



**HAL**  
open science

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

Muhammad Shahid, Emmanuel Ferrand, Eva Schreck, Camille Dumat

► **To cite this version:**

Muhammad Shahid, Emmanuel Ferrand, Eva Schreck, Camille Dumat. Behavior and Impact of Zirconium in the Soil-Plant System: Plant Uptake and Phytotoxicity. *Reviews of Environmental Contamination and Toxicology*, 2013, Vol. 221, pp. 107-127. 10.1007/978-1-4614-4448-0\_2 . hal-00815305

**HAL Id: hal-00815305**

**<https://hal.science/hal-00815305v1>**

Submitted on 18 Apr 2013

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>  
Eprints ID: 6554

**To link to this article:** DOI: 10.1007/978-1-4614-4448-0\_2  
URL: [http://dx.doi.org/10.1007/978-1-4614-4448-0\\_2](http://dx.doi.org/10.1007/978-1-4614-4448-0_2)

**To cite this version:** Shahid, Muhammad and Ferrand, Emmanuel and Schreck, Eva and Dumat, Camille *Behavior and Impact of Zirconium in the Soil-Plant System: Plant Uptake and Phytotoxicity*. (2013) *Reviews of Environmental Contamination and Toxicology*, Vol. 221 . pp. 107-127. ISSN 0179-5953

Any correspondence concerning this service should be sent to the repository administrator: [staff-oatao@listes-diff.inp-toulouse.fr](mailto:staff-oatao@listes-diff.inp-toulouse.fr)

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

Muhammad Shahid, Emmanuel Ferrand, Eva Schreck, and Camille Dumat

## Contents

|   |   |     |
|---|---|-----|
| 1 | Introduction.....   | 108 |
| 2 | Zr Minerals, Isotopes, and Sources.....                             | 108 |
| 3 | Retention, Mobility, and Bioavailability of Zr in Soils.....        | 110 |
| 4 | Zr Speciation.....  | 113 |
| 5 | Plant Uptake of Zr from Soil and Translocation to Aerial Parts..... | 114 |
| 6 | Zr Toxicity to Plants.....  | 116 |
| 7 | Conclusions and Perspectives .....                                  | 118 |
| 8 | Summary.....  | 118 |
|   | References.....   | 119 |

---

M. Shahid (✉)

Université de Toulouse, INP-ENSAT,  
Avenue de l'Agrobiopôle, Castanet-Tolosan, Toulouse 31326, France

EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement), UMR 5245 CNRS-INP-UPS,  
Avenue de l'Agrobiopôle, BP 32607, Castanet-Tolosan, Toulouse 31326, France

Department of Environmental Sciences, COMSATS Institute of Information Technology,  
Vehari 61100, Pakistan  
e-mail: shahidzeeshan@gmail.com

E. Ferrand

Laboratoire d'Etude Radioécologique en milieux Continental et Marin, Service d'Etude et de  
Surveillance de la Radioactivité de l'Environnement, IRSN, Institut de Radioprotection et de  
Sûreté Nucléaire, Direction de l'Environnement et de l'Intervention, Cadarache, BP 3,  
Saint Paul Lez Durance, Gardanne 13115, France

E. Schreck • C. Dumat

Université de Toulouse, INP-ENSAT, Avenue de l'Agrobiopôle,  
Castanet-Tolosan, Toulouse 31326, France

EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement), UMR 5245 CNRS-INP-UPS,  
Avenue de l'Agrobiopôle, BP 32607, Castanet-Tolosan, Toulouse 31326, France

## 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 ( $\text{ZrSiO}_4$ ) and baddeleyite ( $\text{ZrO}_2$ ) 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,  $^{90}\text{Zr}$  is the most common form, comprising 51% of natural Zr. The other four stable isotopes and their relative abundances are  $^{91}\text{Zr}$  (11%),  $^{92}\text{Zr}$  (17%),  $^{94}\text{Zr}$  (17%), and  $^{96}\text{Zr}$  (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,  $^{93}\text{Zr}$  is the longest-lived [half-life ( $T_{1/2}$ ) of  $1.53 \times 10^6$  years] and  $^{110}\text{Zr}$  is the heaviest and shortest-lived artificial isotope ( $T_{1/2}$  30 ms).  $^{93}\text{Zr}$  decays to niobium ( $^{93}\text{Nb}$ ) 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

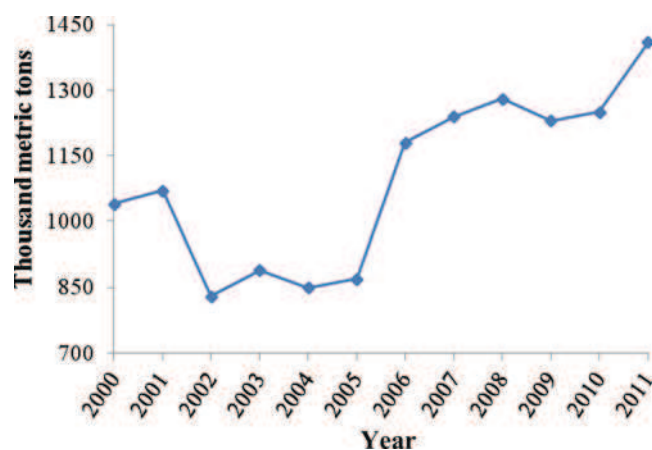


Fig. 1 Annual world mine production of Zr in 000 metric t (from USGS 2012)

90% of the Zr metal that is produced. The  $^{93}\text{Zr}$  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  $^{89}\text{Zr}$  isotope ( $T_{1/2}$  of 78.4 h) is a promising positron-emitting surrogate for  $^{90}\text{Y}$  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 ( $22.54 \text{ e}^2/\text{\AA}$ ), 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  $\text{OH}^-$  and  $\text{F}^-$  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  $\text{H}^+$ /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, <sup>95</sup>Zr 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  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . 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.

