ values (the negative logarithm of the dissociation constant) indicative of the pH of maximum buffer capacity. The monomeric hydrolytic Al species that is produced at each step can undergo further ion-exchange reactions, or in the presence of base, continue to undergo hydrolysis until the original $Al^{3+}$ ion is completely neutralized.

Unlike a polyprotic weak acid, the titration of an $Al^{3+}$-saturated layer silicate mineral does not result in a plot of equivalents of base added versus equilibrium pH with three distinct buffer regions (Figure A7). This is because the chemistry of hydrolysis of $Al^{3+}$ beyond the first hydrolysis reaction ($pK_1 = 5.0$) becomes confounded by secondary polymerization reactions that result in the formation of polynuclear hydroxy-Al species of differing basicity (OH : Al ratios; Bertsch, 1989). Because of their relatively high positive charge density, these polymeric Al species are attracted to and stabilized on the surfaces of the negatively charged layer silicate minerals (Adams, 1984). In soils, they also interact with the functional groups of SOM. These surface bound polymeric Al species continue to undergo hydrolysis and react with added base, but the exact p$K$ values for these reactions are not known. The result of this combination of reactions is that the titration curve of an $Al^{3+}$-saturated layer silicate mineral is in general characterized by only one broad buffer region (Figure A7). Below the average p$K$ for this buffer region, $Al^{3+}$ is the dominant ion both in solution and on the ion-exchange surface of the clay mineral. The actual concentration of $Al^{3+}$ in solution and the observed pH is a function of the concentration and charge of the neutral salt cation used during the titration. With addition of base, polymeric Al species are formed at the expense of exchangeable $Al^{3+}$, and the concentration of $Al^{3+}$ in solution decreases until essentially no exchangeable $Al^{3+}$ remains associated with the layer silicate mineral. This point does not represent 100% neutralization, however, since the charged polymeric species are still bound to the clay surface. The negative charge associated with the layer silicate mineral requires a higher concentration of hydroxyl ions ($OH^-$) in solution to complete the neutralization reaction (i.e., a higher pH). Complete neutralization of the original $Al^{3+}$ results in 100% base saturation of the clay.

An analogous series of reaction occurs when base (e.g., in the form of lime) is added to an acid mineral soil. A pH 5.5 is typically cited as the reference point above which no exchangeable $Al^{3+}$ remains associated with the soil layer silicate minerals. The actual pH at which this occurs will vary between soil types and also within the same soil. Additions of fertilizer increase the concentration of neutral salt cations in the soil solution. This increase in ionic strength will lower the apparent soil pH for the same increment of lime addition (Figure A7). In terms of crop production, this can have the effect of obtaining maximum yields at lower pH values for the same soil series (Adams, 1984), especially for ultisols and oxisols. This salt effect on soil pH measurements is well known and it is recommended that samples from intensively fertilized soils be leached with water before determining soil pH, or that all soil pH measurements be referenced to a relatively concentrated salt solution. The two neutral salts commonly used for this purpose are calcium chloride (0.01 kmol $m^{-3}$ $CaCl_2$) and potassium chloride (1 kmol $m^{-3}$ KCl) (Peech, 1965).

Other acidic cations that can undergo hydrolysis and release $H^+$ ions include $Fe^{3+}$. In the pH range of most mineral soils ($pH > 4$), the hydrolysis of $Fe^{3+}$ displaced from the exchange surface of soil clay minerals is not considered an important source of exchangeable acidity. The equilibrium constants for the hydrolysis reactions of $Fe^{3+}$ favor the formation of the hydrolyzed species at lower pH values than $Al^{3+}$. Hydrolysis of $Fe^{3+}$ following the oxidation of ferrous iron species ($Fe^{2+}$), however, is an important source of acidity and will be discussed later.

The majority of extractable or exchangeable $H^+$ present in acid soils is associated with the acid functional groups of SOM. SOM is formed from microbial decomposition of plant and animal tissue added to soils. As a result, SOM is heterogeneous with respect to composition, chemical structure, and quantity and type of acid functional groups (Stevenson, 1982). These functional groups behave as weak acids and have been assigned p$K$ values, but these are only approximate values and titration of SOM extracts seldom yields defined buffer regions. This is due in part to the distribution of the functional groups within SOM, and the change in stereochemistry that occurs as the net negative charge of SOM increases with addition of base (Stevenson, 1982). Titration curves of SOM tend to be linear over a defined pH range, beyond which the majority of $H^+$ bound to the functional groups, has been neutralized (Magdoff and Bartlett, 1985).

The quantity of extractable $H^+$ removed by a neutral salt solution from SOM is a function of the concentration and charge of the neutral salt cation and the final pH of the soil suspension. It can be argued, therefore, that the $H^+$ associated with SOM is both a source of exchangeable acidity and residual acidity, depending on the laboratory procedure selected and the chemical properties of a particular soil. The density of acid functional groups per unit mass for SOM ($>600$ $cmol_c$ $kg^{-1}$) is substantially greater than that for most clay minerals, such that relatively small amounts of SOM ($<1.5$ to 6.5%) can contain substantial amounts of $H^+$. However, it is generally believed that the potential negative charge represented by this bound $H^+$ is only available following a neutralization reaction. Lime requirement determinations for acid soils containing mostly organic matter (Histosols) now use buffer pH procedures rather than neutral salt solutions (van Lierop, 1990).

## Residual acidity

The acid functional groups associated with SOM, especially the carboxyl groups (R–COOH), are also capable of forming complexes with metal ions (Stevenson and Vance, 1989). In many acid soils, complexation with $Al^{3+}$, $Fe^{3+}$, and $Mn^{2+}$ may account for 60–80% of the potential negative charge of SOM. These ions (especially $Fe^{3+}$ and $Al^{3+}$) are not considered exchangeable with mono- or divalent base cations at the concentrations of base cations typically found in soil solutions. They only react with added base when the ligand competition between $OH^-$ ions and the SOM functional groups favor formation of the monomeric hydrolytic metal species. This typically occurs at pH values >4.5. Additions of organic matter to soils can reduce Al toxicity to crop growth without changing soil pH and can decrease KCl-exchangeable $Al^{3+}$ (Hargrove and Thomas, 1981).

The acid functional groups of the mineral components of soils, which have the greatest abundance and reactivity, are the silanol and aluminol groups. These are present at the edges of layer silicate minerals and on the surface of the Fe and Al oxides and oxyhydroxides. The dissociation of $H^+$ can be represented as follows:

$$-MOH_2^{+N} = -MOH^{+N-1} + H^+ \tag{4}$$

where M represents a Fe, Al, or Si ion that is part of the mineral structure but that comes in direct contact with water molecules. This reaction is similar to that of a weak acid in that the degree of protonation or deprotonation is a function of pH; i.e., the net charge on these surfaces is a function of pH. The $H^+$ bound to these surface functional groups is not considered exchangeable with mono- or divalent base cations. Indeed, the chemistry of these functional groups is such that, at pH values that favor a net positive charge, an increase in ionic strength (addition of neutral salt) favors an increase in net positive charge (removal of $H^+$ from solution) (Parfitt, 1980). Removal of $H^+$ associated with these surface functional groups can only be achieved by neutralization with base.

In many acid mineral soils with variable charge, the hydroxyl silanol or aluminol group associated with the Fe and Al minerals is a significant portion of the total soil acidity. Often, the equivalence of $CaCO_3$ required to shift soil pH from 6.5 to 7.0 can be 2 to 4 times that required from pH 5.5 to 6.0 (Fox, 1980). Attempting to lime these soils to an optimum soil pH, as determined for soils that are dominated by constant-charge layer silicate minerals, can require an exorbitant amount of lime. In such instances, optimum yields are obtainable with neutralization of exchangeable $Al^{3+}$, provided sufficient exchangeable $Ca^{2+}$ is present for root growth. These soils are also more susceptible to over-liming (Fox, 1980).

## Other sources of acidity

The remaining sources of soil acidity are not quantifiable by the routine analytical methods used to estimate exchangeable acidity or lime requirement. These sources of acidity are more temporal in nature deriving from a number of factors including a unique soil characteristic or chemical composition, anthropogenic or natural inputs, and cultural management practices. One, or a combination of two or more of these factors can result in the generation of soil acidity that potentially can have the same deleterious effect on plant growth as the more traditional sources of acidity.

## Oxidation–reduction

Oxidation reactions that follow the drainage of wetlands, or a falling water table, can generate substantial amounts of soil acidity (van Breemen, 1987). The chemical reactions that are the primary source of this acidity are based on the transformations of iron. Ferrous ion ($Fe^{2+}$) is generated from the reduction of ferric oxides and oxyhydroxides if a soil containing organic matter is submerged for more than a few days. Drainage of the soil results in the conversion of the $Fe^{2+}$ ions to $Fe^{3+}$ ions. The resulting $Fe^{3+}$ ions undergo hydrolysis and releases $H^+$ ions to the soil solution. In acid-sulfate soils, soils containing strip mine spoils, or other soils containing significant quantities of pyrite ($FeS_2$), a source of $Fe^{2+}$ ion is already present in the soil and exposure to oxygen can result in very low pH values (pH̃ 2) (McFee et al., 1981). The following overall reaction illustrates the quantity of moles of $H^+$ released as the result of the combined oxidation of the $Fe^{2+}$ cation and sulfide anion, coupled with hydrolysis of the $Fe^{3+}$ ion:

$$2FeS_2 + 7H_2O + 7.5O_2 = 4SO_4^{2-} + 8H^+ + 2Fe(OH)_3 \tag{5}$$

If allowed to go to completion, the above reaction can produce amounts of $H^+$ that make liming impractical as a management alternative. In such instances, the management scheme of choice is to keep the soils flooded as much as possible to prevent the oxidation of pyrite (Thomas and Hargrove, 1984).

## Fertilizers

Commercial fertilizers (especially those containing ammonical-N, P and elemental S) are anthropogenic sources of soil acidity that are added to soils to increase crop yields. These soluble salts react to release $H^+$ and soluble anions, which can promote leaching of base cations from the soil. Microbiologically mediated nitrification is the dominant reaction involving $NH_4^+$-based fertilizers (e.g., $NH_4NO_3$) resulting in the formation of nitric acid (Adams, 1984):

$$NH_4NO_3 + 2O_2 = 2NO_3^- + 2H^+ + H_2O \tag{6}$$

Chemolithotrophic sulfur bacteria (typically *Thiobacilli*) are responsible for the oxidation of elemental S utilizing the energy released to fix carbon dioxide ($CO_2$) into organic matter (Tisdale et al., 1985):

$$CO_2 + S + 0.5O_2 + H_2O = [CH_2O] + SO_4^{2-} + 2H^+ \tag{7}$$

Elemental S has traditionally been used as a soil acidulant to promote soil acidity in the reclamation of alkaline soils. More recently it has been incorporated into commercial fertilizers to increase their S content. For concentrated P fertilizers (e.g., monocalcium phosphate) hydrolysis is the primary reaction that releases $H^+$ ions (Tisdale et al., 1985):

$$H_2O + Ca(H_2PO_4)_2 = CaHPO_4 + H_3PO_4 \tag{8}$$

The potential impact on the soil environment from these soluble salts depends in part on the method of application. Band application concentrates the fertilizer within the soil, favoring conditions that can result in extremely low pH values in the band ($pH < 1.5$ for triple superphosphate). Broadcast application followed by tillage disperses the fertilizer throughout the soil but extremely acid conditions can still form around the individual fertilizer granules. This results in partial dissolution of soil clay minerals and release of $Al^{3+}$ and $Fe^{3+}$ ions. In most soils, this fertilizer-produced acidity is rapidly neutralized, but the net reaction is still an increase in soil acidity.

Identification of the source of the N or P fertilizer allows the calculation of the potential acidity that can be released after addition to the soil (Table A7). For example, if ammonium sulfate is used, about 7.1 kg of pure calcium carbonate ($CaCO_3$) per kg of N added is necessary to neutralize the potential acidity added with the fertilizer. In practice, the amount of acidity generated is substantially less because of competing chemical and biological reactions. These include loss of N as $NH_3$ through volatilization, denitrification of $NO_3$-N, which

**Table A7** Maximum amount of calcium carbonate ($CaCO_3$) required to balance the acidity produced by nitrogen (N) fertilizers[a]

| Material | Nitrogen content ($g\ kg^{-1}$) | $CaCO_3$ equivalent ($kg\ CaCO_3\ kg^{-1}$ of N) |
|---|---|---|
| Ammo-phos A | 110 | 6.8 |
| Anhydrous ammonia | 822 | 3.6 |
| Calcium nitrate | 150 | 0.0 |
| Cottonseed meal | 67 | 3.2 |
| Dried blood | 130 | 3.5 |
| Potassium nitrate | 130 | 0.0 |
| Sulfate of ammonia | 205 | 7.1 |
| Tobacco stems | 28 | 2.5 |
| Urea | 466 | 3.6 |

[a] Source: Tisdale et al., 1985.

**Table A8** Amount of calcium carbonate ($CaCO_3$) required to balance the acidity produced by crop removal of exchangeable calcium (Ca) and magnesium (Mg)[a]

| Crop | Yield ($kg\ ha^{-1}$) | Ca ($kg\ ha^{-1}$) | Average harvest Mg ($kg\ ha^{-1}$) | $CaCO_3$ equivalent ($kg\ ha^{-1}$) |
|---|---|---|---|---|
| Corn[b] | | | | |
| whole plant | 13000 | 52.0 | 32.5 | 264 |
| grain | 5400 | 0.8 | 6.5 | 29 |
| Soybean[b] | | | | |
| whole plant | 6400 | 76.8 | 32.0 | 324 |
| grain | 1900 | 5.7 | 6.7 | 42 |
| Small grains[c] | 5300 | 18.6 | 13.3 | 101 |
| Tobacco[b] | 2240 | 62.0 | 25.0 | 258 |

[a] Sources: Walsh and Beaton, 1973; Westerman, 1990.
[b] Corn (*Zea mays* L.); soybean (*Glycine max* (L.) Merr.); tobacco (*Nicotiana* sp.).
[c] Small Grains: Barley (*Hordeum vulgare* L.); oats (*Avena* sp.)/wheat (*Triticum* sp.).

consumes $H^+$ ions, direct plant uptake of $NH_4^+$ ions, or plant uptake that removes unequal equivalents of anions and cations from the soil solution (Thomas and Hargrove, 1984; Tisdale et al., 1985). Uptake of $NO_3^-$ in excess of cations will result in the release of $OH^-$ and organic acid anions from the plant roots to maintain electrical neutrality. These anions either neutralize or bind with the $H^+$ ions in the soil solution such that the net acidity released from addition of a N-fertilizer could be zero. Such a result is highly unlikely under field conditions and is known not to occur for anions such as sulfate ($SO_4^{2-}$) and phosphate ($H_2PO_4^-$). For most sources of acid producing N, P, and S fertilizers, the actual soil acidity released is assumed to be half to two-thirds the maximum calculated value (Table A7).

## Plant uptake

The extent of soil acidity generated by plant uptake of base cations (predominately calcium and magnesium) is a function of soil type (cation exchange capacity), cropping rotation, and management decisions concerning the crop residues. Plant species vary in their degree of cation uptake but in each case the basic reaction is the exchange of a base cation for a $H^+$ ion at the soil-root interface. Removal of $Ca^{2+}$ and $Mg^{2+}$ ions from the exchange complex of the soil (the primary source of these ions in soil) requires the release of the $H^+$ ions to maintain overall charge balance in the soil solution. Intensive cropping of a soil can remove significant amounts of these base ions, especially if all of the above ground portion of the crop is removed (for example, as with for corn (*Zea mais* L.) silage or tobacco (*Nicotiana* sp.)) (Table A8). Base cation removal with forage crops can be even higher because of the potential for several harvests per growing season. It has been shown that yields of alfalfa (*Medicago sativa* L.) approaching 10 metric tons result in the production of soil acidity requiring 600 kg $CaCO_3\ ha^{-1}$ for neutralization (Nyatsanga and Pierre, 1973). Management schemes that incorporate the crop residue back into the soil minimize the overall change in base cation content of the soil associated with crop production (Power and Legg, 1978). However, the base cations returned in this manner are not immediately available for plant uptake, nor are they capable of neutralizing the acidity released during their incorporation into the growing plant. Furthermore, the uptake of base cations by most crops occurs over a relatively short period of time (10–14 weeks) during a growing season. It is not uncommon to see a decrease in soil pH by 1 pH unit during this period of intense demand for nutrient ions, especially in soils with relatively low cation exchange capacities (e.g., $<5$ cmolc $kg^{-1}$). Limited availability of base cations during this time will have the same deleterious effects on crop growth as an increase in soil acidity.

## Acidic deposition

Another potential source of soil acidity that arises from anthropogenic inputs is acidic deposition. Acidic deposition is composed primarily of N and S acid-forming compounds that undergo gas-phase oxidation and aqueous-phase reactions in the atmosphere to form nitric and sulfuric acids (Tanner, 1989). Partial neutralization of these acids by ammonia ($NH_3$) in the atmosphere results in $H^+$, $NH_4^+$, $NO_3^-$, and $SO_4^{2-}$ being the dominant ions in acidic rainwater (Berdèn et al., 1987) and in dry deposition (Murphy and Sigmon, 1989). Acidic deposition, therefore, represents both an episodic and continuous input of ions into the soil ecosystem. These ions can have both a beneficial and a harmful effect. The inputs of S and N can have a positive impact on plant growth, while the inputs of $H^+$ coupled with the strong acid anions can promote leaching of base cations and mobilization of toxic ions such as $Al^{3+}$.

Current loading rates from acidic deposition are $<2$ kmoles $H^+\ ha^{-1}\ yr^{-1}$ except for areas located near point sources of N and S acid-forming substances, or in high-elevation ecosystems that are also impacted by acidic cloud-water (Berdèn et al., 1987; Aneja et al., 1992; Mohnen, 1992). In many rural areas the loading rate is $<1$ kmoles $H^+\ ha^{-1}\ yr^{-1}$ (Ulrich, 1991), which is equivalent to that neutralized by 50 kg of pure calcium carbonate $ha^{-1}\ yr^{-1}$. Compared to the acidity generated by fertilizer additions and through plant uptake (Tables A7 and A8), the amount of acidity being deposited from atmospheric deposition is small; and it is generally accepted that continued inputs of acidic deposition on intensively managed soil systems will have no effect on soil acidity (McFee, 1983; Tabatabai, 1985). Forages and native pastures, however, represent agronomic ecosystems that can be considered sensitive to acidic deposition (Irving, 1983). The rhizosphere in such ecosystems is concentrated in the top few cm of soil, which remains relatively undisturbed for long periods of time. Due to grazing and mechanical harvesting, there is a regular export of base cations. Replacement of these base cations is generally left to natural weathering processes for pastures that are not highly managed. Forages and pastures located on soils with inherently low buffer capacity, low organic matter content, and receiving low management input will be susceptible to increases in soil acidity due to acidic deposition. Such soils (ultisols and alfisols) are predominant throughout the southeastern United States (Buol, 1983) where substantial acreages (14–16 million ha) are devoted to forages and pastures. The average lime application rate per hectare throughout this region in 1980 was $<220$ kg $yr^{-1}$. Assuming a realistic economic application rate of 4500 kg $ha^{-1}$, only 1 out of every 20 ha received lime. Expressed another way, this means that it will take 20 years before each hectare will receive just one lime application. Acidic deposition during this period will be equivalent to $\sim$1000 kg of $CaCO_3$ $ha^{-1}$. These figures demonstrate what is meant by low management input and suggest that a negative impact of acidic deposition through an increase in soil acidity is a distinct possibility.

Soils associated with forested ecosystems are considered to be the most susceptible to change induced by acidic deposition. For example, at the Walker Branch Watershed, which is located on the U.S. Department of Energy's Oak Ridge Reservation in Anderson County, Tennessee in the USA, the total estimated input of $H^+$ from atmospheric deposition is 1.5 kmoles $H^+$ $ha^{-1}$ $yr^{-1}$ (75 kg $CaCO_3$ equivalent $ha^{-1}$ $yr^{-1}$) (Johnson and Lindberg, 1989).

Internal generation of $H^+$, due to formation of carbonic acid and net accumulation of base cations in the vegetation, is 1.6 kmoles $H^+$ $ha^{-1}$ $yr^{-1}$. The current rates of acidic deposition have essentially doubled the total $H^+$ loading at this location. This in turn has accelerated the leaching of base cations ($K^+$, $Ca^{2+}$, and $Mg^{2+}$) from the forest canopy by 50%. This accelerated loss of cations from the canopy foliage can increase soil acidity if it is not balanced by internal $H^+$ sinks such as weathering, or reaction with the weak acid functional groups associated with SOM or Fe and Al oxides and oxyhydroxides. It has been argued that most forested ecosystems developed on non-calcareous parent material in humid environments cannot compensate for the continued inputs of $H^+$ from acidic deposition (Ulrich et al., 1980). The soils associated with these ecosystems will continue to acidify leading to the loss of soil nutrients due to leaching, and mobilization of toxic metals (primarily $Al^{3+}$ and $Mn^{2+}$) in the soil solution and in the stream waters draining these ecosystems.

Objections to this line of reasoning are based on the argument that the effects of acidic deposition on soils in forested ecosystems can only be evaluated from the standpoint of how these acidic inputs interact with the natural processes of soil acidification (Rosenqvist, 1978; Krug and Frink, 1983; Tabatabai, 1985). Soil formation in humid temperate climates is an acidifying process, and the simple correlation between areas of high acidic deposition ($>1$ kmole $ha^{-1}$ $yr^{-1}$) and the presence of acidic soils and stream waters is not sufficient cause to conclude that acidic inputs will increase soil acidity in these ecosystems. Many of the forests of northern Europe and eastern North America have undergone substantial changes in land use policy in the past 200 years. As many of these forests are now aggrading, the natural soil acidification that accompanies such regrowth cannot be attributed to acidic deposition (Krug and Frink, 1983). Even at the Walker Branch Watershed, intensive studies have indicated that, despite accelerated leaching due to $H^+$ inputs from acidic deposition, a significant change in soil acidity in the next few decades is very unlikely (Johnson and Lindberg, 1989). Lack of an appreciation of natural soil acidification processes, combined with results from intensive studies dealing with whole watersheds receiving acidic deposition, have forced a reevaluation of how these acidic inputs could enhance soil acidity in forested ecosystems (Johnson et al., 1991; Robarge and Johnson, 1992). It is now accepted that it is very unlikely that changes in soil acidity induced by acidic deposition can be quantitatively described by a single index parameter (Matzner, 1989), and that there has probably been too much emphasis on changes in soil pH and cation depletion as a necessary and expected effect of acidic deposition on soil systems (Johnson et al., 1991). Of more importance is how the natural acidification processes within a given ecosystem predispose that system to the way it will respond to acidic inputs, particularly to the inputs of the mineral acid anions $NO_3^-$ and $SO_4^{2-}$. These mechanisms are briefly discussed in the next section and in more detail elsewhere (Matzner, 1989; Ulrich, 1991; Robarge and Johnson, 1992).

