

# Technical Report

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### Uptake of nuclides by plants

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April 2004

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*Keywords:* Biosphere, Ecosystems, Radionuclide.

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author and do not necessarily coincide with those of the client.

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## Summary

This review on plant uptake of elements has been prepared to demonstrate how plants take up different elements. The work discusses the nutrient elements, as well as the general uptake and translocation in plants, both via roots and by foliar absorption. Knowledge of the uptake by the various elements within the periodic system is then reviewed. The work also discusses transfer factors (TF) as well as difficulties using TF to understand the uptake by plants. The review also focuses on species differences. Knowledge necessary to understand and calculate plant influence on radionuclide recirculation in the environment is discussed, in which the plant uptake of a specific nuclide and the fate of that nuclide in the plant must be understood. Plants themselves determine the uptake, the soil/sediment determines the availability of the nuclides and the nuclides themselves can interact with each other, which also influences the uptake. Consequently, it is not possible to predict the nuclide uptake in plants by only analysing the nuclide concentration of the soil/substrate.

# Sammanfattning

Denna rapport har sammanställts för att ge en förståelse för hur växter tar upp olika nuclider. Upptag och transport till skottet, liksom upptag via rötter och skott diskuteras. Kunskapen om alla olika ämnen i det periodiska systemet gällande upptag i växter går igenom. Arbetet diskuterar också överföringsfaktorer (TF) samt svårigheten att använda TF för att förstå upptag i växter. Olika växttypers upptag diskuteras i rapporten. Rapporten försöker även att belysa den nödvändiga kunskap som behövs för att förstå och beräkna växtens inverkan på flödet av radionuklider i ett ekosystem. Växten bestämmer själv över sitt upptag, jorden/sedimentet bestämmer tillgängligheten och nukliderna själva påverkar systemet genom interaktioner. Av den orsaken är det inte möjligt att bedöma en växts upptag av en nuklid genom att analysera koncentrationen av densamma i substratet.

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# 1 Introduction

Nuclear power produces nuclear waste and systems of taking care of the waste have long been discussed, of which deep repository is the most likely. Sites for deep repository in bedrock are being characterised in several projects within the FUD-program.

A future problem may be leakage of nuclear waste, via transports ending up in the earth's ecosystem. An important component in such a transport chain is vegetation, since plants can take up nuclides from soil, air and water and are also food and feed for many animals as well as for human beings. Plants are also good indicators and are used for mapping of pollutants. To be able to predict a possible future problem with nuclide leakage from deep repositories of spent nuclear fuel it is necessary to understand and be able to calculate plant influence on radionuclide recirculation in the environment. This review on plant uptake of elements has therefore been prepared in order to examine how plants take up different nuclides as well as the fate of that nuclide in the plant.

The review discusses the plant elemental uptake in general and more specifically knowledge of the uptake of the various elements of the periodic system, including plant species differences. The work also discusses the commonly used soil-to-plant transfer factors (TF), and the difficulties to use TF, in order to understand the uptake by plants. This work will hopefully be valuable when calculating the nuclide recirculation in various biotopes of the biosphere part in the FUD program.

## 2 Different elements, environments and plant types

Plants take up all elements present in the rhizosphere as well as in the surrounding of leaves and thali, thus, plants are able to take up and translocate all elements of the periodic system. Some of the elements are used in various functions in the plant organism; N, P, K, S, Mg and Ca are used in large amounts whereas Fe, Mn, Mo, Ni, Cu, Zn, B and Cl are used in trace levels. These elements are essential for plants. In addition, plants also use H, O and C, which are taken up as water and carbon dioxide but may sometimes also be taken up as organic substances. Other trace elements have been discussed as being essential for some plants, e.g. La and Ce /Asher, 1991/. However, to be able to find out whether or not an element is essential it must be possible to delete this element from the plants surroundings to find out if 1) the plant is unable to complete its life cycle, 2) the element can not replace a nutrient element, and 3) the element is directly involved in plant metabolism /Marschner, 1995/. There are also beneficial elements, meaning that they can be essential 1) for some plant species, 2) under specific conditions, and 3) despite not being essential, be able to increase the growth rate of plants /Marschner, 1995/. Examples of beneficial elements for some plant species are V, Na and I.

**THE PERIODIC SYSTEM**

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	E	Fm	Md	No	Lw		

	Metals
	Non metals
	Half metals

Figure 2-1. The periodic system.

Elements are available to plants in air and water as well as in soil and sediment. Plants are able to take up elements from all of these media. Thus, higher plants take up elements from water or air by their shoots, and the roots take up elements from the soil or sediment (or the surrounding medium). Mosses accumulate elements from the air using their shoot or thallus, and macroalgae use their thallus to accumulate elements from the water.

The uptake of elements depends on the availability of them in the rhizosphere or in the surrounding medium. The various elements are bound to greater or lesser extents to the soil/sediment particles, which in turn varies depending on organic matter content, pH, redox potential, CEC (cation exchange capacity) of the colloids, as well as salinity and clay content of the matrix /review in Greger, 1999/. Therefore, elements can be differently available to the plant in different soils, sediment and other matrixes.

Water and air function mostly as transport media for the elements, thus having short retention time as well as low concentrations in these media. Soil and sediments instead are considered as sinks ending up in high concentrations. Various elements vary in retention time in different media, thus influencing the element concentration of the medium /Förstner and Wittmann, 1979/. For example, Pb has a very short retention time in water whereas that of Zn is much longer.

In addition, there is equilibrium between the element concentration at the interface of, e.g. water and sediment /Förstner and Wittmann, 1979/. The equilibrium can be influenced by external factors, which in turn affect plant uptake. Such factors include resuspension, bioturbation, and addition of organic matter and changed salinity (common in estuaries). The concentration is often much lower in the water phase than in the sediment, which means that factors releasing elements from the sediment will increase the water concentration of the element to a high degree. The difference in concentration is often even bigger between air and soil, and since most elements are not able to be in a gaseous state, they are unable to form an equilibrium.

The different elements are present in the external media in different forms (species). The speciation of the element is important when dealing with plant uptake since plants cannot take up all forms. For example, Cd in complex with chloride has been shown to be difficult to take up by plants /Greger et al, 1995/. Therefore, Cd in saline water will be present in such complexes and the uptake by plants will decrease with increasing salinity. Some of the metals are taken up as cations (e.g.  $\text{Ca}^{2+}$ ) whereas others as anions (e.g.  $\text{MoO}_4^{2-}$ ). Elements can also be taken up in gaseous form, e.g. Hg, Se, I as well as the oxides of nitrogen, carbon and sulphur, through the stomata of leaves.

Different plant species, and even different genotypes of species have different efficiencies in taking up specific elements. Some plants are capable of high accumulation and thus can hyperaccumulate a specific element and thereby be used in phytoextraction or phytomining /Brooks, 1998/.



### 3 Plant uptake of elements in general

Plants take up and accumulate elements in their tissue but can also be released back into the surrounding medium. The accumulation of an element by the plant therefore is referred to as net uptake and is based on both influx and efflux. Part of the element taken up is translocated further to other plant parts.

The net uptake may be of different magnitude depending on the plant genotype. There are extremes of strategies in some plant genotypes /Baker, 1981/ (Figure 3-1). There are some plants, called excluders, that have low uptake of the element at quite high external concentrations of the element. These plants have some kind of barrier to avoid uptake, but when the external concentrations become too high, this barrier loses its function, probably due to toxic action by the element, and uptake increases massively. Other plants, called accumulators or includers, have high accumulation of elements at very low external element concentrations. These plants have certain detoxification mechanisms within the tissue, which allows the plant to accumulate such high amounts of metals. At high external concentrations, however, these plants do not increase their uptake, probably due to competition between elements at the uptake site. A special case of accumulator is the hyperaccumulator, which shows extreme accumulation of the element in leaves. For example, the concentration in leaves ( $\text{mg}(\text{g dry weight})^{-1}$ ) is shown to be  $> 0.1$  for Cd,  $> 1$  for Pb, Co, Cu, Ni or  $> 10$  for Mn and Zn /Baker et al, 2000/.

The uptake of elements is affected by other ions. There are antagonisms between ions of the same charges. Therefore, a low pH decreases the uptake of cations in a solution culture due to competition between cations and hydrogen ions ( $\text{H}^+$ ) at the uptake sites. However, when soil is involved this is masked by the fact that the low pH releases cations from colloids and consequently increases the concentration of these cations in the rhizosphere, which in turn increases the cation accumulation.

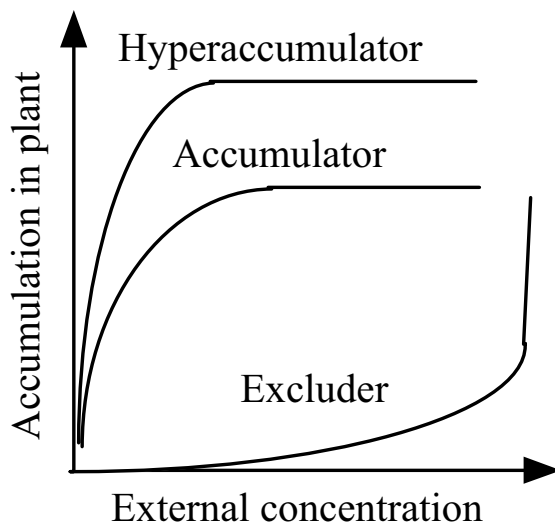


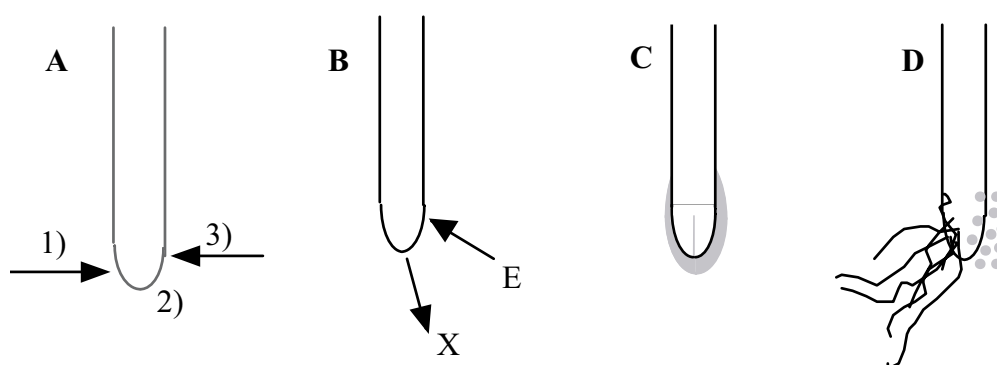
Figure 3-1. Plants with different uptake characteristics.

The absorption area of the roots/leaves also affects uptake. The larger the absorption area the higher is the effective uptake /Greger, 1999/. Furthermore, increased biomass production increases the uptake of elements. However, the accumulation in the tissue will diminish due to dilution caused by biomass increase and that the uptake rate is lower than the rate of biomass production /Ekvall and Greger, 2003/.

### 3.1 Uptake by roots

The movement of mineral elements to the root surface depends on the following (Figure 3-2A): 1) Diffusion of elements along the concentration gradient formed due to uptake generating depletion of the element in the root vicinity. 2) Root interception, where soil volume is displaced by root volume due to root growth. 3) Mass flow, transport of bulk soil solution along the water potential gradient (driven by transpiration) /Marschner, 1995/.

To facilitate or restrict the uptake of elements, plants can release, via the roots, certain substances that bind to certain elements in the rhizosphere (Figure 3-2B). In this way, elements that are firmly bound to soil particles can be released for uptake. One example is phytosiderophores, which facilitate the uptake of Fe, but also Mn and Zn /Römheld, 1991/. This is a system that is used by grasses. Other substances facilitating or restricting the uptake are organic acids, which bind to, e.g. Al, and form large complexes that are difficult for the plant to take up /Jackson et al, 1990/. Plants can also excrete mucilage (Figure 3-2C), a high-molecular-weight gelatinous material consisting mainly of polysaccharides, including 20–50% polyuronic acids depending on plant species /Morel et al, 1986; Ray et al, 1988/. The production of mucilage is positively correlated with the growth rate of roots /Trolldenier and Hecht-Buchholz, 1984/. Microorganisms usually invade the mucilage and, together with soil particles, the material is called mucigel, which facilitates or restricts ion uptake. Since mucigel creates interaction in the soil root interface it is probably of importance for uptake of the micronutrients, toxic heavy metals, aluminium and probably also for other elements.



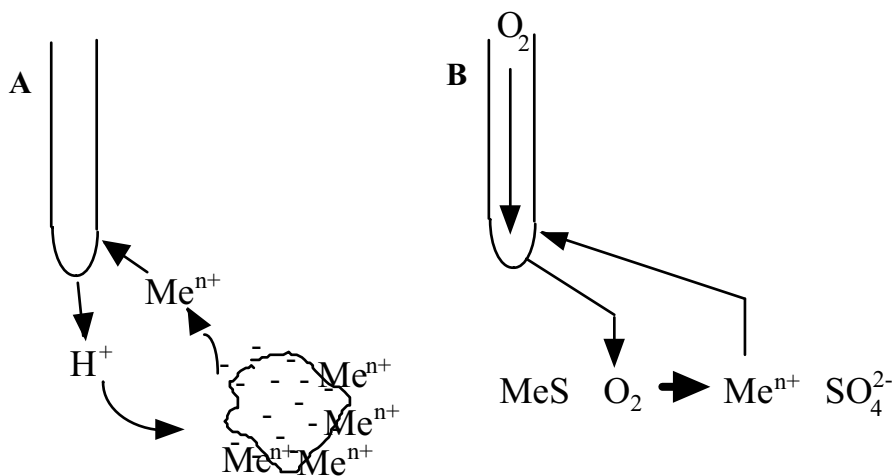
**Figure 3-2.** A. Movement of mineral elements to the root surface by 1) diffusion, 2) interception, 3) mass flow. B. Release of substances (X) from the root to enhance or prevent uptake of elements (E). C. Mucigel, including mucilage (grey) excreted by the plant root may facilitate or restrict the uptake of elements. D. Mycorrhiza (left) and bacteria (right) can enhance or prevent uptake of elements.

Mycorrhiza is known to increase the uptake of phosphorus by plant roots as well as prevent heavy metal uptake /Tinker at al, 1992/ and nitrogen-fixing bacteria help the plant to use atmospheric nitrogen /Marschner, 1995/ (Figure 3-2D). Furthermore, recent investigations show that microbes may also be important for uptake of metals /van der Leilie, 2001, pers comm/.

Plants are able to excrete hydrogen ions ( $H^+$ ) into the rhizosphere, which decrease the pH by one unit within 1–2 mm distance to the root surface /Muranyi et al, 1994/. This in turn gives a cation exchange with metal cations that are bound to the negatively charged colloids, thus the cations will be more available for uptake and the hydrogen ion instead binds to the colloid (Figure 3-3A). In environments with low redox potential, e.g. waterlogged environments, plants are able to translocate oxygen from the shoot to the roots and there oxygenise the rhizosphere, thereby increasing the redox potential (Figure 3-3B) /Armstrong et al, 1992; Chen and Barko, 1988/. This oxygen either originates from the photosynthesis (especially occurring in submerged plants) or has been taken up from air by the leaves (emerged plants).

The exact locality of the ion uptake by roots is somewhat different, depending on the element in consideration. Some elements in some plants are taken up primarily at the apical region; others are taken up over the entire root surface. Uptake depends on both the uptake capacity and the growth characteristics of the root system. When the element uptake by the root is high and the nutrient concentration in the soil is low, element uptake is limited by diffusion. At low diffusion rates compared with the uptake rates, an ion depletion zone adjacent to the root surface will be formed. The roots would rapidly deplete the soil adjacent to their surface if they did not have a capacity for continuous growth to new sites.

The movement of ions from the external solution to the cell walls of the roots is a non-metabolic, passive process driven by diffusion or mass flow /Marschner, 1995/. The primary cell walls consist of a network of cellulose, hemicellulose, pectins and glycoproteins. This network forms pores of different size in which the elemental ions can move. Pectins consist of polygalacturonic acid with negatively charged carboxylic groups acting as cation exchangers. In the smaller pores of the cell wall the cations are attracted to the negative charges of the cell wall. Depending on the density of negative charges the cations can be concentrated, e.g. at the plasma membrane, increasing the concentration gradient across the membrane and thereby promoting transport into the cell. The anions move by repulsion caused by the negative charges of the walls.

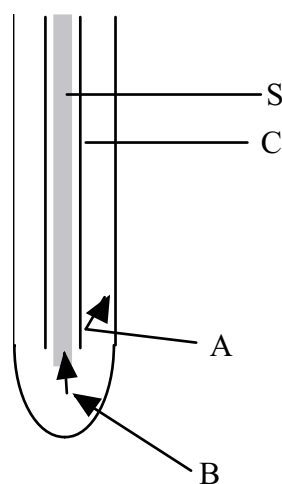


**Figure 3-3.** Mechanisms by which roots increase the cation ( $Me$ ) uptake.

Elements are moving either apoplastically, i.e. in the cell wall system outside the plasma membrane, or symplastically, i.e. in the cytoplasm from cell to cell via plasmodesmata. Elements that penetrate into the cytoplasm can also be shuttled into the vacuole via various mechanisms depending on element. Examples are Cd and Cu, which form complexes with phytochelatin (PC), a polypeptide formed due to the presence of the metal /Steffens, 1990/. The PC-metal complex is translocated into the vacuole, where the bonding is broken due to low pH, and the PC is transported back to the cytoplasm whereas the metal stays in the vacuole, probably linked to an organic acid.

