

Chapter 2

Soil

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2.1 Introduction to Soil and Its Characteristics

The pedosphere is the total surficial layer of the earth that consists of soil and which has complex and dynamic interactive linkages with the lithosphere, the hydrosphere, the biosphere, and the atmosphere¹ (Fig. 2.1). Soil covers a large proportion of the 149 million km² global land area, but only an estimated 93 million km² are biologically productive containing approximately 33 % forest, 32 % pastures and 11 % crop land.² Over the pedosphere, variations in soil properties with depth and across landscapes can be accounted for by several interacting factors including physical and chemical weathering, erosion and deposition, and human and natural disturbances and result from the effects of the different factors of soil formation which include parent material, climate, living organisms (e.g., vegetation), topography and time.^{3,4} An example of the resulting spatial diversity existing in soils is shown by the fact that the National Cooperative Soil Survey of the United States has identified and mapped over 20,000 different kinds of soil in the United States alone.⁵

Soils can be evaluated at different scales, from the molecular level of individual soil components (e.g., soil clay mineralogy), to individual three-dimensional soil

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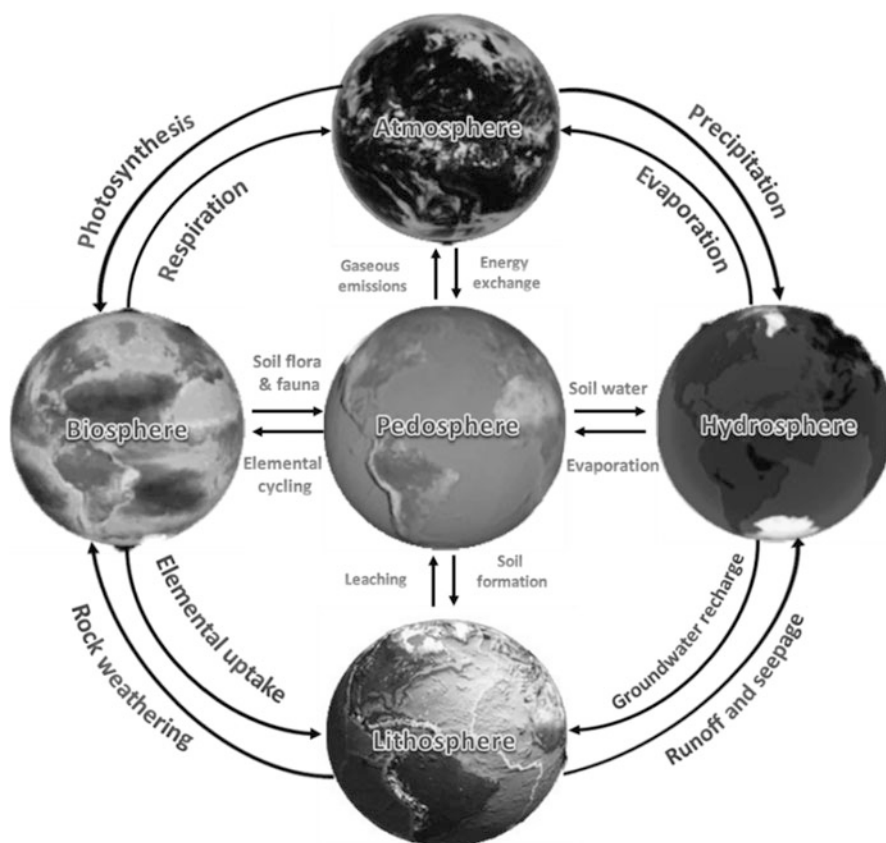
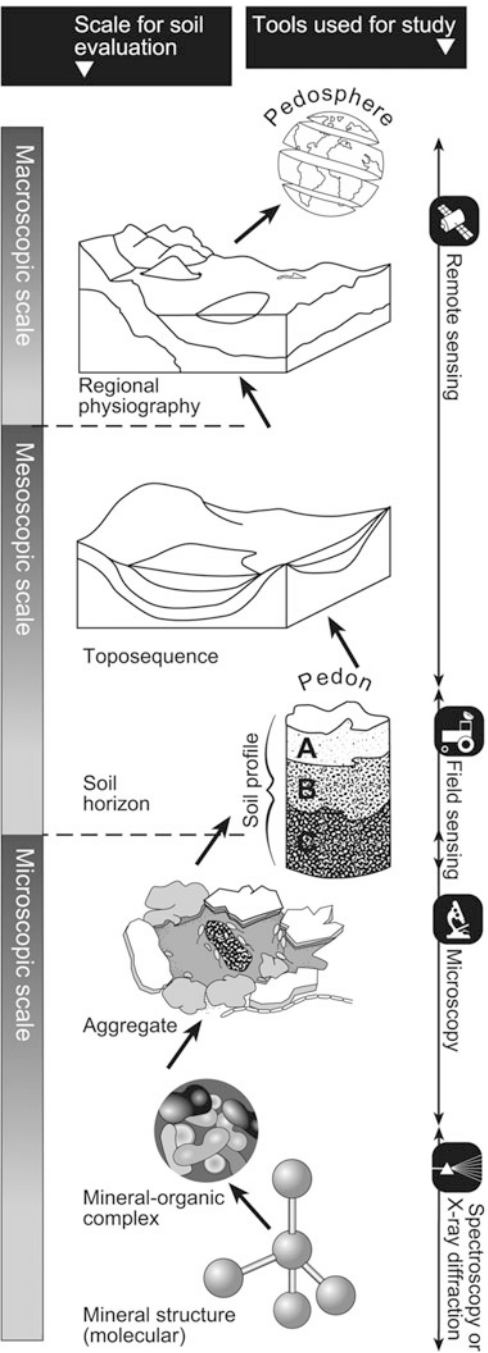


Fig. 2.1 Diagram illustrating the linkage and interactive processes of the pedosphere with other important systems on earth (adapted from reference (1)); Earth images from Exploring Earth (http://www.classzone.com/books/earth_science/terc/content/visualizations/es0102/es0102page01.cfm?chapter_no=visualization) and Utah State Office of Education (<http://utahscience.oremjv.alpine.k12.ut.us/sciber99/8th/earth/sciber/surface.htm>)

bodies (known as pedons), to large-scale soil toposequences and ultimately to the pedosphere itself⁶ (Fig. 2.2). The appropriate tool for measurement of soil properties at each of these scales of soil evaluation may vary (Fig. 2.2) and may be affected by several factors including the objective of the evaluation, technical capabilities for measurement, the observed spatial and temporal variability, and cost.

New tools for assessment of soil physical, biological, and chemical properties are critically needed to better understand the complex processes and spatial and temporal variability that occur in soils at different scales and in interaction with other biotic and abiotic components of terrestrial ecosystems. Increasing pressures for food production, growing human populations, and accelerating environmental degradation require improved soil management, including a better capability to

Fig. 2.2 The broad range of scales at which soil sensor-based evaluation can take place and examples of assessment procedures used for evaluation at each scale (adapted from references (6, 7))



more intensively monitor changes in soil properties and processes, to determine how those changes may affect soil, water, and atmospheric systems, and to provide information for decision-makers to select appropriate land use practices. Such improvements may also require concomitant improvements in data quality control procedures and innovative data management, analysis, and presentation techniques for both short-term and long-term use of the collected soil and supporting information.

2.2 The Unique Nature of Soils: A Heterogeneous, Three Phase System

Soil is a diverse natural material that is characterized by solid, liquid, and gas phases that give it unique chemical, physical, and biological properties. The proportion of solids, liquids, and gases in the soil will vary depending on several factors including the composition of the organic and inorganic constituents in the soil and their physical spatial arrangement (i.e., soil structure). In the U.S. Department of Agriculture classification system, the solid mineral components in soil are categorized based on particle diameter into sand (0.50–2 mm), silt (0.002–0.50 mm) and clay (<0.002 mm) particles.⁸ Other classification systems for particle size limits may also be used from organizations such as the Canada Soil Survey Committee (CSSC), the International Soil Science Society (ISSS), and the American Society for Testing and Materials (ASTM).⁸ Organic and inorganic colloidal material are defined to have particle sizes of <0.001 mm in diameter and these size particles have particular importance environmentally because of their relatively large surface area, charge, mobility, and role in biological activity.⁹

The inorganic components of soils include primary (e.g., quartz) and secondary minerals (e.g., phyllosilicate clays) which are composed primarily of nine chemical elements (i.e., oxygen, silicon, aluminium, iron, carbon, calcium, potassium, sodium, and magnesium). An important characteristic of the secondary soil minerals is their high total surface area ranging from kaolinite with a specific surface area of 7–30 m² g⁻¹ to montmorillonite with a specific surface area of 600–800 m² g⁻¹. Soil organic matter is the organic fraction of the soil that includes organic materials in all stages of decomposition, including a more stable complex organic fraction known as soil humus. The soil organic matter is primarily composed of carbon, hydrogen, oxygen, nitrogen, sulphur, and other elements that are contained in organic materials (e.g., plant residues) that are added into the soil.

Surface charge develops on soil clays and organic matter due to cation substitutions in the crystalline structures of clay (resulting in permanent negative charge) and loss or gain of hydrogen ions from functional groups of inorganic soil minerals and organic matter with changes in soil pH (resulting in pH-dependent

negative or positive charge). The presence of surface charge in soils is critical for cation and anion exchange processes that allow for retention of ionic species on the soil surfaces in equilibrium with ionic species in the soil solution contained in the soil pores.

