
# PHYTOEXTRACTION OF GERMANIUM IN SOIL

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**Abstract**
Germanium (Ge) has proved important characteristics in human health what makes studies about this element that could be found in soils and is absorbed by plants increase. A way to extract Ge in soil it is through the phytoextraction technique that is already used for other elements. Ge is a cognate element of Silicon (Si), whose study is already more advanced, what makes easier to have some information about how Ge works in the plant-soil system. On the other hand, there is a need to identify the species with the greatest potential for germanium accumulation, for our tropical conditions. In this sense, grasses have this characteristic, added to the high capacity to absorb metals compared to other species so, one can think about using edible plants to enrich them with germanium given its beneficial effects on human health. Given the above, this review deals with the importance of Ge for human health, its occurrence in the soil and the factors that influence the phytoextraction of this element.

**Keywords:** Germanium; phytoextraction; soil; plants;

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## INTRODUCTION

Germanium (Ge) is a metalloid (SKOOG, 2013) with a great application in electronic industry (HÖLL et al., 2007; ZOU et al, 2005), his demand increased considerably and a probable cause is the progress of researches about the use of Ge in human health (JIANBO et al, 2002), that has shown anticancer actions, ageing retard, efficiency in rheumatoid arthritis, hypertension, diabetes and asthma treatment (GOA & LIU, 2000; MOURA, 2009)

High concentrations of Ge were found in medicinal plants for a Japanese researcher (ASAI, 1980) what made him deepen studies about the use of Ge in human health and about the relation between plants and Ge. Studies have pointed Ge availability in Brazilian soils in a significant amount (SILVA et al., 2017) that could be measured in terms of accumulation in plants. By the way, phytoextraction it is one of the cheapest ways of studding Ge. This technique consists in use plants to extract a metal from soil or water considering the interaction between plant and metal (EPA, 2000). Different plants species could be used in soil Ge extraction, edible and non-edible plants.

As a cognate element of Silicon (Si), Ge has a similar behavior in the plant-soil system, but it has also differences between them, what make necessary to have increase studies on this element. Thus, the objective of this work is to review what it is already known about the phytoextraction of germanium in soil.

## MATERIALS AND METHODS

This literature review was developed based on books, articles and abstract about phytoextraction of Germanium in soil.

## RESULTS AND DISCUSSION

Ge is widespread in the Earth's crust (WICHE et al., 2017), and is considering the 54th most abundant element (REIMANN et al., 2014) with an average concentration estimated at 1.6 $\mu g.g^{-1}$ (ROSENBERG, 2007). Ge is usually present in basic rocks, such as basalt and amphibolites (SILVA et al., 2017). Then, in the process of soil formation, these rocks are weathered, and the germanium present in the rock passes to the soil (ROSENBERG, 2007). Germanium is widely used in the electronics industry as a semiconductor. Ge began to gain ground in industries in 1960 (CALDER, 1958), with the invention of germanium transistors and semiconductors used as material for radar units. Germanium is often used in the industrial field, mainly in electronics and optics, and also for military applications (RENTSCH et al., 2016). In the field of micro and nanoelectronics, fiber optics, polymerization catalysts and infrared detectors, Ge is frequently applying like a semiconductor (PILLARISETTY, 2011).

In addition to Ge importance in the field of military industries and applications, it has been highlighted as an important element with beneficial effects on human health, this was disclosed by the bodies related to public health (JIANBO et al, 2002). Orthomolecular medicine has been using Ge and obtaining positive results (CURTO, 2015). The compounds containing Ge have anticancer actions, being used in medicines and in human nutrition (GOA & LIU, 2000). It is also efficient in decelerating aging, decontamination by heavy metals, asthma, rheumatoid arthritis, diabetes and hypertension (MOURA, 2009). Another characteristic of this element is its performance as an antioxidant, which makes it a powerful agent in arteriosclerotic and vasculopathic diseases. In addition, it has also been efficient in the treatment of mental pathologies (SILVA et al., 2017). Ge acts on the immune system, it assists in normalizing the function of T cells (stem) and B lymphocytes. It is adsorbed and transported quickly through membranes due to the size of the germanium sesquioxide, thus, the diffusion of oxygen through the cells and tissues is catalyzed and optimized (MOURA, 2009).

