Archives of Environmental Protection
Vol. 48 no. 2 pp. 24–33

PL ISSN 2083-4772
DOI 10.24425/aep.2022.140763

Urban mining: Phytoextraction of noble and rare earth elements from urban soils

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Keywords: platinum group elements, soil, environmental pollution, phytomining, phytoremediation, roads

Abstract: The increasing demand for noble metals boosts their price. In order to meet the increasing demand for elements, a number of technologies are being developed to recover elements already present in the environment. Traffic-related metal pollution is a serious worldwide concern. Roadside soils are constantly subjected to the deposition of metals released by tailpipe gases, vehicle parts, and road infrastructure components. These metals, especially platinum group elements from catalytic converters, accumulating in the soil pose a risk both for agricultural and residential areas. Phytomining is suggested as a novel technology to obtain platinum group metals from plants grown on the contaminated soil, rock, or on mine wastes. Interest in this method is growing as interest in the recovery of rare metals is also increasing. Based on the research of many authors, the sources and amounts of noble metals that accumulate in soil along communication routes have been presented. The paper presents also plants that can be used for phytomining.

Introduction

Environmental pollution is currently a global issue, and constitutes a serious threat to the entire ecosystem we live in. The threat is recognized both by means of satellites and analytical methods. Natural sources of pollution that occur in nature are fires, salt particles brought to the continent by wind, or sand from desert areas and volcano eruptions. High level of these pollutants recorded in urbanized areas evidence their anthropogenic origin. In many cases, the source of emission of such pollutants and their harmful effect on living organisms is identified. Heavy metals (HM) are relatively thoroughly investigated group of pollutants. The group of elements with this arbitrary name includes approximately 40 metals and metalloids. The predominant ones are lead (Pb), zinc (Zn), cadmium (Cd), arsenic (As), mercury (Hg), chromium (Cr) VI, and copper (Cu), and they are usually dominated by one of them. All of them except for mercury occur in the solid phase, but due to high temperatures during the incineration process, they are emitted to the atmosphere in the form of gas. Only after cooling down, they fall down in the solid form at various distances from the emission source. It has been confirmed by research of the team of (Mikołajczak et al. 2017, Çolak et al. 2016, Liang et al. 2019, Liu et al. 2019). According to the authors, *Achillea millefolium* L., *Artemisia vulgaris* L., *Papaver rhoeas* L., *Taraxacum officinale*, and *Tripleurospermum inodorum* absorb rare metals near roads, and accumulate them in their organisms. The highest efficiency was observed for *T. officinale*.

Rare earth elements (REE) are another group of pollutants. They are identified as a group of 17 elements with similar physicochemical characteristics. Of these elements, 15 belong to the group of lanthanides: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutecium (Lu). Two more elements join the REE group, i.e., scandium (Sc) and yttrium (Y) (Ramos et al. 2016).

Platinum group elements, also described as noble metals, occur in nature in very small amounts, and sometimes accompany other elements. The natural presence of these elements in the soil is estimated at a level from 0.5 to 4 $\mu g \cdot kg^{-1}$ (Schafer and Puchlet 1998, Matodzi et al. 2020). At the global scale, the number of places of their abundant occurrence is limited. They are valuable elements. When the environmental conditions and extraction costs allow profit, mines of these elements often appear in such places at present. Owing to the progress in the extraction technology, sites exploited in the past are currently revisited. Unfortunately, the extraction industry is one of the branches causing the greatest environmental damage. A high price of the elements encourages their extraction even at their lower levels. Phytoremediation is applied for their extraction from the surface soil layer. It is worth emphasizing the environmentally friendly character of the technology, because after metal extraction, the area is left with soil in its full condition for the presence of plants and other living organisms. The key factor in the implementation of phytoremediation is the fact that noble metals are easily absorbed by plants (Kowalska et al. 2004, Gawrońska et al. 2018). At the end of the 20th century, when phytoremediation began to be applied in practice, one of the first experiments with gold extraction by means of plants was conducted. In one of the Australian gold mines, in the surface soil layer, the content of gold was so low that it was not cost-effective to extract it by means of industrial methods, but it was refused to be abandoned. The phytoremediation technology based on plants was therefore used. In the experiment, Indian mustard *Brasicca juncea* proved to be the species most efficient in gold recovery. For intensification of gold uptake, several days before harvest, ammonium thiocynate was introduced into the soil as a substrate amendment, because it is commonly used for making gold soluble in mining operation. The compound is toxic for humans, as well as plants which died after such treatment of the soil. The obtained plant material, however, contained considerably greater amounts of gold (Anderson et al. 1998). Recovery of elements by means of this form of phytoremediation is called phytomining. Crop cultivation for extraction of metals the resources of which are limited and demand for which is growing allows for the expansion of places for their recovery. Crop cultivation over large areas for obtaining metals is still being improved and has already been subject to the first book publications. This cultivation system is called agromining (Nkrumah et al. 2018, Van der Ent 2018).