**Acknowledgments** The authors would like to thank the “Agence Nationale pour la gestion des déchets radioactifs” (Andra) for financial support. We thank the Higher Education Commission of Pakistan ([www.hec.gov.pk](http://www.hec.gov.pk)) and the French Society for Export of Educative Resources (SFERE, <http://www.sfere.fr/>) for the scholarship granted to M. Shahid.

## References

- Abollino O, Aceto M, Malandrino M, Mentasti E, Sarzanini C, Barberis R (2002) Distribution and mobility of metals in contaminated sites. Chemometric investigation of pollutant profiles. *Environ Pollut* 119:177–193
- Aja SU, Wood SA, Williams-Jones AE (1995) The aqueous geochemistry of Zr and the solubility of some Zr-bearing minerals. *Appl Geochem* 10:603–620
- Ali S, Bai P, Zeng F, Cai S, Shamsi IH, Qiu B, Wu F, Zhang G (2011) The ecotoxicological and interactive effects of chromium and aluminum on growth, oxidative damage and antioxidant enzymes on two barley genotypes differing in Al tolerance. *Environ Exp Bot* 70:185–191
- Alleman LY, Lamaison L, Perdrix E, Robache A, Galloo J-C (2010) PM10 metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. *Atmos Res* 96:612–625
- Anderson SP, Dietrich WE, Brimhall GH Jr (2002) Weathering profiles, mass balance analysis, rates of solute loss; linkages between weathering and erosion in a small, steep catchment. *Geol Soc Am Bull* 114:1143–1158

- Arshad M, Silvestre J, Pinelli E, Kallerhoff J, Kaemmerer M, Tarigo A, Shahid M, Guiesse M, Pradere P, Dumat C (2008) A field study of lead phytoextraction by various scented *Pelargonium* cultivars. *Chemosphere* 71:2187–2192
- Aznar J-C, Richer-Lafèche M, Paucar-Muñoz H, Bordeleau M, Bégin Y (2009) Is tree growth reduction related to direct foliar injuries or soil chemistry modifications? *Chemosphere* 76:1366–1371
- Baes CF, Mesmer RE (1986) *The hydrolysis of cations*, 2nd edn. Kreiger, New York
- Bain DC, Mellor A, Wilson MJ, Duthie DML (1994) Chemical and mineralogical weathering rates and processes in an upland granitic till catchment in Scotland. *Water Air Soil Pollut* 73:11–27
- Baker AJM (1981) Accumulators and excluders—strategies in the response of plants to heavy metals. *J Plant Nutr* 3:643–654
- Bali R, Siegele R, Harris AT (2010) Phytoextraction of Au: uptake, accumulation and cellular distribution in *Medicago sativa* and *Brassica juncea*. *Chem Eng J* 156:286–297
- Belousova EA, Griffin WL, O'Reilly SY (2006) Zircon crystal morphology, trace element signatures and Hf isotope composition as a tool for petrogenetic modeling: examples from Eastern Australian granitoids. *J Petrol* 47:329–353
- Belousova EA, Griffin WL, O'Reilly SY, Fisher NI (2002) Igneous zircon: trace element composition as an indicator of source rock type. *Contrib Mineral Petrol* 143:602–622
- Benekos K, Kissoudis C, Nianiou-Obeidat I, Labrou N, Madesis P, Kalamaki M, Makris A, Tsaftaris A (2010) Overexpression of a specific soybean GmGSTU4 isoenzyme improves diphenyl ether and chloroacetanilide herbicide tolerance of transgenic tobacco plants. *J Biotechnol* 150:195–201
- Bern CR, Chadwick OA, Hartshorn AS, Khomo LM, Chorover J (2011) A mass-balance model to separate and quantify colloidal and solute redistributions in soil. *Chem Geol* 282:113–119
- Bhuiyan MAH, Parvez L, Islam MA, Dampare SB, Suzuki S (2010) Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. *J Hazard Mater* 173:384–392
- Bi X, Ren L, Gong M, He Y, Wang L, Ma Z (2010) Transfer of cadmium and lead from soil to mangoes in an uncontaminated area, Hainan Island, China. *Geoderma* 155:115–120
- Blumenthal WB (1976) Zirconium-behavior in biological systems. *J Sci Ind Res* 35:485–490
- Blumenthal WB (1963) *The chemical behavior of zirconium* (D. van Nostrand, New York, 1958). Inostrannaya Literatura, Moscow
- Bowen H (1979) *Environmental chemistry of the elements*. Academic, London
- Braun J-J, Ngoupayou JRN, Viers J, Dupre B, Bedimo JPB, Boeglin JL, Robain H, Nyeck B, Freyrier R, Nkamdjou LS, Rouiller J (2005) Present weathering rates in a humid tropical watershed: Nsimi, South Cameroon. *Geochim Cosmochim Acta* 69:357–387
- Brun CB, Åström ME, Peltola P, Johansson MB (2008) Trends in major and trace elements in decomposing needle litters during a long-term experiment in Swedish forests. *Plant Soil* 306:199–210
- Caffau E, Faraggiana R, Ludwig H-G, Bonifacio P, Steffen M (2010) The solar photospheric abundance of zirconium. *Astron Nachr* 999:789–800
- Calagari AA, Abedini A (2007) Geochemical investigations on Permo-Triassic bauxite horizon at Kanisheeteh, east of Bukan, West-Azarbaidjan, Iran. *J Geochem Explor* 94:1–18
- Carvajal M, Martinez-Sanchez F, Alcaraz CF (1994) Effect of titanium (IV) application on some enzymatic activities in several developing stages of red pepper plants. *J Plant Nutr* 17:243–253
- Caspari T, Bäumler R, Norbu C, Tshering K, Baillie I (2006) Geochemical investigation of soils developed in different lithologies in Bhutan, Eastern Himalayas. *Geoderma* 136:436–458
- Chadwick OA, Brimhall GH, Hendricks DM (1990) From black box to grey box: a mass balance interpretation of pedogenesis. *Geomorphology* 3:369–390
- Chaignon V, Hinsinger P (2003) A biotest for evaluating copper bioavailability to plants in a contaminated soil. *J Environ Qual* 32:824–833
- Che VB, Fontijn K, Ernst GGJ, Kervyn M, Elburg M, Van Ranst E, Suh CE (2012) Evaluating the degree of weathering in landslide-prone soils in the humid tropics: the case of Limbe, SW Cameroon. *Geoderma* 170:378–389