## Discussion

The majority of the concepts discussed in the previous sections were reported on and subsequently validated during the 1950s and 1960s (Thomas and Hargrove, 1984). The successful lime requirement programs that have been developed as a result of this work have formed the foundation for modern agriculture for the past 30 years in regions dominated by acid soils. More recent research efforts have focused on the problems associated with soil acidity and changes in modern agriculture management techniques, the challenge of developing low input systems to replace shifting (slash and burn) agriculture, and environmental concerns about the effects of acidic deposition on soil systems. Examples from each of these subject areas are discussed to illustrate that our knowledge concerning the components, mechanisms and interactions that comprise soil acidity is still incomplete.

### Subsoil acidity

In many acid soils, acidity is not confined to the surface of the soil profile but extends down into the subsoil (e.g., ultisols). Root growth is often confined to the surface horizons in these soils because of this subsoil acidity (primarily exchangeable $Al^{3+}$ and $H^+$). The lack of root penetration into the subsoil means that the soil water stored there is unavailable to support plant growth. The inability of plants to gain access to this water is especially important in regions receiving adequate annual rainfall, but that are characterized by growing seasons during which drought conditions frequently occur at critical physiological stages of crop growth (Reicosky et al., 1977). Lack of adequate available soil water during these periods significantly decreases yields. Application of lime to neutralize surface soil acidity in these soils has little immediate effect on subsoil acidity because the overall neutralization reaction requires that the $Ca^{2+}$ ions remain in the surface horizon (Thomas and Hargrove, 1984):

$$2Al^{3+}\text{-soil} + 3CaCO_3 + 3H_2O = 3Ca^{2+}\text{-soil} + 2Al(OH)_3 + 3CO_2 \qquad (9)$$

Deep placement of lime has not proven to be an economic amelioration procedure because of the expense involved in the technique. It is possible to introduce lime slurries into the subsoil but the volume of soil affected is relatively small and the increase in yields obtained, if any, do not justify the costs associated with this procedure.

Amelioration of subsoil acidity is currently accomplished with surface applications of calcium salts; primarily gypsum $Ca(SO)_4 \cdot 2H_2O$ (McCray and Summer, 1990). Limited retention of the $SO_4^{2-}$ anion in the surface horizon provides the necessary mobile anion for movement of the $Ca^{2+}$ ion into the subsoil. The net result is an increase in exchangeable $Ca^{2+}$ at the expense of exchangeable $Al^{3+}$. The exact mechanism for the decrease in exchangeable $Al^{3+}$ is still subject to debate, but may be due to the formation of soluble $AlSO_4^+$ complexes which are leached from the soil, or to the formation of aluminum sulfate precipitates (e.g., jurbanite). The $SO_4^{2-}$ ions would also particiate in ligand exchange reactions at the surface of the Fe and Al oxides and oxyhydroxides:

$$M - (OH)_2 + SO_4^{2-} = M - (OH)SO_4^- + OH^- \tag{10}$$

where M represents either Fe or Al. The $OH^-$ ions released by this ligand exchange reaction would in turn neutralize exchangeable $Al^{3+}$. The adsorbed $SO_4^{2-}$ can either remain on the oxide surface, or form a separate solid phase due to the relatively high concentrations of $SO_4^{2-}$ in the soil solution. This proposed reaction would favor an increase in subsoil pH, but a positive change in pH is not always associated with the application of gypsum. Subsoil pH is not considered a reliable indication of an improvement in conditions that favor root growth.

The amounts of gypsum necessary to ameliorate subsoil acidity depend on soil type, but surface applications may approach 10 Mg $ha^{-1}$. Leaching of exchangeable $K^+$ and $Mg^{2+}$ from the surface horizons is a potential problem at these high loading rates, especially in soils with relatively low cation exchange capacities ($<5$ cmolc $kg^{-1}$). Supplemental additions of K and Mg fertilizers are necessary under these conditions to maintain crop growth (McCray and Summer, 1990).

Addition of gypsum allows the amelioration of subsoil acidity within one or two growing seasons, but it is becoming clear that long term application of fertilizer and lime to surface horizons alone can facilitate the accumulation of sufficient base cations in the subsoil to promote root growth. This is particularly true for the subsoils of ultisols in the southeastern USA (Hardy et al., 1990). Continuous cultivation for over 30 years has resulted in reduction of 23 to 100% of the exchangeable $Al^{3+}$ in subsoils under managed versus unmanaged sites. The primary restriction to plant growth in the argillic horizons of these ultisols is now related to physical properties, and, with the proper subsoiling techniques, soil water stored in these horizons is available for plant growth. Similar changes are occurring in the subsoils of cultivated soils within the middle and upper parts of the Atlantic Coastal Plain and the Piedmont regions of the southeastern United States (Buol, 1985).

## No-till planting

Another tillage practice that can influence soil acidity is no-till planting. No-till crop production systems involve little or no mixing of the soil and leaves crop residues on the soil surface as a protective mulch to minimize soil erosion (Larson et al., 1978). Additional benefits associated with no-till planting include increased water infiltration (minimal surface crusting), decreased soil evaporation, and an increase in SOM content and soil microbial population (Blevins et al., 1983). The disadvantage in regards to soil acidity is that no-till planting precludes mixing of crop residues, lime, and fertilizers with the surface soil. In continuous no-tillage crops such as corn (*Zea mays* L.), N applications are restricted to the soil surface or the top 5 to 8 cm of the soil if incorporated during planting. Release of $H^+$ ions due to nitrification (enhanced by the increase in soil microbial populations), coupled with greater $Ca^{2+}$ loss through leaching due to the presence of $NO_3^-$ anions and increased infiltration of water, combine with crop uptake of base cations to decrease soil pH more rapidly with depth than with conventional tillage treatments (Table A9). This decrease in soil pH and loss of exchangeable $Ca^{2+}$ is matched with an increase in exchangeable $Al^{3+}$, which in turn reduces yields. This increase in soil acidity can also result in the inactivation of herbicides often used to kill the sod before planting. Lower crop yields and poor control of weeds are visual indicators of low surface soil pH in no-till plantings (Thomas, 1986).

Because the acid-producing effect of application of N fertilizers is concentrated in the soil surface, neutralization is accomplished with surface application of lime in no-till plantings. The management questions that need to be addressed, however, are the frequency and amount of lime required to maintain optimum yields. For example, over-liming can result in possible enhancement of N volatilization (as $NH_3$) from urea-based fertilizers. Failure to add enough lime may limit the replacement of base cations removed by crop uptake from deeper in the surface soil. Proper sampling design for determining lime requirement is also a problem. Stratification caused by the acidification reactions limits the usefulness of traditional soil sampling procedures. No-till plantings may require sampling as a function of depth for proper lime recommendations. These management problems illustrate why soil acidity is considered one of the most serious problems encountered in no-till plantings, and why no-till soils require different management techniques than those used with conventionally tilled soils (Thomas, 1986).

## Acid tolerant genotypes

Management schemes that include neutralization of soil acidity by lime assume that an adequate source of liming material is available that can be economically applied and mechanically incorporated into the soil. For low-input agriculture systems this option is often not available. In these systems, successful management techniques must include crops with a genetic tolerance to soil acidity (Foy, 1984). Screening for plant tolerance to acidity must take into account all of the possible toxic conditions that may exist in acid soils (Scott and Fisher, 1989). Acid soil toxicity affects the growth of different plants through different physiological and biochemical pathways, depending

**Table A9** Effect of lime on continuous corn (*Zea mais*) grain yield using no-till planting[a]

| Year | Yield (q $ha^{-1}$) | | Yield increase (%) | Surface pH | |
|---|---|---|---|---|---|
| | No lime | Lime | | No lime | Lime |
| 1965 | 50.2 | 60.9 | 21.3 | 4.8 | 5.1 |
| 1966 | 73.2 | 75.4 | 3.0 | 4.8 | 5.1 |
| 1967 | 65.5 | 79.3 | 21.1 | 4.5 | 5.2 |
| 1968 | 57.5 | 84.1 | 46.3 | 4.5 | 5.7 |
| 1969 | 69.4 | 97.6 | 39.3 | | |
| 1970 | 74.7 | 90.6 | 21.3 | 4.5 | 5.7 |
| 1971 | 73.0 | 98.4 | 34.8 | – | – |
| 1972 | 45.6 | 82.3 | 80.5 | 4.9 | 6.4 |

[a] Source: Tables 1 and 2, Moschler et al., 1973.

**Table A10** Major constraints and responses of plant growth under acid soil conditions[a]

| Constraint | Response | Affected part |
|---|---|---|
| $>$ $H^+$ concentration | $H^+$ toxicity | Root |
| $>$ $Al^{3+}$ concentration | Al toxicity | Root |
| $>$ $Mn^{2+}$ concentration | Mn toxicity | Shoot |
| $<$ base cation concentration | Ca, K, Mg deficiency | Whole plant |
| $<$ P and Mo solubility | P, Mo deficiency | Whole plant |
| Inhibition of root growth | Nutrient and water deficiency | Whole plant |
| Increase in leaching | Nutrient deficiency | Whole plant |

[a] Source: Clark, 1984; Foy, 1984; Marschner, 1991.

on the genetic inheritance of an individual plant species (Table A10).

Because $Al^{3+}$ ions dominate the exchange complex in acid mineral soils, the presence of monomeric $Al^{3+}$ ions in soil solution is considered to be the most common acidity impediment for plant growth (Foy, 1984). Plant response to high Al concentrations includes reduction of cell division in root apices, DNA replication, P availability at root membranes, and interference with sugar phosphorylation enzymes. More recent work has demonstrated that polynuclear hydroxy Al species (especially triskaidekaaluminum; $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ or $Al_{13}$) are also toxic to plant growth (Kinraide, 1991). The fact that these polycationic Al species may be present in aqueous Al solutions used to screen for Al tolerance questions earlier conclusions concerning the role of monomeric Al species in the response of plants to Al toxicity; but it is not yet clear to what extent these polycationic Al species may actually occur in soil solutions. Evidence also continues to accumulate that Al constraints to root growth can be partially alleviated by Ca additions (Alva et al., 1986; Noble et al., 1988). Calcium is important to maintain cell wall structure, membrane stability, and regulation of enzymes in plants (Clark, 1984). Several nutrient culture studies have shown that it is the ratio of Ca to Al that is important in alleviating Al constraints to growth (Cameron et al., 1986; Noble et al., 1988). This suggests that the presence of Ca from the application of gypsum is as important in reducing subsoil acidity as the potential formation of relatively insoluble aluminum-sulfate compounds. Hydrogen-induced root injury occurs at pH $< 4$ (Islam et al., 1980) and involves changes in root membrane permeability, interference in nutrient transport, and loss of organic substrates and absorbed cations (Foy, 1984). Toxicity due to $H^+$ ions is of concern in acid organic soils and possibly from nitrification and hydrolysis reactions of fertilizers. Toxicity from Mn in acid soils is not related to a decrease in root growth, but from the excessive accumulation of Mn in the shoots of plants grown on soils with high exchangeable Mn levels (Kamprath, 1984).

A number of screening methodologies have been developed for identification of acid tolerant genotypes (Howeler, 1991). These methodologies have advantages and disadvantages, and more attention needs to be given to activities of individual species in solution, especially for Al (Kinraide, 1991). These techniques, combined with a growing understanding of the physiological basis of tolerance (Bennet and Breen, 1991; Taylor, 1991), has lead to the identification of acid tolerant germ plasm for a number of crop species, both in the temperate regions and the tropics. However, these screening procedures assume that plants are passive role players in regards to soil acidity. This is not the case, and as living systems, plants can choose between two strategies (tolerance or avoidance) for adapting to acidity constraints (Marschner, 1991). The strategy of choice appears to be avoidance as reflected in the ability of plants to *(a)* increase the pH of the rhizosphere, *(b)* release organics to chelate toxic cations, and *(c)* employ mycorrhizae to increase root surface area. The single factor approach of most acid-tolerant screening procedures do not account for the active response of plants to acid conditions. This may account for the limited success achieved with laboratory selected acid-tolerant species when grown under field conditions. Although evidence continues to accumulate that selection based on laboratory screening techniques can be used to develop genotypes adapted to the toxic conditions of acid soils (Furlani et al., 1991; Ritchey, 1991), and that breeding programs will lead to the development of tolerant cultivars for major crop and pasture species (Howeler, 1991).

## Acidic deposition

Concern about the potential negative impacts of acidic deposition on forested soils is an example of a problem dealing with soil acidity on the scale of whole watersheds, geographical regions, or even whole countries. Liming or selection of acid tolerant species is not a management alternative in these situations. The only effective approach to reduce the potential impacts of acidic deposition is through control of emissions of the acid-forming precursor compounds. Setting goals for emission controls is complicated by the fact that the major constituents of acidic deposition are also components of the natural processes of soil acidification, which occur in all forested ecosystems, especially those found in humid environments. Valid questions that must be addressed are whether current rates of deposition are sufficient to induce change, and whether this change can be detected. The later question is especially important because historical data characterizing forested ecosystems is generally not available, or is subject to different interpretations due to changes in land use patterns with time. In most cases this negates any determination of change induced by acidic deposition by simply comparing bulk soil characterization measurements (e.g., soil pH, cation exchange capacity, or exchangeable $Al^{3+}$ or $Ca^{2+}$). Emphasis instead must be placed on the natural soil acidification processes and how acidic inputs can act to destabilize a forested ecosystem.

Processes within forested soils can be considered as a cycling of ions within an ecosystem (Ulrich, 1983). The major components of this cycle are: inputs (atmospheric deposition, weathering of soil minerals), outputs (leaching), plant uptake, and mineralization (decomposition of organic matter). If an ecosystem is in steady state, the fluxes from inputs and outputs will be equal and net $H^+$ production or consumption will be minimized. Temporal discouplings do occur in these stable ecosystems, for example during N transformations, since many forested soils have a potential for high mineralization and nitrification rates (Swank, 1986; Gundersen and Rasmussen, 1990); but internal buffering reactions (e.g., exchangeable $Ca^{2+}$ and $Mg^{2+}$) act to limit the intensity of these reactions. The $H^+$ generated by nitrification is eventually balanced by $H^+$ consuming reactions (mineral weathering). Inputs of N from acidic deposition, however, can increase the total N pool within a soil and eventually overwhelm the resistance of the ecosystem to $H^+$ production during N transformations (Ulrich, 1983; Gundersen and Rasmussen, 1990). When this occurs, nitrification following mineralization will force a decrease in soil solution pH and the generation of an excess of $NO_3^-$ anions. In these naturally acid soils, the decrease in pH will in turn favor an increase in soil solution Al and an increase in the leaching of base cations. This change in soil acidity is not due to the concentration of $NO_3^-$ in individual acidic deposition events, nor is it due to changes in static soil parameters. The change is due to the dynamics of N cycling within the ecosystem; i.e., the internal cycling of N has become saturated (Ågren and Bosatta, 1988).

Another example of how acidic deposition can destabilize a soil process involves the normal transport of Al within the soil profile (Driscoll and Schecher, 1990). Mobilization and subsequent deposition of Al is an integral part of soil genesis in well-drained acid soils. This is because the bicarbonate anion ($HCO_3^-$) and dissolved organic acids are normally the dominant anions in the soil solution. Bicarbonate concentrations are elevated in the soil solution of the surface soil horizons because of an excess of carbon dioxide ($CO_2$) released from mineralization and root respiration into the soil atmosphere (i.e., there is an increase in the partial pressure of $CO_2$):

$$CO_{2aq} + H_2O = H_2CO_3 = H^+ + HCO_3^- \qquad (11)$$

As the soil solution drains from the surface horizons, there is a drop in the partial pressure of $CO_2$ in the soil atmosphere, which causes the dissolved $CO_2$ to degas, resulting in the removal of the $HCO_3^-$ ion from solution (Reuss, 1991). Since this reaction is a $H^+$ consuming process, it promotes the hydrolysis of $Al^{3+}$ and deposition of an Al oxide or hydroxide, for example:

$$Al^{3+} + 3HCO_3^- = \underset{\text{gibbsite}}{Al(OH)_3} + 3CO_2 \qquad (12)$$

A similar result will occur for dissolved organic acids following mineralization. In either case, the removal of the transient anion must result in the deposition of Al, either within the soil profile or in the sediment of surface waters draining the watershed (Driscoll and Schecher, 1990).

Continued loading of N and S from acidic deposition on these soils results in a gradual change of the dominant anions in the soil solution from $HCO_3^-$ and dissolved organic acids to $NO_3^-$ and $SO_4^{2-}$. Dissolved $NO_3^-$ and $SO_4^{2-}$ are not transient anions and remain in the soil solution as it moves through the soil profile. This in turn results in the apparent mobilization of dissolved $Al^{3+}$, causing elevated concentrations of Al in the soil solution and surrounding surface waters (Driscoll and Schecher, 1990). This change in soil solution $Al^{3+}$ concentrations does not require a change in soil acidity (decrease in soil pH, change in cation exchange capacity, or an increase in exchangeable $Al^{3+}$).

## Summary

Soil acidity is one of the most important factors regulating the species distribution and composition within an ecosystem, and in limiting crop yields. The acidification of soils is the consequence of a combination of natural and anthropogenic processes. Aluminum is generally accepted as the toxic agent in most acid mineral soils, but uncertainty still exists about the toxicity of different species of aluminum in the soil solution and the effect other ions have on mediating this toxicity. In organic soils, aluminum toxicity is probably not the dominant constraint to plant growth. Industrialization has resulted in the release of acids to the atmosphere, much of which has been deposited in terrestrial ecosystems. Our knowledge of soil acidity in regards to liming and crop production has proven inadequate in understanding how these inputs of anthropogenic acids will degrade naturally acid soils and the streams that drain them. Closer examination of natural soil acidification processes is required to understand how anthropogenic acid inputs can cause changes in soil acidity. Continued study of these natural soil acidification processes will in turn answer many questions concerning the ecophysiological mechanisms by which soil acidity limits plant growth. Such information will aid in the development of acid tolerant genotypes for use in low-input agricultural systems as alternatives to shifting (slash and burn) agriculture.

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### Cross-references

Acid Deposition Effects on Soils
Acid Soils
Acidity
Acids, Alkalis, Bases and pH
Buffers, Buffering
Chemical Analyses
Nitrogen Cycle
Podzols
Sorption Phenomena
Sulfur Transformations and Fluxes
Weathering Systems in Soil Science

## ACIDS, ALKALIS, BASES AND pH

These four basic concepts are all related to the concentration of hydrogen ions (protons) in a system. In the case of soil chemistry, the systems considered are always aqueous, and the proton is never present as such, but is hydrated as the $H_3O^+$ ion. Here, the common convention of discussing the four concepts in terms of $[H^+]$ will be followed, the square brackets indicating concentration.

The earliest relevant idea of importance in modern chemistry is the distinction between acidity and alkalinity due to Arrhenius. It is based on the dissociation of water into $H^+$ and $OH^-$ ions. An acid aqueous solution has $[H^+] > [OH^-]$, an alkaline solution has $[H^+] < [OH^-]$, and a solution in which $[H^+] = [OH^-]$ is said to be neutral.

The most general idea of acids and bases is due to G. N. Lewis. A Lewis acid is a chemical species that can accept an electron pair, whereas a Lewis base is capable of donating an electron pair. The most commonly used (and useful) concept in soil and environmental science is the simpler one of Brønsted and Lowry. It defines acid as a proton donor and base as a proton acceptor. In the reaction:

$$HCN = H^+ + CN^-$$

HCN (hydrocyanic acid) is the proton donor and therefore the acid, and $CN^-$ is called the conjugate base. In terms of $H_3O^+$, the reaction is written:

$$HCN + H_2O = H_3O^+ + CN^-$$

By comparison, in the Lewis concept, $H^+$ (as an electron acceptor) is itself considered to be an acid.

The dimensionless parameter pH is defined as the negative logarithm of the thermodynamic activity of the hydrogen ion in an aqueous solution. The pH scale derives from the dissociation constant of water, $K_w$:

$$K_w = [H^+][OH^-] = 10^{-14}$$

or

$$-(\log[H^+]) + \log[OH^-] = 14$$

$$pH = -\log[H^+]$$

so that

$$pH = 14 + \log[OH^-]$$

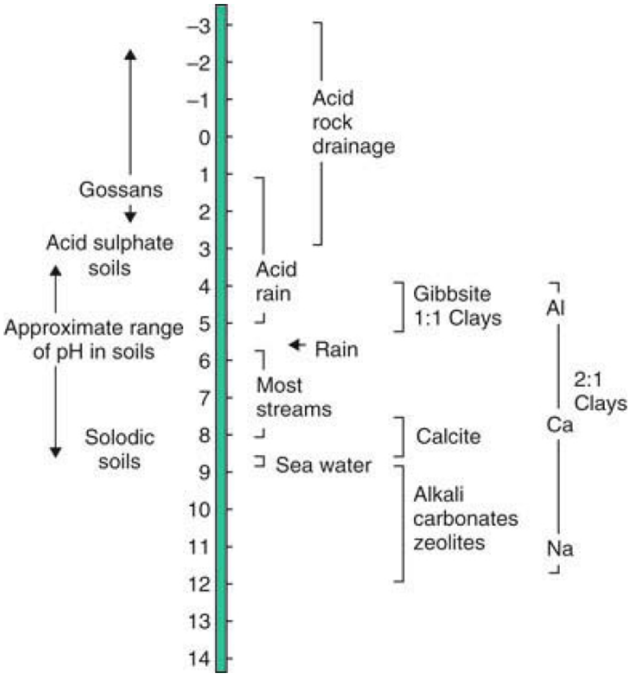

**Figure A8** Approximate ranges of pH values for soils and other materials of the Earth's surface.

Conventionally, pH is shown on a scale of 0 to 14, and a common misconception is that these two values define maximum acidity and maximum alkalinity respectively. In fact values that fall outside of this range are possible, though rare, in weathering systems. Some typical pH values are shown in Figure A8.