Some elements are taken into the cells to a large extent (e.g. K), whereas cellular uptake of other elements is more or less avoided (e.g. Ca) since the latter can cause harm to the cellular activity such as binding to phosphorus, thereby causing phosphorus-deficiency and lack of energy (ATP) /Marschner, 1995/. The latter type of elements are therefore translocated in the tissue via the apoplast and some of these elements, if they are cations, are trapped by the negative charges of the cell walls and can be accumulated there to a high extent. Therefore, the highest concentration of such cations is found in roots whereas they can be found to a lower extent in the shoot. Another reason for a high accumulation in the roots is that the apoplastic translocation from the outside to the xylem vessels, the translocation vessel in centre of the root (steele), ends at the Casparian strips which form a suberinised and impermeable part of the endodermis cell walls surrounding the stele /Collander, 1941/. However, at the root tip the Casparian strips are not yet formed, and thus the elements can be translocated into the xylem in the root tip (Figure 3-4). The mechanism behind the transport into the xylem is not yet known.

Translocation to the shoot will be performed in the xylem and this translocation is promoted by transpiration of water via leaves. A young plant, however, has a small ratio of shoot-to-root mass and in such plants the root pressure determines the translocation of xylem sap to the shoot. The root pressure is formed by the ion uptake that in turn promotes water uptake caused by the formed concentration gradient between the rhizosphere and the root tissue. For some divalent cations translocation is influenced by cation exchange at the negative charges of the xylem vessel walls /Van de Geijn and Petit, 1979/. It should also be noted that there is a transverse translocation from the xylem to the neighbouring cells along the entire stem.

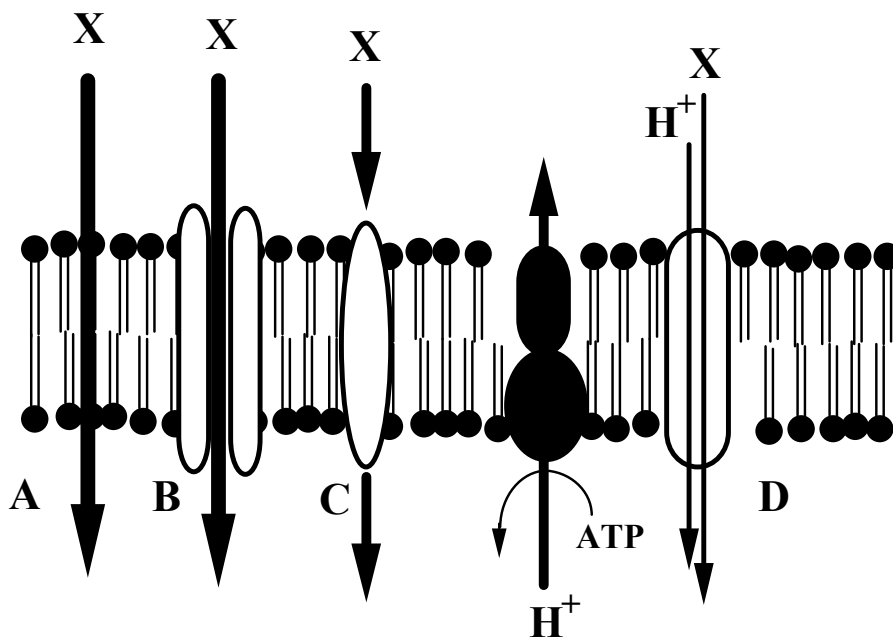


**Figure 3-4.** Apoplastic translocation of elements into the stele (S). Endodermis with Casparian strips (C) prevents element transport (A) whereas at the root tip the absence of Casparian strips promotes translocation (B).

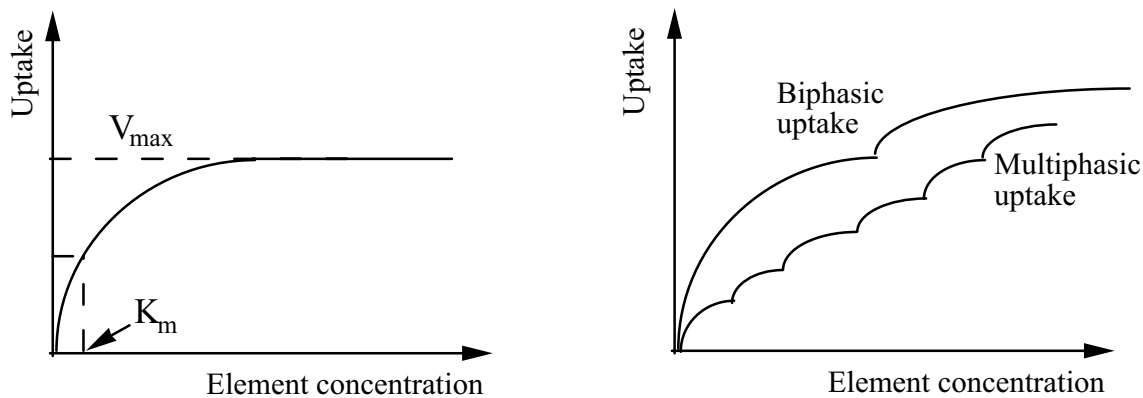
## 3.2 Cellular uptake

Uptake of elements into the cell can be performed by 4 different routes (Figure 3-5) /Taiz and Zeiger, 1998/. Passive uptake occurs when the element concentration outside the cell is higher than that inside. Passive diffusion works for small molecules that are uncharged. Facilitated diffusion is working through open ion channels as well as carriers. When the transport is performed against a concentration, gradient energy is needed and active transport is performed. Actually, the active part is the proton pump by which protons are pumped out to generate a proton gradient (a high  $H^+$  concentration outside and a lower inside the cell), which then facilitates a  $H^+$ -element ion symport (the hydrogen ion together with the element ion is transported to the inside of the cell to create an equilibration of  $H^+$  concentration between the inside and the outside of the cell).

The cellular uptake is influenced by the external concentration (Figure 3-6). The maximum uptake rate is when all available carrier sites are loaded with ions – the maximum uptake rate is denoted with a capacity factor,  $V_{max}$ . The concentration giving half the maximum transport rate is called  $K_m$ . When two different kinds of carriers are working at different concentration ranges, we have a biphasic uptake /Epstein et al, 1963/. One example is K, which is shown to have such an uptake. Furthermore, /Nissen, 1991/ found that the uptake could involve many different carriers – a multiphasic uptake.



**Figure 3-5.** Cellular uptake of cations or anions (X) across a membrane: Passive uptake A, B and C and active uptake D. A) Passive diffusion, B) Facilitated diffusion via channel, C) Carrier, D) Electrogenic proton pump coupled to a cation or anion (X) symport.



**Figure 3-6.** Uptake as a function of the external concentration based on uptake carriers. Left: Maximum transport rate ( $V_{max}$ ) and the concentration giving half the maximum transport rate ( $K_m$ ). Right: Biphasic and multiphasic uptake involving more than one carrier.

### 3.3 Foliar uptake

The outer cell layer of the leaf surface consists of epidermis cells and on top of their cell walls a cuticle layer is formed containing cutin, pectin and cuticular lipids (also called waxes). On top of this, a layer of cuticular lipids is situated, and this layer may appear very different from plant species to plant species and may also vary due to external conditions. Stomata guard cells are situated in the epidermis cell layer. Plants are able to take up elements via the leaf surface both via stomata (gases) and via the cuticle (ions) /Martin and Juniper, 1970; Lindberg et al, 1992; Marschner, 1995/. Thus, the stomata aperture promotes uptake of gases. A high density of stomata can also promote uptake of ions since the uptake occurs to a high degree through ectodesmata. Ectodesmata are nonplasmic “channels” (which are less dense parts of the cuticle layer) that are situated foremost in the epidermal cell wall/cuticular “membrane” system between guard cells (stomata) and subsidiary cells. Elements that occur as cations will penetrate the leaves through the cuticle whereas elements that occur as anion like S, Se, N, I, also are common in gaseous form and thus will be taken up via stomata in gaseous form.

Due to the negative charges of pectic material and non-esterified cutin polymers in the leaf cuticle, the cuticular layer functions as a weak cation exchanger. A distinct gradient from low to high charge density occurs from the external surface towards the cell walls, and thus cation penetration across the cuticle is favoured along this gradient /Yamada et al, 1964/. The mechanisms for uptake into the cell are probably the same as for roots.

The efficiency of uptake into the leaf tissue depends on the composition of the cuticle, ending up in a specific permeability to different ions. There is no close correlation between thickness and the permeability of the cuticle /Mériada et al, 1981/. The permeability is promoted by a high relative humidity, since the cuticle is then in its most open and swollen condition. The permeability may vary between plant species and, e.g. submerged plants often have a much higher uptake due to the high penetration of the cuticle /Greger, 1999/.

When the elements have been taken up they can be translocated to other plant parts via the phloem. This, however, is not true for all elements and such elements as Ca and Cd are probably not translocated in the phloem for the same reason as the prevented uptake into root cells. Instead, these elements will be kept outside the phloem cells not to disturb cell activity. However, in submerged plants, part of the elements taken up by the shoot can be translocated to the roots, and this indicates that they probably have another translocation system /Greger, 1999/.

## 4 Accumulation of nuclides

Nuclides occur naturally in low levels but are also supplied to the environment with emissions and as deposited nuclear waste (Table 4-1). Radionuclide emissions to the atmosphere include; 1) fallout from atmospheric bomb tests of the 1950s and 1960s and major nuclear accidents, e.g. Chernobyl (important isotopes are I, Cs and Sr), 2) satellite re-entry, 3) routine emissions to the atmosphere from reprocessing plants and nuclear power stations (important isotopes are  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{35}\text{S}$  and the radioiodines), and 4) waste disposal sites ( $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ,  $^{135}\text{Cs}$ ,  $^{237}\text{Np}$  and daughters, and  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  and daughters) /Naito and Smith, 1998; Ould-Dada et al, 2001/. Non-volatiles, such as U and Pu, are likely to be deposited in insoluble forms such as oxides, whereas volatile elements, such as I, are more likely to be deposited in soluble forms /Ould-Dada et al, 2001/.

Both above ground (mostly foliar absorption) and below ground (root absorption) plant parts account for the input of nuclides to plant tissue. Nuclides can be deposited on the external plant component directly from the atmosphere by wet or dry deposition, via resuspension from soil, and via contamination from either aspersion or irrigation waters /Coughtrey and Thorne, 1983/. There is also an input to the soil via these sources directly or via dead plant material. In addition, there may also be natural sources of nuclides from the parent material, the organic component, the mineral component and the soil solution as well as leakage from unnatural sources such as buried radioactive materials in the soil. High levels of radionuclides in plants generally are found in soils that have high background levels, namely near ore deposits or on contaminated soils and mine tailings. It may also be noted that uptake of radionuclides is generally higher from solution cultures than from soils /Bell et al, 1988/. In addition, plants can be affected by radiation from radionuclides and doses as low as 5 Gy can result in morphological changes, reduction of stem growth and root biomass and increased leaf density /Thiede et al, 1995/. This, in turn, may affect the uptake.

**Table 4-1. Radionuclide emissions from different sources, waste and half-life /Lindgren and Lindström, 1999; Ould-Dada et al, 2001/. h, hours; d, days; y, years; U, uranium.**

Nuclide	Half life	Emission to air				Waste Inventory at 40 years after discharge Bq U <sup>-1</sup>
		Bomb tests TBq	Chernobyl accident TBq	Reprocessing TBq yr <sup>-1</sup>	ACR reactor TBq yr <sup>-1</sup>	
<sup>108m</sup> Ag	418 y	–	–	–	–	5.0x10 <sup>8</sup>
<sup>241</sup> Am	458 y	–	–	–	–	1.5x10 <sup>14</sup>
<sup>243</sup> Am	7370 y	–	–	–	–	1.2x10 <sup>12</sup>
<sup>241</sup> Am + <sup>242</sup> Cm	458 y/162 d	–	–	6.5x10 <sup>-5</sup>	–	–
<sup>41</sup> Ar	1.8 h	–	–	–	1.81x10 <sup>2</sup>	–
<sup>140</sup> Ba	12.8 d	7.3x10 <sup>8</sup>	1.70x10 <sup>11</sup>	–	–	–
<sup>14</sup> C	5568 y	2.2x10 <sup>8</sup>	–	1.9x10 <sup>-1</sup>	0.78x10 <sup>1</sup>	5.0x10 <sup>10</sup>
<sup>141</sup> Ce	33 d	2.5x10 <sup>8</sup>	1.68x10 <sup>12</sup>	–	–	–
<sup>144</sup> Ce	284 d	3.0x10 <sup>7</sup>	1.37x10 <sup>11</sup>	–	–	–
<sup>36</sup> Cl	3.0x10 <sup>5</sup> y	–	–	–	–	5.5x10 <sup>8</sup>
<sup>242</sup> Cm	162 d	–	9.25x10 <sup>8</sup>	–	–	–
<sup>245</sup> Cm	8500 y	–	–	–	–	9.4x10 <sup>9</sup>
<sup>60</sup> Co	5.3 y	–	–	–	1.00x10 <sup>-2</sup>	–
<sup>134</sup> Cs	2.3 y	–	4.44x10 <sup>10</sup>	–	–	–
<sup>135</sup> Cs	2.3x10 <sup>6</sup> y	–	–	–	–	2.1x10 <sup>10</sup>
<sup>137</sup> Cs	35 y	9.1x10 <sup>5</sup>	8.51x10 <sup>10</sup>	6.2x10 <sup>-4</sup>	–	1.8x10 <sup>15</sup>
<sup>55</sup> Fe	2.7 y	2.0x10 <sup>6</sup>	–	–	–	–
<sup>166m</sup> Ho	1200 y	–	–	–	–	7.5x10 <sup>7</sup>
<sup>3</sup> H	12.3 y	2.4x10 <sup>8</sup>	–	1.7x10 <sup>2</sup>	1.57x10 <sup>1</sup>	–
<sup>129</sup> I	1.7x10 <sup>7</sup> y	–	–	2.5x10 <sup>-2</sup>	–	1.3x10 <sup>9</sup>
<sup>131</sup> I	8 d	6.5x10 <sup>8</sup>	1.67x10 <sup>12</sup>	2.6x10 <sup>-3</sup>	0.16x10 <sup>-2</sup>	–
<sup>85</sup> Kr	10.7 y	–	3.33x10 <sup>10</sup>	9.5x10 <sup>4</sup>	–	–
<sup>54</sup> Mn	303 d	5.2x10 <sup>6</sup>	–	–	–	–
<sup>59</sup> Ni	7.6x10 <sup>4</sup> y	–	–	–	–	8.8x10 <sup>10</sup>
<sup>63</sup> Ni	100 y	–	–	–	–	9.3x10 <sup>12</sup>
<sup>94</sup> Nb	2.0x10 <sup>4</sup> y	–	–	–	–	2.9x10 <sup>9</sup>
<sup>237</sup> Np	2.1x10 <sup>6</sup> y	–	–	–	–	1.5x10 <sup>10</sup>
<sup>239</sup> Np	2.4 d	–	1.67x10 <sup>12</sup>	–	–	–
<sup>231</sup> Pa	3.3x10 <sup>4</sup> y	–	–	–	–	1.8x10 <sup>6</sup>
<sup>107</sup> Pd	6.5x10 <sup>6</sup> y	–	–	–	–	4.9x10 <sup>9</sup>
<sup>239</sup> Pu	2.4x10 <sup>4</sup> y	6.5x10 <sup>3</sup>	2.96x10 <sup>7</sup>	–	–	9.5x10 <sup>12</sup>
<sup>240</sup> Pu	6.5x10 <sup>3</sup> y	4.4x10 <sup>3</sup>	4.44x10 <sup>7</sup>	–	–	1.2x10 <sup>13</sup>
<sup>241</sup> Pu	13 y	1.4x10 <sup>5</sup>	5.92x10 <sup>9</sup>	7.9x10 <sup>-4</sup>	–	–
<sup>242</sup> Pu	3.8x10 <sup>5</sup> y	–	8.51x10 <sup>4</sup>	–	–	1.0x10 <sup>11</sup>
Pu-α	–	–	–	1.0x10 <sup>-4</sup>	–	–
<sup>226</sup> Ra	1600 y	–	–	–	–	1.4x10 <sup>5</sup>
<sup>103</sup> Ru	39.3 d	2.4x10 <sup>8</sup>	1.70x10 <sup>11</sup>	–	–	–
<sup>106</sup> Ru	1.0 y	1.2x10 <sup>7</sup>	2.96x10 <sup>10</sup>	–	–	–
<sup>35</sup> S	88 d	–	–	–	3.00x10 <sup>-1</sup>	–
<sup>79</sup> Se	1.1x10 <sup>6</sup> y	–	–	–	–	2.8x10 <sup>9</sup>
<sup>151</sup> Sm	90 y	–	–	–	–	9.4x10 <sup>12</sup>
<sup>126</sup> Sn	1x10 <sup>5</sup> y	–	–	–	–	2.3x10 <sup>10</sup>
<sup>125</sup> Sb	2.7 y	5.2x10 <sup>5</sup>	–	–	–	–
<sup>89</sup> Sr	50.5 d	9.1x10 <sup>7</sup>	8.14x10 <sup>10</sup>	–	–	–
<sup>90</sup> Sr	29 y	6.0x10 <sup>5</sup>	8.14x10 <sup>9</sup>	1.0x10 <sup>-4</sup>	–	1.2x10 <sup>15</sup>



<sup>99</sup> Tc	2.1x10 <sup>5</sup> y	–	–	–	–	5.7x10 <sup>11</sup>
<sup>132</sup> Te	3 d	–	4.07x10 <sup>11</sup>	–	–	–
<sup>229</sup> Th	7340 y	–	–	–	–	1.0x10 <sup>4</sup>
<sup>230</sup> Th	7.5x10 <sup>4</sup> y	–	–	–	–	1.6x10 <sup>7</sup>
<sup>133</sup> Xe	5.3 d	–	6.29x10 <sup>12</sup>	–	–	–
<sup>91</sup> Y	58.8 d	1.2x10 <sup>8</sup>	–	–	–	–
<sup>233</sup> U	1.6x10 <sup>5</sup> y	–	–	–	–	3.1x10 <sup>6</sup>
<sup>234</sup> U	2.5x10 <sup>5</sup> y	–	–	–	–	4.6x10 <sup>10</sup>
<sup>235</sup> U	7.0x10 <sup>8</sup> y	–	–	–	–	4.5x10 <sup>8</sup>
<sup>238</sup> U	4.5x10 <sup>9</sup> y	–	–	–	–	1.2x10 <sup>10</sup>
<sup>93</sup> Zr	1.5x10 <sup>6</sup> y	–	–	–	–	5.6x10 <sup>10</sup>
<sup>95</sup> Zr	66 d	1.4x10 <sup>8</sup>	1.67x10 <sup>11</sup>	–	–	–

## 4.1 Transfer factors

Most works dealing with uptake of nuclides use the soil-to-plant ‘transfer factor’ (TF), also called transfer ratio (TR), as a measure of uptake /Shaw and Bell, 1994/. The transfer factor is also called the concentration ratio, CR and is discussed by /Mortvedt, 1994/. This is defined simply as the ratio of the specific radionuclide activity in the plant tissue of concern (usually some edible organs or above ground parts) and the soil, with the dry masses of each material usually being taken into account. The soil part is generally the surface soil (10 –20 cm of the soil profile) because the bulk root density is usually found in these surface layers.

$$TF = \frac{\text{Plant specific activity (Bq kg}^{-1}\text{)}}{\text{Soil specific activity (Bq kg}^{-1}\text{)}}$$

This definition is the most commonly used and is adopted by the International Union of Radioecologists (IUR) as the working definition for soil-to-plant transfer database. Ranges of TF values for various nuclides are shown in Table 4-2 and ranges from 1.5x10<sup>-7</sup> for <sup>241</sup>Am to 3.4x10<sup>3</sup> for <sup>99</sup>Tc /IUR, 1989/. It was shown by /Linsalata et al, 1989/ that the TF values decreased in the order: divalent > trivalent > tetravalent cations, at least when dealing with <sup>232</sup>Th, <sup>230</sup>Th, <sup>228</sup>Ra, <sup>226</sup>Ra, La, Ce and Nd. The authors speculated that these differences reflected the relative availability of these metals for plant uptake.