- Chow JC, Watson JG, Ashbaugh LL, Magliano KLCN (2003) Similarities and differences in PM10 chemical source profiles for geological dust from the San Joaquin Valley, California. *Atmos Environ* 37:1317–1340
- Clearfield A (1964) Structural aspects of zirconium chemistry. *Rev Pure Appl Chem* 14:91–108
- Cornu S, Lucas Y, Lebon E, Ambrosi J, Luizão F, Rouiller J, Bonnay M, Neal C (1999) Evidence of titanium mobility in soil profiles, Manaus, central Amazonia. *Geoderma* 91:281–295
- Cotton FA, Wilkinson G (1980) *Advanced inorganic chemistry*, 4th edn. Wiley, New York
- Couture P, Blaise C, Cluis D, Bastien C (1989) Zirconium toxicity assessment using bacteria, algae and fish assays. *Water Air Soil Pollut* 47:87–100
- Davis RV, Beckett PHT, Wollan E (1978) Critical levels of twenty potentially toxic elements in young spring barley. *Plant Soil* 49:395–408
- Davydov YP, Davydov DY, Zemskova LM (2006) Speciation of Zr(IV) radionuclides in solutions. *Radiochemistry* 48:358–364
- Dessureault-Rompré J, Luster J, Schulin R, Tercier-Waeber M-L, Nowack B (2010) Decrease of labile Zn and Cd in the rhizosphere of hyperaccumulating *Thlaspi caerulescens* with time. *Environ Pollut* 158:1955–1962
- Dou X, Zhang Y, Wang H, Wang T, Wang Y (2011) Performance of granular zirconium–iron oxide in the removal of fluoride from drinking water. *Water Res* 45:3571–3578
- Dumat C, Quenea K, Bermond A, Toïnen S, Benedetti MF (2006) Study of the trace metal ion influence on the turnover of soil organic matter in cultivated contaminated soils. *Environ Pollut* 142:521–529
- Dupré B, Gaillardet J, Rousseau D, Allègre CJ (1996) Major and trace elements of river-borne material: the Congo Basin. *Geochim Cosmochim Acta* 60(8):1301–1321
- Duvallet L, Martin F, Soubies F, Salvi S, Melfi AJ, Fortune JP (1999) The mobility of zirconium and identification of secondary Zr-bearing phases in bauxite from Pocos de Caldas, Minas Gerais, Brazil; a mass-balance and X-ray absorption spectroscopic study. *Can Mineral* 37:635–651
- Egli M, Fitze P (2001) Quantitative aspects of carbonate leaching of soils with differing ages and climates. *Catena* 46:35–62
- Ekberg C, Källvenius G, Albinsson Y, Brown PL (2004) Studies on the hydrolytic behavior of zirconium(IV). *J Solution Chem* 33:47–79
- Evangelou MWH, Bauer U, Ebel M, Schaeffer A (2007) The influence of EDDS and EDTA on the uptake of heavy metals of Cd and Cu from soil with tobacco *Nicotiana tabacum*. *Chemosphere* 68:345–353
- Feng J-L (2010) Behaviour of rare earth elements and yttrium in ferromanganese concretions, gibbsite spots, and the surrounding terra rossa over dolomite during chemical weathering. *Chem Geol* 271:112–132
- Feng J-L (2011) Trace elements in ferromanganese concretions, gibbsite spots, and the surrounding terra rossa overlying dolomite: their mobilization, redistribution and fractionation. *J Geochem Explor* 108:99–111
- Ferrand E, Dumat C, Leclerc-Cessac E, Benedetti MF (2006) Phytoavailability of zirconium in relation to its initial added form and soil characteristics. *Plant Soil* 287:313–325
- Flohr MJK, Ross M (1990) Alkaline igneous rocks of Magnet Cove, Arkansas: mineralogy and geochemistry of syenites. *Lithos* 26:67–98
- Fodor M, Hegedus A, Stefanovits-Banyai E (2002) Examination of effect of zirconium ascorbate on wheat seedlings. In: I. Pais (ed) *Proceedings of the 10th international trace element symposium*. Budapest, pp 76–82
- Fodor M, Hegedus A, Stefanovits-Banyai E (2005) Zirconium induced physiological alterations in wheat seedlings. *Biol Plantarum* 49:633–636
- Fodor M, Hegóczki J, Vereczkey G (2003) The effects of zirconium, a less known microelement, on basic fermentation characteristics and protein composition of *Saccharomyces cerevisiae*. *Acta Aliment* 32:353–362
- Gagnevin D, Daly JS, Kronz A (2009) Zircon texture and chemical composition as a guide to magmatic processes and mixing in a granitic environment and coeval volcanic system. *Contrib Mineral Petrol* 159:579–596

