Chapter 6
Inorganic Contaminants in Urban Soils

Andrew W. Rate

Abstract If, in the absence of prior knowledge, we were to guess one feature of urban soils, we might assume that pollution with hazardous inorganic substances, such as ‘heavy metals’ or asbestos, would be widespread. In many cases this is true, and so this chapter deals with the topic of inorganic contaminants in urban soils. We identify nutrients, metals and metalloids, asbestos, plastics, manufactured nanoparticles, radionuclides, and cyanide as contaminants of concern and discuss their sources in urban soils. In addition, we cover the formation and properties of acid sulphate soils. Following this, we explain the behaviour of inorganic contaminants, going into some more detail on soil chemical reactions than was presented in Chap. 4. The discussion addresses the effects of transport processes, time, and soil properties on the relevant chemical reactions. Some further discussion of bioavailability is coupled with a discussion of the effects of urban soil contamination on ecosystem services. The later sections present methods for soil chemical analyses and concepts for understanding soil chemical data. The analytical method component covers total and partial elemental analyses and field measurements. Following this, we examine the concepts of background concentrations, regulatory contamination thresholds, separation of geogenic and anthropogenic sources of contaminants, and contamination indices.

Keywords Soil chemistry · Urban soils · Chemical properties · Nutrients · Metals · Acid sulphate soils · Speciation · Bioavailability · Transport

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What you could learn from this chapter:

- The inorganic contaminants of concern in urban soils and where they come from.
- An introduction to acid sulphate soils in urban environments.
- The processes controlling immobilisation, mobility, and bioavailability of inorganic contaminants.
- Why there are many ways of analysing soil for inorganic contaminants and what information the analyses give us.
- Some ways we can use soil analysis data to distinguish natural and anthropogenic sources of inorganic contaminants.

6.1 Sources of Inorganic Contaminants in Urban Soils

An understanding of the potential sources of contaminants is essential for assessment of urban soil environments. In a formal environmental impact procedure, the likely contaminant sources form part of a conceptual site model (CSM), which will be discussed further in Chap. 9. Substances which are potential contaminants may be subdivided into two categories: first, those elements and substances which are from recognised sources and have usually been added to soils during the *Anthropocene* era (i.e. since about 1950, when accelerating human activity began to significantly change environments on a global scale). Second, contaminants (often the same substances) have also been added to urban soils by humans, in historical times (subjectively, before the twentieth century), which provide indicators of urban/anthropogenic impact (e.g. Strauch et al. 2008).

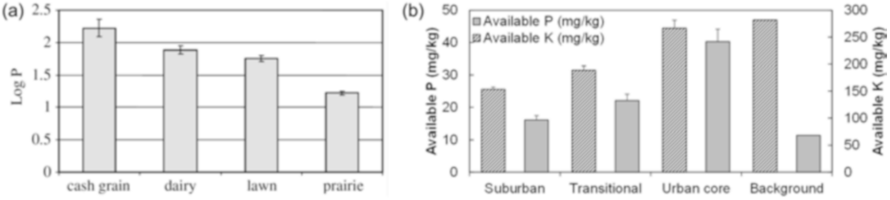

Fig. 6.1 (**a**) Phosphorus concentration ($\log_{10}$(mg/kg); extracted from soil using the Bray-1 'available' P method) in soils under different land uses in and around the Madison urban area, Wisconsin, USA (from Bennett et al. 2005; used with permission from Springer). 'Cash grain' and 'dairy' are agricultural land uses; 'lawn' is residential urban; 'prairie' is remnant natural vegetation. Urban land has less P than agricultural and greater P than natural (significance $p < 0.01$). (**b**) Available P and K in urban soils of Beijing, China (redrawn from data in Mao et al. 2014)

6.1.1 Sources of Nutrients

Since early history (at least as early as the Bronze age; Golyeva et al. 2018), soils in urban areas commonly have become more concentrated in nutrients. This nutrient signature is predominantly manifested as increased phosphorus and carbon contents (both elements are more persistent in soils than nitrogen; see Deevey et al. 1979; Davidson et al. 2006). Urban soils which have received recent fertiliser or organic amendments may also be enriched in nitrogen (Gregory et al. 2016). An excess of nutrients can occur in urban soils on land currently or historically used for horticulture and other forms of plant production, since these soils commonly receive large amounts of synthetic and organic fertilisers (Mann et al. 2002; Sangare et al. 2012; Mao et al. 2014). Soils used primarily for plant growth also include urban lawns (Bennett et al. 2005 – see Fig. 6.1) and those reclaimed from coastal saline environments (Li et al. 2014). The export of nutrients from urban soil (e.g. residential lawns) is strongly dependent on soil properties. Export of nitrogen and phosphorus has been measured to be much higher if soil properties favoured run-off rather than infiltration of rainwater (Easton and Petrovic 2008b; Easton and Petrovic 2008a). Another important source of excess soil nutrients in some urban environments is the discharge of untreated or minimally treated wastewater or solid wastes onto soil, even if the nutrient content of the wastewater represents beneficial reuse of an otherwise discarded material (Anikwe and Nwobodo 2002; Nyenje et al. 2010).

6.1.2 Sources of Metals

Natural inputs. Trace elements occur widely in the parent materials of soils, at concentrations which are broadly dependent on lithology. Global summaries of average concentrations of trace elements in different rock types have been presented by Kabata-Pendias (2011), Alloway (1995), and Adriano (2001), but to present these data here is beyond the scope of this text. Some soils have naturally high concentrations of one or more trace elements, derived from their parent rocks. For example, soils developed on ultramafic or serpentine rocks commonly contain high concentrations of chromium and/or nickel (Gonnelli and Renella 2012). During the process of soil formation, trace elements may become enriched or depleted in different soil horizons. This depends on the soil-forming environment and the predominant chemical reactions for each element (Adriano 2001). For example, Cu and Pb may become enriched relative to parent material in the surface organic horizons, following plant uptake from depth. The metals remain in surface soils because of their strong associations with pedogenic minerals (such as iron oxides and clays) and soil organic matter (Davies 1988; Baker and Senft 1995). External inputs of trace elements include atmospheric deposition, which is minimal in many natural environments (e.g. Ljung et al. 2010) but may be locally important, especially in urban areas (Nriagu 1988).

Anthropogenic Inputs Elevated concentrations of metals in soils are commonly derived from human activity, and (not surprisingly) most research into metal ion *bioavailability* (see Box 6.1) has been concerned with contaminated environments. Anthropogenic sources of trace metals have been reviewed exhaustively (e.g. see Adriano 2001; Kabata-Pendias 2011; Alloway 2012). Industrial inputs include mining and ore processing, smelting, and other metallurgical processes and a wide range of metal-utilising industries (Chen et al. 1997; Wong et al. 2002; Laidlaw et al. 2018). Several agricultural and horticultural activities, such as market gardening, contribute metals, particularly in (peri)urban systems. These sources of trace elements in horticulture include use of fertilisers with trace element supplements or impurities (Mann et al. 2002), application of metal-contaminated organic wastes including sewage sludge or effluents from intensive animal industries (Sterrett et al. 1996), and use of metal-containing pesticides, especially Cu and Zn in fungicides. Enhanced atmospheric deposition of some metals has also resulted from use and disposal of fossil fuels and their residues. Specifically urban sources include road traffic (Adachi and Tainosho 2004; Mielke et al. 2010), construction and weathering of buildings and other infrastructure (Davis et al. 2001), and indirect contributions from road dust (Harrison et al. 1981; Kelly et al. 1996; De Miguel et al. 1997; Banerjee 2003). Urban environments are not always predictably enriched in trace elements on a whole-city basis; for example, Acosta et al. (2015) found that population density does not affect metal concentrations in soil in some Spanish cities.

6.1.3 Sources of Other Contaminants

Asbestos The asbestos group of minerals (such as chrysotile, crocidolite, or tremolite, having fibrous crystal forms) is naturally occurring and has been mined and used widely in commercial products such as insulation, fireproof building materials, some concrete products, and vehicle brake linings (Alloway 2004; USEPA 2008; Department of Health (WA) 2009). In addition, naturally occurring asbestos may exist in soils near natural asbestos deposits (Lee et al. 2008). Asbestos may occur in urban soils following abrasion or disposal of any of these manufactured items or weathering of rocks containing minerals in the asbestos group. Human exposure to asbestos presents well-established health risks, which are discussed in Chap. 10. The risk is dependent on the form of asbestos in soil; the Department of Health (WA) (2009) identifies, in increasing order of risk, asbestos-containing material (intact products or larger fragments present in soil via disposal or spillage), fibrous asbestos (friable and smaller fragments of asbestos), and asbestos fines (free fibres and any fragments or aggregates of asbestos passing a 7 mm sieve). In many countries the use of asbestos, and management of land with asbestos contamination, is heavily regulated.

Plastics Contamination of global environments with plastics, particularly microplastics, is extremely widespread, with significant attention being given to the presence of plastic pollution in marine environments (Derraik 2002; Browne et al. 2011, and see Fig. 6.2a) due to their perceived and actual effects on marine organisms (Gregory 2009). Microplastics are mainly generated in terrestrial environments (Jambeck et al. 2015) and are known to occur in soils (Rillig 2012), though less is known about the occurrence and ecological effects of plastics in soils (Horton et al. 2017; He et al. 2018). An important secondary source of plastic pollution in urban environments is road dust (Abbasi et al. 2017); transport of microplastics occurs through natural drainage networks such as streams (Nizzetto et al. 2016). It is likely that constructed stormwater systems are also conduits for transport of microplastics derived from road dust and other terrestrial sources, but this issue has not yet been addressed significantly in published research. Even waste products such as cigarette butts may represent a source of persistent plastic pollution in urban soils (Green et al. 2019).

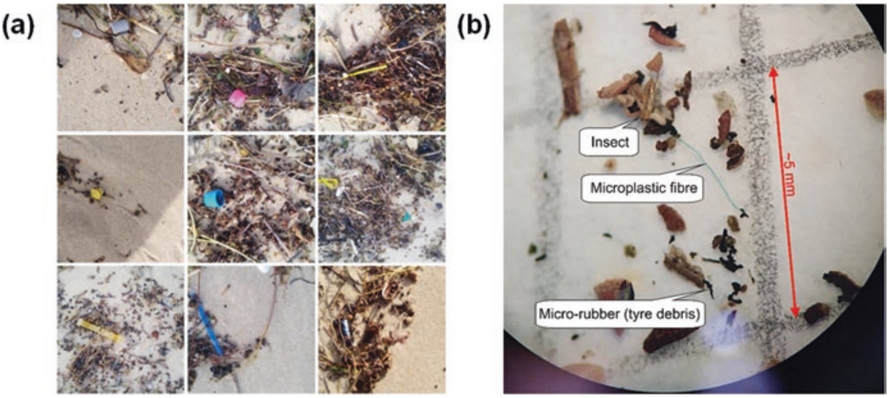

Fig. 6.2 (**a**) Plastic pollution in the wrack zone of a beach; (**b**) optical microscope image of microplastic and micro-rubber particles extracted from urban soil (images by Andrew W. Rate)

Plastics in soils, in particular microplastics (Fig. 6.2b), are of concern because they are known to interact with soil fauna (Huerta Lwanga et al. 2017; Maaß et al. 2017) and because of their capacity to adsorb and transport persistent organic pollutants (Da Costa et al. 2019) and potentially toxic metals (Zhou et al. 2019). The interactions of fauna or pollutants with plastics are not understood sufficiently well for their effects on soil ecosystem services to be assessed.

