

## Sources of environmental radionuclides and recent results in analyses of bioaccumulation. A review

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**Abstract** In principle, there are two sources of environmental radionuclides, namely natural and man-made. In comparison with other environmental pollutants as, e.g., heavy metals, some scientific and technical disciplines profit by the natural radionuclides, using them for age determination of the samples, e.g., hydrology, geology and archaeology. Nevertheless, the environmental radionuclides represent mostly risk for a human health. Therefore, in this review, their sources are shortly described and original recent analyses of some bioaccumulation methods are presented, using either selected plant species or microorganisms, respectively. The different uptakes in all systems were measured to evaluate the possibility of application of the tested biological materials as markers of environmental contamination. It was also demonstrated that the detection methods developed for analyses of bioaccumulation of environmental radionuclides could be applied in radiotracer methodology for a study of bioaccumulation of heavy metals. While gamma spectrometry for soil samples and liquid scintillation spectrometry for water samples were used, autoradiography was applied to analyze the distribution of radionuclides during and/or after bioaccumulation.

**Key words** environmental radionuclides • sources • bioaccumulation • radioisotopes of heavy metals

### Introduction

Ecological investigations concentrate on the biosphere where all life on earth takes place. The biosphere consists of a part of the atmosphere, of a part of the crust of the earth, of the lithosphere and of nearly the whole hydrosphere. In different ecosystems as, e.g., woodlands, rivers, lakes, deserts, oceans, or the deep sea systems, by exchange processes close correlations exist between the living creatures and their habitat. Radionuclides entering the spheres of existence are involved in this exchange. Those from the habitat can be taken up by the animate one, exchanged within the organisms of an ecosystem or passed through to others. Plants living autotrophically by photosynthesis are at the beginning of the food-chain. In contrast, animals are dependent on heterotrophical organic nourishment. Besides the incorporation of radioactive substances from the inorganic compounds, an exchange or passage, respectively between the organisms has to be taken into account. To finish the circuit, particularly adapted microorganisms exist which are nourished saprophytically by decomposition of organic compounds.

In contrast to most chemical substances for which toxicity is commonly related to specific molecular structures, radiotoxicity of the isotopes depends on the radiological characteristics as well as on the molecular structure of the radioactive substance. An alteration of the chemical structure of the molecule comprising a radionuclide does not remove the radionuclide from the environment but merely changes its kinetic behaviour in the biosphere or can lead

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to augmented deposition in different organs. In this way, bioaccumulation can be influenced considerably.

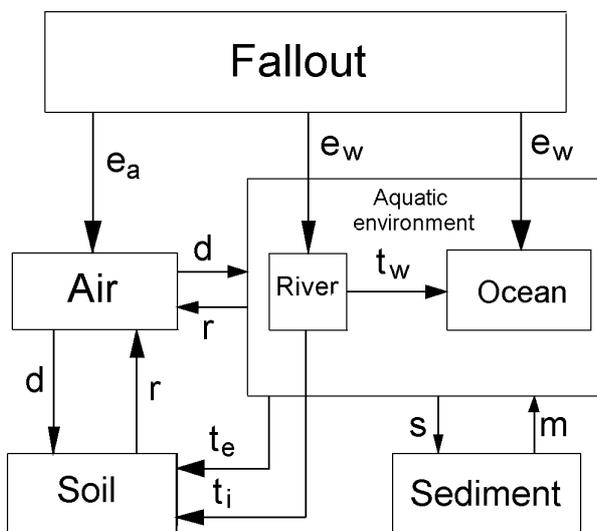
The pathways of radionuclides through the environment are extraordinarily complex. Figure 1 shows clearly that the release of fallout into the air ( $e_a$ ) or into water ( $e_w$ ) starts a complicated migration pattern through the biosphere. Fallout brought to the air is deposited onto the soil, the vegetation and on water surfaces. Transportation by water contaminates rivers, lakes and the sea, many of which are situated far away from the release point. From soil and water, the radionuclides enter the air by resuspension ( $r$ ), e.g., by wind and vaporization. Erosion of the soil transports radioactive substances from the ground to rivers, lakes and the oceans or reversibly by flooding and artificial irrigation again onto the soil or the surface of the vegetation. From the aqueous media the fallout can be deposited as sediment or be remobilized. The uptake of radionuclides in all ecosystems by living organisms called bioaccumulation can be used to decrease the specific activity of soils and waters.