**Table 4-2. Minimum and maximum values of soil to plant transfer factors (TF) for selected radionuclides /IUR, 1989/.**

Radionuclide	TF
<sup>110m</sup> Ag	6x10 <sup>-5</sup> – 4x10 <sup>-3</sup>
<sup>241</sup> Am	2x10 <sup>-7</sup> – 8x10 <sup>-1</sup>
<sup>144</sup> Ce	3x10 <sup>-2</sup> – 3x10 <sup>-1</sup>
<sup>60</sup> Co	4x10 <sup>-4</sup> – 4x10 <sup>0</sup>
<sup>134/137</sup> Cs	2x10 <sup>-4</sup> – 3x10 <sup>1</sup>
<sup>237</sup> Np	4x10 <sup>-5</sup> – 5x10 <sup>-1</sup>
<sup>239/240</sup> Pu	4x10 <sup>-7</sup> – 7x10 <sup>-1</sup>
<sup>90</sup> Sr	8x10 <sup>-3</sup> – 4x10 <sup>1</sup>
<sup>103/106</sup> Ru	5x10 <sup>-3</sup> – 2x10 <sup>0</sup>
<sup>99</sup> Tc	3x10 <sup>-1</sup> – 3x10 <sup>3</sup>

One of the problems involved in interpreting TF data is that TF values are not linearly related to soil concentrations of radionuclides /Martinez-Aquirre et al, 1997/, even though the definition normally assumes that the plant concentration increases linearly with increasing substrate concentration and that the function passes through the origin. In general, TF values decrease with increasing substrate concentrations over a small range in concentrations. Above this range the TF value asymptotically decreases to a given value that does not change with further increases in soil concentrations /Mortvedt, 1994/. It is proposed that radionuclide uptake for a variety of plant species and elements is a non-linear function of substrate concentration /Simon and Ibrahim, 1987/. The uptake response was described as a single or multiphasic saturation curve and the uptake response for some plant species and radionuclides required a threshold of soil activity before uptake was measurable, i.e. above the depletion zone.

There is difficulty in identifying causal relationships between TFs and soil physico-chemical parameters /Frissel et al, 1990/. Transfer factors also differ between different species as well as genotypes of a species since they accumulate elements to various degrees /Landberg and Greger, 1996; Broadley and Willey, 1997; Österås et al, 2000/. Data on TF are therefore completely site and species/genotype specific. /Ng et al, 1979/ proposed that since the TF lacks site-specific data, a reasonable approach would be to adopt a ratio for each main crop that would be conservative for most agricultural soils. It would thus be possible to adopt a reasonable ratio for each main food crop on each main soil type. This would, however, probably be a very difficult task for other plants than cultivated crops. Another important factor is the plant part used in the TF calculation, since elements are often unevenly distributed within the plant. For example, after uptake, the activity is considerably less in reproductive and storage organs than in vegetative parts of a crop /Bell et al, 1988/.

An interesting finding is that the TF value depends on when during the plant development stages the TF is measured. /Ambe et al, 1999a/ found that when growing *Brassica rapa* the TF values for Rb, Tc and Cs, based on leaves, decreased with time. Furthermore, the TF for Mn increased with development stage whereas there was no change in TF for Na, Co, Zn, Se and Sr. /Bell et al, 1988/ suggested that a change in concentration during the growing period is due to a dilution or concentration effect depending on the growth rate in relation to the uptake rate, which was also shown by /Ekvall and Greger, 2003/. There is also retranslocation from roots to newly formed foliage, which means that after grazing of grasses the activity in the remaining roots can be redistributed to the new shoots /Bell et al, 1988/.

In perennial crops the uptake of nuclides is higher than for annual crops /Coughtrey et al, 2001/. Radionuclide concentration in fruit depends on the yield; low yield correlates with high concentration of radionuclides. It may increase because of leaf-to-fruit translocation or soil-to-fruit transfer, then decrease because of growth dilution, and then increase again towards ripening because of water loss by aging. Transfer factors clearly need an equilibrium situation. Further discussions about improvement of TF can be found in /Simon and Ibrahim, 1988/.

Other definitions of the transfer factors used are ‘inventory ratio’ (IR), where the transfer factor is based on the contamination of soils and vegetation on an areal basis /Gilbert and Simpson, 1983/.

$$\text{IR} = \frac{\text{Plant activity per unit area (Bq m}^{-2}\text{)}}{\text{Soil activity per unit area (Bq m}^{-2}\text{)}}$$

In /Mascanzoni, 1990/ one uses another definition of 'TF' based on radionuclide activities on both a mass and an areal basis.

$$\text{'TF'} = \frac{\text{Plant specific activity (Bq kg}^{-1}\text{)}}{\text{Soil specific activity per unit area (Bq m}^{-2}\text{)}}$$

The vegetation density is also important /Garten, 1978/. However, in a magnitude of 1 kg m<sup>-2</sup> the vegetation density could lead to a significant depletion of radionuclides in soil when plant uptake is associated with a transfer factor more than 10 /Coughtrey and Thorne, 1983/.

The soil depth and the soil treatment are, of course, important. Ploughing gave a decreased plant uptake of Sr in comparison with untreated contaminated surface soil /Milbourn, 1960/, which is due to dilution of the contaminant.

Lack of standardization of experimental design, and that spiked soils can change the plant available fraction of the element during the time under study have been mentioned in attempts to work out recommendations to be able to set up a data-bank and be able to use TFs /IUR, 1982/. The following parameters should be given as information: Radionuclide, concentration of radionuclide, species, plant part, unwashed or washed, percent dry matter in crop, soil type (particle size), soil pH, soil organic matter, how the soil was contaminated (spiked or natural pollution), duration of radionuclide in the soil, irrigation (amount), soil depth and container type.

## 4.2 Important factors influencing accumulation

Use of transfer factors is a very simplified way to explain the soil-to-plant transfer. There are numerous disadvantages included in this simplification since there are many factors that influence TF. Three important factors influencing plant accumulation in soil are 1) genetic differences, 2) soil and fertiliser effects, and 3) season and stage of maturity /Underwood, 1977/. This includes moisture status of the soil, botanical composition of the herbage and morphological characteristics of the plant. From the plants point-of-view, the following processes are involved in the plant uptake /Cataldo and Wildung, 1978/ and the degree is species-specific:

- 1) Physiological aspects of ion replenishment in the rhizosphere.
- 2) Kinetic parameters regulating plant absorption of elements.
- 3) Metabolic behaviour of elements and plant tolerance.
- 4) Competition between closely related anions and cations.

The uptake into the whole plant is influenced by both time and root mass (root absorption area, /Greger, 1999/), meaning that the concentration within the plant varies directly and inversely with growth rate according to the formula /Loneragan, 1975/,

$$I_m = \frac{RGR \times [E]}{wr}$$

$I_m$  = rate of absorption of element, E, per unit root weight,  
 $RGR$  = relative growth rate of the whole plant,  
 $[E]$  = average concentration of element, E, in the whole plant,  
 $wr$  = ratio of weights of root to whole plant.

The uptake increases with the size of the root absorption area, however, the larger the root absorption area the lower is the element concentration in the roots due to the uptake not being in a 1 to 1 relation to growth /Greger, 1999; Ekvall and Greger, 2003/. For example, the highest concentration of  $^{85}\text{Sr}$  and  $^{134}\text{Cs}$  was found in plants that were smallest in size /Baeza et al, 1999a/. It is important to notice that not only the root absorption area, where especially the area of root tips is important, but also the proportion of shoot-to-root mass has to be considered. The latter may very well affect the TF factor if using only the green parts when calculating the factor. It was shown that plants with slow growth rate had a lower Cs concentration in the shoots than fast-growing plants, which may depend on the translocation from root to shoot being influenced /Broadley and Willey, 1997/.

Another factor that will influence the TF is the soil element concentration. There is no linear relationship of radionuclide concentrations between crop and soil /Yasuda and Uchida, 1995/. /Greger and Landberg, 1999/ showed that the higher the soil concentration the lower the plant uptake efficiency, and TF for  $^{210}\text{Po}$  and isotopes of U and Th decreased with increased soil concentration /Martinez-Aquirre et al, 1997/. A high soil element concentration but a low uptake could in addition be due to low bioavailable element concentrations in the soil.

The growth stage of the plant when radionuclides are analysed will play an important role in the result, since growth stage and organ influence the accumulation of the radionuclide /Anguissola Scotti, 1996/. The more advanced the vegetative stage is during treatment, the higher the plant concentration.

/Van Dorp et al, 1979/ tried to find a formula that accounted for the mobility of the nuclide in soil, its relative uptake by plant roots and its subsequent translocation. The concentration of the nuclide in the plant part (Cp) is calculated as,

$$C_p = F \times S \times \frac{PT}{P_p} \times TC \times \frac{C_t}{L(q + rkd)}$$

which is based on the concentration of a radionuclide in soil solution (Cs),

$$C_s = \frac{C_t}{L(q + rkd)}$$

and the total plant uptake (U),

$$U = S \times TC \times C_s \times PT$$

Cp = concentration of the nuclide in the plant part of interest,

F = the fraction of the absorbed nuclide that is translocated to the plant part,

S = selectivity coefficient,

U = uptake (Bq plant<sup>-1</sup>),

PT = total production (gDW cm<sup>-2</sup> year<sup>-1</sup>),

Pp = production of plant material (gDW cm<sup>-2</sup> year<sup>-1</sup>),

TC = Transpiration coefficient (ml (gDW<sup>-1</sup>)),

Ct = total amount of nuclide in soil surface (Bq cm<sup>-2</sup>),

L = rooting depth of soil profile (cm),

Cs = concentration in soil solution (Bq ml<sup>-1</sup>),

q = water content of soil (ml cm<sup>-3</sup>),

r = bulk density of soil (g cm<sup>-3</sup>),

kd = Bq absorbed per g soil/Bq dissolved per ml solution (i.e. equilibrium distribution coefficient).

This approach is useful and even though it does not account for differences during growth, a relative growth rate factor could be included.

### 4.3 Above-ground accumulation

The dry deposition is estimated by the concept of deposition velocity ( $V_g$ ) and is defined as the downward flux of aerosol or gas to a vegetation or soil surface, normalized to the ambient atmospheric gas or aerosol concentration above the surface /Chamberlain, 1953/. It is measured in units of radioactivity per unit area and volume such as,

$$V_g = \frac{\text{Bq cm}^{-2} \text{ s}^{-1}}{\text{Bq cm}^{-3}}$$

Deposition velocity is closely and complexly related to particle size. /Moore et al, 1979/ suggested the following  $V_g$  for vegetative surfaces:  $2 \times 10^{-2} \text{ m s}^{-1}$  for reactive gases,  $1 \times 10^{-3} \text{ m s}^{-1}$  for small particles ( $< 4 \mu\text{m}$  diameter) and  $1 \times 10^{-4} \text{ m s}^{-1}$  for relatively unreactive gases.

In the case of gases, the chemical form will play a major role in controlling the  $V_g$  to vegetation. The reciprocal of  $V_g$  is the total resistance ( $r$ ) to uptake of the gas ( $\text{s cm}^{-1}$ ) and can be broken down in parts, each of which is controlled by different processes,

$$r_{\text{total}} = r_a + r_s + r_{\text{int}}$$

where  $r_a$  is the aerodynamic resistance,  $r_s$  stomata resistance and  $r_{\text{int}}$  internal resistance. The aerodynamic resistance influencing the passage of the gas through the boundary layer close to the leaf surface, where there is a transition from turbulent to molecular diffusion. This is controlled by the molecular diffusion coefficient of the individual gas and by the wind speed. The stomata resistance is controlled by the degree of opening of the stomata. The chemical sink for the gas controls the internal resistance. Any factor that influences these resistances will affect the uptake of radioactive gas. Further,  $r_{\text{int}}$  is influenced by the physiological status of the plant,  $r_a$  is controlled by meteorological conditions and  $r_s$  by both of these factors. There are also influences of  $r_{\text{cc}}$  (adsorption onto the surface) and  $r_{\text{ci}}$  (penetration via the cuticle). It should not, however, be forgotten that nuclides in gaseous form penetrate via stomata to the highest extent. Thus, such nuclides are taken up to a higher degree in light than in darkness due to stomata closure in the latter case /Kluczewski et al, 1983/.

In the case of particles, the physical form rather than the chemical characteristics controls the velocity of deposition. Wet foliage is more efficient at capturing particles than dry leaves. Furthermore, wind speed is an important factor, as a wind speed that increases the deposition of smaller particles will also increase the probability of penetration of the laminar bound layer above the vegetation surface /Chamberlain and Little, 1980/. Smaller particles are also most important over larger distances. Particle size controls the processes by which deposition occurs as well as its efficiency. Larger particles ( $> 20 \mu\text{m}$ ) are mainly deposited under gravity, independent of wind speed. Other processes are impaction, where the momentum of the particles causes collision with an obstacle such as a leaf, and interception, which constitutes the filtering action of hairs and other projections on the leaf surface. Smaller particles  $< 0.1 \mu\text{m}$  behave like a gas. For larger particle sizes,  $V_g$  is high due to the dominance of sedimentation, whereas sub-micron particles are deposited efficiently by diffusion, thus the lowest  $V_g$  is found between  $0.1\text{--}1.0 \mu\text{m}$  /Bonka and Horn, 1983/.

The interception factor (if) is the proportion of the total wet and dry deposition retained by the vegetation. The interception and the retention are affected by humidity, precipitation and the form of material applied /Eriksson, 1977/. The relative amount intercepted decreases in the following order: wet-deposited radionuclides > wet-deposited particles > particles dry-deposited on grass wet with rain > particles dry-deposited on grass superficially wet > particles dry-deposited on dry grass, and small particles > larger particles. Using the Chamberlain model as base /Chamberlain, 1970; Miller, 1979, 1980/, a model was constructed where the interception factor, if, is related to the biomass of vegetation,

$$if = 1 - e^{-(\mu \times Yv)}$$

where  $\mu$  is the proportionality constant (absorption coefficient,  $m^2 kg^{-1}$ ) and  $Yv$  is dry weight density of vegetation ( $kg m^{-2}$ ). This formula was well founded for grassland vegetation but less well for agricultural vegetation /Miller, 1980/. /Miller, 1980/ carried out a statistical analysis of the parameter if and could proposed that a single value of if/ $Yv$  should be used for assessment purposes instead of individual uncorrelated values of if and  $Yv$ .

/Chamberlain, 1970/ concluded that under conditions of continuing fallout, most of the activity of herbage is due to foliar uptake. Thus, he introduced the concept of normalised specific activity (NSA), which has a unity of  $m^2 day kg^{-1}$  and is defined as,

$$NSA = \frac{\text{Activity per kg dry matter in foliage}}{\text{Activity deposited per day per meter square of ground}}$$

and is in the range of 27–61  $m^2 day kg^{-1}$ .

Foliar absorption and accumulation in the internal tissue should be distinguished from the external deposition. Adsorbed activity can be washed off by rain and mist and in experiments on plutonium on *Phaseolus vulgaris* foliage it was shown that mist was most effective /Cataldo et al, 1981/. Also absorbed activity can be washed off by cation exchange with  $H^+$ .

Absorption by foliage strongly depends on species. /Bukovac et al, 1965/ showed that 72 hours after treatment *Phaseolus vulgaris* (bush bean) had a 10 times higher absorption of  $^{89}Sr$  than *Zea mays* (maize) and two times higher than *Raphanus sativus* (radish) and *Lactuca sativa* (lettuce). Such differences have also been shown for other other plant species and other elements, e.g. Cd /Greger et al, 1993/.