In soils, the individual mineral and organic particles often bind together to form aggregates of various sizes ranging from 0.5 to 5 mm in diameter. Factors influencing aggregation include soil faunal (e.g., earthworms) and microbial (e.g., soil fungi) activity producing extracellular polysaccharides and hyphae, root growth and exudation, inorganic binding agents (e.g., calcium), and environmental variables (e.g., drying and wetting).¹⁰ Pores or voids formed due to the geometrical packing of the individual soil particles are known as “intra-aggregate” pores and voids formed by the physical arrangement of aggregates are known as “inter-aggregate” pores.¹¹ These pores are categorized by size into macropores (>500 μm radius), coarse mesopores (25–500 μm radius), fine mesopores (5–25 μm radius), and micropores (<5 μm radius).¹² Other pore size limits have also been used to distinguish micropores and macropores (e.g., reference (13)). Soil organic matter can also contain pore space and surface area that facilitates the retention of water. The distribution and continuity of these soil pores affect multiple processes in soils including root growth and nutrient uptake, water infiltration, drainage and storage, gaseous exchange in and out of the soil, and chemical retention and transport. Porosity or the proportion of the soil pore volume to the total soil volume is often approximately 50 % in soils (i.e., when the soil bulk density is 1.3 Mg m^{-3}).

The soil pore space itself is filled with varying proportions of gas and water (known as the soil solution) and this environment provides ideal microhabitats for soil biological activity, although the space occupied by living microorganisms represents generally less than 5 % of the overall space in soils¹⁴ (Fig. 2.3). In addition, almost 80–90 % of soil microorganisms are on solid surfaces. Among the factors affecting the ecology, activity and population dynamics of soil microorganisms in soil pores and on soil surfaces are the availability of carbon and energy sources, the presence of mineral nutrients, the amount and potential of soil water, temperature, pore air composition, pH of soil solution, soil oxidation–reduction potential, the area and charge of soil surfaces, the genetics of the microorganisms and the interaction among microorganisms and other soil biological components (e.g., plant roots).¹⁴ Soil has a large and diverse biological population that includes micro- and macro-fauna and flora. For example, the estimated number of bacterial cells in a gram of soil is typically approximately 10^9 and based on DNA reassociation kinetics, the estimated number of distinct genomes in a gram of soil ranges from 2,000 to 18,000.¹⁵

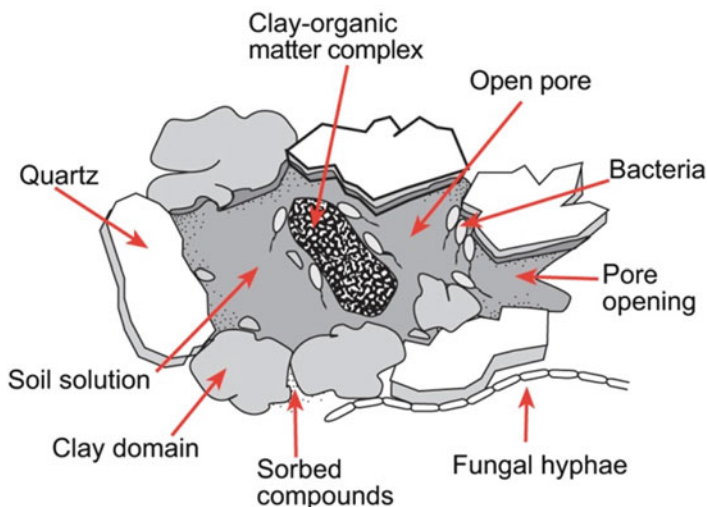


Fig. 2.3 Components and structure of a soil aggregate (adapted from reference (16))

2.2.1 Interactions of Biological, Chemical, and Physical Processes

Several important soil biological, chemical, and physical processes have major effects on the environment and are important for understanding the basis for several important environmental issues including air, soil, and water pollution, climate change, and the fate of pollutants and other materials added to soil. The magnitude and rate of many of these processes are affected by abiotic factors, such as temperature, aeration, soil water content, and soil moisture potential.

2.2.1.1 Buffering

Buffering of soil moisture content and soil temperature relative to air temperature and humidity make soil an ideal medium for plant growth and soil biological activity. The retention of water in soil pores and water's very high specific heat capacity account for the relatively moderate changes in soil temperature compared to changes in air temperature when a soil contains moisture. In addition, the large soil surface area and pore size distribution (i.e., micropores tend to retain more water than macropores) act to reduce soil water loss through evaporation and drainage.

Another type of buffering in soil moderates changes in the chemical composition of the soil solution and ionic species retained on the exchange sites of soil colloids. The process by which charged soil surfaces (i.e., clays, organic matter, sesquioxides, and amorphous minerals) attract and retain ionic species from the soil solution which is bathing the surface is known as adsorption. These sorbed

chemical species are retained at various strengths of retention depending on several factors including the nature and charge of the surface functional groups and the hydrated radius and charge of the sorbed species. These chemical species can also form sparingly soluble precipitates on the soil surfaces. The combined processes of adsorption and precipitation are known as sorption.

The interaction between sorbed chemical species on soil surfaces and chemical species in the soil solution helps to moderate excessive changes in the chemical concentration or activity of chemical species in the soil solution. For example, soil pH is buffered because when H^+ ion is added to the soil solution, some of the H^+ will be sorbed on the soil surfaces and the possible soil pH decrease resulting from that addition of H^+ will be moderated. Similarly, if H^+ is removed from the soil solution, H^+ (and Al^{+3}) will be desorbed from the soil surfaces and the possible soil pH increase due to H^+ removal will be moderated. This chemical solid-solution buffering system in soils affects multiple soil properties and processes including plant nutrient availability, biological activity, and the fate of chemical pollutants. Due to this chemical buffering system, measurement of soil reaction (acidity and alkalinity) for purposes of determining the amount of liming or acidifying material to raise or lower the soil pH for optimizing plant growth must measure both the soil acidity in the soil solution and ‘exchangeable acidity’ or concentrations of H^+ and Al^{+3} on the exchange sites of the soil surfaces. Similar assessments for determining the amount of phosphorus (P) fertilizer to add to a particular soil to raise the soil solution P level to an optimum level for plant growth must also take into account the soil’s P buffering capacity.

2.2.1.2 Filtering and Retention

The capacity of soils to filter and retain organic and inorganic pollutants is an important ecosystem service or function of soils.¹⁷ The filtering process occurs because of the interaction of physical, chemical, and biological processes in soils and is optimized when organic and inorganic pollutants are exposed to soil surfaces and biological activity. Therefore, preferential flow of pollutants through soil channels or cracks, shallow soils, slow infiltration of polluted water into soil causing surface runoff, and sandier-textured soils reduce the amount of potential filtering and retention of pollutants. Optimizing soil filtration is a major objective in the design of septic systems and pollutants from the sewage, such as human enteric viruses, move through soils due to several factors such as rainfall, temperature, soil structure, soil organic matter content, and soil pore water pH.¹⁸

2.2.1.3 Decomposition and Soil Organic Carbon Dynamics

Decomposition is the process by which organic materials are progressively dissociated and ultimately can be converted into inorganic constituents. This process serves two important ecosystems functions—the mineralization of carbon (C) (e.g.,

from organic C to carbon dioxide) and other elements (e.g., from organic to inorganic forms of nitrogen, phosphorus and sulphur), and the formation of soil organic matter.¹⁹ Decomposition is also the primary process in the biodegradation of pollutants²⁰ and affects soil efflux of carbon dioxide into the atmosphere, which is an important component of the global carbon balance affecting climate change. The conversion of C and other elements to mineral forms is called mineralization, and the reverse process by which inorganic forms are incorporated into organic forms in microbial biomass is called immobilization.²¹

Decomposition is primarily a biological process that includes the activity of soil organisms, but abiotic factors can also facilitate mass loss of organic materials through fragmentation, physical abrasion, photochemical breakdown and leaching.²² Among the factors affecting the degree and rate of decomposition are the resource quality of the organic materials, the soil physical/chemical environment (e.g., soil water potentials, oxygen supply, temperature, soil texture and mineralogy, pH) and the physical accessibility of the organic materials to microbial and enzymatic breakdown.^{22–24} Due to the higher proportion of organic matter and biological activity in the soil surface horizons, the highest rates of decomposition most often occur in this zone.

Several factors influence soil organic C stabilization by affecting both plant productivity and the activity of the saprotrophic system.²⁵ These factors include soil temperature, moisture, texture, pH, landscape position, ecosystem type, biological activity, the physicochemical properties of soil organic fractions, soil structure, nutrient availability, and clay mineralogy.^{24,26–29} A primary difficulty in assessing the relative importance of these factors in stabilizing soil organic C is the interactive nature of many of these variables. For example, among the effects of changes in soil moisture are changes in biological activity, in chemical solubility and transport, in plant productivity, and in soil temperature. The soil solid phase can adsorb biological molecules, retain them from transport in the environment, and also protect them from biological decomposition.¹⁴ In addition, loss mechanisms of soil organic C are not confined to decomposition, but also include losses due to soil erosion and leaching of dissolved organic C. These latter C loss processes may have relatively greater significance than decomposition among some soils situated in highly erosive or well-drained environments.