Figure 2 shows a survey on the transfer routes of radionuclides into the food-chain of animals and humans. By migration through the food-chain, radioactive substances may pass from the soil by way of consumable plants into the organism of animals or humans. Whereas pasture cattle may take up radionuclides present in the upper layers of soil and upon the plants, for man this kind of transfer commonly should be excluded because of the cleaning of vegetable food. Transferred to the cattle, radioactive isotopes enter the human body by the intake of milk and meat. Since many animals form the basic nourishment for other animals, radionuclides are secondarily transmitted to these animals.

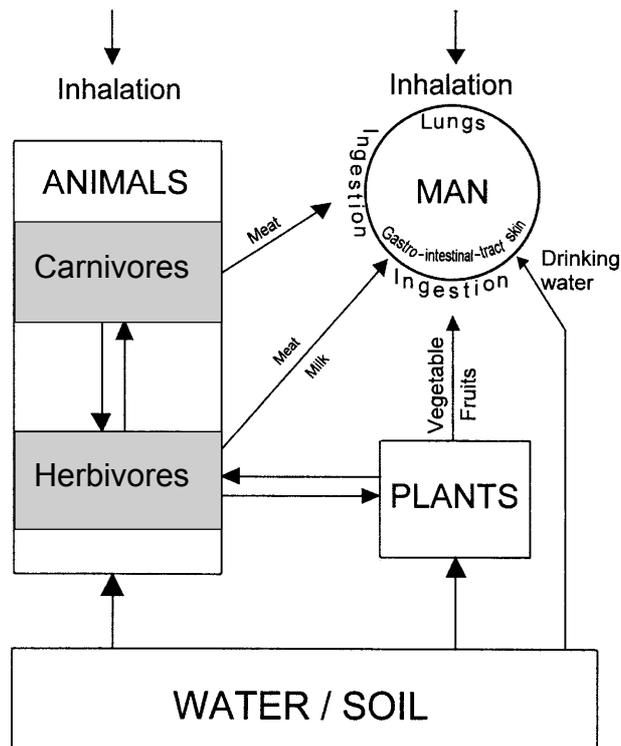
### Sources of radionuclides in the environment

#### Contamination without human influence

A part of naturally occurring radioactive materials existed before the origin of the earth. Others are produced in the atmosphere, the soil, and in the water by influences from



**Fig. 1.** Release of radionuclides in air or in aquatic systems and their main pathways through the different ecological systems.



**Fig. 2.** Migration of radionuclides through the food-chain in the terrestrial and aquatic environment.

the cosmos. From the fission fragments and activation products generated by the spontaneous nuclear reactions of uranium (Oklo phenomenon) it becomes obvious that, in principle, nearly all radionuclides might occur. Short half-lives and low concentrations, however, hinder us in fact from identifying them in the biosphere and application in bioaccumulation.

Carbon, hydrogen, potassium, and also uranium are widely spread in the biosphere. In the Earth's history, geological and meteorological influences have always given rise to changes in the distribution in the biosphere. Also the organisms changed the distribution of natural radioactive substances by their metabolism. Radionuclides were partly concentrated in living matter by selective enrichment, bound and deposited after the death, e.g., in coal (Table 1).

**Table 1.** Concentration of natural radioactivity in coal, fly- and bottom ash from production of electrical power.

	Radioactivity, Bq/kg				
	Coal world wide	Coal from China	Fly ash	Bottom ash	
$^{238}\text{U}$	20	(1–1300)	36	200	48–100
$^{232}\text{Th}$	20	(2–320)	30	70	44–120
$^{226}\text{Ra}$		(7–100)		240	4–250
$^{210}\text{Pb}$		(10–50)		930	30–3900
$^{210}\text{Po}$		(10–41)		1700	7–190
$^{228}\text{Th}$				110	90–560
$^{228}\text{Ra}$		(13–35)		130	20–67
$^{40}\text{K}$	50	(1–800)	104	265	240–1200

**Table 2.** Estimated annual atmospheric release of natural radionuclides from zinc mines.

	Annual atmospheric release, MBq/y							
	<sup>238</sup> U	<sup>234</sup> U	<sup>230</sup> Th	<sup>226</sup> Ra	<sup>222</sup> Rn	<sup>210</sup> Pb	<sup>210</sup> Po	<sup>232</sup> Th
Mining	0.004	0.004	0.004	0.003	8,500,000	0.01	0.006	0.002
Mill	0.06	0.06	0.05	0.03	40,000	0.05	0.07	0.02
Smelter	10	10	5	7	–	20	2	3

**Table 3.** Beginning and latest nuclear test, number of atmospheric (ATM), subterranean shots (SUB), and estimated total yield of atmospheric tests.