In the manufacture of batteries, four chemical elements are particularly important, i.e. La + Ce + Pr + Nd. Lanthanum is typically applied in batteries for hybrid cars, whereas neodymium and dysprosium – for hybrid and electric car motors. Other elements, such as thulium, are used in X-ray equipment, yttrium – in spark plugs and various sensors, holmium – in lasers, samarium, gadolinium, erbium and holmium – in nuclear reactor components including control rods. Neodymium, due to its magnetic properties, has found application in electric generators in wind power stations. The chemical elements referred to above are also used to prevent banknotes against counterfeiting (Jowitt et al. 2018).

In Europe, Poland is a leader in the production of lithium-ion cells used in electric vehicles (Mathieu 2021). Despite Poland, the group of the largest producers of lithium-ion cells includes Germany, Hungary, Norway, Sweden and France. The recovery of rare earth elements as well as lanthanides will become increasingly important (Kim et al. 2021, Moreira et al. 2021). This is confirmed by Pagliaro and Meneguzzo (2019), who note that in the EU, the average recovery of used batteries is 58%, and it is steadily increasing. Dang and Li (2021) point out that for soils contaminated with rare earth metals, where conventional mining techniques for extracting poor ore or for treating metal rich soils are uneconomical, a very good recovery of rare earth metals can be achieved through the use of vegetation. Okoroafor and Wiche (2020) point out that both grasses and herbs are suitable in phytomining and take up 57.32 µg gold per g of dry weight. Also, Moreira et al. (2021) confirm that a range of plants characterized by selective uptake of certain metals and with high biomass can be used for phytomining.

This results in social protests as well as binding legal acts stipulating cleaning of the environment, repair of the damage, and the introduction of clean technologies, or technologies harmful to the environment to a minimum degree. The processes of cleaning the environment revealed the possibility of recovery of many such elements. This particularly concerns metals, especially noble metals and rare earth elements. Their considerable amounts are generated in the course of utilization of devices. Recovery of these elements from the soil, water, and air is a more difficult task. It is required by the economy, and sometimes the implemented circular economy policy. It is worth emphasizing that due to the necessity of environmental protection and limited amount of noble metals and rare earth elements, their recovery is becoming extremely important. Many of these elements are vital for currently developed technologies such as electronics, electric transport, or photovoltaics (Yu et al. 2022). In order to meet the increasing demand for elements, a number of technologies are being developed for recovering elements already present in the environment. The currently developed dedicated technologies based on natural processes occurring in the environment are attractive for this purpose. The metal cycle in the surface soil layer is known to be strongly dependent on biological processes (Reith et al. 2014). In the case of metals and rare earth elements, plants are useful.

These elements occur in the soil in very small amounts, but once absorbed by the plant, they reach higher concentrations in its tissues.Due to their demand, recovery of such elements as nickel (Ni), vanadium (V), thallium (Tl), and copper (Cu) is also attempted.

Plants play an important role in our life. They feed us, provide energy and medicine, and offer wellbeing. Unfortunately, neglectful and exploiting treatment of nature by man has led to changes threatening the very human existence. As a result, to repair the inflicted damage, man turns to plants for help. In this case, we involve them in dirty work, namely extraction of very toxic elements and substances introduced to the environment by man. Progress in knowledge regarding plants in such disciplines as plant physiology, molecular biology, toxicology, microbiology, and soil sciences, has led to formation and development of a new discipline of environmental biotechnology called phytoremediation (Yan et al. 2020). As organisms leading a sedentary lifestyle, sometimes in extreme conditions, plants, in the course of their evolution, developed efficient, and sometimes additional defence mechanisms allowing them to survive in the environment. Another factor making them an attractive partner is the vast total surface of leaves and needles, particularly valuable in phytoremediation of the air. Plants applied in this technology are used for the removal or reduction of the level of pollutants in the soil, water, and air. The diversity of the world of plants is awe-inspiring. Similar differences are observed in their strategies of avoiding and tolerance of absorbed pollutants.