2.3 Importance of Soil Analysis

As a major component of terrestrial cycles, soils are a central component for many important agricultural and environmental issues. Soil degradation is a growing problem in the world while increased food production utilizing soil resources is needed to meet a growing world population (Table 2.1). One estimate is that food production will need to double in 30 years since the world's population is expected to reach 9.2 billion by 2050.³¹ However, approximately 25 % of all global land resources have been highly degraded or trending to high degradation, resulting in

Table 2.1 Major soil and other resource degradation in different agricultural land use types in developing countries (adapted from reference (30))

Land type	On-site soil degradation	Other resource degradation
Irrigated lands	<ul style="list-style-type: none"> • Salinization and waterlogging • Nutrient constraints under multiple cropping • Biological degradation (reduced soil organic matter, agrochemicals) 	<ul style="list-style-type: none"> • Nutrient pollution in ground/surface water • Pesticide pollution • Water-borne disease • Water conflicts
High-quality rain-fed lands	<ul style="list-style-type: none"> • Nutrient depletion • Soil compaction and physical degradation from overcultivation, machinery • Acidification • Removal of natural vegetation, perennials • Soil erosion • Biological degradation (reduced soil organic matter, agrochemicals) 	<ul style="list-style-type: none"> • Pesticide pollution • Deforestation
Densely populated marginal lands	<ul style="list-style-type: none"> • Soil erosion • Soil fertility depletion • Removal of natural vegetation, perennials • Soil compaction, physical degradation from overcultivation • Acidification 	<ul style="list-style-type: none"> • Loss of biodiversity • Watershed degradation
Extensively managed marginal lands	<ul style="list-style-type: none"> • Soil erosion from land clearing • Soil erosion from crop/livestock production • Soil nutrient depletion • Weed infestation • Biological degradation from topsoil removal 	<ul style="list-style-type: none"> • Deforestation • Loss of biodiversity • Watershed degradation
Urban and peri-urban agricultural lands	<ul style="list-style-type: none"> • Soil erosion from poor agricultural practices • Soil contamination from urban pollutants • Overgrazing and compaction 	<ul style="list-style-type: none"> • Water pollution • Air pollution • Human disease vectors

reduced productivity and negative environmental consequences.³² Examples of soil degradation include loss of soil organic matter, a decline in soil fertility and soil structure, increased erosion, salinity, acidity or alkalinity and the effects of toxic chemicals, pollutants, or excessive flooding.¹

Society faces diverse environmental challenges that include soil resources and their management as an important component of these challenges. Current soils-related environmental issues that are being extensively researched include: biogeochemical cycling of carbon and nutrient elements such as nitrogen and phosphorus; the fate of trace elements and other inorganic and organic pollutants (e.g., pesticides, biological agents, waste products, industrial chemicals) in soils; soil erosion processes and impacts; soil greenhouse gas emissions; the impacts of climate change on soil resources; and the effects of land use on soil, air, and water quality in urban and rural areas in different regions of the world.

2.4 Issues Related to Soil Assessment and Testing

Soil assessment for improving agricultural production has a long history of development and, more recently, environmental soil testing has become a major focus of effort to monitor and provide information related to environmental contamination.³³ Other uses of soil assessment include geotechnical investigations to assess physical properties of soils for foundations and earthworks and suitability for waste treatment and drainage.

Soil testing could be defined as any physical, chemical, or biological measurement that is performed on a soil, but for agricultural testing the definition of soil testing has been broadened to include soil sampling and processing, soil analysis, interpretation of the results, and management recommendations.³⁴ Additional important elements in modern soil testing programs have been the use of Global Positioning System (GPS) technology to add geographic references to soil sample information, communication of soil test results to soil testing clients and offering of supporting information and decision tools through use of the World-Wide Web, and improved storage and analysis of historical soil test databases. Environmental soil testing has several of the same features as agricultural soil testing including that the tests have to be rapid, accurate, and reproducible as well as provide some information to interpret the results.³³ However, environmental soil testing often follows standardized procedures that may be officially sanctioned (e.g., by a national agency such as the U.S. Environmental Protection Agency, see <http://www.epa.gov/ne/info/testmethods/>) and accuracy and reproducibility are a greater priority for agricultural soil testing, which often emphasizes rapid turn-around times and lower cost procedures to allow agricultural managers to make timely decisions.

The development of state-based soil testing programs to support agriculture in the United States relied on extensive research that assisted in the selection of appropriate soil testing methods and extractants, correlated the results of soil tests with plant production to allow for the interpretation of soil test results, and provided field calibration to develop nutrient recommendations for plant production based on soil test results. Several methods have been developed to analyse soil for important soil physical, chemical, and biological properties that might affect agricultural production and soil quality (Table 2.2).

2.4.1 *Representative Sampling or Monitoring with Spatial and Temporal Variation*

Representative sampling or monitoring of the soil resource is a major component of soil assessment since most soil samples or monitoring points provide information on a small fraction of the total soil volume contained in a field and may only represent certain locations and depths at a specific point in time. If the soil sampling or monitoring strategy is not designed and conducted correctly based on the

Table 2.2 Common soil properties measured and examples of methods used for agricultural and soil quality assessments

Category	Soil property	Methods used ^a
Physical	<ul style="list-style-type: none"> • Water content • Bulk density • Porosity • Penetrability • Wet aggregate stability • Soil moisture potential • Saturated hydraulic conductivity • Particle size distribution • Soil temperature 	<ul style="list-style-type: none"> • Time domain reflectometry (TDR) • Core or clod methods • Calculation from particle and bulk densities • Penetrometer resistance • Wet-sieving method • Tensiometer or pressure plates • Constant head soil core • Pipette method • Thermocouple thermometry
Chemical	<ul style="list-style-type: none"> • Soil reaction (acidity and alkalinity) • Oxidation-reduction status • Soil salinity and sodicity • Surface charge • Soil organic matter • Exchangeable cations • Other plant nutrients (e.g. nitrate) 	<ul style="list-style-type: none"> • pH meter and exchangeable acidity • Redox potential using probe and meter • Electrical conductivity and analysis for sodium • Sum of base cations plus exchangeable acidity • Total organic carbon by combustion • Atomic absorption (AA) or inductively-coupled plasma emission (ICP) spectrometry • Spectrophotometry
Biological	<ul style="list-style-type: none"> • Microbial activity • Microbial diversity • Active organic carbon • Nitrogen fixation • Nitrogen mineralization • Greenhouse gas flux 	<ul style="list-style-type: none"> • Measure soil microbial respiration or enzyme activity • Polar lipid fatty acid analysis or molecular biological techniques • Potassium permanganate-oxidizable carbon • Acetylene reduction • In-situ ion exchange resins or ex-situ laboratory incubation • Open chamber method and gas chromatography

^aMultiple methods are available for measurement of soil physical, chemical, and biological properties and this table lists some examples of those methods. For more complete discussion of methods of soil analysis, see the Methods of Soil Analysis series published by the Soil Science Society of America

objectives of the soil testing effort and the nature of the targeted soil properties then data and conclusions based on the soil test may be in error or misleading.

An example of an important sampling and monitoring consideration is the selection of the appropriate soil depth and soil depth increments for sampling and monitoring.

A traditional approach in soil sampling for agricultural testing is to take soil samples to the depth of cultivation (also known as the plow layer depth) which is approximately 15–20 cm with conventional tillage. However, the recommended depth for agricultural assessment of soil nitrate nitrogen is deeper, with the preplant soil nitrogen test often recommended to a depth of 60 cm and the pre-sidedress nitrate test (PSNT) to a depth of 30 cm due to the more extensive movement of nitrate in the soil profile. Environmental soil testing may require even deeper testing to determine possible leaching and lateral movement of pollutants, but shallow sampling depths (e.g., 2.5–5 cm) may also be employed in studies related to surface runoff and erosion.

Selected sample depth increments may provide additional information related to vertical variation in soil resources and are often done in uniform increments through the soil profile. Depending on the soil sampling or monitoring objectives, soil depth locations may also be selected based on known morphological differences (i.e., location and width of soil horizons) since these horizons and their different properties may have environmental significance on several processes.

Increasingly for certain soil properties more intensive temporal sampling is being sought to more accurately understand changes in those properties over time due to changes caused by diurnal, seasonal, and disturbance effects. For example, wider time intervals in sampling for assessment of cumulative soil surface greenhouse gas (i.e., carbon dioxide, nitrous oxide, and methane) emissions either over- or under-estimate these emissions compared to shorter time intervals, especially for trace gases such as nitrous oxide.³⁵

Similarly, more intensive spatial soil sampling over land areas is being utilized for multiple objectives including precision agricultural management³⁶ and for assessment of the extent of environmental pollution.³⁷ More intensive spatial soil sampling provides a better understanding of variations in soil properties across landscapes caused by natural and anthropogenic processes, but the cost of sampling and analysis with the larger number of samples may make this approach cost-prohibitive and requires use of more advanced geostatistical techniques (e.g., reference (38)).

Statistical design and analysis are important components of soil sampling and evaluation, and therefore the selection of the statistical approach and the method for statistical analysis are important to consider prior to sample collection. Fuller discussion of this topic can be found in several texts including references (39) and (40).

