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15.1 Introduction

The natural abundance of elements in the soil parent material and the factors controlling their availability to plants and animals provide major links between geology and human medicine and the health of plants and animals in natural and agricultural ecosystems. This is the rock-soil-plant-animal/human pathway, and it is of major importance in the study of medical geology.

The formation of soils (pedogenesis) is closely linked to the weathering of rock-forming minerals and the structural arrangement of organic (mainly humic) and mineral materials to form a soil profile. However, soil formation depends on the involvement of plants, microorganisms, and soil fauna, whereas rock weathering can occur without the biological component and produce a regolith of decomposed rock rather than a soil.

Within the context of soil–plant interactions, the main soil processes controlling the availability of both naturally occurring and contaminant trace and major elements to plants and their leaching down the soil profile to the groundwater are those which influence the sorption and desorption of these elements within the soil. Sorption is the collective term for the retention of metal ions on the surfaces of the solid phase of the soil system. The sorption mechanisms include:

1. Cation or anion exchange in which ions are attracted to oppositely charged sites on the solid surfaces (e.g., negatively charged surfaces in the case of cation exchange and positively charged surfaces in anion exchange)
2. Specific adsorption in which certain metal cations and most anions are held by ligand exchange in the form of covalent bonds
3. Co-precipitation in which ions are precipitated on surfaces simultaneously with other inorganic compounds, such as iron, aluminum, and manganese oxides, or calcium carbonate
4. Insoluble precipitates of elements on surfaces, including the formation of insoluble carbonates, sulfides, phosphates, and hydroxides

5. Organic complexation with solid-state organic matter ligands (in contrast to the formation of low molecular weight soluble complexes)

Desorption is the term for the release of ions from these sorbed forms due to a change in pH, and redox conditions, or the release of plant root exudates (Alloway 1995).

The factors controlling adsorption and desorption of ions in soils, include:

1. The properties, speciation, and concentration of specific trace and major elements
2. The composition of the soil, especially the relative abundance of clay minerals of different types, and total contents of iron, aluminum and manganese oxides, free calcium carbonate, and organic matter
3. Soil physicochemical conditions, which include pH, redox status, and concentrations of other cations and anions

Plant factors, especially genotype, also play a major role in determining the extent to which elements are accumulated in plant tissues, including edible parts, and, ultimately, in the food chain.

However, elements differ considerably in the relative extent to which they are taken up from the soil and accumulated in plant tissues even allowing for the differences in soil properties and plant genotype. The soil–plant transfer of different elements varies in orders of magnitude from relatively unavailable metals such as barium, to the more readily accumulated elements such as cadmium. In general, the essential trace elements with relatively low transfer coefficients ($Tf = M$ Plant/M Soil) are likely to be more prone to being deficient, whereas both essential and non-essential elements with high transfer coefficients would be more likely to pose a problem of toxicity.

15.2 Soil Formation

Pedogenesis is the process by which a thin surface layer of soil develops on weathered rock material, gradually increases in thickness, and undergoes vertical differentiation in morphology to form a soil profile. The soil profile comprises distinct horizontal layers (called horizons), which differ in color, texture, structure, and organic matter content. This soil profile (or solum) is the unit of classification of soils. The basis of soil mapping is to delineate areas of soils with distinct profile characteristics.

Pedogenesis is essentially the processes of chemical weathering of rock fragments in an environment which is generally rich in atmospheric oxygen, moisture, carbon dioxide, humic material, and biochemicals from living and decomposing vegetation (the biosphere). These pedogenic processes are strongly influenced by climatic factors, which include temperature, precipitation, and evaporation. They are also affected by the drainage of the site at which the soil is forming and this depends on the topography (shedding or receiving water) and the permeability of the layers of weathering rock material.

Humus is the name given to the complex organic molecules formed in the soil as a result of microbial action on dead plant material (litter) in the soil. The solid-state humic substances generally have relatively high molecular weights and are distinctly different from biochemical substances found in living and recently dead plant and animal tissues. Low molecular weight, soluble forms of soil organic matter are referred to as dissolved organic compounds and are important in forming soluble complexes containing metals. These soluble organic compounds can desorb metal ions from sorption sites on solid surfaces and thus increase the mobility and plant availability of many elements. Solid-state humus plays several very important roles in the soil. Physically it contributes to the binding of particles to create soil aggregates and a pore system comprising linked voids of varying diameter which are involved in both water transmission and storage and gaseous exchanges with the atmosphere. Chemically, soil humus is a major reserve of carbon, nitrogen, phosphorus, and sulfur which were constituents of the plant tissues that underwent humification. However, humic substances also have relatively strong adsorptive capacities for cations and the presence of humus in soil therefore adds considerably to the sorptive properties of the soil contributed by clay minerals, oxides of iron, and manganese and carbonate minerals.

Soils are formed as a result of the interactions between the geological parent material, climate, vegetation, and topography (especially with regard to drainage status) over time. Jenny (1941) called these the "state factors" of soil formation and expressed them in the form of an equation:

$$Soil = f(cl, \ o, \ r, \ p, \ t)$$

where f is a function, cl is climate, o is organisms (vegetation), r is relief (topography), p is parent material, and t is time.

It is important to note that the parent material is the weathered rock at the surface of the Earth and in many cases this may not be the underlying solid geology but the "drift material" that can be fragmented unaltered or chemically weathered rock, which has been transported and deposited on top of the solid geology. This transport may have been by wind (loess), rivers (alluvium), glaciers (glacial sands, gravels, and boulder clay), and downslope movement (colluvium). However, where the solid geology is exposed at the surface the soils will be formed on weathered fragments of this material.

A typical profile of an uncultivated soil comprises a layer of organic litter (desiccated but undecomposed plant material) on the surface (called the L horizon). Below this can occur an A horizon which is a relatively dark colored mixture of humic and mineral material (formed by the actions of earthworms). In cultivated soils where mixing has occurred often over many centuries through plowing and other tillage, the surface layer of dark colored soil is referred to as the plow layer (or Ap horizon). However, under acid conditions in unplowed soils, dark-colored layers of decomposing plant material may exist beneath the litter horizon. These organic layers differ in the extent to which the plant tissues have decomposed and are designated O1 and O2, etc., with O1 only partially decomposed and O2 more decomposed and so on. The O horizons will often overlie an A horizon, but it will not be as thick or deep as in the less acid soils where deep mixing of the soil by large numbers of earthworms or where regular plowing and cultivation has created a thick Ap horizon.

Beneath the A horizon there may be a zone of a lighter color and different texture called an eluvial (E) horizon. This is the zone in the soil profile from which clay minerals and iron have been removed and translocated down the profile. Beneath the E horizon, a B horizon of accumulation can occur. The B horizon can be designated a Bt horizon where clay has accumulated, or a Bs horizon where sesquioxides of iron and aluminum have been deposited and, in podsol profiles, a Bfe and a Bo horizon can also be found. Beneath this B horizon is found the C horizon—the weathering rock material on which the soil is forming. If solid rock is found beneath this C horizon then it is designated the R horizon. Figure 15.1 shows a diagrammatic soil profile with both the FAO/UNESCO and the USDA Soil Taxonomy horizon nomenclature.

There are two important modifying factors that can affect a soil horizon's appearance and chemical properties, and these are identified in the designation of soil horizons. These are where free calcium carbonate occurs in soil horizons (calcimorphic soils) and where soils are affected by either permanent or intermittent waterlogging (hydromorphic soils). In calcimorphic soils (also called calcareous soils, or calcisols), horizons containing visible calcium carbonate are described as calcareous and identified with a lowercase "ca" as in Aca or Bca and so on. This calcium carbonate (calcite) may have originated either from limestone in the parent material or from precipitation of calcite in the pores of soils in semi-arid areas. In hydromorphic soils (usually called gleys) poor drainage results in the onset of reducing conditions which affect both the appearance and the physicochemical properties of the soil. The waterlogging, which gives rise to the creation of reducing conditions in gley soils can be due to impermeability caused by either fine soil texture (where there is a high proportion of clay-size particles), and/or
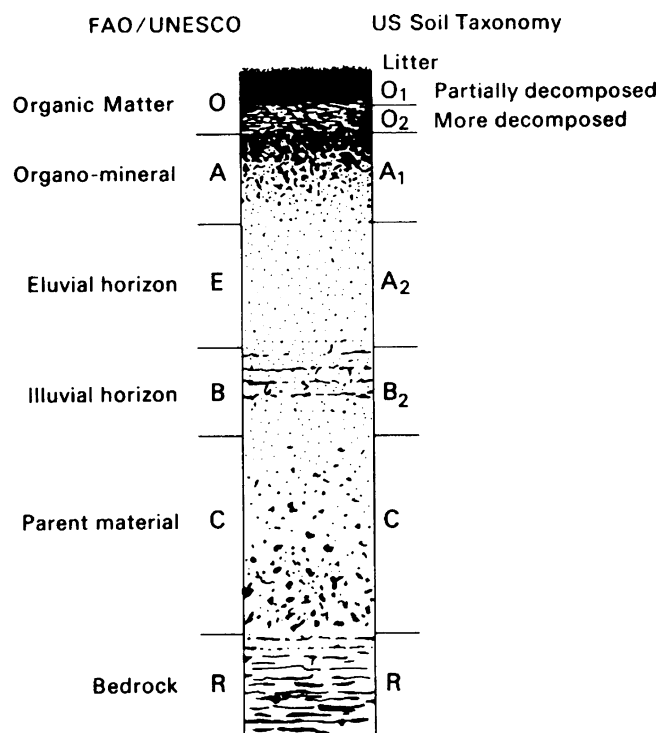
Fig. 15.1 A diagrammatic soil profile with FAO/UNESCO and USDA soil taxonomy horizon nomenclature (From Alloway 1995)

poor structure, or poor site drainage (e.g., in a hollow or at the foot of a slope). Gleying in soils is characterized by pale colors (light brown, gray to bluish green) caused by the reduction of iron oxides. Soils with aerobic, or oxic, conditions normally have darker brown and reddish colors due to the presence of abundant iron oxides.

It should be pointed out that not all soil profiles contain all of the types of distinct horizons mentioned here, but different soil types are characterized by certain combinations of horizons. For example, acidic and strongly leached soils developed on permeable parent material, such as sands or weathered granite, in areas with a high precipitation–evapotranspiration ratio can have a characteristic podsol (or spodosol in the USDA Soil Taxonomy) profile. This podsol comprises a combination of thick organic horizons at the top of the profile—a strongly bleached E horizon, underlain by a Bo horizon of deposited organic matter, over a thin, distinct hard layer of deposited iron (iron pan, Bfe)—which in turn overlies a relatively thick yellowish brown horizon of deposited iron and aluminum sesquioxides (Bs horizon) and this, in turn, overlies the C horizon which is the parent material. This is the distinct profile (L, O1, O2, A, Ea, Bo, Bfe, Bs, C) of a podsol found in many parts of the world with a cool humid climate, such as areas of natural coniferous forest. In contrast, areas underlain by chalk (soft limestone) tend to have a much simpler and shallower profile with a

characteristic deep, dark-colored and humus-rich A horizon underlain by a C horizon of chalk fragments. This AC profile belongs to a shallow calcareous soil called a rendzina found on limestones in central and western Europe. In arid and semi-arid areas, soils with a calcium-carbonate-enriched "calcic" horizon (Bca, or Cca) are commonly found. These calcareous soils are called calcisols and a calcic horizon with more than 15% calcium carbonate (and at least 5% more than in the underlying horizon) is their defining characteristic. Calcisols can develop on limestone parent material or on other parent material in low-lying areas where a high water table with calcium-rich groundwater leads to evaporation from the soil surface and precipitation of calcium carbonate within the pore structure of the soil profile.

The chemical weathering of the geological parent material involves the processes of hydrolysis, hydration, dissolution, oxidation, reduction, ion-exchange, and carbonation. These, together with the physical disintegration of rock, bring about the decomposition of rock-forming minerals, which release cations and anions into solution. New secondary minerals (including clay minerals and iron oxides) can be formed from the products of weathering and precipitates of compounds formed when their solubility products are exceeded. Some of the ions released will remain in solution and be leached down the soil profile. These will either reach the groundwater and move to water courses in humid regions or accumulate in low-lying areas and move up through the soil profile as evapotranspiration of water occurs in arid environments. The latter situation results in the formation of calcified and/or saline soils, which are characteristic of arid and semi-arid regions. Soils with high contents of calcium and a high pH often have low concentrations of plant-available trace elements, such as zinc, and acute deficiencies of this and other essential trace elements can occur in crops growing on them. Low availability of elements to plants can be the result of either low total concentrations in the soil (sometimes referred to as a primary deficiency), to a high degree of sorption leading to low soluble/plant available concentrations, or to antagonistic effects between two or more elements, e.g., copper and zinc, which are both absorbed by the same pathways into plant roots. A relative excess of one element can induce a reduction in the uptake and availability of the other.