Manufactured Nanoparticles Nanomaterials, including a wide range of different type of nanoparticles, are materials manufactured with particle sizes in the range 1–100 nanometres (1 nm = 10^{-9} m). The field of nanotechnology is rapidly expanding, and nanoparticles have a wide range of applications including electronics, medical diagnosis and treatment, advanced solar power generation and storage, 'smart' fabrics, catalysis, and environmental remediation (Independent Working Group for PMSEIC 2005; National Nanotechnology Initiative 2019). The compositions of nanomaterials considered in soil research include silver (Ag), zerovalent iron (Fe), titanium dioxide, (TiO_2), magnetite (Fe_3O_4), stannic oxide (SnO_2), cerium oxide (CeO_2), antimony oxide (Sb_2O_3), zinc oxide (ZnO), carbon nanotubes, and a range of nanoparticulate plastics. Given the wide range of uses of nanomaterials and the high mobility of nanoparticles, a range of nanoparticulate substances are likely to be found in soils. To date, however, there are no measurements of manufactured nanoparticles in soils, except those that have been added experimentally to soils in a research context (Bundschuh et al. 2018). Manufactured nanoparticles need to be distinguished from the diversity of natural nanoparticles in soils (e.g. many Fe oxides, clay particles), meaning that current techniques are extremely complex (e.g. Praetorius et al. 2017 – future methods are also likely to be similarly elaborate).

Radionuclides Natural radionuclides (radioactive isotopes of some elements such as Cs, Ra, Ru, Th, U, etc.) in soils, sediments, and rocks generate the ambient radiation background which can be enhanced by urban construction using these materials (e.g. Medeiros and Yoshimura 2005). Potentially harmful concentrations of radioactive isotopes can be derived from human activities which may occur in urban areas. The most obvious of these are nuclear power generation accidents, such as Chernobyl and Fukushima (Andersson and Roed 1994; Endo et al. 2012). Other radionuclide contamination may be derived from mineral sand mining which can adjoin urban areas (Arogunjo et al. 2009) or from application of phosphogypsum fertilisers (Fernández-Caliani 2012).

Cyanide Simple cyanide compounds, mainly hydrogen cyanide (HCN) and related salts such as NaCN containing the cyanide anion CN^-, are extremely toxic with a very low fatal dose for humans. More complex cyanide compounds (such as the relatively simple $Fe^{II}(CN)_6{}^{4-}$) have substantially lower toxicity (Kjeldsen 1999). The most likely sources of cyanide in urban soils are current or former gas works sites, where extraction of coal gas produces HCN as one of the by-products (Mival et al. 2006). Cyanide is also used in electroplating and extraction of gold from ores, both activities which could conceivably occur in cities. Meeussen et al. (1994)

measured concentrations of free cyanide in groundwater and deduced that the concentrations were controlled by the low solubility of $Fe^{III}_4(Fe^{II}(CN)_6)_3$ (commonly called ‘Prussian blue’) which is formed during purification of coal gas. In a quite different context, Stec et al. (2019) found soil to be contaminated with free cyanide following the tragic Grenfell Tower fire in London, UK, in 2018. The source of cyanide in this instance was the partial combustion of, or volatilisation from, nitrogen-containing organic (e.g. polymer) materials in the fire.

6.1.4 Acid Sulphate Soils

Acid sulphate soils (often abbreviated to ASS) form from the oxidation of sulphide minerals (commonly pyrite, FeS_2) contained naturally in soils, which have previously remained in anoxic conditions due to saturation with water (Moormann 1963; Pons and Van Der Molen 1973). The exposure of such soil materials to atmospheric oxygen results in the oxidation of sulphides and the formation of sulphuric acid; if insufficient acid neutralisation capacity (e.g. carbonate minerals) is present, the soils become very acidic with $pH \leq 4$. The most common landscape category for acid sulphate soils to form in are coastal soils formed from parent materials which were previously inundated with seawater (e.g. during periods of higher sea level), such as estuaries. Drainage of these soils for urban development, such as canal construction, housing, or growing crops, reduces the water-filled pore space in the soil, allowing entry of oxygen and initiating sulphide oxidation (Figs. 6.3, 6.4). Formation of acid sulphate soils also occurs on sulphidic material dredged from drains and natural waterways (e.g. Fig. 2.7 and Fig. 6.4; Fanning 1990; Xu et al. 2018). Prior to oxidation by drainage or dredge-spoil deposition, the sulphidic soils are known as potential acid sulphate soil, or PASS, and these are distinguished from actual acid sulphate soils (sometimes abbreviated AASS) (Ahern et al. 2004).

Acid sulphate soils are known to occur in urban environments. For example, Fanning and Rabenhorst (1990) and Evans et al. (2000) describe formation of acid sulphate soils from material dredged from Baltimore Harbour, USA, within a timescale of a few weeks. Formation of acid sulphate soils on dredged sediment has also been described in the city of Brisbane, Australia (Clark and McConchie 2004). Appleyard et al. (2004) measured acidification of groundwater attributed to excavation and drainage of peat soils in Perth, Western Australia; the acidification also caused increased concentrations of dissolved arsenic, aluminium, and iron. The threats from acid sulphate soils are likely to remain an important issue, since they occur in highly populated areas in developing countries (Ljung et al. 2009). In addition, climate change and water abstraction in urban areas may accelerate their formation, if the groundwater level declines so that sulphidic materials are exposed to oxygen in soil or sediment pores (Salmon et al. 2014).

Acid sulphate soils can also be detrimental to urban infrastructure. For example, Plumlee et al. (2016) describe how the use of dredged materials in dune reconstruction caused corrosion of steel structures used for stabilisation of landforms. Concrete

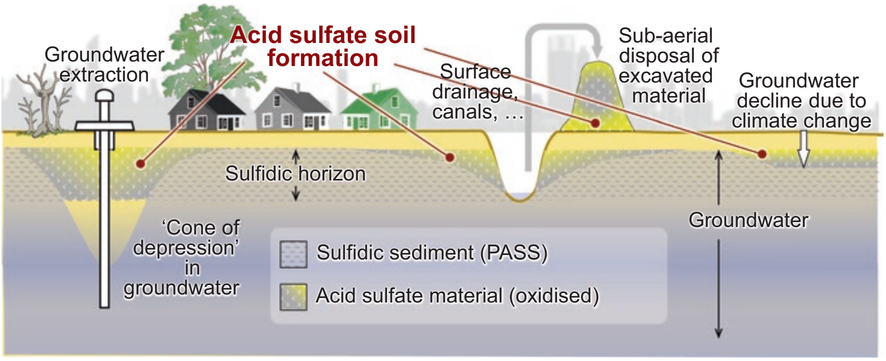

Fig. 6.3 Formation of acid sulphate soils in urban landscapes by processes which expose sulphidic material to atmospheric oxygen: groundwater extraction, excavations such as land drainage, subaerial spoil disposal, and climate change or other processes which lower groundwater such as altered hydrology (graphic by Andrew W. Rate)

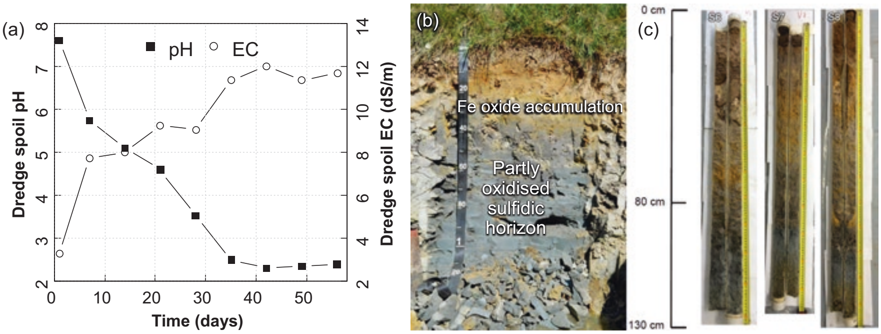

Fig. 6.4 (**a**) Change in pH and EC of dredge spoil after exposure to air (redrawn from data in from Evans et al. 2000); (**b**) acid sulphate soil profile in a peri-urban environment near Fredricksburg, Virginia, USA (coordinates 38.397 N, −77.456 W) (from Rabenhorst 2016 with annotations by Andrew W. Rate; used with permission from John Wiley and Sons); (**c**) soil cores from an acidified dredge spoil in Western Australia (−32.59 S, 115.782 E) (from Xu 2018, used with permission)

and limestone materials are also known to be damaged when exposed to acid sulphate materials (Golab and Indraratna 2009).

6.1.4.1 Other Acidic Urban Soils

Not all acidic urban soils have acidified by acid sulphate processes. Du et al. (2015) describe areas of acidic urban soils in southern China, centred on large urban areas, caused by atmospheric deposition of sulphur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) in rainfall. In this case the SO_2, NO_x, and NH_3 are derived from emissions from industries and other urban sources.

6.2 Controls on Contaminant Behaviour in Urban Soils

6.2.1 Reactions Involving Soil Solid Phases

Many trace elements predominantly exist as cations in natural systems (metallic forms such as $Cu^0_{(s)}$ may exist under some redox conditions, but are uncommon). The aqueous speciation of cationic metals is mostly as stable complexes or ion pairs, as well as aquo complexes and their hydrolysis products. The cationic metals commonly form insoluble oxides, hydroxides, carbonates, phosphates and sulphides. In general, most ionic forms of nutrient and trace elements are associated in soils with solid phases as described below and in Chap. 4.

6.2.1.1 Metals in Mineral Phases

Many trace elements occur as discrete mineral phases containing the element of interest as the primary structural cation (such as hydroxides, carbonates, phosphates, and sulphides) or as ions co-precipitated in variable proportions in the structure of more common minerals such as primary and secondary silicates and oxyhydroxides of Fe, Al, and Mn. While trace metals within primary or pedogenic mineral structures provide useful data on geochemical origins and soil-forming processes, these forms of elements are not usually considered to contribute to biological uptake due to their slow cycling within terrestrial ecosystems. Exceptions to this generalisation include trace metal ions co-precipitated with secondary iron or manganese oxyhydroxides or present in sulphide minerals. Changes in soil redox potential can result in transient fluxes of dissolved metal ions from these minerals via processes such as reductive dissolution of oxides or sulphide oxidation (Gambrell 1994; Singh et al. 1996; Sullivan et al. 2013). There is some evidence to show that over a wide geographical range, several trace elements including As, Cr, Co, Cu, Ni, Pb, and Zn co-occur with iron minerals in soils (Hamon et al. 2004). It should be noted, however, that despite the predominance of metals in mineral phases and their purported lack of bioavailability (Box 6.1), correlations between total metal concentrations in soils and bioavailability as determined by plant uptake have been observed (e.g. McGrath et al. 2000).