2.4.2 Selection of Soil Analytical Methods

The selection of analytical methods for determining soil properties may vary depending on several factors including: the objectives of soil testing; the speed at which the soil analysis must be done; where the soil analysis will occur (i.e., in the field or laboratory); the native properties of the soil; whether the soil can be disturbed; the cost and speed of the analysis; the accuracy and precision of the method; any imposed requirements for standard testing and quality control procedures; the availability of information to interpret the analytical results; the

training of the person doing the analysis; the availability of analytical equipment and reagents; and the necessary time intervals between analyses. As analytical technology and methods have progressed, the capacity and speed of analysis has increased and more options have become available for non-destructive analytical procedures (e.g., remote sensing and proximal sensor technology). These analytical methods have also been linked with GPS and geographic information system (GIS) technologies to geographically reference and store analytical information and provide maps as a basis for management decisions, such as variable rate application of fertilizers in agricultural fields. The possibility of linking the results of analytical methods with other procedures (e.g., with interpretation and management steps) may also influence the selection of a specific analytical method.

A key principle for selection of analytical procedures is to identify methods that provide information on soil properties that are significant to the assessment or management objective or application. For example, selection of an appropriate chemical extractant for measuring plant-available nutrients is a critical element for agricultural soil testing.⁴¹ As a basis of selection of the extractant, the amount of nutrient element (e.g., phosphorus) extracted should have a significant correlation with the amount of nutrient taken up by the plant or with crop performance over a critical period of time, such as the growing season. An environmental testing example is measurement of lead in soils to determine potential health hazards. Total lead contained in the soil can be determined after acid digestion, but this information would not be as significant to assessing the potential health hazard as measuring the bioavailable fraction of lead in the soil through use of dilute acid- or chelate-based soil test extractants.³³

An associated consideration for selection of analytical methods is whether they have been extensively tested for the specific application and, if it is a new procedure, whether it has been compared to standard methods and incorporates quality control (QC) procedures. Uniform use of extensively-tested methods and QC allows for comparisons of data results collected across different studies and environments over time.

2.4.3 Associated Measurements

The collection of associated measurements (e.g., soil water content, soil temperature, soil bulk density, soil classification) in addition to the primary soil test assessment can provide valuable information for interpretation of the results as well as other applications. For example, measurements of soil carbon including total organic carbon and soil carbon fractions are often done on a weight basis, but simulation modellers of soil carbon dynamics who wish to validate their models may need the results on a volume or area basis. The measurement of soil bulk density allows for conversion of the data results from a weight to volume basis and vice versa. In addition, soil properties (e.g., biological properties) may be influenced by changes in soil temperature and water content and, therefore, these associated measurements are useful for understanding the observed results and again may help in simulation modelling.

2.4.4 Use of Soil Test Databases and Networks

Extensive soil testing information has been collected in the United States since the 1940s but maintenance of records of this information (referred to collectively as the soil testing database) has improved with the spread of computer technology since the 1970s.⁴² Private and public soil testing laboratories in the United States analyse and provide recommendations for approximately 3–3.5 million soil samples annually, and therefore a large database of information is generated about soil conditions. For agricultural soil test programs, information accompanying the samples may include client information (e.g., name, address, telephone number), information regarding the soil sample (e.g., type of sample, source of sample, previous crop, previous fertilization, crop to be grown, and yield goal), results of soil or plant analyses, and plant nutrient recommendations.

Traditionally, soil testing databases have been used to examine general trends in soil nutrient levels on county, state, or regional scales and to assess the service performance of the laboratory.⁴² This information can also be used by agricultural extension personnel to determine the geographic effectiveness of their efforts at promoting soil testing, identify priority issues, and to re-allocate extension resources. The relative levels of soil plant nutrients among submitted samples can also be evaluated within regions of a state or among states at the national scale, and problems associated with nutrient deficiencies or excess can be identified. For example, comparison of soil test phosphorus results among states has provided information on issues related to regions with possible phosphorus deficiency for crop growth but also on states where excessive soil test phosphorus may be an environmental issue.⁴³

Currently geographically referenced soil test information is also being generated at a large-scale on agricultural land with the collection of sensor-based information, such as soil apparent electrical conductivity, in support of precision agriculture management practices. This soil test database is also being stored and could have potential uses for improving long-term management and may have commercial and research value for prediction of crop production and other uses, such as validation of computer simulation models. In addition, large-scale environmental monitoring networks (e.g., the Fluxnet network of sites examining exchanges of carbon dioxide (CO₂), water vapour, and energy between terrestrial ecosystems and the atmosphere; see <http://fluxnet.ornl.gov/introduction>) are posing many different challenges for existing data management systems such as the transport, storage, quality control and assurance, gap-filling and analysis of large sets of sensor-generated environmental data.⁴⁴

Properly curating and preserving soil test information and providing the appropriate metadata associated with the collected data is especially important for large soil test datasets for which the information may have long-term value for preservation. Therefore, procedures and policies associated with the collected soil test database may need to be formulated prior to initiation of data collection to incorporate established ecoinformatics practices.⁴⁵

2.5 Application of Proximal Soil Sensors

Various sensing methodologies play a key role in soil analysis. Optical, radiometric, mechanical, electrochemical, and other methods are commonly used in standard laboratory analyses. Some of these methods have been adapted for in-field proximal soil sensing (PSS). Proximal soil sensing has been defined as the use of field-based sensors to obtain signals from the soil when the sensor's detector is in contact with or close to (within 2 m) the soil.⁴⁶ A comprehensive review of PSS methodologies and applications was recently presented.⁴⁷

Operation of PSS may be either stationary or mobile ("on-the-go"), and each of these two sensor deployment models may present different advantages and disadvantages. Mobile sensors are best suited to providing spatially dense, although often temporally sparse datasets. A major application of mobile PSS, as reviewed by references (48, 49), is to generate the spatially dense data needed in precision agriculture, where crop management inputs such as fertilizers and pesticides are varied spatially according to within-variation in the need for the input. Sensor response time is a key factor due to mobile operation, as are durability and reliability with respect to machine vibration.

Stationary PSS are better able to provide temporally dense data; however, the number of feasible sensing locations is often limited by the cost of multiple sensors and data recording devices. Stationary PSS are often organized in sensor arrays or networks, which may consist of multiple sensor types as well as multiple sensors of the same type. Sensors may be arranged vertically in the soil profile to collect data documenting fluxes from one depth to another or horizontally to provide some degree of spatial coverage. Applications include monitoring temporal changes in soil water content to control irrigation of crops⁵⁰ and documenting soil changes at a comprehensive ecological observatory site.⁵¹ Signal-to-noise issues may be a concern if long leads are used in an attempt to connect sensors at multiple locations to the same datalogger. Many newer sensor networks use wireless connectivity to overcome this problem. Stability, durability, and long-term reliability under harsh ambient conditions are important considerations, particularly if sensors are to be deployed for extended periods of time.⁵²

A key issue with application of soil sensors is the inherent heterogeneity of the soil mass. In part, this heterogeneity is caused by the three-phase nature of the soil and its significant biological component (see Sect. 2.2). Depending on the properties of interest, PSS data collection may need to be spatially dense, temporally dense, or both. Soil heterogeneity can cause problems for electrochemical measurements. One approach for dealing with heterogeneity is to measure the properties of interest in soil extracts.⁵³ However, in cases where many sensor measurements are needed to fully characterize the soil, the soil extract approach may be infeasible. Then a detailed understanding of soil heterogeneity is needed for optimal placement of stationary PSS or for developing deployment plans for mobile PSS.⁵¹

Below we discuss applications of electrochemical sensors to soil analysis, categorized by the type of measurement⁵⁴: voltammetric, conductometric, or potentiometric.

2.5.1 Voltammetric Methods

A particular application of voltammetric methods to soil analysis has been in the detection of heavy metals. Heavy metals, unlike organic wastes, are non-biodegradable and can accumulate in living tissues, causing various diseases and disorders.⁵⁵ High levels of toxic elements, such as cadmium (Cd), copper (Cu), zinc (Zn), and lead (Pb) can be found in agricultural soils. They can also be found in stream systems in and around abandoned metalliferous mines due to improper disposal and management of mine wastes.⁵⁶ Moreover, rapid industrialization has become an additional source for environmental contamination by heavy metals, which originates from metal plating, mining activities, and paint manufacture. Therefore, monitoring heavy metal levels in the environment and food samples is necessary to efficiently characterize the contaminated sites and minimize the exposure of humans to heavy metal contaminated crops.