- Garnham GW, Codd GA, Gadd GM (1993) Accumulation of zirconium by microalgae and cyanobacteria. *Appl Microbiol Biotechnol* 39:666–672
- Ghosh S, Sharma A, Talukder G (1992) Zirconium. An abnormal trace element in biology. *Biol Trace Elem Res* 35:247–271
- Goldich SS (1938) A study in rock weathering. *J Geol* 46:17–58
- Grover P, Rekhadevi P, Danadevi K, Vuyyuri S, Mahboob M, Rahman M (2010) Genotoxicity evaluation in workers occupationally exposed to lead. *Int J Hyg Environ Health* 213:99–106
- Gundersen V, Bechmann IE, Behrens A, Stürup S (2000) Comparative investigation of concentrations of major and trace elements in organic and conventional Danish agricultural crops. 1. Onions (*Allium cepa* Hysam) and peas (*Pisum sativum* ping pong). *J Agric Food Chem* 48:6094–6102
- Gupta DK, Huang HG, Yang XE, Razafindrabe BHN, Inouhe M (2010) The detoxification of lead in *Sedum alfredii* H. is not related to phytochelatins but the glutathione. *J Hazard Mater* 177:437–444
- Hao Q, Guo Z, Qiao Y, Xu B, Oldfield F (2010) Geochemical evidence for the provenance of middle Pleistocene loess deposits in southern China. *Quaternary Sci Rev* 29:3317–3326
- Hill SJ, Arowolo TA, Butler OT, Chenery SRN, Cook JM, Cresser MS, Miles DL (2002) Atomic spectrometry update. Environmental analysis. *J Anal At Spectrom* 17:284–317
- Hinsinger P, Bengough AG, Vetterlein D, Young IM (2009) Rhizosphere: biophysics, biogeochemistry and ecological relevance. *Plant Soil* 321:117–152
- Hinsinger P, Brauman A, Devau N, Gérard F, Jourdan C, Laclau J-P, Cadre E, Jaillard B, Plassard C (2011) Acquisition of phosphorus and other poorly mobile nutrients by roots. Where do plant nutrition models fail? *Plant Soil* 348:29–61
- Hirsch AM, Fang A, Asad S, Kapulnik Y (1998) The role of phytohormones in plant-microbe symbioses. *Plant Soil* 194:171–184
- Hodson M (2002) Experimental evidence for mobility of Zr and other trace elements in soils. *Geochim Cosmochim Acta* 66:819–828
- Horvath T, Szilagyi V, Hartanyi Z (2000) Characterization of trace element distributions in soils. *Microchem J* 67:53–56
- Hoskin PWO (2005) Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. *Geochim Cosmochim Acta* 69:637–648
- Jiang W, Liu D (2010) Pb-induced cellular defense system in the root meristematic cells of *Allium sativum* L. *BMC Plant Biol* 10:40
- Jones DL (1998) Organic acids in the rhizosphere—a critical review. *Plant Soil* 205:25–44
- Jung S, Hoernes S, Mezger K (2000) Geochronology and petrogenesis of Pan-African, syn-tectonic, S-type and post-tectonic A-type granite (Namibia): products of melting of crustal sources, fractional crystallization and wallrock entrainment. *Lithos* 50:259–287
- Kabata-Pendias A (1993) Behavioural properties of trace metals in soils. *Appl Geochem* 8:Supplement 2, 3–9
- Kabata-Pendias A, Pendias H (1992) Trace elements in soils and plants, 2nd edn. CRC, Boca Raton, 365 p
- Kamal A, Kumar BA, Suresh P, Shankaraiah N, Kumar MS (2011) An efficient one-pot synthesis of benzothiazolo-4 $\beta$ -anilino-podophyllotoxin congeners: DNA topoisomerase-II inhibition and anticancer activity. *Bioorg Med Chem Lett* 21:350–353
- Klechkovsky VM, Gulyakin IV (1958) Behavior in soils and plants of the micro-quantities of strontium, cesium, ruthenium and zirconium. *Soil Sci* 3:1–15 (In Russian)
- Kopittke PM, Asher CJ, Blamey FPC, Menzies NW (2007) Toxic effects of Pb<sup>2+</sup> on the growth and mineral nutrition of signal grass (*Brachiaria decumbens*) and Rhodes grass (*Chloris gayana*). *Plant Soil* 300:127–136
- Kopittke PM, Asher CJ, Menzies NW (2008) Prediction of Pb speciation in concentrated and dilute nutrient solutions. *Environ Pollut* 153:548–554
- Kovalenko NI, Ryzhenko BN (2009) Comparative study of the solubility of zircon and baddeleyite. *Geochem Int* 47:405–413
- Kruglov SV, Vasil'yeva NA, Kurinov AD, Aleksakhin AM (1996) Distribution of radionuclides from Chernobyl fallout with regard to fractions of the soil-particle distribution of sod-podzolic soils. *Eur Soil Sci* 28:26–35

