Uptake, Translocation, Accumulation, and Phytotoxicity of Platinum Group Elements (PGE) on Potato, Lettuce, and Barley

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Dedicated to:

Yara,

Ranya,

Cornelie,

And

My Mother

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Abstract:

The transition elements platinum, palladium, and rhodium are widely used in the automobile industry. Production of catalytic converters is the principal application field of the so called Platinum Group Elements (PGE). Since the introduction of autocatalysts to reduce the emission of the greenhouse gases; CO, $NO_{X,}$ and HC, the concentration of PGE in environmental samples such as road dusts, soils, and plants is steadily increasing. The uptake pathways, accumulation, and transport of PGE emitted from autocatalysts in crop plants are poorly understood. However, the present study deals with these subjects in addition to the phytotoxicity of these metals on crop plants. Field experiments with lettuce (*Lactuca sativa* L.) were conducted at two sites. The first site lies close to the German Highway A5 and the second site is within the botanical garden of the University of Karlsruhe/Germany. The expected emissions of PGE at the highway site were higher than those at the botanical garden site. In addition to an expected atmospheric uptake by aerial organs, PGE uptake via plant roots was enabled by separate addition of two catalyst's powders containing the three noble metals, platinum, palladium and rhodium. Furthermore, greenhouse experiments using PGE soluble chloride salts; that were added to the hydroponic medium, were conducted with potato (*Solanum tuberosum* L.), barley (*Hordeum Vulgare* L.), and lettuce (*Lactuca sativa* L.) under controlled conditions, whereby the uptake was exclusively made via the plant roots. The crop plants were divided into their organs and the PGE concentrations were determined using HR-ICP-MS. The phytotoxicity of PGE on the crop plants was visibly manifested and some physiological parameters were determined. Lettuce (*Lactuca sativa* L.) plants that were treated with the catalyst's powders showed higher PGE concentrations than the control ones, implying the uptake of the precious metals via the plant roots. PGE concentrations determined in the field grown lettuce (*Lactuca sativa* L.) demonstrate, not only the solubility of platinum, palladium, and rhodium in the soil, but also the higher bioavailability of palladium, rather than platinum and rhodium. Platinum and palladium are mainly retained in the roots of the crop plants grown in the growth chamber. The noble metals are translocated from roots to shoots showing high mobility within the plants and phototoxic symptoms were more severe in potatoes (*Solanum tuberosum* L.) than in lettuce (*Lactuca sativa* L.) and barley (*Hordeum Vulgare* L.). Palladium, to a higher extent than platinum, is mainly retained in plant roots, whilst platinum; to a higher extent, is taken up into aerial organs. The Monocotyledonous (barley) plant showed an overall higher total concentration, but lower shoot platinum and palladium concentrations than the dicotyledonous one (potato). Potato (*Solanum tuberosum* L.) accumulated more platinum and palladium than lettuce (*Lactuca sativa* L.). Palladium is

not only more mobile within the potato and lettuce than platinum, but was also severely toxic on the potato (*Solanum tuberosum* L.) when compared to platinum. There were no severe phytotoxic effects from the PGE on barley (*Hordeum Vulgare* L.) and lettuce (*Lactuca sativa* L.). Visible phytotoxic symptoms observed in the crop plants are stunted growth, chlorosis, blackening of the root system, small leaves, and brown patches on leaves. It has clearly been established that the differences in platinum and palladium concentrations in potato (*Solanum tuberosum* L.) organs were due to the differences in phytotoxic effects of both elements on plants rather differences in amount of platinum or palladium applied for the uptake. The principal difference between platinum and palladium was seen in the portion taken up into either the aerial parts or retained in the roots of the three plant species.

Kurzfassung:

Die Übergangsmetalle, Platin, Palladium und Rhodium werden weltweit in der Automobilindustrie verwendet. Die Herstellung der Autoabgaskatalysatoren zählt zu den Hauptanwendungen der sogenannten Platingruppenelemente (PGE). Seit der Einführung der Autoabgaskatalysatoren, um die Emissionen der Treibhausgase CO, NOx und HC zu reduzieren, nimmt die Konzentration der PGE in den Umweltproben wie Strassensedimenten, Böden und Pflanzen ständig zu. Die Aufnahmepfade, Akkumulation und der Transport der aus den Abgaskataysatoren emittierten PGE in den Nutzpflanzen sind wenig bekannt. Die vorliegende Arbeit befasst sich zusätzlich zu der Phytotoxizität dieser Metalle auf Nutzpflanzen mit diesen Themen. Es wurden an zwei Standorten Feldversuche mit Salat (*Lactuca sativa* L.) durchgeführt. Der erste Standort liegt direkt an der A5 und der zweite innerhalb des Botanischen Gartens der Universität Karlsruhe. Die erwarteten Emissionen der PGE an dem Autobahn-Standort waren höher als die am Standort Botanischen Garten. Zusätzlich zu einer atmosphärischen Aufnahme über die oberirdischen Pflanzenorganen wurde die Aufnahme über die Pflanzenwurzel ermöglicht. Dies geschah durch getrennten Zusatz von zwei Katalysatorenpulver, die die Edelmetalle Platin, Palladium und Rhodium in unterschiedlichen Konzentrationen enthielten.

Überdies wurden Gewächshausversuche mit Kartoffeln (*Solanum tuberosum* L.), Gerste (*Hordeum Vulgare* L.) und Salat (*Lactuca sativa* L.) unter kontrollierten Bedingungen durchgeführt, um die Aufnahme ausschließlich über die Wurzel zu ermöglichen. Als Kontaminationsquelle wurden lösliche PGE-Chloridsalze verwendet. Die Nutzpflanzen wurden in einzelne Pflanzenorgane unterteilt und deren Gehalte an PGE mittels HR-ICP-MS bestimmt. Die phytotoxischen Auswirkungen der PGE auf die Nutzpflanzen wurden visuell manifestiert und die pflanzenphysiologischen Parameter ermittelt. Die Salatpflanzen, die mit Katalysatorpulver behandelt waren, zeigten einen höheren PGE-Gehalt als die Kontrollpflanzen, was die Aufnahme der Edelmetalle über die Wurzeln impliziert.

Die ermittelten PGE Konzentrationen im feldgewachsenen Salat (*Lactuca sativa* L.) sehen nicht nur die Löslichkeit von Platin, Palladium und Rhodium im Boden vorraus, sondern auch die höhere Bioverfügbarkeit von Palladium eher als die von Platin und Rhodium. Platin und Palladium wurden hauptsächlich in den Wurzeln der Nutzpflanzen, die im Gewächshaus angepflanzt waren, retentiert. Die Edelmetalle wurden von der Wurzel in den Spross transportiert, was die hohe Mobilität innerhalb der Pflanzen zeigt. Die phytotoxischen Symptome waren schwerwiegender bei den Kartoffeln (*Solanum tuberosum* L.) als bei der Geste (*Hordeum Vulgare* L.) und dem Salat (*Lactuca sativa* L.), die im Gewächshaus

angezogen waren. Palladium wurde, in größerem Umfang als Platin, hauptsächlichen in den Wurzeln der Gewächshauspflanzen retentiert während Platium in größerem Umfang als Palladium in den Spross aufgenommen wurde. Die monocotyle Pflanze (Gerste) zeigte insgesamt höhere Konzentrationen, aber niedrigere Platin- und Palladiumkonzentrationen im Spross als die dicotyle Pflanze (Kartoffel). Die Kartoffel (*Solanum tuberosum* L.) akkumulierte mehr Platin und Palladium als Salat (*Lactuca sativa* L.). Das Palladium war innerhalb von Kartoffel und Salat nicht nur mobiler als Platin, sondern hatte im Vergleich zu Platin auch sehr toxische Auswirkungen auf die Kartoffelpflanzen, die im Gewächshaus angezogen waren. Hingegen waren keine schweren toxischen Auswirkungen der PGE auf Gerste (*Hordeum Vulgare* L.) und Salat (*Lactuca sativa* L.) zu beobachten. Die sichtbaren phytotoxischen Symptome, die bei den Gewächshauspflanzen beobachtet wurden, waren verkümmertes Wachstum, Chlorosis, Schwärzung des Wurzelwerkes, kleine Blätter sowie braune Flecken auf den Blättern. Es wurde deutlich gezeigt, dass die Unterschiede im Platin- und Palladiumgehalt in den Kartoffelorganen auf die unterschiedlichen phytotoxischen Auswirkungen der beiden Metalle auf die Pflanzen zurückzuführen sind. Diese Unterschiede waren unabhängig von den Mengen an Platin und Palladium, die für die Aufnahme eingesetzt waren. Der Hauptunterschied zwischen Platin und Palladium waren die Mengen, die entweder in den oberirdischen Organen aufgenommen oder in den Wurzeln der drei Pflanzen retentiert wurde.

Chapter I

Introduction and Aim of the Present Study

“Don’t throw a stone in the holy Nile, don’t throw your waste in front of thou neighbour’s house, don’t build your house blocking the sun or the wind from thou of your neighbour; for if you did, the gods shall have no mercy, and will abolish your wealth and shall not escort you on your final trip to eternity…..

The book of the dead, 1500 BC

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I. Introduction and Aim of the Present Study

The present study is devoted to the uptake, accumulation, translocation, and phytotoxicity of PGE being emitted from autocatalysts and added as catalyst's powders to soils or as soluble salts to the hydroponic medium for crop plants. The number of cars fitted with catalytic converters is continuously increasing and the concentrations of PGE in environmental compartments are consequently increasing (Alt et al. 1993; Wei & Morrison 1994a; Farago et al. 1996; Helmers & Mergel 1998; Schäfer et al. 1998; 1999; Laschka & Nachtwey 2000; Palacios et al. 2000a; 2000b; Gómez et al. 2001; Rauch et al. 2001; Zereini 2001a; 2001b; Cinti et al. 2002; Kanitsar et al. 2003; Djingova et al. 2003; Dongarra et al. 2003). There is a great concern about this increase since it has been demonstrated that PGE are mobile in the environment (Fuchs & Rose 1974; Kothny 1979; Pogrebnyak et al. 1986; Wood & Vlassopoulos 1990; Fletcher et al. 1995; Jarvis et al. 2001).

PGE had been found in plants (mainly grass) collected along roads with high traffic density (Helmers et al. 1994; Helmers & Mergel 1997; Schäfer et al. 1998; Djingova et al. 2003; Dongarra et al. 2003; Lesniewska et al. 2004a). The uptake of PGE has been suggested to occur mainly via roots (Sarwar et al. 1970; Kothny 1979; Pallas & Jones 1978; Farago et al. 1979; Ballach 1995; Ballach & Wittig 1996; Lustig et al. 1997). Nevertheless, uptake via aerial parts by adsorption of very fine emitted particles (on which PGE are attached) was also reported (Messerschmidt et al. 1994; Lustig et al. 1997; Dongarra et al. 2003). Studies on the uptake of soluble PGE salts by different plant species have been conducted by Farago et al. (1979), Farago & Parsons (1986a; 1986b; 1994), Klueppel et al. (1998), Verstraete et al. (1998), Ballach (1995), Ballach & Wittig (1996), and Ballach et al. (2000). The accumulation of PGE in roots and the translocation into plant shoots has been demonstrated. In these experiments, PGE were applied as soluble complexes and their concentrations in the nutrient solutions were in most cases relatively high. Phototoxic effects of PGE on plants have also been demonstrated at higher concentration in the nutrient solutions (Michenfelder et al. 1988; Farago et al. 1979; Farago & Parsons 1986a; 1986b; 1986c; 1994). Field experiments, conducted near roads with high traffic density, on the uptake of PGE emitted from catalytic converters by crop plants, are less known. Furthermore, detailed studies on the accumulation of PGE in plant organs as well as their transport and movement within plant species are rare.

The first objective of the present study was as follows:

- Investigate the uptake pathways of PGE by the crop plants barley (*Hordeum Vulgare* L., var. Pasadena) and lettuce (*Lactuca sativa* L., var. Estelle) grown in field.
- Define the PGE accumulating plant organs
- Examine the bioavailability of PGE added to soils as autocatalyst's powders, for plant uptake.

For these purposes, two sites of different traffic density were chosen. The first site was chosen along the German Highway A5 between Karlsruhe and Frankfurt am Main/Germany. According to the Regierungspräsidium in Karlsruhe/Germany, the daily traffic density at this site was estimated at 89,000 vehicle/day (anno 2001). The second site chosen was 200 m from a main street (Adenauer Ring) in Karlsruhe/Germany. Based on the difference in traffic density between the two sites, it is reasonable to compare the PGE concentrations in crop plants grown at both sites. The crop plants were grown on soils originated from these sites after addition of catalyst powder to the soils.

It is suggested that bacteria are able to methylate platinum species, and thus enable easier uptake via plant roots (Brubaker et al. 1975; Lustig et al. 1997). The PGE that were added as autocatalyst's powders to the soil used for experiments with barley, were left in the field for 18 months to allow the formation of bioavailable species in soils by bacteria or related processes prior to conducting the field experiments with lettuce (*Lactuca sativa* L.).

It has been demonstrated that PGE are phototoxic at high and tonic at low concentrations in the hydroponic medium (Sarwar et al. 1970; Bornique et al. 1976; Parsons 1982; Farago & Parsons 1986a; 1986b; 1986c). The uptake of PGE by plants depends on plant species, PGE salt applied, and concentration added to the nutrient solution (Farago & Parsons 1986a; 1986b; 1994). Moreover, Verstraete et al. (1998) pointed out that rye grass (*Lolium perenne*); a monocotyledonous plant, slightly accumulated platinum and cucumber (*Cucumis sativus*); a dicotyledonous plant, strongly accumulated platinum. In the present study, two concentration levels (300 and 2000 µg/l) of platinum and palladium in the nutrient solution were chosen to highlight the toxic effects of PGE on the different plant species and to further to compare the differences in uptake and accumulation by two dicotyledonous and one monocotyledonous plant species, on the other hand.

The second objective was as follows:

- Investigate the accumulation, translocation, and phytotoxicity of the precious metals on the crop plants under controlled experimental conditions.
- Investigate the differences in uptake, accumulation, and phytotoxicity between a monocotyledonous (*Hordeum Vulgare* L.) and a dicotyledonous (*Solanum tuberosum* L.) as well as between two dicotyledonous (*Solanum tuberosum* L. and *Lactuca sativa* L.) plant species.
- Compare the uptake, translocation, and phytotoxicity of PGE on potato (*Solanum tuberosum* L.) at two metal concentrations in the hydroponic medium.
- Study the transport and movement of PGE within potato (*Solanum tuberosum* L.), lettuce (*Lactuca sativa* L.), and barley (*Hordeum Vulgare* L.).

For these purposes, the uptake pathway of PGE via aerial parts was excluded and the uptake via roots was done exclusively by conducting uptake experiments in a greenhouse under controlled experimental conditions. Moreover, soluble PGE salts (platinum and palladium chlorides) were chosen. The platinum and palladium chloride salts were then added to the hydroponic culture containing macro- and micronutrients.

The crop plants studied were subdivided into their different organs (i.e. leaves, leaf stalks, stems, roots, and tubers) in order to define the accumulating organs of PGE. Furthermore, by comparing the noble metal ratios in the different plant organs, a first approach to investigate the movement of PGE within plants has been undertaken.

Chapter II

State of the Art

From a global and life cycle perspective, the catalytic converter is “converting” rather than reducing the environmental impacts.

Amatayakul & Ramnäs (2001)

2.1 Properties, Occurrence and Usage of Platinum Group Elements (PGE)

2.1.1 Some Chemical and Physical Properties of PGE

The six transition elements ruthenium, rhodium, palladium, osmium, iridium and platinum, positioned in Group VIII of the periodic table, are collectively known as platinum group elements (PGE) or as platinum group metals (PGM). Being transition elements, they show strong tendency to form complex ions, pose catalytic effects and exhibit a wide range of oxidation states. The PGE, particularly palladium, platinum and ruthenium, are used as catalysts in hydrogenation and oxidation reactions (Ginzburg 1975) because of their ability to adsorb gases. According to their specific gravities, PGE are divided into light (ruthenium, rhodium, and palladium) and heavy (osmium, iridium and platinum) triads. These noble metals are amongst the world's scarcest elements (Farago & Parsons 1994) and their mean concentrations in the Earth's crust range from 0.001 to 1.0 μg/kg (Wedepohl 1995). The unique chemical, physical and electrical properties of the PGE led to widespread use of technical applications in the chemical, jewellery, dental and medical (dental alloys, anticancer drugs), automobile and electronic industries.

2.1.2 Natural Occurrence and Mining of PGE

Platinum group elements are considered to be highly siderophile elements. More than 99% of the Earth's noble metals reside in the core and only minor amounts are expected to be in the earth's mantle (Rehkämper 2000). The abundances of terrestrial and extraterrestrial PGE were found to be comparable, suggesting the extraterrestrial origin of PGE present in the Earth. Holzheid et al. (2000) concluded that highly siderophile elements were added to the earth from meteorites after the Earth had initially formed and the core had become distinct from the mantle.

The most important primary PGE ore deposits are the South African Bushveld complex, the Russian Urals, the Canadian Sudbury District and the Great Dyke in Zimbabwe (Cawthorn, 1999). Secondary (alluvial) or placer PGE deposits occur in Columbia, Ethiopia and the Urals. South Africa, Russia, USA, Canada, and Zimbabwe are the world's main producers of PGE (Johnson Matthey 2003).

During the mining process, PGE containing ore deposits are crushed, pulverized, and mixed with water, air, and special reagents which cause PGE-containing particles to float (Jones 1999). After the flotation process, PGE are removed from the surface for drying. Since the concentrations of PGE in the host rock are very low, ~ 3 g/ton (Cawthorn 1999), a concentration process of PGE by smelting is necessary. Thereafter, PGE are separated from nickel and copper, and further refined from base metals (Jones 1999). Consequently, significant environmental impacts occur during the mining and production of PGE. However, substantial benefits are gained through atmospheric emission reduction of the greenhouse gases since PGEs are widely used in automobile catalytic converters (Amatayakul & Ramnäs 2001).

Weathering of PGE metal alloys by oxidation in a natural system is considered to be a slow process (Jarvis et al. 2001). Moderately strong oxidizing solutions that contain complexing agents such as chloride or humic matter could accomplish the dissolving process. However, lighter elements, including palladium and rhodium would weather more rapidly than the heavier triad including platinum (Jarvis et al. 2001).

2.1.3 PGE Usage in the Jewellery Industry

Because of the inertness and attractive appearance of platinum (the most common element in the platinum group), one of its major uses is in the manufacture of jewellery. It was discovered by South Americans and was used by pre-Columbian Natives who produced rings and ornaments from platinum nuggets. Ancient Egyptians also used platinum, which was found as a decorative material on a casket from the 7th century BC. In the 18th century, a modern platinum jewellery tradition began. Several years after World War II and in the 1970s, a revival by German jewellers gave platinum a new identity, characterised by modern design and the prevalent use as a satin finish. Palladium, iridium, ruthenium, copper, and cobalt are alloyed with platinum, which is resistant to tarnish and has high strength, in order to fabricate jewellery (Johnson Matthey 2003). White gold is an alloy of gold that is decolorized by the addition of either platinum or palladium. Japan is the largest producer and consumer of platinum jewellery whereas China is the fastest growing market of platinum jewellery (Taylor & Biggs 1999; Johnson Matthey 2003).

2.1.4 PGE for Dental and Medical Usage

In the last three decades and according to their physicochemical properties, some elements of the PGE such as platinum, palladium, and ruthenium are widely used in dentistry and medicine. Since they are known as inert metals, they are used together in a mixture with gold or silver as dental inlays, crowns, and bridges. Platinum; and recently ruthenium, in certain chemical forms have the ability to inhibit cell division (Natile & Coluccia 2001; Johnson Matthey 2003). This important discovery led to the development of drugs based on platinum to treat certain kinds of cancer. The platinum complex *cis*-platin, which is the first anticancer drug discovered, was widely used since the 1970's in cancer therapies to treat head, neck, testicular, and ovarian cancers (Parsons et al. 1987; O'Dwyer et al. 1999; Natile & Coluccia, 2001; Johnson Matthey 2003). *Cis*-platin also has adverse effects on patients treated with this compound (Hann et al. 2001). Furthermore, another compound known as *carbo*-platin, which is similar to *cis*-platin in terms of activity and has less toxic effects, was approved in 1986 (Johnson Matthey 2003). Platinum is excreted by patients after applying antineoplastics. Consequently, hospital effluents have been described by Kümmerer & Helmers (1997) and Kümmerer et al. (1999) as a source for the emission of platinum into waste water and sewage sludge. PGE also have further uses in medicine. For example, platinum is used in the fabrication of very tiny components, which are used as electrodes in pacemakers to treat heart disorders (Johnson Matthey 2003).

2.1.5 PGE Usage in Automobile Industries

Recent data published by Johnson Matthey (2004) illustrated that after the jewellery industry, the automobile industry represents the main consumer of the PGE supplies worldwide. The principal application of PGE in the car industry is in the production of car catalytic converters.

The application of clean air legislation led to the introduction of automobile catalytic converters in the mid 1970s in the USA and Japan, and later (late 1980s, early 1990s) in Europe (Zereini et al. 1997a; Palacios et al. 2000a; Jarvis et al. 2001; Gómez et al. 2002). Moreover, the European Standards and Directive 94/12/EEC implemented since 1993, on ambient air quality require all new automobiles registered in the EU to be equipped with a catalytic converter (Palacios et al. 2000a).

The first generation of autocatalysts (two-way catalysts) was based on platinum and rhodium. The modified autocatalysts (three-way catalysts) are based on platinum, rhodium, and palladium. The three-way catalyst can reduce the emission rate up to 90% for the three main contaminants HC, NOx, and CO present in the exhaust fume (Johnson Matthey 2003). A modern three-way catalytic converter has been designed to promote the reduction of nitrous oxides to nitrogen using rhodium, and simultaneously oxidize carbon monoxide and unburned hydrocarbons to less harmful carbon dioxide and water using platinum and/or palladium (**Figure 1**).

Figure (1): A modern three-way catalytic converter for the reduction of the greenhouse gases carbon monoxide (CO), nitrogen oxides (NOx), and hydrocarbons (HC) (from: Johnson Matthey 2003).

A catalytic converter consists of a highly porous ceramic honeycomb monolithic structure (cordierite skeleton, $5SiO_2.2Al_2O_3.2MgO$). The cordierite is coated with a highly porous "washcoat" of approximately 90% $_{\gamma}Al_2O_3$, which provides a high active catalytic surface area for the catalytic reactions A mixture of base metal additives, mainly oxides of Ce, Zr, La, Ni, Fe, and alkaline earths (Palacios et al. 2000) enhances the catalyst's performance. Furthermore, the "wash coat" is impregnated with the noble metals platinum, palladium, and rhodium in different combinations and concentrations. In European gasoline automobile fitted with three-way converters, the Pt/Rh or Pd/Rh ratio in autocatalysts is usually 5:1. However, the type and size of an engine determine the platinum and rhodium amount used per vehicle. The concentration of the noble metals was given by Zereini et al. (1997a) and Cuif et al. (1997) as follows: 1.5 g of platinum and 0.3 g of rhodium per litre. Nevertheless, the results of radiotracer measurements conducted by Schneider et al. (1999) indicated that an average of 12% additional platinum and 124% additional rhodium was deposited on converter substrates beyond that calculated. Therefore, the results of Schneider at al. (1999) indicated that PGE are present in greater amounts in the catalytic converter than the amounts given by the autocatalyst's

producers. Thermal heating within the catalyst causes the tiny particles of precious metal to agglomerate, thus reducing the catalyst's overall surface area and hence its activity (Helmer 2002).

Platinum group elements (PGE) are not only applied in the catalytic converter production but have also a wide range of uses in the automobile industry. Among them are sensors for automobile emission control, car climate control sensors that detect CO and NO_x concentrations inside the vehicle, air-mass flow sensors to measure the air-flow to each bank of cylinders in the engine, and initiator sensor in air bags (Johnson Matthey 2003).

