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Behavior and Impact of Zirconium in the Soil–Plant System: Plant Uptake and Phytotoxicity

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1 Introduction

Because of the large number of sites they pollute, toxic metals that contaminate terrestrial ecosystems are increasingly of environmental and sanitary concern (Uzu et al. 2010, 2011; Shahid et al. 2011a, b, 2012a). Among such metals is zirconium (Zr), which has the atomic number 40 and is a transition metal that resembles titanium in physical and chemical properties (Zaccone et al. 2008). Zr is widely used in many chemical industry processes and in nuclear reactors (Sandoval et al. 2011; Kamal et al. 2011), owing to its useful properties like hardness, corrosion-resistance and permeable to neutrons (Mushtaq 2012). Hence, the recent increased use of Zr by industry, and the occurrence of the Chernobyl and Fukushima catastrophe have enhanced environmental levels in soil and waters (Yirchenko and Agapkina 1993; Mosulishvili et al. 1994; Kruglov et al. 1996).

Zr is the twentieth most common element in the earth's crust (Fodor et al. 2005). Zr is generally considered to be immobile in soil (Muhs et al. 2007, 2010; Muhs and Budahn 2009; Aznar et al. 2009; Feng 2010, 2011; Little and Lee 2010; Hao et al. 2010; Bern et al. 2011), because it has low water solubility and a strong tendency to polymerize (Clearfield 1964). Moreover, Zr forms strong complexes with soil components, via zirconium dioxide and zirconocene dichloride, among others. The rate of adsorption/desorption of Zr to soil depends on its speciation and the characteristics of the soil involved. This element can be mobile in soil under a wide range of geological settings such as tropical weathering (Duvallet et al. 1999; Kurtz et al. 2000; Hodson 2002; Davydov et al. 2006).

Soil-plant transfer is an important link in the chain of events that leads to radionuclide entry into the human food chain. However, few studies have been performed on Zr transfer to plants (Shi and Guo 2002). Such soil-plant transfer may be influenced by both the characteristics of the plants (species, variety, maturity, etc.) and soils involved. Generally, plants absorb elements as ions or small complexes (Kabata-Pendias and Pendias 1992) in the soil solution.

Compared to other fission products (e.g., Sr, Cs, and Co), few data exist on the environmental behavior and fate of Zr (Couture et al. 1989; Garnham et al. 1993). Our goal in this review is to describe the following aspects of Zr: (1) isotopes and sources; (2) retention, mobility, and bioavailability in soils; (3) speciation in soil; (4) plant uptake and translocation to aerial parts; and finally (5) phytotoxicity.

2 Zr Minerals, Isotopes, and Sources

Relative to other inorganic trace elements, Zr has a high natural abundance in the earth's crust (Jones 1998; Martínez Cortizas et al. 2003; Chow et al. 2003; Alleman et al. 2010; Kumpiene et al. 2011). The natural level of Zr in soils varies from 32 to 850 mg/kg (Kabata-Pendias and Pendias 1992; Fodor et al. 2005). Bowen (1979) gave 400 mg/kg as an average Zr soil concentration, and Pais and Jones (1983)

reported a value of 250 mg/kg. In soil, Zr is more than twice as abundant as copper and zinc and has ten times the abundance of lead. Its geochemistry is dominated by its lithophilic nature: Zr occurs in more than 140 recognized mineral species, but zircon (ZrSiO_4) and baddeleyite (ZrO_2) are the main naturally observed compounds (Ryzhenko et al. 2008). The order of Zr content in various types of rock is ultrabasic rocks < granite rocks < alkaline rocks (Kovalenko and Ryzhenko 2009). A-type granite is characterized by having high concentrations of Zr, and accessory minerals such as zircon and monazite (Jung et al. 2000; Sako et al. 2009). The highest Zr content values appear in apatitic nepheline syenites, carbonatites, and peralkaline granites: 34 mg/kg in ultra basic rocks, 150 mg/kg in intermediate rocks, 200 mg/kg in silicic rocks, 820 mg/kg in alkaline rocks, and 1,120 mg/kg carbonatites (Ryzhenko et al. 2008). Zircon and baddeleyite are weathering resistant and form placers, which are the main commercial sources of Zr (Ryzhenko et al. 2008).