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# ACRISOLS

From Latin *acris* meaning *sour*, *very* acid, indicative of a low base saturation of the cation exchange capacity at pH 7.0.

## Definition

Soils having

1. an *argic* horizon, which has a cation exchange capacity (in 1 M $NH_4OAc$ at pH 7.0) of less than 24 $cmol_c\ kg^{-1}$ clay in some part, either starting within 100 cm from the soil surface, or within 200 cm from the soil surface if the *argic* horizon is overlain by loamy sand or coarser textures throughout, *and*
2. a base saturation of less than 50% (in 1 M $NH_4OAc$ at pH 7.0) in the major part between 25 and 100 cm.

## General characteristics

Soils characterized by the presence of a well-defined B horizon, with a blocky, prismatic, granular or massive structure (depending on water content, amount of Fe sesquioxides, and mineralogy of the fine fraction), which has a markedly increase in clay content (*argic* horizon) relative to the overlying horizons, and a cation exchange complex in which acidic cations (ionic Al species and, to a lesser extent, $H^+$, $Fe^{+2}$, $Mn^{+2}$ among others) predominate over basic cations.

Mineralogical characteristics of the B horizon are variable, including *(i)* soils with 1 : 1 kaolinitic clay type (well-crystallized kaolinites, metahalloysites, or tubular halloysites) with or without the presence of gibbsite, and *(ii)* soils in which small amounts of more or less degraded mica are present. In both cases, the clay fraction is commonly associated with variable amounts of Fe sesquioxides (mainly goethite and/or hematite); the ratio of free Fe over total Fe of these soils is high (generally greater than 40%), which indicates an important degree of weathering and pedogenic evolution. These are, therefore, highly developed soils, formed under a tropical, subtropical, or even wet temperate (warm temperate in FAO usage) climate on old land surfaces, which have remained relatively stable during the recent Quaternary, and have been scarcely affected by recent glacial, fluvial, or colluvial processes.

The dominant pedogenic processes occurring in these soils are:

- *Weathering and argilization* of the most labile minerals present in the parent material, with clay formation under acidic or weakly acidic conditions, which favor the synthesis of 1 : 1 phyllosilicates and gibbsite, as well as the release of Fe with formation of crystalline free Fe forms. It is, therefore, a more or less intense *fermonosiallitization* (Pédro, 1983). The contents of Fe-, Al-, and Ti-oxides are comparable to those of Ferralsols or somewhat lower. The degree of weathering can be very intense, being mainly influenced by *(i)* the type of parent material (greater on igneous and metamorphic rocks of basic character), and *(ii)* both the intensity and duration of cation leaching and acidification processes.
- *Degradation and, ultimately, destruction of micas* present in the parent material with the release of K and transformation of micas to different intergrades mica-vermiculite, or even to Al-hydroxy-interlayered vermiculite, especially frequent in the A horizons. In the more advanced stages, these minerals become destroyed by acid hydrolysis.
- *Desaturation and aluminization* of the cation exchange complex by intense leaching processes, so that the amount of basic cations released by weathering is either similar to or smaller than the amount leached. This leads to a saturation of the CEC by Al and acidic cations, although a relative enrichment of basic cations may occur at surface, due to biotic pumping.
- *Clay translocation* from overlying horizons and the accumulation of clay in the *argic* horizon is not always easy to identify. Only when the amount of 2 : 1 clays is greater than that of 1 : 1 clays, or when kaolinitic clays are very crystalline and the amount of free Fe is low, illuvial features covering pore walls and aggregates are clearly identified. In other soils, illuvial features are very scarce and reduced to the presence of small birefringent bodies (*papules*) integrated into the matrix, which are attributed to either *(i)* features of a previous illuviation process, or *(ii) cutans* produced at the initial weathering stages of the parent material, more frequent at the base of the B2 horizon and in the saprolite. Moreover, in soils with abundance of either *(i)* halloysites, *(ii)* short-range order kaolinites, or *(iii)* kaolinites with significant isomorphic substitution of Al by Fe, illuvial features are hardly identified (even with detailed examination of thin sections). For this reason many researchers have proposed, on one hand, the exclusion of the illuvial genesis as a criterion for the definition of this reference soil group and, on the other, the inclusion of other processes that could explain the textural change. In this sense, it has been proposed as such processes *(i)* the occurrence of clay impoverishment caused by differential erosion in the surface horizons, *(ii)* preferential neoformation of clay in the B horizon (less acidic than the A horizon), or even *(iii)* the existence of textural discontinuities produced by polycyclism, after erosion and surface coverage with new material. Some researchers, and also some soil classifications, are considering the need to introduce a new group that would bring together all those soils of advanced weathering and desaturation, and with abundance of low activity clays (LAC), but that do not meet the requirements for a *ferralic* B horizon, and do not show a clear illuvial genesis. The following terms have been proposed: “Ferrosols” (Chinese classification), “Kurosols” (Australian classification), “red yellow podzolic soils” (Indonesian and Brazilian classification), “LAC-soils”, “Kandisols”, and “Kaolisols” (among others).

## Morphology

Acrisols are characterized by the presence of an *ochric* or an *umbric* A horizon (10 to 30 cm depth), overlying an *argic* Bt horizon, which is deep, generally intensively colored (either yellow or brown to red), and whose structure ranges between prismatic, blocky, or granular, although in some cases, and under certain conditions, it can have a massive appearance. Often, there is either a thin grayish horizon or an *albic* E horizon between these two horizons, which is weakly structured and with an evident impoverishment of colloids, and which generally has an abrupt transition to the underlying Bt horizon. Redoximorphic features (known as gleyic soil properties in FAO usage) may appear at the base of the Bt horizon and, seasonally in the surface horizons in contact with the argic horizon in depressions especially.

### Parent material

Acrisols are found on igneous, metamorphic, or sedimentary materials. Under wet tropical conditions, these soils are more frequently found on igneous and metamorphic rocks of acidic to intermediate character, although they may also be found on already weathered colluvial materials that accumulate in slopes of low hills. At intermediate latitudes, under subtropical to wet temperate climates (warm temperate – FAO) Acrisols tend to form readily on more easily weatherable rocks, such as schists and basic gneisses, granulites, amphibolites, gabbros, and, especially, on old, sedimentary materials with notable permeability, such as *(i)* deposits of major flood events (formations that in the Iberian Peninsula are known as “rañas”, and which are probably of Plio-Pleistocene age), and *(ii)* in the upper levels of Quaternary terraces (soils which tend to be absent in flooding valleys and on Holocene formations, and *(iii)* on fluvio-marine deposits present in old emerged platforms.

### Climate

Formation of Acrisols occurs under climatic conditions that favor both leaching and intense weathering. These conditions are common in regions with a wet tropical/monsoonal, subtropical or warm temperate climate.

### Topography

Formation of Acrisols requires long periods of geomorphologic stability. Therefore, these soils are more common in flat, undulating, or hilly landscapes, with gentle slopes, and with a predominance of conditions of biostasis produced by the presence of permanent vegetation cover. Under these conditions, Acrisols are found on old erosional surfaces and on depositional (piedmont) surfaces receiving already weathered materials from adjacent uplands.

### Time

Even under the bio-physico-chemical conditions, Acrisols require a long formation period, being generally considered as fini-Tertiary to Pleistocene soils. When found under temperate climatic conditions, these soils are often relict soils formed under conditions of greater temperature and/or rainfall than those presently occurring; however, the effect of an acidification process caused by leaching during a long time period may lead to a convergence towards the same stage of evolution.

### Lower level units of Acrisols

The following lower levels units are recognized: leptic, plinthic, gleyic, andic, vitric, umbric, stagnic, cutanic, lamellic and nitic, vetic (ECEC $<6$ mol$_c$ kg$^{-1}$ clay). Moreover, other suffix qualifiers are proposed: abruptic, ferric, alumic, hyperdystric, ($V > 20\%$ in some part starting within 100 cm from soil surface), skeletic, rhodic (redder than 5YR), chromic, etc. (IUSS Working Group WRB, 2006). The criteria used for separation of lower level units are based on aspects such as: presence of hydromorphy, andic materials, Al activity, low activity clay, amount and distribution of organic matter and other characteristics.

### Concordance with Soil Taxonomy

The different types of Acrisol correspond essentially with suborders of the Ultisols (aquult, humults, udults and ustults). Some Acrisols correspond to Oxisols with a kandic horizon. Some Acrisols (and Alisols) classify as alfisols in Soil Taxonomy.

### Distribution

The geographical distribution of Acrisols is shown in the accompanying map (Figure A9). They are found associated and alternating with Nitisols, Ferralsols and Lixisols on old

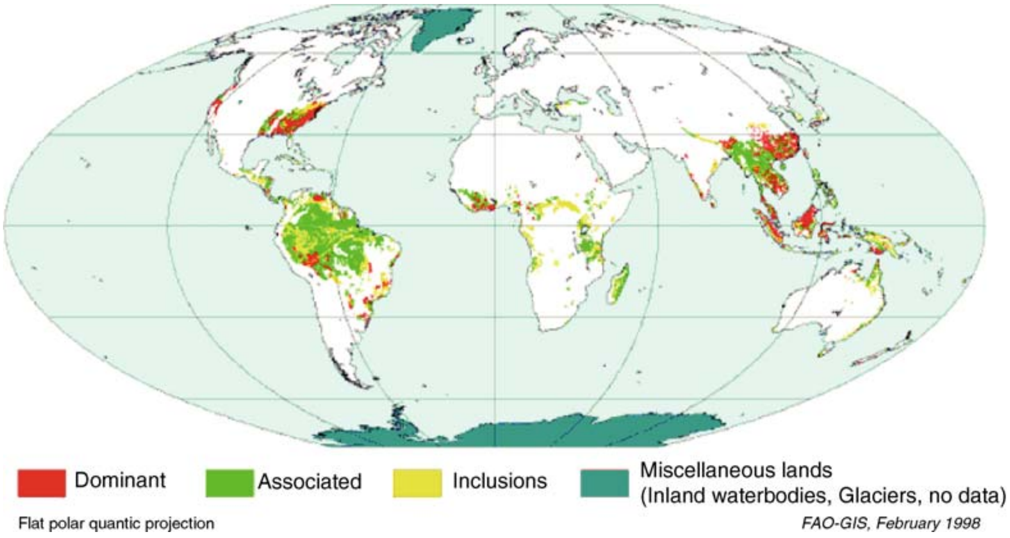

**Figure A9** Acrisols of the world.

erosional surfaces and piedmont locations. On cratonic regions of the humid tropics, they commonly developed as the erosional products of Ferralsols, with the latter occur at a topographically higher level, on stable pediments or uplands. In mountain areas, Acrisols can be found on stable landscape positions of interfleuves, adjacent to Regosols and Cambisols on steeper and less stable slopes. On valley terraces Acrisols may occur on older examples with Luvisols or Cambisols on lower ones. Acrisols may occupy the better-drained areas of alluvial fans in the humid tropics, with Plinthosols and Gleysols in depressions.

### Physical and chemical properties

The chief physico-chemical characteristic of Acrisols is the contrast in properties between the superficial horizons and the underlying argic horizon. The superficial horizons, with their lower clay content are less stable structurally and less capable of retaining water. Where a well-established cover of vegetation has developed, erosion is well controlled. If the cover is removed, erosion becomes a problem, with or without the complimentary problem of compaction. Compaction commonly leads to the retention of drainage waters and the development of darker chromas in the soil. In the B horizon, structural stability is good when Fe is high, though the union between Fe hydroxy phases and negatively charged colloids is less well developed than in Ferralsols, so that aggregates within Acrisols are less stable than in Ferralsols. Consequently clay in the Bt is more easily dispersed.

The acidity of Acrisols is greater in the surface horizons, where it is normally less than 4.5, than in the B, where the range 4.5 to 5.5 is common. At these pH levels soil chemistry tends to be determined by the behavior of Al, which dominates the exchange complex. In addition, the lower the pH the greater the amount of Al in solution in ionic form, either as simple ions, hydroxylated species or complexed to $F^-$. Al toxicity is the common result in Acrisols, and shows up as poor root growth, diminished rate of nitrification, and a high level of phosphate fixation. The domination of Al over exchangeable nutrient elements accounts for the low fertility of these soils.

Cation exchange capacity (CEC) at pH 7 is typical of a low activity clay soil – normally less than 16 $\text{cmol}(+)\text{kg}^{-1}$ of clay. It may be higher if residual mica or halloysite is present. The effective cation exchange capacity (ECEC) is much lower, and in some cases may be as low as 4 $\text{cmol}(+)\text{kg}^{-1}$ of clay). Presence of active Fe and Al surfaces in the solid phases may cause a moderate to high ability to adsorb anions such as phosphate, arsenate, sulfate, and fluoride, as well as organic anions.

Biophile elements (C and N for example) tend to be low in Acrisols as would be expected with low soil fertility. The vegetative cover may be forest, bush or herbaceous, with the species present being those, which tolerate low inherent fertility and high acidity.

### Use

Agricultural use of Acrisols is limited chemically by low fertility, and the toxicity of Al. Physically, cultivation exposes these soils to significant erosion, and truncated profiles are common. The well-drained surficial part of the soil tends to be droughty in drier climates and shallow-rooting crops are at risk.

Liming and fertilization are the management practices necessary for the production of reasonable agricultural yields. Crops include tea, rubber, oil palm, coffee and sugar.

### Environmental significance

In terms of the negative environmental significance of Acrisols, the obvious point is that that once the vegetation cover is removed, the A horizon is easily eroded. The acid nature of the acrisolic environment accounts for a second point. Metal structures, and metal-containing additives may release toxic amounts of metallic ions into the aqueous environment, where Acrisols are the dominant soils. Both of these negative features may be minimized however – the first by geotechnical treatment, contour ploughing, terracing and so on; the second by liming and by the addition of organic wastes and manures, which will tend to immobilize Al and other metals.

The argic horizon of Acrisols has a well-developed capability of filtering and retaining possible contaminants that enter soil water from atmospheric and anthropic sources. In addition the large area of Al and Fe dominant surface afforded by hydroxide and kanditic minerals, provides these soils with a considerable ability to fix anions, thereby protecting groundwater resources from anionic contamination. This latter characteristic is of course a negative feature when judged in terms of phosphate retention in an agricultural soil, but in the case, but in terms of the environmental value of this property, it has the positive effect of affording protection of groundwater from phosphate contamination, as well as providing protection against eutrophication to associated groundwaters.

Felipe Macías

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### Cross-references

Acid Soils
Acidity
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Ferralsols
Tropical Soils
Weathering Systems in Soil Science

## ACTIVITY RATIOS*

### Introduction

Most studies of the composition of solutions in equilibrium with soils measure the concentrations of a single ionic component of interest, such as a plant nutrient element. If, however, incidental experimental variables such as electrolyte concentration or soil/solution ratio are altered, the concentration of that component also alters. This occurs because the surfaces of the clay and humus colloids of the soil contain negative electric

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*This text originally appeared in Soil Science – ISBN 0879331763.

charges, and the incidental experimental variables alter the distribution of cations and anions between the charged surfaces and the solution. Thus it is impossible to characterize a soil with a unique value of the solution of any one ionic component.

This impasse can be overcome by relating the concentration (or better, the activity) of one ion to that of another, in the form of activity ratios (for two ions of similar charge) and activity products (for two ions of opposite charge). This article first explains the theoretical principles and goes on to practical applications and case studies.

## Theory and definitions

### Chemical potential, activity, and concentration

When considering chemical reactions, the term of the Gibbs free-energy *function* that relates to the chemical composition of the system is the *chemical potential*, $\mu$. For a given component, $\mu$ is defined in terms of the *activity*, $a$, by the relationship:

$$\mu = \mu^\circ + \mathrm{R}T \ln a \tag{1}$$

where R is the gas constant, $T$ is the temperature in K, and $\mu^\circ$ is the *standard chemical potential*, an arbitrary reference point given by the value of $\mu$ at unit activity.

The activity can be qualitatively described as "effective concentration," and it is related to the actual concentration, $m$ mol dm$^{-3}$, by the activity coefficient, $\gamma$, that is, $a = m\gamma$. The activity coefficient has a value close to unity for very dilute solutions ($<10^{-4}$ mol dm$^{-3}$); but it decreases as the electrolyte concentration increases. In pure solutions it can be evaluated theoretically or determined experimentally by a variety of techniques (Robinson and Stokes, 1965).

## The electrical double layer

When an electrically charged surface is in equilibrium with a solution, electrical neutrality is maintained by absorbed counter-ions, which produces an *electrical double layer*. The structure of such a double layer around a negatively charged surface is shown diagrammatically in Figure A10. The distribution of cations adjacent to the surface (Figure A10a) shows the *Stern layer*, a localized layer of cations near the surface, and the *Gouy*, or *diffuse layer*, occurring further from the surface. An exponential drop in electrical potential to zero in the external solution (Figure A10b) is associated with the electrical double layer. The excess of cations over anions in the solution balances the negative charge of the surface, their relative concentrations at a distance from the surface being as shown in Figure A10c.

The "thickness" of the double layer is thought of as the distance from the surface of a plane of charge with electrical capacity equal to that of the double layer. This thickness decreases as the valency and concentration of the electrolyte increase. For typical soil systems the double-layer thickness measures between 1 and 10 nm, but the distance from the surface at which the charge is totally neutralized will be several times greater than this (van Olphen, 1977).

## The electrochemical potential

In the electrically charged system described previously, the electrochemical potential of an ion replaces the chemical potential as the appropriate term of the Gibbs free-energy function (Guggenheim, 1929). For a given ion species, this function is defined by:

$$\bar{\mu} = \bar{\mu}^\circ + z\mathrm{F}\Psi + \mathrm{R}T \ln a \tag{2}$$

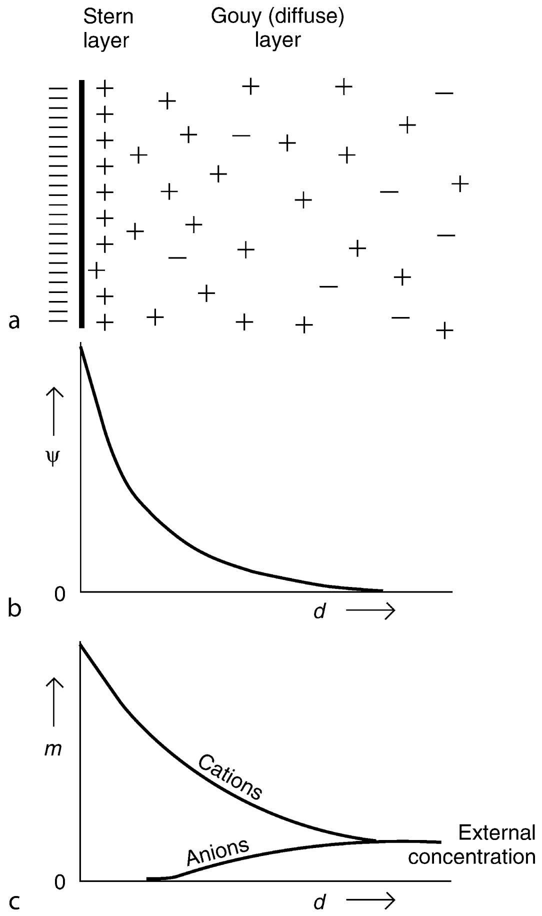

**Figure A10** The electrical double layer. (**a**) Diagrammatic representation of the distribution of counterions adjacent to a negatively charged surface. (**b**) Electrical potential $\Psi$ at a point in the solution as a function of distance *d* from the charged surface. (**c**) Concentration *m* of cations and anions in solution as a function of distance from the surface.

where $z$ is the valency of the ion, F is Faraday's constant, and $\Psi$ is the electrical potential in solution. At equilibrium, $\bar{\mu}$ must remain constant throughout the system, which requires the activity $a$ to vary with distance from the surface because of the variation of $\Psi$. This variation depends on both the concentration of external electrolyte and the charge of the ions in the system.

Consider the electrochemical potential of two ions of differing charge, say, $K^+$ and $Ca^{2+}$, in a plane of constant potential $\Psi$. The electrochemical potentials are given by:

$$\bar{\mu}_{\mathrm{K}} = \bar{\mu}^{\mathrm{o}}_{\mathrm{K}} + F\Psi + \mathrm{R}T \ln a_{\mathrm{K}} \tag{3}$$

and

$$\bar{\mu}_{\mathrm{Ca}} = \bar{\mu}^{\mathrm{o}}_{\mathrm{Ca}} + 2F\Psi + \mathrm{R}T \ln a_{\mathrm{Ca}} \tag{4}$$

Subtracting Equation (4) from (2) × (3), we get:

$$2\bar{\mu}_{\mathrm{K}} - \bar{\mu}_{\mathrm{Ca}} = 2\bar{\mu}^{\mathrm{o}}_{\mathrm{K}} - \bar{\mu}^{\mathrm{o}}_{\mathrm{Ca}} + \mathrm{R}T \ln \frac{(a_{\mathrm{K}})^2}{(a_{\mathrm{Ca}})} \tag{5}$$

which may be simplified to:

$$f(\Delta\bar{\mu}) = \log\frac{(a_{\mathrm{K}})^2}{(a_{\mathrm{Ca}})} \qquad (6)$$

## Activity ratios

Equation (6) shows that a function of the difference in electrochemical potential is directly related to the logarithm of a ratio of the two ionic activities. Since $f(\Delta\bar{\mu})$ is a constant throughout the system, by definition the activity ratio must also be constant, and it defines the chemical potential of one ion with reference to that of another ion, even though the actual concentration of each individual ion may vary.

Similar reasoning may be applied to any ion pair, taking account of the sign and charge of the ions. In many natural soils, $Ca^{2+}$ is the dominant cation, and it is therefore frequently used as the ion to which activities of other ions are related, producing activity ratios and products such as $a_{\mathrm{Mg}}/a_{\mathrm{Ca}}$; $(a_{\mathrm{H}})^2/a_{\mathrm{Ca}}$; $(a_{\mathrm{Al}})^2/(a_{\mathrm{Ca}})^3$; and activity products such as $a_{\mathrm{Ca}} \times (a_{\mathrm{H2PO4}})^2$; $a_{\mathrm{Ca}} \times a_{\mathrm{HPO4}}$. The activity ratios for cation pairs are often expressed in such forms as $\mathrm{AR}_{\mathrm{K-Ca}}$ or $\mathrm{AR}_{\mathrm{Mg-Ca}}$, and it is sometimes convenient to express the "reduced" activity ratio, (such as $a_{\mathrm{K}}/(a_{\mathrm{Ca}})^{1/2}$) on a negative logarithmic scale, which yields functions such as pK–1/2pCa, pH–1/2pCa, and $\mathrm{pH_2PO_4} + 1/2\mathrm{pCa}$, which are frequently, but inaccurately, referred to as "potassium potentials," "phosphate potentials," etc.