Plant use for phytoremediation

All plants conduct phytoremediation by absorbing metals dissolved in soil water. During water transport to the overground organs, they retain part of them in the roots, and transport the remaining part to the stems and leaves. In the case of high content of metal creating very toxic conditions, only a small number of species are able to survive. They are called hyperaccumulators (Brooks 1998, Dinh et al. 2022). The trace element hyperaccumulators – plants which contain in their dry weight foliar tissue (μg·g^{-1}) > 100 cadmium, thallium or selenium, > 300 of cobalt, copper or chromium,> 1000 of nickel, arsenic, lead or rare earth elements (REEs), > 3000 of zinc, or > 10 000 of manganese, when growing in their natural habitat (Van der Ent et al. 2018) Global Hyperaccumulator Data Base contains 721 hyperaccumulator species (523 nickel, 53 copper, 42 cobalt, 1 chromium, 42 manganese, 20 zinc, 2 rare earth elements, 41 selenium, 2 thallium, 7 cadmium, 5 arsenic, and 8 lead) with some species showing hyperaccumulation of more than one element (Reeves et al. 2017) (Table 1).

The toxic impact of heavy metals on plants and their response has already been recognised by Carl Linnaeus, the "father" of taxonomy, who distinguished the leadwort plant family (Plumbaginaceae) represented by species very tolerant to lead. Sea Thrift (*Armmeria maritima*), Cape Leadwort (*Plumbago auriculata*), and some species from genus Limonium producing more biomass are the most common for cultivation at lead polluted sites (Gawroński et al. 2011, Javed et al. 2019, Khalid et al. 2018).

The list of hyperaccumulators throughout the plant kingdom includes slightly more than 400 species, and new species are still very sporadically found. Hyperaccumulators are a very interesting group of plants accumulating high concentrations of metals in tissues (Liu et al. 2020). Unfortunately, they develop small biomass, because the majority of the obtained energy is used for defense against toxic elements. Only several of species develop greater biomass. They are attempted to be used for phytoremediation. This variant of the phytoremediation technology extracting metals from the soil is usually described as phytoextraction. In practice, phytoextraction is conducted with the application of species that absorb less metal from the soil, but develop substantially greater biomass, consequently allowing for obtaining a greater yield of the metal e.g. *Miscanthus gigantheus*.

This purpose usually involves the use of crop species more tolerant to heavy metals, because we can cultivate them. We know their environmental requirements and methods of harvesting of the whole overground biomass without leaving remains saturated with toxic metal. Most annual and perennial plants contain up to 80% water in their overground parts. Therefore, the harvested plant material is left to dry on site to avoid its transportation. Unfortunately, a high number of species crumble after drying, and part of the harvest is lost. Grasses retaining entire dry leaves for a long time after harvesting or completion of vegetation deserve attention. The intensity of absorbing metals from the soil also depends on the properties of a given element, and the role it fulfils in the life of the plant.

Plants absorb metals from the soil solution. Their solubility and water pH therefore play the key role. Heavy metals are more soluble in different ranges of soil acidity. Their uptake

Table 1. Selected hyperaccumulator plants in the Global Database (2017)

Element	Threshold (μg·g^{-1})	Plant (the highest concentration reported to date)	References
Cadmium	>100	*Arabidopsis halleri* (0.36%)	(Stein et al. 2017)
Cooper	>300	*Valtheria Indica* (1.5%)	(Rajakaruna & Bohm 2002)
Nickiel	>1000	*Berkheya coddii6* (7.6%)	(Mesjasz-Przybyłowicz et al. 2004)
Lead	>1000	*Spermacoce mauritiana* (2.8%)	(Rotkittikhun et al. 2006)
Zinc	>3	*Noccaea caerulescens* (5.4%)	(Reeves et al. 2001)
Rare earth elements (REE)	>1000	*Dicranopteris linearis* (0.7%)	(Shan et al. 2003)