Inductively coupled argon plasma (ICP) spectrometry has been the most widely used technique used for metal determination in the environment and food crops, combined with wet or dry ashing procedures for digesting organic matter as a sample pre-treatment process.⁵⁷ Yet, such conventional methods are costly and time consuming, thereby limiting the number of samples tested in the field. Therefore, real-time, continuous analytical methods capable of detecting heavy metal ions with high temporal and spatial resolution are desirable. Recent advances in electronic technology have increased the potential for the development of portable electrochemical sensors for in-field monitoring of heavy metals.⁵⁸

Anodic stripping voltammetry (ASV), which involves preconcentration of a metal phase, a solid electrode surface at negative potentials, and selective oxidation of each metal phase species during an anodic potential sweep, has been considered a powerful technique for detecting trace levels of heavy metals in aqueous samples due to its remarkable sensitivity, fast response, and portability.^{58,59} Two basic electrode systems, a mercury-film electrode and a hanging mercury drop electrode, have been widely used in the development of ASV. Glassy carbon (GC) electrodes have been commonly used with ASV to support the mercury film, because of their wide potential window and low porosity.⁶⁰ However, the use of mercury as an electrode material, historically used in electrochemical methods of analysis for determining Cd, Pb, Cu and Zn, has been recently limited in many countries due to the toxicity of mercury itself, thereby requiring mercury-free electrodes^{59,61,62} (see Chap. 16). Several researchers have reported that bismuth, which is an environmentally friendly element with very low toxicity, could be used as an alternative to mercury for ASV analysis.^{59,63–65}

2.5.2 *Conductometric Methods: Soil EC_a*

Electrical conductivity (or its mathematical inverse, resistivity) of a soil solution is strongly correlated with total salt content. Therefore, laboratory methods involving solution or saturated paste conductivity are often used to assess soil salinity. Electrical conductivity measurements of bulk soil (designated as EC_a for apparent electrical conductivity) were also first used to assess salinity.⁶⁶ Resistivity and conductivity measurements are also useful for estimating other soil properties, as reviewed by⁶⁷ and.⁶⁸ Factors that influence EC_a include soil salinity, clay content and cation exchange capacity (CEC), clay mineralogy, soil pore size and distribution, soil moisture content, and temperature.^{69,70} For saline soils, most of the variation in EC_a can be related to salt concentration.⁷¹ In non-saline soils, conductivity variations are primarily a function of soil texture, moisture content, bulk density, and CEC.⁶⁸ The theoretical basis for the relationship between EC_a and soil physical properties has been described by a model where EC_a was a function of soil water content (both the mobile and immobile fractions), the electrical conductivity of the soil water, soil bulk density, and the electrical conductivity of the soil solid phase.⁷² Later, this model was used to predict the expected correlation structure between EC_a data and multiple soil properties.⁷³

Because EC_a is a function of a number of soil properties, EC_a measurements can be used to provide indirect measures of these properties if the effects of other soil properties on the EC_a measurement are known or can be estimated. In some situations, the contribution of within-field changes in one factor will be large enough with respect to variation in the other factors that EC_a can be calibrated as a direct measurement of that dominant factor. This direct calibration approach was used to quantify within-field variations in soil salinity under uniform management and where water content, bulk density, and other soil properties were “reasonably homogeneous”.⁷⁴ In addition, EC_a can be calibrated to the thickness of soil layers with contrasting conductivities. Examples include EC_a regressions for the depth of flood-induced sand deposition⁷⁵ and for topsoil depth (TD) above a subsoil argillic horizon.^{76–79}

Researchers have related EC_a to a number of different soil properties either within individual fields or across closely related soil landscapes. Examples include soil moisture,^{80,81} clay content,⁸² and CEC and exchangeable Ca and Mg.⁸³ Mapping of areas of differing soil texture⁷⁵ and soil type⁸⁴ have also been reported. In a project relating EC_a to multiple soil properties across a number of locations in the north-central USA, the strongest and most consistent relationships were with clay content.^{78,85} When EC_a was evaluated for delineating a number of soil physical, chemical, and biological properties related to yield and ecological potential it was found useful for delimiting distinct zones of soil condition.⁸⁶ Although many soil factors affecting EC_a are relatively fixed over time (e.g., clay content), others may exhibit strong seasonal dynamics. For example, a time sequence of EC_a maps was related to temporal changes in available soil nitrogen,⁸⁷ suggesting that it might be possible to use EC_a measurements as an indicator of soluble nitrogen gains and

losses in the soil over time. Because soil EC_a integrates texture and moisture availability, two characteristics that both vary over the landscape and also affect productivity, EC_a sensing also shows promise in interpreting crop yield variations, at least in certain soils (e.g., reference (88)).

Soil EC_a has been used to assess soil environmental susceptibility. For example, EC_a was used as an estimator of the partitioning of a triazine herbicide between the soil and soil solution, which could allow mapping soil susceptibility to leaching of the herbicide.⁸⁹ Other researchers have applied EC_a data for measuring and mapping contaminant plumes, including seepage from animal waste lagoons⁹⁰ and industrial waste landfill leachate.⁹¹

2.5.2.1 Soil Conductivity Sensors

Two types of mobile, proximal EC_a sensors are commercially available for soil investigations, an electrode-based electrical resistivity (ER) sensor requiring soil contact and a non-contact electromagnetic induction (EMI) sensor. In the EMI approach, nominal measurement depth depends on coil orientation and operating frequency of the instrument, and is also proportional to the spacing between the coils of the sensor.⁶⁹ Most EMI instruments used for soil investigation operate at a single frequency; however, many allow multiple measurements by reorienting the sensor, or through the inclusion of multiple receiver coils. An EMI-based EC_a sensor widely used for soil investigation is the EM38 (Geonics Limited, Mississauga, Ontario, Canada), which was initially developed for root-zone salinity assessment.⁹² The EM38 is a lightweight bar designed to be carried by hand and provide stationary EC_a readings. It can be operated in two orientations, providing effective measurement depths of approximately 1.5 and 0.75 m. A newer version (EM38-MK2) has multiple receiver coils, and provides simultaneous measurements at two depths. To implement mobile data acquisition, it is necessary for the user to assemble a transport mechanism and data collection system (e.g., references 77 and 93). The EMI approach is also used by the DUALEM sensors (Dualem, Inc., Milton, Ontario, Canada) which provide two or more simultaneous measurements through multiple receiver coils.

The ER sensing approach generally requires a minimum of four electrodes in direct contact with the soil, two to inject an electrical current and two others across which a voltage potential is measured. The measurement depth depends on the spacing between the electrodes. In an early implementation, EC_a was measured with a four-electrode sensor and used to create maps of soil salinity variations in a field.⁹⁴ Later, a version of the electrode-based sensor was tractor-mounted for mobile, georeferenced measurements of EC_a .⁹⁵ Several commercial sensors implementing the electrode-based approach are manufactured by Veris Technologies, Salina, Kansas, USA. Smaller models use four rolling coulters for electrodes and provide a single measurement, while larger models use six rolling coulters and provide two simultaneous EC_a measurements.⁹⁶ Another system, called GEOPHILUS ELECTRICUS, provides five simultaneous measurements.⁹⁷

Operational advantages and disadvantages of each type of commercial proximal EC_a sensor have been summarized.⁷⁸ In addition to the widely used proximal EC_a sensors, there are also commercial penetrometer-based EC_a sensors that allow direct measurement of EC_a as a function of depth.^{98,99}

2.5.3 Potentiometric Methods: Ion-Selective Electrodes

Most of the potentiometric methods employed in soil analysis are based on the use of an ion-selective electrode (ISE) with glass or a polymer membrane, or an ion-selective field effect transistor (ISFET). The ISFET has the same theoretical basis as the ISE, i.e., both ISEs and ISFETs respond selectively to a particular ion in solution according to a logarithmic relationship between the ionic activity and electric potential. The ISEs and ISFETs require recognition elements, i.e., ion-selective membranes, which are integrated with a reference electrode and enable the chemical response (ion concentration) to be converted into an electrical potential signal.¹⁰⁰ Due to an increased demand for the measurement of new ions, and major advances in the electronic technology required for producing multiple channel ISFETs, numerous ion-selective membranes have been developed in many areas of applied analytical chemistry, e.g., in the analysis of clinical or environmental samples.¹⁰¹

2.5.3.1 Issues in ISE/ISFET Application

There are several potential disadvantages of ISE/ISFET sensors, as compared to standard analytical methods. One is chemical interference by other ions, because ion-selective electrodes are not truly specific but respond more or less to a variety of interfering ions. To overcome interference issues, various data processing methods have been used. For example, multivariate calibration models have been proposed to allow cross responses arising from primary and interfering ions to be decoupled, thus allowing accurate determination of individual ion concentrations within mixtures.¹⁰² In some cases, another compound can be added to suppress the interference effect. For example, Ag_2SO_4 can be used to suppress the chloride interference in nitrate sensing.¹⁰³

Another disadvantage is degraded performance over time due to ambient environmental conditions. For example, accuracy can be reduced due to electrode response drift and biofilm accumulation caused by the presence of organic materials and soil microbial activity in environmental samples.¹⁰⁴ In particular, signal drift and biofilm accumulation may be a major concern when considering an in-line management system that includes continuous immersion of ISEs in solution. Particularly for in-situ applications, poor soil-electrode contact is a concern. Although good contact may be attained during installation, the range of environmental conditions encountered during operation, including soil moisture variations

and associated shrinking and swelling of the soil mass, may make it difficult to maintain the required contact. Also, the general challenges associated with environmental sensor measurements must be considered. Temperature variations, excessive moisture, electromagnetic interference, and susceptibility to damage are some of the factors that are more likely to affect field sensor measurements than laboratory measurements.