The absorbed element could be trapped in the cuticle or cell wall of the outer cell or translocated to the phloem and further to other plant parts. Especially in long-lived radionuclides it is important to distinguish between absorbed and translocated activity. Different nuclides react differently. In the case of technetium, tellurium, iodine and cesium, 10% was expected to be translocated to the grain of cereal crops /CEA/NRPB, 1979/, and in the case of molybdenum, chromium, strontium, transuranic and cadmium, translocation from shoot to root was considered insignificant /Bukovac et al, 1965; Nair et al, 1980; Greger et al, 1993/. Various plant species also translocate a nuclide to various degrees. /Brown et al, 1991/ showed that *Calluna vulgaris* (heather) shoots had an extremely high translocation of  $^{134}Cs$  from leaves to other plant parts whereas other members of Ericaceae such as *Erica tetralix* (bell heather) and *Vaccinium myrtillus* (bilberry) showed scarcely any such translocation.

Different factors influencing the foliar absorption of activity and, based on our knowledge of plant hormones and nutrient elements, we can identify that influencing factors are; the contact angle and degree of surface wetting of the plant surface, the age and nitrogen status of the plant, the physical aspect of permeation, structure of the cuticular waxes and the composition of the cuticle, surface chemistry of the particle, degree of penetration into leaves and, if cell penetration is included, structure and properties of the plasma membrane /Boynton, 1954; Van Oberleek, 1956/. The absorption of radionuclides was found to be directly proportional to the length of absorption /Biddulph, 1960/. It was also shown that the closer in time the contamination is to the harvest of the fruit or tuber, the more efficient is the transfer coefficient from leaf to the edible part of  $^{85}\text{Sr}$  and  $^{134}\text{Cs}$  in turnips and bush beans /Baeza et al, 1999a/.

## **4.4 Accumulation by lower plants and mycorrhizas**

### **4.4.1 Lichens**

Lichens take up radionuclides through the thallus, preferably via air. Lighter nuclides such as  $^{137}\text{Cs}$  and  $^{144}\text{Ce}$  are strongly retained at the surface of the thallus, whereas heavier and more particle reactive nuclides such as Pb and Pu isotopes penetrate the thallus more completely /Mattsson, 1975/. On the other hand, nuclides such as  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  have a shorter biological residence time, (1–2 years) than  $^{137}\text{Cs}$  (5–8 years) in lichens /Ellis and Smith, 1987/.

### **4.4.2 Mycorrhizas**

Mycorrhizal fungi are much more prone to accumulate radiocesium than saprophytic fungi /Römmelt et al, 1990/, and many of the Basidiomycete fungi efficient in accumulation of this radionuclide are able to form mycorrhizas with higher plant species /Olsen et al, 1990/. In contrast, fruit bodies of saprophytic fungi accumulate much higher levels of heavy metals (Hg, Pb, Cd) than mycorrhizal fungi /Lodenius et al, 1981/. This is probably due to saprophytic fungi using wood as nutrient source and that heavy metals are firmly bound and highly accumulated in cell walls of plants. Mycorrhizas may in some cases increase the uptake of radionuclides in plants, but not in other cases, as was shown for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  in the case of yellow sweet clover, sudan grass and other tropical grass species infected with VAM (vesicular-arbuscular mycorrhiza) /McGraw et al, 1979; Rogers and Williams, 1986/. In studies on heather, mycorrhizal plants had a lower uptake but a higher translocation of Cs than non-mycorrhizal plants /Clint and Dighton, 1992/. Different grass species with arbuscular mycorrhizas had a higher uptake of both Cs and Sr than plants without arbuscular mycorrhizas /Entry et al, 1999/. The uptakes of  $^{137}\text{Cs}$ , Cs and Rb were higher in mushrooms than in higher plants whereas the opposite was found for Ca and Sr /Yoshida and Muramatsu, 1998/.

**Table 4-3. Trace element contents ( $\mu\text{g gDW}^{-1}$ ) in macroalgae and, in comparison, in reference terrestrial plants as well as hyperaccumulation levels, according to /Markert, 1994/. /From Dunn, 1998/.**

Element	Reference plant	Hyperacc. levels Mean	Macroalgae
Ag	0.2	20	< 0.8
As	0.1	10	8.2
Au	0.001	0.1	< 4
Ba	40	4000	< 40
Br	4	400	643
Ce	0.5	50	0.94
Co	0.2	20	2.5
Cr	1.5	150	2.2
Cs	0.2	20	0.11
Cu	10	1000	12
Hf	0.05	5	0.2
I	3	300	238
La	0.2	20	0.57
Mo	0.5	50	< 0.8
Ni	1.5	150	< 20
Pb	1	100	–
Rb	50	5000	23
Sb	0.1	10	0.11
Sc	0.02	2	0.49
Sr	50	5000	696
Th	0.005	0.5	0.06
U	0.01	1	0.44
V	0.5	50	5.9
Zn	50	5000	37

#### 4.4.3 Macroalgae

Trace elements are found to be hyperaccumulated in some macroalgae (Table 4-3), probably due to their uptake site, which is the whole plant body (thallus) and the uptake medium, which is water with dissolved elements. Of course, there must be a favourable equilibrium of the elements between the sediment and the water.

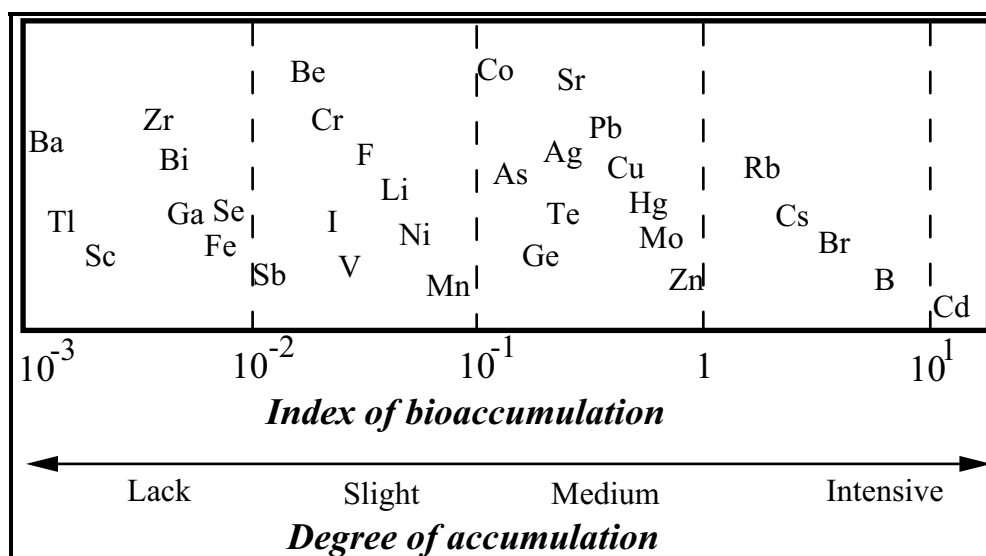


## 5 Different nuclides and plant uptake

### 5.1 In general

Plants accumulate different trace elements to different extents (Figure 5-1). For example, uptake of U is generally greater than that of Th and Po /Mortvedt, 1994/. The reason for this is not clear. In discussions it has been suggested that those elements that are plant nutrients, or those that are similar to plant nutrients, are easier to take up since, in the case of nutrients, plants have a need and thus have an uptake mechanism, for these elements. The elements similar to nutrients (such as Cs and Rb being similar to K, Sr being similar to Ca, and Se being similar to S) follow the same path as the nutrient they are similar to. It is, however, clear that the reason for a high uptake has nothing to do with nutrients although similar uptake sites can be used by other elements and since many elements can be hyper-accumulated by plants without being needed by the plant or having similarity to a nutrient element. One element, which is taken up to high extent without being a nutrient element, is  $^{99}\text{Tc}$  /Wildung et al, 1977; Green and Wilkins, 1995/.

Various elements are bound to soil colloids to different degrees of hardness, which in turn influences the plant-available soil fraction of the element and thus also the uptake. For example,  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$  are firmly bound and rapidly fixed to soil mineral materials, especially the clay fraction, and the degree of soil-to-plant transfer of this nuclide will thus strongly depend on the amount of clay in the soil /Bell et al, 1988; Cremers et al, 1988; Baeza et al, 1999a/. On the other hand,  $^{85}\text{Sr}$  and  $^{90}\text{Sr}$  remains relatively mobile and about 90% is in exchangeable form within the soil /Francis, 1978; Baeza et al, 1999a/. This may be the reason why TF of  $^{90}\text{Sr}$  increases with time whereas that of  $^{137}\text{Cs}$  decreases /Krouglov et al, 1997/. However, at decomposition of leaf litter the reincorporation of Sr into the soil is faster than that of Cs /Baeza et al, 1999c/. The binding time in soil also accounts for an effect on the availability to plants, and in the case of Tc 90% immobilisation is reached first after 30–40 years /Van Loon, 1986/.



**Figure 5-1.** Bioaccumulation of trace elements by plants from soil. Index of accumulation is the concentration of an element in a plant in relation to the concentration in soil. The figure is redrawn from /Kabata-Pendias and Pendias, 1992/.

Various plants accumulate different elements to different degrees. After screening of 32 species for Rb, Co, Sr and Cs, a high uptake of Co was found for broccoli and tomato and high uptake of Rb was found for tomato, chard, sunflower and cucumber. Further, high uptake of Sr was found in cucumber, sunflower and turnip, and for Cs the highest uptake was found for tomato, chard and cucumber /Gouthu et al, 1997/.

The degree of accumulation also depends on competing elements in the soil, at the uptake site or within the plant tissue. Interaction between K and Cs as well as between Ca and Sr may cause a reduced uptake of Sr and Cs when fertilisers with K and Ca are applied /Nisbet, 1993; Shaw, 1993/. Lime reduces the TF of both Cs and Sr /Lembrechts, 1993/, however, in the case of Sr only when the Ca concentration of the soil is low /Milbourn, 1960/. Potassium fertilizers decrease TF for Cs and Sr /Lembrechts, 1993/. Potassium-sulphate fertilizer treatment also lowers the activity concentrations of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  /Whicker et al, 1999/. An interesting aspect is that the Cs uptake in halophytic plants, like Chenopodiaceae, is more susceptible to K addition than in mesophytic plants like Gramineae /Broadly and Willey, 1997/. Furthermore, nitrogen increases not only the growth of plants but also the  $^{137}\text{Cs}$  uptake and it was shown that addition of fertilizers increased the storage of  $^{137}\text{Cs}$  in the root system whereas it decreased the whole plant uptake /Belli et al, 1995/. It was also found that the higher the level of nutritive mineral elements in the soil the smaller is the potential effect that fertilization may have in reducing the transfer factor of Cs and Sr /Lembrechts, 1993/. The Tc uptake of rye grass was decreased by addition of nitrogen /Echevarria et al, 1998/.

It is possible that discrimination between isotopes of the same element occurs. A lower soil-to-plant transfer factor was shown for  $^{137}\text{Cs}$  than for  $^{134}\text{Cs}$  /Shaw and Bell, 1994/. The  $^{235}\text{U}/^{238}\text{U}$  ratio is, in general, higher in plants than in soils collected at the same places /Yoshida et al, 2000/. Furthermore, different isotopes of Pu seem to be differently easy to take up /Dienstbach et al, 1983/, and concentrations of  $^{232}\text{Th}$  in vegetation were lower than those of  $^{230}\text{Th}$  and  $^{228}\text{Th}$  at locations where they were present in similar soil concentrations /Ibrahim and Whicker, 1988/. The plants have a greater  $^{226}\text{Ra}/^{228}\text{Ra}$  ratio than soil and discrimination factors have been calculated and discussed by /Baeza et al, 1999b/. Such differences should be due to differences in element mass, however, in elements of mass number > 20 the kinetic discrimination between isotopes during reactions, such as those involved during passage of membranes, would be expected to be negligible /Bowen, 1979/.

Uptake into roots may also vary; immobile elements may stay attached to the root surface whereas mobile elements will enter the roots and translocate further into the plant. For example, actinides ( $^{234}\text{U}$ ,  $^{238}\text{U}$ ,  $^{238}\text{Pu}$ ) adsorb to the outer layer of roots whereas the more mobile elements such as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  enter the plant tissue /Adriano et al, 2000/. However, there is more translocation of Cs than of Sr within the plant /Baeza et al, 1999c/.

The translocation of elements in plants after foliar deposition into the edible part of plants depends on the element, the plant type and the time between deposition and harvest /Aarkrog and Lippert, 1969, 1971; Aarkrog, 1975; Voigt et al, 1991/. Manganese, Zn, Se, Rb, Sr and Ba were translocated to the leaves and seeds after root addition, whereas Be, Na, Sc, Fe, Co, Y, Nb, Ag, Te, Ce, Pm, Eu, Gd, Tb, Lu, Hf, Ir and Pt were not /Ambe et al, 1995/. After foliar application, Sc, Mn, Co, As, Se, Rb, Sr, Y, Eu, Gd, Ub, Hf, Re and Ir As, Se and Re were accumulated in the leaves whereas Co, Se and Rb were accumulated, particularly in the fruits /Shinonaga et al, 1996; Shinonaga and Ambe, 1998/. A study on different nuclides added to plant roots showed that the uptake maximum for most elements was at 200 h and thereafter the concentration decreased with time /Shinonaga et al, 1999a/. The exceptions were Zn, Tc and Re, which increased up to 360 h after addition and both Tc and Re did not show any decrease with time.

It was found that the photon flux (photosynthesis) influenced the accumulation of radionuclides ( $^7\text{Be}$ ,  $^{22}\text{Na}$ ,  $^{43}\text{K}$ ,  $^{47}\text{Ca}$ ,  $^{46}\text{Sc}$ ,  $^{48}\text{V}$ ,  $^{51}\text{Cr}$ ,  $^{54}\text{Mn}$ ,  $^{59}\text{Fe}$ ,  $^{58}\text{Co}$ ,  $^{65}\text{Zn}$ ,  $^{67}\text{Ga}$ ,  $^{74}\text{As}$ ,  $^{75}\text{Se}$ ,  $^{83}\text{Rb}$ ,  $^{85}\text{Sr}$ ,  $^{88}\text{Y}$ ,  $^{88}\text{Zr}$ ,  $^{95\text{m}}\text{Tc}$ ,  $^{129}\text{Cs}$ ,  $^{131}\text{Ba}$ ,  $^{139}\text{Ce}$ ,  $^{143}\text{Pm}$ ,  $^{147}\text{Eu}$ ,  $^{149}\text{Eu}$ ,  $^{146}\text{Gd}$ ,  $^{149}\text{Gd}$ ,  $^{183}\text{Re}$ ,  $^{192}\text{Ir}$ ,  $^{188}\text{Pt}$ ) in the roots but had no significant effect on the selective absorption coefficients for the leaves /Ambe et al, 1999b/.

## 5.2 Inert gases (He, Ne, Ar, Kr, Xe, Rn)

*(Helium, neon, argon, krypton xenon)*

These elements have a very stable electron structure and thus do not normally form chemical complexes. They are inert and exist as monoatomic molecules because of their non-reactivity. They have no nutrient analogues. Even though it does not take part in any chemical or physiological reaction,  $^{222}\text{Rn}$  is important as an inhalation hazard. If inert gases are taken up, they are absorbed via leaf stomata. If present in plants, the gases can also be transpired from the plant body to the air via stomata. /Lewis and MacDonell, 1990/ investigated this for  $^{222}\text{Rn}$  and showed that  $^{222}\text{Rn}$  release rates from leaf surfaces of corn, fescue and sunflower were unrelated to the quantity of water transpired. Plants tended to release more  $^{222}\text{Rn}$  at  $15^\circ\text{C}$  than at  $30^\circ\text{C}$ , which was explained in part by increased solubility of  $^{222}\text{Rn}$  in water at the lower temperature.

## 5.3 Hydrogen and alkali metals (H, Li, Na, K, Rb, Cs, Fr)

*(Hydrogen, lithium, sodium, potassium, rubidium, cesium, francium)*

Apart from the zero state, the oxidation state of alkali metals is always +I. The chemical bonding with non-metals is always ion bonding. The tendency for alkali metals to form complex ions is very small and this tendency decreases with increasing ionic radii. Francium only exists as a non-stable isotope with a short half-life. Some man-made examples of significant radionuclides,  $^{86}\text{Rb}$ ,  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ , ( $^{134}\text{Cs}$  is an activation product and  $^{137}\text{Cs}$  is a fission product) exist whereas stable isotopes of these elements occur naturally. There are also natural radioactive isotopes of plant macronutrients, such as  $^{40}\text{K}$ , which accounts for  $\approx 0.012\%$  of all K.

Hydrogen is important in the tritium form and may be released to the atmosphere as tritiated water (HTO), tritium gas (HT) and tritiated methane ( $\text{CH}_3\text{T}$ ) with HTO being the dominant chemical form /Murphy, 1993/. The transfer process of tritium between atmosphere, soil and plant include dry and wet deposition, soil migration and diffusion, evaporation, uptake into plants and evapotranspiration from plants. Transfer of tritium into vegetation occurs mainly through stomata on the leaf surface and uptake of soil water /Murphy, 1993; Brudenell et al, 1999/. Uptake via stomata is also highest during conditions with open stomata, such as daytime. Differences in the behaviour of tritium in crops can be ascribed to differences in plant morphology and growth physiology /Brudenell et al, 1999/. Tritium is also incorporated in organic matter (OBT) within crop tissues /Brudenell et al, 1997/ and OBT in plants occurs in either exchangeable or non-exchangeable form, where most is in the latter form /Guenot and Belot, 1984; Diabate and Strack, 1993; Hill and Johnson, 1993/.

Lithium is incorporated in clay minerals and is also lightly fixed by organic matter; therefore the Li content of soil is controlled more by conditions of soil formation than by its initial content in parent rocks /Kabata-Pendias and Pendias, 1992/. Soluble Li in soils is readily available to plants. High levels of Li are found in plants of Rosaceae family, but also in members of Solanaceae, which have a very high Li tolerance /Borovik-Romanova and Bielova, 1974/. Lithium appears to share the  $K^+$  transport carrier and therefore is easily transported into plant cells. In some cases leaves accumulate high levels of Li /Kabata-Pendias and Pendias, 1992/.