Naturally occurring Zr contains five stable isotopes (Ryzhenko et al. 2008; Caffau et al. 2010). Among these, ^{90}Zr is the most common form, comprising 51% of natural Zr. The other four stable isotopes and their relative abundances are ^{91}Zr (11%), ^{92}Zr (17%), ^{94}Zr (17%), and ^{96}Zr (2.8%) (Ryzhenko et al. 2008). In addition to these stable natural isotopes of Zr, 28 artificial isotopes have been manufactured, ranging in atomic mass from 78 to 110. Among these artificial isotopes, ^{93}Zr is the longest-lived [half-life ($T_{1/2}$) of 1.53×10^6 years] and ^{110}Zr is the heaviest and shortest-lived artificial isotope ($T_{1/2}$ 30 ms). ^{93}Zr decays to niobium (^{93}Nb) by emitting a beta particle of 0.02 million electron volts radiation energy. Nb, in turn, decays by isomeric transition by emitting beta and gamma particles of 0.028 and 0.0019, respectively. The Zr isotopes, with mass numbers between 88 and 104, have been characterized by high fission yields ranging from 5.8 to 6.3%.

Both geogenic and anthropogenic sources for Zr exist, the first generally being more abundant (Abollino et al. 2002; Schulin et al. 2007; Brun et al. 2008; Little and Lee 2010). The unique physical–chemical properties of Zr has enhanced its industrial use and has produced higher anthropogenic emissions to the environment from several sources: nuclear fallout, ceramic dusts, and heavy metal mining, improper waste dumping, abandoned industrial activity sites, incidental release (e.g., leakage, corrosion), and atmospheric fallout (Chow et al. 2003; Schulin et al. 2007; Little and Lee 2010; Bhuiyan et al. 2010). The Zr applications most valued by include uses that require high resistance to corrosive agents, component use in vacuum tubes, alloying agent for steel, surgical instrument applications, photoflash bulbs, explosive primers, lamp filaments and as a component of gems. The alloys of Zr are utilized as refractory materials, a cladding material for nuclear fuel elements, and a component of explosive primers, rayon spinnerets and superconductive magnets (Yau 2010). Recently, Dou et al. (2011) reported that a granular zirconium–iron oxide alloy can be used to remove fluoride from drinking water. The increased use of Zr by many industries has increased annual production from mines where it is sourced (Fig. 1; USGS 2012).

Zr has a diversity of uses. Zr is known as an ideal material for nuclear reactor applications, due to its low absorption cross-section for neutrons (Mushtaq 2012). The use of Zr in commercial nuclear power generation now accounts for as much as

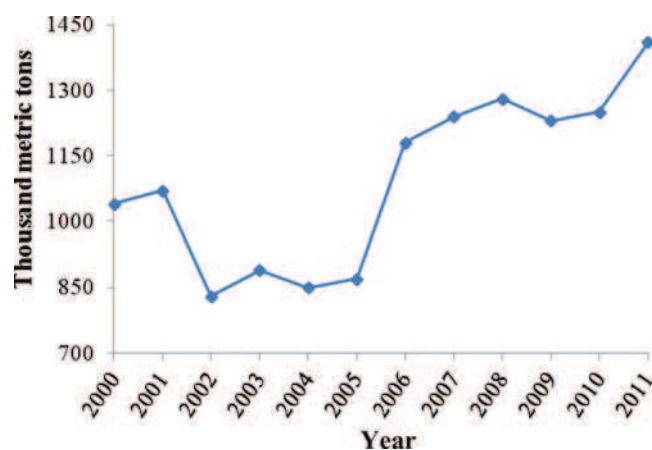


Fig. 1 Annual world mine production of Zr in 000 metric t (from USGS 2012)

90% of the Zr metal that is produced. The ^{93}Zr isotope is long-lived ($T_{1/2}$ of 10^6 years). This isotope occurs largely in radioactive wastes as a fission reaction by-product (Naudet 1974). Because of its relatively short half-life, the ^{89}Zr isotope ($T_{1/2}$ of 78.4 h) is a promising positron-emitting surrogate for ^{90}Y in radio immunotherapy (Verel et al. 2003). Zr is also used for its incendiary effect in weapons such as the BLU-97/B combined effects bomb. Moreover, Zr is detected in phosphate fertilizers and in calcium cyanamide (range 0.38–8.24 mg/kg) (Senesi et al. 1988). Traces of Zr also exist in sewage sludge (5–90 mg/kg), limestone (20 mg/kg), and animal manure (5 mg/kg) (Kabata-Pendias 1993).

Abollino et al. (2002) and Bhuiyan et al. (2010) reported that anthropogenic activities can modify the amount and nature of Zr that is present in soils and should be considered as a possible soil pollutant. Finally, the growing environmental abundance of Zr has increased researcher interest in measuring the levels at which it exists in living organisms (Ghosh et al. 1992).