## The ratio law

Schofield (1947) proposed a "ratio law" governing the distribution of soil cations. He expressed it as follows: "When cations in a solution are in equilibrium with a larger number of exchangeable ions, a change in the concentration of the solution will not disturb the equilibrium if the concentrations of all the monovalent ions are changed in one ratio, those of all the divalent ions in the square of that ratio and those of all the trivalent ions in the cube of that ratio." It appears from this that the ratio Schofield referred to in this statement was that in which the concentration of ions was changed. However, it is clear from his paper that his emphasis was on the index of this ratio to be used for cations of different valency. His statement introduces another factor, namely, a change in the concentration of the solution. This change may be caused either by diluting the whole system (altering the soil/solution ratio) or by adding electrolyte. The ratio law defines the condition under which these changes will not disturb the equilibrium. In these situations the $\Psi$ terms will cancel out in equations similar to Equations (2)–(5), provided the ion distribution at the surface is not altered. Thus the activity ratio should remain constant in spite of these changes.

The ratio law has subsequently been interpreted rather differently since it has been found experimentally that for a number of ion pairs and a variety of soils activity ratios and products remain approximately constant while solution concentrations vary up to 0.02 mol $\mathrm{dm}^{-3}$ (Beckett, 1971). The activity ratio has therefore become accepted as a relatively stable characteristic to describe the cation status of a soil because it changes little with the incidental experimental variables mentioned above.

There are, however, many soils for which the ratio law does not hold or holds only at lower electrolyte concentrations. A fundamental condition for conformity to the ratio law is the effective exclusion of anions from the cation adsorption sites in the inner parts of the electrical double layer (Figure A10). This occurs only if there is a high potential drop between the charged surfaces and the solution, which requires that the external electrolyte concentration is low and that the soils have a high surface negative charge. For soils of low surface negative charge, and particularly for variable charge soils which contain measurable amounts of surface positive charge, small changes in solution composition alter the relative proportions of cations on the soil surfaces, and activity ratios do not remain constant.

## Activity ratios and cation-exchange equilibria

A cation-exchange model, in addition to the electrochemical model outlined previously, may also describe the distribution of cations between a soil surface and the solution. Consider, for example, the cation exchange reaction:

$$\text{soil Ca} + 2\text{KCL soil K}_2 + \text{CaCl}_2$$

There are a number of ways of formulating the equilibrium quotient for this reaction (Bolt, 1967), but the most satisfactory for practical purposes is probably the "corrected rational selectivity coefficient" (Helfferich, 1962), which defines the equilibrium coefficient $K^{\mathrm{K}}_{\mathrm{Ca}}$ in terms of the *equivalent fraction* of cations in the exchanger phase and the *activity* of cations in the solution phase. This treatment reduces to the following equation:

$$K^{\mathrm{K}}_{\mathrm{Ca}} = \frac{(q_{\mathrm{K}})^2}{q_{\mathrm{Ca}}q_0} \times \frac{a_{\mathrm{Ca}}}{(a_{\mathrm{K}})^2} \qquad (7)$$

where $q_{\mathrm{K}}$ and $q_{\mathrm{Ca}}$ are the amounts of $K^+$ and $Ca^{2+}$ adsorbed at the surface, and $q_0$ is the total charge (cation exchange capacity) of the exchanger, measured in mmol of charge per $\mathrm{dm}^3$, $q_0 = q_{\mathrm{K}} + q_{\mathrm{Ca}}$. This selectivity coefficient is not usually constant for all conditions, but it can be related to the thermodynamic equilibrium constant $K$ by introducing terms for the activity coefficients of ions in the adsorbed phase (Bolt, 1967).

According to Equation (7), the *activity ratio in solution* relates to two important properties of the soil: (1) the composition of the exchange phase, i.e., the relative proportions of $K^+$ and $Ca^{2+}$ adsorbed at the negatively charged surface, and (2) the relative affinity of these cations for the soil surface as reflected by the selectivity coefficient $K^{\mathrm{K}}_{\mathrm{Ca}}$. Reasoning similar to that used here for potassium and calcium can be used for any cation pair.

## Measurement and use of activity ratio

The equilibrium activity ratio $\mathrm{AR}^{\mathrm{e}}$ of an ion pair for a soil sample serves to characterize the sample with respect to the free-energy difference of the two ions whether the ratio law holds or not. There are two rigorous ways of measuring this and one approximate way:

- Conventional chemical analysis of the soil solution allows ion concentrations to be determined and activities (hence activity ratios) to be calculated taking account of ion-pair formation. More directly, ion-selective electrodes allow direct determination of the activities of ions of interest, and hence the activity ratio (Yu, 1992).
- An *adsorption-desorption isotherm* is constructed by shaking a number of samples of the soil at a wider soil/solution ratio, say, 1:10, with incremental additions of the ion under investigation such as $K^+$ but at a constant concentration of the reference cation such as 5 or 10 mM $CaCl_2$. Chemical determination of the concentrations of $K^+$ allows the calculation of the amount desorbed or adsorbed ($\Delta$K, mmol per kg

soil) at each point. A typical plot resulting from such an experiment is shown in Figure A11, and the equilibrium activity ratio, $AR^e_{K-Ca}$ for the soil is obtained from the *null* point, $\Delta K = 0$, where potassium is neither lost to nor gained from the solution.

- An approximate value can be obtained by equilibrating a soil sample with a dilute electrolyte, say 5 mM $CaCl_2$ solution if Ca is the dominant cation in the soil at a low soil solution ratio such as 1 : 1. This ratio provides sufficient solution for analysis with a minimum desorption of exchangeable cations.

In addition to demonstrating the equilibrium activity ratio, the sorption isotherm shown in Figure A11 also shows how the activity can be expected to change when the ion is removed from a field soil by leaching or crop uptake or when it is added in fertilizers. The gradient of the isotherm ($\delta\Delta K/\delta AR$) defines the *buffer capacity* of the soil for the ion, but because the isotherms are rarely linear, a comparison of buffer capacities of different soils must be made at some standard AR value. The two linear regions of the curve illustrated in Figure A11 reflect potassium-calcium exchange on two different types of surface sites, and the two intercepts $K_1$ and $K_2$ give the capacity of these sites for retaining potassium.

Plant growth is complex and is controlled by a network of interactions so that the application of cation-activity ratios to growth studies is by no means straightforward (Beckett, 1972). Indeed there has been much controversy over whether plants respond to chemical potentials or to individual ion concentrations (Soon, 1985). This is difficult to resolve experimentally, because to do so requires systems in which both concentration and activity ratio vary independently. This would be very difficult to achieve without involving other nutrient interactions, and to the author's knowledge has not yet been done convincingly. However, the use of activity ratios and products is the only method of defining unambiguously the chemical potential of ions in a charges colloidal system such as soil. The use of individual ion concentrations may be satisfactory when comparing similar soils under similar incidental experimental conditions, but only when this restriction maintains both the reference ion concentration and the activity-coefficients constant.

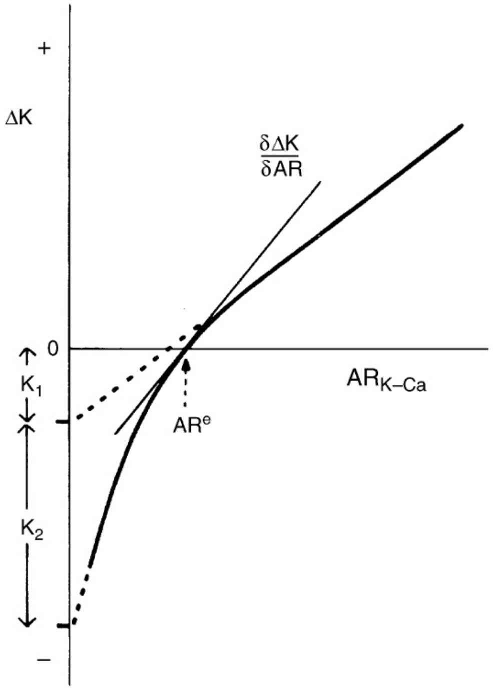

**Figure A11** Sorption isotherm for potassium, with calcium as the reference cation. The diagram illustrates the estimation of the equilibrium activity ratio ($AR^e$), the buffer capacity ($\delta\Delta K/\delta AR$), and adsorption capacities ($K_1$ and $K_2$) of two different types of potassium-adsorbing sites.

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# ADOBE

Unburnt brick made of clay or clay-rich soil, and dried in the sun. Characteristic of building construction in Mexico and adjacent parts of the USA.

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# ADSORPTION

The concentration and bonding of a substance to the surface of a second substance. The bonding is relatively weak and temporary, as for example the adsorption of nutrient ions to clay particles in a soil. The materials in the soil that are capable of adsorbing are known collectively as the adsorption complex. The amount of a chemical species taken up by the adsorption complex at a given temperature may be plotted against the concentration of that species in the co-existing aqueous solution. The resulting graph is called an adsorption isotherm (McBride, 1994, p. 344–345).

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## Cross-reference

Sorption Phenomena

# AGGREGATE

A composite body or granule within a soil, made up of mineral particles loosely held together. Characteristically the binding of the particles is a relatively minor amount of organic matter.

# AGGREGATE STABILITY TO DRYING AND WETTING

*Aggregate stability* may be defined as the extent to which portions of soil remain intact when stressed by environmental factors. Here, the emphasis is on wetting and drying. For dry soil, the maximum possible stress is imposed by immersing portions in water. In the case of wet aggregates, possible weakening due to recent cultivation has to be taken into account. This effect is maximized by remoulding a soil at field capacity and then immersing wet portions in water. In the case of surface soil aggregates, mechanical stress and stress due to wetting are applied simultaneously by raindrops. Only an indirect simulation of the effect of rain is discussed here using end- over-end shaking. An indication of the likely effect of severe rain is also obtaining by finding out how wet a soil can be remoulding before the stability of a wet portion is reduced.

## Breakup of aggregates on wetting

*Slaking.* The initial breakup of aggregates when immersed in water (Figure A12a,b) is caused by differential swelling and entrapped air (Renin, 1938). The relative importance of the two factors depends on the surface area of the clay present and the amount of clay. The magnitude of the stresses induced decreases with increasing water content of the aggregates prior to immersion.

The faster an aggregate is wetted, the greater its tendency to slake. Its rate of wetting depends on both the precise method of wetting used and permeability of the aggregate itself. Organic matter reduces slaking by enclosing the packets of clay particles present in an aggregate rather like a string bag, the packets of clay being free to swell up inside. Another effect of organic matter, if sufficient quantity is present, is to increase the soil-water contact angle so that the rate of wetting is reduced. Slaking of aggregates can also be prevented by engulfing the clay particles in a solid matrix either naturally, by the deposition of silica, for example, or artificially by adding cement.

*Dispersion.* After immersion in water and any slaking, soluble salts present in an aggregate begin to diffuse out into the surrounding water. If the electrolyte content of the water is sufficiently low, then clay particles may gradually separate from the aggregate due to the osmotic pressure difference induced between them (Figure A12c,d). Exchangeable sodium is normally the main cause of dispersion. Its effect is enhanced by the presence of magnesium rather than calcium ions on the other exchange sites, but reduced if sites are occupied by hydroxy aluminum ions. On a larger scale very fine aluminum and iron oxides can prevent dispersion by acting as cationic bridges between clay particles (El-Swaify and Emerson, 1975). By linking particles together, as already indicated, organic matter can also prevent dispersion despite the presence of appreciable exchangeable sodium. The presence of a source of divalent cations such as carbonate reduces dispersion by increasing the electrolyte content of the water.

*Dispersion of wet, sheared aggregates.* An aggregate in which there is no exchangeable sodium present does not normally disperse in water unless it has been sheared first when wet. During shearing water between some of the larger pores is forced in between the clay particles, thereby increasing their average distance apart. Then when the wet soil is immersed in water, the osmotic stress induced between the particles may be sufficient to cause dispersion. The same factors that control the ease of dispersion of unsheared aggregates affect in a similar way the value of the minimum average distance between clay

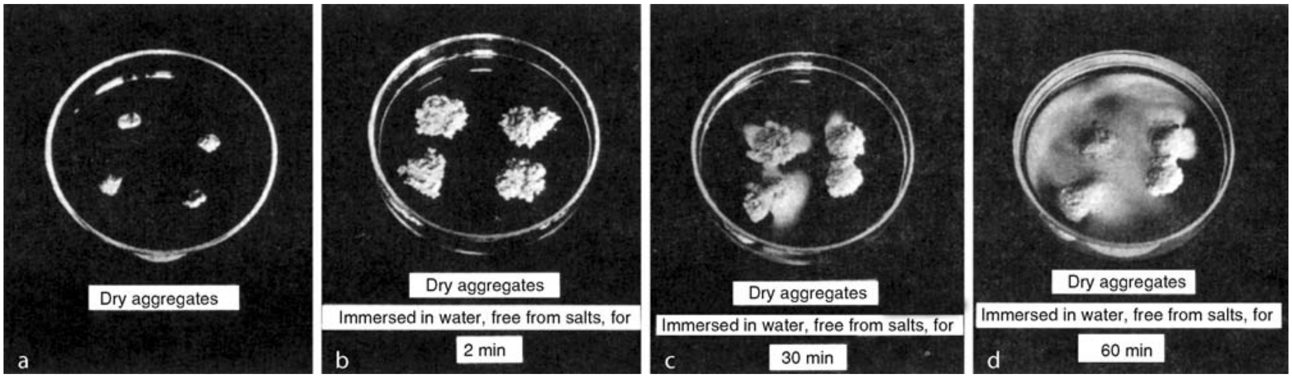

**Figure A12** The breakup of aggregates on wetting where dry aggregates (**a**) at first rapidly slake in water (**b**) and then subsequently release clay at a slow rate by dispersion (**c, d**) (after Emerson, 1967).

particles, minimum water content of the aggregate, before dispersion occurs, with one exception. Organic matter, can act in two ways. First, if there are sufficient organic links between the clay packets, shearing is unable to break the links, and there is reduced dispersion (as for unsheared aggregates). Second, if there are only a few links and when these are broken by shearing, the individual polymer chains act as peptizing agents. Thus for some soils the surface aggregates may be more easily dispersed by shearing than the subsoil aggregates with similar clay content.

## Measurement of aggregate stability

*Water-stable aggregation.* This is usually measured on a macroscale following Tiulin (1928) or a microscale after Middleton (1930). In the first, dry aggregates are wetted, then immersed in tap water and the size distribution of the slaked fragments determined by sieving. Methods of wetting and sieving have been standardized (Kemper, 1965; Kemper and Chepil, 1965). In the second, wetted aggregates are immersed in water contained in a cylinder, which is then shaken end over end. Aggregation is measured by the proportion of particles smaller than 50 µm in suspension compared with the proportion of particles smaller than 50 µm present in the aggregates. This method has been partially standardized (Quirk, 1950). Microaggregation combines breakup of aggregates due to slaking and aggregates due to subsequent attrition.

*Aggregate coherence in water.* In 1967, Emerson suggested classifying the stability of the structure of soil aggregates according to their reactions with water. The first reaction used was the slaking/dispersion of air-dry aggregates when immersed in water. Slaking by itself is an insufficient criterion, although its speed and severity are always assessed (Emerson, 1991). The difficulty is that aggregates may contain sufficient organic matter or inorganic cement to prevent slaking and spontaneous dispersion, but not so much as to prevent dispersion of the aggregates after working wet. In the current scheme (Figure A13), these aggregates are in classes 3–7 depending on the strength of the interparticle bonding. Strongly cemented aggregates are in class 7. No clay is released from such aggregates when shaken vigorously as a 1 : 5 suspension in water. When testing the dispersion of remoulded soil, 5 mm cubes are used instead of just portions of remoulded soil. The water content at which soil is remoulded is still either field capacity or that of aggregates smaller than 2 mm wet up with water at 10 kPa suction. However, class 3 has now been divided into 3a and 3b according to the severity of dispersion of the aggregates. Loveday and Pyle (1973) assessed the dispersion of aggregates in classes 1–3 after 2 h as well as 16 h. This enabled them to develop a *dispersion index, which* allows 16 levels of stability to be distinguished.

## Application in the field

Conventionally the effect of organic content on the stability of soil aggregates to water has been assessed by measuring water-stable aggregation (Clarke and Marshall, 1947). However, these methods are not useful for elucidating the general causes of aggregate instability. For this determining the class number of a soil is a simple but powerful tool (Greenland, Rimmer and Payne, 1975). An advantage of using dispersion as the main diagnostic criterion is that it is easily seen in laboratory tests. When actual dispersion occurs in the field, the results are spectacular. Examples are piping failures through dam walls containing soil in class 1 when rapidly wet with water of low salt content; severe crusting on drying of surface soils in class 3a, if the soils are cultivated wet and rain follows soon after. However, even if actual dispersion does not occur, then the class number helps to show how structural damage can be avoided. For example, where soils are irrigated with water of low salt content, aggregates of clay subsoils in classes 1 or 2 may swell sufficiently to impair drainage. This can be overcome by adding gypsum. If a cultivated soil contains class 3a aggregates, then tillage and traffic under wet conditions should be minimized. Otherwise the structural porosity of the aggregates will be lost. Such damage can be mitigated by increasing the Ca-ion concentration in the soil solution, so moving the aggregates into class 4.

If a duplicate cube of soil is weighed and dried, values for the dry *bulk density* of the soil are obtained. These are the

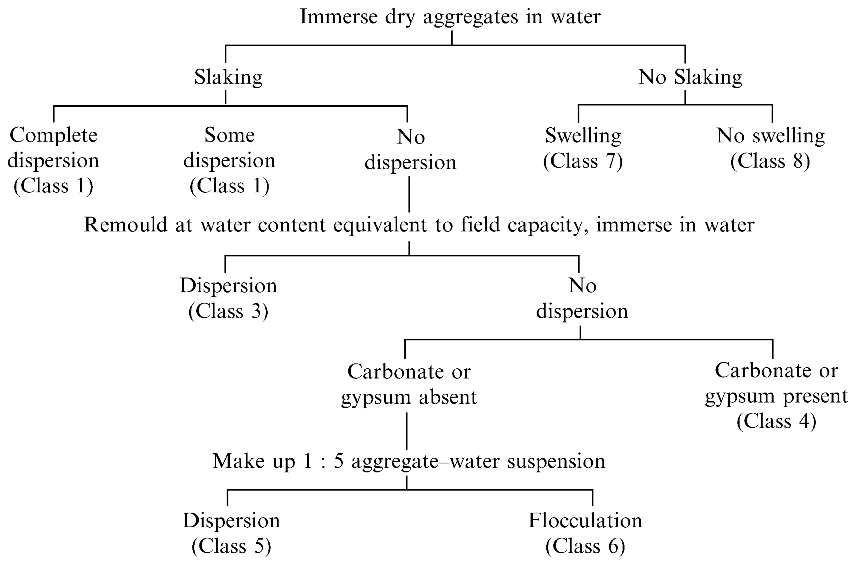

**Figure A13** Scheme for determining class numbers of aggregates.

maximum possible dry bulk densities the soil or aggregates can attain in the field at field capacity or after drying. If the actual field values are measured, then the existing structural porosity can be determined. Values of minimum possible dry bulk density can be found from their values under permanent grass. The current structural status of the soil can then be assessed.

More detailed accounts of the mechanisms of aggregate breakup, inter-particle bonds, and field applications of the aggregate classification are given in Emerson (1991) and under the entry *Soil Structure.* Descriptions of the actual measurement of water-stable aggregation are given in Haver et al. (1972).

W. W. Emerson

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### Cross-references

Aggregation
Bulk Density
Flocculation
Infiltration
Particle Density
Physical Chemistry
Soil Pores
Transport Processes
Water Budget in Soil
Water Movement

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## AGGREGATION

The soil is a complex multi-phase system made up of solid, liquid, and gaseous material. It contains solid particles of sand, silt and clay size. These are usually bound together as structural units called aggregates. An individual soil aggregate, also called a ped (Soil Survey Staff, 1993), can be defined as a naturally occurring cluster, or group, of soil particles in which the forces holding the particles together are much stronger than the forces between adjacent aggregates. The size distribution of the aggregates, their stability, and the amount and size distribution of the pore space between and within the aggregates characterize the soil structure. The terms "aggregation" and "soil structure" should not, however be used interchangeably: "aggregation" represents only one aspect of soil-structure formation while "soil structure" can result either from the building up of aggregates from dispersed materials or from the breaking down of larger coherent masses into favorably sized aggregates (Six et al., 2004).

From an agricultural point of view, the binding of soil particles into aggregates is essential for the production of optimum *soil tilth*. Soil tilth is a general term, which signifies the ability of the aggregates to withstand destruction by the impact of implements, raindrops, or running water so that the air-moisture regime is maintained at a favorable level for plant growth and microbiological activity (see *Tillage*).

### A conceptual model

The five major factors involved in aggregate formation are soil fauna, microorganisms, roots, inorganic components and physical processes in the environment. References to the earlier work in this field will be found in the first edition of this Encyclopedia. Before the 1950s an overall conceptual model was lacking, and it was Emerson in 1959, who provided the breakthrough (Figure A14).

As quartz, clay, and organic matter are the main constituents of the soil aggregate or crumb, the various possibilities of bonding arrangements are summarized *grosso modo* in Figure A14. The clay particles are shown as *domains* consisting of several clay particles held together face to face. The domains may be held edge to face through aluminum bonds or edge to face, edge-to-edge, or face-to-face through organic colloids. These colloids can also bond clay particles to the surface of siliceous silt or sand particles. The critical advances since Emerson's work is summarized in Figure A15, from Six et al., 2004).