The main soil constituents responsible for the adsorption of cations and anions are certain clay minerals, hydrous oxides of iron, manganese and aluminum, calcite, and humus. Therefore, the soil horizons that have relatively high concentrations of these mineral and organic materials will tend to retain ions released from weathering together with ions introduced in fertilizers (especially phosphorus, potassium, and sulfur). Many environmental pollutants (especially trace metals and persistent organic pollutants) will also be retained in these horizons. Nitrogen added to the soil in fertilizers and manures is not retained to any significant extent. It is usually lost from the soil by leaching (mainly as nitrate ions or lost to the atmosphere in gaseous oxide forms [NO_x]). The organic-rich surface horizon, especially in cultivated soils (Ap horizon, topsoil) is usually the horizon with the greatest adsorptive capacity. This horizon is the rooting zone for plants and receives elements cycled through plants and added in fertilizers, manures, and agrichemicals and is also a sink for atmospherically deposited pollutants.

Conversely, horizons of elution where materials, especially clays, have been removed by being washed down the profile, will tend to have lower adsorptive capacities and contents of both nutrient and non-essential elements. In general, sandy textured, well-drained soils tend to have lower adsorptive capacities than soils with a higher proportion of silt and clay-sized mineral particles or iron oxides. However, the humus content can greatly modify this. Intensively cultivated soils generally have lower organic matter contents than soils under permanent grassland or rough grazing in the same climatic zone. Therefore, the texture, organic matter content, and mineral composition of intensively cultivated soils tends to be more important in the dynamics of ions of all types than in grassland soils. In addition to the macronutrients required by plants (nitrogen, phosphorus, potassium, magnesium, calcium, sulfur, and sodium), the trace element content of the parent material will also differ between soils developed on different types of weathered rock. This will include both essential trace elements (boron, cobalt, chlorine chromium, copper, iron, iodine, manganese, molybdenum, nickel, selenium, and zinc) and elements with no known essential function (including arsenic, cadmium, mercury, lead, thallium, and uranium). Therefore, differences in mineralogy and geochemistry of soil parent materials will result in differences in the total concentrations of both major and trace elements found in topsoils and whole soil profiles. Examples of this include soils developed on ultramafic (e.g., serpentinite) rocks where there is a relative excess of magnesium com-pared to calcium and therefore possible problems with a deficiency of calcium and an excess of magnesium and anomalously high concentrations of cobalt, chromium, and nickel. This combination of high magnesium to calcium ratio (Mg:Ca) and elevated concentrations of certain metals has resulted in the evolution of specialized serpentine flora and if non-adapted plants are grown on these soils they could be affected by nutritional imbalances and possibly toxicity.

Of wider importance with regard to areas of land affected are the soils developed directly on clay or shale strata with distinct sedimentary layers (facies) of marine black shales within them and also soils developed on surface drift deposits containing these materials. The marine black shales generally contain anomalously high concentrations of silver, arsenic, cadmium, copper, molybdenum, lead, selenium,
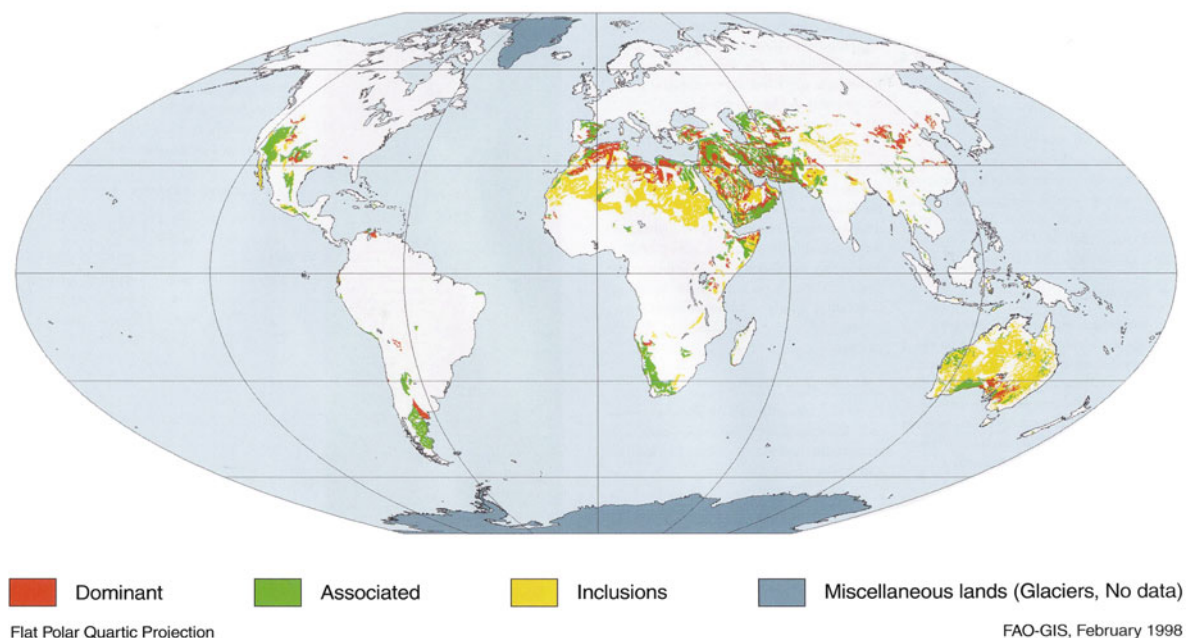
Fig. 15.2 World distribution of calcisols (calcareous soils) (Reproduced from the world reference base for soil resources Atlas, ISSS working group RB 1998, Bridges et al., Eds., by permission of the editors and publisher)

uranium, vanadium, and zinc. There is a distinct possibility of these soils giving rise to elevated concentrations of some or all of these elements in food crops and livestock herbage. Apart from the risk of excess available concentrations of some of these elements, there is also the possibility of antagonistic effects occurring due to interactions between some of the elements present in high concentrations. For example, high molybdenum concentrations can induce copper deficiency in ruminant livestock even though copper itself may be present in elevated total concentrations in the soil and herbage.

In general, soils developed on clay and mudstone formations or drift derived from them tend to have higher concentrations of most essential trace elements than those developed on sandstones and sandy drift deposits. This is due to the clays and mudstones having inherently higher concentrations of these elements and also to the soils having greater adsorptive capacities to retain them against leaching compared with more sandy soils. These geochemical differences, together with variations in soil chemical properties associated with the variations in parent materials and soil forming-factors, will also help to determine the concentrations of elements (both essential and non-essential) that are available to plants (bioavailable fraction). In addition to these geochemical associations, inputs of fertilizers, agrichemicals, and environmental pollutants will also add to the total concentrations, but the nature of the elements concerned and the physicochemical properties of the soil will determine the bioavailability of these substances.

The global distribution of calcisols (ISSS 1998) is shown in Fig. 15.2. These soils are important with regard to the mobility and plant availability of trace elements because their alkaline pH and the presence of free calcium carbonate result in the strong adsorption of many cations. This has serious implications in the case of essential trace elements, which include zinc, iron, copper, and manganese because inadequate concentrations of available forms of these elements can cause deficiencies in both crops and livestock. When crops, such as wheat and rice are affected by deficiencies of essential trace elements, such as zinc, there is both the problem of reduced crop yields and also low concentrations of the elements in the human diet. Therefore, the health of regular consumers could also be affected. Zinc deficiency is a major problem in wheat and other staple crops in arid countries such as Turkey, Syria, Iraq, India, and Pakistan which all have large areas of calcisols.

Soils with a high percentage (>65%) of sand grains are called "arenosols," but in contrast to calcisols, they do not necessarily have one particularly distinctive horizon nor do they always have an alkaline soil pH. They are classified by their distinctive sandy texture, which has certain soil physical and chemical properties associated with it. These sandy soils also give rise to deficiencies of essential trace elements, which include zinc, iron, copper, boron,
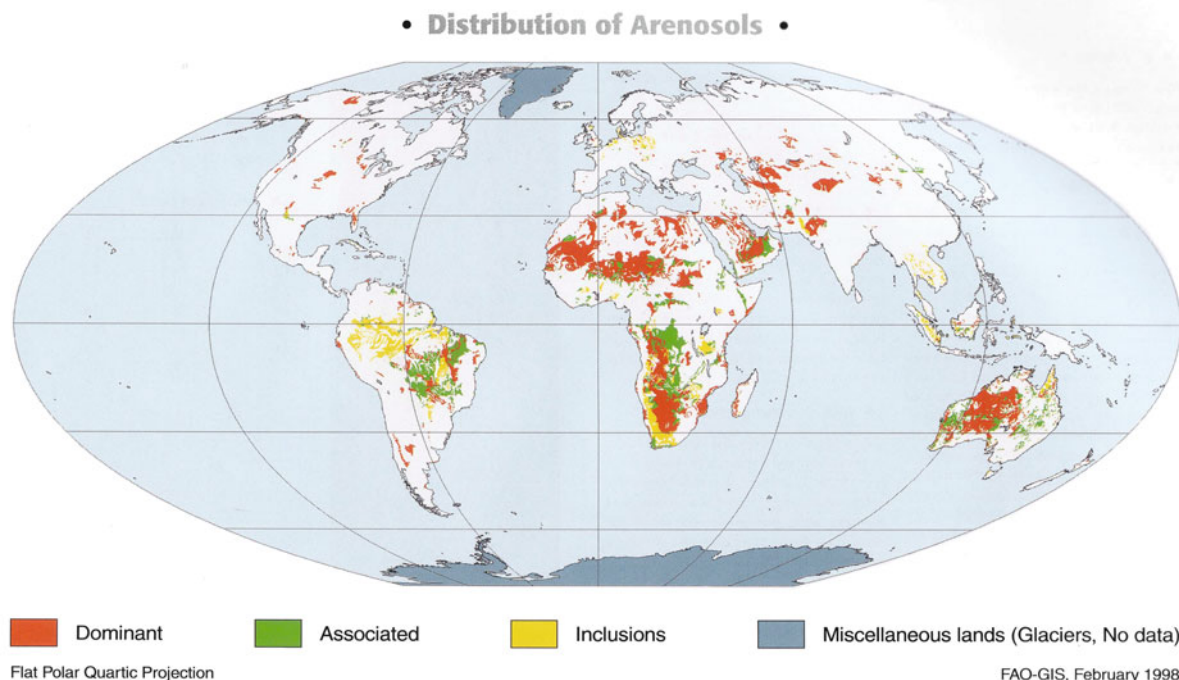
Fig. 15.3 World distribution of arenosols (sandy soils) (Reproduced from the world reference base for soil resources Atlas, ISSS working group RB 1998, Bridges et al., Eds., by permission of the editors and publisher)

manganese, selenium, and cobalt. In this case the cause of the deficiency is the inherently low total concentrations in the sand grains of the soil parent material and the relatively low sorptive capacity of these soils. Their low clay content results in the loss by leaching of nutrient elements reaching the soil by various pathways. Arenosols are commonly found in deserts, but in areas where they are cultivated (usually where the climate is humid or where irrigation is available) deficiencies of essential trace elements are commonly found. The global distribution of arenosols (ISSS 1998) is shown in Fig. 15.3.

Soils rich in iron oxides are characteristic of tropical regions of the world. These oxides are the result of the accumulation of iron and aluminum after all the weatherable minerals have decomposed under the aggressive tropical weathering environment with its high temperatures, high precipitation, and low pH, which favor the chemical weathering of geological minerals. These soils are referred to as oxisols in the USDA Soil Taxonomy. They are also sometimes called ferralitic soils, and they are classified as ferralsols in the *World Reference Base for Soil Resources* (ISSS 1998) and in the FAO/UNESCO World Soil Map. These ferralsols rich in iron oxide are also a potential trace element deficiency problem as a result of both the complete weathering of the original parent material and subsequent leaching and/or the sorption of ions on the iron oxides. The global distribution of ferralsols (ISSS 1998) is shown in Fig. 15.4.