Fuel cells are another important usage of PGE in the automobile industry, whereby platinum is a necessary component of it. The noble metal is dispersed on the proton exchange membrane (PEM), which is considered to be the most researched part of the fuel cell. In a medium-sized passenger car, about 25 g of platinum are required (Borgwardt 2001), which is a concern in terms of cost. Vehicles fitted with fuel cells have environmental and economic advantages which make them equal to zero-emission vehicles (Johnson Matthey 2003).

2.1.6 Further Usages of PGE

The unique physical, chemical, and catalytic properties of PGE led to a wide range of applications of these elements in several industrial sectors. For example, platinum wire, foil, and discs are used as electrodes for various sensors in medical equipments (Johnson Matthey 2003). They are also used in the electronic industry (computer hard discs, electronic circuits), production of nitric acid, watch industry, glass fibre production, crucibles used in the production of high purity crystals, and high technology products such as small rocket engines and space technology (Yuantao & Zhengfen 1999; Fisher et al. 1999). Further applications are in sensors used to detect CO concentration in buildings and in catalysts used in refining high-boiling crude oil fractions (Renner & Schmuckler 1991). Moreover, PGE are used as catalysts for the catalytic oxidation of ammonia in nitric acid production (Büschl et al. 1999).

2.2 PGE Emissions into the Environment

2.2.1 Car Catalytic Converters as a Main Emission Source of PGE

Several studies have been conducted by many work groups around the globe to determine the PGE concentrations in the different environmental compartments near roads with high traffic density (Hodge & Stallard 1986; Alt et al. 1993; Wei & Morrison 1994a; Farago et al. 1996; Alt et al. 1997; Helmers & Mergel 1998; Schäfer 1998; Schäfer et al. 1999; Laschka & Nachtwey 2000; Schierl 2000; Tilch et al. 2000; Gómez et al. 2001; Rauch et al. 2001; Zereini 2001a, 2001b; Cinti et al. 2002; Kanitsar et al. 2003; Djingova et al. 2003; Dongarra et al. 2003; Whiteley & Murray 2003). The PGE have been detected in soils, dusts, sewage sludge, and plants. From their results, the PGE are suggested to be of anthropogenic origin, contributed mainly to the emissions from catalytic converters and in some cases, from sewage sludge samples collected in Pforzheim/Germany due to jewellery industry located there (Lottermoser 1994).

PGE in environmental samples gained more attention after the introduction of the autocatalysts. Fathi Zereini (Johann Wolfgang Goethe Universität, Frankfurt am Main/Germany) is one of the pioneers who conducted several studies to determine the PGE concentrations in environmental samples (Zereini et al. 1993, 1997a, 1997b, 1998, 2001a, 2001b, 2004). PGE sources in environmental samples have been mainly contributed to car catalytic converters (Ravindera et al. 2004 and references therein). A research interest to determine reasons of PGE emissions from catalytic converters, their emission rates, species, and forms has been developed. However, the precious metals (platinum, palladium and, rhodium) are suggested to be emitted from car catalytic converters due to thermal heating and mechanical abrasion (Artelt et al. 1999a; Balgord 1973). Zereini et al. (1997a) pointed out that the catalyst is chemically and physically stressed by fast changing oxidative/reductive conditions within the catalyst's body. All these, in addition to high temperatures and mechanical abrasion, led to the release of PGE-containing particulates into the environment.

PGE emitted from catalysts are deposited on a narrow zone along the roadside (Schäfer & Puchelt 1998; Ely et al. 2001; Gómez et al. 2001; Jarivs et al. 2001; Zereini et al. 2001b). Increased concentration of PGE in the airborne particulate matter were reported in several studies from different countries such as Germany, USA, Sweden, England, and Spain (Hodge & Stallard 1986; Alt et al. 1993; Wei & Morrison 1994a; Farago et al. 1996; Tilch et al. 2000;

Gómez et al. 2001; Zereini 2001a, 2001b). Zereini et al. (2001b) determined platinum concentration in dust samples collected from the city of Frankfurt am Main/Germany, which varied between 22 and 719 µg/kg. Dust samples collected by Aboughalma & Stüben (2003, unpublished data) along the German Highway (A5) showed concentrations of platinum varying between 122 and 536 µg/kg, palladium varying between 50 and 479 µg/kg, and rhodium varying between 19 and 98 µg/kg depending on sampling distance from the highway and sampling height above the ground surface. Zereini et al. (2001b) also pointed out that platinum in samples collected at a height of <1.5 m generally showed the highest concentration. Lower platinum (317 ng/g) and rhodium (74 ng/g) concentration in dust samples collected from Madrid/Spain has been reported by Gómez et al. (2001).

2.2.2. PGE Emission Forms and Amounts Released from Autocatalysts

At present, it is accepted that PGE are emitted from autocatalysts and attached to various particles. The emission form of particles and the size of its grains have not been studied enough due to limitation factors, such as the very low concentration of PGE in dust samples or airborne particulate matter and the detection limits of technical equipments, such as electron microscopy, that are required for detailed experiments.

Although, several studies have been conducted to determine the PGE concentrations near roads (Jarivs et al. 2001; Schäfer & Puchelt 1998; Schäfer et al. 1999; Zereini et al. 2001b), the spatial and seasonal variations of PGE emitted from autocatalysts need further study. Aboughalma & Stüben (2003) conducted experiments along the German Highway (A5) and reported on the spatial distribution of PGE. The amount of PGE decreases with increasing distance from the highway and showed two maxima at 2 m and 15 m, which correlate with coarse and fine grain fractions of PGE-containing particles, respectively. They also added that the PGE are subject to seasonal variations. Further studies conducted by Moldovan et al. (1999) showed that more than 95% of emitted platinum, more than 85% of emitted palladium, and more than 90% of emitted rhodium are released in particulate form at the ng/km level. Moreover, platinum group elements are emitted in metallic and oxide species, which are attached to very fine Al_2O_3 particles (Artlet et al. 2000; Palacios et al. 2000a; Jarvis et al. 2001).

The amount of PGE emitted depends on several factors such as traffic density, driving speed, type of engine, catalyst type and age, and type of fuel additives (Schäfer et al. 1999; Palacios et al. 2000a; Gómez et al. 2001; König et al. 1992; Helmers 1997; Zereini et al. 2001b;

Ely et al. 2001). In this essence, Artelt et al. (1999a) mentioned that approximately four times less platinum was emitted from converters installed on low power engines. There was a tendency towards lower emission values with increasing age of catalysts and driving velocity. High platinum concentration in road dust samples collected from SE England were associated with high traffic densities (Farago et al. 1998).

However, PGE concentrations in the atmosphere are influenced by a variety of different factors including volume of traffic on a particular roadway, the number of cars fitted with catalytic converters, vehicle type and associated emission amounts, particle size of airborne matter, and meteorological and driving conditions (Schäfer et al. 1999; Kanitsar et al. 2003).

2.2.3 PGE Emission Rates from Autocatalysts

Several studies were conducted to determine the emission rates of PGE from car catalytic converters (König et al. 1992; Schäfer et al. 1999; Artelt et al. 1999a; Palacios et al. 2000a; Zereini et al. 1997a). Unfortunately, the data outcome was contradictory and gave no realistic information about the emission rates. This is partly due to the different experimental designs and PGE analysis in such samples because there are no standardized methods for PGE determination in environmental samples. However, different emission rates of PGE from autocatalysts are postulated by different scientists, some estimated higher and others lower emission rates. For example, Palacios et al. (2000a) estimated higher platinum release from diesel than from fresh gasoline catalysts. The mean total amount emitted from diesel catalysts varied between 400 and 800 ng/km, whereas from fresh gasoline catalysts it was approximately 100, 250, and 50 ng/km for platinum, palladium, and rhodium, respectively. König et al. (1992) estimated emission factors ranging from 2 to 40 ng/km; from experiments with two catalysts under four different operating conditions, whereas Artelt et al. (1999a) estimated higher factors ranging from 9 to 124 ng/km which were measured in the exhaust of two different engines. Far higher emission factors of 9700 ng/km and 270 ng/km have been estimated by Helmers (1997) and Zereini et al. (1997a) as well as by Schäfer et al. (1999), respectively. However, sampling, experimental design, and analytical methods might have led to such a wide range of variation during the estimation of the emission rates of PGE.

2.2.4 Importance of PGE Emissions from Autocatalysts

The metallic species of these noble metals are inert, but some of their compounds such as hexachloroplatinate and tetrachloroplatinate complexes are suggested to be powerful sensitizers (Rosner & Merget 1999; Merget & Rosner 2001; Lindell 1997). Moreover, some platinum complexes bind to nitrogen and sulphur in proteins producing a possible reduction in essential enzymatic activity (Merget & Rosner 2001).

Estimation of environmental risks from PGE present in urban air and in road dust sediments remains unclear. However, for human beings, inhalation of the fine grain fraction (such as particles of 0.1-2.15 μm grain size) containing PGE is deposited in the lung alveoli and might pass directly into blood (Kanitsar et al. 2003; Palacios et al. 2000a). Noble metal transformation into bioavailable species, by methylation for example, which is then a subject of uptake by plants, represents another indirect source of intake by humans. Surface deposition of PGE-containing particles onto water bodies represents another risk source to water quality and water organisms (Rauch & Morrison 1999).

2.2.5 Other Emission Sources of the PGE

Since the 19th century some authors reported on properties, volatility, and emission of PGEs from sources other than autocatalysts (Davy 1817; Howe 1900; Crookes 1912; Alcock & Hooper 1960). Effluents from hospitals applying platinum containing cancer drugs represent another important platinum emission source into the environment. In 1996, a total emission of 14.2 kg of platinum from German hospitals and 187.2 kg from automobile catalytic converters, was, estimated by Kümmerer et al. (1999). As mentioned previously, dental alloys containing PGEs seem to be the most important source for triggering individual urinary platinum excretion (Begerow & Dunemann 1999).

Platinum and rhodium are also lost during the oxidation of ammonia used in nitric acid production, as reported by Nilsen et al. (2001) who pointed out that platinum undergoes a chemical transport reaction from the high- to low-temperature zone in oxidizing environments. Ammonia itself does not play a significant role as a chemical transport agent for platinum. Moreover, their mass spectrometric experiments identified Pt^+, PtO^+ and PtO_2^+ as a Pt-containing gaseous species. In another experiment conducted by Nowak (1966) it has been shown that platinum-based ammonia oxidation catalysts undergo surface alteration and erosion

during the production process. He also suggested that volatilization of platinum by oxidation contributes significantly to catalyst losses during this process. Yuantao & Zhengfen (1999) reported that volatile oxides of platinum, palladium, and rhodium (PtO_4, PdO and RhO_2, respectively) are formed on the catalyst's surface during nitric acid production by the oxidation of ammonia. However, platinum is lost during ammonia oxidation due to mechanisms involving erosion of the platinum by a species other than oxygen and the rearrangement of the surface followed by mechanical erosion. Skelland (1974) assumed that the metal loss was due to a chemical reaction followed by transport of gaseous PtO_2 away from the surface.

2.3 Geochemical Behaviour of PGE in Environmental Compartments

2.3.1 PGE in the Atmosphere

The end of the vehicle exhaust pipe is in direct contact with the atmosphere. Not only are vehicle fuel combustion products related, but also other products such as particles from the catalytic converter are thus directly released into the atmosphere. Since oxidation catalytic converters operate in the temperature range from 500°C to 1000°C (mid-bed temperature), it is reasonable to expect some loss of platinum as PtO_2 vapour (Balgord 1973) that would undergo decomposition and subsequent condensation into a finely dispersed platinum aerosol as the exhaust cools. The formation of possible soluble $PtCl_6^{2-}$, $PdCl_4^{2-}$, or $RhCl_6^{2-}$ ($RhCl_3$) organic complexes with carbonyl compounds or 'colloidal PGE' could be favoured at high temperatures and humidities that may be reached in the catalyst and explain the high release of soluble forms (Palacios et al. 2000a). Palladium and particularly rhodium can form carbonyl compounds to which the noble metals are bound through oxygen, sulphur, nitrogen, or phosphorus (Giandomenico 1996).

2.3.1.1 Relationship between Grain Sizes, Seasonal Variations, and PGE Concentration in the Atmosphere

Most experiments on the relationship between PGE concentration in dust samples and grain size analysis showed that PGE are attached to the fine grain fraction (Wei & Morrison 1994a; Artelt et al. 1999a; Zereini et al. 2001a). This fine grain fraction is of great interest since it contains high PGE concentrations and can be inhaled by humans. However, platinum has been shown to be emitted in the form of particles of aluminium oxide "wash coat", in which mainly Pt (0) is attached in addition to small amounts of oxidised PtO_2 adsorbed at the surface (Inacker & Malessa 1996; Schlögl et al. 1987) or in the form of particles containing sulphur (Rauch & Morrison 2000). The distribution of particle size in all conducted tests showed that the larger grain size fraction (> 10.2 µm) was the dominating fraction (mean 66%) and the alveolar fraction (< 3.14 µm) was represented by values between 11% and 36% (Artelt et al. 1999a). Moreover, particle sizes of 0.1-20 µm contained platinum varying between 43 and 88 ng/m³ (Inacker & Malessa 1996).

In road dust samples collected in 1984 and 1991 from Göteborg/Sweden, the concentration of platinum showed an increase in all fractions, whereby fraction less than 63 µm

showed the highest platinum content amongst all other fractions (Wei & Morrison 1994a). An increase in palladium concentration from 1994 to 1997/1998 in road dust samples collected from Munich/Germany was demonstrated by Schuster et al. (1999). Furthermore, by comparing the years 1993 and 1994 with 1995 and 1996, an increase of airborne platinum concentrations was detected by Schierl (2000) in samples collected from Munich/Germany. Zereini et al. (2001a) pointed out that particle fractions between 4.7 and 5.8 µm in diameter contained higher platinum concentrations than other fractions of aerosol samples collected from Frankfurt am Main/Germany. Meanwhile, Kanitsar et al. (2003) suggested that most of the platinum and palladium in aerosol samples collected from Vienna/Austria were present in the coarse aerosol mode (10-30 µm) and the highest value was determined in the grain size fractions with AED (Aerodynamic Equivalent Diameter) between 1 and 2.15 µm. In another study from Spain conducted by Gomez et al. (2001), platinum was associated with a wide range of particle diameters but in most cases was highest in the <0.39 µm grain size fraction. Hill & Mayer (1977) pointed out that 80 % of the particles emitted from autocatalysts have a grain size greater than 125 µm and only 20 % were fine grained.

Neither seasonal variations in platinum content determined in dust samples collected from Dortmund/Germany, nor preference for any particular grain size could be observed by Alt et al. (1993). Similarly, platinum showed no seasonal variations during one year (2 years in Gomez et al. 2002) of sampling conducted by Gomez et al. (2001), and rhodium as well. Weather and seasonal conditions had no influence on PGE concentration of dust samples collected by Tilch et al. (2000) from Berlin/Germany and by Schierl (2000) from Munich/Germany. On the contrary, Aboughalma & Stüben (2003) in a recent study concluded that PGE concentrations in road dust samples were higher in winter than in summer, which imply that PGE are subject of seasonal variations.

2.3.1.2 Solubility of PGE Emitted from Autocatalysts

The exact PGE species emitted from car catalytic converters into the atmosphere remain unknown due to the lack of detailed experiments. Therefore, detailed experiments and accurate data on this subject are urgent. From published data it is not clear which species of PGE are emitted from autocatalysts. Nevertheless, Lustig et al. (1997) suggested that metallic platinum (~ 95% of the platinum in automobile exhaust) is insoluble and therefore not bioavailable for plant uptake. In the meantime, volatile platinum oxide (PtO_2) might form at temperatures above 450°C (Albert 1992), which represents a common temperature in catalytic converters (Rauch &

Morrison 2000). Platinum oxidizes at measurable rates for temperatures above ~800°C producing volatile species such as PtO_2 (Alcock & Hooper 1960).

From solubility experiments with dust samples collected and two solutes (deionized water and simulate rain) from the UK, Jarvis et al. (2001) showed a significant difference in solubility of the three elements (platinum, palladium, and rhodium) in both solutes with 35% of the total palladium being soluble in rain at pH 3. A proportion of rhodium present in road dust was also suggested to be in an easily solublized form, while a smaller percentage of platinum can be readily dissolved. They also suggested that palladium was unlikely to be in the metallic form and for example may be present as chloride species. However, the chemical conversion must be a relatively rapid process. Jarvis et al. (2001) predicted that high solubility of palladium in road dust and the potentially adverse health effects are of serious environmental concern. Alt et al. (1993) also reported low solubility values for platinum extracted in diluted HCl (0.07 mol/L) from road dust samples collected from Dortmund/Germany.

The amounts of soluble PGE especially platinum, estimated in some experiments, varied widely. For example, Rühle et al. (1997) postulated 5% soluble platinum species of the total emitted platinum, whereas Hill and Mayer (1977) suggested approximately 10%. Higher values were estimated by Alt et al. (1993) who reported "soluble" platinum values between 30 and 43% (in dilute HCl) from the total platinum amount that was present in dust samples collected from Dortmund/Germany. Far lower amounts of about 1% soluble platinum from the total emitted amount were also estimated by Artelt et al. (1999b).

These findings indicate that the platinum emitted from catalytic converters has a low solubility. However, there is a great concern within the community of environmental scientists since the ever- increasing use of autocatalysts might lead to a wide dispersion of PGE into the environment emitted from automobiles fitted with a catalytic converter.

2.3.2 PGE in the Pedosphere

After emission of PGE from autocatalysts, they are diffused into the atmosphere before deposition onto the ground surface. The concentrations of PGE in soil samples near highways or in inner cities decrease rapidly with increasing distance from the road and are dependent upon traffic density (Ely et al. 2001; Cicchella et al. 2003; Schäfer et al. 1999; Heinrich et al. 1996; Cubelic et al. 1997; Zereini et al. 1993; Zereini et al. 2001a). Zereini et al. (1997a)

reported that the highest PGE values in soil samples collected from Germany were encountered in the uppermost 40 mm. Furthermore, Schäfer et al. (1999) reported that the highest PGE concentrations have been found in the uppermost soil samples (0-20 mm) collected from Pforzheim/Germany in 1996, and were about four times higher than those collected in 1994. Similar trends have been reported by Zereini et al. (1993) who studied soil samples collected along the Highway A66 in Germany, and Cinti et al. (2002) who studied soil samples from Rome/Italy. However, platinum is suggested to be deposited as particles of different sizes on soil surface and has low mobility in soils (Zereini et al. 1993).

A positive correlation with other traffic-related heavy metals such as Ni, Cu, Zn, Pd, Cr, Sn, Co, Ce, and Y has been suggested by several authors, such as Ely et al. (2001), Whiteley & Murray (2003), Heinrich et al. (1996), and Schäfer & Puchelt (1998). Ely et al. (2001) pointed out that the coarser grain size fraction of the soils studied contained almost an order of magnitude lower abundance of platinum, palladium, and rhodium than the fine grained fraction. A transformation of emitted platinum may occur in the atmosphere, on roads, or in soils where it is deposited (Rauch & Morrison 2000; Wäber et al. 1996).

After deposition of emitted platinum onto the soil surface, soluble Pt-complexes might form due to bacteria present in soil (Brubaker et al. 1975). Platinum and palladium differ in their solubility whereas the latter is suggested to be more mobile in the environment than the former (Kothny 1977). Moreover, palladium can migrate either as a true solute or in colloidal form (Pogrebnyak et al. 1986; Wood & Vlassopoulos 1990; Fletcher et al. 1995). The transport of palladium in solution as $PdCl_4^{2-}$ is clearly feasible in relatively acidic soils such as those found in a relatively humid forested environment (Fuchs & Rose 1974). Chloride concentration in a certain medium plays an important role in the transport of PGE. In the presence of suitable ligands such as Cl^-, a certain amount of colloidal platinum has been found to be soluble (Nachtigall et al. 1996). However, at chloride concentrations of about 5 mg/l, Pd^{2+} becomes the dominant dissolved species and the slight mobility of palladium can be achieved even at low chloride concentrations (Fuchs & Rose 1974).

The enrichment of platinum and palladium in the lower soil horizons (B and C), depletion in the A horizon, and transition horizons is suggested by Fuchs & Rose (1974) who mentioned that palladium may occur in the lattice of some clay minerals emphasizing the less noble, more reactive nature of palladium rather than platinum. Furthermore, Wood & Vlassopoulos (1990) concluded that soils have been found to be depleted in palladium relative to platinum,

suggesting that palladium is preferentially mobilized in solution. However, platinum is suggested to be bound on the organic fraction of soils, sediments, and gully-pot sediments (Wei & Morrison 1994b; Fliegel 2003). A higher organic content of gully-pot sediments is suggested to result in a transformation of platinum from an inorganic to an organic bound species (Wei & Morrison 1994b). The oxidation and further transformation reactions in soil may generate PGE species that are available for plants. These platinum species are not soluble and strongly attached to soil, but can be remobilised with platinophile complexing agents, e.g. EDTA (Lustig et al. 1997).

A considerable proportion of PGE has also been found in sewage sludge samples collected from Karlsruhe/Germany by Schäfer et al. (1999) and from Boston Harbour/USA collected by Tuit et al. (2000). They found higher palladium than platinum concentrations suggesting additional palladium sources (not only traffic) and/or palladium reactivity than platinum.

2.3.3 PGE in Living Organisms

Several experiments showed the influence of some PGE-compounds on animals. Sures et al. (2001) and Zimmermann et al. (2001) conducted experiments to determine the bioavailability and uptake of PGE by European eels and Zebra mussels. They reported that PGE are bioavailable and taken up by aquatic animals exposed to grounded catalyst's materials and road dust.

During the production or recycling of catalytic converters, workers are also exposed to elevated PGE concentrations in the surrounding media. Shaller et al. (1992) mentioned that employees exposed during these processes, showed far higher platinum concentration in their urine and blood compared to non-exposed individuals.

Respiratory hypersensitivities have been reported after inhalation of PGE (platinum, palladium, and rhodium) by motorway maintenance workers. Farago et al. (1998) determined the concentrations of platinum in blood and urine of precious metal workers, motorway maintenance workers, and Imperial College staff. The precious metal workers showed the highest platinum concentrations in their urine and blood amongst the examined persons.

2.3.4 PGE in Plant Species

2.3.4.1 Uptake Pathways of PGE by Different Plant Species

From the general point of view, metals present in soil, water, and the atmosphere are available for uptake by plants depending on the surrounding environment. Both essential (such as Zn, Cu, and Mn) as well as non-essential (such as Cd, Pb, and As) metals are normally taken up by roots. They can also be taken up by shoots when present in gaseous or ionic form. At present, PGE (especially platinum) are considered as non-essential metals (Wittke 2002). Prior to the introduction of autocatalysts there were several studies conducted on the uptake of PGE by plant roots. After the first catalytic converters had been introduced in 1974, Brubaker et al. (1975) suggested that the introduction of platinum containing autocatalysts provides a route whereby platinum could enter the environment.

Maier-Reiter & Sommer (1996) and Lustig et al. (1997) found that platinum was mainly located in the vegetative and not in the regenerative organs of the plants and were considered to be taken up through root system only. Messerschmidt et al. (1994) showed that platinum group elements were subject to uptake by plants via stomata. Furthermore, Lustig et al. (1997) mentioned that plants may take up platinum in above-ground parts by adsorption of airborne particles or by dust deposited on plants. Dongarra et al. (2003) studied pine needles (*Pinus pinea* L.) from the city of Palermo/Italy. In their plants, they observed concentrations ranging from 1 to 102 µg/kg for platinum and from 1 to 45 µg/kg for palladium, which have the same order of abundance observed in grass samples collected by Schäfer et al. (1995) and in leaves of plants studied by Hodge & Stallard (1986) collected near areas of intense traffic. PGE concentrations measured in pine needles (*Pinus pinea* L.) collected by Dongarra et al. (2003) from the city centre of Palermo/Italy were far higher than those occurring outside the town indicating a relationship between PGE concentration in plant samples and traffic density.