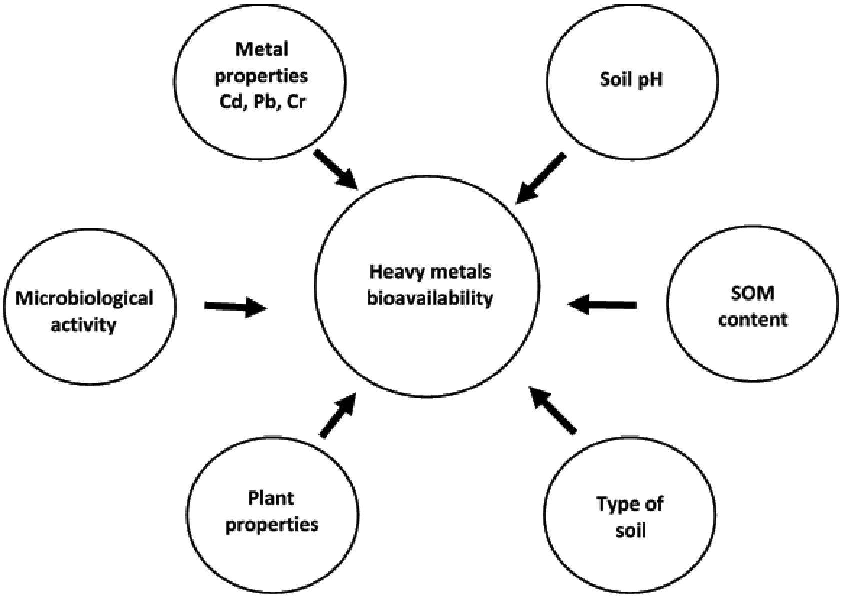

Fig. 1. Trace elements activity in soil

usually increases at lower pH. It should be remembered that the majority of plants usually show high tolerance of soil pH approximate to neutral. Many metals fulfil a substantial role in plant metabolism, but at their high level, they also become toxic to the plants. Uptake of lead (Pb) and chromium (Cr) is limited due to low soil water solubility. Consequently, in the case of these two elements, the phytoremediation technology is hardly practiced, and their presence in higher amounts in plants points to accumulation from polluted air (Gregoratos et al. 2015).

Air pollutants

In an urbanized area, pollution is caused by man, who made the air the depository of their gas contaminants. The primary sources of emission of the toxins include transport, housing heating and preparation of meals, and the industry (Holnicki et al. 2017). The capacity of air to move has made polluted air a global threat. The number one air pollutant is currently a complex mixture of chemical compounds within solid or liquid particles suspended in the air, defined as aerosol. The primary mechanism of their removal from the air is particle dry deposition, or alternatively incorporation within rain droplets (Sun et al. 2014). Solid aerosols, also known as particulate matter (PM), similarly contain metals in the vicinity of the emission source.

Ultimately all solid pollutants sooner or later fall down. If they fall to the soil, they are retained by the sorption complex or leach deeper into the soil profile. They also fall into water that covers a substantial part of the globe. An additional portion of pollutants is supplied to the water environment from urbanized areas with water from paved soil surfaces flowing into stormwater discharge systems, and further to rivers and oceans. It is estimated that in cities, approximately 50% and more surfaces such as roads, pavements, and squares are covered, preventing water from infiltrating the soil (McGrane 2016). In countries that care about the quality of water, before its discharge it is collected in ponds or deliberately designed sediments traps (Müller et al. 2020). The sediment from such sites has a significant list of heavy metals and other pollutants (Flanagan et al. 2021).

The combustion processes currently dominating in obtaining energy by man generate vast amounts of pollutants in the air. Plant biomass is the only factor that can retain pollutants on its surface at a large scale, and absorb part of them (Kończak et al. 2021). It is a perfect opportunity to collect pollutants before they are supplied to the soil or water, where their recovery is much more difficult. Rain removes PM from both the air and surfaces of leaves, contributing to air purification. Nonetheless, between rainfalls, only plants accumulate PM from the air (Sun et al. 2019, Nowak et al. 2006). The deposition of PM on the leaves is greater than the usual fall, because thousands of metabolic compounds contained in the leaf create an electromagnetic charge conducive to their accumulation (Gawrońska and Bakera 2015). During precipitation, PM present on the surface of leaves is washed into the soil, and partly stuck in the wax remains in the harvested biomass. Pollutants caught by rain reach the soil, where metals and organic pollutants are retained in the sorption complex. Metals retained in the soil complex are in ionic equilibrium with the part dissolved in the soil water, and they are taken up from water by plants. Meanwhile, metals also slowly permeate into the deeper layers of the soil.

Next to combustion products, microplastics, tires, brake discs and asphalt are also abrased in an urbanized area. The formation of very fine particles is caused by repeated fragmentation by subsequent vehicles. Data have shown that non-exhaust particles contribute almost equally to the total PM emitted in highly urbanized areas (Gregoratos et al. 2015), and microplastics constitute a part of them. If the toxicity of non-combustion fractions of PM is equivalent to combustion fractions, the introduction of hybrid and electric cars will only partly decrease the human risks associated with PM emissions. Black carbon (BC) particles constituting a product of incomplete combustion, and in the case of transport pollutants are abrased from tyres and asphalt, have a substantial contribution in the composition of PM. The direct toxicity of black carbon is currently subject to more detailed investigation, because it used to be considered as a less toxic product. It is, however, a perfect carrier of pollutants, e.g. metals, on its surface. In recent years it has been evidenced that microplastics (MP) also have a high share in the composition of PM, potentially accounting for its one third (Gasperi et al. 2018). Next to black carbon, microplastic is the second most important component of PM transporting other pollutants on its surface. It is currently investigated whether due to its chemical composition it does not contribute to the tendency for accumulation of particular pollutants on its surface. For us, it is interesting whether any of the aforementioned primary carriers has preferences to accumulate noble metals on its surface due to their specific physical-chemical properties. This question still remains unanswered.