Application of ISE technology to real-time soil sensing requires continuous determination of individual ion concentrations with acceptable sensitivity and stability. In general, stability and repeatability of response are a concern in the use of an array of multiple ISEs to measure ion concentrations in a series of samples because accuracy of the measurement may be limited by drift in electrode potential over time. The use of a computer-based automatic measurement system would improve accuracy and precision because consistent control of sample preparation, sensor calibration, and data collection can reduce variability among multiple electrodes during replicate measurements.¹⁰⁵ Ideally, an automated sensing system would be able to periodically calibrate and rinse the electrodes and continuously measure ions of interest in the solution, while automatically introducing solutions for calibration and rinsing as well as measurement.

2.5.3.2 Application: Soil Nutrient Sensing

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are essential for crop growth, and the use of commercial N, P, and K fertilizers has contributed greatly to the increased yield of agricultural crops. However, excessive fertilizer applications can lead to environmental contamination, primarily of surface and ground waters.¹⁰⁶ Ideally, fertilizer application should be adjusted to match the requirements for optimum crop production at each within-field location, because there can be high spatial variability in the N, P, and K levels found within fields.^{107,108}

To quantify soil nutrient (i.e., N, P, and K) levels at the spatial scale needed for within-field measurements, on-the-go real-time sensors present an attractive alternative to current manual and/or laboratory methods.^{109,110} Mobile sensors could provide measurements at a high spatial density and relatively low cost,⁴⁸ and with an overall accuracy potentially higher than that of conventional methods. This occurs because there are two sources of error in soil testing—analysis error due to sub-sampling and analytical determination, and sampling error due to point-to-point variation in soils. With traditional soil testing, analysis error is relatively low; however, sampling error can be substantial since cost limits the sampling intensity. Mobile sensors can provide a spatial sampling intensity several orders of magnitude greater than traditional methods. Therefore, a mobile real-time soil sensor can tolerate much higher analysis errors while providing greater overall accuracy in mapping soil variability. Reviews of soil nutrient sensing by ISE and other methods have been presented.^{111,112}

2.5.3.3 Nitrate, Potassium, and Phosphate Membranes and Electrodes

Numerous nitrate ion-selective membranes (Table 2.3) have been described for various environmental applications, such as food, plants, fertilizer, soil, and wastewater. Overall, best results were obtained with PVC ion-selective membranes prepared with quaternary ammonium compounds, such as TDDA or MTDA as the sensing element. These membranes were able to determine nitrate across the concentration range important for N fertilizer application management, i.e., $10 \sim 30 \text{ mg kg}^{-1} \text{ NO}_3$. The best membranes also maintained acceptable selectivity levels in mixed solutions, being at least 40 times more sensitive to nitrate than to chloride and bicarbonate.

Valinomycin-based membranes (Table 2.4) have been the predominant choice for potassium sensing in soil and other environmental samples. Considerable research effort has focused on improving the adhesion of the PVC membrane to extend the consistent sensitivity period, and thus, the lifetime of the electrode. Valinomycin ionophores have exhibited strong K selectivity and sensitivity sufficient to quantify variations in the typical range in soil K where additional fertilizer is recommended.¹¹¹

The design of an ionophore for selective recognition of phosphate has been especially challenging for several reasons. Due to the very high hydration energy of phosphate, ion selective membranes have a very poor selectivity for phosphate. The free energy of the phosphate species is very small and the large size of orthophosphate ions prohibits the use of size-exclusion principles for increased selectivity. Reviews^{111,113,128} report work on various phosphate sensors, including polymer membranes based on organotin, cyclic polyamine, or uranyl salophene derivatives; protein-based biosensors; and cobalt-based electrodes (Table 2.5). A recurring problem has been the low selectivity response of such membranes toward many anions that may be present in the soil. At present, the best alternative appears to be the solid cobalt electrode, which has exhibited sufficient sensitivity, selectivity, and durability to provide a quantitative measure of phosphates in soil extracts.^{141,144,145}

2.5.3.4 Laboratory Prototype Systems for Soil Nutrient Sensing

Ion selective electrodes have historically been used in soil testing laboratories to conduct standard chemical soil tests, especially soil pH measurement. Many researchers in the 1970s and 1980s concentrated on the suitability of ISEs as an alternative to routine soil nitrate testing. More recently, researchers whose end goal was a mobile macronutrient sensing system have reported on laboratory tests of components of such systems.

Nitrate and potassium ion-selective electrodes have been evaluated for use in moistened soils as opposed to soil extracts.¹⁴⁶ Soluble nitrate and K content of moist soil samples could be determined in the laboratory ($r^2 = 0.56 \sim 0.94$) if several limitations such as inconsistent contact between soil and electrode and

Table 2.3 Comparison of nitrate ion-selective membranes

Chemicals used	Performance factors ^a				References
	Sensitivity (mV/decade)	Linear range (M)	Detection limit (M)	Selectivity (log K _{ij})	
Tetraoctylammonium nitrate (TDDA); 2-nitrophenyl octyl ether (NPOE); high-molecular-weight polyvinyl chloride (PVC)	-63.4	10 ⁻⁴ ~ 10 ⁻¹		Cl ⁻ = -2.40	114
				HCO ₃ ⁻ = -3.29	
				HPO ₄ ²⁻ = -3.76	
				SO ₄ ²⁻ = -3.76	
				Ac ⁻ = -3.48	
TDDA; dibutylphthalate (DBP); PVC	-56.2		8.3 × 10 ⁻⁷	Br ⁻ = -0.81	115
				Cl ⁻ = -2.30	
				NO ₂ ⁻ = -1.15	
Tetraoctylammonium nitrate (TOAN); trioctyl phosphonate (TOP); aliphatic urethane diacrylate Ebecryl 270 and hexanediol diacrylate (HDDA); 2-2'-dimethoxyl phenylace- tophenone (Irgacure 651)	-62.6	2.3 × 10 ⁻⁵ ~ 6 × 10 ⁻²	1 × 10 ⁻⁵	F ⁻ = -3.0	116
				HCO ₃ ⁻ ≥ -3.30	
				Cl ⁻ = -2.0	
Tetraoctylammonium nitrate (TOAN); DBP; PVC Tridodecylmethylammonium nitrate (TDMAN); NPOE; PVC Tris(4,7-diphenyl-1,10-phenanthroline) nickel(II) nitrate (TDPNN); NPOE; PVC	-54.0 ± 0.6 -56.1 ± 0.9 -55.8 ± 7.1		2.3 × 10 ⁻⁴ 2.8 × 10 ⁻⁴ 7.8 × 10 ⁻⁴		117
Methyltridodecylammonium nitrate (MTDAN); methyltriphenyl phosphonium bromide; NPOE; PVC	-55.6	10 ⁻⁴ ~ 10 ⁻¹		Cl ⁻ = -1.45	118
				HCO ₃ ⁻ = -2.17	
				SO ₄ ²⁻ = -2.74	
Triallyldodecylammonium nitrate (TDDAN); NPOE; Krynac; dicumyl peroxide (DCP)	-57.7	1.2 × 10 ⁻⁵ ~ 10 ⁻¹	8.8 × 10 ⁻⁶	Cl ⁻ = -4.0	119
				HCO ₃ ⁻ = -4.9	
				SO ₄ ²⁻ = -5.0	
TDDA; NPOE; PVC	-54.9 ± 1.3	10 ⁻⁴ ~ 10 ⁻¹	10 ⁻⁵	Cl ⁻ = -2.07	120
				HCO ₃ ⁻ = -3.22	
				Br ⁻ = -1.03	

^aEmpty cells occur when data for that membrane characteristic were not provided in the reference

Table 2.4 Comparison of potassium ion-selective membranes

Chemicals used	Performance factors ^a				References
	Sensitivity (mV/decade)	Linear range (M)	Detection limit (M)	Selectivity (log K _{ij})	
Valinomycin; Benzophenonetetracarboxylic acid tetra- <i>n</i> -undecyl ester (BTCU); High-molecular- weight polyvinyl chloride (PVC)	51.7	10 ⁻⁴ ~ 10 ⁻¹		K ⁺ > NH ₄ ⁺ > H ⁺ > Na ⁺ > Li ⁺ > Ca ⁺	121
Valinomycin; bis (2-ethylhexyl) sebacate (DOS); PVC; potassium tetrakis(4-chlorophenyl) borate (KTPCIPB)	58	1.8 × 10 ⁻⁵ ~ 10 ⁻¹	3 × 10 ⁻⁶	Na ⁺ = -4.2 Li ⁺ = -4.3	122
Valinomycin; KTPCIPB; DOS; Eb270 + HDDA	55.7	7 × 10 ⁻⁵ ~ 0.1	4 × 10 ⁻⁵		116
Valinomycin; DOS; PVC; KTPCIPB	51.5 ± 1.41	10 ⁻⁴ ~ 10 ⁻¹	10 ⁻⁴	Na ⁺ = -2.57 NH ₄ ⁺ = -1.63 Mg ²⁺ = -2.94 Ca ²⁺ = -2.88	120
Valinomycin; Dioctyl adipate; PVC	54.88 ± 1.137	10 ⁻⁵ ~ 10 ⁻¹			123
Valinomycin; Dioctyl adipate; PVC; copolymer VAGH	53 ± 0.6		4 × 10 ⁻⁵	Na ⁺ = -4.0	124
<i>Cis</i> -bis(15-crown-5 ether); 2-nitrophenyl octyl ether (NPOE); PVC	59		9.5 × 10 ⁻⁷	Na ⁺ = -3.69 NH ₄ ⁺ = -2.28 Li ⁺ = -4.07 Cs ⁺ = -2.25	125
Valinomycin; dioctyl adipate; PVC	58–59				126
Valinomycin; bis(2-ethylhexyl) adipate; PVC	56 ~ 59	10 ⁻⁵ ~ 10 ⁻¹	~10 ⁻⁶	Na ⁺ = -3.56	127