15.3 Soil–Plant Transfer of Trace Elements

The soil–plant transfer coefficient (Tf), also called the bioaccumulation ratio (BR), is a convenient method of expressing the relative ease with which elements in soils (total concentrations) are taken up by plants and accumulated in their above-ground tissues. The coefficient is obtained by dividing the concentration of an element in the plant tissues by the total concentration of the same element in the topsoil (Tf = M in plant/M in soil). Plants differ considerably in their ability to absorb trace elements, but Kabata-Pendias and Pendias (1992) have quoted work that considered the relative ranges of BRs or transfer factors for a large number of plant species from data published in the literature. These range from the least accumulated elements such as barium and titanium to those most readily accumulated (cadmium and boron). However, considerable differences in trace element accumulation occur between plant species and between varieties within a species (inter- and intraspecific variations):

1. Elements lacking accumulation (only slightly available) (Tf < 0.001)
   barium > titanium > scandium > zirconium > bismuth > gallium > iron > selenium
2. Elements showing slight accumulation: (Tf 0.001–0.01)
   antimony > beryllium > chromium > iodine > vanadium > fluorine > lithium > nickel > manganese
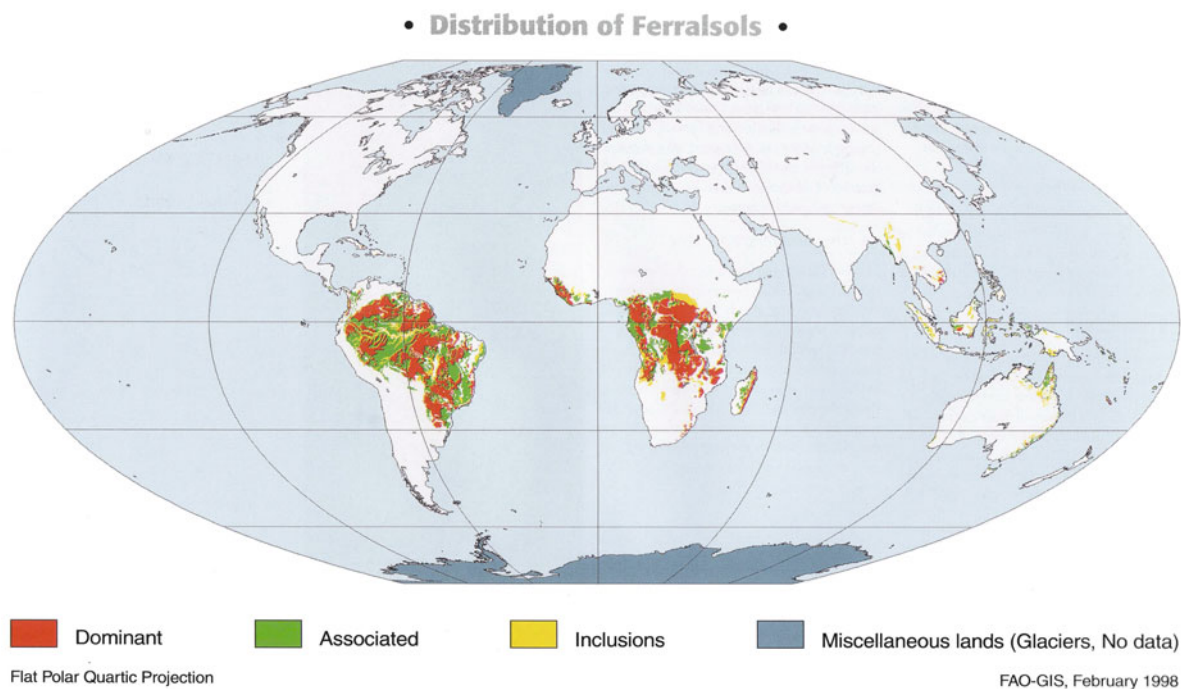
Fig. 15.4 World distribution of ferralsols (iron oxide-rich soils) (Reproduced from the world reference base for soil resources Atlas, ISSS working group RB 1998, Bridges et al., Eds., by permission of the editors and publisher)

3. Elements showing medium accumulation: (Tf 0.01–1.0) cobalt > arsenic > germanium > tellurium > silver > strontium > lead > coppe > mercury > molybdenum > zinc

4. Elements which are intensively accumulated (Tf 1–10) rubidium > caesium > bromine > boron > cadmium

In general, the elements that tend to have relatively low soil–plant transfer coefficients are those that tend to be more strongly sorbed onto the surfaces of soil solids. Those that are more readily accumulated are less strongly adsorbed due to the properties of the ionic forms of these elements. The ions that are strongly sorbed will tend to have lower free ion concentrations in the soil solution and, therefore, be less available for plant uptake and translocation to the aerial tissues of plants.

15.4 Soil Chemical Properties and the Bioavailability of Trace and Major Elements

The soil is a dynamic system comprising solid, liquid, and gaseous phases, which is subject to short-term fluctuations such as variations in moisture status, temperature, pH, and redox conditions. In addition to the non-living mineral and organic constituents, the topsoil contains a highly diverse microbial and mesofauna population and a high density of roots of many different plant species. These living organisms are all intricately involved in the physical, chemical, and biological processes taking place in the soil. In addition to short-term changes, soils also undergo gradual alterations in response to changes in management and environmental factors. Examples of these longer term changes in soil properties include a decrease in the content of organic matter with increasing cultivation and/or increasing temperatures and gradual acidification due to acid precipitation or lack of regular liming in areas of high precipitation relative to evaporation. These short- and long-term changes in soil properties can each have significant effects on the form and bioavailability of trace and major elements (of both indigenous geochemical and external pollution origin). Soils are also inherently heterogeneous at the micro (profile) and macro (field/catchment) scales. For the purposes of soil testing to assess the available concentration of both essential and potentially toxic elements, the spatial variability in soil physical and chemical properties necessitates appropriate and thorough sampling. It is essential to take sufficient samples which include the range of variability in parameters at any site investigated.

15.4.1 Key Soil Chemical Properties

15.4.1.1 Soil pH

The soil reaction (pH) is the most important factor controlling the chemical behavior of ions and many other important

processes in soils. The pH of a soil applies to the hydrogen ion (H^+) concentration in the solution present in the soil pores. This is in dynamic equilibrium with the predominantly negatively charged surfaces of the soil particles with which it is in contact. Positively charged hydrogen ions are strongly attracted to surface negative charges and they have the power to replace most other cations. There is a diffuse layer close to the negatively charged surfaces, which has a higher concentration of H^+ than the bulk solution. When the soil solution is diluted (as when a suspension of soil in water is made to measure pH or in the field after heavy rain), the diffuse layer expands, causing the pH of the bulk solution to increase. This has important implications for soil testing to measure soil pH. It is the normal practice to mix soil with 2.5 times its weight of distilled water. This generally gives a pH value which is 1–1.5 units higher than that of the soil solution in the diffuse layer near the solid surfaces where the reactions take place. However, this dilution effect can be overcome by measuring the pH in a dilute suspension of a neutral salt such as calcium chloride or potassium chloride, which helps to recreate the ionic strength of the real soil solution. When reporting soil pH values, the method used for measuring it is usually given with the results, but if the solvent used is not named, it is normally assumed that the pH was measured in distilled water.

Soil pH is affected by variations in redox potential that periodically occur when the drainage status of soils changes from waterlogged to more freely drained and vice versa. Reducing conditions (gleying) generally cause an increase in pH and oxidation decreases pH. Fluctuations of up to two pH units can occur over a year in soils prone to periodic waterlogging. Oxidation of iron pyrites (FeS_2) in a soil parent material, such as a weathering black shale or drained marshland, can cause a marked decrease in pH due to the formation of sulfate ions and sulfuric acid.

There are several mechanisms in soils that have the effect of buffering pH changes. These include the formation of hydroxy-aluminum ions ($Al(OH)^{2+}$), partial pressure of CO_2, and formation and dissolution of carbonates and cation exchange reactions. However, even with these buffering mechanisms soil pH can vary by as much as one unit diurnally and spatially due to localized conditions in different parts of a field. In humid regions, soil pH usually increases with depth due to the leaching of bases down the soil profile. In arid environments, pH can decrease with increasing depth due to the accumulation of salts of calcium, sodium, and magnesium in the surface horizons through evaporation of the soil solution.

Soils generally have pH values (measured in water) from 4 to 8.5 due to the buffering by aluminum at the lower end and by calcium carbonate at the upper end of the range. Brady (1984) states that the normal pH range of soils in humid regions is 5–7 and 7–9 in the soils of arid regions.

The maximum range of pH conditions found in uncontaminated soils is 2–10.5, but some contaminated soils containing large amounts of cement or mortar may have even higher pH values. In a typical temperate environment, such as the UK, the pH range generally found in topsoils is 4–8. The optimum pH for most arable crops is 6.5 and for grassland mineral soils it is 6.0, but for peaty soils, the optimum pH for grassland is 5.5. Soil pH can be relatively easily raised by liming (with calcium carbonate or calcium hydroxide), but it is normally impractical to acidify agricultural soils more alkaline than these values.

In general, most divalent cationic forms of elements are more mobile and more available to plants; therefore, they are less strongly adsorbed on soil solids under acid conditions than they are at neutral and slightly alkaline pH values. However, the pH of the soil also has a major control on the solubility of soil organic matter, which in turn can modify the behavior of trace elements in the soil. As the soil pH increases toward neutrality and beyond, there is an increase in the amount of DOC. This can have a modifying influence on the solubility of several elements which readily form chelate complexes with soluble organic matter. For example, copper and lead are strongly complexed by soil organic matter so they may become more available with increasing soil pH in soils with a relatively high organic matter content due to the increased concentration of organic ligands in the DOC.

The overall importance of the soil pH in controlling the availability/mobility of elements is due to its effects on (1) the solubility of soil organic matter; (2) the speciation and solubility of elements in the soil solution; (3) the polarity of the charge on solids in soils, such as Fe oxides which have variable charges; (4) the cation exchange capacity of soil solids; (5) the dissolution of certain precipitates and minerals (e.g., calcium carbonate); and (6) effects on soil microorganisms and fauna.

15.4.2 Soil Organic Matter

Soil can be distinguished from regolith (decomposed rock) by the presence of living organisms, organic debris (mainly from plants), and humus. All soils (by definition) contain organic matter although the amount and type may vary considerably. Colloidal organic matter has a major influence on soil physical and chemical properties and can be divided into "non-humic" and "humic" substances. The non-humic substances comprise unaltered biochemicals such as amino acids, carbohydrates, organic acids, lignin, lipids, and waxes that have not changed their form since they were synthesized by living organisms. In contrast, humic substances are a series of acidic substances, yellow to black colored, polyelectrolytes of moderately high molecular weight. They are formed by secondary synthesis reactions involving

microorganisms and have characteristics that are dissimilar to any compounds in living organisms. They have several functional groups, which include carboxyl, phenolic hydroxyl, carbonyl, ester, and possibly quinone and methoxy groups (Hayes and Swift 1978; Stevenson 1979). Although mainly composed of humic substances, soil humus also contains some biochemicals bound to humic polymers. The elemental composition of humus (on an ash-free basis) is 44–53% carbon, 3.6–5.4% hydrogen, 1.8–3.6% nitrogen, and 40–47% oxygen. In general, soil organic matter (humus plus non-humic material) contains about 58–60% organic carbon.

The organic matter contents of soils can vary widely from <1% in intensively cultivated arable soils or soils in semi-arid areas, to more than 10% in permanent grassland soils in cool humid conditions. In poorly drained (gleyed) sites, the soil may be formed on peat and comprise more than 70% organic matter. In general, in hotter drier climates organic matter contents are much lower than those found in cooler humid regions. Within the soil profile, organic matter is always found concentrated in the surface horizon. In cultivated soils this will have been mixed within a deeper layer due to plowing (Ap horizon) and in podsols (usually found in cool humid conditions) and in vertisols (found in hot humid conditions) some organic matter will have been translocated down the profile.

Humus is frequently described as comprising three fractions forming a continuum of compounds varying in molecular weight, carbon, oxygen and nitrogen contents, acidity, and cation exchange capacity in the order: humin > humic acid > fulvic acid. The humic acid fraction has a molecular weight in the range of 20,000–100,000 Da and fulvic acid generally consists of lower molecular weight compounds (some of which may be decomposition products of humic acid) with up to 10% polysaccharides. Humins are humic acid type compounds strongly bound onto minerals.