The source of higher than average presence of noble metals in the environment are combustion vehicles equipped with catalyzers, and sometimes industrial activity (Matodzi et al. 2020) (Figure 2). The elements are released to the environment as a result of high temperatures in the catalyzer and its vibrations.

In practice, platinum (Pt) alloys with rhodium (Rh) or palladium (Pd) in a ratio of 5 to 1 are applied in catalysers.

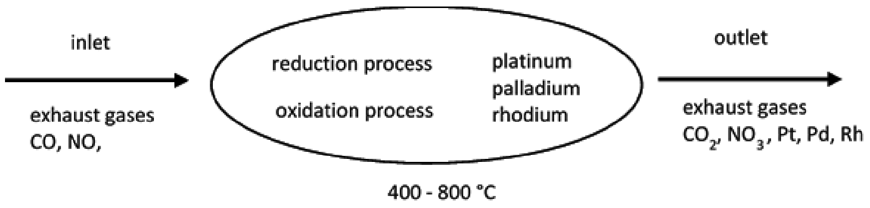

Fig. 2. Catalytic converter operation

They fulfil the function of the "heart" of the catalyzer, and in accordance with their properties, they stimulate the occurring reactions. As a result, cars featuring them usually emit ten times less toxins to the environment. A passenger car releases an average of 0.8 µg of noble metals per kilometer of road from the catalyzer, and small quantities from combusted fuel (Gasperi et al. 2018). Noble metals are heavy, and usually fall at a distance of up to 3 meters from the edge of the road. Particles released from the catalyzer, containing Pt, are in a PM range from a size below 1 µm to 63 µm, whereas 40% of them are soluble (Moreira et al. 2021).

Noble metals – phytomining

The highest amounts of noble metals are recorded in the dust deposited on the roads. This is confirmed by Mleczek et al. (2021) who, next to exhaust fumes, also included dust from abrasion of asphalt, tires, and brake blocks to the primary sources of rare earth elements (REE). Their much smaller amounts are found at a distance of up to 8 meters.

On one of the most important transport routes in Warsaw (Żwirki and Wigury Street, the road was ceremonially opened on 26 August 1934, currently has a length of 5.8 km and connects the center of Warsaw with the Fryderyk Chopin Airport, with an estimated traffic rate of 50 thousand vehicles per day) (Photo 1) the accumulation of platinum and palladium was primarily observed at a distance of up to 8 m from the edge of the road (Figures 3 and 4).

The greatest accumulation of both metals was recorded at a distance of 0.5 m and depth of 5 cm, where 60 µg·kg^{-1} of platinum and 75 µg·kg^{-1} of palladium was found, respectively (Łutczyk 2008). The content of the analyzed elements decreased with distance from the road. Higher than average contents of both elements were found at a distance of up to 2 m from the road. At distances of 4 and 8 m from the road, their content further decreased. The platinum content in a layer of 0–5 cm and a distance of 8 m from the road did not exceed 17 µg·kg^{-1}, and the palladium content did not exceed 2.5 µg·kg^{-1}. According to the study, both elements are transported down the soil profile to a depth of 20 cm, with a considerably decreasing amount. Depending on the distance from the road, the platinum content at a depth of 20 cm decreased from 13 µg·kg^{-1} (at a distance of 0.5 m from the road) to 5 µg·kg^{-1} (for the remaining distances), and the palladium content decreased from 17 to 2.5 µg·kg^{-1}, respectively. With depth, the palladium content decreased faster than that of platinum. The highest contents of both elements were always recorded in soil sampled from a distance of 0.5 m from the road. The platinum content in road dust was 87 µg·kg^{-1}, and that of palladium 136 µg·kg^{-1} (own results Figures 3–4).