3 Retention, Mobility, and Bioavailability of Zr in Soils

Metal bioavailability is defined as the fraction of total metal in soil that can be absorbed by a biological target (Shahid et al. 2012b). The degree to which a metal is bioavailable depends on its soil mobility. Opinions vary on how mobile/bioavailable Zr is in soil. Certain authors (Chadwick et al. 1990; Bain et al. 1994; Hodson 2002) believe that Zr is very slightly mobile in soils as a result of its binding to highly insoluble oxides, chloride, and silicates that are resistant to weathering (Kabata-Pendias 1993; Smith and Carson 1978; Prisyagina et al. 2008). Blumenthal (1963), in contrast, believes that zirconium oxide is almost insoluble in water, acid and alkali solutions, and organic solvents and therefore is not mobile. Indeed, the mobility

and/or bioavailability of Zr depend on its chemical form. Certain chemical forms of Zr (e.g., zirconium carbide and zirconium oxychloride) are slightly soluble, whereas others are insoluble in water (zirconium oxide, zirconium hydroxide, and zirconium phosphate) (Venable 1922).

Zr has a fixed crystalline structure in many of the minerals in which it appears (Horvath et al. 2000). This structure of Zr changes very slowly over time from the effects of weathering. The more Zr minerals are weathered the more they change. Hence, one can use the degree of weathering of Zr-containing minerals that appear in soil to track the geologic age of some minerals. Therefore, Zr is used as a tool to estimate long-term weathering rate for rocks that exist in soils (Hill et al. 2002; Egli and Fitze 2001; Patino et al. 2003; Zacccone et al. 2008).

The total quantity of an immobile element in a given soil horizon is not unaffected by the weathering processes (Hodson 2002), although the element's concentration may change from loss or addition of other elements or from the addition of organic matter. Goldich (1938) and Pettijohn (1941) investigated the durability of Zr in weathered rock and found that zircon was the most persistent mineral in a wide range of igneous, metamorphic and sedimentary rocks. Tejan-Kella et al. (1991) recorded etch-pitted zircon grains only in soils that were 100,000 years old. The chemical composition of zircon mineral is used to elaborate many magmatic processes, including the interaction with hydrothermal fluids (Thomas et al. 2002; Hoskin 2005), crystal fractionation (Pettke et al. 2005; Lowery Claiborne et al. 2006), and/or magma mixing (Wang et al. 2002; Belousova et al. 2006), as well as being a potential source indicator (Aja et al. 1995; Belousova et al. 2002; Gagnevin et al. 2009).

Zr is highly resistant to acidic weathering and is widely used to predict the structure of parent rocks (Valeton et al. 1987; Kurtz et al. 2000; Panahi et al. 2000; Calagari and Abedini 2007). The ratio of Zr to other metals like Hf or Ti is highly useful to determine the crystallization sequences of rocks (Zaraisky et al. 2009). Therefore, Zr/Hf and Ti/Zr concentration ratios are employed to trace possible precursor rock(s) that exist in ores (Kurtz et al. 2000; Zaraisky et al. 2008, 2009; Hao et al. 2010; Bern et al. 2011). The ratios of immobile elements (e.g., Ti/Zr) in bauxite are similar to those of the parent rock (Valeton et al. 1987) and can be used to determine source rocks (Calagari and Abedini 2007). The concentration ratios of other element combinations have been successfully used to infer the derivation of soils (Sommer et al. 2000).

In contrast to the opinion of other researchers mentioned above, Whitfield (2011) and Bern et al. (2011) concluded that Zr was mobile in soils. The mobility of Zr relative to Nd in commercial reactors was also reported by Maeck et al. (1975). Hill et al. (2002) and Kurtz et al. (2000) have shown that immobile elements like Zr (or Y and Th) are redistributed within the weathered soil profile. This redistribution may result from physical, chemical, and biological processes that operate on the earth's surface (Anderson et al. 2002; Che et al. 2012). Petrographic evidence (Rubin et al. 1993; Flohr and Ross 1990) suggests that Zr may be mobile in soil under a wide range of geological settings (Hao et al. 2010; Malandrino et al. 2011; Ribeiroa et al. 2010; Liu et al. 2010).

In addition to origin (whether natural or anthropogenic), several other factors influence the mobility of Zr in soils, such as soil characteristics, interactions with organic matter, and climate (Ferrand et al. 2006; Davydov et al. 2006). These factors, separately or in combination, affect the bioavailability of Zr, particularly when adsorption/desorption processes are involved (Klechkovsky and Gulyakin 1958; Schulin et al. 2007).

The effects of pH greatly influences metal partitioning between the soil solid and solution phases (Peng et al. 2009; Shahid et al. 2011b). Soil pH affects adsorption/desorption reactions, speciation, and mobility of heavy metals in soils (Davydov et al. 2006; Wu and Hendershot 2010; Zou et al. 2009; Bali et al. 2010; Shahid et al. 2011c). In strongly acidic solutions, the polynuclear hydrolysis species are formed and control Zr solubility and mobility in solution. Under less acidic conditions, mononuclear hydrolysis species are more predominate. Under alkaline solutions, solubility increases form the formation of the zirconate ion.