^aEmpty cells occur when data for that membrane characteristic were not provided in the reference

Table 2.5 Comparison of phosphate ion-selective membranes and electrodes

Chemicals used	Performance factors ^a			Selectivity order	References
	Sensitivity (mV/decade)	Linear range (M)	Detection limit (M)		
Measured species: HPO_4^{2-} Bis(tribenzyltin) oxide; 2-nitrophenyl octyl ether (NPOE); high-molecular-weight polyvinyl chloride (PVC)	-30.1	$5 \times 10^{-6} \sim 10^{-1}$	10^{-6}	$\text{HPO}_4^{2-} > \text{Br}^- > \text{NO}_3^- > \text{Cl}^- > \text{Ac}^- > \text{SO}_4^{2-}$	129
Bis(guanidinium); HDTODAB; NPOE; PVC	-32.1		10^{-6}		130
Bis(<i>p</i> -chlorobenzyl)tin dichloride; Dibutyl sebacate; PVC; <i>N,N</i> -dimethylformamide	-33	$2.2 \times 10^{-4} \sim 1.2 \times 10^{-2}$	3.3×10^{-5}	$\text{HPO}_4^{2-} > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$	131,132
3-decyl-1,5,8-triazacyclodecane- 2,4-dione (N3-cyclic amine); dibutyl sebacate; PVC	-29	$10^{-6} \sim 10^{-2}$		$\text{HPO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$	133

Measured species: H_2PO_4^-					
Bidentate organic tin compound; bis(2-ethylhexyl) sebacate (DOS); PVC	-54.6				134,135
Trialkyl/aryl-tin chloride NPOE; PVC; NaTFPB	-60	$10^{-4} \sim 10^{-1}$	7×10^{-5}		136
Uranyl salophene derivative; NPOE; PVC; tetradecylammonium bromide (TDAB)	-59	$10^{-4} \sim 10^{-1}$			137,138
Cobalt rod (99.99 %, 5 mm diameter) coated with Teflon	-55	$10^{-5} \sim 10^{-2}$	5×10^{-6}	$\text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} = \text{AcO}^- > \text{NO}_3^-$	139
Cobalt wire (99.99 %, 0.5 mm diameter)	-38 ± 0.5	$10^{-5} \sim 10^{-3}$	10^{-6}	$\text{I}^- > \text{Br}^- > \text{Ac}^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$	140-143
Cobalt rod (99.95 %, 5 mm diameter) coated with silicone and a plastic body	-32.9 ± 0.9	$10^{-4} \sim 10^{-1}$	10^{-5}	$\text{Ac}^- > \text{HCO}_3^- > \text{Cl}^- > \text{F}^- > \text{Br}^- > \text{NO}_3^-$	144

^aEmpty cells occur when data for that membrane or electrode characteristic were not provided in the reference

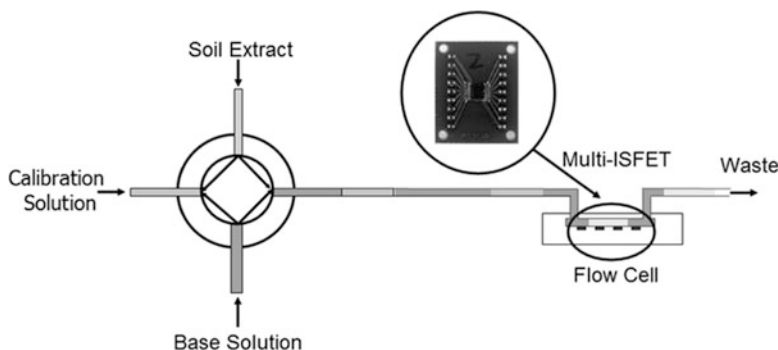


Fig. 2.4 Scheme of an ion-selective field effect transistor (ISFET)—flow injection analysis (FIA) system.¹¹¹ The soil extract sample, calibration, and base solutions are sequentially introduced through a flow injection line system with multiple inlets, and are transported to a multi-ISFET chip with outputs that continuously change due to the passage of the sample through the flow cell

potential drift due to continuous measurements were addressed. Plant-available K of 32 agricultural soils as determined by two ISEs (glass and PVC-based) was highly correlated with values from standard laboratory analysis.¹⁴⁷

A multi-ISFET sensor chip was used to measure soil nitrate in a flow injection analysis (FIA) system using low flow rates, short injection times, and rapid rinsing^{114,148} (Fig. 2.4). The multi-ISFET/FIA system successfully estimated soil nitrate-N content in manually prepared soil extracts ($r^2 > 0.90$) while allowing samples to be analyzed within 1.25 s with sample flow rates less than 0.2 mL s^{-1} . Later, a rapid extraction system was designed for in-field real-time measurement of soil nitrates using these ISFETs.¹⁴⁹ Several design parameters affecting nitrate extraction were studied. Nitrate concentration could be determined 2–5 s after injection of the extracting solution when using data descriptors based on the peak and slope of the ISFET nitrate response curve.

A sensor array including three different ISEs based on TDDA-NPOE and valinomycin-DOS membranes and cobalt rod was evaluated using an automated test stand (Fig. 2.5) to simultaneously determine $\text{NO}_3\text{-N}$, available K, and available P in Kelowna-soil extracts.¹⁵⁰ The nitrate ISE in conjunction with the Kelowna extractant¹⁰³ provided results in close agreement with the standard method. Kelowna-K ISE concentrations were about 50 % lower than those obtained with the standard method due to decreased K extraction by the Kelowna solution. Soil P concentrations obtained with the Kelowna extractant and cobalt P ISEs were about 64 % lower than those obtained by the standard method due both to a lower P extraction by the Kelowna solution, and to lower estimates of P concentrations in the extracts by the cobalt P ISEs. Although P and K concentrations were low, a calibration factor could address this issue because there was a linear relationship between ISE and standard methods ($r^2 = 0.81$ and 0.82 for P and K, respectively). In further evaluation of this system, it was possible to transfer existing calibration equations to new membranes and electrodes.¹⁵¹ An adjustment for the difference in

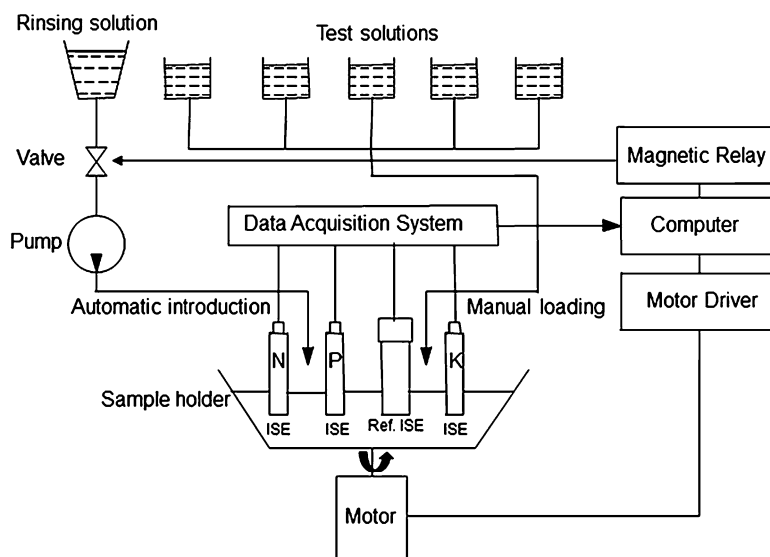


Fig. 2.5 Schematic diagram of a test stand for multiple electrode tests¹⁵¹

extraction efficiency between Kelowna and standard extractants yielded linear relationships with near 1:1 slopes between estimates and actual soil N and K values. However, a relatively large offset between calibrated ISE and standard method concentrations for P was said to require further investigation.

2.5.3.5 Field-Mobile Soil Nutrient Sensors

Beginning in the early 1990s, several prototype real-time on-the-go soil nutrient sensing systems were developed using custom-designed soil samplers and commercially available ion-selective electrodes for sensing nitrate and pH in soils. In a laboratory study nitrate level was estimated by ISE with 95 % accuracy after 6 s of measurement.¹⁵² However, a follow-up study where the ISE was integrated into a tractor-mounted system for field measurement encountered several mechanical and electrical problems.¹⁵³ The functionality of this automated soil sampler was later improved and evaluated with comprehensive performance testing conducted in five fields. There was strong agreement between measurements of soil nitrate by the extraction system and by standard laboratory instruments (slope = 1.0, $r^2 = 0.94$).¹¹⁰

An automated sampling system for soil pH by direct soil measurement (DSM) was based on a flat-surface combination pH electrode in direct contact with moist soil collected by the sampling system.¹⁵⁴ There was a high correlation between the electrode voltage output and soil pH in the laboratory and field ($r^2 = 0.92$ and 0.83 , respectively). The system could measure pH while taking soil samples at a pre-selected depth between 0 and 20 cm every 8 s. Based on these results, a

commercial soil pH mapping system was developed by Veris Technologies, Salina, Kansas, USA.¹⁵⁵ Sensor-based mapping of soil pH provided improved accuracy of lime prescription maps¹⁵⁶ and was used to plan variable-rate liming for eight production fields.¹⁵⁷ In this study a field-specific bias in overall error estimates of 0.4 pH units or greater could be reduced to less than 0.3 pH units through site-specific calibration. Additional tests of the same commercial mobile soil pH system on two fields, one with a uniform soil and the other with six different soil types, showed that the real-time system provided more accurate estimates at the 0–7.5 cm depth ($r^2 = 0.75$ – 0.83) than at the 7.5–15 cm depth ($r^2 = 0.53$ – 0.79).¹⁵⁸ In addition, the inclusion of EC_a as a covariable improved pH estimates in the field with six different soil types, but not the uniform field.