Nanoparticulate minerals. In some cases, metals in nanoparticulate phases in soils may contribute to enhanced bioavailability (Aruoja et al. 2009; Unrine et al. 2010). It is not yet clear whether this bioavailability reflects differences in solubility of, or adsorption onto, nanoparticulate solid phases (Theng and Yuan 2008) or whether nanoparticles themselves can be assimilated by organisms. Some studies in aquatic environments have found that toxicity may be attributed to nanoparticle dissolution, rather than a direct nanoparticle effect (Franklin et al. 2007; Mortimer et al. 2010). In some cases, however, it appears that nanoparticulate Cu and Zn oxides are themselves bioavailable or induce a physiological response (Ivask et al. 2010; Johnston et al. 2010).

6.2.1.2 Metals Retained by Surface Reactions: Chemisorption, Ion Exchange

It is important to make the chemical distinction between metals contained in mineral structures in soils and metal species which are retained at the solid-solution interface by a sorption mechanism.

Chemisorption (adsorption by formation of electron-sharing bonds; see Chap. 4) is likely to be very important in terms of bioavailability, for two main reasons. First, chemisorption removes metal ions from solution and therefore controls the concentration of free ions in that solution. A theory of biological uptake called the *free ion activity model* argues that the amount of uptake of an element is related mainly to the concentration of its free (uncomplexed) ions in solution (assuming that concentration is equivalent to chemical activity, which is an acceptable approximation in dilute solutions). Second, adsorption is a reversible chemical reaction, and desorption (the reverse reaction; release from adsorption) occurs in response to depletion of the dissolved ion. Some desorption reactions are fast enough that release of ions occurs over timescales which allow significant uptake by plants and other organisms. Chemisorption is commonly considered to show poor ‘reversibility’, deduced from observations of desorption hysteresis, that is, an apparently different equilibrium concentration of ions for adsorption compared with desorption (McLaren et al. 1981). Desorption hysteresis is most likely an effect of slow reaction rates (Barrow 1998).

Ion exchange. The occurrence of many metals as cations (e.g. Al^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) means that they can be retained by electrostatic sorption (i.e. ion exchange) on negatively charged soil colloids such as phyllosilicates and organic matter. Since variable charge is more negative at high pH, the capacity of soils to hold cations electrostatically increases as pH increases. The exchangeable fraction of metals usually represents a low proportion of total metal content in soils. Lower concentrations of exchangeable trace metals reflect the unfavourable thermodynamics of electrostatic sorption compared with other mechanisms and competition at charged particle-water interfaces by high concentrations of di- or trivalent major cations (Ca^{2+}, Mg^{2+}, Al^{3+}).

6.2.1.3 Metals in Solution and Aqueous Speciation

Concentrations of metals in soil solution are usually very low compared with those in the solid phase and reflect a combination of equilibrium with sparingly soluble and adsorbed or exchangeable forms of metals and formation of soluble inorganic and organic complexes (Wolt 1994).

6.2.2 Concentrations of Contaminants

Sorption reactions in soils can be considered to occur at ‘sites’ which effectively form a continuum in terms of their affinity for metal cations. At high concentrations of metals in soils, the high-affinity ‘strong’ chemisorption sites are fully occupied by ions. It therefore follows that the lower-affinity ‘weak’ sites then become more important for ion or molecule retention, since these will be the only sites left vacant for further adsorption. As a result, in contaminated soils, compared with uncontaminated, there may be a higher proportion of weakly bound ions or molecules, some of which may be held in ion-exchangeable form.

6.2.3 Transport of Metals and Nutrients

Transport phenomena for trace elements in soils have been reviewed thoroughly by Carrillo-González et al. (2006). Generally, mobility of metals is very low relative to the rate of water movement in soils. This low mobility is a consequence of reactions which retain metal ions in solid phases: (co)precipitation, adsorption, and ion exchange. The thermodynamics of these reactions favour the existence of metals in solid phases, and the low observed mobilities also suggest that rates of metal ion release to the aqueous phase are slow. Factors which affect these equilibria (mainly metal ion identity and concentration, amount and type of adsorbing phases, pH, and reduction-oxidation potential) consequently affect metal transport, as do formation of soluble complexes or adsorption on mobile colloids. The mobility of cationic metals in soils increases in the approximate order $Fe^{3+} < Pb^{2+}$, $Hg^{2+} < Al^{3+}$, Cu^{2+}, $Cr^{3+} < Co^{2+}$, Mn^{2+}, Ni^{2+}, Zn^{2+}, $Fe^{2+} < Cd^{2+}$ Ca^{2+} $Sr^{2+} < Na^{+}$, K^{+}, NH_4^{+} (trace element order from Kabata-Pendias 2011). The mobility of common anions in soils increases in the approximate order $H_2PO_4^{-}$, $H_2AsO_4^{-}$, MoO_4^{2-}, $HS^{-} < H_2BO_3^{-} < SO_4^{2-} < HCO_3^{-}$, NO_3^{-}, Cl^{-}, Br^{-} (Bohn et al. 2002). These rankings are only a guide, however, and the order is not replicated in all studies. For example, McQueen (2009) categorises the mobility of elements differently depending on pH (acidic, alkaline) and redox (oxidising, reducing) conditions, acknowledging that different reactions predominate depending on soil or regolith conditions.

The strong retention of many elements in soils results in small transport distances over observable timescales, which are commonly shown by the retention of contaminant-derived elements (e.g. metals; metalloids like As, Mo, or Se; or phosphate) in surface soil horizons, except in very acidic or sandy soils (Adriano 2001). Low pH, such as that encountered in acid sulphate soils or acid mine drainage, allows relatively large concentrations of metals to leach through soils (Boman et al. 2010). Mass transport of metal cations or oxyanions is likely to be dominated by preferential water flow in large, continuous soil pores (McLaren et al. 2004), and the amounts of metals transported are small reflecting the low concentrations in solution. In addition, there is increasing recognition of colloid transport (transport of sub-microscopic particles with metals or other elements attached) as a mechanism resulting in faster transport of contaminants (Sen and Khilar 2006). Metal ion supply to plants occurs more by diffusion than mass transport in uncontaminated soils (Hinsinger 2001; Degryse et al. 2009); shorter diffusion distances may remove diffusion limitations in contaminated soils. Transport by diffusion depends on the concentration gradient, ionic diffusion coefficient, and physical factors, such as soil water content and water film thickness (Sparks, 1989; Carrillo-González et al. 2006).

6.2.4 Time

Nutrients or trace metals may enter soil as ions or as components of amendments such as fertiliser or sewage sludge. After addition, short-term pedological processes act to change their speciation and bioavailability (Lu et al. 2005; Smolders et al. 2009). There are quite different timescales for urban additions, however, and commonly considered pedogenic timescales. In many cases, urban phenomena are very recent, and this represents a key difference for urban soils in which pedogenesis has had limited time to occur. Laboratory studies (Parfitt et al. 1989; Backes et al. 1995) commonly demonstrate that if nutrient or metal ions react longer with soil components they desorb less, and the desorbed fraction is released more slowly than for shorter reaction times. A contrasting concept is the ‘time bomb’ hypothesis, where it is thought that metals applied in organic residues such as sewage sludges will increase in bioavailability in the medium to long term, following mineralisation of organic adsorbing phases and associated acidification. McGrath et al. (2000), however, found that Zn and Cd extractability from soil did not change significantly more than 20 years following sewage sludge application, results which do not support either increased or decreased bioavailability in the long-term. Some steps towards resolution of this issue have been made by Bergkvist and Jarvis (2004), who show by a modelling approach that long-term changes in metal bioavailability vary according to soil and sewage sludge properties and metal content and that no universal outcomes exist. The general outcome for metal bioavailability, however, shown by Smolders et al. (2009), is for aging of metal-contaminated soils to decrease metal bioavailability (Fig. 6.5). Multiple mechanisms explain decreased bioavailability with aging, including leaching-induced changes in soil solution properties and adaptation of organisms (Smolders et al. 2009) as well as the changes in solid-state speciation implied by decreased desorption rates. Regulatory guidelines, such as the Australian National Environment Protection Measure (National Environment Protection Council 2013b), distinguish between aged and fresh contamination, with acceptable concentrations of some elements in aged contaminated soils being lower than for freshly contaminated soils.

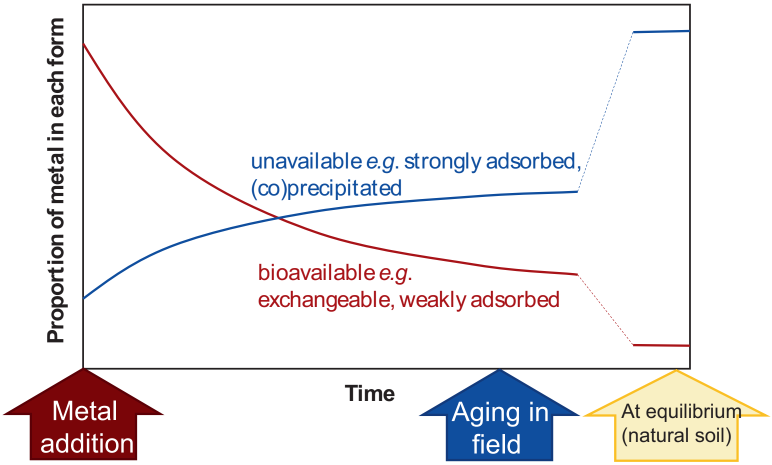

Fig. 6.5 Simplified effect of time on forms of metals in soils

6.2.5 Soil Properties

Numerous studies have shown that a range of bulk soil properties have observable effects on the behaviour of elements in soils.

6.2.5.1 Soil pH

Soil pH affects elements in different ways depending on their dominant forms and reactions in soils.

Nitrogen Low pH reduces overall decomposition of soil organic matter which is the largest store of nitrogen in soils (Haynes 1986). Nitrification (microbial oxidation of ammonium to nitrate) is more sensitive than ammonification to low pH, so ammonium tends to accumulate in acidic soils. Since there is a large range of soil biota contributing to organic matter decomposition and release of soluble nitrogen species, overall nitrogen availability is relatively insensitive to soil pH (McLaren and Cameron 1990).

Phosphorus Low pH reduces the availability of phosphorus, since dissolved concentrations of Al^{3+} and/or Fe^{3+} are greater in acidic soils, and the solubility of aluminium and iron phosphate minerals (e.g. strengite, variscite) is low. Similarly, at high pH, the dominant exchangeable cations in soils are usually Ca^{2+} and Mg^{2+} (Lindsay et al. 1989), which maintain greater equilibrium concentrations of Ca^{2+} and Mg^{2+} in soil solution. Consequently, at high soil pH, calcium and/or magnesium phosphates may exceed their solubility products and precipitate. For these reasons, the bioavailability of phosphorus is at a maximum at near-neutral pH (approximately pH 6–7).