- Krzeslowska M, Lenartowska M, Mellerowicz EJ, Samardakiewicz S, Wozny A (2009) Pectinous cell wall thickenings formation—a response of moss protonemata cells to lead. *Environ Exp Bot* 65:119–131
- Krzeslowska M, Lenartowska M, Samardakiewicz S, Bilski H, Wozny A (2010) Lead deposited in the cell wall of *Funaria hygrometrica* protonemata is not stable—a remobilization can occur. *Environ Pollut* 158:325–338
- Kumpiene J, Brännvall E, Taraškevičius R, Aksamitauskas ū Zinkutis R (2011) Spatial variability of topsoil contamination with trace elements in preschools in Vilnius, Lithuania. *J Geochem Explor* 108:15–20
- Kurtz AC, Derry LA, Chadwick OA, Alfano MJ (2000) Refractory element mobility in volcanic soils. *Geology* 28:683–686
- Langmuir D, Herman JS (1980) The mobility of thorium in natural waters at low temperatures. *Geochim Cosmochim Acta* 44:1753–1766
- LeRiche HH (1973) The distribution of minor elements among the components of a soil developed in loess. *Geoderma* 9:43–57
- Liao YC, Chien SWC, Wang MC, Shen Y, Hung PL, Das B (2006) Effect of transpiration on Pb uptake by lettuce and on water soluble low molecular weight organic acids in rhizosphere. *Chemosphere* 65:343–351
- Little MG, Lee C-TA (2010) Sequential extraction of labile elements and chemical characterization of a basaltic soil from Mt. Meru, Tanzania. *J Afr Earth Sci* 57:444–454
- Liu X, Wang Q, Deng J, Zhang Q, Sun S, Meng J (2010) Mineralogical and geochemical investigations of the Dajia Salento-type bauxite deposits, western Guangxi, China. *J Geochem Explor* 105:137–152
- Lomonte C, Doronila AI, Gregory D, Baker AJM, Kolev SD (2010) Phytotoxicity of biosolids and screening of selected plant species with potential for mercury phytoextraction. *J Hazard Mater* 173:494–501
- Louvel M, Sanchez-Valle C, Petitgirard S, Cardon H, Daniel I, Cauzid J (2009) Zr speciation and partitioning in SiO<sub>2</sub>-rich aqueous fluids and silicate melts. *Goldschmidt Conference Abstracts*. p 73
- Lowery Claiborne L, Miller CF, Walker BA, Wooden JL, Mazdab FK, Bea F (2006) Tracking magmatic processes through Zr/Hf ratios in rocks and Hf and Ti zoning in zircons: an example from the Spirit Mountain batholith, Nevada. *Mineral Mag* 70:517–543
- Lyubenova L, Schröder P (2011) Plants for waste water treatment—effects of heavy metals on the detoxification system of *Typha latifolia*. *Bioresour Technol* 102:996–1004
- Maeck WJ, Spraktes FW, Tromp RL, Keller JH (1975) Analytical results, recommended nuclear constants and suggested correlations for the evaluation of Oklo fission-product data. In: IAEA Vienna. *Le Phénomène d'Oklo*, pp 319–324
- Maestri E, Marmiroli M, Visioli G, Marmiroli N (2010) Metal tolerance and hyperaccumulation: costs and trade-offs between traits and environment. *Environ Exp Bot* 68:1–13
- Malandrino M, Abollino O, Buoso S, Giacomino A, La Gioia C, Mentasti E (2011) Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite. *Chemosphere* 82:169–178
- Maria GES, Cogliatti DH (1988) Bidirectional Zn-fluxes and compartmentation in wheat seeding roots. *J Plant Physiol* 132:312–315
- Martínez Cortizas A, Gayoso EG-R, Muñoz JCN, Pombal XP, Buurman P, Terribile F (2003) Distribution of some selected major and trace elements in four Italian soils developed from the deposits of the Gauro and Vico volcanoes. *Geoderma* 117:215–224
- Meyers DER, Auchterlone GJ, Webb RI, Wood B (2008) Uptake and localisation of lead in the root system of *Brassica juncea*. *Environ Pollut* 153:323–332
- Mirza N, Mahmood Q, Pervez A, Ahmad R, Farooq R, Shah MM, Azim MR (2010) Phytoremediation potential of *Arundo donax* in arsenic-contaminated synthetic wastewater. *Bioresour Technol* 101:5815–5819
- Mosulishvili LM, Shoniya NI, Katamadze NM, Ginturi EN (1994) Environmental radionuclide distribution in the republic of Georgia after the Chernobyl catastrophe. *Zh Anal Khim* 49:135–139