Very similar results regarding the distribution and content of platinum on roads and in their vicinity were obtained by

Fot 1. Żwirki and Wigury Street (Szulc 2021)

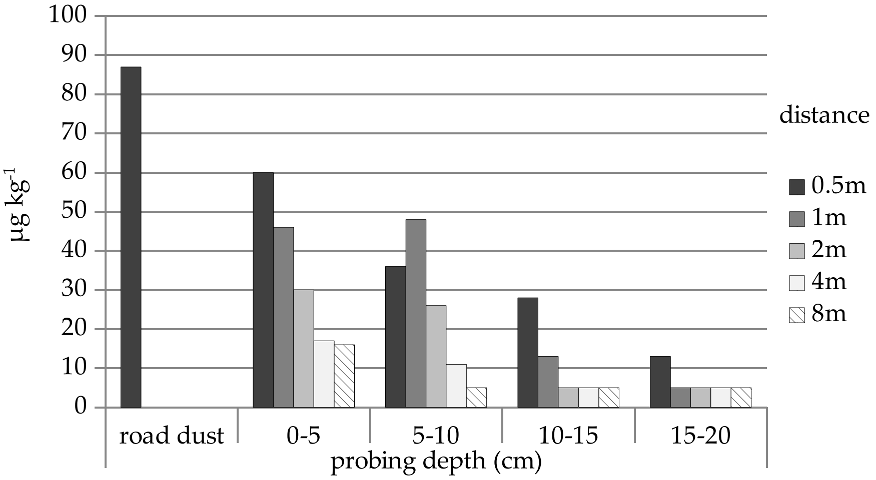

Fig. 3. Concentrations of platinum in roadside soils at Żwirki and Wigury Street in Warsaw

other scientists (Schafer and Puchlet 1998, Ladonin 2017). Particles containing Pt released from the catalyzer are in a PM range from a size below 1 µm to 63 µm, whereas 40% of them are soluble (Reith et al. 2014).

There are multiple possibilities of the recovery of platinum, palladium, and rhodium on roads and in their vicinity. The first place of interest regarding the presence of the elements is the vicinity of roads with high traffic intensity. It is specifically the 3 m belt of land adjacent to the road, and the middle belt if the road is a two-lane road. Plants growing in these areas accumulate noble metals on their overground surface, and simultaneously absorb them from the soil. A number of plant species efficiently absorb noble metals from the soil in the vicinity of roads (Schafer et al. 1998). According to the authors, palladium is absorbed the most efficiently, followed by platinum, and rhodium. The maintenance of the vicinity of roads involves mowing plants in these areas. In other words, nature conducts the first stages of phytoremediation.

Our task was mowing, collection, and controlled combustion of the obtained biological material. The obtained ash contains many elements, including noble metals the recovery of which from the obtained "ore" can be performed by means of methods applied in traditional extraction. Due to the technique of its maintenance, the vicinity of roads is usually subject to sawing of a mixture of grasses. The collected biomass contains both metals accumulated on plants from the air and those absorbed from the soil. In the temperate zone, mixtures of grass species that adjust to the existing environmental conditions are sawn in the vicinity of roads. One of the dominant grass species is perennial ryegrass (*Lolium perene* L.). In our experiments, it proved to be a species easily absorbing platinum in hydroponic cultivation. At platinum concentration of 500 µg·l^{-1}, leaves were found to contain 8.42 µg·g^{-1}, and roots as much as 50.8 µg·g^{-1} (Kowalska et al. 2004). Such high absorption of platinum, more than a thousand times greater than in nature, results from hydroponic cultivation, when the entire roots are in contact with the solution, unlike in the soil. This, however, points to high tolerance of oatgrass to platinum, and its good absorption. Unfortunately, pursuant to the already mentioned principle, the species most efficient in absorption of metals develop small biomass. Some grasses, in this case sheep fescue (*Festuca ovina* L.), are added as a certain percent share of the mixture, because they better tolerate the unfavorable environmental conditions. Grasses develop a fibrous root system with many roots primarily located in the surface humic layer of the soil, also containing metals. In cities, increasingly frequently instead of lawns, "flower meadows" are introduced, including up to several dozen species of plants. In the future, species with even greater abilities of absorbing noble metals could be introduced to the belt adjacent to the road. Other possibilities of intensification of the bioavailability and absorption of Pt and Pd are also searched for through the development of a complex with siderophores produced by bacteria inhabiting the soil. Their primary purpose is the development of chelate with metal, and particularly absorption of largely unavailable iron, although the process is not very selective, and noble metals are also absorbed (Dahlheimer et al. 2007).