High concentrations of Ge were observed in medicinal plants by a Japanese researcher (ASAI, 1980) and this, coupled with reports from Russia on the role of rejuvenation and action against cancer, led him to study whether Ge alone would be useful for health. One of the notes of the Japanese researcher's study was that the quality of the soil in which the plant grows is linked to the variation in the amount of germanium present in the plant, and also that the addition of Ge in the soil causes the plants to grow in a significant (ASAI, 1980). Foods of plant and animal origin have low concentrations of Ge, according to Moura, 2009. The organic chemical form with therapeutic properties is known as germanium L32, sesquioxide of 2 carboxyethyl germanium ($Ge - CH_2 - CH_2 - COOH$) 2O3, it is not toxic, nor accumulates in the body. It is the most expensive form of Ge, as it is found in minimal amounts in vegetables (SILVA et al, 2017). Studies have already indicated the availability of Ge in some Brazilian soils in significant quantities (SILVA et al., 2017) and this must be evaluated regarding its accumulation in plants.

Germany Analysis Methods

The determination of Ge in solid environmental samples is challenging because the analytical concentrations are in general low, in addition, there is the occurrence of interferences of the sample matrix during the measurement. Yet, another problem of Ge analysis is due to the lack of certified reference materials for instrument calibration, accuracy checks and Ge recovery during the development of the method and quality control, because of that, data from older studies must be treated with care. Even today, these materials are scarce, and when not costly (WICHE, 2018). The most appropriate analytical methods are those with high sensitivity for determining Ge at trace levels are atomic spectrometric methods (mainly atomic absorption in graphite furnace (GF-AAS)), optical emission spectrometry with inductively coupled plasma (ICP- OES) and mass spectrometry (ICP-MS), these last two however, due to the treatment and determinations in the liquid phase, they still have difficulties regarding the openness of the samples for detection of germanium, requiring further studies (ROSENBERG, 2007). Due to the low levels of germanium in the samples, in general, mainly for the determination of Ge in environmental samples requires pre-concentration and extraction of the matrix, which are obtained via pre-treatment techniques, such as, for example, sorption, liquid-liquid extraction, coprecipitation and membrane filtration (SOYLAK & YIGIT, 2015), or even instrumentally using the cloud point method (BOYUKBAYRAM & VOLKAN, 2000), or hydride generation (HG ) and cryo-trapping. Currently, dilution of HG-ICP-MS isotopes with cryotrapping may be one of the most sensitive and accurate methods for determining Ge in environmental samples (MORTLOCK & FROELICH, 1996).

Phytroextraction

One of the ways to study Ge that is gaining relevance is phytoextraction, which is one of the phytoremediation techniques. Phytoextraction is a technique where plants are used to extract this metal from the soil and water, with the interaction of the metal with the plant being observed (EPA, 2000). However, the efficiency of phytoextraction depends on the species of the plant and the type of metal present in the soil (ALI et al, 2013b).

The availability of Ge for plants is the result of different interactions of factors associated with plants, such as the presence of sets of labile and potentially available elements for plants in the soil and the ability of plants to obtain a certain set of elements. Studies have shown that the presence of Ge in the soil derives from the interactions between primary, secondary and biogenic sources of Ge, mineral dissolution, mineral transformation, absorption by plants, adsorption in the secondary phases and export in the soil profile. The way in which each process affects the chemical composition and processes in the soil solution depends on factors such as climate, soil type, anthropogenic use of the land and the species that form the vegetation (WICHE, 2018).

Ge mobility in soils is generally low and largely depends on actors like the mineral composition of the bedrock, the intensity of the climate to the mineralogy formation of the soil, the biological activities and his functional properties. Under most climatic conditions, soil formation appears to connect Ge in newly formed phases, limiting his mobility and consequently enriching the topsoil (WICHE, 2018). The action of the chemical weathering on rocks tends to release Ge, together with Si, from primary minerals, and it can be strongly fixed in aluminosilicates (LUGOLOBI et al., 2010) and Fe(III)-oxyhydroxides (POKROVSKY et al., 2006), as well as in soil organic matter (VIERS et al., 1997). How much of Ge is accumulated in relation to Si will depend on the climatic conditions that control the formation of the type of clay mineral (CORNELIS et al., 2010). Although Ge and Si have similar chemical properties, Ge is more reactive than Si (DELVIGNE et al., 2009) and unlike Si, it is toxic to plants with moderate to high supply (HALPERIN et al., 1995). Other observation about the relation between Ge and Si is plant species, it was observed that plant species with high concentrations of Si also had high concentrations of Ge, and also it has been noted that the concentrations of Ge and Si were 10 times higher