- Mou D, Yao Y, Yang Y, Zhang Y, Tian C, Achal V (2011) Plant high tolerance to excess manganese related with root growth, manganese distribution and antioxidative enzyme activity in three grape cultivars. *Ecotoxicol Environ Saf* 74:776–786
- Muhs D, Budahn J (2009) Geochemical evidence for African dust and volcanic ash inputs to terra rossa soils on carbonate reef terraces, northern Jamaica, West Indies. USGS Staff—published research
- Muhs DR, Budahn J, Avila A, Skipp G, Freeman J, Patterson D (2010) The role of African dust in the formation of Quaternary soils on Mallorca, Spain and implications for the genesis of Red Mediterranean soils. *Quaternary Sci Rev* 29:2518–2543
- Muhs DR, Budahn JR, Prospero JM, Carey SN (2007) Geochemical evidence for African dust inputs to soils of western Atlantic islands: Barbados, the Bahamas, and Florida. *J Geophys Res* 112:126
- Mushtaq A (2012) Producing radioisotopes in power reactors. *J Radioanal Nucl Chem* 292:793–802
- Naudet R (1974) Summary report on the Oklo phenomenon. French CEA Report. *Bull Inf Sci Tech* 193:7–85
- Oliva VJ, Dupre B, Fortune JP, Martin F, Braun JJ, Nahon D, Robain H (1999) The effect of organic matter on chemical weathering: study of a small tropical watershed: nsimi-zoetele site, cameroon. *Geochim Cosmochim Acta* 63:4013–4035
- Owojori OJ, Reinecke AJ, Rozanov AB (2010) Influence of clay content on bioavailability of copper in the earthworm *Eisenia fetida*. *Ecotoxicol Environ Saf* 73:407–414
- Pais I, Jones JB (1983) The handbook of trace elements. St Lucie Press, Boca Raton
- Pais I (1983) The biological importance of titanium. *J Plant Nutr* 6:3–131
- Panahi A, Young GM, Rainbird RH (2000) Behavior of major and trace elements (including REE) during Paleoproterozoic pedogenesis and diagenetic alteration of an Archean granite near Ville Marie, Quebec, Canada. *Geochim Cosmochim Acta* 64:2199–2220
- Patino L, Velbel M, Price J, Wade J (2003) Trace element mobility during spheroidal weathering of basalts and andesites in Hawaii and Guatemala. *Chem Geol* 202:343–364
- Patra M, Bhowmik N, Bandopadhyay B, Sharma A (2004) Comparison of mercury, lead and arsenic with respect to genotoxic effects on plant systems and the development of genetic tolerance. *Environ Exp Bot* 52:199–223
- Peng J-F, Song Y-H, Yuan P, Cui X-Y, Qiu G-L (2009) The remediation of heavy metals contaminated sediment. *J Hazard Mater* 161:633–640
- Pettijohn FJ (1941) Persistence of heavy minerals and geologic age. *J Geol* 49:610–625
- Pettke T, Audetat A, Schaltegger U, Heinrich CA (2005) Magmatic-hydrothermal crystallization in the W–Sn mineralized mole granite (NSW, Australia)—Part II: evolving zircon and thorite trace element chemistry. *Chem Geol* 220:191–213
- Pokrovsky O, Schott J (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chem Geol* 190:141–179
- Pourrut B, Perchet G, Silvestre J, Cecchi M, Guiesse M, Pinelli E (2008) Potential role of NADPH-oxidase in early steps of lead-induced oxidative burst in *Vicia faba* roots. *J Plant Physiol* 165:571–579
- Prisyagina NI, Kovalenko NI, Ryzhenko BN, Starshinova NP (2008) Experimental determination of ZrO<sub>2</sub> solubility in alkaline fluoride solutions at 500°C and 1000 bar. *Geochem Int* 46:1164–1167
- Quenea K, Lamy I, Winterton P, Bermond A, Dumat C (2009) Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water. *Geoderma* 149:217–223
- Qureshi MI, D'Amici GM, Fagioni M, Rinalducci S, Zolla L (2010) Iron stabilizes thylakoid protein-pigment complexes in Indian mustard during Cd-phytoremediation as revealed by BN-SDS-PAGE and ESI-MS/MS. *J Plant Physiol* 167:761–770
- Rascio N, Navari-Izzo F (2011) Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting? *Plant Sci* 180:169–181