Cationic Metals The combined effects of cation exchange, adsorption, and co-precipitation reactions in soils, as described in Chap. 4, mean that metal bioavailability (Box 6.1) decreases as pH increases (McBride 1994; Sauvé et al. 2000). Since soil pH exerts such an important control, especially on metal behaviour, it is used to adjust guideline concentrations in contaminant regulations (e.g. the Australian National Environment Protection Measure·, National Environment Protection Council 2013b).

6.2.5.2 Cation Exchange Capacity

Cation exchange capacity (CEC) in soils is a key property affecting contaminant behaviour. The CEC itself is dependent on (and probably integrates the effects of) other soil properties such as pH (see above) and the content of soil components bearing negative charge (such as organic matter and clays; see below). Smolders et al. (2009) showed that effective CEC (i.e. CEC measured at the soil's unadjusted pH) was able to explain a significant proportion of the variation in toxicity to organisms at any given total metal concentration. Like soil pH, CEC is an important control on metal behaviour and is also used to adjust regulatory guideline concentrations of contaminants (e.g. National Environment Protection Council 2013b).

6.2.5.3 Soil Organic Matter or Organic Amendments

Effects on Nutrients Soil organic matter is a dominant contributor to soil cation exchange capacity and therefore has a large influence on the behaviour of exchangeable cations in soils. Greater soil organic matter content has been shown to decrease leaching of K^+ and NH_4^+ (Griffioen 2001; Vogeler et al. 2011). In addition, the greater CEC of organic materials retains a reserve of plant-available nutrients, and organic matter added to soils may itself contain useful nutrient contents (Gallardo-Lara and Nogales 1987; Weber et al. 2007). The addition of *organic amendments* to soils, especially those containing larger proportions of easily mineralisable ('labile') carbon compounds, can lead to greater than normal decomposition of pre-existing soil organic matter. This is known as a *priming effect* and is caused by the ability of organic amendments to increase the activity and/or growth of the soil microbial population. In addition, some other microbially driven processes in soils related to nutrient cycling (e.g. sulphate reduction, denitrification) are promoted by an external source of labile carbon compounds (Thangarajan et al. 2013).

Effects on Cationic Metals It is well known that metal cations adsorb to organic matter in soils (Young 2012) and that this adsorption renders the metals both immobile and unavailable to organisms. Some external sources of organic matter, especially those derived from urban waste materials such as sewage sludges (biosolids) or municipal solid waste composts, may contain relatively concentrations of potentially toxic trace elements including cationic metals (Alloway 2012). In many cases, the metal content of added organic materials is great enough that application to soils to meet nutrient requirements may result in exceeding guideline concentrations for potentially toxic trace elements. Some research has evaluated the so-called time bomb hypothesis which predicts that the organic matter in metal-containing soil amendments will eventually decompose, reducing the ability of the soil systems to adsorb metals and creating a sudden increase in metal bioavailability (Chang et al. 1997). The 'time bomb' increase in metal bioavailability may or may not occur, however, depending on how much the organic amendment increases the natural adsorption capacity of the soil, whether the organic amendment also contains an inorganic fraction which can immobilise metals, and the actual metal content of the organic amendment (Bergkvist and Jarvis 2004). Organic matter in soils may also exist in dissolved form and provide ligands which form soluble complexes with trace element cations. In such cases the mobility of metals may actually increase as a result of addition of an organic amendment (Kabata-Pendias 2004).

6.2.5.4 Soil Redox Potential

Effects on Nutrients In aerobic soils (i.e. with an adequate supply of oxygen via air-filled soil pores), nitrogen and sulphur are most stable as the oxyanions NO_3^- and SO_4^{2-}. For nitrate (NO_3^-) in particular, this can result in leaching of N into groundwater due to the minimal retention of NO_3^- by most soils. Under reducing conditions (e.g. in saturated soils), nitrate is depleted by denitrification, and the conversion of ammonium (NH_4^+) to NO_3^- is suppressed. Prolonged reducing conditions allow microbial sulphate reduction to occur in soils to form sulphide species (HS^-/S^{2-}; see Table 4.2). The other macronutrient elements (e.g. P, K) are not directly affected by redox processes but can be affected indirectly; the main indirect effect is release into solution of adsorbed phosphate ($H_2PO_4^-/HPO_4^{2-}$) from iron oxides under reducing conditions, since anoxia favours reductive dissolution of Fe^{III} (hydr)oxides, with simultaneous release of many adsorbed ions.

Effects on Trace Elements Iron (Fe) and several minor or trace elements (including As, Cr, Co, Cu, Mn, Ni, and V and the rare-earth elements Ce and Eu) are able to exist in more than one oxidation state, depending on soil redox potential, over the range of redox potentials typically encountered in soils (McBride 1994). In aerobic soils, elements normally existing as cations remain in cationic form; trace element oxyanions are also stable, and both are predominantly adsorbed to soil colloids or present in the mineral structure of various solid phases. Changes in redox species are important reactions for some elements, and we mainly consider chromium (Cr) and arsenic (As) due to the high potential toxicity of both elements.

Chromium generally exists in the trivalent (Cr^{3+}) oxidation state in both oxidised and reduced soils in species such as mineral forms like $Cr(OH)_3$ or adsorbed $Cr(OH)_2^+$ (Gonnelli and Renella 2012). In some oxidised soils, however, including soils contaminated with chromium, the more mobile, toxic, and carcinogenic Cr^{6+} species (mainly chromate CrO_4^{2-} or dichromate $Cr_2O_7^{2-}$) can persist – these are usually called ‘chromium six‘and abbreviated to Cr^{VI}. Persistence of Cr^{VI} is greater if Mn oxides are abundant or if minimal concentrations of typical electron acceptors for the reduction of Cr^{VI} species exist. Under natural soil conditions, it is generally soil organic matter which reduces Cr^{VI} to non-toxic Cr^{III} species (Gonnelli and Renella 2012).

Arsenic is mainly present in aerobic soils as the oxyanionic As^{V} species AsO_4^{3-} (arsenate) as a structural ion in mineral solid phases or as adsorbed $H_2AsO_4^-$ or $HAsO_4^{2-}$ (still arsenate; these are the protonated forms, which are predominant when arsenate is dissolved in water). Under reducing conditions, there are two pathways for transformation of arsenate, depending on the soil organic matter content. In most soils, the product of chemical reduction is the As^{III} species arsenite $H_3AsO_3^0$; in highly organic soils, methylated forms of arsenic(III), such as methylarsonic acid or trimethylarsine oxide, can form (Wenzel 2012; Young 2012).

Reductive dissolution of iron(III) (hydr)oxides (and in some soils, Mn(IV) oxides), as for phosphate above, releases trace element cations or oxyanions which were adsorbed onto or co-precipitated with the oxide mineral (Stone and Morgan 1987). Typically, reduction of Fe and Mn oxides occurs prior to sulphate reduction in the ‘redox cascade’ (McBride 1994). The increase in dissolved metal concentrations may be transient, since precipitation of trace element cations may occur by formation of hydroxides at the higher pH commonly associated with reducing conditions or as sulphate reduction proceeds (see below). Organic ligands present in saturated soil environments may also prolong or enhance dissolved metal concentrations (Grybos et al. 2007).

Formation of sulphide minerals occurs under reducing conditions, with the onset of sulphate reduction, which produces free sulphide as HS^- (or H_2S). The sulphide produced by sulphate reduction reacts with cationic metals and arsenic, resulting in precipitation of discrete trace element sulphides or co-precipitation of trace elements within iron(II) sulphide minerals. Sulphide minerals maintain trace elements in forms with extremely low bioavailability, so long as reducing conditions persist (e.g. by continued saturation/submergence of soil) (Gambrell 1994). The risk of subsequent oxidation is affected by recrystallisation during early diagenesis; the initial minerals to form such as amorphous ferrous monosulphide (FeS), or mackinawite, have extremely rapid rates of oxidation, whereas more stable (recrystallised) minerals such as pyrite (FeS_2) oxidise more slowly (Morgan et al. 2012).

6.2.5.5 Soil Mineral Phases/Major Elements

The existence of mineral phases containing trace elements, or associations of trace elements with specific minerals or major elements, is difficult to prove experimentally. We cannot simply rely on correlation analyses showing a positive relationship between a trace element and a mineral or major element, since these never imply causation. In addition, the very widely used sequential selective extraction methods largely categorise trace elements into operational fractions, which are not completely specific or which overlap, so sequential extraction does not provide sufficient evidence either. More compelling data is obtained from microchemical techniques, such as energy dispersive X-ray microanalysis (EDX or EDS) which is conducted in combination with electron microscopy or micro-X-ray fluorescence (μ-XRF) which requires a synchrotron radiation source. The 'gold standard' method is obtaining X-ray or electron diffraction patterns on samples of a few microns or less in diameter, which can be used to identify individual mineral phases and which requires a transmission electron microscope. In this textbook we have tried to cite research using at least one microchemical method to support their conclusions.

Clay Content In strictly chemical terms, the role of phyllosilicate (layered aluminosilicate) clays should be distinguished from the effects of 'clay' as a soil textural category, since Fe, Al, and Mn oxides and other reactive minerals may be present in the ≤0.002 mm grain size fraction. Using a range of advanced techniques, phyllosilicate clay minerals have been shown to host trace element ions released by chemical weathering and redistributed in soils by formation of secondary minerals during pedogenesis (e.g. Batista et al. 2018). Trace element cations are also retained by clay in soils by surface reaction mechanisms such as adsorption (Schulthess and Huang 1990) and ion exchange (Majone et al. 1998; Abanda and Hannigan 2007).

If the simple grain size definition of clay is accepted, numerous studies show a positive correlation between metal content and clay content. Some weaker evidence that this relationship is due to the presence of aluminosilicate clays would be a similar positive correlation between metal content and aluminium content (e.g. Pardue et al. 1992) or information that other mineral phases are not present in the ≤0.002 mm fraction from an X-ray diffraction technique.

Iron/Fe Oxides and Hydroxides Very large databases of soil properties demonstrate relationships between trace element and iron concentrations across multiple soil environments worldwide (Hamon et al. 2004); see Fig. 6.6. The most likely explanation for these globally consistent relationships is the association, by adsorption or co-precipitation, of trace metal ions with iron(III) oxides and/or hydroxides (e.g. Singh and Gilkes 1992; Matera et al. 2003; Daṃbkowska-Naskręt 2004).

Calcium/Carbonate Minerals A number of cationic trace elements (including Cu, Ni, Pb, and Zn) are known to form discrete carbonate mineral phases or associations with carbonate minerals (Yarlagadda et al. 1995; Adamo et al. 1996; Dermatas et al.