Potassium is a macronutrient for plants /Marschner, 1995/. Uptake into the cells occurs to a large extent and also more or less directly into the outer cells of the root tissue (the rhizodermis including root hair cells) and the element is easily transported in the tissue both symplastically and apoplastically. It mostly occurs as a free cation and is important for the maintenance of the electro-chemical potentials of plant cells and thus of ion fluxes across membranes. The uptake is highly selective due to the high degree of cellular uptake and its close coupling to metabolic activity (Figure 3-5). Its uptake has been shown to be biphasic, meaning that low affinity carriers and high affinity carriers are involved, depending on the external K concentration /Marschner, 1995/. More about the K-carriers can be found in the review by /White and Broadley, 2000/. Sodium, Rb and Cs follow the uptake route of K; the radius of hydrated  $Rb^+$  is similar to that of hydrated  $K^+$ , thus the binding site at the plasma membrane of root cells does not appear to distinguish between these two cations /Erdei and Trivedi, 1991/. That is why  $^{86}Rb$  is commonly used when studying K uptake. However, this may give misleading results under certain circumstances as is also true for the flux rates /Behl and Jeschke, 1982/.

Sodium uptake is closely related to that of K, and plants can be natrophilic or natrophobic, depending on the property to accumulate Na and translocate it to the shoot /Marschner, 1995/. This is mainly due to the level of selectivity in the uptake of K in relation to that of Na and there are both species differences and genotypic differences within the same species in root uptake of Na. This is due to several factors such as different activities/capacities of Na efflux pumps, to passive sodium permeability of the root plasma membranes, but probably not to differences in response of the root plasma membrane bound ATPase to Na /Schubert and Läuchli, 1990; Mills and Hodges, 1988/. Sodium is referred to as beneficial; it may be essential for certain plant species, it may replace K functions in plants, and it may have additional growth enhancement effects /Marschner, 1995/. Halophytes are plants that can use Na in osmotic adjustments, since these plants have a high salt requirement for osmotic adjustment, for which Na is more suitable than K. Sodium is also required for some plants with C4 photosynthesis to reach the high efficiency in  $CO_2$ -utilization at low ambient  $CO_2$  concentrations.

Rubidium is firmly bound to acidic igneous rocks and sedimentary aluminosilicates /Kabata-Pendias and Pendias, 1992/. Weathering of Rb is closely linked to that of K, but its bindings to silicates appear to be stronger than those for K. The transfer factor of Rb is about 0.3. This low value relates to the slow rate of supply from soil in relation to root activity. Therefore, available Rb in the immediate vicinity of active plant roots is rapidly depleted and further uptake appears to be diffusion controlled. Thus, various soil factors are important for the Rb uptake /Coughtrey and Thorne, 1983/. It is suggested that pH-dependent reactions regulate the  $Rb^+$  solubility in soils and are major conditions accounting for differences in plant uptake of  $Rb^+$  from contrasting soils; the pool size of exchangeable Rb seems to be of less importance /Tyler, 1997/. Its uptake into plant tissue follows that of K and the distribution factor for  $^{86}Rb/K$  in plants is  $\approx 1$  /Menzel, 1965/. However, there is a slight but constant discrimination by plants against Rb compared with K and the  $^{86}Rb/K$  ratio differs between plant parts /Menzel and Heald, 1955/. Rubidium generally concentrates in flowers and young leaves relative to K /Menzel and Heald, 1955/. Thus,

<sup>86</sup>Rb appears to be selectively accumulated within reproductive structures and young tissues. The translocation after uptake by foliage is very fast /Penot, 1976/.

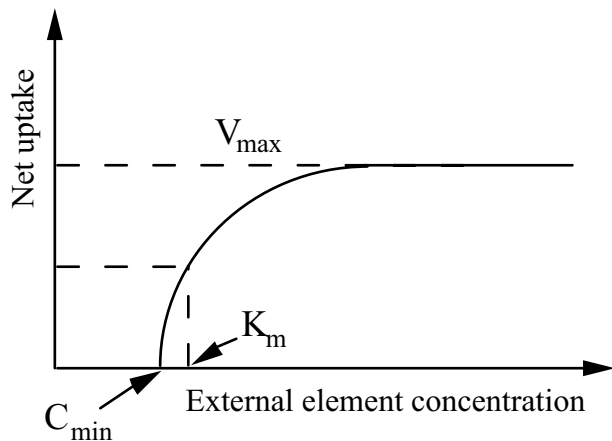
Geochemical characteristics of Cs are similar to those of Rb, but Cs appears to have a greater affinity to aluminosilicates. The content of clay in soil is one of the main variables affecting plant uptake, where an increase in clay content decreases the uptake /Andersen, 1967/. It is known that clay strongly binds Cs and thus depresses the root uptake, whereas organic matter content may increase the uptake of Cs by plants /Cornell, 1993; Valcke and Cremers, 1994; Dumat et al, 1997/. Furthermore, the availability of Cs decreases with increasing soil moisture, extractable K and percentage of very fine sand and silt /Garten and Paine, 1977/. Similarly to Rb, it is soil processes rather than the potential or capacity of plants, that influence the uptake of Cs.

Plants relatively easily take up cesium and in solution it is present as a monovalent cation /White and Broadley, 2000/. Uptake of Cs is related to K and these elements are interrelated in a complex, concentration-dependent, manner rather than by simple competition /Cline and Hungate, 1960/. The root uptake seems not to be parallel to K absorption /Coughtrey and Thorne, 1983; Bunzl et al, 2000/. Instead, the differences between K and Cs are thought to be in the selectivity of the xylem loading process /Buysee et al, 1995/. According to /Handley et al, 1973/, a metabolic process is involved in the uptake of Cs by roots. It is also shown that uptake is affected by temperature /Haghiri, 1962; Resnik et al, 1969/, water stress and osmotic conditions /Van der Borgh et al, 1967/, and it is proposed that Cs uptake is controlled by diffusion /Shalhevet, 1973/. The Cs influx into cells and its use of K transporters is discussed in greater detail in the review by /White and Broadley, 2000/. In a study on Na, K, Rb, Li and Cs /Sutcliffe, 1957/ it was found that the uptake mechanism of Cs was different from that of the other chemical similar elements. Compared with K and Rb, the affinity of the binding sites for Cs is low and, thus, in general K distinctly depresses the Cs uptake /Erdei and Trivedi, 1991/. It was shown that Ca + Mg depressed the Cs uptake and the effect was suggested to be on the Cs loading in the apoplast of the root cortex /Smolders et al, 1997/.

After application to roots, Cs is found in areas of cell expansion and active metabolism, thus in parts of increased requirement for water and nutrients, i.e. nodes, leaf tips, young leaves and shoot meristems /Vanek et al, 2001/. Cesium uptake from soil depends on the stage of plant development. It is shown that the transfer of Cs from soil to plants is higher in grasses than in grain crops /Eriksson and Rosén, 1991/.

A substantial portion of applied soluble Cs can be absorbed by leaves, suggested to be primarily via metabolic processes linked to the developmental status of the species /Coughtrey and Thorne, 1983/. It is expected that about 5–30% of the deposited Cs is absorbed by plant leaves and a substantial portion is translocated to other plant parts. Both foliar and root absorbed Cs is extremely mobile in plants.

No plant group is characterised by a particularly high or low accumulation of Cs, but differences have been found between species /Broadley and Willey, 1997/. Species differences in grasses were found in  $V_{max}$  and  $C_{min}$  /Broadley et al, 1999/ (Figure 5-2). However, the <sup>137</sup>Cs level was very high in *Nymphaea candida* /Nelin and Nylén, 1994/, and the concentration decreased in the order: herbs > grasses > woody plants > trees and shrubs /Rosén et al, 1995/. In tree trunks, <sup>137</sup>Cs is relatively uniform in the wood xylem /Momoshima and Bondietti, 1994/. The same was found in sweet potatoe, where <sup>137</sup>Cs distributed homogeneously in both storage roots and leaves /Wang et al, 2000b/. In *Picea abies*, <sup>134</sup>Cs is predominantly accumulated in fine-roots /Riesen and Brunner, 1996/. *Caluna vulgaris* has a very high accumulation of <sup>134</sup>Cs, whereas low concentrations are measured in dead plant material /Salt and Mayes, 1993/. Heather with mycorrhiza have higher uptake of <sup>134</sup>Cs than plants without mycorrhiza /Strandberg and Johansson, 1998/.



**Figure 5-2.** Net uptake as a function of external concentration. Maximum net uptake rate ( $V_{max}$ ) when the external concentration tends to infinity, the concentration giving half maximum net uptake rate ( $K_m$ ) and the highest concentration with no net uptake ( $C_{min}$ ).

## 5.4 Alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra)

### (Beryllium, magnesium, calcium, strontium, barium, radium)

Of these elements Ca and Mg are the most common in nature. Oxidation state is +II and the heavier metals form complexes with ionic bindings, whereas complexes with beryllium often additionally consist of covalent bindings. The tendency to form complexes is higher than for alkali metals. Most of the metals form difficultly dissolved complexes with sulphate, carbonates and phosphates, whereas they form easily dissolved complexes with nitrate, chloride, sulphides and cyanides. Radium is formed in the declining series of uranium. In general, Sr, Ba and Ra are considered to be approximate chemical and physiological analogues of Ca, with important radionuclides as  $^{90}\text{Sr}$ ,  $^{140}\text{Ba}$  and  $^{226}\text{Ra}$ .

Beryllium most often is found as  $\text{Be}^{2+}$  but can also be found in complexes with oxygen and in alkaline environments with carbonate /Kabata-Pendias and Pendias, 1992/. Beryllium is also known to attract to organic material. It is quite immobile in soil but as soluble salts, such as  $\text{BeCl}_2$  and  $\text{BeSO}_4$  it can be available to plants. In soluble form, Be is easily taken up by plants if in a soluble form. Absorption of Be seems to be similar to that for Mg and Ca. Beryllium can also replace Mg in some plants. *Vaccinium myrtillus* has been found to be a hyperaccumulator of this element /Wedepohl, 1969–1974/. Root accumulators have been found among the Leguminosae and Cruciferae families /Gribovskaya et al, 1968/.

Magnesium and Ca are nutrient elements in plants /Marschner, 1995/. Roots take them up when they exist as divalent ions. Both elements are mobile in the plants. The uptake into cells of these ions is passive and Ca is taken up by a facilitated diffusion, via a specific Ca channel. However, at the cells the Ca concentration is restricted to the cell walls and the cell compartments so as not to interfere with phosphorus in the cytoplasm, since Ca easily forms complexes with phosphate and thereby may affect the energy metabolism. An active efflux mechanism is therefore important for Ca. Calcium is restricted to the apoplast and is translocated apoplastically. The root uptake is mainly through the root tips. Calcium is needed for cell division, cell wall and membrane functions. On the other hand, as with K, magnesium is also involved in osmotic adjustments and electro-potential regulation and thus, is commonly found in ionic form in the cells. Since Mg is important in the photosynthesis, both as a component of the chlorophyll molecule and in carbon fixation, translocation to the shoot is

important. Calcium and Sr exist largely as immobile complexes with glutauronic acids and pectate in the plant tissue /Mortensen and Marcusiu, 1963; Myttenaere and Masset, 1965/.

Strontium is often associated with Ca and sometimes also with Mg, and the ratio between Sr and Ca is relatively stable in the biosphere. Strontium mainly occurs as  $\text{Sr}^{2+}$  ions, also in chelating forms. It is easily mobilized during weathering and is then incorporated in clay minerals and strongly fixed to organic matter. Thus, the availability of Sr is dependent on soil pH and soil organic matter content, and in addition it is most mobile in acid and anaerobic soils /Coughtrey and Thorne, 1983/.  $^{90}\text{Sr}$  is produced in many nuclear processes and is one of the most hazardous elements to man. The root uptake of Sr from soil is related to the mechanisms of both mass-flow and exchange diffusion /Elgawhary et al, 1972/. In plants, 10 to 1500  $\mu\text{g Sr gDW}^{-1}$  is commonly found. The availability in soils may, however, be depressed by Ca, Mg, K and Na /Kabata-Pendias and Pendias, 1992/. After foliar deposition  $^{85}\text{Sr}$  was considered to be moderately mobile in the plant body /Shinonaga et al, 1999b/. The radial distribution of  $^{90}\text{Sr}$  in tree trunks differs depending on tree species /Momoshima and Bondietti, 1994/.  $^{90}\text{Sr}$  is found to be more concentrated in leaves than in storage roots of sweet potatoes /Wang et al, 2000b/. In *Picea abies*,  $^{85}\text{Sr}$  is predominantly accumulated in fine-roots /Riesen and Brunner, 1996/.

In geochemistry, Ba is usually associated with K because of its very similar ionic radii. However, Ba is not very mobile and it precipitates with sulphates and carbonates and is strongly absorbed by clay. Barium is easily taken up from acid soil. Barium is present in plant tissue, ranging between 1–198  $\mu\text{g gDW}^{-1}$ . The highest concentrations of Ba, up to 10 000  $\mu\text{g gDW}^{-1}$  have been reported for different trees and shrubs and in Brazil nuts /Shacklette et al, 1978/.

Radium occurs in the environment as radioactive nuclides  $^{224}\text{Ra}$ ,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , decay products of uranium and thorium, and where  $^{226}\text{Ra}$  is the most stable and frequent in the biosphere. The concentration of Ra in vegetation ranged from 0.03 to 1.6  $\text{pg gDW}^{-1}$  /Kabata-Pendias and Pendias, 1992/, and the transfer factors show wide variations ( $0.1 \times 10^{-2}$  to  $40 \times 10^{-2}$ ) in different species /Markose et al, 1993/. *Echinops echinatus* seems to have a preferential uptake of Ra /Markose et al, 1993/. In studies on spruce tree rings, Ra did not show any radial translocation /Haas and Müller, 1995/. Accumulation in fruit of  $^{226}\text{Ra}$  is two orders of magnitude lower than that of leaves and roots /Markose et al, 1993/.

## **5.5 Boron group (B, Al, Ga, In, Tl)**

### **(Boron, aluminium, gallium, indium, thallium)**

The oxidation state of +III is most common for these elements. Gallium, indium and thallium are rare elements whereas aluminium is very common in the earth's crust. Boron is not a metal, whereas the others are. Boron forms covalent bindings, whereas in Al complexes ionic bindings are more common. Aluminium oxides are amphoteric meaning that they can react both as acid and base.

Boron, which is a plant micronutrient, is taken up as boric acid and soil pH is one of the most important factors affecting its availability to plants. The uptake process is discussed /Moore, 1972; Price et al, 1972; Loneragan, 1975/. It seems, however, that a metabolic component within the cell membrane is of minor importance and that the absorption mainly follows the water flow through the roots. Boron is relatively immobile in plants but is translocated in the xylem and is accumulated in old leaves with the highest content in tips

and margins /review in Kabata-Pendias and Pendias, 1992/. It is indicated that B can be translocated from leaves to fruits and seeds. The transpiration stream primarily governs its distribution in the plants although it is also phloem-mobile and might be retranslocated in considerable amounts /Shelp, 1993/. Dicotyledonous plants have a higher requirement of B than monocots and thus also a higher level in the tissue.

Aluminium is very closely related to soil and water pH. It forms a lot of different complexes with OH-groups also containing several Al-units, which are more cationic at low pH becoming more anionic at higher pH. At neutral pH, a non-ionic form of  $\text{Al}(\text{OH})_3$  is formed. Uptake of Al by plants will probably be in the form of  $\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ . Some species may contain more than 0.1% of Al and thus are Al-accumulators /Kabata-Pendias and Pendias, 1992/. Aluminum binds to phosphate and thus P can decrease Al uptake or Al may affect the energy metabolism in plants.

Only two minerals of Ga are known, sulfide and hydroxide. Gallium is found in plants in a range of 3–30  $\mu\text{g gDW}^{-1}$  /Shacklette et al, 1978/. There is a higher ratio of Ga to Al in terrestrial plants than in soils, which reflects a selective uptake of Ga by plants /Kabata-Pendias and Pendias, 1992/.

Plants take up indium although not always above the detection limit. According to /Smith et al, 1978/, In occurs in various plants at 1–2  $\mu\text{g gDW}^{-1}$  after being grown in culture solution with In, and up to 2.1  $\mu\text{g gDW}^{-1}$  in plants from contaminated sites.

Thallium is incorporated with various minerals, mainly sulphides. Chemical behaviour is analogous with K. Herbage and woody plants apparently contain larger amounts of Tl than other plant species. /Shacklette et al, 1978/ found up to 100  $\mu\text{g gDW}^{-1}$  in pine trees and the concentration was higher in needles than in stems. Up to 17 000  $\mu\text{g gDW}^{-1}$  was found in flowers of *Galium* sp /Zyka, 1972/. Rape has been shown to accumulate high Tl levels, 33 mg  $\text{kgDW}^{-1}$  of rape seeds was reported, and with TF factors for shoot and seeds of > 1 and > 3, respectively /Tremel et al, 1997/.

## 5.6 Carbon group (C, Si, Ge, Sn, Pb)

### (Carbon, silicon, germanium, tin, lead)

This group consists of non-metals, half-metals and a metal and the oxidation state of this group can be both +II and +IV. Carbon and Si are very common in earth crusts. Carbon is found in organic compounds originally from living material, in gaseous form  $\text{CO}_2$  and CO, and in complexes such as  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . Silicon is common as silica oxide. Germanium, Sn and Pb are trace elements and show chalcophilic properties in the terrestrial environment, where  $^{210}\text{Pb}$  is an important radionuclide.

Carbon-14 may be released to the atmosphere as  $\text{CO}_2$ , CO,  $\text{CH}_4$ , HCHO and COS /Ould-Dada et al, 2001/. Carbon is taken up as carbon dioxide via air through leaves; the  $^{14}\text{CO}_2$  form is incorporated into carbohydrates via photosynthesis. However, uptake also occurs via roots since  $\text{CO}_2$  diffuses into the soil /Morgan and Betham, 1990/. Carbon is also taken up as hydrocarbon via roots. Carbon can be taken up as glucose, mannose and citric acid /Jones and Darrah, 1992/. Also unnatural compounds such as 2,4,6-trinitrotoluene (TNT), or their decomposition products, can be taken up /Sens et al, 1999/. Important C-fluxes in the rhizosphere are resorption by roots, uptake by the microorganisms and release of C by the roots /Jones and Darrah, 1992/. High environmental mobility and long half-life are the main factors contributing to the radiological importance of  $^{14}\text{C}$ .