Soil texture also influences the behavior of Zr. Metals generally have a strong affinity for the soil-clay fraction (Owojori et al. 2010), and that fine soil fraction is often pollutant enriched. In contrast, Zr is mainly present as zircon grains in the coarse fractions of soils (Stiles et al. 2003; Caspari et al. 2006). However, Zr sorption onto the solid surfaces of soil may influence its mobility and bioavailability (Klechkovsky and Gulyakin 1958; Udovic and Lestan 2009; Rascio and Navari-Izzo 2011). Competing ions (viz., H, Ca, Mg, Na, Fe, and K) affect these adsorption reactions.

Soil organic matter (SOM) also plays a key role in governing the mobility/bioavailability of metals in soil (Dessureault-Rompré et al. 2010). Soil organic content affects the mobilization of Zr, because this element may be adsorbed by it, or may form stable complexes with it (Ferrand et al. 2006). Such interactions may result from the interaction of metal ions with the acidic binding sites on carboxylic and phenolic hydroxyl groups of SOM (Oliva et al. 1999; Viers et al. 2000; Pokrovsky and Schott 2002). Oliva et al. (1999) and Viers et al. (2000) recorded relatively high Zr concentrations (0.01–0.6 g/kg) in organic-rich soils (10–35 µg/g dissolved organic carbon). Oliva et al. (1999) measured high Zr concentrations in a small tropical watershed in South Cameroon and believed that they were the result of zircon weathering that was enhanced by organic matter. LeRiche (1973) detected Zr in hydrogen peroxide extracts of soils, which indicated that Zr may be associated with the organic matter fraction of soils. SOM also indirectly affects metal mobility in soil via its effects on soil properties (i.e., pH, cation exchange capacity, particle size distribution, cracking pattern and porosity, soil solution composition, microbial and enzyme activities) (Shahid et al. 2012b).

The extent of Zr mobility also varies according to climatic conditions. Under temperate and tropical weathering conditions, biotite is decomposed and zircon is released into the soil column, and it is subsequently redeposited in deep horizons (Swindale and Jackson 1956; Cornu et al. 1999). Under low rainfall, Zr may precipitate or coprecipitate with Fe oxides and become immobilized. In contrast, Zr may become mobile under more severe weathering conditions and the presence of high organic matter content (Dupré et al. 1996; Hodson 2002; Braun et al. 2005).

In soils exposed to intensive chemical weathering, topsoil generally contains higher amounts of Zr as zircon minerals, compared to deeper horizons (Hodson 2002; Stiles et al. 2003). Abollino et al. (2002) reported higher concentrations of Zr in chemically weathered surface than in deep soil samples. Hence, there is a notion that the mobility of Zr is site-specific.

4 Zr Speciation

The biogeochemical behavior of an inorganic element in an ecosystem, and its potential effects on plants, are strongly influenced by its speciation (Stojilovic et al. 2005; Fodor et al. 2005; Davydov et al. 2006; Dumat et al. 2006; Ryzhenko et al. 2008; Prisyagina et al. 2008; Kopittke et al. 2008; Louvel et al. 2009; Uzu et al. 2009; Shahid et al. 2012b, c). Speciation is the existence of a metal in different chemical forms as a result of being exposed to different environmental conditions (Dumat et al. 2006; Louvel et al. 2009; Shahid et al. 2011c). As mentioned, Zr speciation strongly depends on soil pH and SOM interactions. Zr exists in several forms in the soil and in liquid media, and these forms have different levels of solubility and bioavailability (Fodor et al. 2005; Davydov et al. 2006; Ryzhenko et al. 2008; Prisyagina et al. 2008; Louvel et al. 2009). Different Zr species affect the solubility, mobility, and uptake of Zr by plants (Davydov et al. 2006; Ferrand et al. 2006; Ryzhenko et al. 2008). Therefore, although it is relatively easier to measure, one cannot rely on the total Zr content in a plant as an indicator of uptake and toxicity (Shahid et al. 2012b). Therefore, to improve the understanding of risk and what constitutes realistic remediation depends heavily upon measuring the relevant species of Zr that exists in soil as well as those taken into plants.