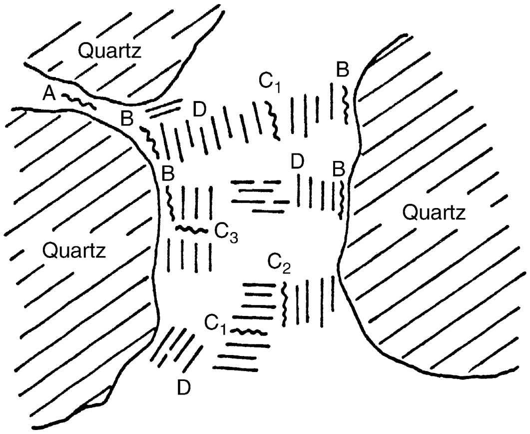
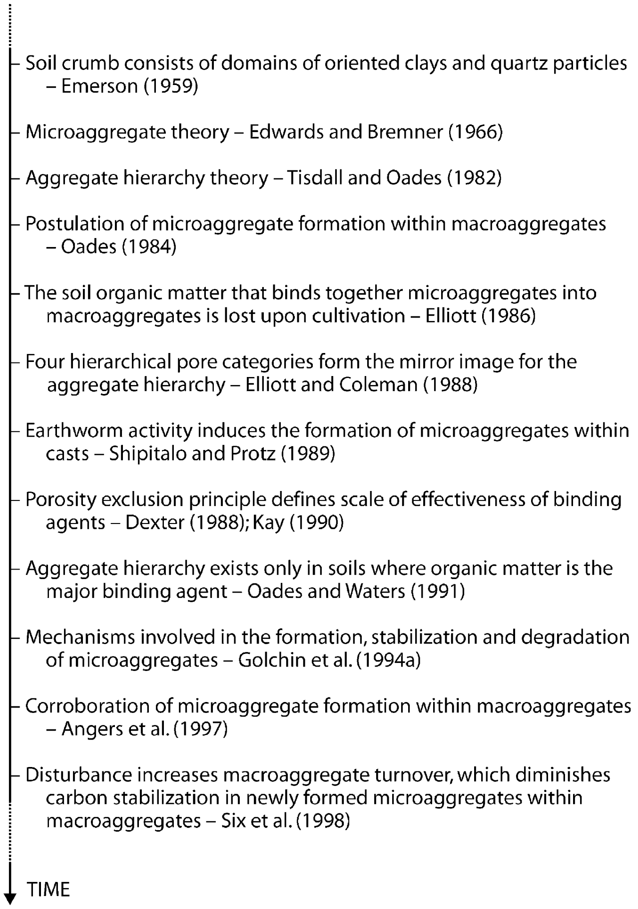


**Figure A14** Suggested arrangements of quartz particles, clay domains, and organic matters in a soil *aggregate. A:* Quartz-organic colloid-quartz; *B:* quartz-organic colloid-clay domain; *C:* clay domain-organic colloid-clay domain; $C_1$: face-face; $C_2$: edge-face; $C_3$: edge-edge; *D*: clay domain edge-clay domain face (after Emerson, 1959).



- Soil crumb consists of domains of oriented clays and quartz particles – Emerson (1959)
- Microaggregate theory – Edwards and Bremner (1966)
- Aggregate hierarchy theory – Tisdall and Oades (1982)
- Postulation of microaggregate formation within macroaggregates – Oades (1984)
- The soil organic matter that binds together microaggregates into macroaggregates is lost upon cultivation – Elliott (1986)
- Four hierarchical pore categories form the mirror image for the aggregate hierarchy – Elliott and Coleman (1988)
- Earthworm activity induces the formation of microaggregates within casts – Shipitalo and Protz (1989)
- Porosity exclusion principle defines scale of effectiveness of binding agents – Dexter (1988); Kay (1990)
- Aggregate hierarchy exists only in soils where organic matter is the major binding agent – Oades and Waters (1991)
- Mechanisms involved in the formation, stabilization and degradation of microaggregates – Golchin et al. (1994a)
- Corroboration of microaggregate formation within macroaggregates – Angers et al. (1997)
- Disturbance increases macroaggregate turnover, which diminishes carbon stabilization in newly formed microaggregates within macroaggregates – Six et al. (1998)

**Figure A15** Critical advances in the understanding of aggregation in soils, since Emerson's work.

The diversity of soil constituents implicated as aggregating agents has produced many theories explaining the processes involved in soil aggregation, with the role of the clay fraction or organic material being particularly stressed. Martin et al. (1955) for example, emphasized the importance of clay as the predominant binding agent in soil aggregation. They suggested that organic materials do not act primarily to hold clay, silt, and sand grains together, but rather their chief role may be to modify the forces by which clay particles *per se* are attracted to one another. According to this view, cohesiveness between clay particles is the binding force in aggregation rather than the cementing action of organic molecules. Other investigators have stressed the importance of organic substances, produced largely through microbial activity, to soil aggregation. From the point of view of soil structure, aggregation requires a binding together of flocculated particles. Nevertheless, flocculation and aggregation are not synonymous. The former is primarily electrokinetic, although *flocculation* (*q.v.*) can occur as a result of electrostatic attraction between the positive edges and negative forces of clay minerals. Thus flocculation may *aid* the aggregation process, but is not aggregation in itself.

As the formation of aggregates comprises a complex interrelationship of physical, biological, and chemical reactions, different kinds of mechanisms have been proposed to explain the formation of aggregation in the soil (see Six et al., 2004, for a thorough review).

## Clay particles

The clay particles themselves cohere and thus entrap or bridge between larger sand and soil grains. The cohesive forces between the particles arise from physicochemical mechanisms such as:

- The van der Waals forces, which vary inversely as the cube of the distance between particles.
- The electrostatic attraction between negatively charged clay surfaces and positively charged clay edges.
- The linking of the particles together through cationic bridges. There is a linking system between particles consisting of the negatively charged surface of a particle and oriented water molecules.
- The cementation effects of organic matter, aluminum, and iron oxides. The iron oxides, in particular, may serve a dual purpose in aggregation. That part in solution may act as a flocculating agent, and the other part, which is more gelatinous in nature, may exert a cementation action.
- The surface tension of the curved menisci at the air-water interfaces that are mostly present in the soil. Cohesion in wet soils takes place between the molecules of the liquid phase as bridges or films between adjacent particles.

## Organic matter

The organic colloidal material, produced largely through microbial activity, together with clay is responsible for the major portion of soil aggregation. Moreover, it is more effective than clay in causing the formation of stable aggregates with sand. The beneficial effects on soil aggregation originate from the integrated activity of microorganisms, fauna, and vegetation. Changes in aggregation following addition of organic material to soil indicate that aggregating effectiveness relates directly to microbial decomposition.

Organic residues and other products of microbial decomposition in the soil are thought to surround the soil particles and thus hold them together through cementing or encapsulating action. Organic material itself without biological transformation has little effect on soil structure. The conditions that favor high microbial activity result usually in early increased rates of aggregate formation due to fungal mycelia. However, high microbial activity also results in an increased rate of aggregate degradation due to an accelerated decomposition of the organic aggregating substances. Diverse bacteria, fungi, and actinomycetes are able to synthesize soil-binding substances. The major mechanism by which microorganisms effect soil aggregation involves the production of polysaccharides during microbial metabolism of organic matter in soil. The formation of aggregates by microorganisms may be explained by adsorption phenomena, physical entanglement, and cementation by microbial mucilages.

The action of organic compounds in effecting aggregation may be very complex and at best is little understood. Many have postulated that soil particles are held together in aggregates by the organic compounds. There is, however, considerable evidence that another important role of these compounds may be in modifying the expression of cohesive forces between clay particles through adsorption on the surfaces of the clay. Thus active organic materials may be thought of as acting both to hold soil particles together and in other cases to hold clay particles apart.

## Aggregate formation

In light of the previous discussion, the following seems to best explain how aggregates are formed in agricultural soils. Aggregates result primarily from the action of natural agencies or any process by which parts of the soil are caused to clump together and separate from adjacent masses of soil. If soils are initially dispersed, flocculation is essential for aggregate formation; if they are partially puddle (see *Puddling*) or solid, fragmentation into smaller units is the first essential. Thus there are two kinds of processes involved. The first concerns the building up of aggregates from dispersed materials; the second involves the breaking down of large coherent masses into favorably sized aggregates. Since most soils become more dense and compact with continued farming, the second case is of greater interest.

Separation of parts of the soil mass may result from several factors such as the action of small animals, particularly earthworms as they ingest and intermix soil with partially decomposed organic matter and excrete the ingested material as surface casts or subsurface deposits, and the effect of *tillage* (*q.v.*), which is a function of the soil moisture content at the time of tillage.

*Climate-dependent environmental variables* include the effect of freezing and thawing where the aggregating action of frosts relates inversely to the rate of freezing and depends on the manner in which soil moisture crystallizes. Slow freezing results in the formation of few large ice crystals and large aggregates of soil particles. Since there is about a 9% increase in volume when water changes to ice, the pores are enlarged, which loosens the soil. Water is drawn from around the clay particles to the ice crystals during this process, creating a dehydration effect. The combination of ice-crystal pressure and dehydration causes aggregation. On the other hand, large numbers of small crystals are formed if the cooling is rapid and the integrated effect of many expansions is the breakdown of soil aggregates.

The effect of *wetting and drying* on aggregation is a function of the type of soil, the aggregate moisture at the time of wetting, and the intensity of the wetting treatment. The dehydration of a soil mass cannot be uniform, especially if the drying process is rapid. Consequently, unequal strains arise throughout the mass that tend to form *clods*. At least two processes operate to cause disruption of the clod into smaller units when the dried clod is wetted. The rapid intake of water causes unequal swelling throughout the clod, which produces fracturation and fragmentation along the cleavage planes. Moreover, the sorption of water into the capillaries results first in a compression of the occluded air and finally in a virtual explosion within the clod, as the pressure of the entrapped air exceeds the cohesion of the particles.

The *plant root system* is tremendously important, acting to separate and compress small clumps of soil, causing shrinkage and cracking due to desiccation, and making conditions favorable for the activity of microorganisms at the surface of these units. The exact mechanism of aggregate formation by plant root systems has not been established. The earliest explanation was based on pressures exerted by growing roots, which causes a separation to the soil particles adjacent to the root and a pressing together of these units into aggregates. In other words, each root hair that penetrates into large aggregates introduces a point of weakness. The penetration of sufficient root hairs produces granules. However, attempts to form aggregates by applying artificial pressure have failed to duplicate the water stability of natural field aggregates. This failure suggests that mechanical pressures of roots or soil fauna may not be basic aggregating mechanisms. Another possible aggregating factor is the dehydration of the soil in the vicinity of the root system as water is absorbed by the plant. This dehydration produces localized shrinkage and formation of fracture surfaces.

*To conclude:* aggregation is a complex process involving five major factors, with the current consensus, as reviewed by Six et al., 2004, emphasizing interactions between clay particles, polyvalent cations and soil organic matter. There is still a great need for the quantification of such interactions.

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## Cross-references

Aggregate Stability to Drying and Wetting
Flocculation
Humic Substances
Microhabitats
Microstructure, Engineering Aspects
Physical Chemistry
Soil Structure
Sorption Phenomena
Tillage

## AGRICHEMICAL

Pertaining to the various chemicals used in agriculture to fertilize crops, manage weeds and pests, or which are produced from agricultural crops. Examples: fertilizers, herbicides, biofuels such as ethanol.

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Hester, R.E., and Harrison, R.M., eds., 1996. *Agricultural Chemicals and the Environment.* Cambridge, UK: Royal Society of Chemistry, 127 pp.

## AGROECOLOGY

Agroecology is the attempt to apply ecological principles to agricultural systems, with the objective of sustaining those systems in an environmentally sound manner (Thomas and Kevan, 1993).

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### Cross-reference

Ecology

## AGROECOSYSTEM

An ecosystem that has been modified by the practice of agriculture. This will involve the replacement of native species by domesticated plants and animals, and the application of fertilizers, pesticides and other agrichemicals, in order that the domesticates may compete successfully with wild species.

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## AGROGEOLOGY

Agrogeology, a subdiscipline of geology, is the scientific study of the origin, nature, composition, distribution and utilization of soils from a geological viewpoint. Geology is the scientific study of the Earth, and defines the soil as the uppermost geologic layer, or substratum, that supports plant life on the Earth's land surface. Critical data have been drawn together from several fields of natural science disciplines to provide an understanding of the cycling of elements and minerals in the course of time and explain the complexity of the terrestrial system.

The continental part of the Earth's crust – the lithosphere, comprises about one third of the Earth's surface and is composed of various rocks. The Earth's crust was formed throughout its 4.5 billion-years history. The principal materials in the crust (minerals, rocks, soils and water) on or near the surface of the Earth have been created and destroyed by numerous physical, chemical and biological processes. These processes are collectively referred to as the geological cycle, which comprises of a group of subcycles, including the rock, hydrolic and geochemical cycles.

The rock cycle is a sequence of processes that produces the three rock families: igneous, sedimentary and metamorphic. These migratory processes could be discussed in terms of the processes of magmatism, sedimentation and metamorphism and belong to the fields of geochemistry, mineralogy and petrology. In the lithosphere, the rock cycle begins with the initial crystallization of magma, proceeds with the alteration and weathering of the igneous rocks and the transport and deposition of the sediments. It then continues with the diagenesis and lithification of sedimentary rocks followed by their metamorphism to successively higher grades until eventually, through melting, magma is regenerated. The geochemical cycle involves the migration and distribution of elements during geological changes encompassing the chemistry of lithosphere, asthenosphere, hydrosphere, atmosphere and biosphere. The rock and geochemical cycles are closely related to one another and intimately related to the hydrolic cycle, which provides water necessary to many chemical and physical processes and supports life on Earth.

Intimate interactions between the rock and hydrolic cycles produce weathered rock materials that are the basic ingredients of soils. As opposed to the forces of tectonism and volcanism, which tend to build up the landscape, there are other processes that tend to wear it down. These subtle destructive processes are called weathering processes. Weathering is usually divided into physical disintegration or mechanical breakdown of rocks without chemical alterations; chemical weathering or decomposition of minerals with, often irreversible, chemical change; and biological weathering which is affected by the growth and movement of plants and animals.

Weathering can therefore be defined as the disintegration and alteration of rocks and minerals by physical, chemical and biological processes. The nature and rate of weathering depend of several factors such as: rock type, climate, topography and time. Physical weathering processes involve the disintegration of rocks and minerals by mechanisms of brittle fracture and subsequent decrease in the size of their particles without chemical alteration. The major factors in physical weathering environments are temperature, water, ice and wind, while the main activating agents are unloading, thermal processes (thermoclasty), growth and expansion of materials in pore space such as ice (gelification) and various salts (haloclasty).

Chemical weathering is the decomposition and alteration of minerals, and is a consequence of crystal structure breakdown at the molecular scale a leading to the formation of new minerals of completely different chemical composition, such as secondary oxide and hydroxide minerals, or clay minerals. The most important chemical agents involved in the weathering of minerals are water supplied by rainfall and $CO_2$ from root respiration and microbial degradation of organic matter. Temperature, rainfall and humidity are known by the term climate.

Hydrolysis, or the effect of water containing active hydrogen protons, is the most important and widespread process and is generally the method by which feldspars and micas are chemically weathered. There are also several other processes: carbonation, a reaction of carbonate and bicarbonate ions with minerals associated with hydrolysis of feldspars; hydratation, which involves the adsorption of water; solution, a reaction in which calcite or dolomite are altered to soluble bicarbonates; and oxidation and reduction reactions which involve the transferring of electrons.

Biological processes play a major role in rock and mineral weathering either as living organisms or dead soil organic matter, and have a significant effect on weathering and soil genesis. To recognize the importance of organisms and organic matter in weathering and soil formation two types of processes are distinguished: biological and biochemical weathering. Biological weathering occurs with the participation of live organisms. Tiny cracks in mineral crystals could be penetrated by bacteria, algae, fungal and lichen hyphae. Live roots growing into the cracks of minerals and rocks could contribute to physical weathering process.

Biochemical weathering is related to reactions of primary minerals with chemical compounds exuded by plant roots or microbial secretions as well as interactions with decomposition products of organic matter. Microorganisms cause precipitation and dissolution of minerals and control the distribution of elements in diverse environments at and near the surface of the Earth. The effect of chelation on mineral dissolution by organic (humic, fulvic, oxalic, acetic, salicylic, citric, etc.) acids is assumed to be more effective than geochemical hydrolysis. Complex extracellular polymers (polysaccharides, siderophores, and proteins) produced by a variety of microorganisms are involved in the formation of organomineral complexes in soils.

The soil is product of the interplay of several variables including geological parent rock, climate, organic activity, topography and time. Soil forming processes tend to produce distinctive soil layering or horizons, which lead to profile development. The horizons and relative profile development are an important concept of soil classification. Soil scientists have developed two modern systematic classifications of soils known as the Soil Taxonomy with 10 orders, of the Soil Conservation Services of the United States and the World Soil Map with 26 orders, of the Food and Agriculture Organisation of UNESCO. These classifications are based on soil morphology, color, physical and chemical properties of the soil profile and are emphasized by generic terminology. They are especially useful for agricultural purposes and related land-use planning.

The most active mineral constituents in soils are clays. Clays have a high surface area comprised of fine particles and special structural conditions of certain clay minerals. Most of soils contain only a small percentage of organic matter and much higher amounts of clays or mineral particles in the fraction of less than 2 micrometers (μm) in diameter.

Argillogenesis, or the study of the ways and conditions of birth, development, variability and decay of clay minerals is so complex, that as a consequence it is increasingly approached by inter- or multi-disciplinary methods. Several methods are currently used in the study of soil mineralogy, but the X-Ray Diffraction (XRD) method remains the most favorable. As a geologist, one should keep in mind that microscopy as well as detailed field work must still be associated with the XRD laboratory analyses, and that other instrumental methods, such as: electron microscopy, infra-red spectroscopy, geochemistry, isotopic analyses etc., are also extensively practiced. They have improved the study of mineralogical and geochemical processes within the soil horizons during soil formation as well as understanding of soil properties.

The relation between landforms and geology has been recognized by engineers and geologists since the first geological map was produced in Great Britain. A change in landforms always reflects a change in subsurface conditions. The shape of the landform reflects the history of weathering of different rock types and so the recording of changes in landform distinguishes areas with different geological and geomorphological history. The factors controlling the development of the landscape are considered as the effects of process, geology and time. The main processes include weathering, erosion and deposition, and the distinction between erosional and depositional landforms is very significant in landform analysis. In addition to geomorphological history, the effect of time is important in relation to the processes that are essential in understanding landforms and the soils with which they are covered.

Soils and life have been intimately associated almost from the earliest periods of geological time. The paleosols are products of complex terrestrial ecosystems existing at that time. For a long geological time plants and animals and surface processes were involved in developing of the paleosoil. A great deal of evidence has been collected concerning evolution of factors of soil formation during the geological history, particularly during the Pleistocene. Paleosols, formerly the integral component of the landscapes, apart from characteristics of the epoch of their formation have inherited features that correspond to previous natural climatic conditions as well as indications of subsequent changes. Orbitally forced Milankovitch-type cycling can be detected in paleosol series in the Pleistocene loess in many places across the Northern hemisphere.

Today, the application of classic geological principles to soil mapping and modern landscape-analysis methods has been enhanced by sophisticated methods of remote sensing, GPS and GIS techniques. Information from detailed lithological and soil maps could be extremely useful for land use planning and environmental protection especially when considering land capability for particular land use such as: agriculture, forestry, engineering, urban practice, etc.

Nikola Kostic

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van Straaten, P., 2006. Farming with rocks and minerals: challenges and opportunities. *An. Acad. Bras. Ciênc.*, **78**(4).

## Cross-references

Biomes and their Soils
Fertilizer Raw Materials
Geography and Soils
Geology and Soils
Ice Erosion
Landscape and Soils
Neolithic Revolution

## AGRONOMY

The management of land, particularly soil, in the production of crops.

### Bibliography

Acquaah, G., 2004. *Principles of Crop Production: Theory, Techniques, and Technology.* Upper Saddle River, NJ: Pearson Prentice, 740 pp.

## ALBELUVISOLS

Albeluvisols have a horizon of clay illuviation within a meter of the soil surface. This has an irregular upper boundary as a consequence of deep tongues of bleached soil material penetrating the clay horizon. This article is based on the descriptions in FAO (2001).

*Connotation.* From L. *albus*, white, and L. *eluere*, to wash out.

*Synonyms.* Podzoluvisols (FAO), derno-podzolic or orthopodzolic soils (Russia) and several suborders of the alfisols (Soil Taxonomy).

*Definition.* Within a meter of the surface, 'albeluvic tongues' occur in which a clay illuviation horizon is deeply tongued by bleached soil material from above so that the eluvial–illuvial boundary is broken and irregular.

*Parent material.* Mostly unconsolidated glacial till, materials of lacustrine or fluvial origin and of aeolian deposits (loess).

*Environment.* Flat to undulating plains under boreal taiga, coniferous forest or mixed forest. The climate is temperate to boreal with cold winters, short and cool summers, and an average annual precipitation sum of 500 to 1000 mm. Precipitation is evenly distributed over the year or, in the continental part of the Albeluvisol belt, has a peak in early summer.

*Profile development.* Mostly AEBtC profiles with a dark, thin ochric surface horizon over an albic subsurface horizon that tongues into an underlying brown clay illuviation horizon. *Stagnic soil properties* are common in boreal Albeluvisols.

*Origin.* Translocation of clay (*argilluviation* – see Luvisols) and various cool to cold climate factors play a role in the genesis of Albeluvisols. The characteristic albeluvic tonguing results from periglacial freeze–thaw sequencing at the end of the last glaciation. Movement of clay into a horizon of illuviation commonly causes poor drainage, such that periodic saturation produces redoximorphic characteristics (mottling, nodule formation, movement of Fe downwards and even out of the soil, for example). A fragipan is not uncommon at the interface between eluvial and illuvial horizons.

*Use.* Short growing season (frost!), acidity, low nutrient status, tillage and drainage problems are serious limitations of Albeluvisols. Most Albeluvisols are under forest; livestock farming ranks second; arable cropping plays a minor role. In Russia, the share of arable cropping increases towards the south and west of the Albeluvisol belt, especially on relatively nutrient-rich endoeutric Albeluvisols (see Figure A16).