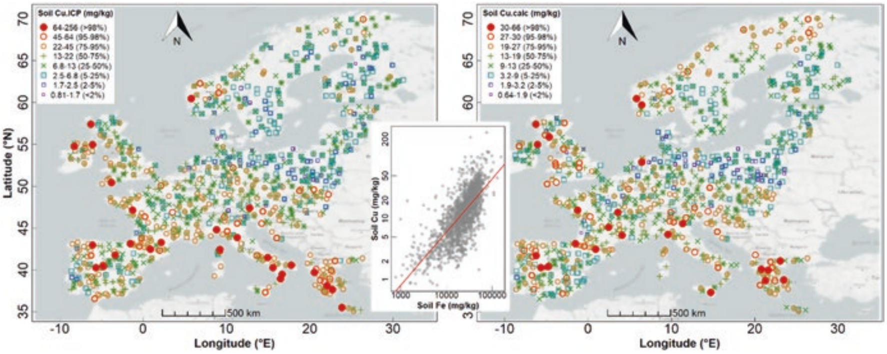

Fig. 6.6 An example of continental-scale trace element-iron relationship: copper concentration ranges in European soils (left), relationship between copper and iron concentrations (inset), and copper predicted from iron concentration (right). Data from the FOREGS survey (Salminen et al. 2005); graphic by Andrew W. Rate

2006). The existence of cadmium carbonate ($CdCO_3$, octavite) has been inferred from soil pore water concentrations of Cd^{2+} and CO_3^{2-} which appear to have an ion product close to the K_{sp} for octavite and therefore to be controlled by octavite solubility (e.g. Street et al. 1977).

Sulphides Sulphide precipitation is important for many trace elements in reduced soils, as discussed above.

Other Materials Numerous other mineral phases containing trace elements, including oxides, phosphates, sulphates, and silicates, have been detected in soil environments (e.g. Adamo et al. 1996; Buatier et al. 2001; Ettler et al. 2008).

6.3 Effects of Inorganic Soil Contaminants on Ecosystem Services

6.3.1 Nutrients

6.3.1.1 Soil Environments

The most important effects of high concentrations of nutrients in soil are related to the likelihood that the soil's retention capacity (e.g. by adsorption or ion exchange) may be exceeded. In many cases this results in export or loss of nutrient(s) from the soil system into a *receiving environment* (this issue is discussed in the following subsection below).

Soils having excessive concentrations of nutrients, or *eutrophic* soils, may show different ecosystem biodiversity and functioning than natural soils (Schindelbeck et al. 2008). For example, in some environments, nutrient toxicity to native plant species from soil eutrophication, such as the sensitivity of some Proteaceae to phosphorus, may limit land rehabilitation efforts (Nichols and Beardsell 1981; Wolff et al. 2017). The consequences of soil eutrophication for the ecology of soil microorganisms and fauna will be addressed in Chap. 8.

6.3.1.2 Receiving Environments

Concentrations of nutrient elements in soil in excess of the capacity of organisms to absorb them will often result in transfers out of the soil system or losses. Nutrients can be lost from soils by leaching (mass transport with water), soil erosion, and for some elements by soil to atmosphere fluxes (such as volatilisation of gas-phase ammonia or hydrogen sulphide or denitrification to produce nitrous oxide) (Carpenter et al. 1998; Groffman et al. 2002).

The effects of loss of nutrients into waterways is common to cause excess concentrations of nutrients in water, or *eutrophication*. The high concentrations of nutrients remove limitations to biomass production for aquatic photosynthetic organisms such as algae, causing phenomena such as algal blooms. In aquatic systems (such as streams, rivers, lakes, and estuaries), productivity is most commonly limited by the supply of phosphorus or nitrogen (Carpenter et al. 1998; Peters and Donohue 2001). Eutrophication and algal blooms have their own adverse environmental effects, such as oxygen depletion, toxicity, and formation of sedimentary organic ooze, which are beyond the scope of this book.

Gas phase losses of nutrients from soils have different types of environmental consequences. Volatilisation of ammonia or hydrogen sulphide can cause toxicity to plants, but, especially at higher concentrations, they are more commonly a nuisance odour to humans (Iglesias Jiménez and Perez Garcia 1989; Muezzinoglu 2003). Denitrification is more insidious; in theory, the end product of denitrification is the environmentally benign nitrogen gas (N_2). In reality, reaction intermediates such as oxides of nitrogen are released during denitrification in soils, in particular nitrous oxide (N_2O) which is a powerful greenhouse gas (on a mass basis, 298 times more effective at trapping solar radiation than CO_2 (IPCC 2007)). Nitrous oxide is also an ozone-depleting substance and is the most important ozone-depleting gas following the widespread ban on halocarbons in the late twentieth century (Ravishankara et al. 2009).

6.3.2 Trace Elements

6.3.2.1 Plants

It is well known that high concentrations of trace elements in soils can lead to toxic effects on plants (Nagajyoti et al. 2010). Metals have a range of biochemical effects on plants (e.g. interfering with essential enzymatic systems) which result in reduced growth related to higher concentrations of metals in plant tissues. The uptake of potentially toxic metallic or metalloid elements by plants confers the possibility of transfer of metals through food chains to higher trophic levels, including consumption of metal-contaminated produce by humans (McBride 1995; Abrahams 2002; Bolan et al. 2013).

6.3.2.2 Soil Microbiota, Meso- and Macrofauna

Soil pollution with potentially toxic trace elements is well-known to affect the growth, functioning, and diversity of soil microorganisms, mesofauna, and macrofauna (He et al. 2005; Smolders et al. 2009; Pauget et al. 2013). These issues will be discussed in much more detail in Chap. 8.

6.3.2.3 Humans

Humans can be affected by soil contamination with potentially toxic trace elements by consumption of plant produce grown on contaminated soils, as discussed previously (Abrahams 2002; Laidlaw et al. 2018). This pathway for ingestion of contaminants is of particular concern due to the growing importance of both community gardening and urban agriculture for food production (Thebo et al. 2014; Egendorf et al. 2018). A number of other mechanisms also result in soil to human transfers of trace elements. Dust entering the atmosphere from contaminated soil (Ljung et al. 2009) potentially results in a decline in air quality and the potential for adverse health effects due to inhalation of fine (< 10 μm) dust. Children are known to accidentally or deliberately consume soil, and this is a known vector for lead poisoning and ingestion of other potentially toxic elements (Mielke et al. 1999; Ren et al. 2006). Finally, trace elements may leach from contaminated soils as dissolved or colloidal forms, particularly at low pH or in very sandy soils (Imperato et al. 2003; Appleyard et al. 2004), posing a threat to water used for human consumption.

6.4 Measurements and Data

Total analyses are those which measure the total concentration of an element regardless of chemical species or physical location in the soil. The methods used are based on complete dissolution of a soil sample using a mixture of concentrated acids, fusion of the soil sample with a flux (e.g. lithium metaborate/tetraborate) followed by dilute acid dissolution, or using a spectroscopic instrumental technique such as X-ray fluorescence or neutron activation analysis (Sparks et al. 1996). Total elemental analyses do not generally correlate well with biological uptake (McLaughlin et al. 2000; Nolan et al. 2003; Rayment and Lyons 2010) and include background concentrations of contaminants as well as anthropogenic additions to soils.

Partial analyses aim to measure an actual species, such as exchangeable metals, or a conceptual chemical form, such as bioavailable phosphorus, of a nutrient or metal in soils. Despite the importance of chemical speciation in soils, however, methods for accurately determining speciation require further refinement. For example, the existence of some elements in specific mineral phases in soils may be established using electron microscopy in conjunction with microprobe techniques such as EDS (having relatively high detection limits, e.g. Essington and Mattigod 1991), synchrotron X-ray spectroscopic techniques (Xia et al. 1997), or SIMS (Chardon et al. 2008). Determination of truly dissolved forms of elements (e.g. 'free' ions) remains complicated by the difficulties in separating truly aqueous species from dispersed colloids. Techniques which target a conceptual fraction (such as 'bioavailable', 'mobile', or 'plant available') rather than a discrete species may, in fact, be more useful in predicting biological uptake than true speciation methods (see Box 6.1; McLaughlin et al. 2000; Zhang et al. 2001).

Box 6.1: Concepts for Bioavailability in Soils

Bioavailability and bioaccessibility. Semple et al. (2004) discuss two related concepts, bioaccessibility and bioavailability. A substance such as a potentially toxic trace element is bioavailable if a transfer from soil into an organism can occur (Fig. 6.7). A substance is bioaccessible if it is able to resupply the bioavailable pool, but organisms are not presently in the same space in the soil, or if a slow process limits release of the bioavailable forms.

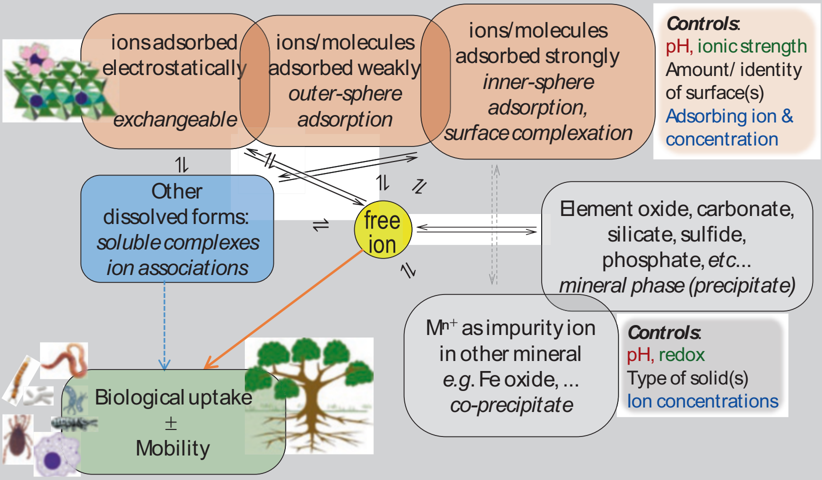

Fig. 6.7 Interactions between chemical species in soils and their relationships with bioavailability – example for metal ions (graphic by Andrew W. Rate)

(continued)

Box 6.1 (continued)

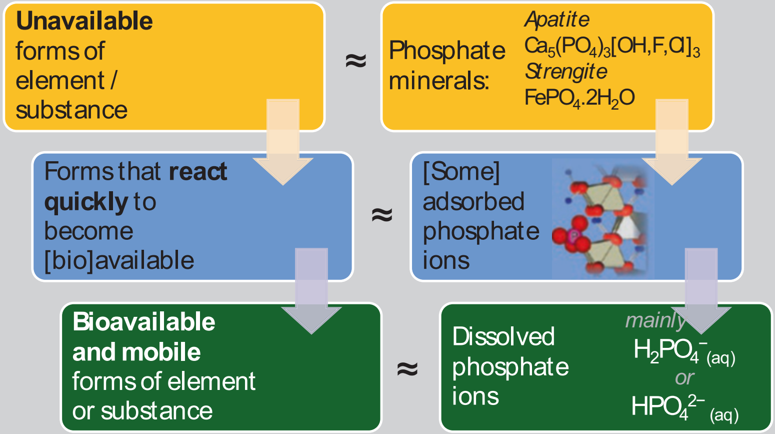

Fig. 6.8 Simplified relationship between chemical speciation and bioavailability for phosphorus (P) in soils (graphic by Andrew W. Rate)

Relationships of bioavailability to speciation. The chemical form of trace elements has a very large effect on those elements' availability or accessibility to organisms (Fig. 6.8). It is commonly assumed that 'bioavailability' continuously decreases from free ions in solution to exchangeable ions, chemisorbed ions, with ions within pedogenic, then primary, mineral structures having the lowest bioavailability (Kabata-Pendias 2004). Bioavailability of nutrients also includes elements such as N, P, and S contained in organic molecules, released ('mineralised') by soil microorganisms during decomposition processes (Stevenson 1994). The ionic forms (NH_4^+, NO_3^-, $H_2PO_4^-$, SO_4^{2-}, K^+) are those bioavailable to plants, with potentially bioavailable forms being exchangeable ions for N and K (NH_4^+ and K^+), and weakly adsorbed forms, or higher-solubility minerals, for P and S (Wild 1988; Hinsinger 2001).