Zr presents different oxidation states (varies from +2 to +4), +4 being the form of the predominant stable valence; bonding with oxygen is the prevailing and most common reaction for Zr (Kabata-Pendias 1993). The Zr crustal abundance ranges from 20 to 500 mg/kg, and its aqueous chemistry is dominated by the quadrivalent oxidation state (valence electron configuration $4d^2 5s^1$) (Ryzhenko et al. 2008). The lower oxidation states of Zr (0, I, II, and III) occur only in nonaqueous solvents and fused salts (Cotton and Wilkinson 1980). Due to high ionic potential ($22.54 e^2/\text{\AA}$), Zr is the most polarizing among the heavier transition and post-transition quadrivalent cations. The extent of hydrolysis and polymer stoichiometry depends on the nature of the ionic media (Davydov et al. 2006), with tetramer and trimer forms being the most common stoichiometry. Moreover, hydrolysis and polymerization reactions dominate in the presence of high field strength cations that are capable of rupturing H–O bonds. Similarly, hydrolysis and polymerization is promoted in alkaline solutions and with increasing temperatures.

How Zr reacts in aqueous media (soil solution) is still the subject of controversy. The zirconium oxide and hydroxide have low solubility and precipitate at low pH. This is because Zr hydrolyses and precipitates as polynuclear species in strongly acidic solutions ($\text{pH} < 1$) (Baes and Mesmer 1986; Ekberg et al. 2004). Davydov

et al. (2006) and Ryzhenko et al. (2008) evaluated the hydrolysis and precipitation of Zr as a function of pHs between 0 and 14 and generally show that Zr precipitation reactions occur at low pH (about 2) (Ryzhenko et al. 2008; Prisyagina et al. 2008). In the pH range 0.6–2.3, potentiometric measurements indicated the presence of both the mononuclear form $[\text{Zr}(\text{OH})_3]^+$ (at a low Zr concentration) and the polymeric species $[\text{Zr}_4(\text{OH})_8]^{8+}$ and $[\text{Zr}_2(\text{OH})_6]^{2+}$. This latter polymeric species predominated at low total Zr concentrations (10^{-5} M). At higher pH, solvent extraction measurements indicated the presence of three mononuclear species: $[\text{Zr}(\text{OH})_2]^{2+}$, $[\text{Zr}(\text{OH})_3]^+$, $\text{Zr}(\text{OH})_4$ (Davydov et al. 2006; Ryzhenko et al. 2008). Under tetravalent oxidation conditions, Zr acts as a hard acid: electrostatic, rather than covalent forces dominate its complexation with inorganic ligands in the following order of decreasing stability: $\text{OH}^- > \text{F}^- > \text{PO}_4^{2-} > \text{ClO}_4^{2-} > \text{SO}_4^{2-} > \text{CO}_2^- > \text{NO}_3^- > \text{Cl}^- > \text{ClO}_4^-$. Complexation reactions involving OH^- and F^- ions have received the most attention, and speciation studies have generally been conducted in perchlorate media.

5 Plant Uptake of Zr from Soil and Translocation to Aerial Parts

Soil–plant transfer is an important link in the chain of events that leads to the entry of metals into the food chain. Unfortunately, little data are available concerning the transfer of Zr to plants (Wang et al. 2000; Shi et al. 2002). Zr is less soluble than other metals (e.g., Pb and Cd) and tends to exist as an insoluble particulate. Consequently, only a small fraction of zirconium is available for plant uptake (Ferrand et al. 2006; Uzu et al. 2009; Hao et al. 2010; Muhs et al. 2010; Feng 2011; Bern et al. 2011), because of strong binding with organic and inorganic ligands in soils (Sammut et al. 2010; Vega et al. 2010; Shahid et al. 2012b). By contrast, Sako et al. (2009) stated that the least mobile elements (e.g., Zr, Ti, Sc, Al, and Th) have a low residence time in the soil solution. However, Tematio et al. (2009) concluded that Zr is more strongly available in the B soil horizons.

Unlike other heavy metals (e.g., Pb, Cd, and Ni), the way Zr enters plants is not well understood. The main pathway by which Zr is taken up by plants is soil–root transfer (Ferrand et al. 2006). Zr is mainly taken up as the tetravalent cation in soil solution (Whicker and Schultz 1982). Zr adsorption on root surfaces (Chaignon and Hinsinger 2003) is a minor phenomenon and such absorption is mainly driven by nonselective water and nutrient fluxes (Ferrand et al. 2006). Zr may enter roots passively and follow translocating water streams. At the molecular level, the mechanism by which Zr enters roots is still unknown. Zr can enter the plant roots via different pathways, especially through ionic channels as does Pb. Entry into plants by Zr may depend on the functioning of an H^+ /ATPase pump to maintain a strong negative membrane potential in rhizoderm cells (Hirsch et al. 1998). Some authors suggested that kinetic-dependant absorption of the metal occurs; the initial phase representing rapid entry into root-free space and binding to the cell walls, and the subsequent slower phase resulting from transport across the plasma membrane into the cytoplasm (Maria and Cogliatti 1988).