Verstraete et al. (1998) studied the uptake of $[Pt(NH_3)_4](NO_3)_2$ by grass (*Lolium perenne*) cultivated on a sandy loam soil and cucumber (*Cucumis sativus*) plants grown hydroponically. They concluded that grass (monocotyledonous) slightly and cucumber (dicotyledonous) plants strongly accumulated platinum. This was referred to the amount of platinum added to each

experiment or to the difference in plant species since dicotyledonous accumulate metals to higher extent than monocotyledonous plants.

Lustig et al. (1997) reported that maize (*Zea mays* L), radish (*Rephanus satvius* L.), potato (*Solanum tuberosum* L.), onion (*Allium cepa* L.), and broad beans (*Vicia faba* L.) took up less than 1% of platinum naturally present in the control soil (0.15-0.11 μg/kg), whilst the same plants grown in soil treated with platinum containing tunnel dust took up slightly more platinum. Platinum was found in radish bulbs and in potato peel (treated and control) that contained higher platinum than the storage tissue. However, Lustig et al. (1997) concluded that the amount of platinum uptake is independent of the plant type, whereas Brenchley (1934) demonstrated that the responses to $PdCl_2$ were dependent on the plant species. The uptake of metals, both by roots and leaves, increases with increasing metal concentration in the external medium (Greger 1999).

2.3.4.2 Accumulation of PGE in Different Plant Parts

After the uptake of metals by the root system of plants, they are transported via xylem to the other plant organs, mostly the aerial ones. The transport of metals from the external medium into the cell walls is a non-metabolic passive process driven by diffusion or mass flow (Marschner 1995). During their transportation through the plant, metals get bound largely on the cell walls, which explain why most of the metal taken up by plant roots is commonly found in the roots (90-75%) and smaller amounts are distributed in the shoot (Greger 1999).

However, platinum and palladium were mainly accumulated in plant roots (Sarwar et al. 1970; Malone et al. 1974; Kothny 1979; Pallas & Jones 1978; Rencz & Hall 1992; Ballach & Wittig 1996; Lustig et al. 1997), whilst other researchers mentioned that it was translocated and accumulated in tops (Farago et al. 1979; Farago & Parsons 1986a, 1994; Klueppel et al. 1998; Verstraete et al. 1998; Ballach et al. 2000).

In a study conducted by Farago et al. (1979) on the uptake of platinum and palladium by tomato (*Lycopersicon esculentum* L.), bean (*Phaseolus vulgaris*) , and corn (*Zea mays* L.), there was some transfer to the noble metals to the leaves, and like platinum, palladium was deposited in plant roots. The transport of PGE to the upper organs of the plants is documented in a study conducted by Pallas & Jones (1978). From their results, they concluded that the roots of all species studied contained considerable amounts of platinum, and cauliflower (*Brassia oleracea*

L.), radish (*Raphanus sativus* L.), and bell pepper (*Capsicum annuum* L.) showed uptake into the aerial parts. Furthermore, they found that platinum was accumulated in the cell wall of the roots which could be similar to hydroponic studies conducted by Malone et al. (1974) with corn plants exposed to palladium.

A limited transport of platinum to the shoots of poplar cuttings (*Populus maximowiczii* L.) was suggested by Ballach & Wittig (1996). After six weeks exposure of poplars to 34.8 µg/l of platinum chloride in the nutrient medium, they pointed out that the accumulation of platinum in roots exceeded that of lead, and that platinum was bound even more strongly to cell walls than lead. Moreover, platinum was translocated to upper plant parts to a lower extent than lead. Older leaves of poplar cuttings studied by Ballach (1995) showed very low platinum levels (31.4 µg/kg) indicating a very small transport in the xylem.

From the above mentioned studies, it is clear that PGE were mainly accumulated in plant roots and a transport to the shoots was also considered. Conversely, Sarwar et al. (1970) studied the uptake of palladium by Kentucky bluegrass (*Poa pratensis* L.) grown in the nutrient solutions at different ambient pH with fixed amount of palladium chloride in the nutrient medium. They found 16 µg/g of palladium in roots but no traces of this metal were detected in leaves of Kentucky bluegrass. Moreover, platinum was accumulated in the roots but was not translocated to the tops of water hyacinth (*Eichhornia crassipes*) studied by Farago & Parsons (1994), tomato (*Lycopersicon esculentum* L.) and bean (*Phaseolus vulgaris*) plants studied by Farago et al. (1979), South African grass (*Setaria verticillata*) studied by Farago & Parsons (1986a, 1986b), cucumber (*Cucumis sativus*) studied by Verstraete et al. (1998), and grass (*Lolium multiflorum*) studied by Klueppel et al. (1998).

There are no detailed studies on the accumulation of PGE by the different plant organs. A plant may accumulate high or low amounts of metals depending on which plant organ is analyzed (Greger 1999). Verstraete et al. (1998) indicated that the stem has a significantly higher platinum concentration than the leaves, but roots of grass (*Lolium perenne*) and cucumber (*Cucumis sativus*) plants accumulated the highest concentrations of this metal. In another study conducted by Alt et al. (2002) the palladium content in different parts of endive (*Cichorium endivia* L.) ranged from 7 ng/g and to 17 ng/g (fresh weight), whereas its concentration of edible parts was only determined to be 8.7 ng/g (fresh weight), confirming the uptake of this element.

2.3.4.3 Phytotoxicity of PGE on Plant Species

Since it has been demonstrated that platinum-complexes had marked phytotoxicological effects on plants, there has been interest in the possible effects of PGE on different plant species. Hydroponic experiments conducted on several plant species grown in nutrient media demonstrated the phytotoxicity of PGE compounds on plants. Responses of plants to PGE compounds depend not only on the plant species but also on PGE complexes applied and their concentration in the nutrient solution. Low concentration of PGE complexes in the nutrient solution stimulated the growth of plants (Sarwar et al. 1970; Farago & Parsons 1986a; 1986b).

The phytotoxicity of palladium (II) chloride on plants has been demonstrated in studies conducted by Coupin (1901) and Brenchley (1934). The latter demonstrated that the responses of the crop plants to $PdCl_2$ were dependent on the plant species.

The relationship between phytotoxic symptoms and the metal concentration in the nutrient solution was shown in experiments conducted by Farago et al. (1979). They showed that there was evidence of chlorosis and a slowing of growth at 0.5 mg/l and 2.5 mg/l platinum concentrations in the nutrient medium, whereas little growth was apparent at 5.0 mg/l and roots were yellow and stunted. In addition, there was no growth, severe yellowing and stunting of roots, and necrotic spots on the lower leaves of tomato (*Lycopersicon esculentum* L.), bean (*Phaseolus vulgaris*), and corn (*Zea mays* L.) at higher platinum levels (30 mg/l). At palladium levels between 0.5 and 2.5 mg/l, the plants showed drop off in yield and similar effects were found with platinum treated plants although less drastic than palladium.

In another experiment conducted by Pallas & Jones (1978) there was a relationship between the metal concentration, plant species, and phytotoxic symptoms. The uptake of platinum by radish (*Raphanus sativus* L.), cauliflower (*Brassia oleracea* L.), snapbean (*Phaseolus vulgaris* L.), sweet corn (*Zea mays* L.), pea (*Pisum sativum* L.), tomato (*Lycopersicon esculentum* L.), bell pepper (*Capsicum annuum* L.), broccoli (*Brassia oleracea* L.), and turnips (*Brassia rapa* L.), which were treated with $PtCl_4$ at different concentrations (0.057, 0.57, 5.7 mg/l Pt) and grown hydroponically in a growth chamber, was examined. From their results, they showed that the dry weights were significantly reduced in tomato, bell pepper, and turnip tops as well as in radish roots at the 5.7 mg/l treatment level. After treatment with 5.7 mg/l platinum, the buds and immature leaves of most species became chlorotic and the total Mn content decreased in turnip tops.

The addition of 2920 µg $PdCl_2$ per tray did not affect the growth of Kentucky bluegrass adversely (Sarwar et al. 1970). Furthermore, it has been shown that palladium stimulated the growth of Kentucky bluegrass in concentrations of $PdCl_2$ up to 2000 µg per tray, but it was toxic at 115,000 and 575,000 µg causing the plants to die after one week and after two days, respectively. Endive plants that were grown in nutrient solution containing 100 µg $Pd(NO_3)_2$ at pH 8, showed extreme stress symptoms after two days of treatment where water uptake was reduced and the leaves began to be whitish (Alt et al. 2002).

Hamner (1942) reported that thin sections of leaves showed a thickening of the walls of the leaf tissue, fewer intercellular spaces, more closed stomata, and greater density of protoplasm in the case of the plants which had received the platinum chloride. He also concluded that bean plants treated with platinum chloride were inhibited in growth, had smaller leaf area, higher osmotic pressure, low transpiration rate, resisted wilting much longer than controls, and were less succulent. Tomato plants were inhibited in growth, had chlorotic lower leaves, and resisted wilting longer than controls. Low levels of platinum stimulated water loss of bell pepper and tomato, whereas higher levels decreased water loss within 2 or 3 days.

Metal species and the oxidation state of a metal in its salt applied also play a role. The different PG-metals and their oxidation states have been shown to possess different influences on the plant species. Tso et al. (1973) reported that tobacco (*Nicotiana* L.) plants treated with rhodium chloride showed a slight increase in weight over controls (+0.7%), whereas decreases in weight for other PGE were noted in the order Ru, Ir (-1.9%), Pd (-13.7%), Pt (-21.2%), and Os (-22.7%).

A comparison between the influences of two different oxidation states of the same metal on a plant species has been shown in some studies. Farago & Parsons (1983a, 1983b, 1983c, 1986a, 1986b) showed that Pt (II) was far more toxic than Pt (IV), whereas Rh (III) was relatively non-toxic to *Eichhornia crassipes* and *Setaria verticillata* compared with the other platinum metals. Platinum (II) complexes have been reported to suppress the growth of corn (*Zea mays* L.) roots (Ivanov et al. 1976).

At low concentration levels in the nutrient solution, PGE have tonic effect on plants. For example, low concentration of Rh (III) was not toxic to tomato, bean, and corn but stimulated the growth of tomato and appeared to have a tonic effect (Farago et al. 1979, 1986a, 1986b) as well as for tobacco plants (Tso et al. 1973). Furthermore, platinum as well as rhodium

complexes stimulated the vegetative reproduction in the water hyacinth studied at lower platinum levels (Parsons 1982). Farago & Parsons (1986b) and Bornique et al. (1976) found similar results with *Allium sativum*. Palladium has also been shown to stimulate the growth of Kentucky bluegrass at low concentrations, but it was phytotoxic at higher concentrations (Sarwar et al. 1970; Farago & Parsons 1986a).

2.3.4.4 Species and Binding of PGE in Plant Material

Studies on PGE species in plant materials are rather rare. Nevertheless, some studies were conducted by Messerschmidt et al. (1994, 1995) who found only one platinum species in the molecular weight range of 160-200 kD in native (untreated) grass and several platinum species in platinum-treated grass extracts. They recognized no species in the low molecular weight range (1-2 kD) of their native grass. Klueppel et al. (1998) mentioned that platinum in native grass appears mainly bound to a protein of high molecular mass and in platinum treated cultures, different fractions of low molecular masses dominated. Recently, Weber (2004) pointed out that lettuce grown in palladium treated soil contained low amounts of palladium, which was subdivided into at least 20-25 palladium species differing considerably in their molecular weight.

Alt et al. (2002) found 40% of the total amount of palladium in the cytosol of endive plants (soluble high molecular weight fraction >10 kDa) which was similar to respective values for cadmium in spinach (*Spinacia oleracea* L.) by Guenther et al. (2000) and 60% in the insoluble pellet (residue). Farago & Parsons (1986b) observed that 35% insoluble platinum in grass (*Setaria verticillata*) was associated with α-cellulose and lignin as well as 9.5% associated with soluble pectate. A considerable proportion of platinum (14%) was found to be associated with proteins and amino acids, which could mean that enzymes may be inactivated to a high degree by platinum. Farago & Parsons (1983a) examined platinum-treated roots of *Eichhornia crassipes* by an electron microscope and concluded that platinum was accumulated in the epidermal region and lesser amounts were found in the cortex. In the water hyacinth, the cell wall acts as an ion exchange column trapping most of the platinum, though some was found bound to water soluble pectates (Farago & Parsons 1983a; 1983b).

Chapter III

Methodology

3.1 Experimental Design and PGE Exposure

3.1.1 Field Experiments (Catalyst's Powders)

3.1.1.1 Introduction

The uptake of PGE by plant roots has been postulated by several authors from their experiments which were mainly conducted in growth chambers or glass houses under controlled experimental conditions. Field experiments on the uptake of PGE by crop plants under "natural" conditions are rare. Such experiments near roads are thus of a special interest because they provide a "real" estimation of environmental risk of PGE emissions on plant species that grow near highways or roads with high traffic density. However, the present study deals with the uptake pathways, translocation, and accumulation of PGE in the different organs of two crop plants grown under field (barley (*Hordeum Vulgare* L.) and lettuce (*Lactuca sativa* L.)) and of those plants grown under greenhouse controlled conditions (potato (*Solanum tuberosum* L.), barley (*Hordeum Vulgare* L.) and lettuce (*Lactuca sativa* L.)). It has been reported that heavy metals and PGE are subject to uptake by above-ground organs of plants (mainly grass) collected near roads with high traffic density (Helmers et al. 1994; Helmers & Mergel 1997; Schäfer et al. 1998; Djingova et al. 2003; Dongarra et al. 2003; Lesniewska et al. 2004a).

Both essential (such as Cu, Zn, Fe, P, S, and Mn) and non-essential (Cd, Pb, Hg, Ag, Pt, and Pd) nutrient elements are normally taken up via plant roots and to a certain extent via plant shoots depending on the surrounding environment. Field experiments were conducted to define the uptake pathways of PGE by the crop plants in the present study. The uptake of metals via above-ground plant organs depends on metal concentration in the atmosphere. The PGE concentrations depend on the traffic density since they are emitted from car catalytic converters. Field experiments under "natural" conditions were conducted at two locations. One of the locations is of high and the other of low traffic density. The PGE uptake via aerial parts and their accumulation in organs of crop plants grown at both sites was compared.

The first site was chosen close to the German Highway A5 between Karlsruhe and Frankfurt/Main (SW Germany). The distance between the highway edge and the experimental field is 11 m. The field area, which belongs to Landesamt für Umweltschutz - Baden-Württemberg in Karlsruhe/Germany, is ca. 10 m wide and 25 m long. According to the

Regierungspräsidium/Karlsruhe (2001), the daily traffic density was estimated at ca. 89,500 vehicle/day. Therefore, high amounts of PGE emitted from autocatalysts are expected at this site because PGE determined in grass samples by Wäber et al. (1996), dusts, and soil samples studied by work groups such as Zereini et al. (1993; 1998; 2001a; 2001b) and Verstraete et al. (1998) indicated elevated concentrations along roads with high traffic density.

The second site, which lies in the botanical garden of the University of Karlsruhe/Germany, was chosen as a location without direct influence of traffic. It lies about 200 m from a main street (Adenauer Ring) in Karlsruhe/Germany and is surrounded by high trees, walls, and buildings.

As previously mentioned, the uptake of macro- as well as micronutrients by plants occurs via the roots which represent the principal uptake pathway. The PGE supplied for uptake by the crop plants barley (*Hordeum Vulgare* L.) and lettuce (*Lactuca sativa* L.) via roots was added to the soils as fine-pulverized unused autocatalyst's powders. The PGE concentrations in these powders as provided by the autocatalyst's producer, are listed below in **Table (1)**. The first powder (***CAT$_{Pt}$***) contains a high concentration of platinum in addition to a lesser amount of rhodium. The second powder (***CAT$_{Pd}$***) contains a high concentration of palladium, whilst rhodium content is nearly similar to that of the first powder (***CAT$_{Pt}$***).

Table (1): PGE concentration in the two autocatalyst's powders used in the present field experiments.

Element/Powder	***CAT$_{Pt}$*** Powder	***CAT$_{Pd}$*** Powder
Platinum (µg/kg)	2410 ± 30	<40
Palladium (µg/kg)	< 40	2660 ± 30
Rhodium (µg/kg)	602 ± 7	614 ± 7
Ratio of Pt/Rh and Pd/Rh	4	4

3.1.1.2 Field Experiment with Barley

The first field experiment on the uptake of PGE emitted from catalytic converters by barley plants was conducted at both sites using the autocatalyst's powders listed in **Table (1)**. At the highway site, 15 pots (volume 20 l) were filled with soil from this site which were previously removed (upper 250 mm), homogenized on a plastic sheet (**Picture 1; Plate 1; Appendix A**) and filled into the pots before mixing the catalyst's powders with the pot soils. Furthermore, soil

from a barley field (Owner Mr. Thomas Bacher, Forst/Germany, **Picture 2, Plate 1; Appendix A**) which lies far away (ca. 1500 m) from the same highway was removed (upper 250 mm), homogenised, and filled into 14 plastic pots (volume 20 l). Thereafter, these pots were transported to the botanical garden site. At the highway site 5 pots were treated with $\boldsymbol{CAT_{Pt}}$ (HW-Pt) and 5 pots with $\boldsymbol{CAT_{Pd}}$ (HW-Pd) catalyst's powder in addition to 5 pots that remained untreated as controls (HW-C, control treatments). The same was applied at the botanical garden site (**Table 2**) but with only 4 pots as control treatments of the same soil from the barley field. The experimental design at both sites is illustrated below in **Figure** (**2**).

The upper 100 mm of the soil in each pot was removed and placed on a paper sheet (except control pots), as shown in **Figure (3)**. Then 10 ± 0.02 g of fine grained (≤10 µm) unused autocatalyst powder was added and homogenized by hand mixing it with each pot soil (**Figure 4**) and then refilled again into the pots.

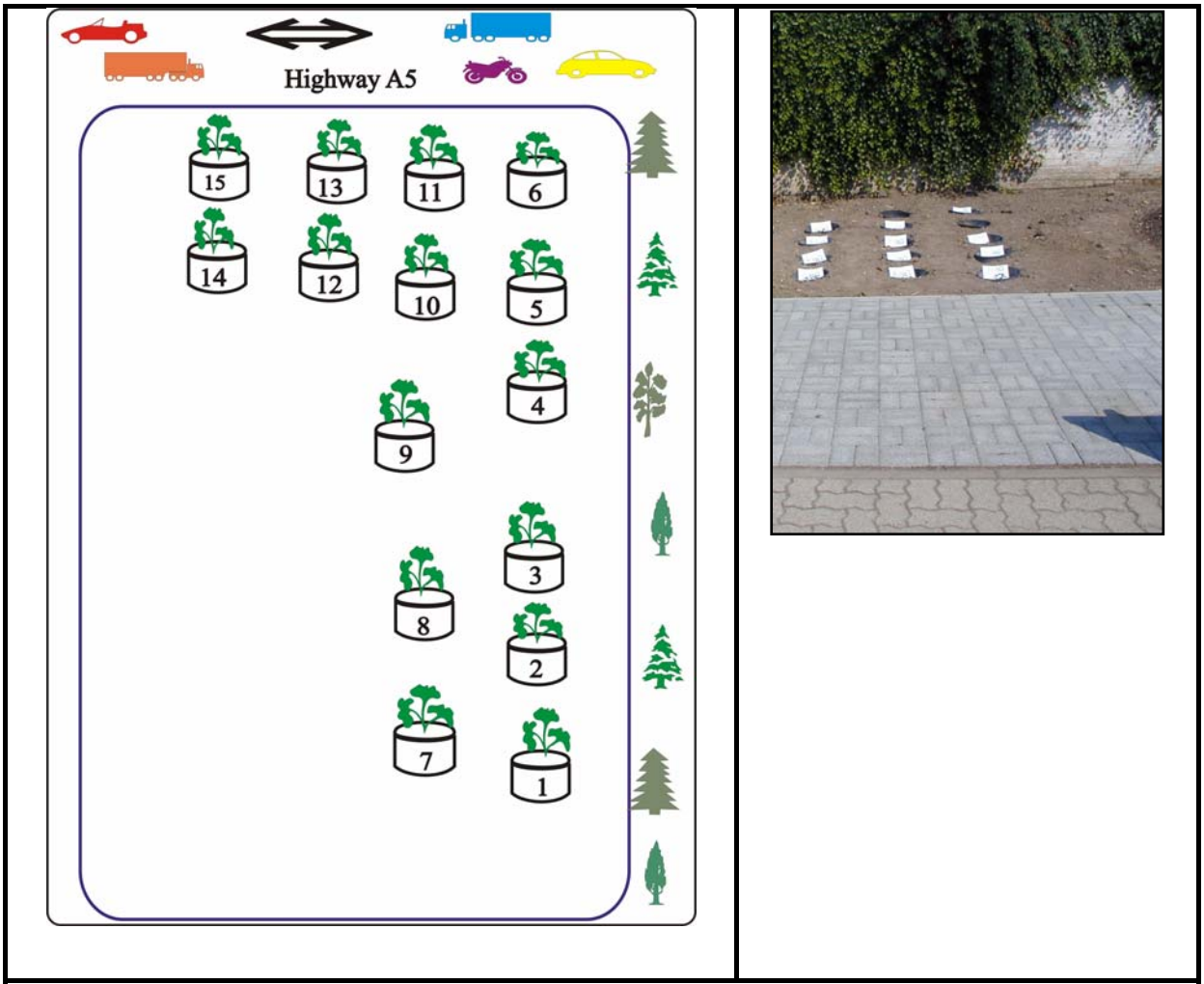

Figure (2): Approximate experimental design of the field experiments with crop plants at the highway (left) and the botanical garden site (right).

Twenty five selected barley seeds (*Hordeum Vulgare* L., var. Basadena) were distributed along five rows of each pot surface (surface area of a pot = 0.06 m^{-2}). The number of barley seeds per pot was calculated using the recommendations of the ZG-Raiffeisen, Karlsruhe/Germany, where the sowing density given is 340 seeds per square meter. The barley seeds in the treated and untreated pots were then covered with a 20 mm thick soil layer and finally irrigated with 5 l of tap water. All plants were irrigated twice weekly with 3 l of tap water except during the rainy weeks (**Picture 3; Plate 1; Appendix A**).

Table (2): Treatment type, label, as well as number of pots from the field experiment with barley (and later lettuce) at both locations. (*) Only three lettuce plants because one plant died.

Locality	**Highway**			**Botanical Garden**		
Treatment Type	***CAT_{Pt}***	***CAT_{Pd}***	***Control***	***CAT_{Pt}***	***CAT_{Pd}***	***Control***
Label	HW-Pt	HW-Pd	HW-C	BG-Pt	BG-Pd	BG-C
Number of Pots	5	5	5	5	5	4(3*)

Figure (3): Preparing the pot soil for treatments with catalyst powder at the botanical garden.

Figure (4): Soil of a pot at the botanical garden after adding and homogenising of 10g grounded catalyst powder for the experiment with barley (later lettuce).

Two fertilizers were prepared to support plant growth: magnesium and phosphorus fertilizers prepared from magnesium sulphate and di-ammonium hydrogenphosphate, respectively. Fertilization was applied during the months of May and June 2002 for the whole

growth period of barley. All chemicals used were of analytical grade (Merck, Darmstadt/Germany). For dewatering of the pot's soil, 12 holes (diameter = 8 mm) were drilled on the base of each pot. Field experiments with barley were conducted from March 29th 2002 until harvesting on August 28th, 2002.

3.1.1.3 Field Experiment with Lettuce

After harvesting the barley in August 2002, the pots of these experiments were left standing in the field until July 28th 2003 to allow PGE present in the soil of the pots (initially added as catalyst's powders) to form soluble species. Rauch & Morrison (2000) and Wäber et al. (1996) suggested that the transformation of emitted platinum may occur in the air, on the road, or in the soil where it is deposited. Furthermore, Brubaker et al. (1975) pointed out that bacteria are able to methylate soluble platinum-complexes which could lead to the formation of toxic complexes. Lustig et al. (1997) mentioned that oxidation and further transformation reactions in soil may generate species available for plant uptake. They also added that platinum was taken up by plants through roots only, which could be due to bacteria methylating platinum species thus enabling easier uptake by roots. Accordingly, PGE present in the autocatalyst's powders, which were added to pot soils in the field experiment with barley, are therefore expected to form bioavailable species in soils by bacteria or other processes.