The contribution of organic matter (humic and non-humic) to the chemical properties of a soil are

1. In the adsorption of cations to negatively charged sites (created by deprotonation of carboxyl and phenol groups)
2. In the mobility and protection of some metal ions from adsorption through the formation of soluble complexes (e.g., chelates) with low molecular weight humic substances (DOC)
3. In the retention of many elements in the higher molecular weight, solid forms of humus by chelation

Soil organic matter is the main reservoir of carbon, nitrogen, phosphorus, and sulfur in soils. These can be gradually released as leachable ionic or gaseous forms (not phosphorus) through the action of soil microorganisms. The carbon locked up in the organic matter of the world's soils is a major consideration in model predictions of global climate change.

Table 15.1 Summarized values for pH and organic carbon in soils in England and Wales, Northern Europe (Baltic area), and the United States

Country	Number of samples	Minimum	Median	Maximum
England and Wales[a]				
pH (water)	5,679	3.1	6.0	9.2
Organic C (%)	5,666	0.1	3.6	65.9
Baltic area[b]				
pH (water)	774	3.7	6.1	8.7
Organic C (%)	774	1.8	7.1	97.2
United States[c]				
pH (water)	3,045	3.9	6.1	8.9
Organic C (%)	3,045	0.09	1.05	63.0

[a]Soils collected on 5 × 5 km grid (From McGrath and Loveland 1992)
[b]Soils collected on a 2,500-km grid over an area of 1,800,000 km^2 from 10 European countries surrounding the Baltic Sea (From Reimann et al. 2000)
[c]Soils from sites with healthy crops remote from obvious contamination (Holmgren et al. 1993)

Several trace metals show particularly high affinities for soil organic matter. These include cobalt, copper, mercury, nickel, and lead and these are probably held principally in chelated form within humus (Adriano 2001). Other trace metals, such as cadmium appear to be mainly sorbed in the soil by cation exchange and specific adsorption and are not retained as strongly on solid-state soil organic matter.

Table 15.1 gives the summarized results of large-scale surveys of soils in England and Wales, a large area of northern Europe surrounding the Baltic Sea, and the United States for soil pH (measured in water) and percentage organic carbon. The surveys differed in that the samples from England and Wales were collected on a formal 5 × 5 km grid, the Baltic area on a grid of one sample per 2,500 km^2, and the American samples from sites selected as free from obvious contamination. The pH data are remarkably similar but the organic matter data show a much lower median value for the American samples, which is probably a reflection of the hotter climate in many agricultural areas of the United States. In contrast, northern Europe has a cooler, more humid climate which is reflected in more peaty soils and pastures with relatively high organic matter contents.

15.4.3 Chemically Active Mineral Constituents

The inorganic constituents of soils usually comprise more than 90% of the mass of soils, and it is the adsorption and desorption of ions on the surfaces of these materials that exerts an important effect on the plant availability and mobility of macro elements and trace elements. The inorganic fraction can comprise a wide range of rock fragments and minerals undergoing weathering; newly synthesized and recycled clay minerals; oxides of iron, aluminum, and

manganese; free carbonates of calcium and magnesium; and, in more arid regions, crystals of salts such as calcium sulfate and sodium chloride.

15.4.3.1 Clay Minerals

Clay minerals are either products of rock weathering or are synthesized as new minerals from the products of weathering. They have marked effects on both the physical and chemical properties of soils. Their contribution to soil chemical properties results from their comparatively large surface area and permanent negative charge on their surfaces which adsorb cations. The clay fraction of a soil is defined as the mass of the dispersed inorganic constituents which are less than 2 μm in diameter. Although this is based on particle size rather than mineralogy, in most cases it is the mineralogically distinct group of clay minerals that comprise most of the material in this size fraction (together with iron oxides in many cases). Due to space limitations in this book, it is not possible to cover the crystallography of these phyllosilicate minerals; however, they all share two main types of building blocks in their structure. These are a continuous sheet of silicon (Si) oxygen (O) tetrahedra (the silica unit) and another of aluminum (Al) hydroxide (OH) octahedra (the gibbsite unit). In many cases some of the silicon and aluminum ions in the crystal lattice of the minerals may be replaced by other ions.

The most common types of clay mineral include: (1) the kaolinites with one silica sheet and one gibbsite sheet (a 1:1 clay); (2) the illites which contain two silica sheets with one gibbsite sheet between them (a 2:1 clay); (3) the smectites which also have two silica sheets and one gibbsite sheet (2:1 clay); and (4) the vermiculites which have two silica sheets, one gibbsite sheet, and one brucite sheet containing magnesium, which is not found in the other types of clay minerals (2:2 clay). In all the clay minerals except kaolinite, isomorphous substitution within the mineral lattice leads to a permanent charge imbalance which gives rise to a net negative charge on the surface of the mineral. For example, this can be caused by Al^{3+} substituting for Si^{4+}, and Mg^{2+} or Fe^{2+} substituting for Al^{3+}.

In kaolinites the 1:1 units are tightly bound together by hydrogen bonds between hydrogen and oxygen atoms of adjacent layers. These kaolinites have a smaller surface area than the other clay minerals (5–40 $m^2 g^{-1}$) and their cation exchange capacity is relatively low (3–20 $cmols_c kg^{-1}$) because little isomorphous substitution has occurred.

Illites have their 2:1 units bonded by potassium ions and their specific surface and cation exchange capacity are larger than those of kaolinites (100–200 $m^2 g^{-1}$ and 10–40 $cmols_c kg^{-1}$, respectively). Smectites have the largest specific surfaces (700–800 $m^2 g^{-1}$) due to relatively weak interlayer bonding, which allows them to expand when they are wetted, and consequently they have high cation exchange capacities (80–120 $cmols_c kg^{-1}$). They shrink on drying and can give rise to cracks during prolonged dry periods in soils in which they predominate. Vermiculites have an intermediate surface area and a high cation exchange capacity (100–150 $cmols_c kg^{-1}$).

15.4.3.2 Oxides of Iron, Manganese, and Aluminum

Oxides of iron, manganese, and aluminum in soils are often referred to as the hydrous oxides, or in the case of iron and aluminum, as sesquioxides. They play important roles in the chemical properties of soils. In temperate regions they generally occur in the clay size fraction (<2 μm) mixed with the clay minerals and have a disordered structure. The main iron oxides include gelatinous ferrihydrite ($Fe_2O_3.9H_2O$), goethite (FeOOH), hematite (α-Fe_2O_3), and lepidocrocite (γ-FeOOH). Precipitation of Fe^{3+} is initially in the form of ferrihydrite, which gradually dehydrates with aging to form more stable minerals. However, ferrihydrite is more likely to be subsequently dissolved again than the other iron oxide minerals when a decrease in redox potential (Eh) or pH occurs. These oxides generally occur as mixtures and are often referred to generically as "iron oxides" or "hydrous iron oxides," but goethite is the iron oxide mineral most frequently found in soils. In tropical regions where there is a more aggressive chemical weathering regime and the soils are usually much older (10^4–10^6 years), the oxides of iron and aluminum are often the predominant soil minerals. This is because all the primary (rock-forming) minerals and most of the clay minerals will have been chemically decomposed (weathered). The characteristic brown color of most soils throughout the world is due to the presence of iron oxides. Nevertheless, the colors of soils vary widely depending on the amounts of iron in the parent material, the presence of other strongly colored minerals, the drainage (redox) status, and the organic matter and calcium carbonate contents.

Gibbsite is the common form of aluminum oxide found in soils, but it is much less abundant than iron oxides. Manganese oxide minerals are generally present in smaller quantities than iron oxides but have stronger adsorptive properties for several cations.

Freshly deposited soil oxides are the most active in adsorbing and co-precipitating trace and major elements. As a result of its large surface area, freshly deposited ferrihydrite acts as a scavenger, sorbing both cations and anions, especially phosphate and arsenate ions (HPO_4^{2-}, H_2PO_4, and AsO_4^{3-}). If oxidizing conditions persist for a long time and/or temperatures remain high, the oxide crystals age and become dehydrated and less strongly charged. Therefore retention of metal ions by oxide surfaces is inversely related to the degree of crystallinity of the oxide minerals (Okazaki et al. 1986).

The adsorptive properties of iron and manganese oxides depend on the soil pH, which determines whether they are positively or negatively charged. Generally speaking, their charge is negative under neutral-alkaline conditions and positive under acid conditions. The pH at which the charge is neutral (called the point of zero charge, PZC) varies for the pure forms of different oxides. The PZC for iron oxides lies in the region pH 7–10, for gibbsite it is in the pH range 8–9.4, and for manganese oxides the pH range is 1.5–4.6. However, when mixed with clay minerals in soils, the PZC values tend to be much lower than these. In acid soils, the positively charged iron oxides are the main adsorptive medium for soil phosphate and arsenic anions. Soil organic matter also has a pH-dependent charge, but its PZC is around pH 2 which is not normally encountered in soils, so this material is nearly always negatively charged. It is, therefore, an important contributor to the cation exchange capacity of a soil.

The presence of chemically active forms of metal oxides in soils is very dependent on the drainage status of the soil at any site. Where waterlogging occurs either as a result of an impermeable soil mineral fraction, such as a high proportion of swelling clays, or topographic position, as in a depression or receiving site, then reducing conditions will predominate. In soils with developing reducing conditions (called gleying), oxides will be reduced and the iron and manganese ions will be mobilized together with the ions of other elements that had been adsorbed on their surfaces. Permanently waterlogged (gleyed) soils have low concentrations of iron and manganese because the oxides of these elements will have been dissolved, transported away, and deposited in an oxygenated environment over a long period of time. Fluctuating redox conditions (such as in paddy rice soils) can result in the periodic mobilization and precipitation of oxides. Certain specialized bacteria, including *Thiobacillus ferrooxidans* and *Metallogenum* spp. are also involved in the precipitation of iron and manganese oxides, respectively.

15.4.3.3 Free Carbonates

The predominant carbonate mineral found in soils is calcite ($CaCO_3$) and more rarely dolomite ($Ca, Mg(CO_3)_2$). These minerals can be present as a result of soils forming on weathering limestone rocks and, in addition, in arid regions from the accumulation of calcite in the pores of soils due to the evaporation of water vapor from calcium-rich ground waters. This latter process is referred to as calcification.

The presence of free carbonate in soils has such a dominant effect on the soil's morphology and chemical properties that they are specially classified as members of the "calcimorphic" group of soils. These include the calcisols (Fig. 15.2) and other soils with relatively high calcium carbonate contents, such as rendzinas, which do not have a horizon of distinct calcium carbonate enrichment within their profile. The carbonate minerals control the soil pH and tend to keep it between 7 and 8.5, and they bind a wide range of cations and certain anions to their surface. Major elements such as phosphorus are strongly bound forming apatite minerals (calcium phosphates) and many trace elements, which include cadmium and zinc are sorbed and rendered less available and less mobile. The agricultural practice of liming soils, where either calcium carbonate or calcium hydroxide is added to soils, has the effect of converting the soil to a near neutral or calcareous soil with a significant proportion of free carbonate surface area. Liming is frequently carried out to remediate soils contaminated with trace metals which include cadmium, copper, lead, and zinc. In naturally calcareous soils, the plant-available concentrations of essential trace elements, including boron, iron, copper, manganese, and zinc, are often inadequate for many agricultural crops. These crops are found to suffer from deficiencies of essential trace elements which can cause major reductions in yield and sometimes crop failure unless appropriate prophylaxis is carried out. This usually involves applying salts of the elements, such as zinc sulfate, copper sulfate, manganese sulfate, and sodium borate to the soil, or other forms, including chelates, as foliar applications to the crops themselves.

15.4.4 Redox Conditions

The balance of reducing and oxidizing conditions (redox status) in the soil is important due to its effects on the speciation of several very important elements including: carbon, nitrogen, sulfur, iron, manganese, chromium, copper, arsenic, silver, mercury, and lead. All of these elements can exist in soils in more than one oxidation state. The main factor determining the redox status is the degree of waterlogging which prevents the movement of oxygen through the soil profile in the larger diameter, air-filled pores. Redox equilibria are controlled by the aqueous free electron activity which can be expressed as either a pE value (negative log of the electron activity) or as a redox potential, Eh, (the millivolt difference in potential between a Pt electrode and a standard H electrode). Large positive values of pE or Eh (+300 to +800 mV) indicate the presence of oxidized species and low or negative Eh values (+118 to −414 mV) are associated with reducing conditions. Eh can be converted to pE by the factor: Eh (mV) = 59.2 pE (Lindsay 1979).