Otto Spaargaren

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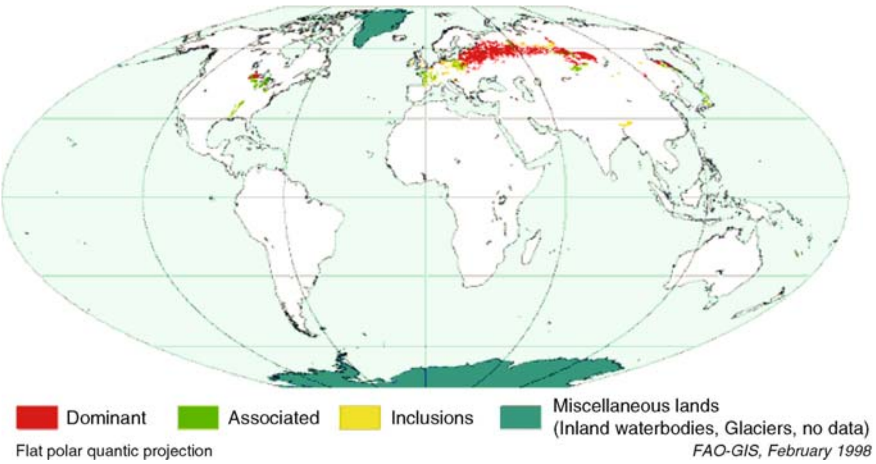
### Cross-references

Acid Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles

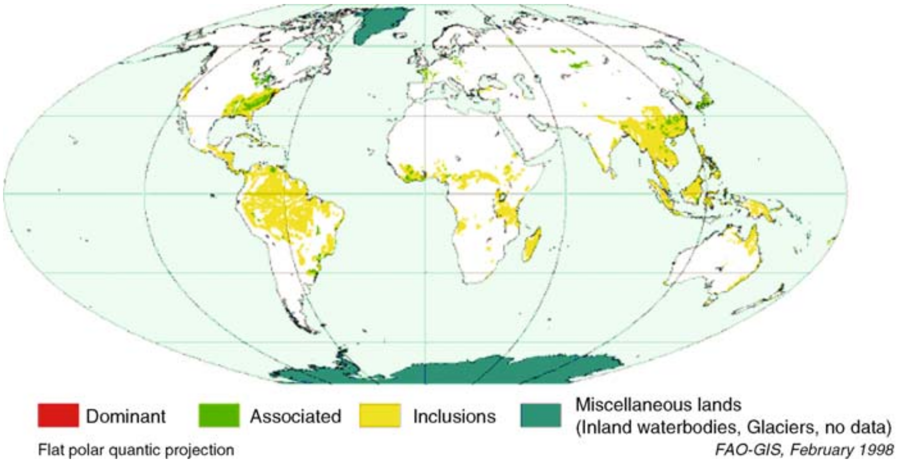
## ALISOLS

Alisols are strongly acid, generally unproductive soils, with accumulated high activity clays in their subsoils. Al dominates the exchange complex. The following is derived from FAO (2001).



FAO-GIS, February 1998

**Figure A16** Distribution of Albeluvisols.



Flat polar quantic projection

*FAO-GIS, February 1998*

**Figure A17** Distribution of Alisols.

*Connotation.* Strongly acid soils with subsurface accumulation of high activity clays that have more than 50% Al$^{3+}$ saturation; from L. *aluminium*, alum.

*Synonyms.* 'Red yellow podzolic soils' with high-activity clays (Brazil), 'ultisols' with high-activity clays (Soil Taxonomy) and 'fersialsols' and 'sols fersiallitiques très lessivés' (France).

*Definition.* Defined by FAO (2001) as soils with

1. an argic horizon, which has a cation exchange capacity (1 M $NH_4OAc$ at pH 7.0) of 24 cmol(+)kg$^{-1}$ clay or more, either starting within 100 cm from the soil surface, or within 200 cm from the soil surface if the argic horizon is overlain by loamy sand or coarser textures throughout, and
2. alic properties in most of the layer between 25 and 100 cm from the soil surface, and
3. no diagnostic horizons other than an ochric, umbric, albic, andic, ferric, nitic, plinthic or vertic horizon.

*Parent material.* Alisols can form in a wide variety of parent materials having high-activity clay minerals such as vermiculite or smectite. Most occurrences of Alisols reported so far are on weathering products of basic rocks.

*Environment.* Most common in old land surfaces with a hilly or undulating topography, in humid (sub-)tropical and monsoon climates (see Figure A17).

*Horizonation.* ABtC profiles. Much of the variation among Alisols is related to the truncation of A horizons in eroded lands. The only diagnostic horizons present are ochric, albic, andic, ferric, nitic, plinthic, or vertic; and the following subclasses are recognized:

a. Plinthic Alisols: with plinthite in the top 125 cm
b. Gleyic Alisols: water saturation produces gleyic properties in the top 100 cm
c. Stagnic Alisols: standing water produces stagnic properties within 50 cm of the surface
d. Humic Alisols: with a mollic or umbric A horizon
e. Ferric Alisols: showing ferric properties
f. Haplic Alisols: all other Alisols

*Origin.* Alisols are found on old landscapes where weathering over the long term has essentially removed virtually all primary minerals except quartz. The clay fraction is dominated by high activity clays, which under appropriate, humid climate conditions, undergo hydrolysis with loss of silica, and alkaline and alkaline-earth cations by leaching, and with the release of Al. Three steps in the genesis of Alisols are recognized:

1. Weathering of bedrock to produce saprolite, which becomes the soil parent material. Most weatherable primary minerals are destroyed and secondary high-activity clays form. On basic and intermediate rocks these are predominantly smectitic, and on acid rocks, vermiculitic.
2. Movement of clay particles in the developing soil, either vertically (illuviation) or laterally. In the most acid soils (pH below about 5) the movement of fine clay tends to be impeded on account of the presence of a significant concentration of Al$^{3+}$, which causes flocculation. Step 2 may overlap the next step.
3. Weathering of secondary high-activity clay. These are unstable in highly leached environments depleted in silica and alkaline and alkaline earth cations. Their weathering liberates Al$^{3+}$ into solution and, where primary ferromagnesian minerals were originally present, iron and magnesium are released from the octahedral inner layers of (2 : 1) clay minerals. Since the solum of an Alisol is an oxidizing environment Fe precipitates as a ferric hydroxyl phase and imparts a reddish color to some Alisols such as the Rhodic Alisols of the Caribbean region.

A common, further change is for a mature landscape to be truncated by surface erosion of the ancient landscapes on which these soils are found. Subsoil horizons then become exposed at the surface.

*Use.* Alisols contain low levels of plant nutrients (except for Mg$^{2+}$ in some cases) whereas soluble inorganic Al is present in toxic quantities. If liming and full fertilization is no option, use of these soils is generally restricted to crops, which accommodate with low nutrient contents and tolerate high levels of free Al. Alisols are traditionally used in shifting cultivation and for low volume production of undemanding crops. In the past decades, Alisols have increasingly been planted to Al-tolerant estate crops such as tea and rubber, and also to oil palm.

Otto Spaargaren

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## Cross-references

Acid Soils
Biomes and their Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils

# ALKALI

See *Acids, Alkalis, Bases and pH*.

# ALKALINE SOILS

Alkaline soils are taken here to include all soils in which soil pH is generally higher than 7 throughout the solum. Other authors consider alkaline soils those that have $pH > 8.5$. This includes Calcisols, Gypsisols, saline and sodic soils, and those soils such as Chernozems and Kastanozems that have subsurface calcite, and which are generally found in sub-humid to semi-arid regions. It excludes those soils of the humid zone in which calcite may be present in sub-surface horizons and which are treated in the article on calcareous soils (Luvisols for example).

## Ambient conditions

Alkaline soils so defined, are characteristic of the drier climates of the world, and tend to be concentrated in deserts and adjacent regions (Figure A18). The significant characteristic is that evapotranspiration exceeds precipitation for at least part of the year. Calcisols represent the least arid part of the spectrum and are found at the edges of the short grass prairie with a sparse vegetation of xerophytic shrubs and ephemeral grasses. With increasing aridity, Gypsisols, so called "desert soils", become dominant. Where salts are present in the parent material or in groundwater, capillary uprise during a pronounced dry period can bring salt to the surface or at least to the upper part of the solum, and saline and sodic soils may form and encourage a halophytic vegetation.

In terms of Eh (pe)–pH conditions, the general field of the alkaline soils is shown in Figure A19.

## Physico-chemical processes

Two physical processes dominate the genesis of alkaline soils. The first is the evaporation of water from the upper part of the solum during dry periods, and the second is the consequent capillary uprise of water from depth. The resulting chemical changes in the soil depend on the chemistry of parent materials and hydrological sources, both of which are highly variable. Generally speaking, the dominant aqueous species that accumulate in soil waters undergoing evaporation are $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $SO_4^{2-}$ and $H_4SiO_4^0$. As a first approximation, the sequence of precipitates that might be expected, following their relative solubilities, is calcium, followed by magnesium, and followed by sodium salts, as evaporation proceeds. In detail a good deal of variation is found in nature, and a concise way to explain this is as a consequence of what Eugster and Hardie (1978) call "chemical divides".

Figure A20 demonstrates the way in which a sequence of chemical divides may lead to the formation of the commonest types of saline soil waters during the process of evaporation. The critical factor is the initial composition of the water. Specifically, this dictates the relationship between carbonate alkalinity ($mHCO_3^- + mCO_3^{2-}$) and the concentration of $Ca^{2+}$ and $Mg^{2+}$ ions.

Figure A21 is a magnified section of Figure A19 showing the usual sequence of alkaline soils found in sub-humid to arid climates, with pH and salinity both increasing with aridity.

Ward Chesworth, Felipe Macías, and Marta Camps Arbestain

## Bibliography

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Zech, W., and Hintermaier-Erhard, G., 2007. Soils of the World. Heidelberg, Berlin: Springer-Verlag, 130 pp.

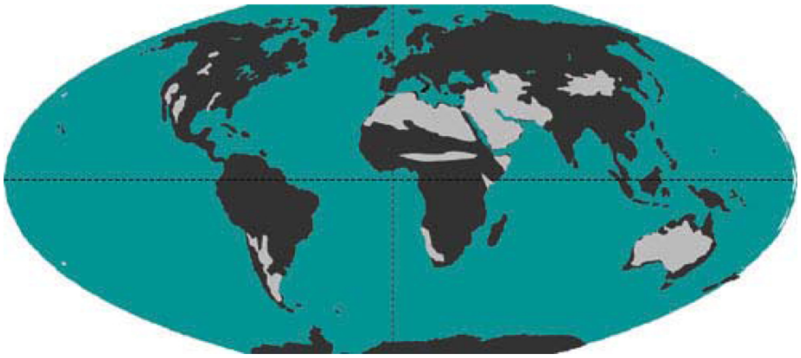

**Figure A18** Major zones of occurrence of alkaline soils. These coincide essentially with regions of arid and semi-arid climate.

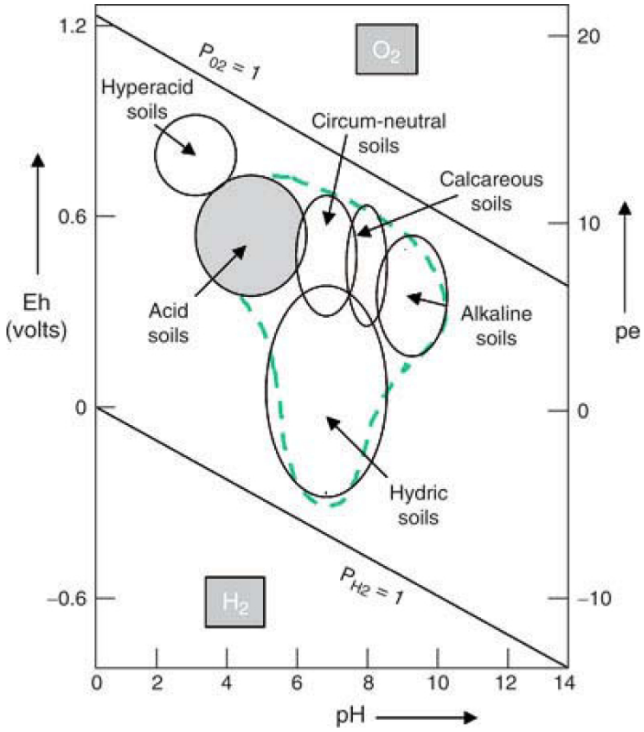

**Figure A19** Alkaline soils defined in terms of the parameters Eh (pe) and pH. The heavy dashed line is the approximate field of the common mineral soils.

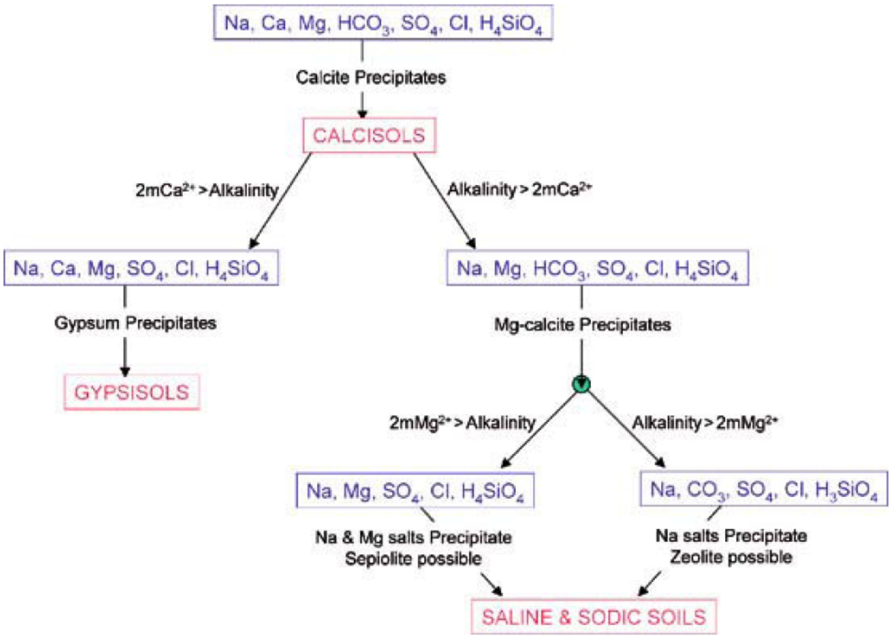

**Figure A20** Chemical divides and the genesis of alkaline soils. The diagram shows the dominant ions in the soil solution at each stage of

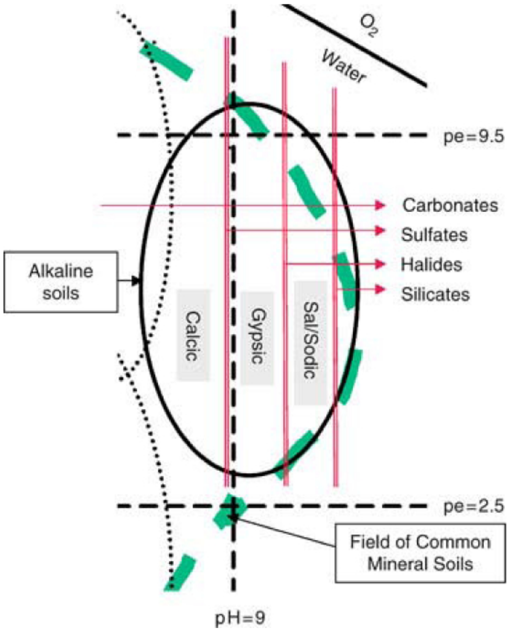

**Figure A21** The alkaline soils field of Figure A19, magnified to show the approximate ranges of precipitation of carbonates, sulfates, halides and silicates in soils. The pH of an evaporating soil solution depends mainly on the concentrations of carbonate species in the system. The precipitation of neutral salts such as gypsum and halite is not pH dependent. The lower pH limits of sulfate and halide precipitation ranges shown in the diagram are based simply on empirical observation. A good deal of variability is possible depending principally on the initial composition of the soil solution.

### Cross-references

Calcisols
Gypsisols
Solonchaks
Solonetz

## ALKALIZATION

Generally used for processes which increase the pH of soils such that they become alkaline (pH greater than 7) or alkali (pH greater than 8.5). Synonym: alkalinization. McBride (1994, p. 274) states that mineral dissolution and the release of ions into solution are invariably involved in the generation of alkalinity.

### Bibliography

McBride, M.B., 1994. *Environmental Chemistry of Soils.* New York: Oxford University Press, 406 pp.

## ALLITIZATION

An advanced stage of weathering in which Al and Fe accumulate at the expense of other ions and species such as the alkalis, alkaline earths and silica, which are removed from the soil in the aqueous phase (Pedro, 1983, table 1).

### Bibliography

Pédro, G., 1983. Structuring of some basic pedological processes. *Geoderma*, **31**: 289–299.

## ALLOGENIC

Describes components transported into the soil from some external place of origin. Equivalent to the geological term allochthonous. See *Authigenic*.

## ALLUVIUM

Alluvial sediment deposited from flowing water; or pertaining to a deposit formed in that way. The parent material of alluvial soils.

### Bibliography

Gerrard, J., 1987. *Alluvial Soils.* New York: Van Nostrand Reinhold, 305 pp.

## ANDOSOLS

### Introduction

Andosols are soils of active volcanic areas. They exhibit unique soil properties that place them apart from other soils. The term ‘andosol’ is derived from Japanese, ‘an’ meaning dark, and ‘do’ connotating soil (Figure A22). Andosols are also found outside active volcanic regions when environmental conditions favor their formation. Andosols have a limited extent (1–2%) of Earth’s land surface, but many such areas are densely populated.

The discussion of this entry follows the terminology of the World Reference Base for Soil Resources (WRB, FAO, 1998). Andosols are termed slightly different, or andisols according to the U.S. Soil Taxonomy (Soil Survey Staff, 1998). The soils discussed in this entry include tephra-rich soils, many of which are not considered Andosols, according to the WRB or Soil Taxonomy, but have various notations in international soil literature, such as vitrisols, (Iceland), vitrandosols (France), Pumice Soils (New Zealand), and vitrons (FitzPatrick’s system).

Andosols were the subject of a book edited by Shoji et al. (1993a), which is the most comprehensive discussion of Andosols to date. Other publications devoted to Andosols include three special issues of scientific journals (Fernandez Caldas and Yaalon, 1985; Bartoli et al., 2003; Arnalds and Stahr, 2004), overview chapters, for example by Wada (1985) and Kimble et al. (2000), a monograph by Dahlgren et al. (2004), and a compilation of benchmark papers about Andosols (Tan, 1984).

### The concept of Andosols

The development of the concept of Andosols has roots in the U.S. Soil Taxonomy, first presented as the andept suborder of inceptisols (Smith, 1986), but from 1990 as andisols, based on a work of international working group (ICOMAND), as was reviewed by Parfitt and Clayden (1991). The concept of the Andosol soil group, as used in the WRB, is similar to that of Soil Taxonomy (see Shoji et al., 1996).

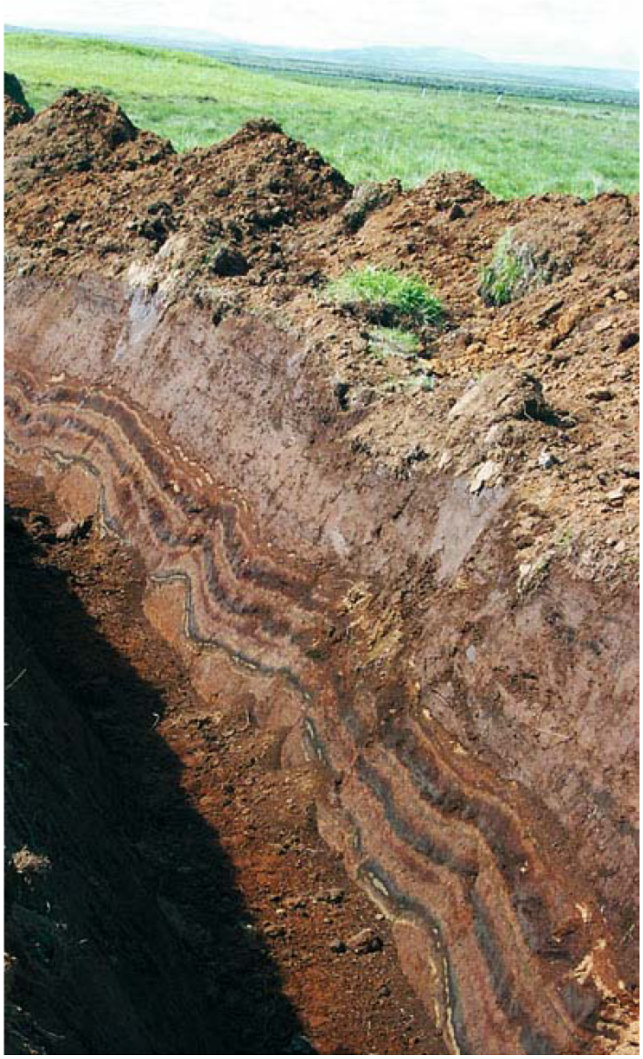

**Figure A22** Andosol in Iceland. The profile is about 190 cm thick. Many distinct tephra layers are evident, disturbed by cryoturbation. Basaltic and andesidic tephras are dark, but thin light colored rhyolitic tephras are also seen near the middle and near the bottom of the profile. The soil contains considerable carbon in most horizons, also at depth.

The concept of andosols is tied to soils that develop in volcanic ejecta. The rapid weathering of volcanic tephra results in precipitation of short-range order minerals and/or metal–humus complexes, a process that is sometimes referred to as 'andosolization' (e.g., Duchaufour, 1977). These colloidal constituents provide the soils with properties that distinguish Andosols, such as low bulk density, variable charge characteristics, thixotropy, and strong phosphate retention. The measure of Andosol colloidal constituents is used for the identification of Andosols. However, the term not only reflects products of soil genesis, as vitric parent materials are also used as a diagnostic criterion for these soils according to the WRB and Soil Taxonomy.

## Mineralogy and metal–humus complexes

### The parent materials

The most common parent material of Andosols is *tephra*. It should be noted, however, that Andosols do form in other types of materials, as will be discussed later.

*Tephra.* This is a collective term for all airborne volcanic ejecta, regardless of morphology, size, and composition. Volcanic ash is tephra which is <2 mm in diameter (MacDonald, 1972). The nature of tephra materials varies substantially according to the nature of the volcanic eruption that produces the tephra and it can be differentiated on several criteria. *Volcanic glass* is a term commonly applied to tephra but strictly speaking it refers to the part of the tephra that has cooled rapidly. The term *vitric* refers to glass (from Latin 'vitr' = glass) and it is used as a diagnostic criterion for poorly developed Andosols/Andisols (FAO, 1998; Soil Survey Staff, 1998), and to coin the terms such as vitrisols and Vitric Andosol. It should be noted that Andosols form in the bulk of parent materials, not only in the Vitric component. Fisher and Schmincke (1984) and Heiken and Wohletz (1985) provided discussion on tephra materials.