For these reasons, field experiments with lettuce were conducted in these pots. One (in some pots 2) lettuce plant (*Lactuca sativa* L., var. Estelle) was planted in each pot **(Picture 4; Plate 1; Appendix A**). However, because the Summer of 2003 was relatively warm, plants were irrigated so that soils at both sites were kept moist by daily irrigation with 3 l of tap water during the warm days. The field grown lettuce plants were not fertilized. Field experiments on PGE uptake by lettuce were conducted from 28th July 2003 until harvesting on 3rd October 2003.

3.1.2 Greenhouse Experiments (Soluble PGE Chloride Salts)

3.1.2.1 Introduction

To exclude the uptake of PGE via aerial parts of crop plants and make it exclusively via roots, experiments under controlled conditions without atmospheric deposition were required. For this purpose, the uptake of PGE that were supplied as soluble chloride salts were conducted

in a growth chamber located in the Forschungszentrum Umwelt (FZU), University of Karlsruhe/Germany.

The crop plants; potato (*Solanum tuberosum* L.), barley (*Hordeum Vulgare* L.), and lettuce (*Lactuca sativa* L.) were grown in hydroponic cultures in the growth chamber with lamps providing a light intensity of 250 µmol m^{-2} s^{-1}, relative humidity of 70% and day/night cycle of 16 h/8 h, and at temperatures of 18 and 15 °C, respectively. The hydroponic medium was a diluted and modified Murashige & Skoog (1962) solution (MS) containing the macro- and micronutrients listed below in **Table (3)**. During the first 3 weeks of the experiments with potato and barley as well as during the whole course of the experiment with lettuce, one-half strength MS hydroponic medium was applied. The pH of the nutrient solution was adjusted to 5.7 using diluted HCl and NaOH during the course of all hydroponic experiments.

Table (3): Composition of the MS nutrient solution modified after Murashige & Skoog (1962).

Macroelements	**Symbol**	**Conc. [mg/l]**	**Microelements**	**Symbol**	**Conc. [mg/l]**
Ammonium nitrate	NH_4NO_3	1650			
Potassium nitrate	KNO_3	1900	Potassium iodide	KI	0.83
Magnesium sulfate hyptahydrate	$MgSO_4.7H_2O$	370	Boric acid	H_3BO_3	6.2
Calcium chloride dihydrate	$CaCl_2.2H_2O$	440	Manganese sulfate tetrahydrate	$MnSO_4.4H_2O$	16.9
Potassium phosphate (monobasic)	KH_2PO_4	170	Zinc sulfate hyptahydrate	$ZnSO_4.7H_2O$	8.6
Iron source (mg/L)			Sodium molybdate dihydrate	$NaMoO_4.2H_2$	0.25
Disodium EDTA	Na_2EDTA	37.3	Cupric sulfate pentahydrate	$CuSO_4.5H_2O$	0.025
Ferrous sulfate	$FeSO_4.7H_2O$	27.8	Cobalt chloride hexahydrate	$CoCl_2.6H_2O$	0.025

3.1.2.2 High versus Low Platinum and Palladium Concentrations in the Hydroponic Medium

There is no data available on the proportion of PGE present in natural soils and bioavailable for plant uptake. Nevertheless, several experiments were conducted on the uptake and phytotoxicity of PGE soluble salts on different plant species grown in hydroponic media. Michenfelder et al. (1988) reported that visible phytotoxic effects occur at PGE concentrations in

the nutrient medium that were higher than 2.5 mg/l. Furthermore, Farago & Parsons (1986b) conducted experiments on the effects of platinum and rhodium applied at different levels of concentration to grass. They concluded that at 0.5 mg/l levels, platinum and rhodium showed tonic effects, but at a concentration of 2.5 mg/l and higher, the noble metals were phytotoxic. In the present study two different platinum and palladium concentrations were chosen. One high (2000 µg/l) and one low (300 µg/l) noble metal concentration in the hydroponic medium were added to compare their uptake via roots only, translocation into crop plant shoots, accumulation by the organs of different crop plant species, and their phytotoxicity on the plant species under study.

The uptake of heavy metals by monocotyledonous plants is lower than dicotyledonous plants. Verstraete et al. (1998), who after experiments with grass and cucumber plants concluded that the dicotyledonous plant (*Cucumis sativus*) accumulated platinum to a higher extent than the monocotyledonous plant (*Lolium perenne*). Potato (*Solanum tuberosum* L.) and lettuce (*Lactuca sativa* L.) are dicotyledonous plants, whereas barley (*Hordeum Vulgare* L.) is a monocotyledonous plant. Therefore, potato (**I**) and barley were exposed to a high platinum and palladium concentration (2000 µg/l) to compare differences in uptake, translocation, and accumulation between a dicotyledonous and a monocotyledonous plant. Furthermore, to compare two dicotyledonous plants, potato (**II**) and lettuce were exposed to a low (300 µg/l) concentration of platinum and palladium as soluble chloride salts, which were added to the hydroponic medium. To differentiate between the two treatments applied to potato plants, experiments with potato were labelled as follows: Potato (**I**) which was treated with a high-concentration (2000 µg/l) and Potato (**II**) which was treated with a low-concentration (300 µg/l) of platinum and palladium chloride salts.

Platinum and palladium were added separately to the nutrient medium as chloride complexes ($PtCl_4$ and $PdCl_2$), which were supplied by Alfa Aeser, Johnson Matthey GmbH. Karlsruhe/Germany, as Specpure® AAS-Standard solution (1000 ± 2 mg/l in 20% HCl). After the addition of platinum and palladium chlorides to the nutrient solution, the pH was adjusted to 5.7 and the solution was left over night to react. Prior to the transfer of the nutrient medium into the pots, the pH was again adjusted to 5.7.

Four pots were treated with $PtCl_4$ (Pt-treatments), 4 with $PdCl_2$ (Pd-treatments), and 4 controls remained untreated during the experiments with potato (**II**), barley, and lettuce, whereas potato (**I**) only two pots of each treatment were used. Nutrient medium in all pots was

continuously aerated using an aquarium pump to circulate the solution and was changed weekly. Furthermore, the nutrient solution was replenished once time every week so that the roots of all plants, but not all potato tubers, remained submerged and the pH was adjusted.

3.1.2.2.1 High-Level Platinum and Palladium Treatments (2000 µg/l)

3.1.2.2.1.1 Growth Chamber Experiment with Potato (I)

Potato tubers with a single sprout and of equal size ((*Solanum tuberosum* L., var. Christa) obtained from the Landesanstalt für Pflanzenbau Forchheim, Saatbauamt Donaueschingen/Germany were germinated in darkness, then planted in small plastic pots filled with peat in a greenhouse, and irrigated with tap water until the plantlet height was about 100 mm. Before transferring plantlets to the growth chamber, similar plantlets (in terms of growth) were chosen and their roots were cleaned from peat under tap water. Thereafter, the plantlets were transferred to cylindrical plastic pots (one plantlet per pot) which were filled with 3 l of a MS nutrient solution (see **Table 3**). Before transferring the plantlets into the growth chamber, the nutrient medium stood for one week in the growth chamber to allow sufficient aeration of the medium. The exposure of potato plants to 2000 µg/l platinum and palladium chlorides started after day 42 of planting the plants in the growth chamber. Nutrient medium containing 2000 µg/l PGE salts was changed twice (i.e. the exposure duration was for two weeks).

3.1.2.2.1.2 Growth Chamber Experiment with Barley

Barley seeds (*Hordeum Vulgare* L., var. Pasadena) obtained from LUFA (Staatliche Landwirtschaftliche Untersuchungs- und Forschungsanstalt Augustenberg, Karlsruhe/Germany) were germinated in darkness in a box filled with styrofoam and watered with a diluted MS medium. Selected plantlets (20 plantlets per pot) of equal size and length were transported to 3 l plastic pots filled with MS medium one week before. After planting in the pots, plants were grown for 40 days before exposure to platinum and palladium chloride complexes for an additional 28 days.

3.1.2.2.2 Low-Level Platinum and Palladium Treatments (300 µg/l)

3.1.2.2.2.1 Growth Chamber Experiment with Potato (II)

At the low-concentration levels (i.e.300 µg/l) of platinum and palladium, the same procedures in terms of tuber source, germination, planting in the growth chamber, and nutrient medium were applied as shown in the first experiment with potato (**I**). The exposure of potato plants to 300 µg/l platinum and palladium chlorides started after day 33 of planting the plantlets in the growth chamber. Nutrient medium containing 300 µg/l platinum and palladium chloride salts was changed four times. The total exposure duration was 28 days.

3.1.2.2.2.2 Growth Chamber Experiment with Lettuce

Lettuce (*Lactuca sativa* L., var. Estelle) plantlets (80 mm height) were obtained from Fa. Postweiler, Karlsruhe/Germany and after removing the peat from the roots using tap water, they were planted in plastic cylindrical pots containing 3 l of MS medium (one-half strength during the whole course of the experiment). After two weeks of planting in the growth chamber, the lettuce plants were exposed to $PtCl_4$ and $PdCl_2$ for a period of 31 days. During this period, the nutrient solutions containing platinum and palladium chloride complex were changed four times.

3.1.2.2.3 Visible Phytotoxic Symptoms after Treatment with $PtCl_4$ and $PdCl_2$

Visible phytotoxic symptoms were manifested during the course of all experiments. The physiological situation of all treated and untreated plants was documented continuously. Changes in leaf colour, leaf area, root properties, and plant growth were documented using photographs. Selected photographs are shown in **Plates 2 and 3; Appendix A.**

3.1.3 Determination of Plant Physiological Parameters

In addition to the manifestation of the phototoxic symptom of the greenhouse plants, further physiological parameters were determined to describe the effects of PGE application on the crop plants. Gas exchange and fluorescence measurements, pigment content, leaf area, and fresh and dry weight were determined as shown below.

3.1.3.1 Photosynthetic Gas Exchange and Transpiration

Photosynthetic gas exchange and transpiration were measured by Porometer (LCA-4, Analytical Development Co. Lmt., ADC, Hoddesdon, UK). All measuring parameters were automatically saved on a LCA-4 data card every 30 s. A measuring sequence consisted of:

- 5 minutes in darkness (darkened with black felt cloth) – dark respiration.
- 30 minutes (15 minutes for barley) under white light (halogen light source 50 W, PAR = 1100 µmol/m²/s at leaf surface) – net photosynthesis.
- The following parameters displayed on Porometer were selected for describing the state of health of the plants:

CO_2 gas exchange (µmol/m²/s)

This gives (a) the amount of CO_2 released during mitochondrial respiration in the dark and (b) the amount of CO_2 uptake during the light period, which represents the total of photosynthetic CO_2 uptake and CO_2 released by mitochondrial respiration and photorespiration (= net photosynthesis). With increasing light intensity, net photosynthesis rises up to a saturation maximum. The height of this maximum depends on the growth conditions of the plants (it is low for plants grown under shade and high for plants grown under full sun light). The highest values for Photosynthetically Active Radiation (PAR) under cloudless sky in high summer months in Karlsruhe are usually around 1700 µmol/m²/s (Buschmann 2002, personal communication). Under light conditions chosen in the present experiments, the CO_2 uptake due to the photosynthetic activity is much higher than CO_2 release due to the two respiration processes and the net photosynthesis being saturated.

Transpiration (mmol/m²/s)

The transpiration rate gives the amount of water released by leaves. Irrespective of the opening state of the stomata, this water is mainly released through the opened stomatal pores and to a smaller amount by the total leaf surface (cuticular transpiration). The transpiration rate depends on the opening of the stomata (see stomatal conductance below), the availability of water in the leaf, and the capacity for water uptake of the air surrounding the leaf.

Stomatal conductance (mmol/m²/s)

The stomatal conductance describes the opening state of the stomata. Low values of the stomatal conductance (mmol/m²/s) indicate that stomata are supposed to be closed, whilst increasing values describe open stomata. The stomatal conductance is expressed as a value, which controls (either restricts or allows) the transpiration rate.

From each plant (treated und untreated), 4-5 selected lettuce (4th and 5th leaf from the apex), barley (flag leaves), and potato (leaves from the 3rd apical branch below the apex of the main branch) were used for the photosynthetic gas exchange measurements. The measurements using a Porometer were conducted after 56, 25, 32, and 35 days from planting of potato (I), barley, potato (II), and lettuce, respectively, in the growth chamber. All measurements were conducted in the greenhouse under the following experimental conditions:

PAR: 1100 µmol/m²/s
Leaf chamber mass flow [µmol/s]: 250 (Potato I and lettuce), 300 (Potato II), 150 (barley).
Leaf area [cm²]: 6.25 for all plants except barley (was calculated and implemented in the Porometer software before measuring).

3.1.3.2 Chlorophyll Fluorescence

The chlorophyll fluorescence induction kinetics were measured with a portable two-wave length Fluorometer (CFM-636973, Institute of Atomic Physics, Technical University of Budapest/Hungary). The fluorescence measurements have been conducted on leaf discs which were punched out from the plant leaves by a cork borer (diameter 6-8 mm). Prior to measurement, the leaf discs were pre-darkened for 15 minutes. Fluorescence data were collected for 3-5 minutes. The intensity of the excitation light was set to 4.5 – 3.0 mW. Data collected by the fluorometer were converted into an Excel worksheet on an external computer. The following parameters were chosen for describing the state of health of plants:

Rfd: ratio fluorescence decrease (Lichtenthaler et al. 1983).

The Rfd values describe the potential strength of photosynthetic light quanta conversion. It is directly related to the function of the photosynthetic electron transport around photosystem II

(for review, see e.g. Strasser et al. 2000). Some authors call it a "Vitality index" which is directly correlated with photosynthetic CO_2 fixation under open stomata (Babani & Lichtenthaler 1996). Rfd values lie usually in the range between 0 and 5, where 0 means photosynthetic inhibition and 5 represents a maximum photosynthetic quantum conversion. From each plant (treated und untreated), one leaf disc from: 4-5 selected lettuce (4^{th} and 5^{th} leaf from the apex), barley (flag leaves), and potato (leaves from the 3^{rd} apical branch below the apex) on which the photosynthetic gas exchange was previously applied, were separated and used for leaf pigment extraction.

3.1.3.3 Content of Chlorophylls and Carotenoids

3.1.3.3.1 Chlorophylls and Carotenoids Determined in Acetone Extract

Chlorophyll *a* and *b* and the sum of carotenoids (in green leaves mainly: Lutein, beta-carotene, violaxanthin, antheraxanthin, and neoxanthin) were determined from acetone extract. Leaf discs were punched out from the plant leaves using a cork borer (diameter 6-8 mm) and immediately frozen at – 24°C. The extract was prepared with acetone as solvent using a mortar or a micro dismembrator II (Braun Melsungen AG., Germany). The extract was filled up to a volume of 4 ml and then centrifuged for 5 minutes at 1500 rpm (Varifuge RF Inert, Heraeus Sepathech, Hanau/Germany) to get a clear solution.

Finally, the absorbance of the extract was measured by a two-beam spectrometer (Perkin Elmer, Lambda 2 UV/VIS Spectrophotometer) at the wave lengths 470, 644.8, 661.6, and 750 nm. The quantity of chlorophylls and carotenoids was calculated after Lichtenthaler (1987) and then expressed on a leaf area basis (mg/m²). The content of leaf pigments (chlorophylls and carotenoids) is a primary indicator for plants state of health since the leaf pigment guarantees the absorption of light energy necessary for photosynthesis. High amounts of carotenoids compared to chlorophylls are visualized as yellowish green leaves (e.g. very young leaves or older leaves under stress conditions). From each plant (treated und untreated), two leaf discs from: 4-5 selected lettuce (4^{th} and 5^{th} leaf from the apex), barley (flag leaves), and potato (leaves from the 3^{rd} apical branch below the apex), were separated and used for leaf pigment extraction.

3.1.3.3.2 Chlorophylls Determined by SPAD Measurement

The Chlorophyll-meter (SPAD 502, Minolta Camera Co., Ltd., Osaka, Japan) is a tool for non-destructive chlorophyll detection in intact plant leaves. From transmittance measurements in the red (650 nm) and near infrared light (940 nm) a value (called SPAD units), which correlates with the chlorophyll contents of the leaves (Richarson et al. 2002) was calculated.

From each crop plant (treated und untreated), the SPAD units of 5-10 selected leaves was determined. Ten to fifteen separate measurements from each leaf were conducted at several leaf positions and an average value was calculated.

3.1.3.4 Leaf Area Index

The leaf area was determined on the same leaves used for photosynthetic gas exchange, pigment extraction, SPAD, and fluorescence measurements. This was applied by using a portable leaf area meter (Li 3000; Li-COR Inc., USA).

3.1.3.5 Fresh and Dry Weight

The fresh and dry weights were determined by punching out two leaf discs using a cork borer (diameter 6-8 mm) from the plant leaf. The leaf discs were immediately weighed and thereafter air-dried at 90° C over night.

3.2 Sampling and Sample Preparation

The roots of field grown plants were not considered in the present study due to the high concentration of PGE added to the soils as catalyst's powder which is difficult to remove from root surface by washing. Therefore, PGE concentration in roots of the field grown plants were not determined to avoid data misinterpretation.

To define the PGE accumulating organs, plants were divided into their different organs. The potato plants grown in the growth chamber were divided into leaves, leaf stalks, stems, tubers, and roots including stolons. The tubers of the growth chamber potatoes were not peeled due to their small size and the lesser amount of tubers obtained from the experiment with Potato I conducted with high platinum and palladium concentration (2000 µg/l) in the nutrient solution.

The field grown barley plants were harvested in October 2001 and divided into 4 groups: Leaves, stalks, seeds, and kemps. Barley plants grown in the growth chamber were divided into shoots and roots only due to the short growth period. The shoots of the field grown lettuce plants were harvested in October 2003 and not subdivided into leaves and stems (the above-ground parts were used for the PGE determination), whereas those grown in the growth chamber were subdivided into leaves, stems, and roots.

All samples of field grown plants were carefully washed using distilled water in an ultrasonic path for 7 minutes to remove any surface soil or dust deposits and rinsed using bi-distilled water. The ultrasonic washing step was not applied for greenhouse plants including roots, but were washed under tap water and rinsed with bi-distilled water. All samples were placed on a plastic net and were allowed to dry under room conditions for one day before freezing.

All plant samples collected from the field and growth chamber experiments were freeze dried. A test with non-experimental tubers was conducted to choose the suitable drying method. The freeze drying of plant samples was more suitable than air drying, especially in the case of potato tuber samples.

The freeze dried potato samples were ground in an agate mill for either 4 (leaves, leaf stalks, and tubers) or 7 minutes (stems). All barley samples were ground in agate mill for 6 minutes. The lettuce samples were ground for either 4 (leaves of field and growth chamber grown plants) or 6 minutes (stems of growth chamber plants). The grinding step of all plant samples was designed to grind all samples of the control treatments before the treated ones. The platinum treated plants were ground before the palladium treated plants. During the grinding of PGE treated plant samples, plant organs with expected low concentration were ground before those with expected high PGE concentrations. For example, potato organs were ground separately as follows: tubers, stems, leaves, leaf stalks, and finally roots. The agate mill was carefully cleaned and washed after grinding of each treatment and plant organ from the same treatment. This was done by grinding 3 ml quartz sand and washing using distilled water.

Since PGE concentrations in environmental samples are low, a pre-concentration step of PGE in plant samples was necessary. However, the finely ground plant samples were weighed into a glass beaker and ashed for 12 h at 250°C and 450°C for an additional 12 hours in a muffle oven. After a complete cooling the loss on ignition was calculated (**Table 1B to 5B; Appendix B**). During the ashing process the PGE are pre-concentrated, some matrix elements are eliminated and Pd is oxidized to the more soluble PdO (Dunn et al. 1989).

3.3 Analytical Methods of PGE Determination in Plant Samples

3.3.1 Microwave Digestion of the Plant Samples

About 0.5g to 1.0g of ashed plant sample was weighed into a 100 ml PTFE-Microwave (ETHOSplus 1600, MLS GmbH Leutkirch/Germany) vessel. After sample weighing, different spike solutions containing ^{198}Pt, ^{105}Pd, ^{99}Ru, and ^{191}Ir (Oak Ridge National Laboratory, Oak Ridge/USA) were added to the field grown plant samples. The spike addition to growth chamber plant samples was applied depending on the treatment type. This means a proper amount of platinum spike solution (^{198}Pt) was added to the platinum treated plants and palladium spike (^{105}Pd) was added to the palladium treated ones. This was applied for the aerial plant organs as well as the potato tubers of the growth chamber plants, whereby the root samples were not spiked due to the expected very high PGE concentration in these plant organs.

Table (4): Operating settings of the microwave digestion procedure of the plant samples.

	Time (min)	Temperature (°C)	Power (W)
Microwave program Nr. 12			
Step 1	3	180	250
Step 2	1	180	0
Step 3	3	180	400
Step 4	5	180	0
Microwave program Nr. 14:			
Step 1	3	180	500
Step 2	2	180	0
Step 3	4	180	500
Step 4	2	180	0
Step 5	4	180	600
Step 6	1	180	0
Step 7	4	180	600
Step 8	45	-	0

Thereafter, the microwave decomposition was applied by adding 5 ml HNO_3 (65 vol. %, sub-boiled, Merck, Darmstadt/Germany), 3 ml HCl (30 vol. %, s.p., Merck, Darmstadt/Germany) as well as 0.5 ml of the oxidative agent H_2O_2 (30 vol. %, s.p., Merck, Darmstadt/Germany) to each plant sample. The microwave digestion of the plant samples was conducted by running the two microwave programs 12 and 14, as recommended by the producer for plant samples. The operating parameters of the microwave apparatus are listed in **Table (4)**. However, the field grown barley samples were decomposed by further addition of 0.250 ml HF before the microwave decomposition step to dissolve silicates present in these samples.

A microwave decomposition patch consisted of 9 samples and a blank, which was treated in the same manner as the plant samples. After each microwave decomposition patch, all vessels were cleaned by adding aqua regia HCl: HNO_3 (ratio = 1:3) and applying the two microwave programs 12 and 14 as listed in **Table (4)**. The cleaning step of the microwave vessels was repeated twice to guarantee clean vessels for the next microwave digestion of other plant samples. The microwave vessels were left to cool and degas before opening for filtration.

To avoid the so called "memory effect" in the microwave vessels, samples with expected low PGE concentrations, such as control treatments, were digested before the PGE-treated ones of the same experiment.

3.3.2 Tellurium Co-Precipitation

After the microwave decomposition step, samples were filtrated using cellulose acetate filters (pore size 0.45 µm, Sartorius AG, Göttingen/Germany) followed by evaporation near dryness on a hot plate and a further decomposition in HCl (30 vol. %, s.p., Merck, Darmstadt/Germany). The analytes were separated by the co-precipitation on Tellurium (Te plasma standard solution, Specpure®, Te 10.000 µg/l, Johnson Matthey, Karlsruhe/Germany) using $SnCl_2 . 2H_2O$ (GR for analysis, Merck, Darmstadt/Germany**)** as a reducing agent.

After complete reduction, the precipitate was filtered on a cellulose acetate filter, rinsed with 1 M HCl (30% vol., s.p, Merck, Darmstadt/Germany), and finally re-dissolved in aqua regia (HCl: HNO_3; ratio = 1:3, s.p. and sub-boiled, respectively, Merck, Darmstadt/Germany). After evaporation to about 1-2 ml the solution was made up to 10 ml with 1% HNO_3 (65 vol. %, sub-boiled, Merck, Darmstadt/Germany) for determinations of PGE. This method is described in Dunn et al. (1989); Hall et al. (1990); Jackson et al. (1990); Rencz & Hall (1992). It should be

mentioned that ashed samples of some plant organs such as the stems of growth chamber lettuce were sometimes low in weight (i.e. lower than 0.5 g). Nevertheless, the sample weighed into microwave vessels was almost kept at one gram ashed sample.