Adjustment of concentrations using soil properties. Metal bioavailability can also be estimated using soil metal concentrations in combination with other quantitative soil chemical information. McBride et al. (1997) advocated using total concentrations of Cu, Zn, Cd, and Pb in soils, together with values of soil pH and organic carbon content which affect metal ion speciation, to estimate concentrations of these metals in soil solution. The work of Smolders et al. (2009) showed that the best empirical predictor of toxicity to plants or invertebrates (earthworms or collembolans), over a large range of soils, was the ratio of total concentration of metal in soil to the soil's effective cation exchange capacity (ECEC). More accurate predictions were obtained if this ratio was corrected for leaching and/or aging of contaminated soils in the

(continued)

Box 6.1 (continued)

field. Just because the metal to ECEC ratio is useful, however, does not prove that exchangeable metal ions are the actual bioavailable species. Considerable uncertainty still surrounds the ability to predict bioavailability from soil measurements (Smolders et al. 2009).

Free ion activity model(s). It is usually assumed that plants or soil microorganisms can only take up the free, uncomplexed metal ion from solution (Parker and Pedler 1997). This is the basis for the 'free ion activity model' of bioavailability. Many studies have shown a positive relationship between free metal ion activity and plant uptake (e.g. Zhang et al. 2001). The free ion activity model has conceptual shortcomings, however, since it does not account for resupply of metals from soil solid phases and also does not allow for chemical reactions on organism surfaces. The free ion activity model would probably be too simplistic for a complex environment such as a soil (Parker and Pedler 1997).

Models based on metal resupply. We now understand that metal ion uptake by plants is controlled by both the free ion concentration **and** the rate of resupply (e.g. desorption) from soil solid phases. In particular, Zhang et al. (2001) showed that the 'effective concentration' of Cu (C_E) measured by a technique called 'diffusive gradients in thin films' (DGT) was the best predictor of copper uptake by plants. DGT analysis measures the concentration of ions released by diffusion over a fixed time interval, so it closely resembles the mechanism for biological uptake. Oporto et al. (2009) and Degryse et al. (2009), however, found that DGT is not a good predictor of plant metal uptake at high concentrations of metals in soil, as would be the case in contaminated soils. In contaminated soil environments, biological uptake may not be limited by diffusion.

Bioavailability models which consider reactions at organism surfaces. The biotic ligand model (BLM) considers competitive, pH-dependent, chemical interactions between ions in soil solution, reactive solid phases, and the biological receptors on organisms (Di Toro et al. 2001). Thakali et al. (2006) showed that a BLM could predict toxicity of Cu^{2+} and Ni^{2+} to plants (measured as decreased root growth), from the amount of Cu^{2+} or Ni^{2+} bound to a biotic ligand (e.g. the root surface). Predictions by the soil BLM were made only for relatively large total metal ion concentrations, since the emphasis was on toxicity caused by contaminated soils. A simplified biotic ligand model has been shown to predict Cu toxicity for a wide range of organisms, particularly plants and invertebrates, with toxicity effects commencing at uncontaminated soil Cu concentrations (<10 mg/kg) (Qiu et al. 2013).

Practical use of bioavailability concepts. In practice, the most useful approach for incorporating the principles of bioavailability into managing soil contamination is to adjust the maximum permissible concentrations using soil

(continued)

Box 6.1 (continued)

properties. The critical soil properties are those known to affect bioavailability – usually pH, cation exchange capacity, clay content, and organic carbon content. Whether the contamination is recent or 'aged' is also important. These concepts have entered regulatory frameworks in the USA and Europe (Naidu et al. 2015), Australia (National Environment Protection Council 2013b), and in the UK (Martin et al. 2017).

There are a wide range of methods for both total and partial analyses of nutrients and metals in soils. Some of the more commonly used methods, or types of methods, are outlined in the following subsections.

6.4.1 Total Elemental Analyses

The analysis of soil for inorganic contaminants is done for numerous reasons. Some measurements, such as pH, redox potential, or clay content are used as supporting information, to characterise the soil environment for a better understanding of the behaviour of the contaminants of interest. For the measurement of nutrients or contaminants in soils, there are two main options.

Nitrogen The most convenient method for total nitrogen (and carbon) in soil is by high-temperature combustion in a specialised instrument. The nitrogen is converted to N_2 gas which is measured with a thermal conductivity detector. Total nitrogen can also be measured by 'Kjeldhal' digestion in concentrated sulphuric acid, which converts all nitrogen into ammonium which can be measured by automated colourimetric analysis (Rayment and Lyons 2010).

Phosphorus, Sulphur, and Potassium The simultaneous measurement of P, S, and K, and most other major elements, in soils is most conveniently achieved using X-ray fluorescence (XRF). Total P and K can also be measured by a fusion/dissolution method followed by separate analyses for the resulting dissolved phosphate and potassium. Total S can be measured by high-temperature combustion and detection of the evolved SO_2 gas by infrared spectrometry (Rayment and Lyons 2010).

Major Elements – Na, K, Mg, Ca, Al, Fe, Si The 'gold standard' method for major element analyses in soils is X-ray fluorescence (XRF) (Karathanasis and Hajek 1996). Comparisons in the author's laboratory indicate that, for major and minor elements in soil and regolith samples, results comparable with XRF are obtained using fusion in a lithium metaborate/lithium tetraborate flux, followed by dissolution in dilute hydrochloric acid with analysis of the solution using ICP-OES (e.g. see Du et al. 2012).

Minor and Trace Elements Most metal and metalloid contaminants are present in soils at concentrations ≤0.1% (1000 mg/kg) by weight and so are categorised as minor or trace elements. Metal contaminants which are of interest in urban soils (not a complete list of possibilities!) include Ag, As, B, Cd, Cr, Co, Cu, Hg, Li, Mn, Mo, Ni, Pb, V, and Zn, with rising interest in the rare-earth elements such as Ce, Gd, La, and Nd due to their increasing use in electronics, medical imaging, and other technologies. The detection limits of XRF are too high (≥ 5 mg/kg for some elements), and so acid dissolution or fusion methods are more commonly used, followed by a more sensitive technique such as inductively coupled plasma-optical emission spectrometry (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS) (Geboy and Engle 2011).

6.4.2 Partial Analyses

Nitrogen The most common method for ‘available’ nitrogen (mainly dissolved and exchangeable NH_4^+ and NO_3^-, with trace concentrations of NO_2^-) in soil is by extraction in 2 mol/L KCl solution. The NH_4^+ and $NO_3^- \pm NO_2^-$ in the resulting extract are usually determined using colourimetric techniques, often automated (Mulvaney 1996; Rayment and Lyons 2010).

Phosphorus There are numerous methods for measuring ‘available’ phosphorus, typically using solutions able to displace weakly adsorbed phosphate such as sodium bicarbonate (Rayment and Lyons 2010) or dilute acids (e.g. acetic acid, sulphuric acid – see Kuo (1996) for more detail). The extracting solution contains dissolved $H_2PO_4^-$ and/or HPO_4^{2-} which can be measured colourimetrically.

Sulphur The analysis of ‘available’ sulphur (dissolved and adsorbed sulphate) is conceptually similar to that for phosphate. A phosphate solution is used to displace sulphate ions into solution, and ICP-OES can be used to measure dissolved sulphur (assuming this is mostly SO_4^{2-}) (Rayment and Lyons 2010).

Potassium Plant-available potassium is often considered to be equivalent to exchangeable potassium; soil is extracted with a solution containing a competing cation (commonly ammonium or calcium salts, although the phosphate-extracting solution, sodium bicarbonate, is also used), following which K can be determined by ICP-OES (Sparks et al. 1996; Rayment and Lyons 2010).

6.4.2.1 Partial Analyses for Metals and Metalloids

Trace elements. There are probably even more choices of extracting solution for metals and metalloids than for nutrients, reflecting multiple analytical objectives (e.g. plant nutrition, environmental assessment, or mineral exploration) and the influence of soil properties. Some wet chemical extraction methods (e.g. 0.01 M $CaCl_2$; Whitten and Ritchie 1991) appear to selectively determine trace metal cations in the ion-exchangeable fraction, although this may not have been the original intention of the method. The success of some of these methods, in predicting plant uptake, may reflect the importance of weakly adsorbed and/or exchangeable ions as a buffer to replace removal of ions from the soil solution. A simple assumption we can make is that the fractions of metals in soils measured by partial chemical extraction represent the bioavailable and/or bioaccessible component, without the need to explain how or why the analysis 'works'. This is the rationale behind the numerous chemical extraction techniques for measuring 'bioavailable' or 'mobile' metals in soils. These methods extract soil with solutions containing (singly or in combination) electrolytes, dilute acids and/or buffers, complexing agents, oxidising agents, or reducing agents (Chao 1984); some examples appear in Table 6.1. Another theory is that bioavailability should be assessed by simulating the chemical conditions within an organism. For example, Ma et al. (2009) and Smith et al. (2010) assumed that using an extractant which simulates the composition of earthworm gut fluids (e.g. relevant enzymes, anoxia) will more accurately reflect uptake and toxicity than total metal and other extractable metal concentrations.

6.4.3 Field Measurements

Measurements of soil chemical properties in the field offer the advantages of immediacy of obtaining data, and there may also be benefits if samples change between sampling and laboratory analysis, for example, following exposure to CO_2 or O_2 in the atmosphere. Simple field analyses of soil properties such as pH and electrical conductivity (EC) are routine, using appropriate electrodes and battery-powered meter (calibrated with standard or buffer solutions) on a standard suspension of soil in water or electrolyte solution (e.g. 0.01 mol/L $CaCl_2$) (Rayment and Lyons 2010). The electrical conductivity measurement can be converted to an approximate content of soluble salts in soil. Measurement of soil pH in the field after oxidation with 30% hydrogen peroxide (H_2O_2) solution can also allow semi-quantitative estimation of the presence of potential acid sulphate soil materials, using the difference between pH in water and pH after peroxide oxidation (Ahern et al. 2004). Less commonly, soil reduction-oxidation potential may also be measured in field soils using a platinum electrode, but the analysis suffers from poor electrical contact in dry soils and variability due to the presence of redox microenvironments.