Country	Year		Number		Total yield (Mt)
	begin	last	ATM	SUB	
United States	1945	1993	193	<sup>a</sup> 815	138.6
Soviet Union	1949	1990	142	508	357.5
United Kingdom	1952	1991	21	24	16.7
France	1960	1996	45	160	11.9
China	1964	1996	22	20	20.7

<sup>a</sup> Pollution from non-nuclear activities.

During the combustion in power plants at temperatures up to 1700°C, the mineral substance of the coal is transformed to a glassy ash. Incompletely burnt organic matrix and heavier ash accumulates on the ground of the furnace as bottom ash or slag. The lighter components, the fly ash, together with volatile minerals and the flue gases reach the chimney, where they escape more or less into the atmosphere. In the absence of organic matrix in the ash, the concentrations in ash and slag increase by about one order of magnitude, and are, compared with earth's crust, significantly higher (Table 1).

Besides combustion, another important sources of environmental pollution by radionuclides represent phosphate and mining industries. The mining of mineral resources – metals or non-metals – integrates in the subsequent processing natural radioactive substances, because of their ubiquitous presence in the earth's crust. At the exploitation and processing they partly escape in an undesirable way into the biosphere, or are disengaged as waste products (Table 2).

### Pollution from nuclear techniques

Radium, as one of the first radioactive elements, was immediately and widely introduced into medicine and laboratory procedures. Today on luminous dials, instead of <sup>226</sup>Ra, tritium or promethium are used. Thorium has been used as “Welsbach mantle” in gas lamps, producing luminescence. During operation, the secondary products <sup>224</sup>Ra, <sup>212</sup>Bi, and <sup>212</sup>Pb are released. Furthermore, thorium is used as an additive in lamps and in special sorts of glass, in the glaze of pottery, and in welding rods.

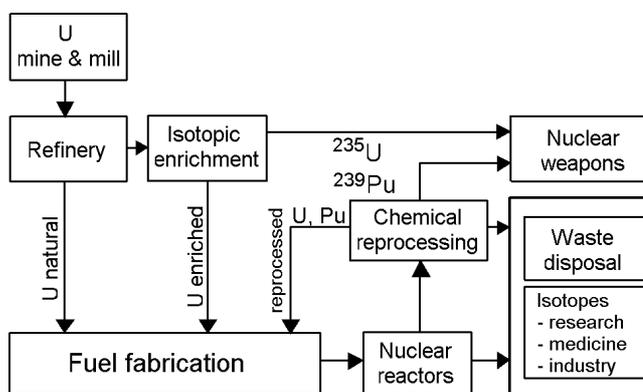
Uranium achieved great importance by the discovery of nuclear fission. For construction of the first atomic bomb, starting in 1942 with the “Manhattan project”, large amounts of uranium were needed. For the production of

electric energy from nuclear processes, the need for uranium as fuel was considerably augmented. Naturally occurring uranium contains 99.8% <sup>238</sup>U, 0.72% <sup>235</sup>U, and 0.0058% <sup>234</sup>U, all being radioactive nuclides. Therefore, mining and processing of uranium, cause these radionuclides together with their progenies to be released into the environment. In Fig. 3 the fundamental steps of the nuclear fuel circuit are outlined.

### Production and tests of nuclear weapons

By producing and testing of nuclear weapons (Table 3), a considerable amount of radioactive material was released. For a long time, consideration was seldom given to the environment. The atmospheric bomb tests having polluted the whole earth by their fallout.