3.3.3 Isotope Dilution and Spike Optimization

The PGE concentration in all plant samples was determined by high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) after isotope dilution and tellurium co-precipitation. The isotope dilution has long been regarded as the most accurate means of measuring elemental abundances, provided that isotope ratio can be measured with sufficient accuracy and precision (Heumann 1988). However, there is a limiting factor for the isotope dilution technique which includes the difficulty in finding two isotopes free from isobaric interferences and the need for some ability to predict likely sample concentrations so as to optimize spike amounts (Heuzen et al. 1989).

To estimate the concentration of the PGE in the different plant organs, and to optimize the amount of PGE-spikes to be added for the isotope dilution analysis, plant samples from each experiment were chosen for this purpose. One sample from each plant organ was chosen and analyzed in a first "estimation" step before the main course of PGE determinations without addition of any spike solutions. After the estimation of the PGE concentration in a plant organ, a proper amount of spike solution(s) was added to each plant organ. Roots of plants grown in the growth chamber were not spiked due to the expected very high PGE concentration in these organs since they are in intimate contact with the hydroponic medium.

3.3.4 Analytical Techniques

3.3.4.1 Mass Spectrometry

The PGE concentration in samples was determined by high resolution ICP-MS (Axiom, VG Elemental, Cheshire/England). Calibrations were carried out by preparing standard solutions (0.1, 0.2, 0.5, 1.0, 2.5, 5.0, 10.0, 25.0, 100.0*, 250.0*, 500.0* and 1,000.0* µg/l, whereby (*) indicate standards prepared for growth chamber plants as well as roots) from a PGE multi-element standard (ICP-Multielement Standard C, Spex CertiPrep, Metuchen/USA, 10,000 µg/l).

The following atomic mass units were measured: ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{198}Pt, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{103}Rh as well as ^{104}Pd, and ^{110}Pd to check interferences on Pd. Furthermore, some heavy metals such as ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{178}Hf, ^{181}Ta, ^{182}W, and ^{111}Cd that might be present in the sample matrix after the tellurium co-precipitation were also measured since they can cause interferences on PGE during the ICP-MS measurements.

Platinum concentration in the plant sample digest was determined by calculating the isotope ratios: $^{194}Pt/^{198}Pt$ $^{195}Pt/^{198}Pt$, and $^{196}Pt/^{198}Pt$. The final platinum concentration in each sample was determined by calculating the mean value of the two non-spiked isotopes (^{195}Pt, ^{196}Pt). Rhodium concentration was determined without using isotope dilution since rhodium is a mono-isotopic element. However, rhodium concentration in plant samples was determined from a calibration line.

Table (5): Instrumental settings of the Axiom (VG Elemental, Cheshire, England).

Instrument:	**Axiom (VG Elemental)**
Forward power:	1350 W
Reflected power:	< 20 W
Sampling uptake rate:	1 ml/min
Scan mode:	Magnet scan
Torch:	Quartz torch (Glass Expansion, Melbourne/Australia)
Nebulizer:	Meinhardt (Glass Expansion, Melbourne/Australia)
Spray chamber:	Conical impact wall (bead)
Temperature of spray chamber:	10 ± 1°C
Cones:	
Sampling cone:	Ni, 1.0 mm
Skimmer cone:	Ni, 0.7 mm
Argon gas flows:	(l/min)
Cool gas:	13.5-14.1
Auxiliary gas:	0.55-0.65
Nebuliser gas:	0.80-0.90
Data Acquisition parameters:	
Acquisition mode:	Pulse counting
Runs:	3
Acquisition time:	
Wash time:	115 s
Dwell time: 40 ms (for Resolution = 9000), 30 ms (for Resolution = 1000)	
Points per peak width:	20
Sweeps per peak:	1
Resolution m/Δ m (isotopic abundance %): 1,000 (^{195}Pt (33.8), ^{196}Pt, ^{198}Pt); 9,000 (^{104}Pd, ^{105}Pd (22.23), ^{106}Pd, ^{108}Pd, ^{110}Pd and ^{103}Rh (100))	

After separation of PGE from matrix elements present in plant samples by tellurium co-precipitation, mono- as well as poly-atomic interferences on palladium isotopes during the ICP-MS measurements must be corrected. The isobaric interferences of ^{104}Ru on ^{104}Pd and ^{110}Cd on ^{110}Pd as well as the polyatomic chlorine clusters $^{35}Cl_3H$ and $^{35}Cl_2{}^{37}ClH$ on ^{106}Pd and ^{108}Pd, respectively, must be eliminated. These have been mathematically corrected by implementing equations of Kramar (2002, personal communication) in the Axiom software package supplied by Thermo Elemental® as follows:

The isobaric interferences of ^{104}Ru on ^{104}Pd and ^{110}Cd on ^{110}Pd are explained on the following example of ^{104}Ru on ^{104}Pd:

$$I(^{104}Pd)corr. = I(^{104}Pd)meas. - [I\,(^{101}Ru)meas. - A_{ii}/A_{ir}]$$

Whereby:

$I(^{104}Pd)corr.$ → = corrected counts per second (CPS) of ^{104}Pd after elimination of the isobaric interference

$I(^{104}Pd)meas.$ → = CPS of ^{104}Pd measured by ICP-MS

$I\,(^{101}Ru)meas.$ → = CPS of ^{101}Ru measured by ICP-MS

A_{ii}/A_{ir} → = ratio between the natural abundances of the isotope interfered (^{104}Ru) and a reference isotope of the same element (^{101}Ru)

$A_{ii}/A_{ir}\,(^{104}Ru/^{101}Ru) = 1.09$

$A_{ii}/A_{ir}\,(^{110}Cd/^{111}Cd) = 0.97$

The $^{35}Cl_2{}^{37}ClH$ clusters on ^{108}Pd were mathematically corrected as follows:

$$I(^{108}Pd)corr. = I(^{108}Pd)meas. - 0.47\,[I\,(^{106}Pd)meas. - I(^{108}(Pd)meas.)]$$

Whereby:

$I(^{108}Pd)corr.$ → = corrected counts per second (CPS) of ^{108}Pd after elimination of the polyatomic interference

$I(^{108}Pd)meas.$ → = CPS of ^{108}Pd measured by ICP-MS

0.47 → $= H(^{37}Cl)/(H(^{35}Cl) - H(^{37}Cl))$

$H(^{x}Y)$ → = natural abundance of the isotope Y with the mass number x

$I\,(^{106}Pd)meas.$ → = CPS of ^{106}Pd measured by ICP-MS

$I(^{108}(Pd)meas.$ → = CPS of ^{108}Pd measured by ICP-MS

The elements; ^{165}Ho, ^{169}Tm, ^{115}In, and ^{209}Bi were used as internal standards. Instrumentation and operating settings of the HR-ICP-MS (Axiom, VG-Elemental, Cheshire/England, with Meinahrdt nebulizer) are summarized in **Table (5)**.

The mean concentration and standard deviation of PGE (platinum, palladium, and rhodium) in the different plant organs of all experiments are shown in **Appendix B**.

3.3.5 Limit of Detection

The Limits of Detection (LOD) were calculated as three times the standard deviation of Pt, Pd, and Rh concentrations determined in all procedural blanks (**Table 6B and 7B; Appendix B**), which were prepared in the same manner like the plant samples (chemical amounts, digestion, and Te co-precipitation).

Method detection limit is that concentration equivalent to three times the standard deviation (3* Σ) of all blanks taken through the procedures of sample decomposition, separation and analysis. The LODs determined were: 0.35, 0.44, and 0.02 µg/l for platinum, palladium, and rhodium, respectively. Furthermore, limit of determination of ICP-MS was calculated by running blanks consisting of 1% HNO_3 during the PGE determinations in plant samples. The limit of determinations calculated were: 0.03 µg/l for platinum and palladium and 0.002 µg/l for rhodium.

3.3.6 Analytical Reproducibility

Although there is a wide range of analytical techniques available for the quantitative determination of the platinum group elements in the different environmental samples, there is no Biological Standard Reference Material for the precious metals in vegetation containing certified concentrations of PGE. Therefore, isotope dilution is considered as a powerful method to determine trace amounts of PGE in environmental samples, provided interferences caused by matrix elements are eliminated. Tellurium co-precipitation has been applied to eliminate these matrix elements present together with PGE in plant samples.

However, our results using this methodology for platinum, palladium, and rhodium in plant organs agree very well with those obtained from independent methodologies conducted by Dr. F.

Alt (Institute of Spectrochemistry and Applied Spectroscopy (ISAS), Dortmund/Germany). The platinum and rhodium concentrations in some replicate potato samples were determined by adsorptive voltammetry analysis and palladium was determined by total reflection X-ray fluorescence (TR-XRF). Data are listed in **Table 8B; Appendix B**.

Figures 5, 6 and 7 show the comparison of PGE determinations conducted at the Institut für Mineralogie und Geochemie (IMG), Universität Karlsruhe/Germany and ISAS. Data from Klueppel et al. (1998) showed that the ICP-MS determination of platinum in grass samples was lower than the adsorptive voltammetry analysis of PGE (**Figure 8**). This was the same case for platinum and rhodium in the present study.

Moreover, potato samples were analyzed in duplicate and showed reproducibility very well, indicating well sample preparation and the homogeneous distribution of PGE in all plant samples examined here **(Figures 9, 10 and 11; Table 9B; Appendix B).**

Furthermore, a leaf sample of field grown potato plants was prepared. The PGE concentration in this sample was determined by applying PGE replicate measurements (9 replicates). Results are shown in **Figure (12)** that also indicates reproducibility very well.

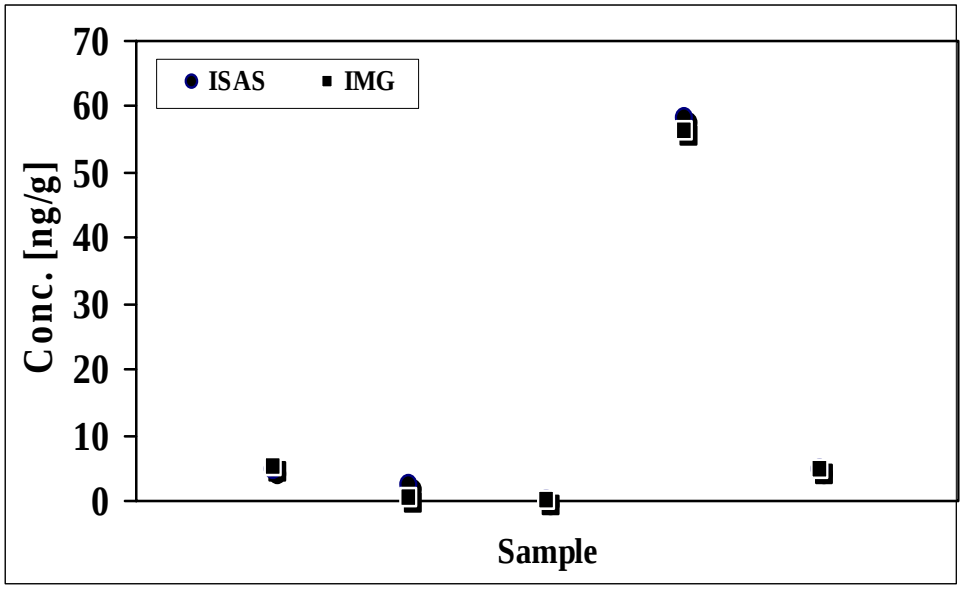

Figure (5): Platinum concentration (ng/g DW) in potato samples determined at ISAS and IMG.

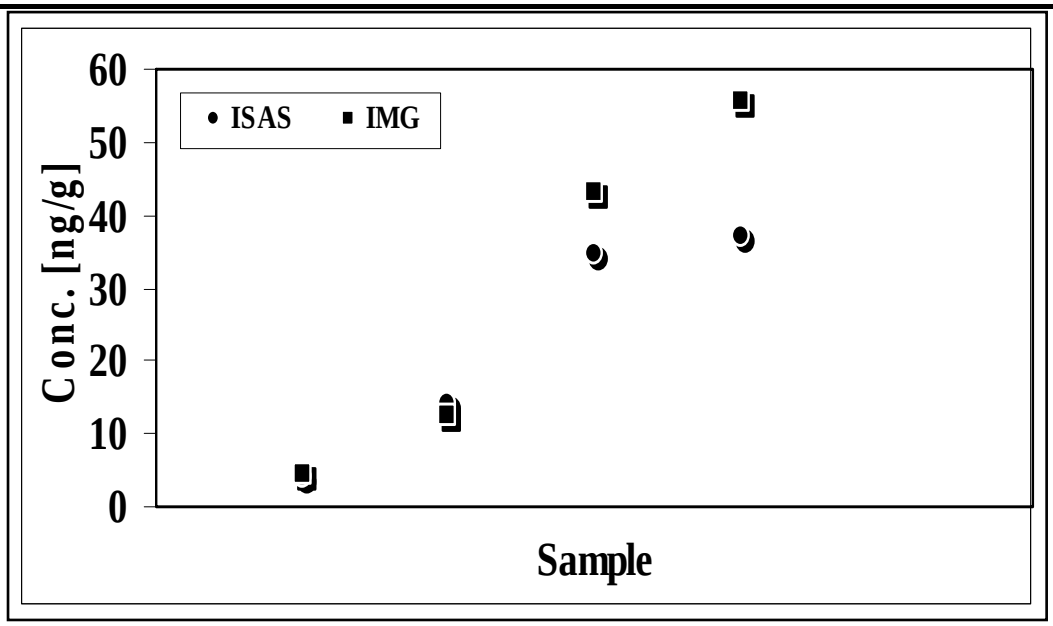

Figure (6): Palladium concentration (ng/g DW) in potato samples determined at ISAS and IMG.

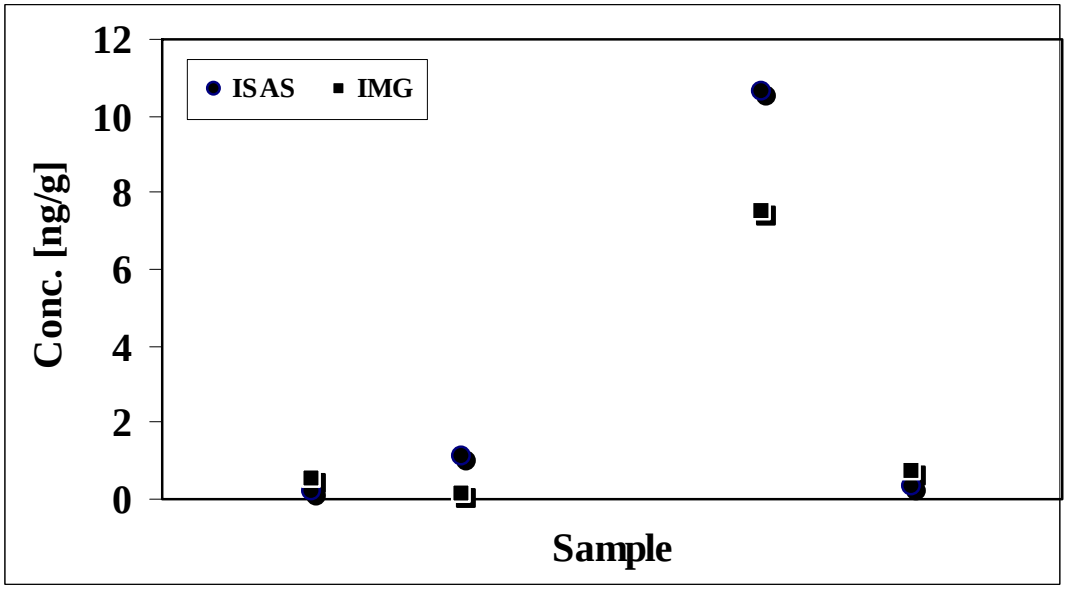

Figure (7): Rhodium concentration (ng/g DW) in potato samples determined at ISAS and IMG.

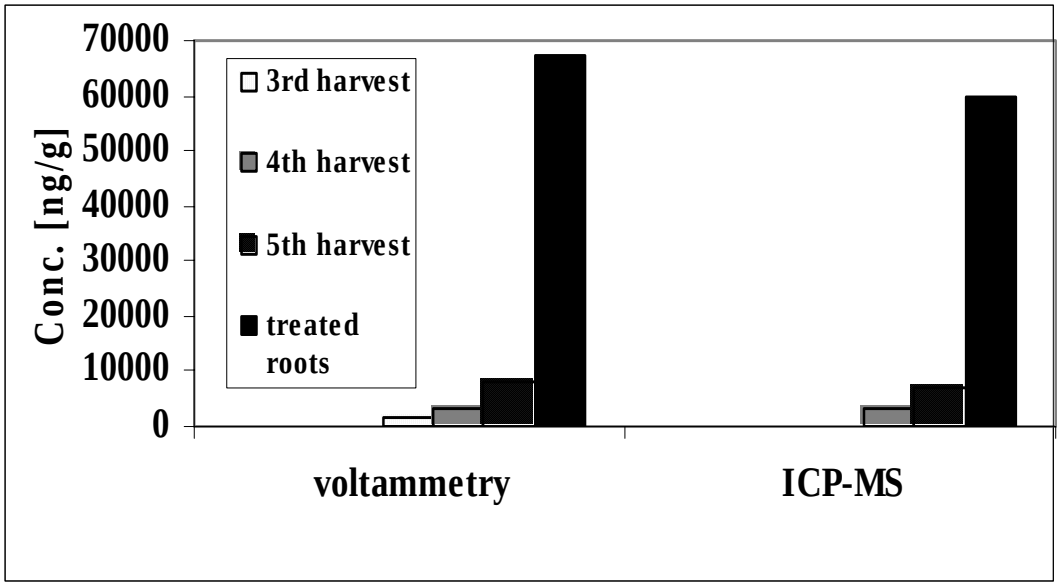

Figure (8): Comparison between platinum concentration (ng/g DW) in grass samples determined by voltammetry and ICP-MS (Data from Klueppel et al. 1998, see **Table 10B; Appendix B).**

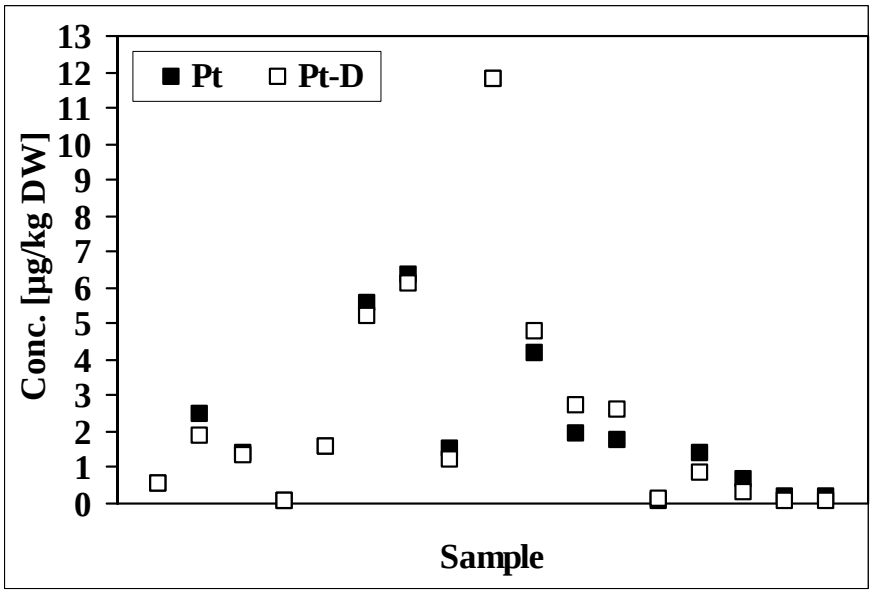

Figure (9): Platinum concentration (µg/kg DW) in duplicate potato samples.

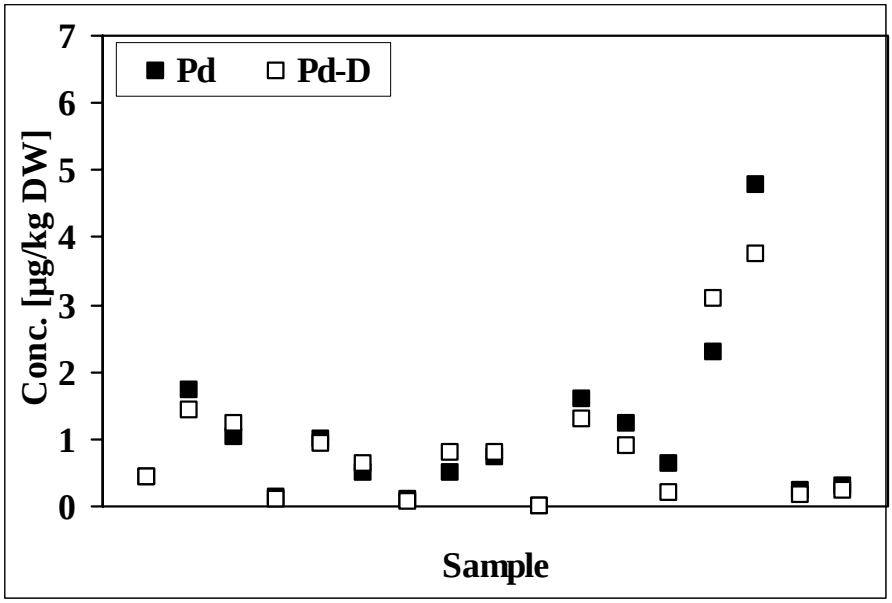

Figure (10): Palladium concentration (µg/kg DW) in duplicate potato samples.

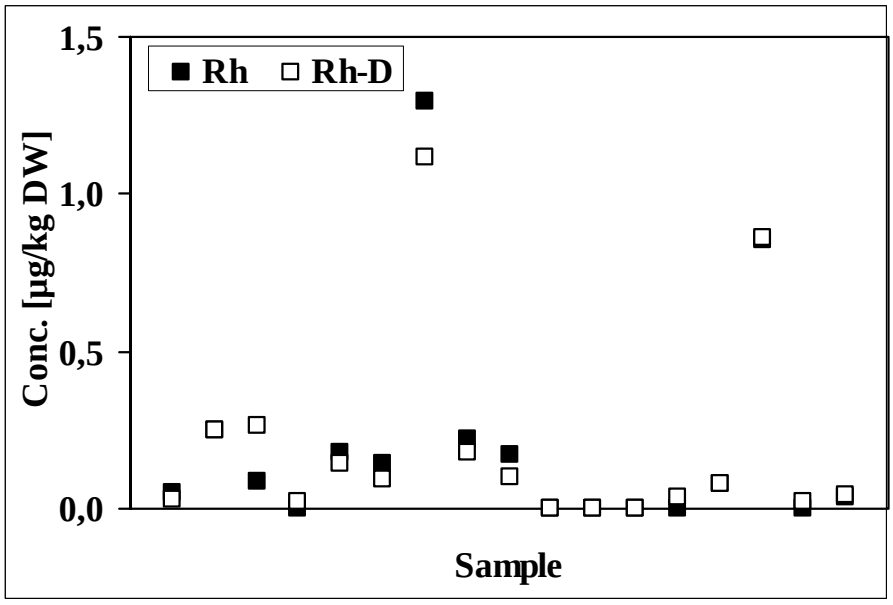

Figure (11): Rhodium concentration (µg/kg DW) in duplicate potato samples.