Redox conditions control the precipitation and dissolution of iron and manganese oxides and, therefore, have a direct influence on the soil's adsorptive capacity for anions and cations. In gleyed (periodically or permanently waterlogged) soils, those elements which are normally sorbed to iron oxides tend to be more bioavailable than in freely

drained (oxic) soils. These include cobalt, iron, nickel, vanadium, copper, and manganese. However, boron, cobalt, molybdenum, and zinc do not undergo changes in valency themselves when changing redox conditions but are sorbed or desorbed and co-precipitated or dissolved according to the effects of redox on the iron and manganese oxides.

Oxic soils tend to have red and brown colors, whereas gleyed soils with strong reducing conditions tend to have pale colors, such as grayish brown and gray to blue-green colors determined by the presence of ferrous ions (Fe^{2+}). However, strong colored parent materials may mask the color changes to a certain extent. Under severely reducing conditions, several elements may be precipitated as sulfides which renders them insoluble and therefore unavailable to plants. The sulfide ion (S^{2-}) comes from the reduction of sulfate (SO_4^{2-}) or from the degradation of sulfur-containing compounds in soil organic matter. In general, the soil pH in acid soils increases slightly under reducing conditions, but in alkaline soils there is a slight pH decrease. If there are cyclic reducing-oxidizing conditions, such as occur in a rice paddy soil with periodic flooding and drying, sulfides, such as iron pyrites (FeS_2) and cadmium sulfide (CdS) (if the soil has been contaminated by this element) will become oxidized and the metal ions released. However, the formation of sulfate ions (SO_4^{2-}) from the oxidation of sulfide when a waterlogged soil dries out results in the soils becoming strongly acidified and elements such as cadmium rendered highly mobile and bioavailable to plants. This situation was responsible for the heavily contaminated paddy soils of the Jinzu Valley in Japan, which caused the outbreak of itai-itai disease in women who had subsisted on locally grown rice (see Sect. 15.7.3).

15.4.5 Adsorption and Desorption of Ions in Soils

The surfaces of the organic and mineral colloidal solids in soils are able to retain ions by several different mechanisms. Frequently, this retention is referred to by the general term "sorption" because in addition to true adsorption by attraction forces, some ions may reside on surfaces as a result of the formation of insoluble precipitates and by chelation.

15.4.5.1 Cation and Anion Exchange
Cation exchange is the term applied to the electrostatic attraction of positively charged cations to negatively charged surfaces. This occurs on several clay minerals, organic matter, and Fe oxides at higher pH values. It is the formation of outer sphere complexes with the surface functional groups to which they are bound electrostatically. The "exchange" part of this mechanism is due to the exchange between counter ions in the soil solution near the charged

surface. The ability of an adsorbent (mixtures of colloidal clays, oxides, and organic matter) to attract and retain cations is refer-red to as the cation exchange capacity (CEC) and its units of measurement are centimoles of charge per kg ($cmols_c\ kg^{-1}$). The CEC of mineral soils can range from around 3 to 60 $cmols_c\ kg^{-1}$, but in organic soils this can rise to 200 $cmols_c\ kg^{-1}$. The importance of pH and PZC in determining the charge of oxides was discussed above. In general, oxides contribute little to the CEC of soils below pH 7 although they can be involved in specific adsorption reactions in acid soils.

Anion exchange occurs where negatively charged anions, such as Cl^-, SO_4^-, and NO_3^- are attracted to positively charged sites on soil solids. These are usually variable charge sites at pH values below the PZC. Soil in which positively charged surfaces predominate, such as ferralsol, at low pH will have the ability to retain various anions against leaching. Maximum anion exchange capacities (AEC) for sesquioxides (iron and aluminum oxides) are 30–50 $cmol_c\ kg^{-1}$ (White 1997). The exchange of Cl^- and NO_3^- is straightforward, but the exchange of other anions including sulfates, phosphates, and molybdates is more complicated due to specific reactions between these anions and the adsorbent. The CEC of soils is generally greater than their AEC due to the greater number of negative charges on the colloid surfaces.

Table 15.2 gives typical CEC values for colloidal constituents of soils and shows that soil organic matter has a much higher CEC than all other soil constituents except vermiculite clays aluminum.

Cation exchange has the following characteristics: it is reversible, diffusion controlled, stoichiometric, and there is some degree of selectivity for one ion over another by the adsorbing surface. This selectivity gives rise to an order of replacement determined by the concentration of ions, their valency, their degree of hydration, and hydrated radius. The higher the valency of an ion, the greater its replacing power. However, the only exception to this is H^+ which behaves like a polyvalent ion. The greater the degree of hydration, the lower the replacing power of an ion, other things equal. The commonly quoted order of replaceability on the cation

Table 15.2 Typical cation exchange capacity values for soil constituents

Soil constituent	CEC ($cmols_c kg^{-1}$)
Soil organic matter	150–300
Kaolinite (clay)	2–5
Illite (clay)	15–40
Montmorillonite (clay)	80–100
Vermiculite (clay)	150
Hydrous oxides of iron, manganese and aluminum	4

From Ross (1989)

Table 15.3 Typical orders of replacement of trace element cations on various soil constituents

Soil constituent	Selectivity order	Ref.
Montmorillonite	Ca > Pb > Cu > Mg > Cd > Zn	Bittel and Miller (1974)
Illite	Pb > Cu > Zn > Ca > Cd > Mg	Bittel and Miller (1974)
Kaolinite	Pb > Ca > Cu > Mg > Zn > Cd	Bittel and Miller (1974)
Smectite, vermiculite and kaolinite	Zn > Mn > Cd > Hg	Stuanes (1976)
(ferrihydrite)	Pb > Cu > Zn > Ni > Co > Sr > Mg	Kinniburgh et al. (1976)
Fe oxides- (hematite)	Pb > Cu > Zn > Co > Ni	MaKenzie (1980)
(goethite)	Cu > Pb > Zn > Co > Cd	Forbes et al. (1976)
Peat	Pb > Cu > Cd = Zn > Ca	Bunzl et al. (1976)
Fulvic acid	Fe^{3+} > Cu > Zn > Mn > Ca > Mg	Murray and Lindler (1983)
Humic substances	Cu > Pb > Zn = Ni > Co > Cd > Mn > Ca > Mg	Tipping and Hurley (1992)

exchange complex (comprising colloidal organic matter, clay, and oxides) is:

$$\text{Lithium } (Li^+) = \text{sodium } (Na^+) > \text{potassium } (K^+)$$
$$= \text{ammonium } (NH_4^+) > \text{rubidium } (Rb^+)$$
$$> \text{caesium } (Cs^+) > \text{magnesium } (Mg^{2+})$$
$$> \text{calcium } (Ca^{2+}) > \text{strontium}$$
$$(Sr^{2+}) = \text{barium } (Ba^{2+}) > \text{lanthanum } (La^{3+})$$
$$= \text{hydrogen } (H^+) = \text{aluminium } (Al^{3+})$$
$$> \text{thorium } (Th^{4+})$$
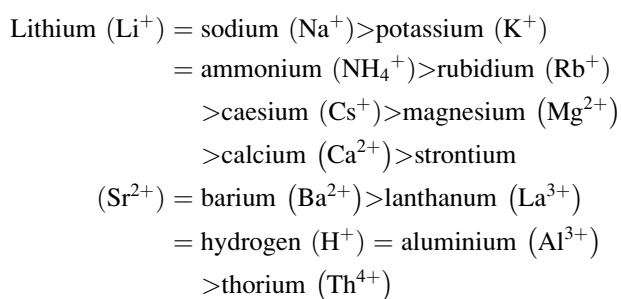
Examples of replacing power of different trace element ions on specific soil constituents are shown in Table 15.3.

From Table 15.4 it can be seen that metal ions such as cadmium and zinc, which were shown in Sect. 15.3 to have relatively high soil–plant Tfs, tend to have low replacing powers and are therefore not strongly retained on soil surfaces. These ions are therefore more readily available for uptake by plants and are also more easily leached down the soil profile than ions with higher replacing powers such as lead and copper.

15.4.5.2 Specific Adsorption

This mechanism involves the exchange of cations of several elements and most anions with surface ligands on solids to form partly covalent bonds with lattice ions. This mechanism is highly pH-dependent and is related to the hydrolysis of the sorbed ions. The pK (equilibrium constant) values of the reaction $M^{2+} + H_2O = MOH^+ + H^+$ determine the adsorption behavior of different ions. Specific adsorption increases with decreasing pK value. However, where the pK values are the same, the ion with the greater radius will be the more strongly adsorbed. Brummer (1986) gave the order for increasing specific adsorption as:

Cd (pK = 10.1) < Ni (pK = 9.9) < Co (pK = 9.7) < Zn (pK = 9.0) << Cu (pK = 7.7) < Pb (pK = 7.7) < Hg (pK = 3.4).
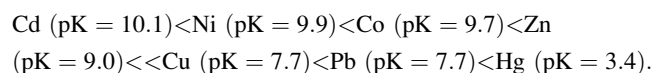
Those ions retained by specific adsorption are held much more strongly than they would be by cation exchange and the CEC of the soil constituent may not reflect the extent of sorption by this different mechanism. For example, it has been shown that the sorptive capacities of iron and aluminum oxides were between 7 and 26 times greater than their CECs at pH 7.6 (Brummer 1986).

In addition to sorption on colloid surfaces, some ions can diffuse into minerals, such as iron and manganese oxides, illite and smectite clays, and calcite. The rate of diffusion into the minerals increases with pH up to a maximum, which is equal to the pK value for when $M^{2+} + H_2O = MOH^+ + H^+$ on the mineral surface. Above this pH, the $MOH^+ > M^{2+}$ and diffusion rate decreases. This can be related to the ionic radius of the ions involved. For example, the maximum relative diffusion rates for cadmium, nickel, and zinc decrease in the order: Ni > Zn > Cd where the ionic radii are Ni 0.69 nm, Zn 0.74 nm, and Cd 0.97 nm (Brummer 1986).

15.4.5.3 Co-precipitation

Co-precipitation is defined as the simultaneous precipitation of a chemical in conjunction with other elements by any mechanism and at any rate (Sposito 1983). The types of mixed solids formed include clay minerals, iron and manganese oxides, and calcite in which isomorphous substitution has occurred. In addition to co-precipitation, replacement of Ca^{2+} in $CaCO_3$ by other elements can occur. For example, cadmium can diffuse into $CaCO_3$ and form cadmium carbonate ($CdCO_3$) (Papadopoulos and Rowell 1988). Typical co-precipitated elements in different minerals are shown in Table 15.4.

15.4.5.4 Insoluble Precipitates of Elements in Soils

When the concentrations of cations and anions in the soil solution exceed the solubility products of compounds they can form, then insoluble precipitates of these may be formed that will have an important effect in controlling

Table 15.4 Trace metals normally found co-precipitated with secondary minerals in soils

Mineral	Co-precipitated trace metals
Iron oxides	V, Mn, Ni, Cu, Zn, Mo
Manganese oxides	Fe, Co, Ni, Zn, Pb
Calcite	V, Mn, Fe, Co, Cd
Clay minerals	V, Ni, Co, Cr, Zn, Cu, Pb, Ti, Mn, Fe

From Sposito (1983)

the concentrations of ions in solution in addition to electrostatic adsorption reactions. Examples of some compounds that can be formed and occur in the solid state in soils include:

1. Phosphates of calcium ($Ca_{10}(OH)_2(PO_4)_6$), cadmium ($Cd(PO_4)_3$), and lead ($Pb_5(PO_4)_3Cl$)
2. Carbonates and bicarbonates of calcium ($CaCO_3$, $Ca(HCO_3)_2$), magnesium ($MgCO_3$), sodium (Na_2CO_3), cadmium ($CdCO_3$), and zinc ($ZnCO_3$)
3. Sulfides of iron (FeS_2), cadmium (CdS), and mercury (HgS, Hg_2S)
4. Chlorides of sodium ($NaCl$) and mercury ($HgCl_2$)
5. Iron (ferrite) forms of copper ($Cu_2Fe_2O_4$), molybdenum ($Fe_2(MoO_4)_3$), and zinc ($ZnFe_2O_4$)

15.4.5.5 Organic Complexation

The solid-phase humic material is involved in the retention of trace elements by forming complexes, such as chelates, in addition to comprising part of the colloidal cation exchange complex. Humic substances with reactive groups, which include hydroxyl, phenoxyl, and carboxyl groups, form coordination complexes with metal and other ions. Carboxyl groups are particularly important in binding by the humic and fulvic acid fractions of humus. The stability constants of chelates with elements tend to be in the following order:

Soluble, low molecular weight organic compounds (DOC) of both humic and non-humic origin can form soluble complexes with many trace elements and thus prevent them from being sorbed onto solid surfaces. This has the effect of making these elements more readily leached down the soil profile and/or more available for plant uptake.