The rate of Zr entry into plant roots significantly depends on its chemical form in the soil solution. Ferrand et al. (2006) observed higher Zr concentrations in the roots of *Pisum sativum* and in tomato plants for the acetate and oxychloride forms than the hydroxide or oxide forms. Shi and Guo (2002) studied the absorption of Zr by *Brassica rapa* that was cultivated on a loamy soil. They observed that when Zr was applied by soil surface irrigation, ⁹⁵Zr was distributed equally between root and shoot. However, when Zr was applied as spray on plant leaves, Zr concentration was greater in roots than shoot. Zirconium ascorbate has been reported by Fodor et al. (2003) to be accumulated from nutrient solution at a significant rate by *Chlorella pyrenoidosa* cells (Simon et al. 1998). This phenomenon may have practical importance in removing Zr from contaminated aquatic environments. Interactions between organic ligands and metals in natural media have been extensively studied because of their affect on metal availability (Ferrand et al. 2006; Quenea et al. 2009; Yip et al. 2010). Synthetic or natural organic ligands have been extensively used to enhance plant uptake of metals in remediation studies (Evangelou et al. 2007; Saifullah et al. 2009, 2010; Yip et al. 2010; Shahid et al. 2012b). In addition to organic ligands, plant root exudates, which generally include acetic, oxalic, fumaric, citric, and tartaric acids, also affect Zr solubility in soil and its uptake by plants (Hinsinger et al. 2009, 2011). Langmuir and Herman (1980) showed that for thorium (a chemical analogue of Zr), oxide solubility and availability were increased by organic ligand addition.

The penetration of an element into a plant can be assessed by assessing the transfer factor (TF) from soil to plant (TF is generally defined as the ratio between the concentration in plants and the soil) (Arshad et al. 2008; Bi et al. 2010; Liu et al. 2010). This TF depends on soil physical and chemical properties and plant type (Arshad et al. 2008; Bi et al. 2010; Liu et al. 2010). The TF value permits researchers to integrate information on the initial total stock of Zr, and therefore to better compare Zr availability under various experimental conditions (Ferrand et al. 2006). A TF value equal to 0.01 corresponds to a low metal absorption rate and a TF value of 10 indicates that the plant accumulates the metal. The mean TF value obtained by Tome et al. (2003) for Zr uptake by grass-pasture grown in soils near a uranium mine was 0.09. Actually, several authors have reported that Zr accumulates in various food crop parts if the crops were grown on Zr-contaminated soil (Sanzharova and Aleksakhin 1982; Fodor et al. 2002). Sanzharova and Aleksakhin (1982) concluded that Zr was taken up by barley, corn, and alfalfa. Gundersen et al. (2000) observed that Zr was absorbed by *P. sativum* (between 0.425 and 5.29 µg/kg of Zr per fresh wt). In any event, plants accumulate significantly lower Zr concentrations than exists in the soil in which they grow (Smith and Carson 1978; Sanzharova and Aleksakhin 1982). Kabata-Pendias (1993) indicated that the Zr levels found in food plants vary from 0.005 to 2.6 mg/kg.

After penetrating the central plant cylinder, metals translocate to shoots via the water flow of the vascular system (Krzyszowska et al. 2010). While passing through the xylem, Zr may form complexes with amino acids such as histidine, or organic acids, as do Pb and Cd (Ferrand et al. 2006; Vadas and Ahner 2009; Maestri et al. 2010; Rascio and Navari-Izzo 2011), or may be transferred in inorganic form. Transportation of metals from the roots to the shoots requires movement through the

xylem (Verbruggen et al. 2009) and is probably driven by transpiration (Liao et al. 2006; Shahid et al. 2011b). The translocation rate of Zr in higher plants is low (Sanzharova and Aleksakhin 1982; Kabata-Pendias 1993; Ferrand et al. 2006). Like Pb, generally more than 90% or more of absorbed Zr is accumulated in plant roots (Kabata-Pendias and Pendias 1992; Wang et al. 2000; Shi et al. 2002; Klechkovsky and Gulyakin 1958; Ferrand et al. 2006; Yan et al. 2010; Gupta et al. 2010; Jiang and Liu 2010).