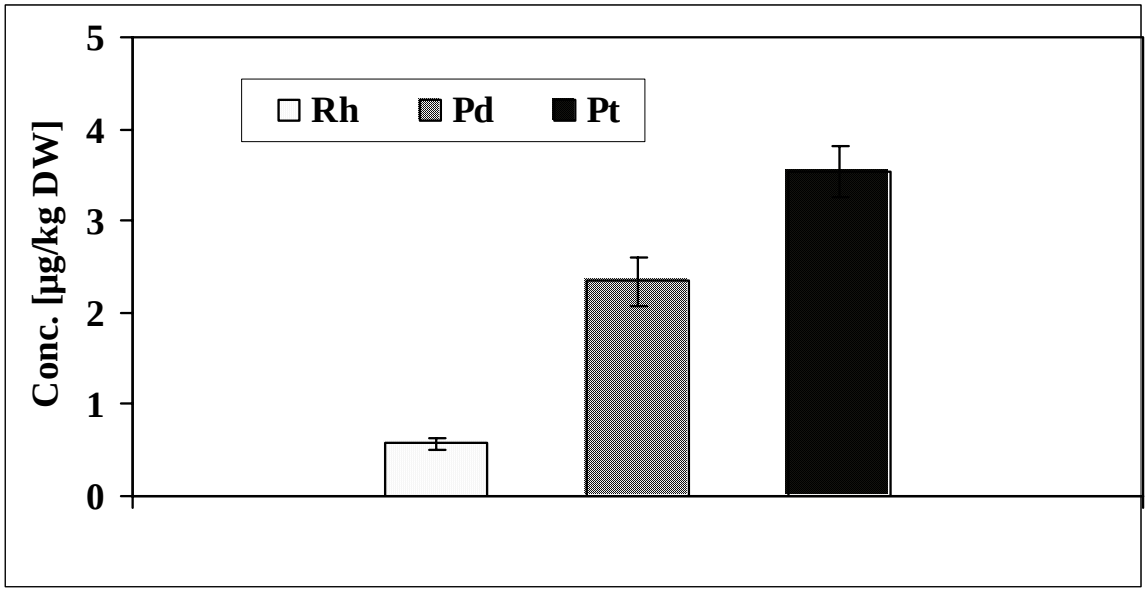

Figure (12): Repeated platinum, palladium and rhodium determinations in a potato sample [n=9, SD: Rh = 0.1, Pt and Pd = 0.3]

Chapter IV

Results

"Geochemists appear to have been misled on the geochemistry of platinum group elements by over-emphasis on the chemical inertness of these elements……."

Cousins (1973)

I Distribution of PGE in Field Grown Crop Plants

4.1 Distribution of PGE in Barley Plants

The PGE concentrations in barley (*Hordeum Vulgare* L.) will not be discussed here due to the low amount of ashed sample material collected after harvesting. Furthermore, zirconium and hafnium interferences on the low PGE concentration in the barley samples during the HR-ICP-MS measurements did not allow proper interpretation of the data collected.

4.2 Distribution of PGE in Lettuce Plants

Generally, the control lettuce (*Lactuca sativa* L.) plants grown at both experimental sites (HW and BG) showed far lower PGE concentrations than the $\boldsymbol{CAT_{Pt}}$ and $\boldsymbol{CAT_{Pd}}$ treated ones (**Figure 13 and 14**). In the aerial organs of control plants grown at both sites, the rhodium concentration varied between <LOD and 2 µg/kg DW.

The control plants grown at the botanical garden site showed platinum concentrations that varied between 7.0 and 32.0 µg/kg DW (**Figure 13**). Furthermore, the palladium concentrations in the same control plants grown at the same site varied between 17.0 and 42.0 µg/kg DW (**Table 11B; Appendix B**).

However, in the control treatments of lettuce grown at the highway site, the aerial organs showed platinum concentrations which varied between 2.0 and 21.0, whilst palladium varied between 6.0 and 21.0 µg/kg DW (**Table 11B; Appendix B**). The higher platinum and palladium concentration in the control plants grown at the botanical garden site than those grown at the highway site, are due to analytical reasons. Unfortunately, roots of platinum and palladium treated plants (grown in the growth chamber) were digested in the microwave vessels before digesting of the field grown control lettuce plants which was the last experiment conducted in the present study. This might have led to the higher PGE in control plants grown at the botanical garden than at the highway site.

Platinum determined in the lettuce plants grown at both experimental sites and treated with the $\boldsymbol{CAT_{Pt}}$ catalytic powder showed nearly similar mean concentration and variation (standard

deviation). In the $\boldsymbol{CAT_{Pd}}$ treated plants, platinum concentrations were slightly higher in the plants grown at the botanical garden site than those grown at the highway site (**Figure 13 and 14**).

Palladium concentrations in the lettuce plants grown at both experimental sites were generally higher than platinum. Moreover, palladium concentrations of lettuce treated with the $\boldsymbol{CAT_{Pd}}$ powder were higher in plants grown at the botanical garden than those grown at the highway site. In the $\boldsymbol{CAT_{Pt}}$ treated plants grown at the highway site, palladium mean concentrations were higher than in the plants grown at the botanical garden site (**Figures 13 and 14**).

Rhodium mean concentration in the $\boldsymbol{CAT_{Pt}}$ and $\boldsymbol{CAT_{Pd}}$ treatments were similar at the same experimental site. Meanwhile, it was higher in lettuce grown at the botanical garden site than those grown at the highway site.

4.2.1 Pt/Rh and Pd/Rh Ratios in Lettuce

Ratios of Pt/Rh and Pd/Rh have been postulated by some authors as an indicator for the common source of these noble metals in environmental samples (Zereini et al. 1997a; Cuif et al. 1997). However, in the present study, the Pt/Rh and Pd/Rh ratios calculated from the metal concentrations listed in **Table (1)** were equal to 4, which is lower than the postulated value of 5:1. As mentioned previously, the soils used for the experiments with lettuce were left for a long period of time (18 months) in the field before planting lettuce in these pots. This has been done to allow PGE to form soluble species through reactions with soil components. It is expected that soluble PGE species might have formed during the period of time between experiments with barley and lettuce. By calculating the Pt/Rh and Pd/Rh ratios in the lettuce plants, it might provide an evidence for the bioavailability of PG-Elements in the experimental soils for plant uptake.

However, the Pt/Rh ratios in lettuce plants were similar at both sites (Pt/Rh = 4), whereas Pd/Rh ratios of plants grown at the botanical garden (Pd/Rh = 7) were higher than those ratios found in plants grown at the highway site (Pd/Rh = 5). Furthermore, the Pd/Rh ratios in the lettuce plants grown at both sites were higher than the Pt/Rh ones (**Figure 15**).

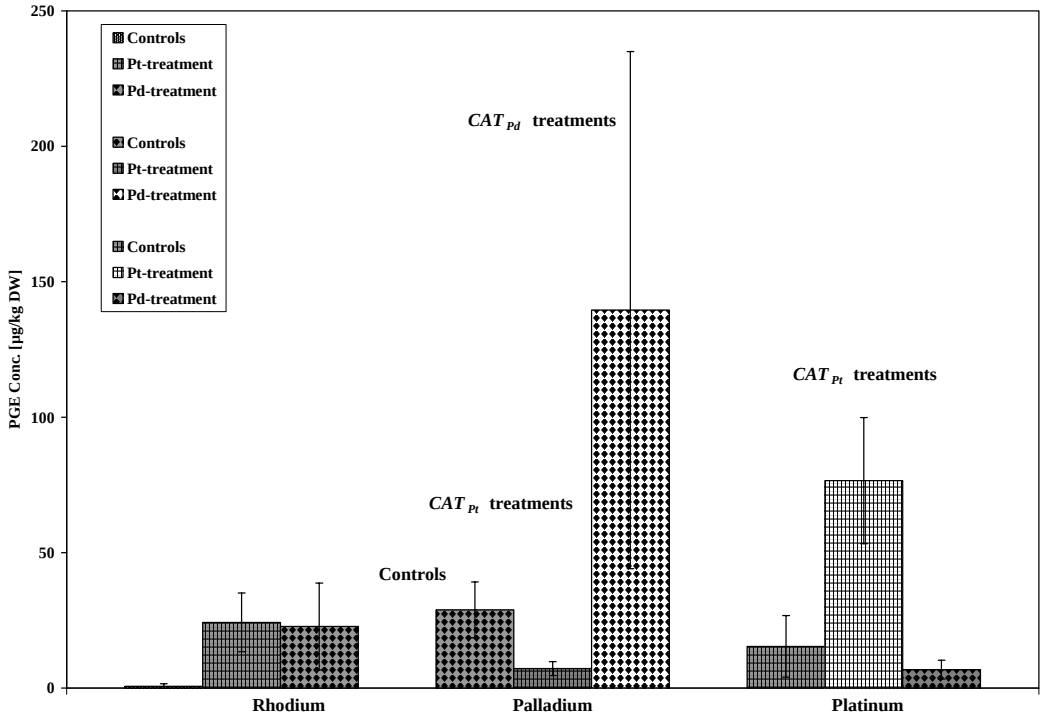

Figure (13): Distribution of rhodium, palladium, and platinum in lettuce shoots grown at the botanical garden (BG) site (Control plants = 1st bar, CAT_{Pt}-treatment = 2nd bar, and CAT_{Pd}-treatment = 3rd bar) (mean ± SD).

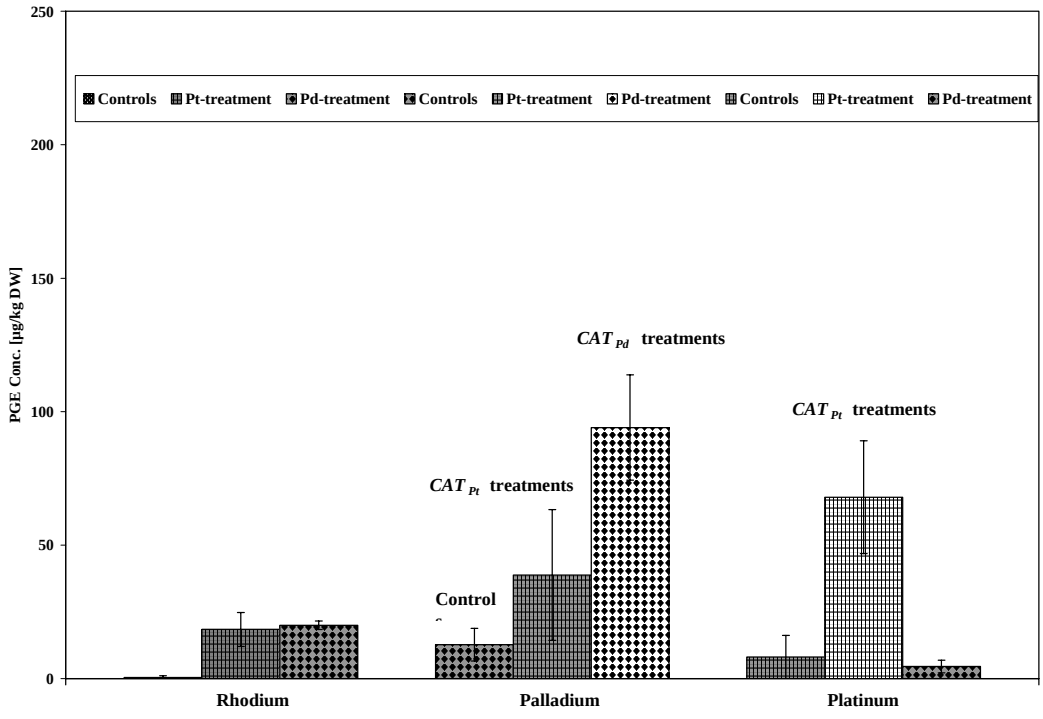

Figure (14): Distribution of rhodium, palladium, and platinum in lettuce shoots grown at the highway (HW) site (Control plants = 1st bar, CAT_{Pt}-treatment = 2nd bar, and CAT_{Pd}-treatment = 3rd bar) (mean ± SD).

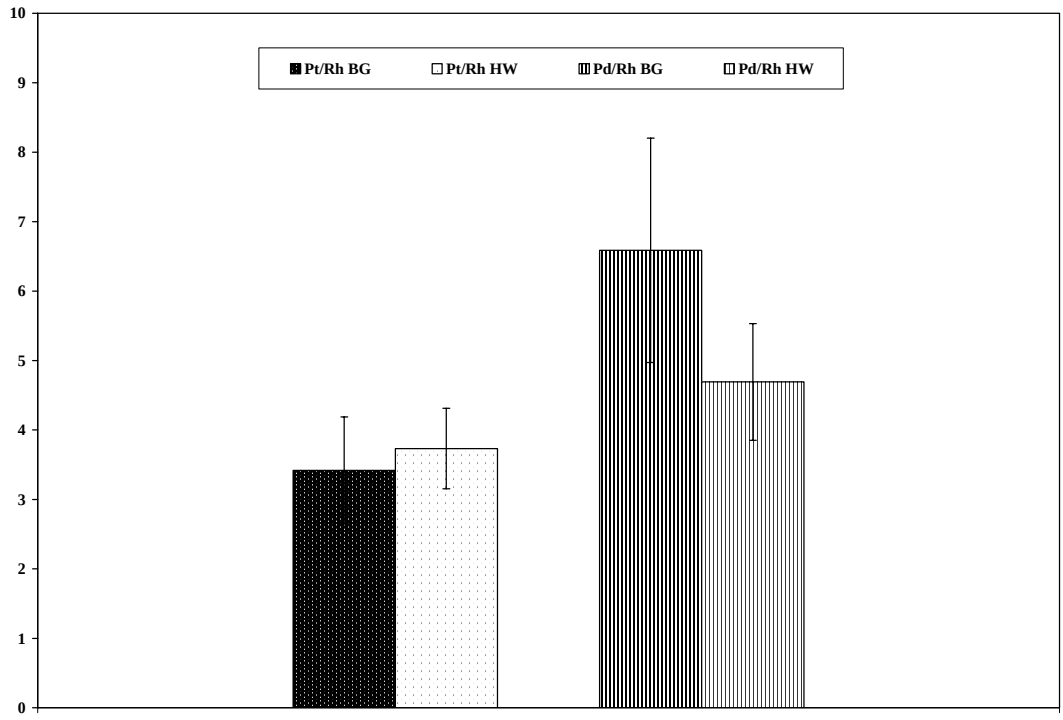

Figure (15): The ratios of Pt/Rh and Pd/Rh in shoots of CAT_{Pt} and CAT_{Pd} treated lettuce grown at both sites (mean ± SD).

II Distribution of Platinum and Palladium in the Greenhouse Plants

Some scientists suggested that the uptake of PGE by plants depends on plant species, PGE salt applied, and the concentration added to the nutrient solution (Farago & Parsons 1986a; 1986b; 1994). In the present study three different plants [two dicotyledonous i.e. potato (*Solanum tuberosum* L.) and lettuce (*Lactuca sativa* L.), and one monocotyledonous plant i.e. barley (*Hordeum Vulgare* L.)] were chosen for the PGE uptake experiments. The uptake of platinum and palladium by potato (*Solanum tuberosum* L.), lettuce (*Lactuca sativa* L.), and barley (*Hordeum Vulgare* L.) was examined under two different concentration levels of the two noble metals in the nutrient medium.

4.3 Distribution of Platinum and Palladium in Low-Level Treated Plants (300 µg/l)

4.3.1 Accumulation of Platinum and Palladium by Potato (II) and Lettuce

The total (mean) platinum and palladium concentrations were generally higher in lettuce than potato (II) plants treated with 300 µg/l soluble PGE salts. However, platinum concentrations in the shoots of potato were higher than lettuce, whereas palladium concentrations were higher in lettuce than potato shoots **(Figure 16)**. Meanwhile, platinum concentrations in lettuce roots were three times higher than those of potato, and palladium concentrations were two times higher (**Figure 16**).

The potato plants accumulated higher amounts of platinum but slightly lower palladium in their leaves than the lettuce (**Figure 17)**. The lettuce accumulated similar amounts of platinum but higher palladium in their stems than potato.

Comparing the concentration of platinum to those of palladium in the aerial organs as well as roots, it is clear that palladium was mainly accumulated in the plant roots, whilst platinum was mainly accumulated in the aerial parts of potato but not of lettuce (**Figure 16**).

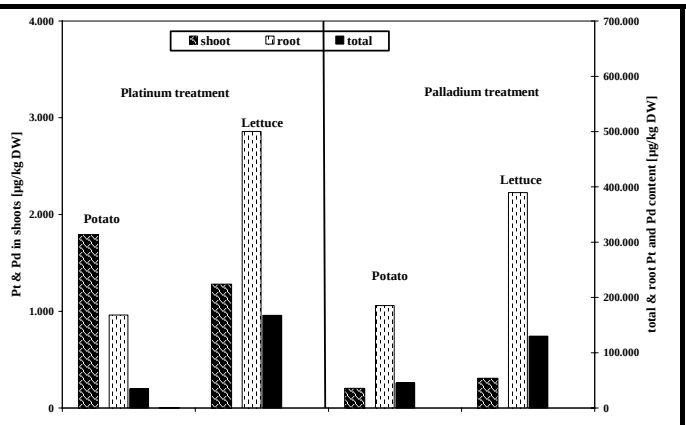

Figure (16): Comparison between platinum and palladium concentration in potato (II) and lettuce plants treated with 300 µg/l chloride salt (shoots, roots, and total concentration). Left y-axis: shoot content, right y-axis: Total (average) and root content of Pt and Pd treated plants.

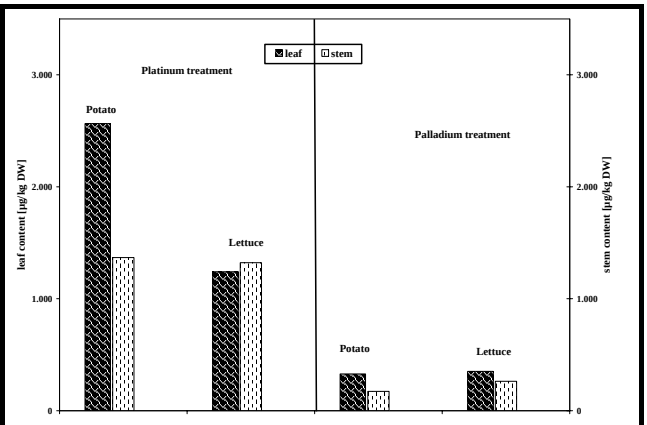

Figure (17): Comparison between platinum and palladium concentration in leaves and stems of potato and lettuce plants treated with 300 µg/l platinum and palladium chloride salts. Left y-axis: leaf content, right y-axis: stem content of Pt and Pd treated plants.

A. Accumulation of Platinum and Palladium in Potato Organs

Platinum concentrations in the potato plants varied between 443 µg/kg DW and 209,158 µg/kg DW (**Table 14B; Appendix B**). However, the lowest platinum concentration was found in the tubers, whilst the highest among all potato plant organs was detected in the roots. Platinum concentrations in the aerial organs were far higher in leaves than leaf stalks and stems, which were in turn similar (**Figure 18**). Palladium concentrations in all aerial organs were lower than that of platinum. Nevertheless, palladium contents of roots were similar to platinum in roots **(Figure 19)**.

In the aerial plant organs, palladium follows generally the same distribution as platinum, (i.e. highest levels were found in leaves, followed by leaf stalks and stems, which showed no significant difference in their concentration). The tubers contained palladium that was similar to stems but higher than leaf stalks (**Figure 18**). In the platinum treated plants, the tubers contained lower platinum than all other aerial organs.

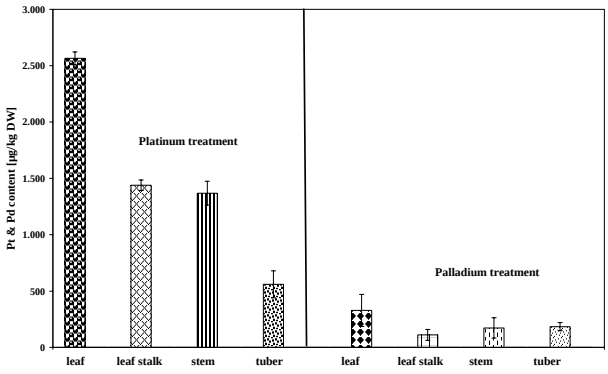

Figure (18): Distribution of platinum (left) and palladium (right) in aerial parts as well as tuber of potato plants treated with 300 µg/l platinum and palladium chloride salts (mean ± SD).

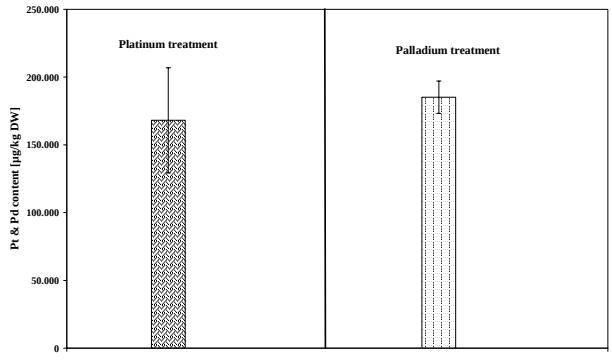

Figure (19): Distribution of platinum (left) and palladium (right) in roots of potato plants treated with 300 µg/l platinum and palladium chloride salts (mean ± SD).

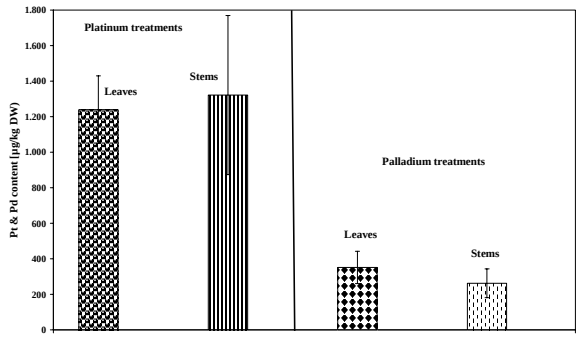

Figure (20): Distribution of platinum (left) and palladium (right) in leaves and stems of lettuce plants treated with 300 µg/l platinum and palladium chloride salts (mean ± SD).

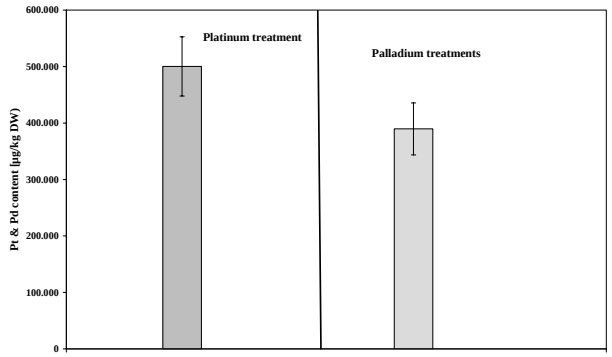

Figure (21): Distribution of platinum (left) and palladium (right) in roots of lettuce plants treated with 300 µg/l platinum and palladium chloride salts (mean ± SD).

B. Accumulation of Platinum and Palladium in Lettuce Organs

The stems of lettuce plants showed slightly higher platinum but lower palladium concentrations than the leaves **(Figure 20).** Platinum concentrations in roots were higher than palladium (**Figure 21**). However, roots contained higher platinum and palladium than the leaves and stems of lettuce.

4.4 Distribution of Platinum and Palladium in High-Level Treated Plants (2000 µg/l)

4.4.1 Accumulation of Platinum and Palladium by Barley and Potato (I)

Generally, the total platinum and palladium concentrations were higher in barley than in potato (**I**) plants (**Figure 22**). This is similar to the case of potato and lettuce treated with 300 µg/l chloride salts. Moreover, platinum and palladium concentrations were higher in potato (average concentrations) than barley shoots, whilst the barley roots contained higher amounts of the two noble metals than the potato roots (**Figure 22**). The distribution of platinum and palladium in potato and barley is thus similar to that of lettuce and potato treated with 300 µg/l chloride salts.