15.4.5.6 Quantitative Description of the Sorption of Ions in Soils

A great deal of research has been conducted on the adsorption of elements by soils, especially trace metals that can pose a potential risk of toxicity in plants, animals, and humans. It has been found that two different adsorption equations are very useful in describing most of the adsorption measured. These are the Freundlich and Langmuir equations.

The Freundlich equation is expressed as : $x/m = KC^{1/n}$

where x/m is the amount of solute adsorbed per unit mass, C is the concentration of solute in solution at equilibrium, and K and n are equation constants. This equation provides an effective means of summarizing adsorption that follows a hyperbolic relationship with the greatest amount occurring at lower concentrations and gradually decreasing with higher concentrations.

The Langmuir equation is expressed as:

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b}$$

where C is the concentration of the ion in the equilibrium solution, x/m is the amount of C adsorbed per unit mass, K is a constant related to the bonding energy, and b is the maximum amount of ions that will be adsorbed by a given sorbent.

These and other applicable adsorption isotherm equations can then be used in models of trace element availability to plants.

15.5 Concentrations of Selected Trace and Major Elements in Rocks, Soils, and Crop Plants

The concentrations of macro and trace elements in soils vary widely as a result of differences in the mineralogy of the soil parent material and, in the case of trace elements, the amount of contamination from external sources can also vary widely. The ranges of concentrations of both macro and trace elements given in Table 15.5 include soils from around the world developed on highly diverse parent materials that have been subject to varying degrees of contamination. Almost all soils in the technologically advanced regions of the world and also in many parts of developing countries are subject to a certain amount of contamination, often from atmospheric deposition.

The data for elements in soils presented in Table 15.5 are for "normal" agricultural soils not considered to be markedly contaminated. Total concentrations of trace elements, such as lead, copper, and zinc can reach very high concentrations in some overtly contaminated soils such as those near metalliferous mines and smelters, other industrial sources of atmospheric emissions, and on land that has received heavy applications of sewage sludge. The concentrations of metals including cadmium, copper, lead, and zinc in sewage sludges have decreased markedly in most industrialized countries as a result of strict pollution controls and structural changes in industry. Nevertheless, soils that received heavy, repeated applications of sewage

Table 15.5 Concentrations of selected trace and major elements in the lithosphere, agricultural soils, and food crops ($mg\,kg^{-1}$ dry matter)

Element	Content in lithosphere	Common range for agricultural soils	Selected average for soils	Typical range in food crops
Silver (Ag)	0.10	0.03–0.9	0.05	0.03–2.9
Arsenic (As)	5	<1–95	5.8	0.009–1.5
Barium (Ba)	430	19–2,368	500	1–198
Boron (B)	10	1–467	9.5–85	1.3–16
Calcium (Ca)	36,000	7,000–500,000	13,700	1,000–50,000
Cadmium (Cd)	0.2	0.01–2.5	0.06–1.1	0.13–0.28
Cobalt (Co)	40	0.1–70	7.9	8–100
Chromium (Cr)	200	1.4–1,300	54	0.013–4.2
Copper (Cu)	70	1–205	13–24	1–10
Fluorine (F)	625	10–1,360	329	0.2–28.3
Iron (Fe)	51,000	5,000–50,000	38,000	25–130
Mercury (Hg)	0.1	0.05–0.3	0.03	0.0026–0.086
Iodine (I)	0.3	0.1–10	2.8	0.005–10.4
Potassium (K)	26,000	400–30,000	8,300	20,000–50,000
Magnesium (Mg)	21,000	20–10,000	5,000	1,500–3,500
Manganese (Mn)	900	270–525	437	15–133
Molybdenum (Mo)	2.3	0.013–17	1.8	0.07–1.75
Sodium (Na)	28,000	750–7,500	6,300	–
Nickel (Ni)	100	0.2–450	20	0.3–3.8
Phosphorus (P)	1,200	200–5,000	600	3,000–5,000
Lead (Pb)	16	3–189	32	0.05–3.0
Sulfur (S)	600	30–10,000	700	1,000–5,000
Selenium (Se)	0.09	0.005–3.5	0.33	0.001–18.0
Tin (Sn)	40	1–11	–	0.2–7.9
Titanium (Ti)	6,000	1,000–9,000	3,500	0.15–80
Vanadium (V)	150	18–115	58	0.5–280
Zinc (Zn)	80	17–125	64	1.2–73.0

Compiled from Lindsay (1979), Kabata-Pendias and Pendias (1992), Adriano (2001), and Marschner (1995)

Note: The typical plant concentrations for the macronutrients calcium, potassium, phosphorus, and sulfur are those for optimum growth and not the full range that may be actually found in crops around the world

sludge in earlier periods when metal contents in sludges were much higher are still likely to retain relatively high total concentrations of several metals for many years (see also Chap. 4, this volume).

Heavily contaminated soils can sometimes contain hundreds of mg kg^{-1} of cadmium, when the safe maximum limits are considered to be around 1–3 mg kg^{-1}; hundreds or thousands of mg kg^{-1} of lead and zinc when the safe maximum values for human health is considered to be in the range 125–450 mg kg^{-1} for lead, and the safe maximum for plants for zinc is around 200–300 mg kg^{-1}. However, in most cases the sites with very high concentrations of metals arising from contamination are generally of relatively small extent in comparison with the total area of agricultural land. Perhaps the most insidious contamination problem is with inputs of cadmium in phosphatic fertilizers which are used in most parts of the world, at least where high-yielding crops are grown. Some of the phosphate rock used for making these fertilizers can contain relatively high concentrations of cadmium (<100 mg kg^{-1}).

15.6 The Bioavailability of Trace and Major Elements to Plants

Uptake of ions by roots can involve several processes including cation exchange by roots, transport inside cells by chelating agents and other carriers, and rhizosphere effects.

Uptake of ions by roots is controlled by the release of ions and organic compounds which include amino acids (e.g., aspartic, glutamic, and prolinic acids). These exudates vary with plant species, microorganism association, and plant growth conditions (e.g., supply of essential trace elements).

15.6.1 Uptake of Trace Elements by Plants

The uptake of trace elements by plants is a key stage in the soil-plant-animal/human pathway and is second only to intake via drinking water with regard to the link between geochemistry and human health apart from where there is excessive ingestion of soil.

Plants readily take up ionic or soluble complexed forms of trace elements present in the soil solution. The factors affecting the amounts of elements absorbed through the roots are those controlling: (1) the concentration and speciation of the element in the soil solution, (2) movement of the element from the bulk soil to the root surface, (3) transport of the element from the root surface into the root, and (4) its translocation from the root to the shoot. Absorption of mobile ions present in the soil solution is mainly determined by the total quantity of this ion in the soil. However, in the case of strongly adsorbed ions, absorption into the root is more dependent on the amount of root produced and its ability to explore a large volume of soil. Mycorrhizae are symbiotic fungi which effectively increase the absorptive area of the root and can assist in the uptake of nutrient ions such as orthophosphates and micronutrients when concentrations of these are low. Roots also possess a significant CEC, mainly due to the presence of carboxyl groups, and this probably forms part of the mechanism transporting ions through the outer part of the root to the plasmalemma where active absorption takes place. Evapotranspiration (flow of water into roots, up through the plant and out of leaf canopy) is an important factor controlling root uptake of elements because plants that have more rapid evapotranspiration will absorb greater volumes of soil solution containing ions and complexes in solution.

Absorption of ions by plant roots can be both passive and metabolically active processes. Passive uptake involves diffusion of ions in the soil solution to the root endodermis. In contrast, metabolically active absorption takes place against a diffusion gradient but requires the expenditure of energy so it is vulnerable to inhibition by toxins. The type of mechanism appears to differ with different elements; for example, lead is passive whereas the uptake of copper, molybdenum, and zinc is considered to be metabolically active or a combination of both active and passive mechanisms. Ions which are absorbed into the root by the same type of mechanism are likely to have an antagonistic relationship through competition with each other. For example, zinc absorption is inhibited by copper and hydrogen, but not by manganese and iron. Copper absorption is inhibited by zinc, ammonium ions, calcium, and potassium (Barber 1984; Graham 1981).

The rhizosphere is a narrow zone (1–2 mm thick) between a root and the surrounding soil. It is a zone of intense microbiological and biochemical activity because it receives appreciable amounts of organic substances from the roots that provide a substrate for a diverse microbial population. These organic substances include exudates, mucilage, and sloughed-off cells and their lysates (Marschner 1995). As a result of the processes taking place in the rhizosphere which include acidification, redox changes, and organic complex formation, some ions adsorbed onto the soil in the vicinity of the root may be desorbed and become available

for absorption into the root. Phenolic compounds and amino acids are known to be involved in the mobilization of oxidized forms of iron and manganese (Fe^{3+} and Mn^{4+}) (Marschner 1995).

Cereal plants experiencing a deficiency of iron and/or zinc appear to have exudates containing substances (usually referred to as phytosiderophores) such as phytosiderophore $2'$-deoxymugineic acid, which are effective in mobilizing these and other elements co-precipitated with them, including cadmium and copper, from iron and manganese oxides and other sorption sites in the vicinity of the root (Kabata-Pendias and Pendias 1992). Tobacco plants have root exudates that increase the absorption of cadmium but decrease that of iron (Mench and Martin 1991).

Kabata-Pendias and Pendias (1992) summarized the main points in the literature relating to the absorption of trace elements from solutions as:

- One of the most important factors determining the biological availability of trace elements is the extent to which they are bound to soil constituents.
- Plants take up the species of trace elements that are dissolved in the soil solution in either ionic or chelated and complexed forms.
- Absorption usually operates at very low concentrations.
- Adsorption depends largely on the concentrations in solution, especially at low ranges.
- The rate of absorption depends on the occurrence of H^+ and other ions.
- The intensity of absorption varies with plant species and stage of development.
- The processes of absorption are sensitive to some properties of the soil environment, such as: temperature, aeration, and redox potential.
- Absorption by a plant may be selective for a particular ion.
- The accumulation of some ions can take place against a concentration gradient.
- Mycorrhizae play an important role in cycling between media (e.g., soil) and roots.
- Root absorption can be by both passive (non-metabolic) and active (metabolic) processes.

In addition, Marschner (1995) stressed that there can be marked differences in ion uptake by different plant species (and cultivars within species; see Sect. 15.6.3).

15.6.2 Uptake of Major Elements by Plants

The major elements are present in much higher concentrations in plant tissues than trace elements and are referred to as "macronutrients." Trace elements are usually present at concentrations of <100 mg kg^{-1}, whereas macronutrients are present at levels of 1,000–40,000 mg kg^{-1} ($<4\%$) in the dry matter.

Wild and Jones(1988) and Marschner (1995) summarized the concentrations of macronutrient elements in crop plants as follows:

1. Calcium has a normal concentration range of 0.1–2.5% in plant dry matter but has a low mobility in plants and thus is not redistributed. Therefore the relatively high concentrations do not necessarily reflect the plants' metabolic requirements. Calcium plays a key role in the maintenance and integrity of membranes.

2. Magnesium generally occurs in the dry matter at lower concentrations than calcium (0.2–0.56%), but this element is more mobile than calcium. Magnesium is a specific constituent of chlorophyll. On serpentine soils, there may be a disproportionately large amount of available magnesium compared with calcium and this has lead to the development of specialized flora.

3. Sulfur is usually present at concentrations of 0.1–1% (dry matter) and is a constituent of the amino acids cysteine, cystine, and methionine, and therefore of proteins containing these. Biochemically, sulfur is a very important element because it is a constituent of enzymes and other key proteins. Crops take up 15–50 kg Sha^{-1} a^{-1}.

4. Phosphorus is present in plants at around 0.2% in the dry matter of shoots and is a key component in metabolic processes involving phosphorylation (e.g., ADP-ATP). It is present in the soil solution mainly as HPO_4^{2-} and $H_2PO_4^{-}$ but is taken up mainly as $H_2PO_4^{-}$. It is relatively strongly bound in most soils, in the organic matter, and sorbed to iron oxides (acid soils) or calcium carbonate with which it reacts to form apatite in calcareous and heavily limed soils.