All silicate minerals are based on a fundamental structural unit,  $\text{SiO}_4$ , the so-called tetrahedron. The most resistant mineral is quartz,  $\text{SiO}_2$ , and opal, a noncrystalline form having a biological origin. The concentration of Si in plants is high in grasses (0.3–1.2%), which need Si for their structure. Diatoms, sedges, nettles and horsetail contain even higher Si levels. Rice plants are known accumulators of Si, up to 10–15% /Carlisle et al, 1977; Kitagishi and Yamane, 1981/. Silicon is absorbed as monosilic acid or silica, and since uptake normally is proportional to the soil concentration and the water flow the uptake is suggested to be passive. However, in rice plants it seems to involve an active process /Tinker, 1981/. In addition, some clovers restrict the uptake of Si, either they exclude  $\text{H}_4\text{SiO}_4$  or bind it within the root tissue, thus reducing the Si concentration in the xylem sap to about 6% of that of the external solution /Carlisle et al, 1977/. /Körös, 1985/ showed that special complexes were isolated from *Thuja plicata* and most of the Si taken up was either monomeric silica acid or organic complex, which was deposited in plant tissue as opaline silica. Silicon strengthens the plants by impregnating the walls of epidermal and vascular tissue /Kaufman et al, 1969/. This reduces water loss and retards fungal infections.

The lowest Ge concentrations are found in calcareous sediments and mafic magmatic rocks. Mobilized Ge is fixed as  $\text{Ge}(\text{OH})_4$  to clay minerals, Fe oxides and organic matter. Germanium occurs as divalent cation, but also as  $\text{HGeO}_2^-$ ,  $\text{HGeO}_3^-$  and  $\text{GeO}_3^{2-}$ . Germanium occurs in plants. High levels have been found in Spanish mosses ( $15 \mu\text{g gDW}^{-1}$ ). Germanium is accumulated in plants at a relatively high rate, possibly as  $\text{GeO}_2$  /Kitagishi and Yamane, 1981/. The tops of rice plants seem to have a high accumulation of  $\approx 1\%$  /Matsumoto et al, 1975/.

Tin is known to occur as  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  and to form several complex anions of oxides and hydroxides. The mobility is pH dependent. In soil, Sn is less available and is not found in all plants. In solution, plants easily take up Sn but most is remaining in the roots. Tin can be accumulated up to  $2000 \mu\text{g gDW}^{-1}$  in plants /Peterson et al, 1976/, and sedges and mosses are found to be the best Sn accumulators /Griffitts and Milne, 1977/.

Most of Pb in the soil is not available to plants. According to /Zimdahl, 1975/ and /Hughes et al, 1980/, Pb is taken up passively via root hairs and is accumulated in the cell walls. Very little of what has been taken up is translocated to the shoot. There is an uptake of Pb also via the aerial parts, but most of it is adsorbed to the applied surface (about 80%) /Isermann, 1977/. When applied to needles of white spruce at low pH (4.0),  $^{207}\text{Pb}$  was translocated towards the shoot tip /Watmough et al, 1999/. There are *Brassica juncea* cultivars which hyperaccumulate Pb /Brooks and Robinson, 1998/. According to /Baker et al, 2000/, 14 taxa and 6 families of plants, e.g. *Minuartia verna*, hyperaccumulate Pb.

## 5.7 Nitrogen group (N, P, As, Sb, Bi)

### (Nitrogen, phosphorus, arsenic, antimony, bismuth)

Non-metals, half-metals and a metal are also found in this group. The most important oxidation states are +V, +III and –III, however, nitrogen can have all states from +V to –III. The higher the atom number the more likely it is that the oxidation state is +III, and it dominates in the case of Bi. Nitrogen is found in gaseous form as  $\text{N}_2$  and  $\text{NO}_x$ , in soluble complexes as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  and in organic substances. Phosphorus is present as  $\text{PO}_4^{2-}$  form.

Nitrogen is a macronutrient and is taken up as  $\text{NO}_3^-$ ,  $(\text{NO}_2^-)$  or  $\text{NH}_4^+$ . The latter is less energy consuming and is, if present, taken up first /Marschner, 1995/. Ammonium is taken up in the cell along with a release of hydrogen ions. Within the root cells, ammonium has to be incorporated to aminoacids, since ammonium is toxic also at low concentrations. Nitrate is taken up along with protons and thus increases the pH of the surrounding medium. Nitrate can be translocated to the shoot via the xylem and be stored in vacuoles without detrimental effects on the cells /Marschner, 1995/. However, nitrate has to be converted to ammonium if nitrogen should be able to be incorporated to organic substances. Nitrite is rarely accumulated in plants under normal conditions. In addition, plant leaves can take up nitrogen from the air via the open stomata when nitrogen is in gaseous form.

Phosphorus is also a plant nutrient and is taken up in anionic form along with hydrogen ions,  $2\text{H}^+ + \text{PO}_4^{2-}$  /Marschner, 1995/. It is translocated to the shoot. Phosphorus occurs in the whole plant since it is closely involved in the energy metabolism of the plant. Phytate is a storage form of phosphorus in grains and seeds.

The behaviour of arsenate ( $\text{AsO}_4^{3-}$ ) resembles that of phosphate and vanadate. Several strains of bacteria accelerate the oxidation of arsenites to arsenate and are also involved in methylation and alkylation of As, thus the microbiota governs the process of As migration, precipitation and volatilization. Phytotoxicity of As depends on the soil properties, where heavy soil seems to be less toxic compared with light soil. It is suggested that As is taken up passively by the water flow due to the linear relationship between uptake and the soil concentration. However, it has also been suggested that arsenic is taken up across cell membranes in a similar way to phosphate since phosphate and arsenate are similar /Marschner, 1995/. For that reason, plants are less intoxicated when supplied with phosphate. Some plants are good at taking up As, e.g. Douglas fir ( $140\text{--}8200 \mu\text{g gDW}^{-1}$ ), and recently it was shown that the brake fern *Pteris vittata* hyperaccumulates As /Warren et al, 1968; Ma et al, 2001/. Arsenic is translocated in the plants. The highest As concentration, however, was always reported in roots and old leaves /Thoresby and Thornton, 1979/. After foliar deposition,  $^{74}\text{As}$  was shown to have moderate mobility in the plant body /Shinonaga et al, 1999b/.

The common occurrence of Sb in waters, its concentrations in carbon and its association with Fe hydroxides indicate a relatively high mobility in the environment /Kabata-Pendias and Pendias, 1992/. Also sewage sludge seems to contain Sb. Plants take easily up Sb when it is in a soluble form.

Bismuth is a rare element in the earth crust, however, accumulation of Bi in coal and graphite shales of  $5 \mu\text{g gDW}^{-1}$  has been reported /Kabata-Pendias and Pendias, 1992/. Bismuth has, according to /Shacklette et al, 1978/, been found in about 15% of the species tested and these ranged from 1 to  $15 \mu\text{g gDW}^{-1}$ . It was also found that *Lycopodium* sp contained between 1 and  $11 \mu\text{g gDW}^{-1}$  of Bi /Erämetsä et al, 1973/.

## 5.8 Chalcogen group (O, S, Se, Te, Po)

### (Oxygen, sulphur, selenium, tellurium, polonium)

Of these elements oxygen and sulphur are the most common. These elements are also non-metals, half-metals and metals with high electro negativity, which decreases with increasing atom number. Oxidation states are from +VI to -II. Oxygen is found in different oxides in both ionic forms and gaseous form, as well as in the forms of  $\text{O}_2$  and ozone,  $\text{O}_3$ . Oxygen

is also found in organic substances. Sulphur is found in gaseous form ( $\text{SO}_2$ ), as ions such as  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$  and sulphides. Selenium is also found as  $\text{SeO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$  and in a gaseous form. Tellurium is a very rare element and polonium only exists in very small quantities as radioactive nuclides, such as  $^{210}\text{Po}$ , in the natural decline series.

Oxygen and sulphur are needed by plants and can be considered as macronutrients. Plants take up oxygen from air by gaseous compounds containing oxygen, such as carbon dioxide. It enters the plant both via air, root and shoot in the form of water, and via roots it can enter in complexes with other elements such as phosphate and sulphate.

$^{35}\text{S}$  may be emitted to the atmosphere from  $\text{CO}_2$ -cooled reactors as carbonyl sulphide (COS) and hydrogen sulphide ( $\text{H}_2\text{S}$ ) /Ould-Dada et al, 2001/. COS is the dominant chemical species during normal operating conditions and the release of  $\text{H}_2\text{S}$  can occur during start-up. COS has low aqueous solubility and high chemical stability. The atmospheric residence time is also longer for COS than for  $\text{H}_2\text{S}$  /Dollard, 1989/. Sulphur is normally taken up by plants in the form of  $\text{SO}_2$  in gaseous form via stomata and as  $\text{SO}_4^{2-}$  via roots.

Selenium occurs as organo-Se or in anionic form in the soil, and the uptake of anions increases with increased pH /Wang et al, 2000/. Selenium is taken up in plants in the form of  $\text{SeO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$  but also as selenomethionine /Abrams et al, 1990/. Selenate is taken up in strong preference to selenite and competes for the same uptake site as sulfate /Asher et al, 1977/. There are selenium accumulators, e.g. many species of the genus *Astragalus* that can accumulate up to  $4000 \text{ mg Se kgDW}^{-1}$ , which be compared with  $10 \text{ mg Se kgDW}^{-1}$  for *Zea mays* /Shrift, 1969/. Selenite is accumulated in the roots and is transferred to aminoacid-Se to a higher extent than selenate, which is translocated to the shoot /Asher et al, 1977; Gissel-Nielsen, 1987/. There is also a volatilization of Se from the plant leaves /Terry et al, 1992/. After foliar deposition,  $^{75}\text{Se}$  was shown to be mobile in the plant body /Shinonaga et al, 1999b/.

The biological cycling of Te resembles that of Se. Bacteria capable of methylating As and Se can also methylate Te and reduction of tellurite to Te is also influenced by micro-organisms /Weinberg, 1977/. The Te concentration in plants is often lower than that of Se. Vapours from some plants smell like garlic and contain dimethyl telluride. In onion and garlic high concentrations of Te ( $300 \mu\text{g gDW}^{-1}$ ) have been reported /Schroeder et al, 1967/.

Polonium occurs naturally in the biosphere with  $^{210}\text{Po}$  and several other short-lived radio-nuclides. In soil, the concentration of  $^{210}\text{Po}$  is  $10\text{--}220 \text{ Bq kg}^{-1}$  and in terrestrial plants  $\approx 10 \text{ Bq kg DW}^{-1}$  /Kabata-Pendias and Pendias, 1992/.

## 5.9 Halogenes (F, Cl, Br, I, At)

### (Fluorine, chlorine, bromine, iodine, astatine)

This group is the most electronegative in the periodic system and attracts one electron. Most of the elements are non-metals with oxidation states of  $-I$ , however, chlorine can have all even oxidation states between  $-I$  to  $+VII$ . These elements can be present in gasous form as well as in ionic form, e. g.  $\text{Cl}^-$  and  $\text{IO}_3^-$ .  $^{129}\text{I}$  is a radioactive longlived hazardous isotope whereas  $^{127}\text{I}$  is stable. Astatine is rarely present and then as radioactive nuclides of very short life.

Fluorine mobility in soil is very complex and under natural soil conditions F is slightly mobile. The soluble F fraction of soil is thought to be taken up passively by roots and that an F-complex is more easily taken up than F-ions. Fluorine is easily translocated within the plant, and  $^{18}\text{F}$  follows the water flow /Kume et al, 1997/. The F concentration in plants is not directly related to F in soil, instead the F concentration in foliage is more correlated to that of the air. Thus, airborne F is more important than that in the soil. From the air, F is taken up in gaseous form via stomata but if precipitated on the leaf surface a cuticular uptake may occur /Chamel and Garrec, 1977/. Higher concentrations of F in aerial than in other parts of the plants are commonly found. The concentration of  $30\ \mu\text{g F gDW}^{-1}$  in plants is common in unpolluted areas. Fluorine is also the most hazardous phytotoxic air pollutant. Asparagus, bean, cabbage, carrot and willow are shown to be F-tolerant species /Kabata-Pendias and Pendias, 1992/.

$^{36}\text{Cl}$  is formed by neutron activation of  $^{35}\text{Cl}$  present in low concentrations as impurity of nuclear fuels, and  $^{36}\text{Cl}$  is interesting since it has a long half-life and is mobile in soil /Ould-Dada et al, 2001/.  $^{36}\text{Cl}$  is also used in the form of chlorate-36 instead of nitrate to investigate the nitrate uptake carrier of plasma membranes. This, of course, can be performed since it is thought that these two ions have the same transport route, which is not absolutely certain. The predominant form in the environment is the inorganic anion ( $\text{Cl}^-$ ), which is highly mobile /Coughtry and Thorne, 1983/. Like the other halogens, chlorine decreases in the soil with increasing distance from the sea. Chlorine is an essential element for plants and is used for metabolic processes involved in maintaining electro- and chemical potentials in plant cell tissue. The availability of Cl to plants in soil is related to the associated cations and more with monovalent than with divalent cations. Root-absorbed Cl readily translocates to both stems and leaves /Coughtrey and Thorne, 1983/. Chlorine can also be directly absorbed from air by leaves. Foliar absorption of soluble and gaseous chlorine compounds occurs readily and rapidly with considerable variation both between and within plant species, and the foliar translocation is very fast /Lessani and Marschner, 1978/. The content of Cl in normal plants is about  $10\text{--}20\ \mu\text{g gDW}^{-1}$  whereas 10 times higher content is found in halophytes, such as sugar beet /review in Kabata-Pendias and Pendias, 1992/. Up to  $5500\ \mu\text{g gDW}^{-1}$  has been found in potato tubers /Bergmann, 1988/. Transfer factors were shown between 0.8 to 170 for Cl /Sheppard et al, 1999/.

Carbon and organic matter accumulate bromine, which has a strong correlation with organic carbon /Kabata-Pendias and Pendias, 1992/. Marine plants in general contain higher Br levels, more than 250 times higher level than terrestrial plants, which is  $\approx 40\ \mu\text{g gDW}^{-1}$ . The concentration is usually higher in leaves than in roots. Bromine is able to substitute for Cl in plants, but is not an essential element.

Iodine is emitted to the atmosphere in its elemental form ( $\text{I}_2$ ), as hydrogen iodide (HI), hypoiodous acid (HOI), methyl iodide ( $\text{CH}_3\text{I}$ ), other organo-iodide compounds, and as particulates /Ould-Dada et al, 2001/. The oxidation of iodide to iodate and further alteration to elemental I may occur in soils, and also exchange of volatile I compounds between soil and atmosphere is reported /Davies, 1980/. Several ionic forms,  $\text{I}^-$ ,  $\text{IO}_3^-$ ,  $\text{I}_3^-$ ,  $\text{IO}^-$ ,  $\text{IO}_6^{3-}$ ,  $\text{H}_4\text{IO}_6^-$ , may occur in the aquatic phase of the soil, of which the first two are the most common /Garrels and Christ, 1965/. Liming is found to decrease the availability of I to plants. Only a small fraction of I is available /Fuge and Johnson, 1986/. Soluble forms of I are easily available to plants. Therefore, terrestrial plants contain much less I than marine plants, which are known to concentrate  $50\text{--}8800\ \mu\text{g gDW}^{-1}$  /Shacklette and Cuthbert, 1967/. It is also found that I in flooded soil is an order of magnitude more soluble than in drained soil, whereas the TF in wild rice did not show the same difference /Sheppard and Motycka, 1997/. The TF of  $^{131}\text{I}$  was not affected by  $^{131}\text{I}$  soil concentration, but, was affected by the plant mass /Yu et al,

2000/. Levels as high as 5 mg I kg<sup>-1</sup> soil may have detrimental effects on terrestrial plants /Sheppard and Evenden, 1995/. Plants have often higher I levels in tops than in roots, and a seasonal variation in I levels, with the lowest in summer, is found /Hartmans, 1974; Davies, 1980/. The reason for the high level of I in shoots has to be due to plants absorbing I from the atmosphere, via stomata, when I is in gaseous form. Both elemental and organic iodine can enter plants by direct foliar absorption /Ould-Dada et al, 2001/. The content of I in plants largely originates from the atmosphere.

## **5.10 Transition metals**

### **5.10.1 Scandium group (Sc, Y, La, Ac)**

**(Scandium, yttrium, lanthanum, actinium)**

This group also includes the lanthanides and actinides (see below). These elements have the oxidation state +III and form covalent complexes. Yttrium and lanthanum are the most common of the elements in this group. Perhaps the most radioecologically important nuclide within this group is <sup>90</sup>Y (the decay product of <sup>90</sup>Sr).

The concentration of Sc is enriched in mafic rocks and in argillaceous sediments, whereas it is low in sand and limestone. Therefore, the lowest Sc concentration is found in sandy and light organic soils and higher in granitic and volcanic rocks. Also enrichment of Sc in phosphorites can be expected. It was observed that the largest amount of Sc was taken up from sandy soil by plants /Ozoliniya and Kiunke, 1978/. The Sc content seemed to be higher in old leaves than in young leaves, and a high concentration was reported in flax plants (0.014–0.026 µg gDW<sup>-1</sup>) and tea leaves (0.013–0.14 µg gDW<sup>-1</sup>). Also lichens and bryophytes contain high levels (0.3–0.7 µg gDW<sup>-1</sup>) /reviewed in Kabata-Pendias and Pendias, 1992/. After foliar deposition, <sup>46</sup>Sc was shown to be immobile in the plant body /Shinonaga et al, 1999b/.