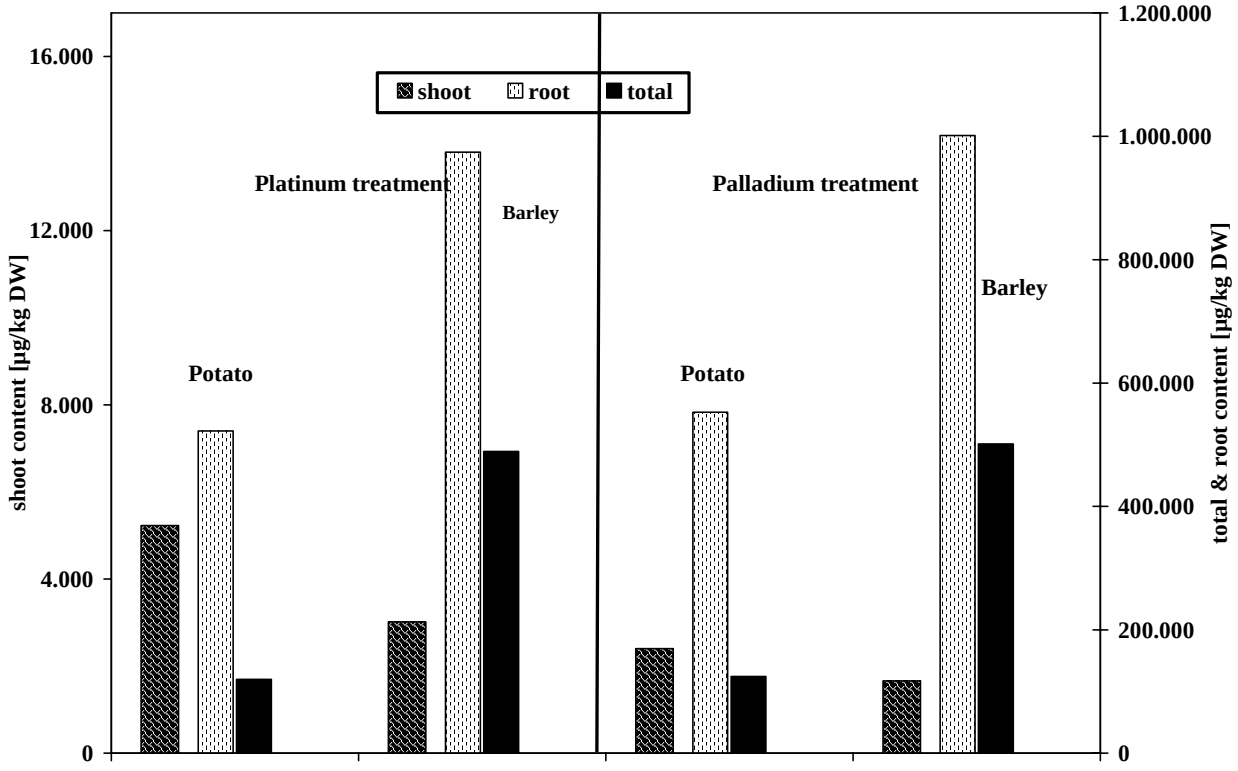

Figure (22): Comparison between platinum and palladium concentrations in potato and barley plants treated with 2000 µg/l platinum and palladium chloride salts (shoots, roots, and average concentration).

A. Accumulation of Platinum and Palladium in Potato Organs

Similar to the low-level treatments (300 µg/l), the lowest platinum concentration was detected in the tubers and the highest was found in the roots. Platinum concentration in the potato plants treated with 2000 µg/l platinum chloride varied between 751 µg/kg DW and 553,255 µg/kg DW (**Table 15B; Appendix B**). In the aerial organs of potato plants platinum concentrations were higher in the leaves than in the leaf stalks and stems (**Figure 23**).

Palladium concentrations in the potato plants treated with 2000 µg/l palladium varied between 1204 and 673,074 µg/kg DW (**Table 15B; Appendix B**). Similar to platinum distribution in potato organs, palladium showed the lowest concentration in tubers and the highest in roots. In the aerial organs, palladium concentrations were highest in leaves followed by stems and leaf stalks.

However, platinum and palladium concentrations in the leaves were approximately two times higher than that in leaf stalks and stems (**Figure 23**). The platinum concentration of stems was slightly lower than that of leaf stalks, whilst palladium concentration was higher in the stems

than in leaf stalks. This is in agreement with platinum distribution in potato treated with 300 µg/l platinum. Palladium concentrations in all plant organs were lower than that of platinum except in roots, which showed higher concentrations than platinum treated plants (**Figure 24**). The tubers showed higher palladium (1204 µg/kg DW) than platinum (741 µg/kg DW) concentration (**Figure 23**).

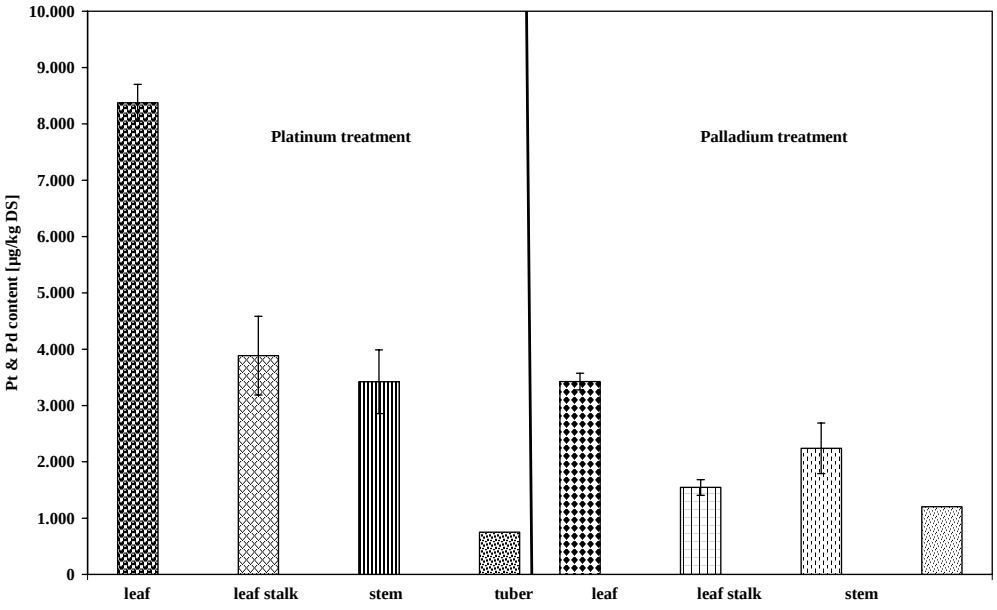

Figure (23): Distribution of platinum (left) and palladium (right) in aerial organs as well as tubers of potato plants treated with 2000 µg/l platinum and palladium chloride salts (mean ± SD).

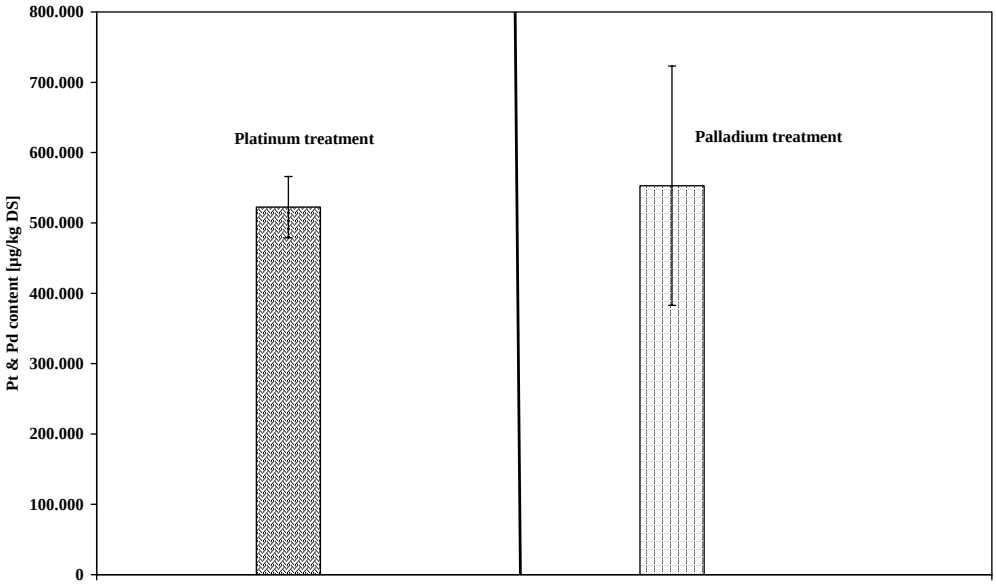

Figure (24): Distribution of platinum (left) and palladium (right) in roots of potato plants treated with 2000 µg/l platinum and palladium chloride salts (mean ± SD).

B. Platinum and Palladium Accumulation in Barley Shoots and Roots

Platinum concentration was higher than palladium in barley shoots but similar in the roots (**Figure 25 and 26**).

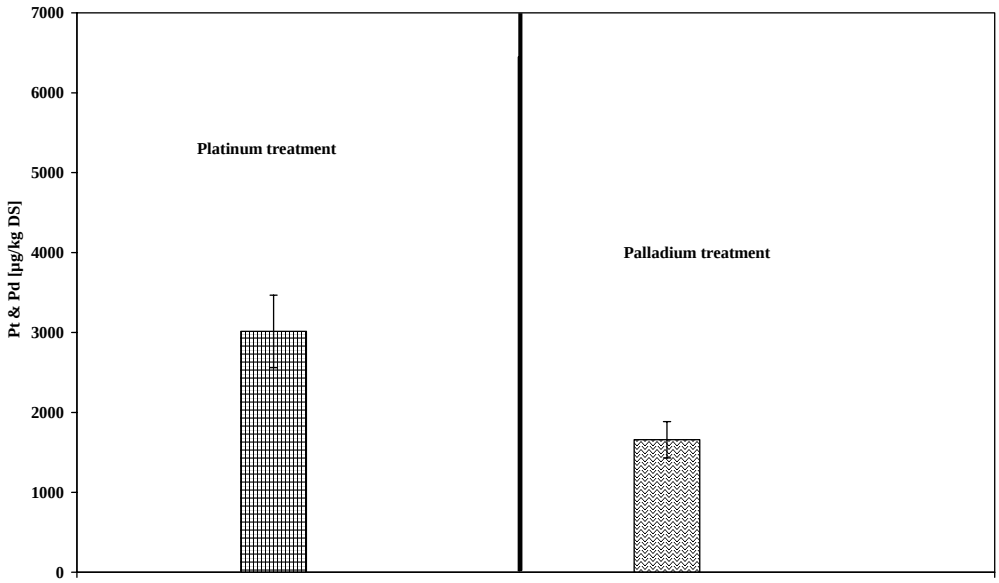

Figure (25): Distribution of platinum (left) and palladium (right) in barley shoots treated with 2000 µg/l (mean ± SD).

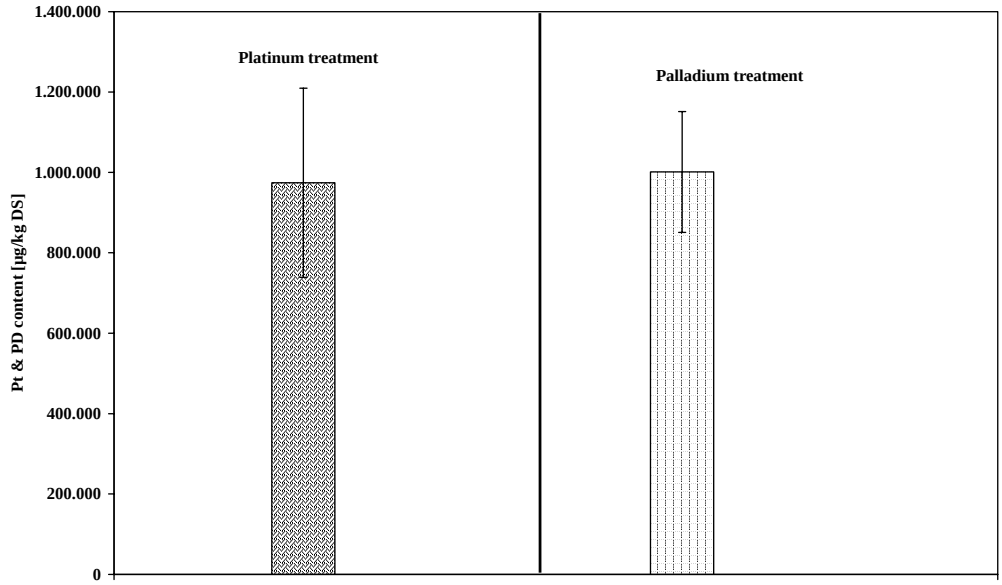

Figure (26): Distribution of platinum (left) and palladium (right) in barley roots treated with 2000 µg/l platinum and palladium chloride salts (mean ± SD).

4.5 Platinum and Palladium Ratios in the Different Plant Organs

4.5.1 Platinum and Palladium Ratios in the Low-Level Treated Plants (300 µg/l)

Introduction

As mentioned previously, platinum and palladium concentrations in potato were determined by separately analyzing each plant organ (leaves, leaf stalks, stems, tubers, and roots). Since the different aerial parts of potato (i.e. leaves, leaf stalks, and stems) are not equal in their volume and mass compared to the total green fresh mass of the whole plant, their platinum and palladium contents cannot be added to calculate their total shoot content. Alternatively, the platinum and palladium content of shoots was determined by calculating their average concentration in the dry weight (DW).

However, the shoot : root (S : R) ratio or the root : shoot (R : S) ratio was calculated by dividing the average concentration (in dry matter) of platinum or palladium in the shoots by the content in the roots and vice versa.

Similarly, the average concentration of platinum or palladium (in dry matter) was determined by calculating the mean concentration in the leaves and stems of lettuce before calculating the S : R or R : S ratios.

A. Potato

The calculated mean of the S : R ratio was 0.011 for platinum and 0.001 for palladium, whereas theR : S ratio was 94 and 897 for platinum and palladium treated potato plants, respectively. However, platinum showed higher shoot : root ratio than palladium, whereas the latter showed about 9 times higher root : shoot ratio than the former (**Figure 27 and 28**).

In the aerial potato organs and tubers, the platinum ratios were generally higher than those of palladium, whereby the platinum leaf : tuber (L : T), leaf stalk : stem (LS : Sm), leaf stalk : tuber (LS : T), and stem : tuber (Sm : T) ratios were higher than those of palladium and only lower in the case of leaf : leaf stalk ratio (**Figure 29**).

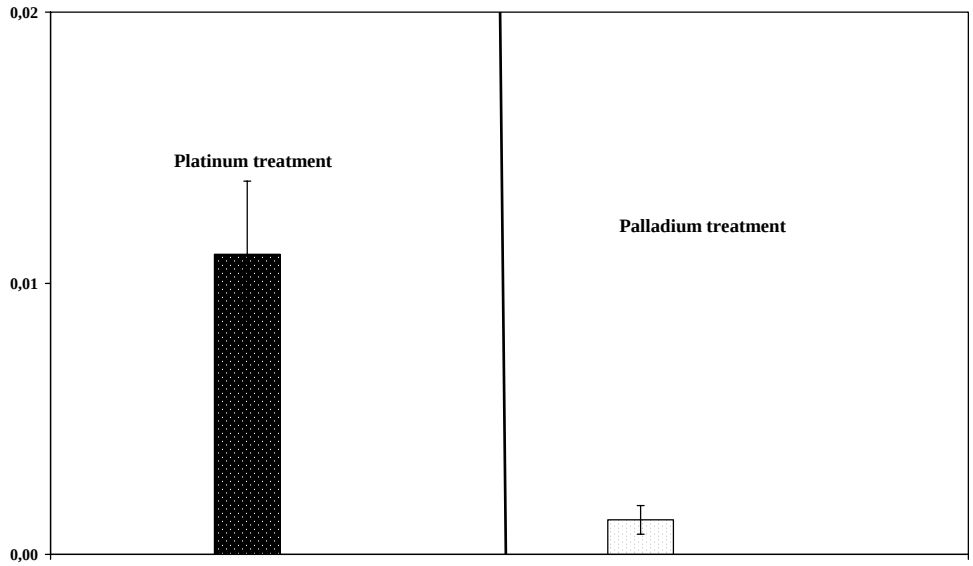

Figure (27): Shoot : root ratio of platinum (left) and palladium (right) in the low-level (300 µg/l) treated potato plants (mean ± SD).

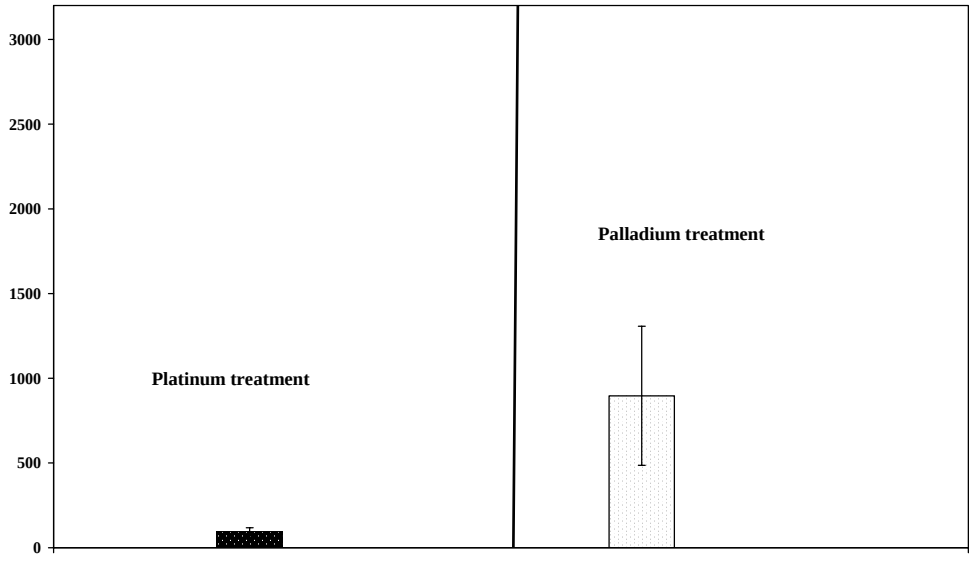

Figure (28): Root : shoot ratio of platinum (left) and palladium (right) in the low-level (300 µg/l) treated potato plants (mean ± SD).

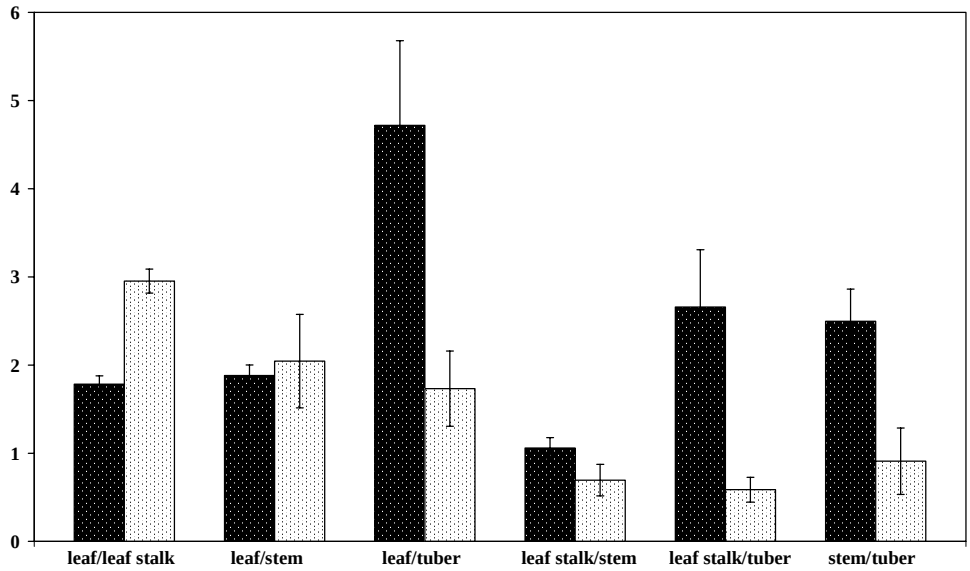

Figure (29): Ratios of platinum (dark bars) and palladium (white bars) in the low-level (300 µg/l) treated potato plants organs (mean ± SD).

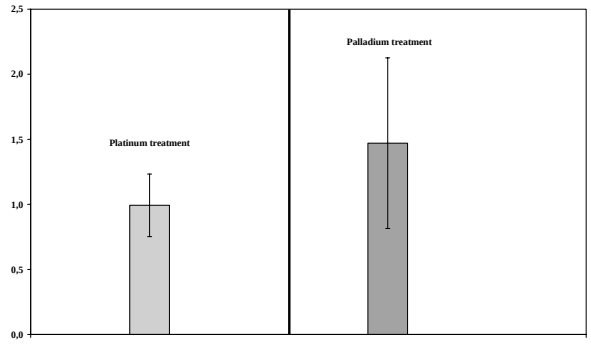

Figure (30): Leaf : stem ratio in lettuce plants treated with 300 µg/l platinum (left) and palladium (right) salts (mean ± SD).

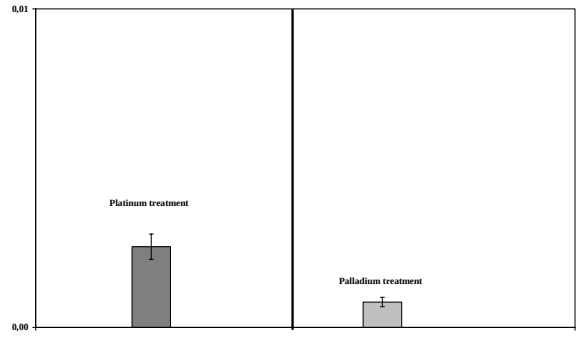

Figure (31): Shoot : root ratio in lettuce plants treated with 300 µg/l platinum (left) and palladium (right) salts (mean ± SD).

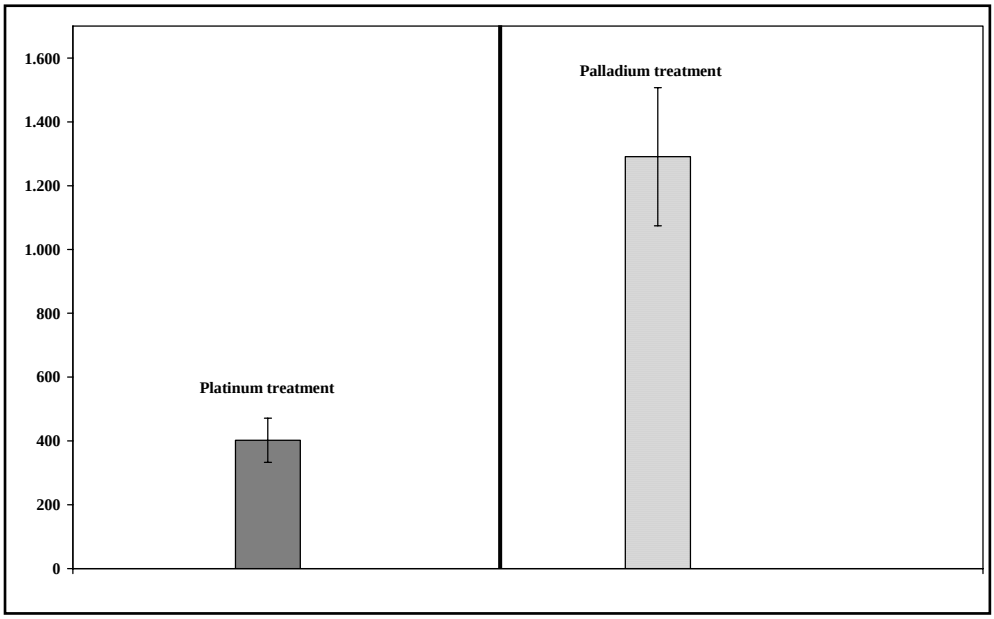

Figure (32): Root : shoot ratio in lettuce plants treated with 300 µg/l platinum (left) and palladium (right) salts (mean ± SD).

B. Lettuce

The lettuce plants were subdivided into leaves, stems, and roots. The L : Sm and R : S ratios calculated for palladium were higher than those for platinum, which showed only higher s : R ratio than palladium (**Figure 30, 31, and 32**).

4.5.2 Platinum and Palladium Ratios in High-Level Treated Plants (2000 µg/l)

A. Potato

The S : R ratio calculated for platinum was higher than palladium (**Figure 33**), but lower in the case of the R : S ratio (**Figure 34**). However, in the high-level (2000 µg/l) treated potato plants, platinum and palladium concentrations in the aerial plant organs showed similar L : LS ratio. The metal ratios for L : Sm and LS : Sm were higher for platinum than palladium (**Figure 35**).