5. Potassium occurs in similar concentrations as nitrogen in plants (1.4–5.6% in the dry matter) and is the most abundant cellular cation, but it can often be in short supply in crops. Crops can take up <500 kg Kha^{-1} a^{-1}, (400–500 kg Kha^{-1} a^{-1} in a 15th a^{-1}DM grass crop, 300 kg Kha^{-1} a^{-1} in a normal crop of potatoes, and <300 kg Kha^{-1} a^{-1} in a 10th a^{-1} (grain) crop of cereals).

6. Nitrogen can be present at 1.6–4% in the dry matter and is the fourth most abundant element in plants after carbon, hydrogen, and oxygen. Nitrogen has an essential role as a constituent of proteins, nucleic acids, chlorophyll, and growth hormones. It can be absorbed into the roots as either nitrate or ammonium ions but whatever the source, ammonium is the intermediate for the formation of amino acids, amides, and subsequently proteins.

15.6.3 Differences in Trace Element Accumulation Between and Within Plant Species

The amount of a trace element taken up from any particular soil will depend on plant factors as well as soil properties. Most important of the plant factors is the genotype or genetic makeup of the plant. Differences between plant families and species and also between varieties (cultivars) within a species are clearly shown in the case of cadmium. Grant et al. (1999) reviewed the literature on cadmium accumulation in crops and reported the general trend between plant families as:

1. Low accumulators: Leguminosae
2. Moderate accumulators: Graminae, Liliacae, Cucurbitacae, and Umbelliferae
3. High accumulators: Chenopodiacae, Cruciferae, Solanacae, and Compositae

However, marked differences can occur within families of plants and within species. For example, many varieties of durum wheat (*Triticum durum*) accumulate significantly more cadmium than common spring or winter (bread) wheats (*T. aestivum*).

In a review, Welch and Norvell (1999) reported that median cadmium concentrations in the seeds of seven different grain crops show a 100-fold variation, ranging from low values in rice and maize, to non-durum wheat, with durum wheat containing higher concentrations than non-durum wheat, and sunflower and flax containing the highest cadmium concentrations. Intraspecific variations of 40-fold have been reported for cadmium in 20 inbred lines of maize.

With regard to the risk to the health of consumers, it is not just the amount of a potentially toxic element, such as cadmium, which occurs in the whole plant that is important, but the concentrations found in the edible portions. Many plants (e.g., oat, soybean, timothy grass, alfalfa, maize, and tomato) tend to concentrate cadmium in their roots which implies that fruits, seeds, or leaves will be less enriched. Other species tend to have higher cadmium concentrations in their leaves, and these include the green leaf crops: lettuce, carrot, and tobacco. Lettuce and tobacco have a higher risk to consumers because of this characteristic distribution within the plant. It is considered that differences between varieties of some crops can be due to variations in the proportions of cadmium translocated around the plant from the roots (e.g., durum wheat).

The finding that varieties of key food crops can vary significantly in their accumulation of potentially hazardous elements such as cadmium does open up the possibility that plant breeders could use this to select new varieties with minimal concentrations in their edible parts. This is a distinct possibility for potatoes, rice, wheat, maize, lettuce, sunflower, and soybean. On the other hand, essential trace elements, such as zinc and copper, also show marked genotypic variations in plant species so plant breeders could exploit this trait. By selecting cultivars of food crops which contain higher concentrations of essential trace elements, such as zinc, it would be possible to match crops to marginally deficient soils and thus reduce the amount of trace element fertilizers needed to rectify the deficiency problems. The diets of people in many developing countries contain marginal to deficient concentrations of zinc and this can have marked effects on health.

15.7 Trace Elements in Soils and Crops and Human Health

Soils used for growing food crops in domestic gardens and commercial horticulture and agriculture can become contaminated with potentially toxic chemicals. In cases where the contamination is not sufficiently great to cause phytotoxicity and/or possible crop failure, there is a possible risk that livestock or people consuming large quantities of crop products grown on contaminated soil could suffer illness and even death from the chronic intake of contaminants or by the direct ingestion of the soil itself.

15.7.1 Concentrations of Selected Trace Elements in Soils in Different Parts of the World

Cadmium and lead are the elements in contaminated soils that are generally considered to constitute the widest possible health risk to humans through the plant uptake-dietary route. Surveys of soils in various countries have been carried out to determine the total (and sometimes bioavailable) concentrations of a range of trace elements, some of which are often found to have been elevated from anthropogenic

sources of pollution. The concentrations of cadmium, lead, copper, and zinc in England and Wales, the United States, Florida, China, and Poland are shown in Table 15.6. These data show that all four elements are generally present at higher concentrations in England and Wales than in the other countries and state. This can be explained, at least in part, by the grid sampling (5×5 km cells) for England and Wales which included sites contaminated from various sources including metalliferous mining and heavy applications of sewage sludge. In the United States, the samples were collected on a more selective basis which avoided obvious sources of contamination either from sewage sludge or atmospheric deposition from nearby industries.

15.7.2 Concentrations of Cadmium and Lead in Food Crop Products

Surveys of the concentrations of potentially toxic elements, such as cadmium and lead, in food crops have also been undertaken in various countries and these help to show the extent to which anthropogenic contamination and/or geochemically enriched soil parent materials have influenced the composition of food crops consumed in the countries or areas considered (see also Chap. 8, this volume).

Table 15.6 Total concentrations of selected elements in topsoils in various countries or states (mg kg^{-1})

Country	Element	Mean	Minimum	Maximum	Median
England & Wales (n = 5,692)[a]	Cadmium	0.8	<0.2	40.9	0.7
	Lead	74.0	3.0	16,338	40
	Copper	23.1	1.2	1,508	18.1
	Zinc	97.1	5.0	3,648	82.0
United States (n = 3,045)[b]	Cadmium	0.265	<0.01	2.0	0.2
	Lead	12.3	7.5	135.0	11.0
	Copper	29.6	<0.6	495.0	18.5
	Zinc	56.5	<3.0	264.0	53.0
Florida (n = 448)[c]	Cadmium	0.07	0.004	2.8	0.004
	Lead	11.2	0.18	290	4.89
	Copper	6.1	0.1	318	1.9
	Zinc	8.35	0.9	169	4.6
China (n = 4,095)[d]	Cadmium	–	0.2	0.33	–
	Lead	–	9.95	56.0	–
	Copper	–	7.26	55.1	–
	Zinc	–	28.5	161.0	–
Poland (n = 127)[e]	Cadmium	–	0.1	1.7	–
	Lead	–	7.1	50.1	–
	Copper	–	2.0	18.0	–
	Zinc	–	10.5	154.7	–

[a]McGrath and Loveland (1992)
[b]Holmgren et al. (1993)
[c]Chen et al. (1998)
[d]Wei et al. (1990)
[e]Dudka (1992)

Consumption of grain, potatoes, and leafy vegetables is considered to account for more than 50% of total cadmium intake by people in most countries (Adriano 2001). In the UK, the largely wheat-based diet gave an intake of 8 µgCd day^{-1} which is only 11% of the WHO limit of 70 µgCd day^{-1}. The concentration of Cd in wheat grain decreased from 0.052 mgCd kg^{-1} in 1982 –0.042 in 1992 and 0.038 in 1993 due to reductions in atmospheric deposition, change to lower cadmium content phosphorus fertilizers, and increased yields giving rise to a dilution effect (Adriano 2001).

The European Union (EU) has legally defined maximum permissible concentrations for cadmium and lead in a range of foodstuffs including wheat (*T. aestivum* L.) and barley (*Hordeum vulgare* L.) grain. For cereals, excluding wheat grain, bran, germ, and rice, the maximum permissible cadmium concentration is 0.1 mg kg^{-1} (fresh weight), and the limit for the excluded crops mentioned above is 0.2 mg kg^{-1} (fresh weight). For lead the maximum permissible concentration in all cereals is 0.2 mg kg^{-1}. Assuming an 85% dry matter content, the effective limiting concentration on a dry matter basis is 0.118 mg kg^{-1} for cadmium in cereals excluding wheat grain, bran, germ, and rice and 0.235 mg kg^{-1} for the excluded categories. The dry matter based limiting concentration for lead is 0.235 mg kg^{-1} in all crop products.

A survey of the cadmium and lead concentrations in 250 samples of wheat grain and 233 samples of barley grain from throughout the UK after the 1998 harvest is reported by Adams et al. (2001). In the samples of wheat, they found overall mean concentrations (in the dry matter) of 0.063 mg kg^{-1} for cadmium and 0.025 mg kg^{-1} for lead. Only one sample of wheat had a cadmium concentration above the maximum permissible cadmium concentration. The 230 barley samples showed an overall mean value of 0.022 mg kg^{-1} for cadmium and 0.039 mg kg^{-1} for lead. Only one sample of barley exceeded the maximum permissible level for cadmium and two samples exceeded the maximum level for lead (Adams et al. 2001).

Both the wheat and barley samples showed small but significant differences between cultivars in mean concentrations of cadmium. The wheat samples also showed significant cultivar differences in lead concentrations (Adams et al. 2001).

Lead concentrations in samples of rice (*Oryza sativa*) from 17 areas of the world were reported by Zhang et al. (1996). The grand means for different countries ranged from 0.002 mg kg^{-1} in Australia to 0.039 mg kg^{-1} in Indonesia. Samples from within China showed a 76-fold variation in mean lead contents (0.016–0.152 mg kg^{-1}) in different parts of the country. A later paper (Zhang et al. 1998) reported lead and cadmium concentrations in 59 samples of several types of cereals and 34 samples of pulses from open markets in northeastern China. Average lead concentrations were 0.031 mg kg^{-1} for the cereals and 0.026 mg kg^{-1} for the pulses. Mean cadmium concentrations were higher in pulses than cereals (0.056 mg kg^{-1} pulses, 0.009 mg kg^{-1} cereals). Foxtail millet (*Stetaria itaica*) was found to contain the highest amounts of lead (0.054 mg kg^{-1}) and cadmium was highest in soya beans (*Glycine max*; 0.074 mg kg^{-1}). There were some possible links between food crop composition and human health effects. It had earlier been found that the consumption of Foxtail millet was a leading determinant of blood lead concentrations in Shandong Province and there was concern about the elevated levels of cadmium in pulses which are an important source of protein and lipids in Asia.

A much larger survey of cadmium and lead in 4,113 samples of rice and other cereal products in Japan was reported by Shimbo et al. (2001). They found a grand geometric mean for cadmium in polished, uncooked rice of 0.05 and 0.019 mg kg^{-1} in wheat flour. Mean lead concentrations were much lower for both rice and wheat flour ranging from 0.002 to 0.003 mg kg^{-1}. Rice was therefore shown to be a more important source of cadmium than wheat flour for Japan as a whole.

These four examples show how varying concentrations of elements, such as cadmium and lead in soil, together with genotypic differences between species and cultivars can give rise to variations in the trace element composition of food crops. The soil concentrations are a result of both the geochemical composition of the parent material and inputs from anthropogenic sources.

Examples of significant human health effects occurring as a result of soil contamination include (1) lead poisoning in children ingesting lead-rich garden soils and house dust, (2) skeletal deformity and death due to excessive cadmium intake by multiparous women living in the Jinzu Valley in the Toyama Province of Japan, and (3) tumors due to arsenic poisoning in people drinking contaminated water and eating vegetables and other crops from soils irrigated with arsenic-rich groundwaters in Bangladesh, India, and Taiwan (see Chap. 12).

15.7.3 Examples of Contaminated Soils Affecting Human Health

15.7.3.1 Exposure of Children to Lead in Contaminated Domestic Garden Soils

Domestic gardens can contain relatively high concentrations of lead from weathered and scraped painted interior and exterior surfaces (especially important around timber houses), deposition of lead from vehicle exhaust emissions

when gasoline used to contain relatively high levels of lead as an anti-knock agent, and other diffuse sources. Prior to the 1950s, some house paints contained more than 50% of lead in the dry matter. It was estimated in the late 1980s that up to 11.7 million children in the United States could have been at risk due to exposure to excessive amounts of lead in contaminated garden soils and house dusts (Millstone 1997). Culbard et al. (1988) conducted a survey of soil in 3,550 urban gardens in the UK and found the following geometric mean concentrations (in mg kg^{-1}): lead 230 (<14,125), cadmium 1.2 (<17), copper 53 (<16,800), and zinc 260 (<14,568). The geometric mean concentrations of metals in 579 gardens in greater London were significantly higher than for the rest of the country: lead 647 mg kg^{-1}, cadmium 1.3 mg kg^{-1}, copper 73 mg kg^{-1}, and zinc 424 mg kg^{-1}. This reveals that urban gardens in large cities, such as London, can be relatively heavily contaminated with potentially toxic elements including lead and zinc. However, zinc in high concentrations is normally regarded as more of a potential toxicity hazard to plants than to humans or animals.