Studies indicate that the concentration, mobility and binding strength of Ge in soils are derived from factors such as: the degree of weathering of the soil, the presence of different minerals, pH, Eh, the presence of organic binders, water flows and nature and stability of soil phases under different climatic conditions (WICHE, 2018). Wiche and Heilmeier (2016) made an experiment using five different species belonging to the functional group of grasses (*H. vulgare, Z. mays, A. sativa, P. miliaceum and P. arundinacea*) and four species from the group of herbs (*L. albus, L. angustifolius, F. esculentum and B. napus*), and they noted that Ge concentrations in grasses were significantly higher compared to the herbs, and they observed too that bioavailability of Ge in soil for the plants depends on the characteristics of the soil like pH and organic matter (Table 1). Rentsch et al. (2016) also considers grasses good species to be used in Ge phytoextraction, like ribbon grass (lat. Phalaris arundinacea L.), because this plant species, called accumulator plant, can concentrates high level of germanium in aerial plant biomass. Wiche et al. (2017) also gets the same conclusions and beyond this, they noted that if you made processes in the rhizosphere of soil-grown plants it might contribute to have good results in Ge phytoextraction from soil (Table 1).

Table 1. Examples of Ge concentrations in different plant species.

| Plant species | Functional group | Plant part | Ge in plant (µg g- 1) | Ge in soil (total) (µg g- 1) | Reference |
|---|---|---|---|---|---|
| Hordeum vulgare | Grass | Shoot | 0.22 | 1.6 | Wiche and Heilmeier (2016) |
| Avena sativa | Grass | Shoot | 0.28 | 1.6 | Wiche and Heilmeier (2016) |
| Phalaris arundinacea | Grass | Shoot | 0.34 | 1.6 | Wiche and Heilmeier (2016) |
| Panicum miliaceum | Grass | Shoot | 0.33 | 1.6 | Wiche and Heilmeier (2016) |
| Zea mays | Grass | Shoot | 0.36 | 1.6 | Wiche and Heilmeier (2016) |
| Lupinus albus | Forb | Shoot | 0.008 | 1.6 | Wiche and Heilmeier (2016) |
| Lupinus angustifolius | Forb | Shoot | 0.031 | 1.6 | Wiche and Heilmeier (2016) |
| Fagopyrum esculentum | Forb | Shoot | 0.011 | 1.6 | Wiche and Heilmeier (2016) |
| Brassica napu | Forb | Shoot | 0.05 | 1.6 | Wiche and Heilmeier (2016) |
| Brassica napu | Forb | Shoot | 0.004 | - | Wiche et al. (2017) |
| Zea mays | Grass | Shoot | 0.071 | - | Wiche et al. (2017) |
| Hordeum vulgare | Grass | Shoot | 0.177 | - | Wiche et al. (2017) |
| A. pratensis | Grass | Shoot | 0.072 | - | Wiche et al. (2017) |
| A. elatius | Grass | Shoot | 0.114 | - | Wiche et al. (2017) |
| L. vulgaris | Forb | Shoot | 0.025 | - | Wiche et al. (2017) |
| P. arundinacea | Grass | Shoot | 0.449 | - | Wiche et al. (2017) |

## CONSIDERATIONS

Germanium's promising path not only on an industrial scale but also in terms of its applications in human health are incentives for further research with this element. Thinking about these researches using phytoextraction, a clean and cheap method, considered a green method, makes it even more conducive to deepen the studies with Ge.

Another research possibility is the development of analytical methods that can provide, in addition to high sensitivity, a high selectivity for the determination of Ge.

All the authors mentioned concluded that germanium is promising, however it needs more studies to understand its cycle in the soil, as well as its behavior and application in human health. In addition, there is a need for studies on tropical soils.

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