- Ribeiro J, da Silvab EF, Li Z, Ward C, Flores D (2010) Petrographic, mineralogical and geochemical characterization of the Serrinha coal waste pile (Douro Coalfield, Portugal) and the potential environmental impacts on soil, sediments and surface waters. *Int J Coal Geol* 83:456–466
- Rubin JN, Henry CD, Price JG (1993) The mobility of zirconium and other “immobile” elements during hydrothermal alteration. *Chem Geol* 110:29–47
- Ryzhenko BN, Kovalenko NI, Prisyagina NI, Starshinova NP, Krupskaya VV (2008) Experimental determination of zirconium speciation in hydrothermal solutions. *Geochem Int* 46:328–339
- Saifullah ME, Qadir M, de Caritat P, Tack FMG, Du Laing G, Zia MH (2009) EDTA-assisted Pb phytoextraction. *Chemosphere* 74:1279–1291
- Saifullah ZMH, Meers E, Ghafoor A, Murtaza G, Sabir M, Zia-ur-Rehman M, Tack FMG (2010) Chemically enhanced phytoextraction of Pb by wheat in texturally different soils. *Chemosphere* 79:652–658
- Sako A, Mills AJ, Roychoudhury AN (2009) Rare earth and trace element geochemistry of termite mounds in central and northeastern Namibia: mechanisms for micro-nutrient accumulation. *Geoderma* 153:217–230
- Sammut ML, Noack Y, Rose J, Hazemann JL, Proux O, Depoux M, Ziebel A, Fiani E (2010) Speciation of Cd and Pb in dust emitted from sinter plant. *Chemosphere* 78:445–450
- Sandoval R, Cooper AM, Aymar K, Jain A, Hristovski K (2011) Removal of arsenic and methylene blue from water by granular activated carbon media impregnated with zirconium dioxide nanoparticles. *J Hazard Mater* 193:296–303
- Sanzharova DI, Aleksakhin RM (1982) Uptake of  $^{22}\text{Na}$ ,  $^{32}\text{P}$ ,  $^{65}\text{Zn}$ ,  $^{86}\text{Sr}$  and  $^{90}\text{Sr}$  by crops. *Pochvovedeniye* 9:59–64
- Schulin R, Curchod F, Mondeshka M, Daskalova A, Keller A (2007) Heavy metal contamination along a soil transect in the vicinity of the iron smelter of Kremikovtzi (Bulgaria). *Geoderma* 140:52–61
- Senesi N, Padovano G, Brunetti G (1988) Scandium, titanium, tungsten and zirconium content in commercial inorganic fertilizers and their contribution to soil. *Environ Technol Lett* 9:1011–1020
- Shahid M, Arshad M, Kaemmerer M, Pinelli E, Probst A, Baque D, Pradere P, Dumat C (2012a) Long term field metal extraction by pelargonium: phytoextraction efficiency in relation with plant maturity. *Int J Phytorem* 14:493–505
- Shahid M, Dumat C, Silvestre J, Pinelli (2012c) Effect of fulvic acids on lead-induced oxidative stress to metal sensitive *Vicia faba* L. plant. *Biol Fert Soils*. [10.1007/s00374-012-0662-9](https://doi.org/10.1007/s00374-012-0662-9)
- Shahid M, Pinelli E, Dumat C (2012b) Review of Pb availability and toxicity to plants in relation with metal speciation; role of synthetic and natural organic ligands. *J Hazard Mater*. [10.1016/j.jhazmat.2012.01.060](https://doi.org/10.1016/j.jhazmat.2012.01.060)
- Shahid M, Pinelli E, Pourrut B, Silvestre J, Dumat C (2011a) Lead-induced genotoxicity to *Vicia faba* L. roots in relation with metal cell uptake and initial speciation. *Ecotoxicol Environ Saf* 74:78–84
- Shahid M, Pourrut B, Dumat C, Winterton P, Pinelli E (2011b) Lead uptake, toxicity, and detoxification in plants. *Rev Environ Contam Toxicol* 213:113–136
- Shahid M, Kirmani SAA, Zaidi SAH (2011c) Effect of pH and fulvic acid on cadmium speciation. *Int Poster J Sci Technol* 1:83–88
- Shahid M (2010) Lead-induced toxicity to *Vicia faba* L. in relation with metal cell uptake and initial speciation. PhD Thesis, INPT, Toulouse-France
- Shi JJ, Chen H (2002) Dynamics of accumulation and disappearance of zirconium-95 in the maize/soil and soybean/soil ecosystem. *J Environ Sci* 23:109–113
- Shi JJ, Guo JF (2002) Uptake from soil and distribution of  $^{95}\text{Zr}$  in Chinese cabbage. *J Agric Sci* 139:431–435
- Shi JJ, Guo JF, Chen H (2002) Dynamics of  $^{95}\text{Zr}$  in the rice/water/soil system. *Appl Radiat Isot* 56:735–740
- Shi JJ, Li MY (2003) Migration and distribution of  $^{95}\text{Zr}$  in a simulated marine fishes/seawater/sediment ecosystem. *Acta Ecologica Sinica* 23:330–335

- Simon L, Hajdu F, Balogh Á, Pais I (1998) Effect of titanium on growth and photosynthetic pigment composition of *Chlorella pyrenoidosa* (green alga). II. Effect of titanium ascorbate on pigment content and chlorophyll metabolism of *Chlorella*. In: Pais I (ed) New results in the research of hardly known trace elements and their role in the food chain. University of Horticulture and Food Science, Budapest, pp 87–101
- Smith IC, Carson BL (1978) Trace metals in the environment: vol 3—Zirconium. Ann Arbor Sci Pub Inc, Ann Arbor, p 405
- Sommer M, Halm D, Weller U, Zarei M, Stahr K (2000) Lateral podzolization in a granite landscape. *Soil Sci Soc Am J* 64:1434–1442
- Stiles CA, Mora CI, Driese SG (2003) Pedogenic processes and domain boundaries in a Vertisol climosequence: evidence from titanium and zirconium distribution and morphology. *Geoderma* 116:279–299
- Stojilovic N, Bender ET, Ramsier RD (2005) Surface chemistry of zirconium. *Prog Surf Sci* 78:101–184
- Swindale LD, Jackson ML (1956) Genetic processes in some residual podzolised soils of New Zealand. In: 6th International Congress of Soil Science, vol 37. Paris, pp 233–239
- Tejan-Kella MS, Chittleborough DJ, Fitzpatrick RW (1991) Weathering assessment of heavy minerals in age sequences of Australian sandy soils. *Soil Sci Soc Am J* 55:527–538
- Tematio P, Fritsch E, Hodson ME, Lucas Y, Bitom D, Bilong P (2009) Mineral and geochemical characterization of a leptic aluandic soil and a thapto aluandic-ferralsol developed on trachytes in Mount Bambouto (Cameroon volcanic line). *Geoderma* 152:314–323
- Thomas JB, Bodnar RJ, Shimizu N, Sinha AK (2002) Determination of zircon/melt trace element partition coefficients from SIMS analysis of melt inclusions in zircon. *Geochim Cosmochim Acta* 66:2887–2901
- Tome FV, Blanco Rodriguez MP, Lozano JC (2003) Soil-to-plant transfer factors for natural radionuclides and stable elements in a Mediterranean area. *J Environ Radioact* 65:161–175
- Udovic M, Lestan D (2009) Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching. *Chemosphere* 74:1367–1373
- USGS (United States Geological Survey) (2012) <http://minerals.usgs.gov/minerals/pubs/commodity/zirconium/>. Assessed 23 Apr 2012
- Uzu G, Sobanska S, Aliouane Y, Pradere P, Dumat C (2009) Study of lead phytoavailability for atmospheric industrial micronic and sub-micronic particles in relation with lead speciation. *Environ Pollut* 157:1178–1185
- Uzu G, Sobanska S, Sarret G, Muñoz M, Dumat C (2010) Foliar lead uptake by lettuce exposed to atmospheric fallouts. *Environ Sci Technol* 44:1036–1042
- Uzu G, Sobanska S, Sarret G, Sauvain J, Pradère P, Dumat C (2011) Characterization of lead-recycling facility emissions at various workplaces: major insights for sanitary risks assessment. *J Hazard Mater* 186:1018–1027
- Vadas TM, Ahner BA (2009) Cysteine- and glutathione-mediated uptake of lead and cadmium into *Zea mays* and *Brassica napus* roots. *Environ Pollut* 157:2558–2563
- Valeton I, Biermann M, Reche R, Rosenberg F (1987) Genesis of nickel laterites and bauxites in Greece during the Jurassic and Cretaceous, and their relation to ultrabasic parent rocks. *Ore Geol Rev* 2:359–404
- Vega FA, Andrade ML, Covelo EF (2010) Influence of soil properties on the sorption and retention of cadmium, copper and lead, separately and together, by 20 soil horizons: comparison of linear regression and tree regression analyses. *J Hazard Mater* 174:522–533
- Venable FP (1922) Zirconium and its compounds (American Chemical Society, Monograph Series). The Chemical Catalog Company, New York
- Verbruggen N, Hermans C, Schat H (2009) Molecular mechanisms of metal hyperaccumulation in plants. *New Phytol* 181:759–776
- Verel I, Visser GWM, Boerman OC, Van Eerd JEM, Finn R, Boellaard R, Vosjan MJWD, Stigter-Van Walsum M, Snow GB, Van Dongen GAMS (2003) Long-lived positron emitters zirconium-89 and iodine-124 for scouting of therapeutic radioimmunoconjugates with PET. *Cancer Biother Radiopharm* 18:655–661