Lead has a relatively low phytotoxicity compared with most other trace metals: cadmium > copper > cobalt, nickel > arsenic, chromium > zinc > manganese, iron > lead (Chino 1981). Therefore, crops grown in lead-contaminated gardens are unlikely to show symptoms of toxicity. However, the greatest risk to children and some adults is not through consumption of vegetables which have accumulated lead by uptake through their roots but by direct ingestion of lead-contaminated soil. This soil may have been ingested accidentally on unwashed vegetables and eating with unwashed hands. However, the greatest risk is to children who intentionally eat soil (*pica*) (see also Chap. 18, this volume).

A model has been proposed by Wixson and Davies (1993) to calculate safe guideline values for lead in soils where there may be a risk of soil ingestion by children. This model is:

$$S = \frac{(T/G^n - B)}{(\delta)} 1,000$$

where S is the soil guideline value, a geometric mean concentration of lead in gPbg^{-1} of soil, T is the blood lead guideline or target concentration in μg Pbdl^{-1} whole blood, G is the geometric standard deviation of the blood lead distribution (typically 1.3–1.5 but may be higher, e.g., in mining areas), B is the background or baseline blood lead concentration in the population from sources other than dust, n is the number of standard deviations corresponding to the degree of protection required, and δ is the slope or response of the blood Pb–soil Pb relationship and has units of μg Pbdl^{-1} blood increase per 1,000 μgPbg^{-1}.

15.7.3.2 Cadmium Contamination in Japan and Great Britain

The Jinzu Valley in the Toyama Province of Japan has metalliferous mining and smelting industries located near the Jinzu River together with intensive paddy rice cultivation around the urban and industrial areas on the alluvial soils of the valley floor. Over many years leading up to WWII the mining and smelting operations had resulted in the contamination of the paddy soils with cadmium, lead, and zinc. Because of the cycle of reducing and oxidizing conditions associated with the flooding and drying out of the soils in the paddy fields, the contaminants, especially cadmium, underwent marked changes in speciation. In the flooded soils with strong reducing conditions, cadmium is present as an insoluble sulfide precipitate (CdS). As the growing rice approaches maturity, the paddy fields are drained to facilitate harvesting and it is during this period that the cadmium sulfide becomes oxidized and forms Cd^{2+} and SO_4^{2-}, which result in a massive uptake of cadmium ions into the rice plant and translocation into the grain (Asami 1984). As a consequence of this, rice grain grown in Jinzu Valley had significantly elevated concentrations of cadmium, and the people consuming this rice were exposed to a high risk of cadmium poisoning. It was the women who had had several children who were the worst affected by any kidney damage and an acute skeletal disorder known locally as itai-itai disease, which translated from Japanese means "ouch, ouch" due to the pain experienced by the sufferers when their bodies were touched. More than 200 elderly women living in the Valley during the 1940s who had borne several children were found to have been disabled by the disease and a further 65 women died from its effects. At that time, the rice-based subsistence diets of the peasant farmers were generally deficient in protein, calcium, and vitamin A, which all exacerbated the cadmium poisoning. In addition to the intake of cadmium in the rice, water taken from the river for drinking and cooking was also significantly contaminated with cadmium.

The average concentration of cadmium in the rice grown on the contaminated paddy soils was 0.7 mgCd kg^{-1}, which was more than ten times greater than the average cadmium concentration in local control samples of rice (0.07 mgCd kg^{-1}). The maximum content of cadmium found in rice was 3.4 mgCd kg^{-1}.

The mean cadmium intake for the residents of the Jinzu Valley was estimated to be around 600 mg day^{-1}, which is around ten times greater than the maximum tolerable intake. The Japanese government has set 1mgCd kg^{-1} in rice as the maximum allowable limit, and it has been found that 9.5% of paddy soils in Japan have been polluted with cadmium to the extent that the concentrations in rice are greater than this

value. Even in areas considered to be unpolluted with cadmium, rice is estimated to be the source of more than 60% of cadmium in the diet. Much of this cadmium is probably derived from phosphatic fertilizers.

An interesting comparison can be made with the village of Shipham in Somerset, England, where a relatively large number of houses had been built in the 1950s and 1960s on land contaminated with cadmium, lead, zinc, and other elements from historic metalliferous mining (Morgan and Sims 1988). Although the total concentrations of cadmium were in some cases more than 100 times those in the Jinzu Valley soils (<360 mgCd kg^{-1}), the cadmium was less bioavailable due to the mining-contaminated soils in Shipham containing appreciable amounts of free calcium carbonate and, consequently, a higher pH and a significant amount of chemisorption (Alloway et al. 1988). The Shipham soils were also contaminated with zinc and lead ($<37,200$ mgZn kg^{-1} and 6,540 mgPb kg^{-1}) and antagonistic reactions with these metals may have also played a role in reducing cadmium uptake. Nevertheless, the mean concentration of cadmium in vegetables grown in gardens in Shipham was 0.25 mgCd kg^{-1} DM, which is nearly 17 times higher than the UK national average of 0.015 mgCd kg^{-1} DM. Some samples of leafy vegetables growing on the most highly contaminated soils contained much higher concentrations but these were not common. Health studies on approximately 500 inhabitants of Shipham village revealed some small but significant differences in biochemical parameters, but there was no evidence of adverse health effects in the participants in the investigations.

15.8 Widespread Deficiencies of Essential Trace Elements

Large areas of the world have soils which are unable to supply staple crops, such as rice, maize, and wheat with sufficient zinc. Smaller, but still significant areas of the world are affected by deficiencies of boron, copper, iron, and manganese. In crops, acute deficiencies of essential trace elements result in visible symptoms of stress, such as chlorosis (yellow coloration due to impaired chlorophyll production) and reduced dry matter growth and yield of edible crop products. However, marginally deficient amounts of certain trace elements, such as copper and zinc, can give rise to hidden deficiencies in which yields can be reduced by up to 30% or more without the appearance of obvious visible symptoms of stress. Plants may be smaller but unless normal (sufficient) crops are available nearby for comparison, marginal deficiencies are often difficult to detect. This can result in crop yields which may be very much less than optimal due to a trace element deficiency that could be easily treated by either application of fertilizers to the soil or foliar sprays to the crop.

The impact of deficiencies of essential trace elements on crop yields and quality is much greater overall than that of toxicity due to pollution. In several countries, large proportions of the arable soils are affected by deficiencies, such as in India where around 45% of soils are deficient in zinc, 33% deficient in boron, 8.3% deficient in iron, 4.5% deficient in manganese, and 3.3% deficient in copper (Singh 2001). Apart from lost food production in terms of tonnes of carbohydrates and protein, the trace element composition of the crop products is also affected. The zinc status of many people in developing countries, such as India and Pakistan, is considered to be suboptimal and therefore low zinc concentrations in food products will exacerbate this problem. Cereal staples, such as rice, wheat, and maize contain relatively large amounts of phytate which tends to make zinc in the diet less available. Phytate concentrations tend to be higher in crops receiving high levels of phosphorus fertilizer, such as the new, high-yielding varieties.

Deficiencies of essential trace elements in crops can be caused by low total concentrations of elements in the soil parent material (such as sandstones and sandy drift deposits), by low availability due to high soil pH, high concentrations of calcium (in calcareous soils on limestones or in semi-arid or arid areas), high organic matter contents (peaty soils), and waterlogged (gleyed) conditions. Zinc deficiency is the most widespread essential trace element deficiency problem in the world and many large areas of land in hot arid climates have severe zinc deficiency problems in calcareous soils (such as in the Middle East) and in rice paddy soils (as in India, Philippines, and Bangladesh).

As with other plant species, crops such as wheat, rice, and maize have been found to vary widely in their ability to tolerate deficiencies of essential trace elements such as zinc. "Zinc-efficient" cultivars of wheat are those that are able to grow and yield reasonably well on soils in which less tolerant cultivars would be acutely affected by zinc deficiency. The zinc efficiency character will enable plant breeders to produce new hybrids that are better suited to zinc-deficient soils. Although any zinc-deficient soil can be fertilized with a zinc compound (such as zinc sulfate) to raise its plant-available concentration of zinc, the use of zinc-efficient cultivars would enable plants to be matched to the soils, rather than the soils fertilized to match them to the crop's requirements. This is particularly important in areas where zinc fertilizers are difficult for farmers to obtain.

As discussed in Selenium Deficiency and Toxicity in the Environment (in this volume), widespread deficiencies of selenium are also related to soil parent materials containing low concentrations of this and other essential trace elements.

15.9 Summary

The health of people and animals can be affected by imbalances in their dietary intake of trace and major elements and therefore the rock-soil-plant-animal/human pathway is of major importance in considerations of medical geology. Soils can differ widely in their total concentrations of both macro and trace elements due to variations in the mineralogy of the geological parent material on which the soil has formed, even without inputs from environmental pollution or agricultural husbandry. Concentrations of essential trace elements can be anomalously low on parent materials such as sandstones and sandy or gravelly glacial drift. These can be due to both low concentrations of these elements in the predominant mineral (quartz) and the relatively low adsorptive capacities of sandy soils (arenosols) due to their very low clay contents. On the other hand, anomalously high concentrations of both essential and potentially toxic elements can occur in soils formed on geological materials which themselves have anomalously high concentrations of certain elements. Examples of this are marine black shales enriched in arsenic, cadmium, copper, chromium, mercury, molybdenum, lead, and zinc and serpentinite rocks enriched in magnesium, cobalt, chromium, and nickel.

Given that marked variations can occur in the total concentrations of elements in the soil, the mobility and bioavailability of these elements is going to be controlled by a range of soil factors of which the pH is probably the most important. The adsorptive capacity of a soil is dependent on its mineralogy, especially the amount and type of clays; the amounts of iron, manganese, and aluminum oxides and free carbonates; and the organic matter content. The redox conditions will have a marked control on the oxide content and the free carbonates will have a major effect on the soil pH.

Even after the bioavailable concentrations have been determined by the soil and parent material factors, the plants growing on the soil have both an effect on the soil and also vary markedly in their ability to accumulate trace and major elements due to differences in their genotypes. Therefore, the potential impact of geology on the dietary intake of trace and major elements by humans and livestock is dependent on a range of soil and plant factors. Fortunately many of the mechanisms in soils are reasonably well understood and in due course it will become possible to model their behavior and make more realistic risk assessments of both potential toxicity and deficiency problems. With regard to the plant genotypic factor, with the continual breeding of new crop varieties, there is an ongoing need to screen these for their ability to accumulate both essential and non-essential elements as they come into use. This would enable the most suitable crop varieties to be grown. This could apply to varieties of crops that have a high efficiency of use of essential trace elements such as zinc in areas where there is a major problem of deficiencies both limiting yields and the dietary available concentrations of trace elements essential for humans consuming the crops. Conversely, where soils have relatively high concentrations of potentially harmful elements, such as arsenic and cadmium, either as a result of anomalous geochemical composition or environmental pollution, then crops which accumulate relatively low concentrations of these elements would be most suitable. Amelioration of soils by manipulation of soil chemical properties, such as pH, can be carried out, but selecting the most appropriate plant species and cultivars would also help to mitigate the problems.

Apart from the uptake of elements by plants followed by the consumption of crop products by people, there are other ways (dealt with elsewhere in this book) by which the composition and properties of soils can affect human health. These range from the inhalation and ingestion of atmospheric dusts containing soil minerals eroded by the wind from land, the intake of elements in drinking water which has been affected by the leaching of elements through soil profiles, and, lastly, to the intentional eating of soil (geophagia). The soil is bviously a key consideration in medical geology.

See Also the Following Chapters. Chapter 17 (Soils and Iodine Deficiency) • Chapter 18 (Geophagy and the Involuntary Ingestion of Soil) • Chapter 19 (Natural Aerosolic Mineral Dusts and Human Health) • Chapter 20 (The Ecology of Soil-Borne Human Pathogens)

Further Reading

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