The Y concentration differs widely between various rock types. In the form of Y<sup>3+</sup> it is incorporated into several minerals, of which silicates, phosphates and oxides are most frequent. Yttrium concentrations above the detection limits were found in about 10% of some analysed plants /Connor and Shacklette, 1975; Shacklette et al, 1978/. After foliar deposition, <sup>88</sup>Y was shown to be immobile in the plant body /Shinonaga et al, 1999b/. Woody seed plants can accumulate high levels of Y, up to 700 µg gDW<sup>-1</sup> /reviewed in Kabata-Pendias and Pendias, 1992/. /Erämetsä and Yliroukanen, 1971/ showed that mosses and lichens contained between 2 and 200 µg gDW<sup>-1</sup> of Y.

### **5.10.2 Titanium group (Ti, Zr, Hf)**

**(Titanium, zirconium, hafnium)**

Zirconium and hafnium are very similar to each other. In this group, +IV is the most common oxidation state. The covalent part of the bindings is high and <sup>95</sup>Zr is an important radionuclide. Minerals of Ti are very resistant to weathering and therefore occur practically undecomposed in soils. Zirconium prefers to bind to oxygen and is only slightly mobile in soil.

Hafnium is taken up by plants and after foliar deposition  $^{175}\text{Hf}$  is shown to be immobile in the plant body /Shinonaga et al, 1999b/. Titanium is considered to be relatively unavailable to plants and not easily mobile in them /Kabata-Pendias and Pendias, 1992/. The availability of Zr to plants is very limited and Zr has a low mobility in plants. On the other hand, Zr is easily taken up from water /Smith and Carson, 1978/. Some herbage plants, especially legumes, as well as shrubs and mosses, are likely to concentrate more Zr than other plants /Kabata-Pendias and Pendias, 1992/.

### 5.10.3 Vanadium group (V, Nb, Ta)

#### (Vanadium, niobium, tantalum)

The oxidation state of these elements is +V but also +II, +III and +IV exist. The chemical characteristics are strongly dependent on its oxidation state. One important radionuclide in this group is  $^{95}\text{Nb}$ .

Vanadium is concentrated mainly in mafic rocks and in shales. This element tends to be associated with organic matter, and therefore its elevated concentrations in organic shales and bioliths are common /Kabata-Pendias and Pendias, 1992/. An especially wide range of V in some coals and crude oil has often been observed, probably due to the existence of plants with much higher V content during former geologic periods than found today in plants with normal uptake characteristics. High V concentration in organic sediments as the result of  $\text{V}^{3+}$  sorption by lipids and cholins, the basic compounds in further formation of porphyrins, was shown by /Yen, 1972/. This element is essential for some algae and cyanobacterias and is known to stimulate the photosynthesis of these organisms /Kabata-Pendias and Pendias, 1992/. Vanadium is a specific catalyst of  $\text{N}_2$  fixation and may partially substitute for Mo in this function.

Soluble V is easily taken up by plant roots and it is thought that the absorption is passive /Welch, 1979 in Kabata-Pendias and Pendias, 1992/. The uptake is strongly depends on pH, where a high pH decreases the uptake. It is indicated that  $\text{VO}^{2+}$ , which occurs under acid conditions, is more rapidly absorbed by roots than are  $\text{VO}_3^-$  and  $\text{HVO}_4^{2-}$ , species that predominate in neutral and alkaline soil solutions /Welch, 1979/. It seems that biotransformation of V from vanadate ( $\text{VO}_3^-$ ) to vanadyl ( $\text{VO}^{2+}$ ) during plant uptake occurs /reviewed by Morrell et al, 1986/, and a reduction of V in plants is beneficial since  $\text{V}^{5+}$  is a potent inhibitor of several enzymes whereas  $\text{V}^{4+}$  is not very harmful to plants. Some bryophytes and fungi, especially *Amanita muscaria*, accumulate high levels of V, up to  $345 \mu\text{g gDW}^{-1}$  with a TF of 50 /Lepp et al, 1987/. Bryophytes are most sensitive to aerial sources of V. Other accumulator plant species are also known /Cannon et al, 1977/.

Niobium, with +5 in valence state, is the most stable one. The presence of organic complexing agents mobilises Nb. Under humic conditions, Nb is relative mobile and therefore available for uptake by plants. A common value of Nb in plants is  $\approx 1 \mu\text{g gDW}^{-1}$ , however, up to  $10 \mu\text{g gDW}^{-1}$  has been found in selected plants such as *Rubus arcticus* /Tiutina et al, 1959/.

Tantalum closely resembles Nb in geochemical behaviour, however, it is less mobil than Nb since Ta has a lower solubility and a weak stability of organic complexes. Therefore, the Nb to Ta ratio varies /Kabata-Pendias and Pendias, 1992/. Not much has been published on Ta and plants.

#### 5.10.4 Chromium group (Cr, Mo, W)

##### *(Chromium, molybdenum, tungsten)*

The oxidation state varies between +II and +VI. All three metals form complex ions with oxygen.

Chromium is taken up by plants but at a low rate due to the mechanism of root uptake. Chromate seems to be absorbed in roots by the same transport system as sulphate, therefore, sulphate is a strong inhibitor of chromate uptake /Kleiman and Cogliatti, 1997/. Root tissues are not capable of stimulating the reduction of  $\text{Cr}^{3+}$  to readily soluble  $\text{Cr}^{2+}$  (the same process as with Fe) /Tiffin, 1972; Cary et al, 1977/. The most available form is  $\text{Cr}^{6+}$ , but is the most unstable and toxic one. There are also reports on  $\text{CrO}_4^{2-}$  absorption by cells /Pacha and Galimska-Strypa, 1988/. The Cr/Fe ratio is fairly stable in plants and is possible due to the similarity in uptake processes /Cary et al, 1977/. It seems that Cr is translocated as anionic complexes, and trioxalatochromate in plant leaves has been reported /Tinker, 1981/. It is also found that  $\text{Cr}^{6+}$  can be transformed in plant cells into  $\text{Cr}^{3+}$ . Due to its low solubility,  $\text{Cr}^{3+}$  is not translocated across cell membranes /Tobin et al, 1984/.

Molybdenum is a nutrient element and is taken up in anionic form as molybdate. Molybdenum is moderately mobile in plants and it has been suggested that it could be translocated as a Mo-S aminoacid complex in the xylem /Tiffin, 1972/. Some native plants, especially leguminous species, are known to accumulate high levels of Mo /Murphy and Walsh, 1972/.

The geochemical behaviour of W resembles that of Mo. It seems also resemble to Mo in the case of plants. The element is easily available to plants and is possibly taken up in anionic form,  $\text{WO}_4^{2-}$  /Wilson and Cline, 1966/. /Bell and Sneed, 1970/ reported a high accumulation of  $^{185}\text{W}$ , released from nuclear reactions, in plant roots. Concentrations of 5–100  $\mu\text{g W gDW}^{-1}$  have been found in trees and shrubs in the Rocky Mountains /Shacklette et al, 1978/, whereas values below 1 seem to be most common in other plant types /Kabata-Pendias and Pendias, 1992/. Tungsten is moderately toxic to plants /Gough et al, 1979/.

#### 5.10.5 Manganese group (Mn, Tc, Re)

##### *(Manganese, technetium, rhenium)*

Both technetium and rhenium are rare, and technetium only exists as a radioactive isotope. Manganese, on the other hand, is a very common element. The oxidation states are between +II and +VII. Important radionuclides are  $^{99}\text{Tc}$ ,  $^{99\text{m}}\text{Tc}$  and  $^{54}\text{Mn}$ .

Manganese availability is high in acid and flooded soil. Manganese is a plant micronutrient, which is taken up as  $\text{Mn}^{2+}$  by plants. Manganese uptake in plant cells seems to be metabolically controlled but at high external concentrations the uptake is passive. Manganese is known to be rapidly taken up and translocated in plants, most likely in a free cationic form and not bound to any insoluble organic ligands either in root tissue or xylem sap /Tiffin, 1977; Tinker, 1981/. However, in the phloem, Mn has been found in complexes with organic molecules /Van Goor and Wiersma, 1976/. Manganese is translocated mostly to meristematic tissues and is therefore observed in young expanding tissue. After foliar deposition,  $^{54}\text{Mn}$  was shown to have moderate mobility in the plant body /Lin et al, 1995; Shinonaga

et al, 1999b/, whereas when added to the stem bark surface, less than 1% of the adsorbed  $^{54}\text{Mn}$  was translocated to other plant organs /Lin et al, 1995/. Manganese resistant genotypes of plant species are found to accumulate above 1 mg Mn gDW<sup>-1</sup> /Gough et al, 1979/.

Rhenium is found in anionic form as  $\text{ReO}_4^-$ , which is readily soluble. It can be taken up by plants and is found in concentrations of 70–300  $\mu\text{g gDW}^{-1}$  /Shacklette et al, 1978/. After foliar deposition  $^{183}\text{Re}$  was shown to have medium mobility in the plant body /Shinonaga et al, 1999b/.

Technetium is a non-naturally occurring element,  $^{99}\text{Tc}$  is a long-lived ( $\approx 200\,000$  years) fission product of  $^{238}\text{U}$  whereas  $^{99\text{m}}\text{Tc}$  is an activation product with short ( $\approx 6$  h) half life. Technetium has a long immobilization time in soil and thus is very bioavailable to plants /Van Loon, 1986/. The uptake occurs probably in the form of  $\text{TcO}_4^-$  and there are antagonistic effects with  $\text{NO}_3^-$  and other anions /Van Loon, 1986/. Technetium is probably also transported as  $\text{TcO}_4^-$  across plasmamembrane into the cytosol /Lembrechts et al, 1985/. Two processes determine the Tc uptake, i.e. the transport of  $\text{TcO}_4^-$  across the cell membrane, probably an active mechanism, and the reduction of  $\text{Tc}^{\text{VII}}$  /Hattink et al, 2000/. Reduction from  $\text{TcO}_4^-$  ( $\text{Tc}^{7+}$ ) to  $\text{Tc}^{5+}$  is probably mediated by ferredoxin within the chloroplast, and up to 10 bioorganic complexes with Tc were found in spinach leaves /Lembrechts et al, 1985/. The reduction of Tc in duckweed was highly correlated with light intensity and temperature /Hattink et al, 2000/. Technetium seems to interact with S at the subcellular level and to be reduced and incorporated into amino nitrogen-containing products instead of S /Cataldo et al, 1989/. In tomato plants, Tc-cystein, Tc-glutathione and Tc-proteins occur /Krijger et al, 1999/. The transfer factor of Tc is higher for leaf vegetables than for edible parts of non-leaf vegetables /Yanagisawa and Muramatsu, 1993/.

### **5.10.6 Iron and platinum metals (Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt)**

***(Iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum)***

These metals have many different oxidation states and form complicated complexes. Some of these elements have important radionuclides, i.e.  $^{55}\text{Fe}$ ,  $^{59}\text{Fe}$ ,  $^{57}\text{Co}$ ,  $^{60}\text{Co}$ ,  $^{103}\text{Ru}$  and  $^{106}\text{Ru}$ .

Low iron availability in soil is the biggest problem in Fe nutrition to plants. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are soluble at low pH level, about 3. To be able to take up Fe at higher pH a chelating agent such as phytosiderophores can be excreted from grass roots /Zhang et al, 1989/ or other chelating agents can be excreted by the plant roots, to be able to release Fe from the colloids /Marschner, 1995/. The Fe uptake is metabolically controlled and is absorbed as  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  or Fe chelates. The ability of roots to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is fundamental in the absorption of this cation by most plants. In xylem exudate, Fe is found in citrate complexes or as  $\text{FeOOH}$ . Iron is also bound to phytoferritin since this element causes oxidative stress in plant cells and thus cannot be in free ionic form. Iron is not readily translocated in plant tissues, and therefore deficiency appears first in young plant parts.

Nickel is the most recently discovered nutrient element /review in Marschner, 1995/. Nickel uptake is positively correlated with Ni concentrations in solutions and the mechanism is multiphasic /Cataldo et al, 1978/. Like other divalent cations,  $\text{Ni}^{2+}$  is known to form organic compounds and complexes. Nickel bound to anionic organic complexes in xylem exudates has been found /Tiffin, 1977/. Although the transport and storage of Ni seems to be metabolically controlled, this metal is mobile in plants and is likely to be accumulated in both leaves and seeds /Halstead et al, 1969; Welch and Cary, 1975; Diez and Rosopulo, 1976/. A lot of nickel accumulators are described and this is the element of which there are most hyperaccumulating species (over 300) all over the world on serpentine soils /Brooks, 1998/. These species are commonly also Co accumulators.



Cobalt is not a plant nutrient but is necessary for nitrogen fixation. Cobalt is taken up by plants and is, like other elements, dependent on the availability in soil. In plants, it is translocated bound to organic substances. The leaf easily takes up cobalt through the cuticle. After foliar deposition  $^{58}\text{Co}$  was shown to be mobile in the plant body /Shinonaga et al, 1999b/.

The platinum group metals are concentrated mainly in ultramafic and mafic rocks and are known to be associated with Ni-Cu ore bodies where Pd and Pt are the most abundant /Kabata-Pendias and Pendias, 1992/. These metals do not readily unite with other elements, however, Ru and Os may form easily volatile oxides ( $\text{RuO}_4$  and  $\text{OsO}_4$ ). Plants apparently readily absorb some of the Pt metals when they occur in easily soluble forms in the substrates /Fuchs and Rose, 1974/. The toxicities of metal species to plants vary and decrease in the following order:  $\text{Pt}^{2+} \approx \text{Pd}^{2+} > \text{Os}^{4+} \approx \text{Ru}^{3+} > \text{Ir}^{3+} \approx \text{Pt}^{4+} > \text{Rh}^{3+}$  /Farago and Parsons, 1985/.

The availability of Ru in soil is reported to be relatively high, and a large proportion of Ru is concentrated in roots /Kirchmann and D'Souza, 1972; Schulz and Babcock, 1974/. The translocation to shoots is thus not very high. However, under specific conditions the concentration in wheat can be fairly high /Grogan et al, 1987/. Concentrations in terrestrial plants have been about 0.4–200 ng gDW<sup>-1</sup> /Duke, 1970/.

Osmium can be released to the environment as a volatile tetroxide ( $\text{OsO}_4$ ) during metal processing, and may possibly be taken up by plant leaves. When  $\text{Os}^{4+}$  occurs in soluble species, it is easily phytoavailable and relatively toxic /Farago and Parsons, 1985/.

Plants take up iridium. Terrestrial plants contain below 20 ng gDW<sup>-1</sup> of Ir and accumulate Ir in the leaf margins, at least in corn plants /Doyle and Fletcher, 1977/. After foliar deposition  $^{192}\text{Ir}$  was shown to be immobile in the plant /Shinonaga et al, 1999b/.

The palladium concentration, which can be about 30–400 ng gDW<sup>-1</sup> of plants, seems to change due to climatic conditions and stage of plant growth /Kothny, 1979/. Palladium seems to be easily taken up by plants and is probably taken up as  $\text{Pd}^{2+}$  and may be able to replace  $\text{Mn}^{2+}$  in metallo-enzymes.

In normal soil a Pt concentration in plants of 12–60 ng gDW<sup>-1</sup> is found, however, up to 6600 ng gDW<sup>-1</sup> was found in plants grown on metamorphic and Pt-bearing ultramafic rocks /Shacklette et al, 1978; Kabata-Pendias and Pendias, 1992/. Platinum is chemically inert, however,  $\text{Pt}^{2+}$  complexes are easily taken up into the plant and are accumulated mainly in roots. Furthermore,  $\text{Pt}^{4+}$  seems to be less toxic to plants than  $\text{Pt}^{2+}$  /Farago and Parsons, 1985/.

### **5.10.7 Coinage metals (Cu, Ag, Au)**

#### ***(Copper, silver, gold)***

All three metals form stable complexes. Silver does not oxidise in water or air and gold is very difficult to oxidise at all. The oxidation state is +I and +II for Cu, +I for Ag and +I and +III for Au.

Copper forms several minerals of which the common primary minerals are simple and complex sulfides, it interacts with mineral and organic components of the soil. Copper is taken up as  $\text{Cu}^{2+}$ , and possibly also as  $\text{Cu}^+$ , by plants and the uptake into cells at low concentrations may include an active component, whereas it is passive at higher concentrations. Copper is a nutrient element in plants and there are also mechanisms for increased Cu uptake in some genotypes coupled to a special chromosome, 5R /Graham et al, 1987/.

Various Cu hyperaccumulators are also found, especially in Asia and Africa /Brooks, 1998/. A copper accumulator is also found in Sweden, "Copper dandelion" *Lychnis vescaria*.

The geochemical characteristics of Ag are similar to those of Cu, but at a 1000 times lower level. Silver is easily released by weathering and then precipitated in alkaline reduction-potential media and in media enriched in S compounds. Cations ( $\text{Ag}^+$ ,  $\text{Ag}^{2+}$ ,  $\text{AgO}^+$ ) and anions ( $\text{AgO}^-$ ,  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ,  $\text{Ag}(\text{SO}_4)_2^{3-}$ ) of Ag are formed. Silver complexes are immobile above pH 4, and  $\text{MnO}_2$  has a significant affinity for Ag. Silver is taken up by plants and the uptake differs between time of the year, apparently being higher in spring than in autumn /Horowitz et al, 1974/. It seems that the concentration in plants follows the concentration in soil /Kabata-Pendias and Pendias, 1992/. Silver ions have great affinity for binding sulphhydryl groups of some organic compounds.