Even simpler field tests are based on use of colour indicators, but these are seldom used due to the reliability and availability of electrode-based pH and EC

Table 6.1 Examples of partial analysis methods, based on extracting solutions, for metals in soils

Solution	Chemical basis	Species or fraction targeted	Reference	Extracting solutions targeting similar fractions
0.005 M[a] DTPA [b], 0.1 M triethanolamine, 0.01 M $CaCl_2$, pH 7.3	DTPA forms stable, soluble complexes with metal ions; triethanolamine buffers pH, Ca^{2+} suppresses $CaCO_3$ dissolution	Plant available micronutrient metals – Also used for potentially toxic metals, probably dissolved, exchangeable and weakly adsorbed metal ions	Lindsay and Norvell (1978)	EDTA [c] (Snowdon and Birch 2004)
0.01 M $CaCl_2$	Ca^{2+} in solution can displace exchangeable metal ions	Dissolved and exchangeable metal ions	Whitten and Ritchie (1991)	Ammonium acetate, NH_4NO_3, $CaCl_2$, $MgCl_2$, $BaCl_2$, $Mg(NO_3)_2$ (Chao 1984; Shuman 1985; McLaughlin et al. 2000)
4 M HNO_3	Dilute acid will not dissolve primary minerals	Metals in some secondary minerals, plus dissolved, exchangeable, and adsorbed metal ions (unless removed by prior extraction(s))	Chao (1984)	1 M HCl (Morgan et al. 2012)
1 M sodium acetate adjusted to pH 5.0 with acetic acid	Acidity will dissolve carbonate minerals, but pH is too high to dissolve oxides	Metals in carbonate minerals, plus dissolved, exchangeable, and weakly adsorbed metal ions (unless removed by prior extraction(s))	Tessier et al. (1979)	Acetic acid (Chao 1984)
0.25 M $NH_2OH{\cdot}HCl$ in 0.25 M HCl, pH <2, 60 °C	$NH_2OH{\cdot}HCl$ is a strong reducing agent able to dissolve amorphous Fe^{III} and Mn^{IV} (hydr) oxides	Metals in reducible minerals, plus dissolved, exchangeable, and adsorbed metal ions (unless removed by prior extraction(s))	Hall et al. (1996)	Ammonium oxalate (pH 3) (Shuman 1985)
0.1 M sodium pyrophosphate, pH 10	Pyrophosphate forms very stable complexes with Fe^{3+} and Al^{3+} which would otherwise precipitate organic matter. Organic matter is ionised at pH 10	Metals associated with soil organic matter, plus dissolved, exchangeable, and adsorbed metal ions (unless removed by prior extraction(s))	Chao (1984)	H_2O_2, NaOCl (Chao 1984; Shuman 1985)

[a]M = moles per litre of solution (mol/L); [b]diethylenetriaminepentaacetic acid; [c]ethylenediaminetetraacetic acid

measurements. For example, Rayment and Lyons (2010) describe the use of a universal pH indicator in which a small volume of indicator solution is added to soil, followed by a white $BaSO_4$ powder to more easily visualise the colour. Less-commonly used field colour tests have been developed as well, for example, for dissolved aluminium for use in acidic soils or ferrous iron (Fe^{2+}) to show whether reducing conditions exist, but neither are used routinely.

Instrumental Methods Field-based instrumental methods generally have lower measurement precision and accuracy than laboratory-based methods but may allow rapid preliminary assessment of field soils without destructive sampling. The most widely used portable analytical instrument in field analysis of soils is the portable X-Ray fluorescence spectrometer (pXRF) available in preliminary forms since about the 1980s. The use of pXRF in the field can allow more rapid and cost-effective screening of metal contaminants, with acceptable accuracy and precision of measurement (Taylor et al. 2004). Field-based pXRF measurements have been used to assess the spatial distribution of contaminants such as As, Cu, Mn, Pb, V, and Zn (as well as non-contaminant elements) in urban soils (Carr et al. 2008; Schwarz et al. 2012; Paulette et al. 2015). Portable XRF has also been used for field measurements in archaeology to locate features of historical human settlements (Save et al. 2020).

Other field-portable instrumental techniques are under development. For example, Wang et al. (2020) used a handheld Fourier-transform infrared (FTIR) spectrometer to map the distribution of petroleum hydrocarbons at a site contaminated with fuels and lubricants. Similarly, visible-infrared spectroscopic methods are able to determine mineral abundances in geological applications such as core logging (Schodlok et al. 2016), but so far there have been no applications of this technique for urban soils. It remains to be seen whether or not field-based instrumental methods (even the relatively common pXRF technique) will achieve widespread use in the chemical assessment of urban soils.

Remote Sensing In Chap. 5 we discussed the use of airborne radiometrics, a remote sensing method that allows estimation of some soil chemical and parameters based on the signals from radioisotopes of potassium, thorium, and uranium. The most promising application was probably the use of depletions in the thorium signal to infer the distribution of acid sulphate soils (Bierwirth and Brodie 2005).

6.4.4 Background Concentrations

If a soil is contaminated, the contamination is understood in the context of naturally occurring concentration of that contaminant – the background or baseline concentration. This a more complex issue than it may appear initially; most recent understanding of background concentrations reflects the idea that 'background concentration' is a variable quantity rather than a constant value (Reimann and Garrett 2005). Background concentrations of nutrients and metals in soils vary with time, scale of investigation, soil depth sampled, specific location, soil properties, and type of sample preparation and analysis – factors which are all, to some extent, interdependent (Hamon et al. 2004; Reimann and Garrett 2005; Johnson and Ander 2008). In soils across several continents, many elements in soils show a positive correlation with iron content, leading Hamon et al. (2004) to recommend that background concentrations should be variable and based on soil iron concentrations. Reimann and Garrett (2005) noted that single subcontinental-scale concentrations of elements were not useful for establishing site-specific backgrounds. They also showed that a common practice, of assuming that deeper soil horizons could be analysed to determine the local background concentrations, was invalid as it failed to account for differences in concentrations resulting from pedogenesis. In some cases, background concentrations (single values or variable functions) can be estimated following analysis, mapping, and modelling of large datasets (Reimann and Garrett 2005; Johnson and Ander 2008).

6.4.5 Regulatory Contamination Thresholds

Using the current Australian 'NEPM' guidelines (National Environment Protection Council 2013b) as an example, there are a number of issues that need to be considered:

- The actual or intended land use of the area from which the soil was sampled. The NEPM considers four land use categories, in decreasing order of risk to humans, from susceptible residential to commercial/industrial.
- The age of contamination.
- Soil properties which control the bioavailability of contaminants. Depending on the contaminant involved, the NEPM considers soil pH, cation exchange capacity, and soil texture.
- The background concentration of contaminants, valid for the site or area under investigation. The NEPM considers background concentrations only for the inorganic contaminants As, Cu, Cr(III), Ni, Pb, and Zn.

The concepts and methodology for establishing guideline concentrations are addressed in Chaps. 9 and 11.

6.4.6 Distinguishing Geogenic from Anthropogenic Contamination

In the preceding sections, we have already discussed two methods which attempt to separate natural concentrations of contaminants from those added by humans. Background concentrations (Sect. 6.4.4) are considered to represent the geogenic contributions to total nutrient or metal concentrations in soils, and the difference between measured concentration and background represents the anthropogenic addition (National Environment Protection Council 2013a). Background concentrations can be based on a statistical threshold based on multiple measurements. For example, Biasioli et al. (2012) calculated background concentrations for soil data from peri-urban and rural areas as the 90th percentile of observations, after outliers above the Tukey threshold were removed (see Fig. 3.14; this followed ISO 19258). In contrast, the National Environment Protection Council (2013a) recommends that the ambient background concentration for metals be set at the 25th percentile from a dataset derived from analysis of urban and rural soils. An alternative, valid for some trace elements, is that widely consistent regression relationships between trace elements and Fe or Mn can be used to estimate background concentrations for a site if Fe and/or Mn concentrations are known and do not themselves represent contamination (Hamon et al. 2004; National Environment Protection Council 2013a).

The final approach we will discuss for establishing background concentrations is based on analysis of a comparable but uncontaminated soil material. The US EPA (2002) recommends taking physical samples at a reference area which has the same physical, chemical, geological, and biological characteristics as the site being investigated but has not received contamination from activities on the site. Sufficient numbers of background samples need to be collected to make statistical comparisons with sufficient statistical power. In some instances, it is assumed that deeper soil horizons are uncontaminated (e.g. if the only known source of potential contamination is aeolian diffuse-source pollution). In this case the subsoil material has been used to represent geogenic background concentrations (Biasioli et al. 2012).

The calculation of enrichment factors (Sect. 6.4.7, e.g. Fabietti et al. (2010)) also relies on valid background concentrations being known and is the ratio of sample concentration of a contaminant element to the concentration of the same element in the reference material, both normalised using the concentration of a reference element. Ideally the reference element is one that behaves conservatively (e.g. not added anthropogenically, nor enriched or depleted by pedogenic processes); examples of reference element for urban soil environments include Al (Liu et al. 2014), Mn (Yongming et al. 2006), Sr (Yaylalı-Abanuz 2011), and Ti (Szolnoki et al. 2013), and Sc, Fe, and Zr have also been used.

The use of regression model analysis builds on concepts outlined by Rose et al. (1979) and Hamon et al. (2004). For example, Rate (2018) developed separate multiple regression models for a range of trace elements in soil in an urban parkland. The positive residuals (deviations from model predictions) were attributed to addition of potential contaminant elements, above a variable background which depended on soil properties. An example illustrating the use of regression analysis to identify unusual values is shown in Fig. 6.9.

6.4.7 *Contamination Indices*

A complement to using contaminant concentrations alone to characterise urban soil is to use a form of contamination index. The simplest forms of contamination index are for individual elements and are calculated as ratios between sample and

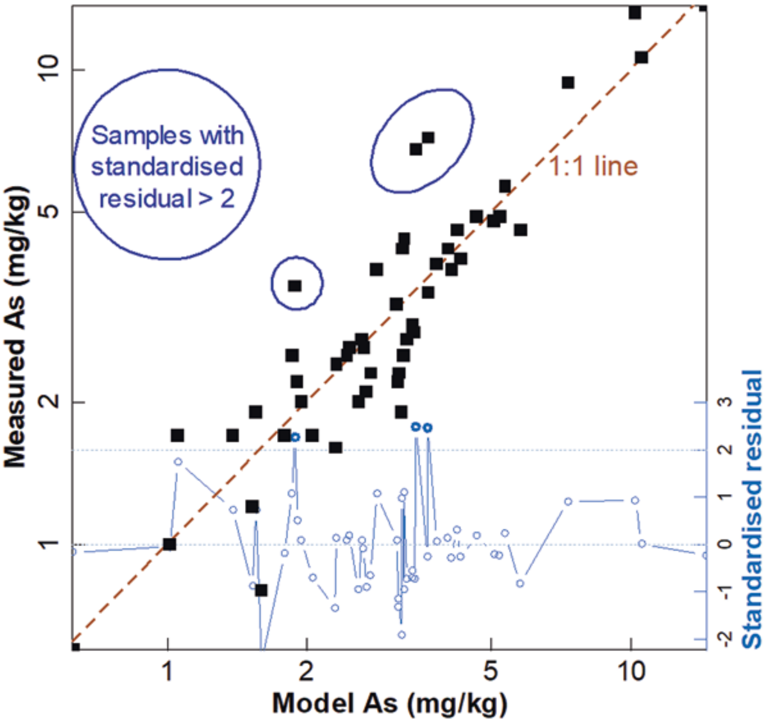

Fig. 6.9 Example of using analysis of residuals from a regression model (see Chap. 3) to identify unusual observations in a dataset with a variable background (graphic by Andrew W. Rate). Note that the unusual samples do not have the highest arsenic (As) concentration

background concentrations of the contaminant of interest (Table 6.2). Other indices recognise that soil contamination is very often multivariate and is essentially sample/background ratios for several contaminants which are averaged in some way (e.g. using arithmetic mean or geometric mean values; see Table 6.2).