*Composition.* The differentiation of tephra by silica content is perhaps the most useful division of the tephra (basalt, andesite, dacite, rhyolite) and is widely used in geology. It affects weathering rates and the genesis of Andosols as discussed later.

*Morphology and mineralogy.* Many terms are applied to the morphology of tephra, such as glass, lapilli, cinders, and pumice. Grain size is an elusive term for tephra, as it is often quite porous and has a large active surface area. It is also difficult to determine the mineralogy of tephra because of microcrystallinity and/or non-crystalline nature of the materials. Such terms as colored glass (basaltic-andesitic and some dacite tephra) and non-colored glass (rhyolitic) are commonly used (e.g., Dahlgren et al., 1993).

### Genetic mineral components

The dominant clay minerals in Andosols are allophane, imogolite, ferrihydrite, and halloysite. Notable publications on allophane and imogolite include those of Wada (1989), Harsh et al. (2002), Dahlgren et al. (1993), and Dahlgren (1994). These are not layered lattice clay minerals such as smectite and kaolinite, but are described by terms such as 'spherical', 'tubular' and 'gel-like'. Their crystallinity has been subject to debate and these constituents have been described as 'amorphous', 'X-ray amorphous', 'poorly crystalline', 'noncrystalline', and 'short-range order' .

The tephra parent materials of Andosols weather rapidly, resulting in high concentrations of Al, Fe, and Si. The poorly crystalline (short-range order) morphological forms of these minerals are the result of rapid crystallization of Al and Si (allophane and imogolite) and Fe (ferrihydrite) from such soil solution. However, these minerals are not exclusive to Andosols as they are also commonly found in Podzols, but to a lesser degree.

*Allophane and imogolite*

Allophane is an aluminum and silica mineral that forms hollow spherules which are about 5 nm in diameter. The ratio between Al and Si is somewhat variable, most commonly 1–2, but values <1 have been recorded (Parfitt and Kimble, 1989). These minerals have an extremely large surface area and a high negative charge that is pH-dependent (variable charge), which increases rapidly with pH. In addition, allophane has considerable anion exchange properties.

Imogolite is tubular and often appears thread-like viewed with a transmission electron microscope. It usually has an Al/Si ratio close to 2, but similar properties to allophane.

*Ferrihydrite*

Ferrihydrite is a poorly ordered $Fe^{III}$ mineral (Schwertmann, 1985), consisting of well aggregated spherical particles (Bigham et al., 2002) which often appear with gel-like structure. Its structure has been debated and ideas about the nature of ferrihydrite are still evolving. Ferrihydrite is very common in Andosols, especially where the parent materials are rich in iron, as in Iceland. It has a large surface area and a pH dependent cation and anion exchange capacity (Bigham et al., 2002).

*Halloysite and other clay minerals*

Halloysite is a common mineral in Andosols, especially in Si-rich environments, and is often associated with dry environments (Dahlgren et al., 1993, 2004) with distinct dry season. Its morphology varies, but it is believed to be closely related to kaolinite (see White and Dixon, 2002). Halloysite is often reported as representing more weathered environment than allophane dominated soils (e.g., Ndayiragije and Delvaux, 2004). Other minerals are found in many Andosols, especially when Andosols become mature, with the Andosol minerals being transformed to other minerals, such as kaolinite, smectite and Al/Fe oxides and chloritized 2 : 1 minerals (e.g., Shoji et al., 1985). Opalline silica is also often reported in Andosols, especially under grassland vegetation (e.g., Shoji et al., 1993b).

### Allophane–humus and metal–humus complexes

The original concept of Andosols ('an-do') reflects the dark color of many andosols, which mainly results from the accumulation of organic matter. Large contents of organic matter characterize well-developed andosols. Appreciable amounts of carbon are found at depths, and the distribution is often quite erratic. There are two main pathways of organic accumulation in Andosols: the formation of allophane–organic matter complexes and metal–humus complexes.

Allophane and organic matter form bonds that are relatively stable, which results in soils that commonly have >6% C in both A and B horizons. This effect is enhanced when $Al^{3+}$ and $Fe^{3+}$ form stable bonds with organic matter by ligand exchange (metal–humus complexes). This means of carbon accumulation is effective at a relatively low pH. Research has confirmed the stability of these constituents, which can be >100 000 yr old in Hawaii (Torn et al., 1997).

In some areas, other environmental factors can enhance the accumulation of organic materials in Andosols, such as poor drainage and cold climate resulting in OC 12–20% (Arnalds, 2004).

## Genesis

The rapid weathering of tephra constituents is perhaps what distinguishes the genesis of Andosols the most. It leads to a soil solution oversaturated with regard to Al, Si, and frequently Fe or organic molecules, which results in the precipitation of the colloidal Andosol constituents. The nature of the parent materials (most often tephra) and climate, which influences the rate of weathering and therefore the release of Al, Fe and Si, are the dominant factors shaping the formation of Andosols. Humid climate enhances the weathering of tephra and the majority of the world's Andosols are therefore found under humid conditions, but <10% under aridic or xeric moisture conditions (Wilding, 2000).

Andosols are most commonly considered youthful soils. Soils on slopes of volcanoes often show a trend from less weathered vitric or andic soils at high elevations (young PM/cold/coarse tephra) to allophanic soils, metal–humus complex dominated soils, and finally to more weathered soils of other types, such as Vertisols (warm, less tephra inputs, fine tephra). A range of soils can develop from Andosols, including Podzols, Mollisols, Vertisols, and Oxisols, (e.g., Dahlgren et al., 2004; Yerima et al., 1987). However, if the climate is dry and especially when the parent materials are silicious, vitric characteristics may dominate for a long time. Andosols also form in tephra redistributed by wind long distances away from where the volcanic materials were originally deposited, as in Iceland (Arnalds et al., 1995).

The nature of Andosols implies that these soils often become buried by new volcanic materials, both tephra and lava.

### Allophanic, vitric and metal–humus complex andosols

Vitric (*vitrandic*), allophanic (*silandic*) Andosols, and Andosols dominated by metal–humus complexes (*aluandic*) can be viewed as three 'end-members' of Andosols (Shoji et al., 1996). The rate of cation release and the pH of the soil solution largely determine whether allophanic Andosols or soils dominated by metal–humus complexes are formed. Allophane formation is favored by a high pH, while it does not form when pH is under 5 (Figure A23a). Under such acidic pH conditions, the formation of metal–humus complexes becomes a dominant process (Figure A23b). The 'aluandic' soils often contain considerable amounts of phyllosilicates, such as chloritized 2 : 1 minerals (Shoji et al., 1985), under a variety of climatic conditions, which contribute to their physical and chemical behavior (see also Ndayiragije and Delvaux, 2003).

The weathering of basaltic tephra is rapid, resulting in areas of high chemical denudation (Stefansson and Gislason, 2001), rapid formation of allophane and ferrihydrite. The surface area of basaltic tephra can be quite high or $>10\ m^2\ g^{-1}$ (Wolff-Boenisch, 2004). Young basaltic tephra soils, which appear to have not been subjected to much weathering, can therefore meet criteria for Andosols (Arnalds and Kimble, 2001).

The weathering of basaltic or andesitic tephra releases an abundance of cations, which maintain the pH. The system can be continuously recharged with cations by weathering of new materials deposited by repeated volcanic eruptions. If not, the soil pH will eventually become low with depletion of tephric materials, and the formation of metal humus complexes becomes a dominant process.

Weathering rates of silicious (rhyolitic) tephra are slower than in basalt with less abundance of cations released to maintain the pH. Weathering often results in more acidic soils, especially in humid-wet areas. Dry climates can alternatively result in relatively unaltered parent materials.

The formation of metal–humus complexes becomes dominant at $pH < 5$, when humic substances form bonds with Al and Fe (predominantly). Their formation is influenced by the rapid release of Al (and Fe), as in the formation of the mineral colloids (allophane, imogolite and ferrihydrite). In Iceland, both mineral colloids and metal humus complexes seem to form when pH is 5–6 (Agricultural Research Institute, unpublished data). Metal–humus complexes have been shown to be quite stable against biodegradation (e.g., Nanzyo et al., 1993), and more stable than allophane–

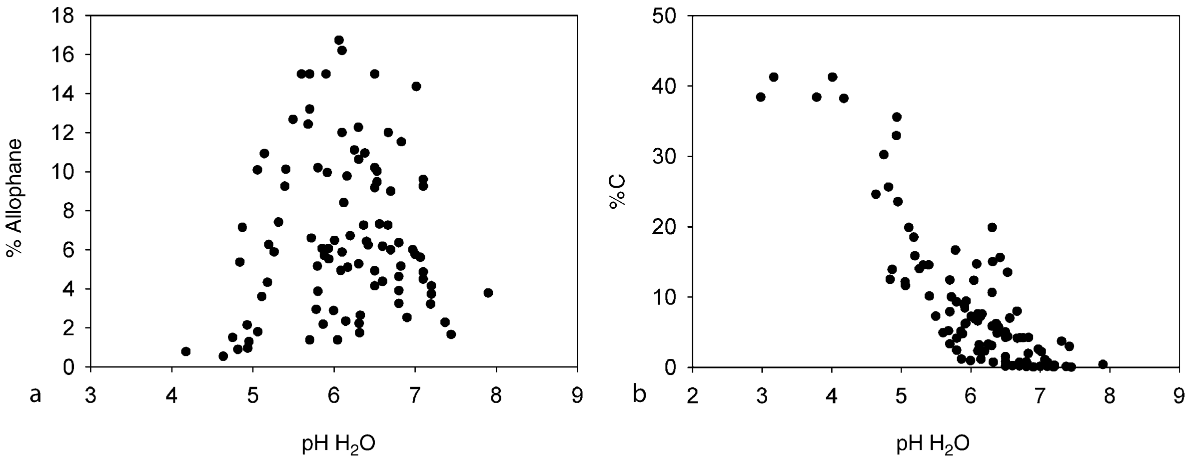

**Figure A23** Allophane and organic carbon as a function of soil reaction in Icelandic Andosols and Histosols (surface horizons). Allophane does not form when pH becomes lower than 4.9 (**a**) and reaches a maximum around pH 6. Organic content rises rapidly with decreased pH, which also represents less tephra input in Iceland (**b**). With less tephra, there is less release of cations by weathering to maintain the pH. The gradient continues into Histosols, which have >20% organic carbon (figure based on O. Arnalds, unpublished data).

humus complexes (Boudot, 1992). Metal–humus complexes can be stable for >20 000 yr, and even >100 000 yr as exemplified by old soils in Hawaii (Torn et al., 1997).

The effect of vegetation on Andosol formation is often emphasized (e.g., Shoji, 1988), with darker soils rich in organic matter (melanic horizons) forming under grassland vegetation, but lighter colored fulvic horizons under woodlands.

### Formation in redistributed volcanic rocks and other parent materials

Andosols have been reported to form in other materials than volcanic when environmental conditions result in a weathering environment characteristic of andosols. Andosols have formed in gabbros and amphibole parent materials in Galicia, Spain (Garcia-Rodeja et al., 1987), in low-activity clay regolith in India (Caner et al., 2000), in granite in Austria (Delvaux et al., 2004), and in non-volcanic materials in Nepal (Baumler and Zech, 1994). Old volcanic rocks, often reworked by glaciers or redistributed as sediments, can also serve as parent materials for Andosols, such as reported in Washington (Hunter et al., 1987) and France (reviewed by Quantin, 2004).

## Properties

### Morphology

When considering the horizonation and morphology of Andosols, it is important to bear in mind that the soil environment is characterized by deposition of parent materials, with the youngest materials on top, gradually or repeatedly being buried under new fresh vitric materials. However, some Andosols also form in volcanic bedrocks that for example have been reworked by Quaternary glaciers (see Quantin, 2004).

Andosols are usually dark soils rich in organic matter, but the morphology varies considerably according to the type of andosols. The color of Vitric Andosols is partly determined by the nature of the tephra materials, which range from black basaltic to light colored rhyolitic materials.

Horizonation typically follows an A–Bw–C sequence, but often with buried sequences due to repeated deposition events. Argillic horizon is usually not present. Clear tephra layers result in abrupt horizon boundaries. Tephra layers are sometimes distinct and can be important markers for dating.

While the surface horizon commonly has well expressed granular structure, the structure of the B horizon is usually poorly developed and difficult to identify. Young or poorly developed Andosols can contain various types of coarse fragments, which are described by specific terminology such as ashy, pumiceous, and cindery (see Shoji et al., 1993c).

Andosols tend to be very friable when lacking phyllosilicates, and non-plastic. Roots often extend far into the soils. However, hard-pans are also common under moist climates, which impede both root growth and water transport.

### Physical properties

The many peculiar physical properties characterize Andosols such as strong silt sized aggregation and thixotropic nature, as was reviewed by Maeda et al. (1977). Vitric materials do not show these properties as clearly as allophanic or metal–humus Andosols, but their physical behavior depends on their type and degree of weathering (see Warkentin and Madea, 1980).

#### *Aggregation and bulk density*

Low bulk density is one of the diagnostic criteria for Andosols. Density of $<0.9$ g cm$^{-3}$ is required. This low bulk density is a result of high organic content, aggregation of soil materials, and sometimes low density vitric materials. Icelandic research points to two main axes of influence, with density slowly decreasing with increased allophane content, but organic matter having more influence on bulk density with lowest values (0.2 g cm$^{-3}$) recorded in Histic Andosols (>12% C). The mineral colloidal fraction also forms stable silt-sized aggregates, which greatly influence the physical properties of Andosols (Maeda et al., 1977), and make conventional mechanical particle size determinations useless for Andosols. Drying can cause irreversible decrease in water retention and increase in bulk density.

*Water retention and transport*

Great water retention is one of the main characteristics of Andosols, hence the low bulk density. Common 1.5 MPa tension water contents are >60%, but the term 'hydric' is used to describe Andosols when water retention is >100% at this tension based on dry weight of the soil. While allophane, imogolite and ferrihydrite contribute to this strong water retention, the effect of organic matter (metal–humus complexes, allophane–humus and humus alone) is much greater, following the two line pattern shown earlier for bulk density. Andosols have a large proportion of both large and intermediate pores, which allow for rapid water transport. Water infiltration, and both saturated and unsaturated hydraulic conductivity are rapid compared to most other soils (see Warkentin and Maeda, 1985; Basile et al., 2003). The silty aggregate behavior of the clay constituents and extremely high water retention leads to high frost susceptibility of Andosols (Arnalds, 2004).

Vitric materials can also have substantial water holding capacity, and extremely high infiltration rate and saturated hydraulic conductivity, enhancing their use for agriculture.

*Atterberg limits and thixotropy*

Andosols possess a special property, which has been called thixotropy. The soils can contain large amounts of water and yet appear relatively dry. When disturbed, the water is released. In other words, the soil can reach the liquid limit upon disturbance (Figure A24). This property is also expressed by very high liquid limits but a low range where the soil is plastic, resulting in very low plasticity index (often near 0). This property explains in part why andosols are quite susceptible to slope failures when disturbed.

## Chemical properties

*pH*

Andosols can have a range of soil pH ($H_2O$). Metal–humus-dominated soils tend to be acid (<5) with low base saturation and they can show signs of Al toxicity. Soils dominated by allophane often have pH 5.5–6.5 (Nanzyo et al., 1993). If fresh basic parent materials are still present, pH is maintained by recharge of basic cations during weathering, which in Iceland sometimes leads to pH > 6.5 (Arnalds, 2004). Older, mature Andosols tend to have lower pH than younger soils, and can be quite acid. Soil reaction measured in KCl tends to be 0.5–1.5 units or more lower than the pH $H_2O$, the greatest difference between the two appears where metal–humus complexes are present (Nanzyo et al., 1993). Soil reaction measured in KCl provides important information about soil acidity in acid Andosols.

Soil reaction of Andosols rises rapidly when NaF is added to the soil solution, with $F^-$ replacing $OH^-$ from active surfaces. This is sometimes used to identify the presence of andic soil materials, both in laboratory and in the field.

*Ion exchange*

One of the most distinguishing features of Andosols is their pH-dependent charge. Allophane, imogolite, ferrihydrite and metal–humus complexes all have large reactive surface areas, but cation exchange capacity rises rapidly with increasing pH (see Wada, 1985). Determination of CEC is therefore very dependent on the pH used in any particular method and care should be taken when interpreting both CEC and base saturation values (see Madeira et al., 2003). Common CEC values reported for Andosols range between 10–40 $\mathrm{cmol_c\ kg^{-1}}$. Andosols also exhibit anion exchange properties, which can be important for nutrient retention (e.g., $Cl^-$, $NO^{3-}$, $SO_4^{2-}$).

Exchange characteristics make Andosols susceptible to heavy metal and $Cs^{137}$ pollution (e.g., Adamo et al., 2003) by retaining the pollutants quite effectively, especially when soils are not very acid (Nanzyo et al., 1993). Andosols often sustain dense populations, and pollution problems have been recorded in many areas, such as near Napoli, Italy (Adamo et al., 2003).

## Classification

The development of early concepts and selection of classification criteria were reviewed by Parfitt and Clayden (1991) for Soil Taxonomy, and the subsequent evolution of the WRB criteria was discussed by Shoji et al. (1996). The colloidal constituents of Andosols, clays and metal–humus complexes, provide them with their distinctive characteristics. The identification of Andosols is therefore primarily based upon the measure of these constituents and their accessory properties.

## Diagnostic properties

Identification of Andosols is based on the identification of an 'andic horizon' in WRB (FAO, 1998), but 'andic soil properties' according to Soil Taxonomy (Soil Survey Staff, 1998). Acid ammonium oxalate preferentially extracts the poorly ordered colloid constituents of Andosols and can be used to calculate the amount of allophane, imogolite and ferrihydrite (Parfitt and Childs, 1988; Parfitt and Wilson, 1985). The treatment also extracts Al and Fe associated with metal–humus

**Figure A24** Thixotropy. Undisturbed clod is shown on to the left, but disturbed clod to the right. The soil reaches the liquid limit when disturbed with gentle pressure, even though the clod appears relatively dry. The soil is hydric andosol from the Azores (Portugal).

complexes. The primary diagnostic criteria for andic horizon is that it has $\geq 2\%$ oxalate extractable Al and ½Fe $(\text{Al} + \text{½Fe})_o$. Additional criteria used for identifying andosols are bulk density $<0.9$ g cm$^{-3}$, P-retention $\geq 70\%$, and thickness of $\geq 30$ cm. WRB also defines a 'vitric horizon' , which is at least 30 cm thick, containing $>10\%$ volcanic glass in the fine earth fraction and has either $(\text{Al} + \text{½Fe})_o$ of $>0.4\%$, or bulk density $>0.9$ g cm$^{-3}$, or P-retention $>25\%$. Soil Taxonomy uses similar criteria for vitric materials, which are included with andic soil properties, by decreasing the requirements for $(\text{Al} + \text{½Fe})_o$ with increasing amount of vitric materials (0.4% $(\text{Al} + \text{½Fe})_o$ when vitric glass $>30\%$). In addition, tephric material (un-weathered) is defined by the WRB.

It should be noted that the tendency of Andosols to accumulate large amounts of organic matter is given special consideration by allowing andic soil horizons to have up to 20% C, while under other conditions $>12\%$ C (no clay) would normally result in Histosol classification (FAO, 1998). This breakpoint is at 25% C in Soil Taxonomy (Soil Survey Staff, 1998).

### Andosols, subclasses

The WRB separates Andosols based on many criteria. Andic horizons are divided depending on whether they are allophanic (silandic), metal–humus complex dominated (aluandic) or vitric. Melanic and fulvic horizons are andic horizons with $>6\%$ C, but the melanic horizon is darker than the fulvic, but a distinction between the two is also based on the so-called melanic index (see FAO, 1998; Shoji, 1988). The term 'hydric' is used for Andosols with $>100\%$ water at 1.5 MPa tension. Andosols also include vitric and silic (allophane rich) subgroups. There is a range of other subunits of Andosols based on criteria common to other soil groups of the WRB, such as histic, mollic and gleyic. Tephric soil material is also used by the WRB for vitric soils.

## Distribution

Andosols are found in volcanic regions, which are widespread on Earth, in all climatic regimes but more commonly in humid areas than dry (Wilding, 2000). Vitric soils are also widespread, but are not recognized as Andosols according to the WRB. Reviews by Kimble et al. (2000), Dahlgren et al. (2004) and FAO (2001) provided good accounts of aerial distribution of Andosols. They are common along the Pacific coast of the Americas, with notable areas are in Alaska (100 000 km$^2$, Kimble et al., 2000) the Pacific North-West USA, Mexico, Peru and Chile. Andosols are found in volcanic areas of Africa, e.g., Ethiopia, Rwanda, Kenya and Tanzania (FAO, 2001). Large areas are found in Asia, including the Kamchatka Peninsula (Russia), Japan, Indonesia and the Philippines, and New Zealand. Andosols are also found in active volcanic areas of mainland Europe (e.g., Italy, France). They are major soils of the volcanic islands in the Atlantic, including the Azores, Madeira the Canaries, and in Iceland. FAO estimate (2001) for global distribution of andic soils is 1.1 million km$^2$, but recent USDA-NRCS estimates are 1.2 million km$^2$ (Kimble et al., 2000) and 0.91 million km$^2$ (Wilding, 2000) (see Figure A25).

Areas affected by volcanic ash are much larger then the close vicinity of volcanoes, as volcanic materials can be transported long distances during eruptions or by aeolian/fluvial redistribution.

## Andosols and land use

The low bulk density and lack of cohesion make Andosols susceptible to disturbance, such as made by heavy machinery. The soils are susceptible to failure when disturbed on slopes, which can cause them to reach the liquid limit (thixotropic property). Landslides are therefore common on slopes covered by Andosols, and this has caused many catastrophes in volcanic areas such as near Napoli, Italy in 1998 (e.g., Basile et al., 2003). Mantling of harder bedrock by andic soils and the platy character arising from tephra layers can form planes of failures. Considerable resources are spent on stabilizing Andosols (Figure A26).