For manufacture of nuclear weapons the fissile isotopes <sup>235</sup>U, <sup>239</sup>Pu, <sup>238</sup>U are used together with the radionuclide <sup>3</sup>H as “intensifier”, which is needed for the amplification of the neutron flux by means of the thermonuclear reactions

**Fig. 3.** The principal steps in the nuclear industries.

$^3\text{H} + ^2\text{H} \rightarrow ^4\text{He} + n + 17.6 \text{ MeV}$  or  $^3\text{H} + ^3\text{H} \rightarrow ^4\text{He} + 2n + 11.3 \text{ MeV}$ . These reactions are the main component of thermonuclear devices as well.

### Emissions by nuclear installations

The hazard to the environment from emissions of nuclear plants or research reactors during normal operation usually at most affects the population living directly in the neighbourhood. When problems arise, however, further sections of the population may be affected by emitted radionuclides, which, due to their half-life and mobility in the environment, may spread widely and get into the food-chain. Reprocessing facilities of burnt up reactor fuel elements take also part in the environmental pollution by radionuclides.

The last but not least source of radioactive pollution is represented by accidents in nuclear facilities. There were many different accidents, the mostly known of which was 1987 in Chernobyl.

More details about sources of radionuclides can be found in our book published recently [4].

### Recent analyses of bioaccumulation using plant species or microorganisms

In this part, our recent analyses of bioaccumulation of  $^{137}\text{Cs}$ ,  $^{226}\text{Ra}$  and uranium are described using in indoor or outdoor experiments either different plant species or selected microbial strains. Different measured uptakes are evaluated in relation to possible markers of environmental contamination.

### Laboratory analyses of $^{137}\text{Cs}$ uptake by sunflower, reed and poplar [3]

The  $^{137}\text{Cs}$  uptake by three plant species (*Phragmites australis* L., *Helianthus annuus* L., *Populus simonii* L.) was analyzed in



Fig. 4. Distribution of  $^{137}\text{Cs}$  in poplar after 16 days of cultivation.

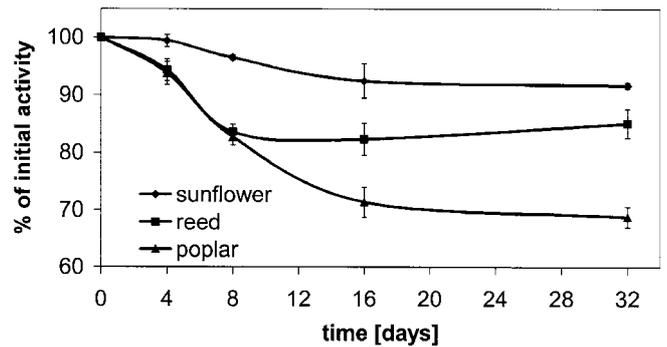


Fig. 5. Disappearance of  $^{137}\text{Cs}$  activity from cultivation medium by different plant species.

Table 4.  $^{226}\text{Ra}$  accumulation in different plant species<sup>a</sup>.

Plant tested	Relative $^{226}\text{Ra}$ activity
Vetch ( <i>Vicia tenuifolia</i> )	4.15
reed ( <i>Phragmites australis</i> )	4.21
Poplar ( <i>Populus tremula</i> )	4.34
white Sweet-Clover ( <i>Melilotus albus</i> )	6.29
silver Birch ( <i>Betula pendula</i> )	8.55
Evening-Primrose ( <i>Oenothera biennis</i> )	9.12
Spurge ( <i>Euphorbia esula</i> )	9.31
Strawberry ( <i>Fragaria vesca</i> )	10.57
perforate St Johnswort ( <i>Hypericum perforatum</i> )	11.07
Blueweed ( <i>Echium vulgare</i> )	11.26
Centauray ( <i>Centaureum erythraea</i> )	11.95
Sunflower ( <i>Helianthus annuus</i> )	12.14
creeping Thistle ( <i>Cirsium arvense</i> )	12.58
bladder Campion ( <i>Silene vulgaris</i> )	13.33
Dewberry ( <i>Rubus caesius</i> )	13.46
corn ( <i>Zea mays</i> )	13.84
Chee Reedgrass ( <i>Calamagrostis epigeios</i> )	17.36
black Medick ( <i>Medicago lupulina</i> )	17.74
Lupin ( <i>Lupinus polyphyllus</i> )	20.25
white Mustard ( <i>Sinapis alba</i> )	22.52
Wild carrot ( <i>Daucus carota</i> )	23.27
Pea ( <i>Pisum sativum</i> )	23.40
corn Mint ( <i>Mentha arvensis</i> )	25.16
silverweed ( <i>Potentilla reptans</i> )	25.72
Hemp ( <i>Cannabis sativa</i> cv. Beniko)	27.04
Sudan grass ( <i>Sorghum bicolor</i> )	27.30
Amaranth ( <i>Amaranthus caudatus</i> )	29.56
Mercury weed ( <i>Mercurialis annua</i> )	35.85