Gold is found in soil in mobile complexes such as  $\text{AuCl}_2^-$ ,  $\text{AuBr}_4^-$ ,  $\text{AuI}_2^-$ ,  $\text{Au}(\text{CN})_2^-$ ,  $\text{Au}(\text{CNS})_4^-$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ . In soils, Au is transported often in organometallic compounds or chelates /Boyle et al, 1975/ and no simple Au cation exists in soil solution /Lakin et al, 1974/. Gold is absorbed by plants and is easily translocated to the top of the plant. In reducing medium, however, Au precipitates on the cell surface and thus inhibits the membrane permeability /Kabata-Pendias and Pendias, 1992/. Root exudate of cyanogenic plants is known to dissolve Au. These plants and deciduous trees are able to accumulate high levels of Au /Shacklette et al, 1970; Lakin et al, 1974/. Horsetail is a good indicator of Au. The herbaceous plant *Phacelia sericea* appeared to be the best Au accumulator /Girling et al, 1979/. It is postulated that a  $1 \mu\text{g gDW}^{-1}$  of Au in plants very well could be called hyperaccumulation since this is about 200 times higher than normal /Brooks, 1998/.

### 5.10.8 Zinc group (Zn, Cd, Hg)

#### (Zinc, cadmium, mercury)

The oxidation state of +II dominates. However, mercury can have +I in a  $\text{Hg}_2^{2+}$  complex.

Zinc is a micronutrient for plants. It is taken up as  $\text{Zn}^{2+}$  and hydrated Zn. It is possible that several other complex ions and Zn-organic chelates may also be absorbed /Tiffin, 1972; Loneragan, 1975/. It is believed that Zn uptake in cells is metabolically controlled but it can also be a non-metabolic process, probably both. Also in the case of Zn, the uptake from soil colloids can be facilitated by root exudates containing phytosiderophores /Zhang et al, 1989/. Several findings support the general statement that Zn generally is bound to soluble low molecular weight proteins, however, the formation of Zn-phytate and other insoluble Zn complexes was also reported /Tinker, 1981/. In the xylem fractions, Zn bound to light organic compounds occurs and the mobility in the plant is among the highest of the heavy metals /Van Goor and Wiersma, 1976; Tiffin, 1977/. The concentration of Zn is almost always higher in roots than in shoots, however, this may depend on the species and genotype /Landberg and Greger, 1996/. The metal is also likely to be accumulated in vacuole fluids and in cell membranes /Tinker, 1981/. There is a specific Zn shuttle that transports Zn from the cytoplasm into the vacuole in complexes with malate and in the vacuole Zn is first released from malate and then bound to oxalate /Mathys, 1977/. After foliar deposition, about 50%  $^{65}\text{Zn}$  is translocated to the rest of the plant body, whereas when added to the stem bark surface less than 1% of the adsorbed  $^{65}\text{Zn}$  was translocated to other plant organs /Lin et al, 1995/. When applied to white spruce needles, however, no translocation of  $^{67}\text{Zn}$  from the application site was found /Watmough et al, 1999/.

Cadmium is a toxic heavy metal and is readily absorbed by plant roots and via the leaf cuticle /Greger, 1999/. The uptake is affected by different soil factors such as pH. It is taken up as Cd<sup>2+</sup>. The origin of Cd seems to be important and /Grupe and Kuntze, 1988/ showed that anthropogenic Cd was taken up to higher extent than Cd of lithogenic origin. Root cells passively absorb Cd, but at low levels also a metabolic component may be involved /Smeyers-Verbeke et al, 1978/. Big differences are found between species and genotypes in accumulating and translocating Cd /Chaney and Hornick, 1977; Greger, 1999/. It is thought that Cd is translocated as Cd<sup>2+</sup> and by water flow and cationic exchange at the xylem vessel walls /Van Gein and Petit, 1979/. The translocation of Cd from leaves via foliar uptake is either very low /Greger et al, 1993/ or is found in the roots /Kitagishi and Yamane, 1981/. Cadmium is also bound to cell walls.

Mercury exists in at least five forms: Hg<sup>2+</sup>, Hg<sup>+</sup>, Hg<sup>0</sup>, HgCH<sub>3</sub><sup>+</sup> and Hg(CH<sub>3</sub>)<sub>2</sub>. Plants take up mercury via roots in both inorganic form and as organic methyl mercury /Kabata-Pendias and Pendias, 1992/. Since Hg is also in a Hg<sub>2(g)</sub> form it can be accumulated via leaves. The translocation both from root to shoot and from shoot to root is poor. There is no known plant hyperaccumulating Hg.

## 5.11 Lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)

*(Lanthanium, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium)*

Lanthanides are also called rare earth elements. The oxidation state of these elements is mostly +III. The most common ones are cerium and neodymium, the other ones are more rare. All isotopes of promethium are non-stable and very small amounts of this element can be found in uranium ores. The most important mineral is monazite CePO<sub>4</sub> where cerium ions can be replaced by other lanthanides or thorium.

**Table 5-2. Concentrations of lanthanides in soils, µg gDW<sup>-1</sup>, and plants, ng gDW<sup>-1</sup>. From /Kabata-Pendias and Pendias, 1992/ and /Bowen, 1979/.**

Element	Soil	Various terrestrial plants
La	26.1	3 – 15 000
Ce	48.7	250 – 16 000
Pr	7.6	60 – 300
Nd	19.5	300
Sm	4.8	100 – 800
Eu	1.2	30 – 130
Gd	6.0	2 – 500
Tb	0.7	1 – 120
Dy	3.6	50 – 600
Ho	1.1	30 – 110
Er	1.6	80 – 380
Tm	0.5	4 – 70
Yb	2.1	20 – 600
Lu	0.3	30

Dealing with terrestrial abundance, the contents of lanthanides decrease with the increase in their atomic weights and, according to Oddon-Harkins rule, the element with the even atomic number is more frequent than the next element with the odd atomic number (Table 5-2).

The geochemical properties of the lanthanides are fairly similar. They show an affinity for oxygen, and are likely to be concentrated in phosphorites and in argillaceous sediments. Two subgroups of lanthanides are distinguished: the first (La to Gd) is composed of more basic and more soluble light metals, and the second (Tb to Lu) is composed of less basic and less soluble metals. During weathering processes, the relative enrichment in the weathered material is relatively high, especially for the light sub-group.

The TFs of lanthanides are very low and lanthanides are strongly excluded by plants /Menzel, 1965/. When adding chelating agents, such as DTPA, the uptake increases drastically /Coughtrey and Thorne, 1983/. Accumulation of La, Ce, Pr and Nd in wheat increases with increasing concentration at low fertilization whereas the accumulation decreases at increased addition at high fertilization /Zhang and Shan, 2001/. The concentrations of these elements in plants follow their occurrence in soil, thus the order of the content of lanthanides in plants decrease with increase in atomic number and also in line with the Oddon-Harkins rule (Table 5-2). It should therefore be possible to calculate the concentration of an unknown lanthanide element once the relationships of elements to each other are known /Markert, 1987/. Woody plants seem to have the highest ability to absorb lanthanides, and hickory trees are most often reported as lanthanide-accumulating plants /e.g. Robinson et al, 1958/. It is not possible to identify any plant group as accumulating or discriminating any of the individual elements. However, it is suggested that concentrations of neodymium in plants are higher than those of the other elements of the lanthanide series (excepting La and Ce), which is also consistent with the relatively greater abundance of this element in soils, also shown in Table 5-2.

This group of elements is known to be toxic in cell metabolism. It is known that  $\text{La}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  inhibit, specifically and competitively, the Ca accumulation by mitochondria of microorganism cells /Weinberg, 1977/ and therefore they are used as inhibitors in laboratory experiments on cellular levels.

The distribution of lanthanides to other plant parts shows a decreasing concentration with distance from the roots if they were supplied with lanthanides. After foliar deposition,  $^{149}\text{Eu}$ ,  $^{146}\text{Gd}$  and  $^{169}\text{Yb}$  was shown to be immobile in the plant body /Shinonaga et al, 1999b/.

Perhaps the most radiologically important nuclide within this group is  $^{144}\text{Ce}$ , a fission product. Apparently,  $\text{Ce}^{4+}$  in oxygenated form is less available to plants than the other lanthanides. Clay and organic matter affect the root uptake of Ce more than soil pH. Cerium is classified as an element strongly excluded by plants /Coughtrey and Thorne, 1983/. It is also concluded that the uptake is not only controlled by soil availability but also by various plant factors. The translocation of Ce is very low in both directions, i.e. after foliar application and after root uptake /Scott-Russell, 1966/. However, one exception is root crops in which there is a much higher concentration in shoots than in roots after root application of  $^{144}\text{Ce}$  /Coughtrey and Thorne, 1983/. Ce applied to foliage is also absorbed to a lesser extent, which is probably the reason for the low translocation.

## 5.12 Actinides (Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, E, Fm, Md, No, Lw)

**(Actinium, thorium, protactinium, uranium, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, lawrencium)**

All of these metals have non-stable isotopes and only thorium ( $^{232}\text{Th}$ ) and uranium ( $^{238}\text{U}$  and  $^{235}\text{U}$ ) are present in nature in any higher degree. This group includes various isotopes of Pu, Am, Cm and Np, of which  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  are longlived, highly radiotoxic and of greatest concern. Plutonium and neptunium have been found in nature in very small amounts. Thorium is found in monazite and uranium in pechblende  $\text{U}_3\text{O}_8$  and uranite  $\text{UO}_2$ . The transuranium elements (actinides except Th, Pa and U) are largely produced by artificial bombardment of uranium and are generally poorly absorbed by organisms /Shaw and Bell, 1994/. Uranium and Th exist in the 4+ and 6+ oxidation states in most geologic environments. During weathering, U forms complexes, mainly organic, easily soluble and mobile. Actinides generally form strong complexes with oxygen ligands /Kabata-Pendias and Pendias, 1992/.

The soluble fraction, and thus available, appears to be largely present as particulates of hydrated oxides and as organometal complexes. It was stated that the root uptake of actinides such as Pu- $\alpha$ ,  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  is negligible and thus the surface contamination on plants is more important, at least in foodchain transfer /IUR, 1990/. However, the soluble fraction of actinides in soils seems to be readily absorbed by plants. In the case of Pu, it is not only accumulated by roots but also translocated to the shoot /Wildung and Garland, 1980/. However, different isotopes of Pu seem to be differently easy to take up /Dienstbach et al, 1983/. Uranium has been found in a protein complex in leaves of *Coprosma australis*, whereas a mineral precipitate, i.e. autunite,  $\text{Ca}(\text{UO}_2\text{PO}_4)_2$ , was found in plant roots /Jones et al, 1990/. No accumulator plant has been found for actinides, but it was shown that microorganisms have a great capability to accumulate U in their tissue, up to 300 times that of the soil /Letunova and Kovalskiy, 1978/. On the other hand, /Dunn, 1986/ reported that twigs of black spruce (*Picea mariana* Mill) contained U concentrations  $> 100 \mu\text{g g}^{-1}$  ash weight. The U concentration of several tree species decreased in the following order: twigs  $>$  leaves  $>$  roots  $>$  trunk /Dunn, 1986/. Uranium is accumulated to higher extent in older leaves than in younger ones /Saric et al, 1995/.

Rain seems to lower the level of Th and U in plants and U is taken up from the water and Th from both water and sediment by *Typha dominguensis* /Jurado Vargas et al, 1997/. Squash did not take up U /Baumgartner et al, 2000/. Uptake of actinides is lowered by fertilizer ( $\text{K}_2\text{SO}_4$ ) treatment /Whicker et al, 1999/. In general, TFs across all tested crops for the actinides were in the order:  $^{244}\text{Cm} > ^{241}\text{Am} > ^{238}\text{U} > ^{232}\text{Th} > ^{239}\text{Pu}$  and  $^{240}\text{Pu}$  /Whicker et al, 1999/. In investigations of spruce tree rings it was found that  $^{234}\text{U}$ ,  $^{238}\text{U}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  were hardly taken up by the roots /Haas and Müller, 1995/.

## 6 Discussion

To be able to understand and calculate plant influences on radionuclide recirculation in the environment the plant uptake of that specific nuclide and the fate of the nuclide in the plant must be understood. Uptake by plants is a complicated story and even though the nuclides to a large extent are taken up into the plant body by a passive process, this process is more than a simple “pump”. Plants themselves determine the uptake, the soil/sediment determines the availability of the nuclides and the nuclides themselves can interact with each other, which also influences the uptake. Consequently, it is not possible to predict the nuclide uptake in plants by analysing the nuclide concentration in the soil/substrate.

Plants take up all kinds of nuclides that are available, which in turn are affected by soil properties such as organic matter content, pH, cation exchange capacity and so on. The plants do not, however, absorb all molecules of a nuclide that are available. The amount absorbed depends on the concentration of available nuclides in the surrounding medium and the lower the external concentration the more is taken up in relation to the external concentration /Greger, 1999/. The uptake can proceed until a depletion concentration has been obtained, the magnitude of which differs depending on nuclide and occasion. Absence of uptake due to the depletion concentration can be counteracted by roots exploring new areas of soil with higher concentrations of the nuclide. In the case of aquatic plants and leaf uptake, the surrounding medium is moving and the external nuclide concentration changes by that physical process; depletion is therefore rarely found in that case.

The plants can also change the availability in soil of nuclides. Substances excreted by the roots can release nuclides from the soil colloids and in some cases bind up the released nuclides, thus making the nuclides more or less available for uptake (Figure 3-2). Furthermore, plant roots are able to change the surrounding pH in the vicinity of the root surface, thus increasing or decreasing the available nuclide concentration and thereby the uptake.

Some nuclides can be taken up to a higher extent by some plants than by others due to the plant having an especially high accumulation of that nuclide, maybe even hyperaccumulating that element. Furthermore, a nuclide of an element can be taken up to higher degree than another nuclide of the same element. The availability of the nuclide can also be higher in a specific soil. It is therefore important to know which plant, which soil and which nuclide are of interest before making any calculations of environmental recirculation of the nuclide in question.

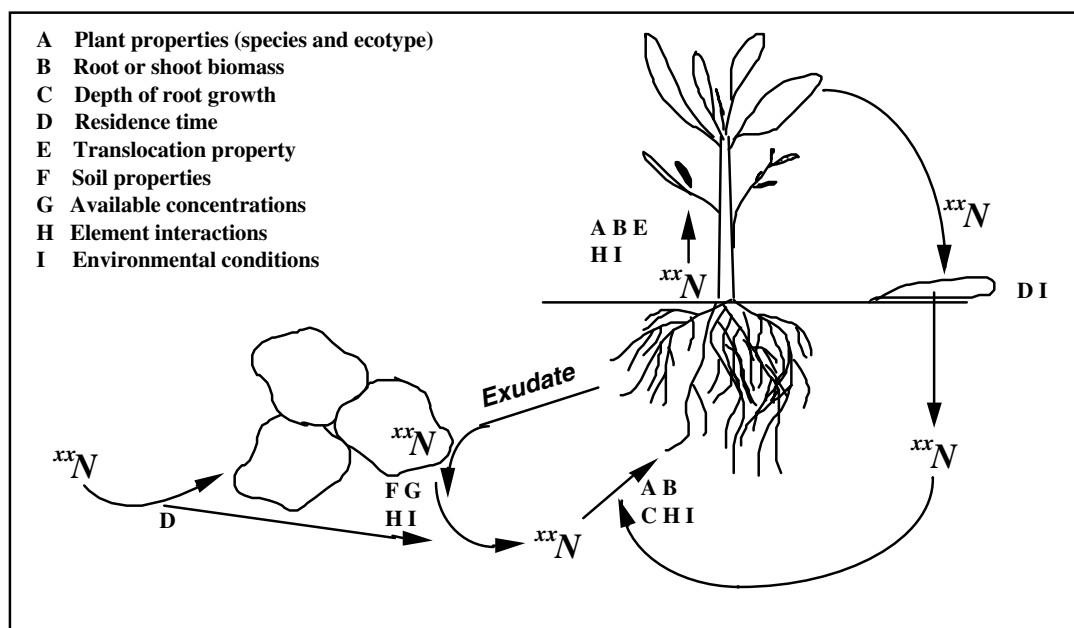
Various nuclides that are supplied in the ground, e.g. via leakage from radioactive waste deposition deep in the bedrock, have different residence times in the water phase before binding up to soil/sediment particles, and the residence time of, e.g.  $^{99}\text{Tc}$ , is very long.  $^{99}\text{Tc}$  is therefore more available to plants than those nuclides with low residence time. This is shown by the very high soil-to-plant transfer factor of that specific element (Table 4-2).

Another important factor is the biomass of the plant. The biomass of roots as well as the amount of root tips, where the most nuclides are taken up, can influence the uptake parameter. The higher the biomass the more is taken up in relation to the external concentration. This is probably due to the density of uptake sites in the apoplast of the root tissue and the availability of the sites. This means that the higher the biomass the more is the internal nuclide concentration diluted ending up in low tissue concentration, even though the total

uptake increases with increasing biomass /Ekvall and Greger, 2003/. A high root biomass often means numerous roots exploring the soil, thus having a higher uptake than plants with small root biomass. The magnitude of shoot biomass also influences the uptake from water in relation to water concentration in aquatic environments in the same way as roots influence the uptake from soil. Furthermore, a high shoot biomass also may enhance the translocation of nuclides from root to shoot. In addition, various plant species translocate different amounts of nuclides to the shoot. The amount translocated is also due to the nuclide in question, and probably also differs between nuclides of the same element. Most elements with high mass have a very restricted translocation to the shoot, often less than 10% of the uptake. In addition to biomass, the translocation of a nuclide to the shoot also depends on various factors such as interactions with other elements in the tissue, transpiration stream, leaf sizes and shape, cuticle permeability and humidity.

Plant roots generally grow in a layer of 30-cm depth, however, in drought conditions roots can grow much deeper. Thus, depending on where in the soil the nuclide is situated it can be absorbed by plant roots. When the plant roots have taken up the nuclide some of it will be accumulated in the leaves. Grazing of leaves and leaf litter decomposition may increase the entrance of the nuclide into the food chain.

To draw correct conclusions of the involvement of plants in recirculation of nuclides in environment, the above-mentioned has to be considered, which is summarised in the figure below.



**Figure 6-1.** Influence of various factors on uptake and fate of nuclides ( $^{xx}\text{N}$ ) in plants.

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