Andosols are light and easy to plow, which favors their cultivation. The high water holding capacity and good hydraulic conductivites enhance their use for agriculture, but coarse layers of tephra can, however impede unsaturated water flow. Good quality products are often associated with Andosols, such as of wine and coffee. However, fertility varies greatly between Andosol types, especially between the acid metal–humus complex Andosols and the allophanic soils. Vitric soils are

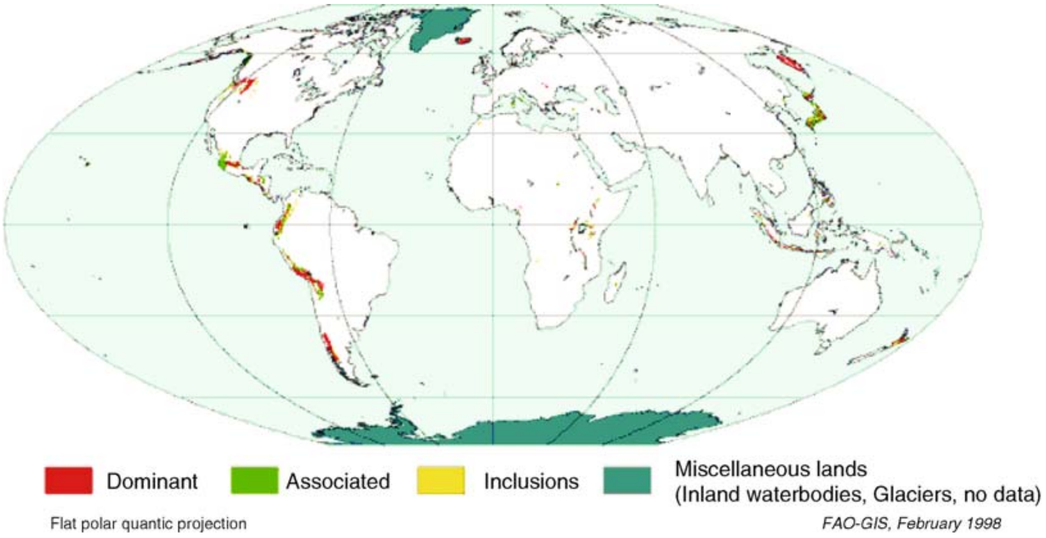

**Figure A25** Andosols of the world.

**Figure A26** Road construction in Hokkaido, Japan. Much effort is made to stabilize the slopes, but landslides are common in Andosol areas.

widespread, especially under dry temperature regimes (e.g., Africa, Mediterranean), and are successfully used for various crops, depending on local conditions, such as seasonal rainfall pattern and possible source of irrigation water.

Extreme examples of the value of Andosols and vitric materials for cultivation is the transport of andic soil materials to the lowlands of the Canary Islands for intensive cultivation (*sorriba*) (see Armas-Espinel et al., 2003) and the use of tephra as mulch for water conservation in the Canaries (Tejedor et al., 2003).

Hard pans commonly form in Andosols, which greatly affect their management possibilities, such as Mexico's *tepetates* (Servenay and Prat, 2003) and in the Azores (Pinheiro et al., 2004). Andosols have an especially strong tendency to retain phosphate, hence the P-retention classification criterion, and often require phosphorous additions for intensive crop production. Allophanic soils in the tropics are often heavily populated as a result of their fertility. Heavy land use can lead to pollution of these soils, enhanced by their colloid charge characteristics.

Much of the organic carbon in global cycling is retained in soils. The tendency of andosols to accumulate more carbon than other mineral soils (Eswaran et al., 1993) make them important in relation to the global carbon cycle and climate change, in spite of their limited distribution.

Olafur Arnalds

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## Cross-references

Acid Soils
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Geography of Soils
Iron Oxides

# ANTHROPOGENIC

Used of soils, landscapes, or ecological systems generally, to indicate modification by human activities. Recognized as the group Anthrosols in the WRB System of Soil Classification, in terms of diagnostic anthropogenic horizons:

A terric horizon (from L. *terra*, earth) results from addition of earthy manure, compost or mud over a long period of time. The terric horizon has a non-uniform textural differentiation with depth. The source material and/or underlying substrates influence the color of the terric horizon. Base saturation (in 1 M $NH_4OAc$ at pH 7.0) is more than 50%.

An irragric horizon (from L. *irrigare*, to irrigate, and agricolare, to cultivate) is a light colored (Munsell color value and chroma, moist, both greater than 3), uniformly structured surface layer, developed through long-continued irrigation with sediment-rich water. Clay and carbonates are evenly distributed and the irragric horizon has more clay, particularly fine clay, than the underlying soil material. The weighted average organic carbon content exceeds 0.5%, decreasing with depth but remaining at least 0.3% at the lower limit of the irragric horizon.

A plaggic horizon (from Dutch plag, sod) has a uniform texture, usually sand or loamy sand. The weighted average organic carbon content exceeds 0.6%. The base saturation (in 1 M $NH_4OAc$ at pH 7.0) is less than 50%. The content of $P_2O_5$ extractable in 1% citric acid is more than 0.25% within 20 cm of the surface (frequently more than 1%).

A hortic horizon (from L. *hortus*, garden) results from deep cultivation, intensive fertilization and/or long-continued application of organic wastes. It is a dark colored horizon with Munsell color value and chroma (moist) of 3 or less. The hortic horizon has a weighted average organic carbon content of 1% or more, and more than 100 mg $kg^{-1}$ (0.5 M $NaHCO_3$ extractable) $P_2O_5$ in the fine earth fraction of the upper 25 cm layer. Base saturation (in 1 M $NH_4OAc$ at pH 7.0) is 50% or more.

An anthraquic horizon (from Gr. anthropos, human, and L. *aqua*, water) represents a puddled layer or a plow pan. Characteristically, plow pans have a platy structure; they are compacted and slowly permeable to water. Yellowish-brown, brown or reddish-brown rust mottles occur along cracks and root holes. The bulk density of the plow pan is at least 20% greater than that of the puddled layer, whereas its porosity is 10 to 30% less than that of the puddled layer. Non-capillary porosity is 2 to 5%.

A hydragric horizon (from Gr. hydros, water, and L. *agricolare*, to cultivate) is a subsurface horizon with characteristics associated with wet cultivation:

- iron-manganese accumulation or coatings of illuvial Fe and Mn; or twice as much dithionite-citrate extractable iron than in the surface horizon(s), or more, or 4 times as much dithionite-citrate extractable manganese or more; or
- redoximorphic features associated with wet cultivation; and
- thickness of more than 10 cm.

## ANTHROSOLS

Anthrosols are soils that have been significantly altered by the agricultural, horticultural, domestic and other activities of humankind. This article is based on the descriptions in FAO (2001).

*Connotation*. Soils with prominent characteristics that result from human activities; from Gr. anthropos, man.

*Definition*. FAO (2001) defines Anthrosols as soils that have been formed or modified by human activities such that

1. a *hortic*, *irragric*, *plaggic* or *terric* horizon 50 cm or more thick is present; or
2. an *anthraquic* horizon and an underlying *hydragric* horizon occur with a combined thickness of 50 cm or more.

*Parent material*. Virtually any soil material, modified through cultivation, excavation, or by addition of material.

*Environment*. Plaggic Anthrosols are most common in northwest Europe; hydragric Anthrosols in Southeast and East Asia, and irragric Anthrosols in the Middle East.

*Profile development*. The influence of *Homo sapiens* is normally restricted to the surface horizon(s); the horizon differentiation of a buried soil can still be intact at some depth. Qualifiers are used to indicate the type of anthropogenic modification that has influenced soil development. Common anthropedogenic horizons and the soils they occur in, are:

*Plaggic Anthrosols – soils modified by additions of sods*. Occur for example in areas of glacial sand and loess of Europe such as Arenosols and Podzols. The *plaggic* horizon (from Dutch *plag*, sod), uniform in texture, commonly sand or loamy sand.

*Terric Anthrosols* are most noticeable in wetland areas with Fluvisols, Gleysols and Histosols or with in regions of acid/unfertile soils such as Albeluvisols, Arenosols or Podzols. The *terric* horizon (from L. *terra*, earth) forms where there has been long-term addition of earthy manure.

*Irragric Anthrosols* are most common in sub-humid to arid regions, with Calcisols, Gypsisols, Solonchaks and Solonetz, as well as with Regosols and Cambisols. The *irragric* horizon (from L. *irrigare*, to irrigate and *agricolare*, to cultivate) is a light colored, with a uniform structure, developed where irrigation with sediment-rich water has been practiced over the long-term.

*Hydragric Anthrosols* are found in river systems with Gleysols and Fluvisols, in uplands with Alisols, Acrisols, Lixisols and Luvisols in upland areas, and in volcanic districts with Andosols. The *hydragric* horizon (from Gr. *hydros*, water, and L. *agricolare*, to cultivate) is a subsurface horizon with the redoximorphic features associated with wet cultivation.

*Anthraquic Anthrosols* occur particularly as modifications of clay to loamy-clay soils, Mollisols and Fluvisols for example, or of soils with a low bulk density such as Andosols. The

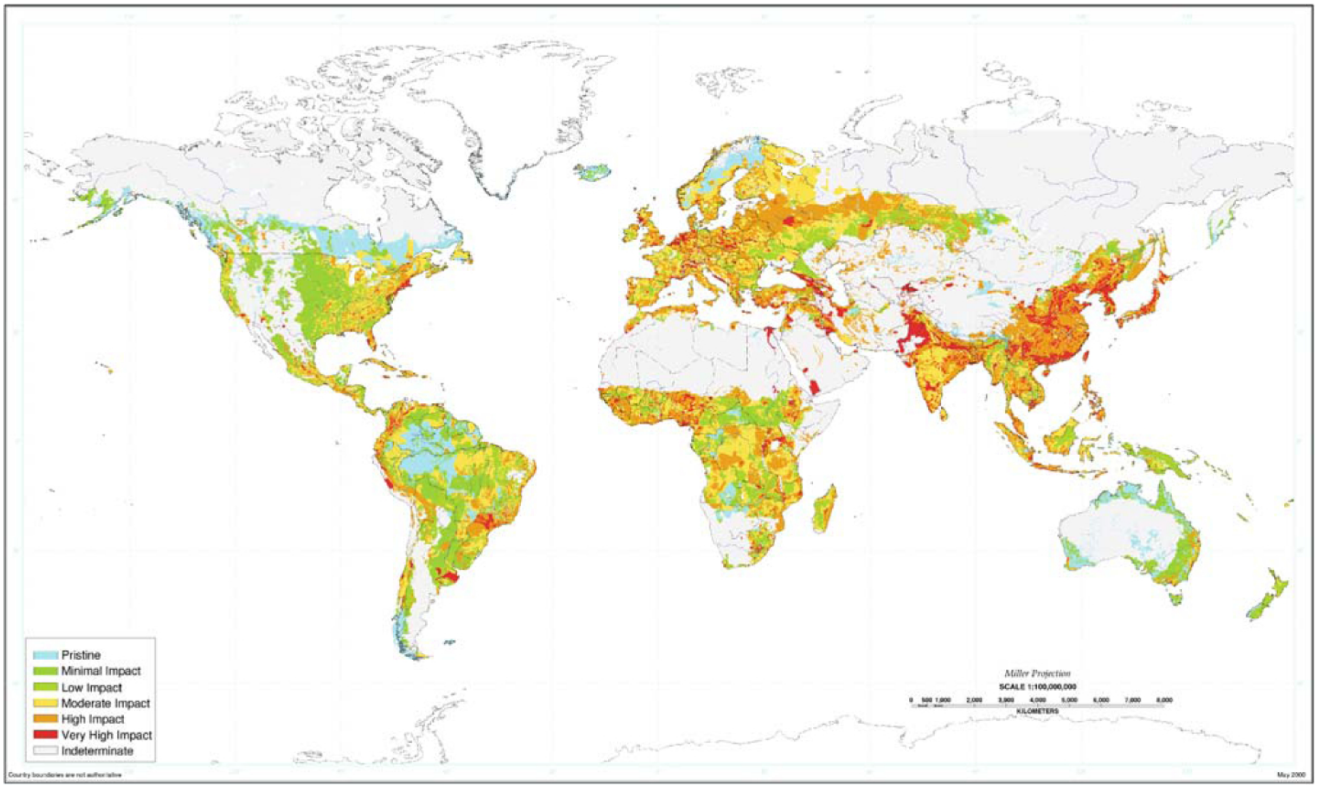

Figure A27 Anthropic landscapes. Courtesy USDA-NRCS, Soil survey division.

*anthraquic* horizon (from Gr. *anthropos*, human, and L. *aqua*, water) is a puddled layer or a plow pan, with low permeability.

*Hortic Anthrosols* can occur alongside virtually any reference soil group. The *hortic* horizon (from L. *hortus*, garden) is produced by deep cultivation, intensive fertilization and/or long-term application of organic wastes.

## Origin

Human activities may modify a soil simply in terms of the activity itself (as in plowing), or by virtue of the addition of materials to the land surface (in land fills for example). In the latter case the material added, '*anthropogenic soil material*', is not itself an Anthrosol until pedogenetic change is evident. Typical '*anthropedogenic processes*' are

1. *deep working*, i.e., below the normal depth of tillage (e.g., in terraced lands in the Mediterranean Region, the Arab Peninsula, the Himalayas and the Andes);
2. *intensive fertilization* with organic/inorganic fertilizers *without* substantial additions of mineral matter (e.g., manure, kitchen refuse, compost, night soil);
3. *continuous application of earth* (e.g., sods, beach sand, shells, earthy manures);
4. *irrigation* adding substantial quantities of sediment;
5. *wet cultivation* involving puddling of the surface soil and human-induced wetness.

*Use*. European Anthrosols were traditionally grown to winter rye, oats, and barley but are now also planted to forage crops, potatoes and horticultural crops; in places they are used for tree nurseries and pasture. Irragric Anthrosols occur in irrigation areas where they are under cash crops and/or food crops. Hydragric Anthrosols are associated with paddy rice cultivation whereas hortic Anthrosols are (mainly) planted to vegetables for home consumption (see Figure A27).

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## Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations, 334 pp.

FAO, 2006. *World reference base for soil resources, 2006: A framework for international classification, correlation, and communication*. Rome: Food and Agriculture Organization of the United Nations. 128 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin: Springer-Verlag, 130 pp.

## Cross-references

Anthropogenic
Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Technosols

# ARENOSOLS

Arenosols are sandy soils, developed on quartzose (and sometimes calcareous) sands of diverse origins, for example from residual materials remaining after the long term weathering of acid rocks, from aeolian deposits, or from fluviatile sediments including post glacial deposits. The following account follows FAO (2001).

*Connotation*. Sandy soils; from L. *arena*, sand.

*Synonyms*. Arenosols are equivalent to 'siliceous, earthy and calcareous sands' and various 'podzolic soils' (Australia), 'red and yellow sands' (Brazil) and the Arenosols of the FAO Soil Map of the World. In Soil Taxonomy Arenosols occur in part as Psamments and Psammaquents, and when deep, with an argic or spodic horizon within 200 cm from the surface, as 'grossarenic' subgroups within the alfisol, ultisol and spodosol orders. In France Arenosols correlate with taxa within the "Classe des sols minéraux bruts" and the "Classe des sols peu évolués".

*Definition*. Essentially sandy soils developed on sandy parent materials, formally defined by FAO (2001) as soils having:

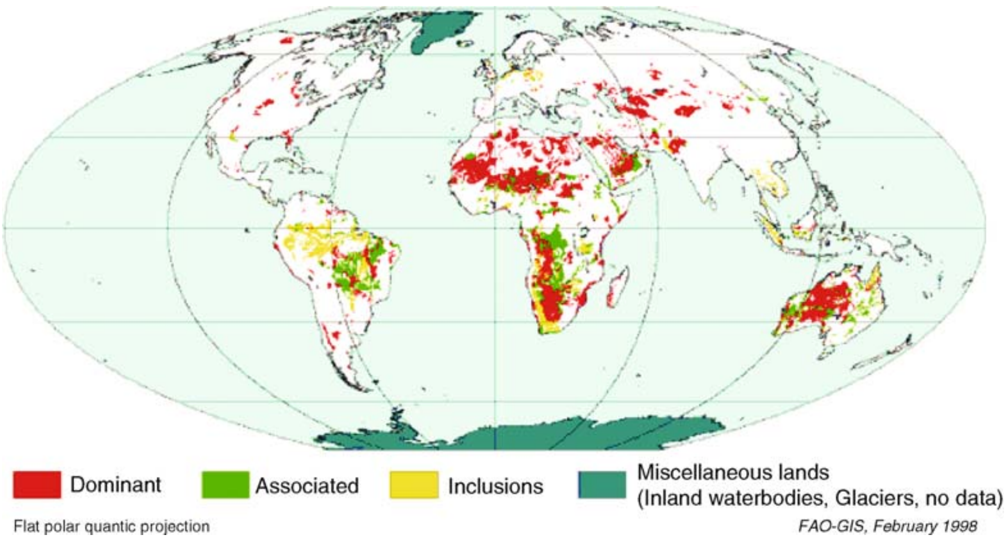

**Figure A28** Distribution of Arenosols.

1. a texture, which is loamy sand or coarser *either* to a depth of at least 100 cm from the soil surface, *or* to a *plinthic*, *petroplinthic* or *salic* horizon between 50 and 100 cm from the soil surface; and
2. less than 35% (by volume) of rock fragments or other coarse fragments within 100 cm from the soil surface; and
3. no diagnostic horizons other than an *ochric*, *yermic* or *albic* horizon, or a *plinthic*, *petroplinthic* or *salic* horizon below 50 cm from the soil surface.

*Parent material*. Unconsolidated, in places calcareous, translocated sand; relatively small areas of Arenosols occur on residual sandstone or siliceous rock weathering.

*Environment*. From arid to (per)humid and from extremely cold to extremely hot; landforms vary from recent dunes, beach ridges and sandy plains under scattered (mostly grassy) vegetation, to very old plateaus under light forest.

*Profile development*. A(E)C profiles. In the dry zone, an *ochric* surface horizon is the only diagnostic horizon. Arenosols in the perhumid tropics tend to develop thick *albic* eluviation horizons; most Arenosols of the humid temperate zone show signs of alteration or transport of humus, iron or clay, but too weak to be diagnostic.

*Origin*. Under dry climates Arenosols have minimally developed profiles either because the parent materials are young, or because soil forming processes are relatively inactive during long droughty. In humid regions, the profile will be more mature, and in the limit achieved in the humid tropics, a giant Podzol may form with a thick albic E-horizon.

*Use*. Most Arenosols in the dry zone (see Figure A28) are used for little more than extensive grazing but they could be used for arable cropping if irrigated. Arenosols in temperate regions are used for mixed arable cropping and grazing; supplemental (sprinkler) irrigation is needed during dry spells. Arenosols in the perhumid tropics are chemically exhausted and highly sensitive to erosion. They are best left untouched.

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### Bibliography

FAO, 2001. Lecture notes on the major soils of the world. World Soil Resources Reports, 94. Rome: Food and Agriculture Organization of the United Nations. 334 pp.

Zech, W., and Hintermaier-Erhard, G., 2007. *Soils of the World.* Heidelberg, Berlin Springer-Verlag, 130 pp.

### Cross-references

Classification of Soils: World Reference Base (WRB) for Soil Resources
Classification of Soils: World Reference Base (WRB) Soil Profiles
Soils of the Coastal Zone

## ARGILLACEOUS

Describes geological materials rich in clay: shales for example. Not normally applied to soils, the roughly equivalent term in pedology being argillic, as in argillic horizon. Soils developed on argillaceous materials tend to be heavy, with clay minerals inherited or derived from sheet silicates in the parent rock. Where soils have developed on so-called "black" (i.e., organic-rich) shales, elements such as Cu, Mo, Ni, Zn, Cr, V, As and F, may be present in toxic amounts (e.g., Fang et al., 2001).

### Bibliography

Fang, W., Hu, R., and Wu, P., 2001. Influence of black shales on soils and edible plants in the Ankang Area, Shaanxi Province, P. R. of China. *Environ. Geochem. Health*, **24**: 35–46.

## ARGILLAN

See *Cutan*.

## ARID

Adjective applied to climates with a low annual precipitation in the range 50 to 250 mm. Precipitation in the range 250 to 500 mm per year is considered to be semi-arid. In Soil Taxonomy an aridic moisture regime is recognized and is one of the diagnostic features of the aridisol order.

## ARRHENIUS' EQUATION

Arrhenius' Equation is commonly expressed in the form shown in Figure A29. T is temperature in °Kelvin; R is the gas constant; $E_A$, is the activation energy, the minimum energy in joules per mole needed for the reaction to take place; e is 2.71828; and A is essentially constant over the small temperature range of typical soil systems, and is related to such factors as stericity, and the number of collisions between molecular particles.

The rate of a given reaction is a function of the rate constant and the concentrations of all reactants. For reactions under earth surface conditions, with activation energies of about 50 kJ $mol^{-1}$, the rate of reaction approximately doubles for a 10 °C rise in temperature.

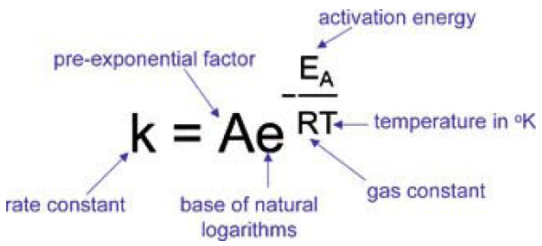

**Figure A29** Arrhenius' Equation.

## ASSOCIATION

A loose grouping of soils that occur together on a landscape, within a given ecological zone, or which develop on a particular parent material.

### Bibliography

Dent, D., and Young, A., 1981. *Soil Survey and Land Evaluation*. London, Boston: Allen & Unwin. 278 pp.

## AUGER

An instrument for boring into soil and obtaining a subsurface sample for examination. Commonly with a handle at right angles to the shank to facilitate penetration of the soil by manually twisting the instrument. Several varieties are used, a common one being the probe, which has a small chamber with a cutting edge at its lower end for retrieving the soil sample. (Tarnocai, 1993, 755–759).

### Bibliography

Tarnocai, C., 1993. In Carter, M.R., *Soil Sampling and Methods of Analysis,* Chap. 71. Boca Raton, FL: Lewis Publishers, 823 pp.

## AUTHIGENIC

Used to describe soil constituents that formed within the soil. The process is called neoformation. The equivalent term used by geologists is autochthonous, a word used in soil science only when referring to certain microorganisms. See *Allogenic*.

## AZONAL SOIL

See *Order*.