<sup>a</sup> The relative  $^{226}\text{Ra}$  activity in % expressed as 100x ratio of specific  $^{226}\text{Ra}$  activity of the plant species (S.D. <  $\pm 10\%$ ) to the mean value of specific  $^{226}\text{Ra}$  activity in the soil surrounding the roots (S.D. <  $\pm 10\%$ ).

a hydroponic medium ( $14 \text{ MBq L}^{-1}$ ;  $0.5 \text{ mM CsCl}$ ) during cultivation. The radioactivity disappearance from the medium was measured after 2, 4, 8, 16 and 32 days of cultivation. Radioactivity distribution within the plant was determined by autoradiography (Fig. 4). We did not find differences between uptake of radioactive and stable caesium isotopes. Relations between the uptake of  $^{137}\text{Cs}$  and concentration of potassium and ammonium ions in medium were also tested. The highest uptake of radiocaesium by sunflower was obtained for medium with  $1 \text{ mM K}_2\text{SO}_4$ . Disappearance of the initial activity was evaluated to compare the capability and rate of  $^{137}\text{Cs}$  phytoremediation of different plant species (Fig. 5).

Field analyses of  $^{226}\text{Ra}$  uptake from soils into different plant species [2]

Accumulation of  $^{226}\text{Ra}$  into different plant species from contaminated soils was measured *on site* within an area of an uranium mill. Marinelli beakers and NaI(Tl) spectrometer were used for measurement of dried and weighted samples. While the specific  $^{226}\text{Ra}$  activity in soil *on site* ranged from  $7.12$  to  $25.60 \text{ Bq/g}$  (S.D.  $< \pm 10\%$ ) in the tested plant species it ranged from  $0.66$  to  $5.70 \text{ Bq/g}$  (S.D.  $< \pm 10\%$ ). The comparison for more than twenty different plant species is given in Table 4. No significant differences in  $^{226}\text{Ra}$  accumulation were found after cultivation of selected plant species in a glasshouse in relation to the outdoor experiments.

Bioaccumulation of uranium from waste water using different strains of *Saccharomyces cerevisiae* [1]

Five different strains *Saccharomyces cerevisiae* were tested to analyze the bioaccumulation of uranium from waste water containing competitive ions. Samples of water passing out from a previous uranium mill were used. The accumulation capacities of the tested strains were different (Fig. 6). The kinetics of bioaccumulation, the leaching degree, the influence of cell density and their origin were analyzed. Under the applied working conditions, more than a half of the total activity could be accumulated after 60 min contact time of  $1 \text{ mL S. cerevisiae}$  suspension and  $5 \text{ mL}$  of water.

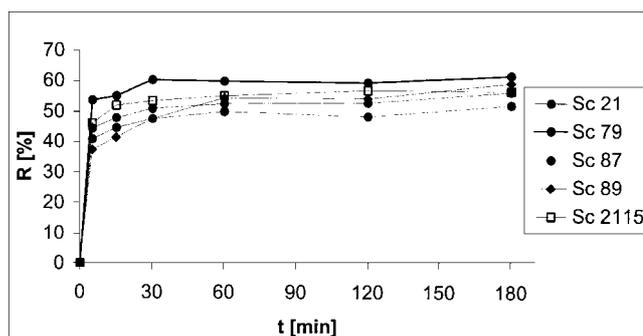


Fig. 6. Uranium bioaccumulation in five strains of *Saccharomyces cerevisiae*.

The heavy metals effectively competed the uranium accumulation.

### Application of radiotracer methodology for heavy metals

All bioaccumulation analyses described above can be applied for heavy metals using their radioisotopes. So, e.g., we used  $^{210}\text{Pb}$  lead nitrate (Amersham, code number RBS 2A) to study lead accumulation which was found (P. Soudek – private communication) almost exclusively in root systems in all plant species tested.

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