- Viers J, Dupre B, Braun JJ, Deberdt S, Angeletti B, Ngoupayou JN, Michard A (2000) Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameroon): constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments. *Chem Geol* 169:211–241
- Wang HF, Takematsu N, Ambe S (2000) Effects of soil acidity on the uptake of trace elements in soybean and tomato plants. *Appl Radiat Isot* 52:803–811
- Wang X, Griffin WL, O'Reilly SY, Zhou XM, Xu XS, Jackson SE, Pearson NJ (2002) Morphology and geochemistry of zircons from late Mesozoic igneous complexes in coastal SE China: implications for petrogenesis. *Mineral Mag* 66:235–251
- Whicker FW, Schultz V (1982) *Radioecology: nuclear energy and the environment*, vol I. CRC press, Boca Raton, Florida
- Whitfield CJ (2011) Evaluation of elemental depletion weathering rate estimation methods on acid-sensitive soils of north-eastern Alberta, Canada. *Geoderma* 166:189–197
- Wu F-L, Lin D, Su D (2011) The effect of planting oilseed rape and compost application on heavy metal forms in soil and Cd and Pb uptake in rice. *Agric Sci China* 10:267–274
- Wu Y, Hendershot WH (2010) The effect of calcium and pH on nickel accumulation in and rhizotoxicity to pea (*Pisum sativum* L.) root—empirical relationships and modeling. *Environ Pollut* 158:1850–1856
- Xu H, Song P, Gu W, Yang Z (2011) Effects of heavy metals on production of thiol compounds and antioxidant enzymes in *Agaricus bisporus*. *Ecotoxicol Environ Saf*. [org/10.1016/j.ecoenv.2011.04.010](https://doi.org/10.1016/j.ecoenv.2011.04.010)
- Yadav SK (2010) Heavy metals toxicity in plants: an overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. *S Afr J Bot* 76:167–179
- Yan ZZ, Ke L, Tam NFY (2010) Lead stress in seedlings of *Avicennia marina*, a common mangrove species in South China, with and without cotyledons. *Aquat Bot* 92:112–118
- Yau TL (2010) 3.14—corrosion of zirconium and its alloys. *Shreir Corros* 3:2094–2134
- Yip TCM, Yan DYS, Yui MMT, Tsang DCW, Lo IMC (2010) Heavy metal extraction from an artificially contaminated sandy soil under EDDS deficiency: Significance of humic acid and chelant mixture. *Chemosphere* 80:416–421
- Yirchenko YP, Agapkina GI (1993) Organic radionuclide compounds in soils surrounding the Chernobyl Nuclear Power Plant. *Eur Soil Sci* 25:51–59
- Zaccone C, Coccozza C, Cheburkin AK, Shotykh W, Miano TM (2008) Distribution of As, Cr, Ni, Rb, Ti and Zr between peat and its humic fraction along an undisturbed ombrotrophic bog profile (NW Switzerland). *Appl Geochem* 23:25–33
- Zaraisky G, Aksyuk A, Devyatova V, Udoratina O, Chevychelov V (2008) Zr/Hf ratio as an indicator of fractionation of rare-metal granites by the example of the Kukulbei complex, eastern Transbaikalia. *Petrology* 16:710–736
- Zaraisky G, Aksyuk A, Devyatova V, Udoratina O, Chevychelov V (2009) The Zr/Hf ratio as a fractionation indicator of rare-metal granites. *Petrology* 17:25–45
- Zeng F, Ali S, Zhang H, Ouyang Y, Qiu B, Wu F, Zhang G (2011) The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ Pollut* 159:84–91
- Zou Z, Qiu R, Zhang W, Dong H, Zhao Z, Zhang T, Wei X, Cai X (2009) The study of operating variables in soil washing with EDTA. *Environ Pollut* 157:229–236