Restrictions in metal translocation may result from blockage by the Casparian strip, accumulation in plasma membrane, precipitation as insoluble Zr or immobilization by negatively charged exchange sites within the cell wall, or sequestration in the vacuoles of rhizodermal and cortical cells. Kabata-Pendias and Pendias (1992) reported a higher increase of Zr content in nodules and roots of legumes than in aerial parts. Wang et al. (2000) found the same result for soybean plants that were cultivated in a radio contaminated soil, even for a longer growing period (up to 60 days after sowing). Shi et al. (2002) found that Zr in *Oryza sativa* was concentrated in the roots and lower part of the stem. Ferrand et al. (2006) observed a several fold increase in the accumulation of Zr in root of *P. sativum* and *Solanum lycopersicum* plants, when the plants were grown in Zr-spiked soil. Enhanced sequestration in root cells, with limited translocation to shoot tissues is a typical feature of metal excluders (Baker 1981). A low Zr concentration in the edible parts of plants, even in very contaminated soils is an important result in terms of sanitary risk linked to vegetable eating. Additional studies on Zr that address movement and accumulation in numerous other plant species are needed. In particular, data are needed on the distribution of Zr in leafy or root vegetables and should emphasize the consumed parts of the vegetables.

6 Zr Toxicity to Plants

Metal toxicity depends not only on total concentration but also on metal speciation and interactions with soil components. Zr has no known biological function in plant or animal metabolism (Blumental 1976). Although effects vary with Zr dose and speciation, exposure has produced either stimulatory or toxic effects in algae, yeasts, bacteria, fish, and higher plants (Smith and Carson 1978; Couture et al. 1989; Abollino et al. 2002; Shi and Chen 2002; Shi and Li 2003; Fodor et al. 2005). Although data are scarce, it appears that the stable isotopes of Zr have low toxicity to organisms (Blumental 1976; Couture et al. 1989). Zr caused slight toxicity in young *Hordeum vulgare* by decreasing biomass (Davis et al. 1978). A significant influence of Zr–Ascorbate on intracellular chemical composition or chlorophyll content was observed to occur in various plants exposed to Zr: *C. pyrenoidosa* or *Triticum aestivum* (Simon et al. 1998; Fodor et al. 2005). Ferrand et al. (2006) reported a slight decrease in dry weight of *P. sativum* and *S. lycopersicum* plants from a high accumulation of Zr.

Zr is also reported to stimulate or inhibit enzymes in plant cells. Inhibition of Zr-induced phosphate-dependent enzymes was reported by Smith and Carson (1978). Fodor et al. (2005) reported a Zr-induced increase in peroxidase (POD) activity, whereas decreased ascorbate peroxidase (APX) and glutathione reductase (GR) activities occurred in *T. aestivum*. Simon et al. (1998) reported a Zr-induced modification of enzymatic activity in *C. pyrenoidosa*. Similar results were obtained by Ti-ASC (which has similar physical and chemical activities as that of Zr) in *T. aestivum* and *Zea mays* (Pais 1983) and in *Capsicum annuum* (Carvajal et al. 1994). Furthermore, after Zr application, Fodor et al. (2005) reported a marked decrease in the total phenol content of plant tissues.

The mechanism behind Zr-induced inhibition of growth or modification in enzyme activities is not known, but may be explained in terms of the possible mechanisms responsible for these physiological changes in plants. Heavy metal accumulation in plant tissue is toxic to most plants and interferes with various morphological, physiological, and biochemical process (Shahid 2010). Inside a cell, these metals impair photosynthesis, respiration, mineral nutrition, and enzymatic reactions (Maestri et al. 2010; Ali et al. 2011). The primary response of plants to heavy metal toxicity is the generation of reactive oxygen species (ROS) (Pourrut et al. 2008; Mirza et al. 2010; Rascio and Navari-Izzo 2011; Ali et al. 2011; Xu et al. 2011). Such ROS include, superoxide radicals ($O_2^{\cdot-}$), hydroxyl radicals ($\cdot OH$), and hydrogen peroxide (H_2O_2) and are also produced during normal cell metabolism in the chloroplast, either as by-products of the reduction of molecular oxygen (O_2) or its excitation in the presence of highly energized pigments. Excess ROS formed within cells from heavy metal exposure can provoke oxidation and modification of cellular amino acids, proteins, membrane lipids, and DNA and produce oxidative stress (Pourrut et al. 2008; Grover et al. 2010; Yadav 2010; Qureshi et al. 2010; Rascio and Navari-Izzo 2011).