Siderophores are produced by bacteria and fungi, and among plants by the botanical family of grasses. Interest in the potential application of siderophores in bioremediation of metals has been increasing in recent years (Ahmed et al. 2014). In order to increase the bioavailability of platinum group metals, research is also conducted regarding the use of other natural and chelating chemical compounds such as L-methionine and citric acid (Zereini et al. 2016). Prices of noble metals are subject to considerable fluctuations in the stock exchange market. It is worth mentioning that ash obtained from combustion of biomass can be easily stored, and recovered when prices of the elements are sufficiently high (Table 2).

Places for recovery of noble metals are lanes of roads on which they are simply deposited. Roads in cities are cleaned, and as mentioned above, the content of noble metals in dust collected from roads is the highest. Dust collected from roads is therefore a valuable "ore" for their recovery. This valuable raw material is currently regarded as toxic and stored in landfills. Collection of dust pollutants from lanes of intensively used roads should be obligatory. Whenever it is not done, rain washes them into our rivers, and finally oceans. Unfortunately, it is also caused by the practice of washing squares and streets with water. Removal of dusts from roads is necessary, because vehicles further crush them into smaller particles that are easier to resuspend in the air. Collecting dusts from roads is therefore

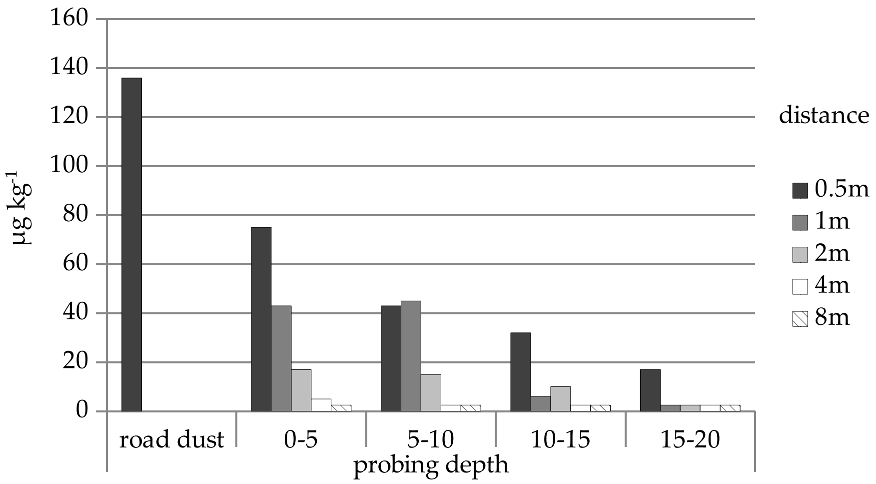

Fig. 4. Concentrations of palladium in roadside soils at Żwirki and Wigury Street in Warsaw

of double value, because it limits the pollution of our rivers and oceans, and permits recovery of valuable metals with no damage to the earth's surface.

There are places in the vicinity of newly constructed roads where pollutants containing metals are already collected into sedimentation tanks built at natural road elevations and bridges where water flows down during rainfall. Water from these sedimentation tanks, purposely polluted, has no outflow, the sediment contains almost the entire periodic table of elements, and the contained metals are possible to recover. The level of metals is higher, because on roads leading uphill motors operate much more intensively, like in the case of higher speeds of driving vehicles. Release of noble metals to the environment is also more intensive in older cars, and after 100 thousand km it can reach up to 2 µg per km (Helmers 1997). High pollution in these closed-drainage sedimentation tanks in the presence of water is confirmed by the presence of bulrush (*Typha latifolia* L.) and common reed (*Phragmites australis* Cav) – water species very resistant to pollution. The above-mentioned species and other plants accumulate the greatest amount of metals in their roots and harvesting the biomass together with the roots significantly improves the metal yield. It is worth mentioning that the deposited mineral material is very fine, and the extraction process does not require a financially expensive and environmentally harmful process of griding the raw material. The older the sedimentation tanks, the more valuable the material for recovery obviously becomes. Express roads are surrounded by closed-drainage ditches to avoid the supply of pollutants to agricultural fields, particularly in the case of accidents involving transport of chemicals. Roads usually maintain a certain level, therefore the overflowing water permeates into the soil in their vicinity, and there the growing vegetation absorbs pollutants.

More and more cities are draining rainwater that collects pollutants from the sealed city surface, not discharging it directly into rivers, but building sediments traps or simply open reservoirs where pollutants settle, and much cleaner water continues to flow through the catchment area. As a consequence, sediments are a site of degradation and accumulation of pollutants. Pollution-resistant species of aquatic plants from all three groups are used: free-floating, subemergent and emergent (Delgado-González et al. 2021, Ali et al. 2020). Together with their microbiome, they break down organic pollutants and accumulate elements present in the biomass, including precious metals (Bonanno 2011) and valuable REE.