The DSM approach was investigated for soil K, NO_3 , and Na as well as pH, but good results were only obtained for pH.¹⁵⁹ The reason for decreased accuracy for K, NO_3 , and Na was hypothesized to be a lower level of variability of the sensed properties in the soil samples tested. Another approach was the agitated soil measurement (ASM)-based integrated system that placed ISEs into a suspension of soil and water.^{160,161} The effects of various measurement parameters on sensor performance were investigated and the system was evaluated for on-the-go mapping of soil pH, soluble K, and residual NO_3 under laboratory conditions. Calibration parameters were stable during each test for pH and K electrodes. However, significant drift was observed for the NO_3 electrode. Both accuracy and precision errors were low with good correlations to the reference measurements ($r^2 = 0.67$ – 0.98 for means).

2.6 Future Outlook and Considerations

Soil sensing is an area of considerable research interest and activity, as documented in numerous recent reviews.^{47,111,112,162} In addition to developments in the sensors themselves, other related advancements are helping further the application of PSS. For example, the ability to extract useful information from the large spatial datasets generated by mobile PSS has improved because of advances in mathematical and statistical methods. Improved electronics and imbedded computer technology, made possible by advancements in the consumer and automotive sectors, have made it possible to readily control and obtain data from sensors. Wireless data transfer from mobile PSS and wireless sensor networks for stationary PSS are now available to facilitate more seamless integration of PSS data with other measurements, computer models, and expert interpretation. These advances in data handling are particularly important when PSS data are combined for analysis across multiple sites, whether for integrated soil nutrient management across fields and farms, or to evaluate environmental changes across a network such as the National Ecological Observatory Network (NEON) in the USA.⁵¹ Each PSS application will require consideration of particular issues. Below we discuss in detail the specific application of soil nutrient sensing.

2.6.1 *Considerations in Soil Nutrient Sensing*

Soil nutrient sensing is one area where the application of electrochemical sensing technology would seem to be relatively straightforward. As discussed earlier in this chapter, progress has been made on developing ion-selective elements for soil macronutrients. However, automation of the process of obtaining a representative soil sample and creating an extract for analysis requires further work. Approaches that circumvent this step and directly place ISEs in contact with moist soil have generally been unsuccessful except for soil pH. Other ways to increase accuracy, such as sensor fusion (discussed below), may hold promise. Sensor measurements must also be considered within the context of the overall nutrient management system. System issues include how well the sensed value can be calibrated against plant response to applied nutrients and how that information can be integrated into an intelligent fertilizer application system.

2.6.1.1 **Sensor Fusion**

There are several limitations to current on-the-go nutrient sensing systems. Although electrochemical systems can directly measure soil nutrient levels, there are implementation issues. Direct electrochemical measurement of moist soil, while shown to be viable for pH and perhaps nitrate, seems to be less feasible for the other soil macronutrients. Thus, a complex set of steps is generally needed to acquire a sample from the field, create a soil slurry or extract, and then complete the measurement. Spectroscopic sensing,¹¹¹ while less invasive, generally measures soil nutrients indirectly, through correlations with other soil properties. Thus, local calibrations are generally necessary and results have been of variable accuracy.

One potential approach for improved accuracy is sensor fusion, whereby readings from multiple, functionally different sensors are combined to estimate the soil properties of interest. For example, a commercial mobile sensor platform¹⁶³ (Fig. 2.6) combined the soil pH sensing system described in reference (155) with soil apparent electrical conductivity (EC_a) sensing. As EC_a provides a strong indication of soil texture variations,⁸⁶ the combination of the pH and EC_a data was useful for establishing lime requirements. An NIR reflectance sensor was later added to this multi-sensor platform.¹⁶⁴

In a laboratory-based example of sensor fusion, both ISE and spectral reflectance data were obtained for 37 surface soil samples from the US states of Missouri and Illinois.¹⁶⁵ Although ISE estimates of P and K were of good accuracy ($r^2 \geq 0.87$), they were further improved ($r^2 \geq 0.95$) by including both ISE and spectral data in the calibration model. The authors attributed the increased accuracy to the ability of the spectral data to provide an estimate of soil texture.



Fig. 2.6 Commercial sensor system integrating soil electrical conductivity and pH mapping (Veris pH manager, Veris Technologies, Salina, Kansas, USA)

2.6.1.2 Sensor Calibration

Widespread adoption of on-the-go soil nutrient sensing may be somewhat limited by the degree to which precise sampling and rapid extraction of the macronutrients in the sample can be achieved in a real-time system. Because extraction efficiency is strongly affected by the extraction time and because the time required for complete extraction may not be feasible in a real-time system, this approach may provide different results as compared to traditional soil testing methods. In this regard, research will be needed to calibrate sensor-based nutrient measurements against plant nutrient response, so that agronomists and growers gain confidence in the applicability of the new methods. Such a calibration might be implemented in the same way that past calibrations to standard laboratory measurements were developed. However, this process would require numerous field experiments with different crops and soil types. An alternative method, whereby sensor measurements were directly calibrated to laboratory nutrient measurements across a broad range of conditions, might be preferable. Although the calibration to plant response would be an indirect one with this approach, it would be considerably less costly and time-consuming.

2.6.1.3 Integration with Fertilizer Application Equipment

Control decisions for variable rate application can be implemented either on-line or off-line. In the on-line, or sensor-based approach, the controlled equipment incorporates onboard sensors and the sensor data are used immediately for automatic control. In the off-line, or map-based approach, data are collected and stored in one operation, and the controlled equipment uses the information in a separate field operation. The map-based approach allows more flexibility in data manipulation and pre-processing but requires multiple field operations. Most systems currently available are map-based, but more on-line systems will likely become available as real-time sensing technologies become more mature. Hybrid systems which rely on a combination of both mapped and real-time data may also come into more widespread use.

Development and implementation of a variable-rate application system presents a number of engineering challenges. Physical connectivity and data flow in such a system can be quite complex (Fig. 2.7). The general system consists of both office tasks and vehicle tasks. Office tasks include interpreting input data, developing management plans, and determining application rate maps. Vehicle tasks include using these application rate maps in conjunction with onboard sensors and actuators to apply fertilizer, chemicals, or inputs in the field, along with any real-time sensing that may be employed. In any given system, the elements shown in this general schematic (Fig. 2.7) may not be present. For example, a system may or may not

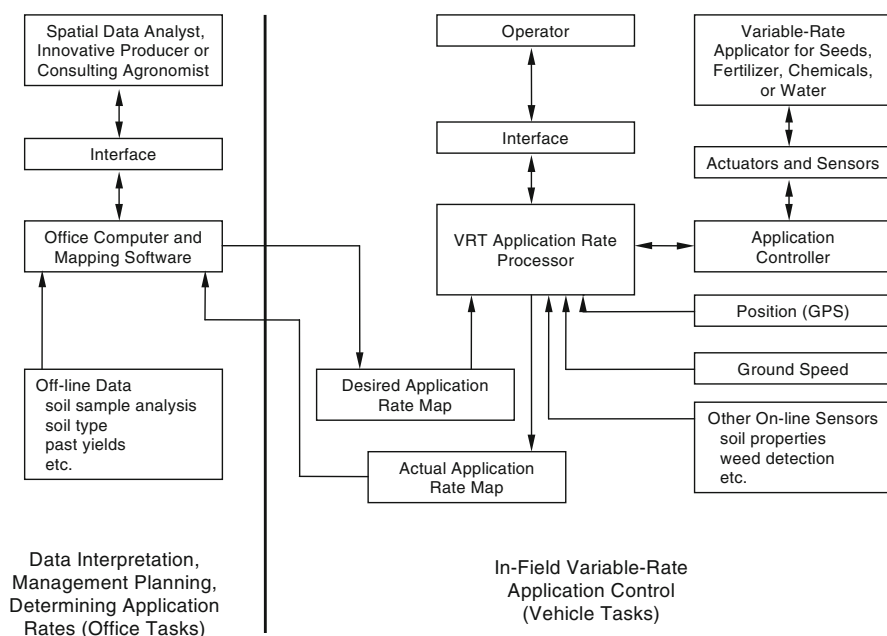


Fig. 2.7 Generalized schematic of data flow in a variable-rate application system

include on-line sensors and may or may not generate an actual application rate map. It is worth noting that the information to drive a map-based system could also come from on-the-go sensor measurements. Decoupling the sensing and application operations might make sense if sensor operating requirements, such as a long delay time for sensing nutrient levels in a soil extract, precluded sensing and application in the same operation.

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