To combat oxidative damage and prevent cell injury and tissue dysfunction, plants employ protective mechanisms (Benekos et al. 2010; Xu et al. 2011). First, plants may resist metal entry into their cells by exclusion or by binding them to the cell wall or other ligands such as organic acids and amino acids, thereby rendering them harmless, as happens with Pb (Wu et al. 2011; Xu et al. 2011; Zeng et al. 2011). Preventing metal entrance into roots is the first and major protective mechanism adopted by plants against harmful metal effects (Meyers et al. 2008; Jiang and Liu 2010). Metal complexation with carboxyl groups of pectins that exist in plant cell walls is the most important plant-cell resistant reaction to most metals like lead (Patra et al. 2004; Kopittke et al. 2007; Meyers et al. 2008; Krzeslowska et al. 2009, 2010; Jiang and Liu 2010). In this manner, metals are accumulated in root cells and are not translocated to shoot tissues. Although Zr is generally not considered to be a toxic metal, its entry into plants via roots is blocked by its bonding with cell wall exchange sites (Ferrand et al. 2006). Several authors have reported that Zr accumulates in plant root cells and thereby reduces the amount translocated to shoot tissues (Kabata-Pendias 1993; Sanzharova and Aleksakhin 1982).

A secondary defense system against metal toxicity is manifested via antioxidants that combat increased production of ROS that are caused by metal exposure.

These antioxidant enzymes include superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), ascorbate peroxidase (APX), and glutathione reductase (GR). There are also antioxidants of low molecular weight such as proline (PRO), cysteine (Cys), nonprotein thiol (NPT), ascorbic acid (AsA), and glutathione (GSH) that scavenge ROS, thereby prohibiting cell injury and tissue dysfunction (Lyubenova and Schröder 2011; Mou et al. 2011; Lomonte et al. 2010; Ali et al. 2011).

7 Conclusions and Perspectives

Zr is a typical lithophile element that has special properties that render it useful for several former and present industrial and other applications. In this chapter, we address the biogeochemical behavior of Zr in soil–plant systems and its impact on the plants. The conclusions we reached from having performed this review are as follows.

1. Zr is abundant in the earth's crust and forms stable complexes in soil with many different compounds, particularly with inorganic ligands like Cl^- and SO_4^{2-} . The behavior of Zr is strongly affected by its geologic origin and speciation. Low pH and complexation with soil organic matter affects zirconium behavior in soils and increases its phytoavailability. The recent growing use of Zr in different industrial processes has produced increased concentrations in different environmental compartments and in some cases has modified the speciation of Zr.
2. Despite its presence and retention at quite high quantities in ecosystems, Zr has not yet been accused of affecting the specific metabolic system of any organisms. Although zirconium enters plants, mainly through the roots from the soil solution, its mechanisms for doing so are still unknown. Once in the roots, Zr becomes sequestered in root cells and a limited amount is translocated to plant shoots. Depending on its speciation, Zr can induce phytotoxicity, such as affecting chlorophyll content or modifying enzyme activity. Plant antioxidant enzymes may be a protective strategy against the toxicity of Zr.
3. Finally, our review has disclosed that more data on the plant–soil behavior of Zr are needed. In particular, new plant species that are cultivated on different soil types that contain Zr are needed. Future studies should emphasize the mechanisms that are involved in uptake and phytotoxicity of Zr and should assess the potential health risks associated with Zr-polluted plants that are consumed by humans. These are important goals in the context of the increasing amounts of Zr emissions to the environment.

8 Summary

Zirconium (Zr) is a transition metal that has both stable and radioactive isotopes. This metal has gained significant attention as a major pollutant of concern, partly because it has been prominent in the debate concerning the growing anthropogenic

pressure on the environment. Its numerous past and present uses have induced significant soil and water pollution. Zr is generally considered to have low mobility in soils. The behavior of Zr particularly depends on the characteristics of the media in which it exists, and even its presence in the biosphere as a contaminant may affect its behavior. In this chapter, we describe the relationship between the behavior of Zr and its speciation in soils, its uptake and accumulation by plants, its translocation and toxicity inside plants, and mechanisms by which plants detoxify it.

Zr is abundant and occurs naturally in the earth's crust. Zr emissions to the atmosphere are increasing from anthropogenic activities such as its use in industry and nuclear reactors. Zr forms various complexes with soil components, which reduces its soil mobility and phytoavailability. The mobility and phytoavailability of Zr in soil depend on its speciation and the physicochemical properties of soil that include soil pH, texture, and organic contents. Despite having low soil mobility and phytoavailability, amounts of Zr are absorbed by plants, mainly through the root system and can thereby enter the food chain.

After plant uptake, Zr mainly accumulates in root cells. Zr does not have any known essential function in plant or animal metabolism. Although little published data are available, we conclude that the phytotoxicity of Zr is generally low. Notwithstanding, Zr can significantly reduce plant growth and can affect plant enzyme activity. When exposed to Zr-induced toxicity, plants possess numerous defense mechanisms to cope with the toxicity. Such strategies include Zr sequestration in plant roots and activation of various antioxidants. Because Zr may have impact on the biosphere, we believe it deserves to be evaluated in supplementary studies that will enhance the understanding of its behavior in soil–plant systems.

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