The Earth Air Purification (EAP) technology developed by the Japanese company Fujita (https://www.fujita.com) offers promising possibilities for the future recovery of valuable elements. It involves pumping polluted air from the bottom of the substrate in which plants grow. In the substrate, heavy metals, including noble metals, are retained by the sorption complex, and organic and gas pollutants are decomposed by the microbes present in the substrate. It is composed of soil bacteria and rhizobacteria present on roots of plants, largely multiplying the presence of bacteria. The substrate and the presence of plants are therefore of key importance for the functioning of the EAP technology. The extraction of metals from the substrate is not a problem, and their recovery can be further improved by increasing its sorption capacity and facility of their recovery. In this technology, volatile compounds are strongly reduced: PM, sulphur dioxide, and carbon oxide in 90%, nitrogen dioxide in 80%, and organic compounds in 75%. Another important issue are materials included in the composition of the substrate in a way making degradation of pollutants sufficiently efficient, and costs of energy of pumping air as low as possible. Much cheaper than industrial technologies, this technology is primarily applied in cleaning air from tunnels, air from large garages in city centres, and road crossings with intensive traffic. The substrate with EAP contains considerably higher amounts of metals, including noble metals, than any other place related to transport-generated pollution. The level of metal in the substrate increases with time, because it does not require replacement for a number of years.

The increasing demand for noble metals increases their price. Their recovery is also supported by the circular

Table 2. RRE and noble metals accumulator plants

Plant	Range ($mg \cdot kg^{-1}$)	Element	References
H'robertii (Robyns) Duvign. El Planckc	10720	Co	(Baker & Brooks 1989)
Crotalaria cobalticola Duvign	3100	Co	(Baker & Brooks 1989)
Tobacco, *Brassica juncea,* *Helianthus annus L.,* *Brassica napus*	60 760 19.2 1.5–10	Au	(Krisnayanti et al. 2016,) (Haverkamp et al. 2007) Wilson-Corral et al. 2011) (González-Valdez et al. 2018)
Tobacco, *Brassica juncea,* *Brassica napus*	54.3 730 15000	Ag	(Krisnayanti et al. 2016,) (Haverkamp et al. 2007) (González-Valdez et al. 2018)
Arabidopsis thaliana (L.) Heynh.	12000–16000	Pd	(Harumian et al. 2017)
Dicranopteris linearis	1400–2450	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y	(Delgado-Gonzales et al. 2021)
Dicropteris dichotoma *Pronephrium simplex*	7000	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y	(Shan et al. 2003)

economy policy. Such activities support their removal from the environment, and make it safer while observing the economic principles.

Conclusions

The increasing demand for noble metals boosts their price. In order to meet the increasing demand for elements, a number of technologies are being developed for obtaining elements already present in the environment. The currently developed dedicated technologies based on natural processes occurring in the environment are attractive for this purpose. The recovery of these elements The recovery of elements is also supported by the circular economy policy. One such technology is phytomining. This method is based on the recovery of platinum group metals and rare earth elements from plants grown on the contaminated soil, rock, or on mine wastes. Plants that take up large amounts of noble metals and can be phytomining are e.g. tobacco, *Brassica juncea* L., *Helianthus annus* L., *Brassica napus* L. Such activities support their removal from the environment, and make it safer while observing the economic principles.

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Górnictwo miejskie: fitoekstrakcja pierwiastków ziem szlachetnych i rzadkich z gleb miejskich

Streszczenie: Aby sprostać rosnącemu zapotrzebowaniu na metale szlachetne poszukuje się technologii odzyskiwania pierwiastków już obecnych w środowisku. Gromadzące się w glebie metale, zwłaszcza pierwiastki z grupy platynowców pochodzące z katalizatorów, stanowią zagrożenie dla środowiska. Fitoekstrakcja jest technologią wykorzystywaną do pozyskiwania metali z grupy platynowców z roślin rosnących na zanieczyszczonej glebie, skale lub odpadach kopalnianych. Zainteresowanie tą metodą rośnie wraz ze wzrostem zainteresowania odzyskiem metali rzadkich. Na podstawie wyników badań różnych autorów przedstawiono ilości metali szlachetnych gromadzących się w glebie wzdłuż szlaków komunikacyjnych. W pracy przedstawiono także rośliny, które można wykorzystać do fitoekstrakcji.