More complex composite indices such as the Nemerow integrated pollution index (Yang et al. 2011) have also been used to assess pollution in urban soils.

A complement, or an alternative, to calculation of contamination indices is the use of multivariate numerical methods to analyse multielement soil data. The most common methods include principal component analysis (PCA – see Chap. 3) and one of the various types of cluster analysis. The main use of these multivariate statistical methods appears to be to identify groupings of contaminants, which are then used to infer contaminant sources (usually in combination with other data or statistical analysis – a detailed explanation is given by Reimann et al. 2008). More recently the positive matrix factorisation (PMF) technique, more commonly used for characterising atmospheric particulates, has been applied to urban soils for identification of the source of inorganic chemical contaminants (Li et al. 2016;

Table 6.2 Examples of contamination indices used in urban soil studies

Index name	Calculation and parameters		Reference
Geoaccumulation index, I_{geo}	$I_{geo} = \log_2(C_n / 1.5B_n)$	C_n = measured concentration of element, B_n = background concentration	Wei and Yang (2010)
Pollution index, PI	$PI = C_i / S_i$	C_i = measured concentration of element, S_i = background concentration	Sun et al. (2010)
Integrated pollution index, IPI	$IPI = \left(\overset{n}{\underset{i=1}{?}} \left(C_i / S_i \right) \right) / n$	$\sum$ means the *sum* of terms 1 to n, C_i = measured concentration of i^{th} element, S_i = background concentration of i^{th} element, n = number of elements	Sun et al. (2010)
Pollution load index, PLI	$PLI = \left(\overset{n}{\underset{i=1}{?}} \left(C_i / S_i \right) \right)^{1/n}$	$\prod$ means the *product* of terms 1 to n, C_i = measured concentration of ith element, S_i = background concentration of ith element, n = number of elements	Madrid et al. (2002)
Enrichment factor, EF	$EF = [C_n / C_{ref}] \div [B_n / B_{ref}]$	C_n = concentration of n^{th} element in soil, C_{ref} = concentration of reference element in soil, B_n = background concentration of n^{th} element, B_{ref} = background concentration of reference element	Yongming et al. (2006)
Nemerow index, P	$P = \sqrt{\frac{\left(\frac{C_i}{S_i} \right)_{max}^2 + \left(\frac{C_i}{S_i} \right)_{avg}^2}{2}}$	C_i = measured concentration of ith element, S_i = background concentration of ith element, subscript 'max' refers to the maximum value, and subscript 'avg' refers to the mean value	Gong et al. (2008)

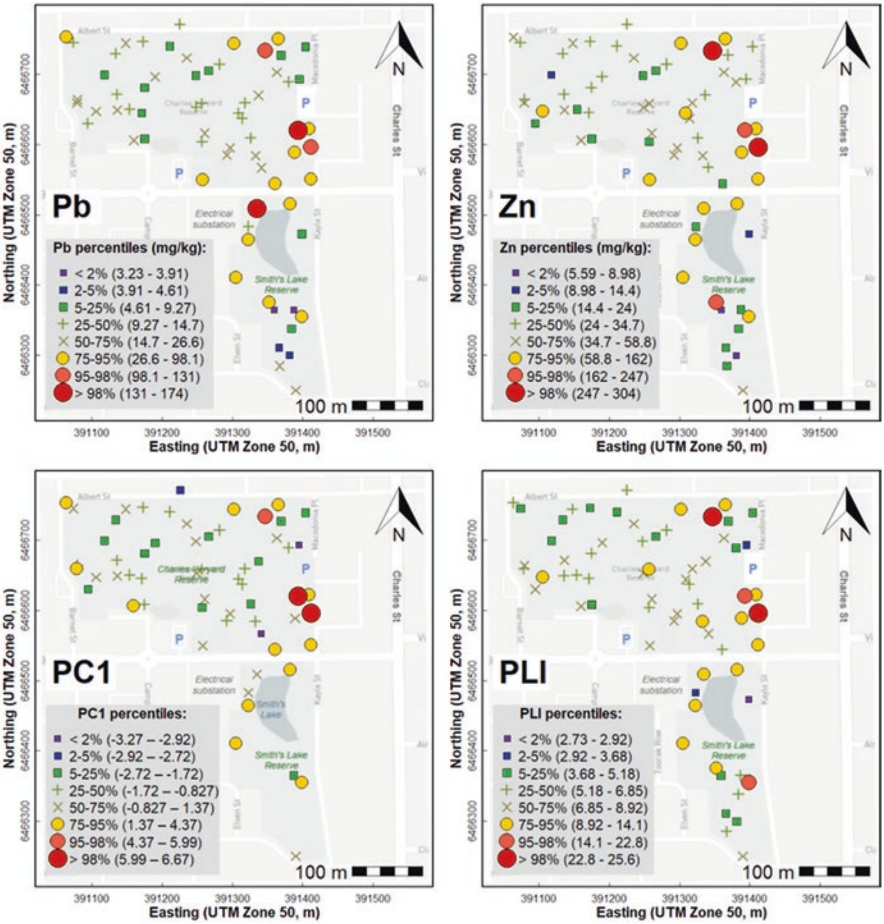

Fig. 6.10 A comparison of maps of single element concentrations for Pb and Zn with indices derived from calculation of principal component (PC1) and the pollution load index (PLI) from Table 6.2 (graphic by Andrew W. Rate). Calculation of principal components was done on centred-log-ratio transformed concentrations, and PC1 (plotted) has its greatest variable weightings from Pb, Cu, Zn, and Cd. Calculation of PLI was based on concentrations of As, Ba, Cr, Cu, Mn, Pb, and Zn using background concentrations from Rate (2018)

Rastegari Mehr et al. 2017). Figure 6.10 shows a comparison of using single-element concentrations, a multivariate index, and a contamination index to map pollution in an urban parkland. While the spatial patterns based on each type of data are similar, Fig. 6.10 emphasises the importance of different analyses of data; for example, both the indices plotted miss the high Pb concentration near an electrical substation.

The specialised discipline of risk analysis also indexes the health risk index, hazard quotient, and hazard index. These parameters are based on a likely proportion of toxic dose for humans, based on risk analysis of possible pathways for human ingestion (examples for urban soils include De Miguel et al. 2007; Nabulo et al. 2010; Thornton 2010; Liu et al. 2014; Abbasi et al. 2017).

6.4.8 Heterogeneity of Soil Chemical Properties

Although this issue has already been addressed in Chap. 3, it is worth remembering that substantial short-scale heterogeneity in soil chemical composition or properties exists (this is also the case for 'natural' soils). Very few studies have investigated urban soil variability at scales of a few metres or less. In practical terms, soil chemical properties such as contaminant concentrations may vary over soil volumes smaller than can be managed or treated efficiently. Consequently, detailed mapping of soil chemical properties is unlikely to result in changes in the management or classification of urban soil.

6.5 Further Reading

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6.6 Summary

- The main inorganic contaminants that we consider in urban soils are nutrients (mostly nitrogen and phosphorus), trace elements (metals and metalloids), asbestos, radionuclides, plastics, manufactured nanoparticles, and cyanide.
- The sources of contaminants in urban soils are very numerous and differ from site to site. Common sources include historical agriculture and horticulture, including manures, fertilisers, and pesticides; solid wastes and wastewater; mining and related activities; various industries; fossil fuels; road traffic; building construction; and weathering.
- Acid sulphate soils are a specific example of soil 'contamination' (the actual added substance is oxygen!) which can result in export of contaminants into receiving environments.
- The chemical behaviour of inorganic contaminants is governed by reactions with fine-grained solid phases: adsorption, ion exchange, and (co)precipitation. In turn, these reactions are controlled by system variables such as pH, redox potential, contaminant concentrations, a wide range of other soil properties, and time.

- Urban soil contaminants in high concentrations cause adverse effects on living organisms. Nutrients are rarely toxic but alter ecological balances. Trace elements, asbestos, radionuclides, and cyanide can be extremely toxic to a wide range of organisms and may also have other deleterious effects such as carcinogenicity. The adverse effects of plastics and manufactured nanoparticles are poorly defined at present.
- The total concentration of an inorganic contaminant in soil is often poorly related to bioavailability, since total concentrations include forms of elements which are inaccessible to any organisms. Various forms of partial analysis of soil contaminants may be more useful to assessing the risk to biota including humans.
- To distinguish between natural 'geogenic' concentrations of inorganic contaminants and the amounts added by humans, various comparisons or numerical analyses are possible. These include determining background concentrations, comparison with regulatory guidelines, calculation of contamination indices, or use of statistical (e.g. regression) models.

6.7 Questions

6.7.1 Checking Your Understanding

1. Identify the main differences and similarities between sources for nutrients, trace elements (metals and metalloids), asbestos, and cyanide in urban soils.
2. Explain how acid sulphate soils form in urban environments, and suggest some ways in which their formation could be avoided.
3. Why does the mobility of cationic metals in soils approximately increase in the order $Fe^{3+} < Pb^{2+}$, $Hg^{2+} < Al^{3+}$, Cu^{2+}, $Cr^{3+} < Co^{2+}$, Mn^{2+}, Ni^{2+}, Zn^{2+}, $Fe^{2+} < Cd^{2+}$ Ca^{2+} $Sr^{2+} < Na^{+}$, K^{+}, NH_4^{+} (i.e. Fe^{3+} least mobile; Na^{+}, K^{+}, NH_4^{+} most mobile)? Explain in terms of chemical reactions.
4. Explain the differences between total and partial analyses for inorganic contaminants in soils and the situations in which we would use each type of analysis.
5. Describe the various methods for distinguishing natural 'geogenic' concentrations of inorganic contaminants in soils and the amounts of inorganic contaminants added to soils by humans. Is any of these approaches the 'best' one to use?

6.7.2 Thinking About the Topics More Deeply

6. Describe a sequence of events for a soil which begins in aerobic conditions and ends with long-term submergence of the soil.

7. Radionuclides (such as some isotopes of caesium or thorium) occur naturally in some soils in significant concentrations. Should we be concerned about this? Why (or why not)?
8. Can we manipulate chemical reactions in soils to make inorganic contaminants less bioavailable or mobile? How might this work?
9. If the bioavailability of some inorganic contaminants in urban soils decreases with increasing time, could one management strategy simply be to leave urban land unused or seal the surface? Explain why this might (or might not) be successful and/or practical.

6.7.3 A Question 'Out of Left Field'

10. Shouldn't we just leave all the plastic waste from urban environments in landfills? Discuss the issues involved!

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