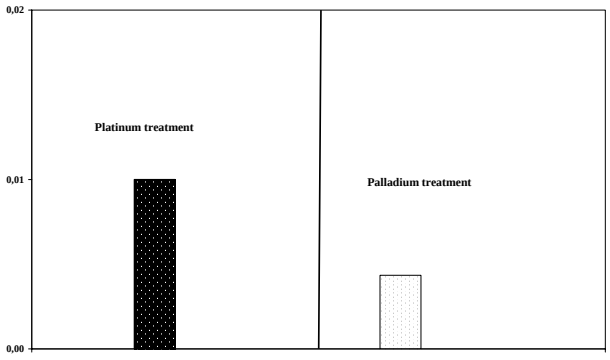

Figure (33): Shoot : root ratio calculated for platinum (left) and palladium (right) in the organs of 2000 µg/l treated potato plants.

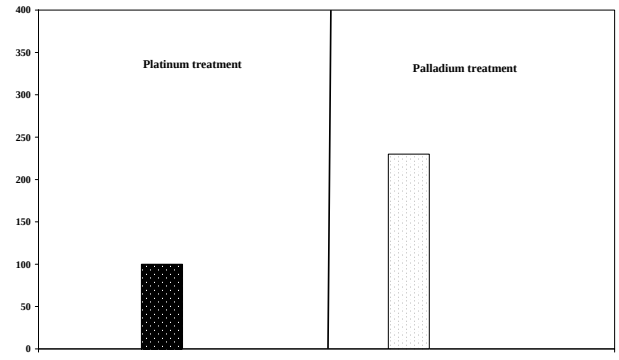

Figure (34): Root : shoot ratio calculated for platinum (left) and palladium (right) in the organs of 2000 µg/l treated potato plants.

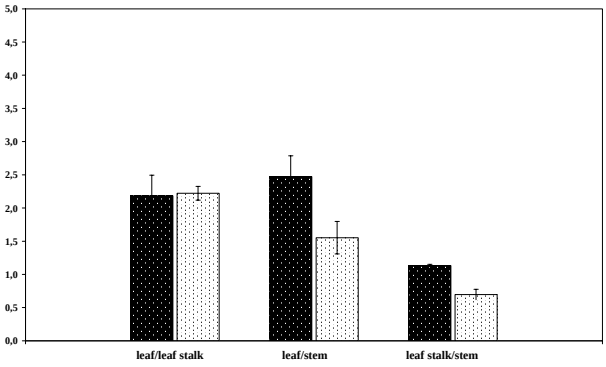

Figure (35): Ratios calculated for platinum (dark) and palladium (white) in the organs of the 2000 µg/l treated potato plants (mean ± SD).

A. Barley

Platinum showed higher S : R ratio but lower R : S ratio than palladium (**Figure 36 and 37**).

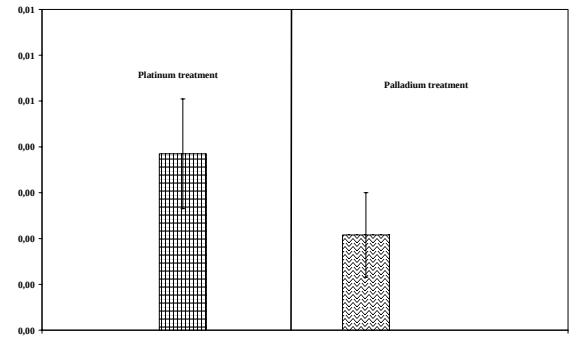

Figure (36): Shoot : root ratio calculated for platinum (left) and palladium (right) in barley plants treated with 2000 µg/l platinum and palladium chloride salts (mean ± SD).

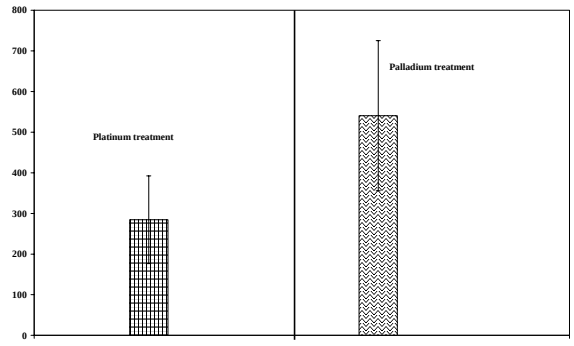

Figure (37): Root : shoot ratio calculated for platinum (left) and palladium (right) in barley plants treated with 2000 µg/l platinum and palladium chloride salts (mean ± SD).

4.6 Comparison of Platinum and Palladium Ratios in Potato at Low-Level (300µg/l) and High-Level (2000 µg/l) Treatments

The uptake of platinum and palladium by the potato plants was examined at two different concentrations for the noble metals in the hydroponic medium, i.e. low- (300 µg/l) and high-levels (2000 µg/l). The S : R and R : S ratio of platinum and palladium concentration in the different plant organs at the two different levels were calculated. The ratio LS : Sm ratios calculated for platinum and palladium were similar at the two treatment concentrations (**Figure 38 and 39**). The L : LS and L : Sm ratios calculated for palladium were higher in the low-level than in the high-level treatment, but were lower for platinum (**Figure 38 and 39**). The ratios of noble metal concentrations in source to sink organs (i.e. leaves and tubers) showed generally the highest ratios of all (**Figure 38 and 39**).

The L : T metal ratios were higher for platinum and palladium at the high-level (2000 µg/l) than the low-level (300 µg/l) treatments. Furthermore, the LS : T and Sm : T metal ratios of platinum were approximately twice as high as palladium, not only at the same metal concentration in the hydroponic medium but also higher at the high-level than at the low-level treatments (**Figure 38 and 39**).

The S : R and R : S ratios of platinum were mostly similar in both treatments. Palladium S : R ratio was higher at the low-level (300 mg/l) than the at high-level (2000 µg/l) treatments, whilst the R : S ratio was higher at the low-level than at the high-level treatments (**Figure 40**).

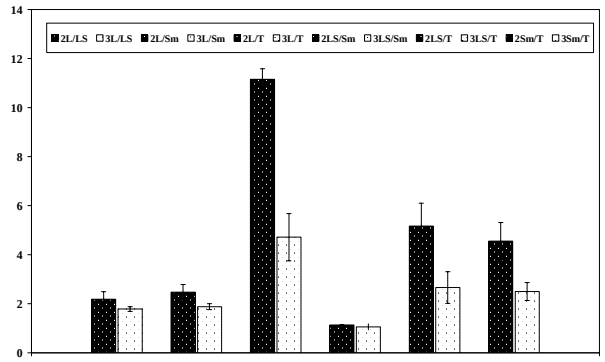

Figure (38): Comparison between platinum ratio in the different organs of potato plants treated with 300 and 2000 µg/l platinum chloride salt (mean ± SD).

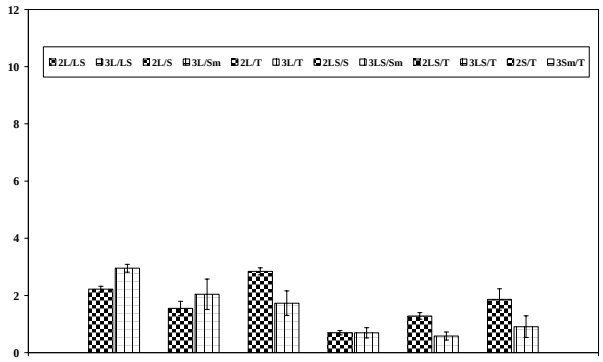

Figure (39): Comparison between palladium ratio in the different organs of potato plants treated with 300 and 2000 µg/l palladium chloride salt (mean ± SD).

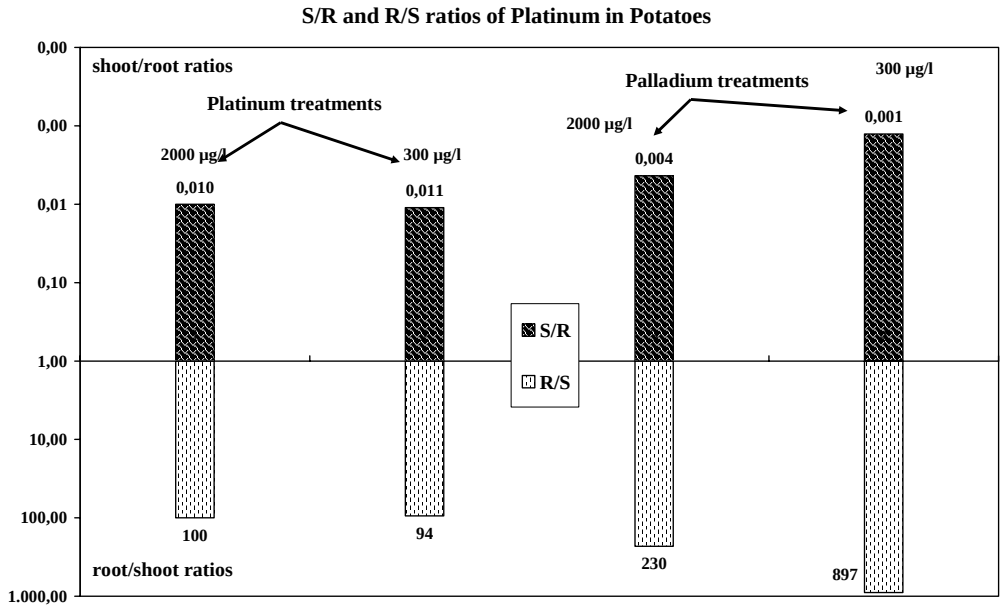

Figure (40): Comparison of shoot : root and root : shoot ratio of platinum (left) as well as palladium (right) in potato plants treated with 2000 and 300 µg/l platinum and palladium chloride salts.

4.7 Visible Symptoms of Platinum and Palladium Phytotoxicity on Crop Plants

Physical manifestations of platinum and palladium phytotoxicity were observed at the low-level (300 µg/l) as well as the high-level (2000 µg/l) treated crop plants during the entire course of the experiments. Potato plants at both levels developed severe visible phytotoxicity symptoms. Plants grown at both treatment levels (300 µg/l and 2000 µg/l platinum and palladium chloride salts in the hydroponic medium) were chlorotic, exhibiting brown edges on middle and upper leaves, brown patches on tips of the leaves (**Figure 41 and Picture 5 and 6; Appendix A, Plate 2**), and the upper leaves of the treated plants were smaller in comparison with the controls. Plants treated with 2000 µg/l showed clearly yellow (**Figure 41**), smaller upper leaves. The roots of platinum and palladium treated potato, lettuce, and barley appeared generally darker (**Figure 45, 46, 48 and 49**) than the control plants (**Figure 44 and 47**).

However, the effects of palladium and platinum phytotoxicity included stunted growth, chlorosis, and blackening of the root systems, especially in the case of potato plants, whereas the roots of lettuce and barley treated with platinum and palladium were darker than the controls. These phytotoxic effects were more intensive in the case of palladium treated plants than platinum treated ones (compare **Figures 41, 42, 43, 45 and 46**).

The tubers of potato plants treated with 2000 µg/l platinum and palladium chloride salts in the nutrient medium were smaller and fewer in number than the 300 µg/l treated ones. Moreover, the tubers of potato plants treated with 2000 µg/l platinum and palladium salts in the hydropnic medium were shortly bulked before plant harvest. Furthermore, the addition of platinum and palladium to the hydroponic medium accelerated the tuber bulking which was faster in the case of palladium than platinum treatments. The control plants showed retardation in their tuber bulking compared to potato plants treated with chloride salts of platinum and palladium. In addition, the root system of control plants was clearly whiter with fewer tubers than the treated plants (**Figure 44 and Picture 14; Appendix A, Plate 3**).

The results of physiological parameters measured on the crop plants are listed in **Appendix C**.

Figure (41): Phytotoxic symptoms: chlorosis and brown leaf edges of potato leaves treated with platinum salt (2000 µg/l).

Figure (42): Platinum (300 µg/l) treated potato plants showing phytotoxic symptoms but less drastic than the palladium treated ones (**Figure 43**)

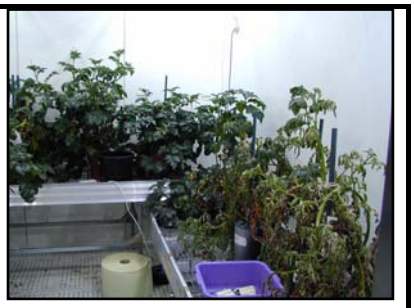

Figure (43): Early death of palladium (300 µg/l) treated plants (right) compared to controls (left).

Figure (44): Clear white roots of a control potato plant but lower tuber yield than platinum and palladium treated plants (**Figure 45 and 46**).

Figure (45): Dark brown roots and more tuber yield of a platinum (300 µg/l) treated potato plant compared to a control in **Figure 44**.

Figure (46): A palladium (300 µg/l) treated potato plant showing dark roots and more tuber yield than control plant in **Figure 44**.

Figure (47): A control lettuce plant showing whiter roots than platinum and palladium treated ones.

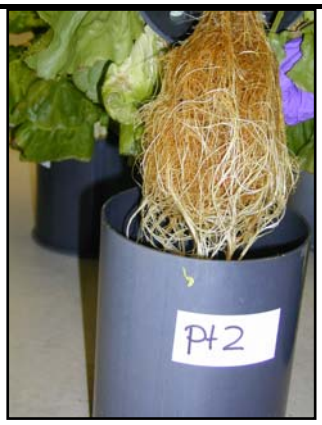

Figure (48): A platinum (300 µg/l) treated lettuce plant showing brown roots (compare to **Figure 47**).

Figure (49): A palladium (300 µg/l) treated lettuce plant showing brown roots (compare to **Figure 47**)

Chapter V

Discussion

“To have an independent mind, to think for ourself, not to follow fashions, not to seek honor or decorations, not to become part of the establishment”.

Marcel Schlumberger (1884-1953)

5.1 The Influence of Traffic Density on PGE Uptake by Crop Plants

The uptake of metals either by roots or leaves increases with increasing metal concentration in the external medium (Greger et al. 1993). The PGE determined in dust samples collected at both sites during the vegetation periods indicated that platinum, palladium, and rhodium concentrations at the highway site were far higher than those determined in samples collected at the botanical garden site (Aboughalma & Stüben 2003, unpublished data).The lettuce (*Lactuca sativa* L.) plants grown at the highway site contained higher platinum and lower palladium than those grown at the botanical garden site. This point will be discussed in detail later in this chapter. It is suggested that PGE concentration in the aerial parts depends on traffic density and hence their concentration in the atmosphere. This is in agreement with a study conducted by Dongarra et al. (2003) who concluded that pine needles (*Pinus pinea* L.) collected from downtown of Palermo/Italy contained far higher PGE concentrations than those collected from sampling sites located in the surrounding areas.

Direct uptake of atmospheric trace metals can account for more than 90% of the metal burden in grasses and parts of herbaceous plants (Tjell et al. 1979). It has also been suggested that direct uptake through bark or foliage may be a major pathway by which metals enter trees, particularly in heavy polluted areas (Baes & MacLaughlin 1987; Lepp 1975; Robitaille 1981).

The concentration of palladium in plant samples collected along roads with high traffic density was lower than platinum (Schäfer et al. 1995; Jarvis et al. 2001; Dongarra et al. 2003; Lesniewska et al. 2004a). This might be due to the low number of vehicles fitted with catalytic converter based on the palladium metal.

An increase of PGE concentrations from 1994 to 1996 in urban dust, road dusts, soil, and sewage sludge samples collected from Southwest Germany was proved in a study conducted by Schäfer et al. (1999). Moreover, PGE concentrations in road dust samples collected by Jarvis et al. (2001) from locations near London/England showed an increase (doubling of concentration) throughout one year of sampling (July 1995 to June 1996). PGE concentrations in dust samples collected by Aboughalma & Stüben (2003, unpublished data) from the same locations where the field experiments with crop plants in the present study were conducted, showed an increase from summer 2002 (May to July) to winter 2002 (November to December 2002).

Since the control lettuce (*Lactuca sativa* L.) plants were carefully washed, it is reasonable to conclude that the considerable amounts of platinum, palladium, and rhodium in these plants indicate the uptake of PGE via the aerial organs. In addition, because the PGE concentrations in plants grown at the highway site were higher than those grown at the botanical garden site, the PGE uptake via aerial plant parts is suggested to be dependent upon traffic density and the noble metal concentrations in the atmosphere. Therefore, the present study is in agreement with other studies conducted by Helmers & Mergel (1997), Dongarra et al. (2003), and Lesniewska et al. (2004a).

5.2 Uptake Pathways of PGE by Field Grown Lettuce

The noble metals, to a great extent, were taken up by the roots of lettuce (*Lactuca sativa* L.) plants grown at the botanical garden site. The lettuce plants treated with catalyst's powders showed higher platinum, palladium, and rhodium than the control plants grown at both sites (**Figure 13 and 14**). These findings imply that the main PGE uptake route by lettuce grown at both sites and treated with catalyst's powders was via the plant roots, to a greater extent, and by the aerial parts, to a lower extent. The main uptake route of PGE by control plants grown at both sites is via plant leaves since no PGE were added to the soils.

However, the uptake of noble metals by the aerial organs of lettuce was sequestered by the higher PGE portion taken up via the roots than that taken up by the aerial organs (**see Figure 13 and 14**). Nevertheless, control treatments of lettuce showed considerable amounts of PGE in their aerial parts revealing the atmospheric uptake of these metals (**Figure 13 and 14**).

The leaves of lettuce have large surface area, which, according to Bargagli (1998), leaf surface area is an important factor for airborne trace metal accumulation. Mehra & Farago (1994) pointed out that the foliar uptake of metals is believed to consist of two phases: non-metabolic cuticular absorption which is generally considered to be the major route of entry, and metabolic mechanisms which account for element accumulation against a concentration gradient.

It is therefore suggested that the leaves of lettuce acted as a trap for airborne PGE in aerial organs of lettuce. Bargagli (1998) mentioned that particles may also enter the leaves, although the waxy cuticle covering the leaf epidermal cells provides an effective barrier to the penetration

of particulate pollutants. Both essential and non-essential metals can be taken up by leaves (Greger et al. 1993). When in the form of gases, they enter the leaves through the stomata, while as ions they mainly enter through the leaf cuticle (Martin & Juniper 1970; Lindberg et al. 1992; Marschner 1995). In radiotracer experiments conducted on the uptake of Cd^{109} by potato (*Solanum tuberosum* L.) plants, Cakmak et al. (2000) demonstrated that Cd can be translocated from the source leaf via phloem to sink organs such as new leaf and root tissues.

Since low amounts of PGE emitted from autocatalysts are suggested to be in volatile and soluble species (Albert 1992; Rauch & Morrison 2000), they may enter the leaves through the leaf cuticle and stomata. Platinum is assumed to be emitted as soluble PtO_2 species in addition to platinum-containing particles of diameter lower than 1 µm (Schlögl et al. 1987; Albert 1992; Alt et al. 1993; Inacker & Malessa 1996; Rauch & Morrison 2000). Therefore, PGE are likely to enter easily leaves through stomata (which according to Bargagli (1998) open to 5-30 µm). Furthermore, Lustig et al. (1997) suggested that platinum may be taken up in aerial organs by adsorption of airborne particles or dust deposited on above-ground organs of the plants. Messerschmidt et al. (1994) speculated that the uptake by stomata may play a role since particles containing platinum in the sub-µm range are emitted from catalytic converters.

The foliar uptake of ^{137}Cs by onion (*Allium cepa* L.) (Bystrzejewska-Piotrowska & Urban 2004), of ^{109}Cd by potato (*Solanum tuberosum* L.) (Reid et al. 2003), and of ^{100}Mo by potato (Saumer 1995), supports the uptake of PGE by leaves in the present study. Hovmand et al. (1983) conducted experiments on barley (*Hordeum Vulgare* L.), kale (*Brassica* L.), wheat (*Triticum* L.), and rye (*Secale* L.) that were carried out in rural areas of Denmark. They concluded that Cd deposited on aerial surfaces of plants can be taken up by leaves and transported within plants and thus can represent a significant source of Cd entering the food chain.

Accumulation of PGE in aerial organs of plants can also be affected by atmospheric deposition of PGE emitted from autocatalysts directly on leaf surfaces. There is little experimental evidence concerning the uptake of PGE by leaves. Accordingly, the results of the present study reveal the PGE uptake by the aerial organs of lettuce.

5.3 Bioavailability of PGE from Catalyst's Powders and their Mobility in Soils

PGE added to the soils in the present study were initially present in a metallic form (Palacios et al. 2000) in the fine grained catalyst's powders. The concentration of rhodium in the two catalyst powders was equal (**Table 1**). After mixing the unused catalyst's powder with the soils in the current experiments, all of the field experiment pots with lettuce stood for a period of time (from March 2002 until harvesting of lettuce in October 2003). It has been reported that palladium is more mobile in the environment (Kothny 1979) than platinum and can migrate either as a true solute or in colloidal form (Pogrebnyak et al. 1986). Furthermore, Fuchs & Rose (1974) pointed out that palladium is more environmentally mobile and thus more available for plants than platinum. According to Wood (1974), the metals Pt, Pd, Cd, and Co belong to a class of very toxic and relatively accessible elements. He also added that one can predict that palladium, platinum, and gold will be methylated in the environment.

The Pd : Rh ratios were higher than Pt : Rh ratios in lettuce grown at both sites (**Figure 15**) implying very well the higher mobility of palladium in soil than platinum under the current experimental conditions. Furthermore, palladium showed higher concentrations in lettuce plants grown at both sites than platinum (**Figure 13 and 14**) revealing its higher bioavailability for uptake by lettuce than platinum. However, the present study shows that palladium is more mobile than platinum, in the soil. It was also taken up by lettuce to higher extent more than platinum indicating its bioavailabilty. Accordingly, the mobility of PGE in soil, as well as preference for plant uptake, can be arranged as follows: Pd > Pt ≈ Rh. Based on these results, it is reasonable to conclude that palladium is preferred for plant uptake more than platinum.

5.4 Uptake und Accumulation of Platinum and Palladium: Differences between Monocotyledonous and Dicotyledonous Plant Species

Field experiments on the uptake of PGE by crop plants were conducted by adding the three noble metals platinum, palladium, and rhodium that were present together in the autocatalyst's powders, to the soils. To study the individual uptake and transport mechanisms of platinum and palladium in crop plants, metals were added separately as soluble salts to the hydroponic medium. Furthermore, the difference between platinum and palladium uptake by monocotyledonous (barley; *Hordeum Vulgare* L.) and dicotyledonous (potato; *Solanum*

tuberosum L. and lettuce; *Lactuca sativa* L.) plant species were compared. This has been done by treating potato (**II**) and lettuce with 300 µg/l (low-level treatment), and potato (**I**) and barley with 2000 µg/l (high-level treatment) soluble platinum and palladium chloride salts.

At the high-level treatments (2000 µg/l), the higher total (average) platinum and palladium concentrations in barley in comparison to potato plants indicate that the monocotyledonous plant accumulate higher amount of the two noble metals than the dicotyledonous one, especially in their roots (**Figure 22**). It should be mentioned that barley plants were treated with platinum and palladium salts for 4 weeks, whilst potato (**I**) plants were treated for two weeks, which led to the higher platinum and palladium concentrations in barley than in potato roots. Nevertheless, potato plants accumulated higher platinum in their shoots than barley and lettuce (**Figure 16 and 22**). Potato accumulated more palladium than barley but less than lettuce (**Figure 16 and 22**). Although, palladium mainly, and platinum to a lesser extent, were retained in the roots of potato, lettuce, and barley they were taken up into the plant shoots.

High green mass production of a plant, which is the case of potato plants, has been given as a reason for a high metal uptake and accumulation (Greger 1999) and suggested to occur in organs with high mass production (Huang et al. 1997). These findings indicate that the uptake of platinum and palladium depends on plant species which is in agreement with other studies. Alt et al. (1988) found relatively higher amounts of platinum in barley (monocotyledonous) than radish (*Raphanus sativus* L.) and tobacco (*Nicotiana* L.) (dicotyledonous) roots. However, tobacco leaves contained relatively higher platinum concentration than radish leaves. Moreover, cucumber (*Cucumis sativus*) plants (dicotyledonous) accumulated more platinum than rye grass (*Lolium perenne*) (monocotyledonous) suggesting that dicotyledonous accumulates metals to a higher extent more than monocotyledonous plant species (Verstraete et al. 1998). Furthermore, Fitzgerald et al. (2003) found that copper accumulated primarily in the roots of the monocotyledonous and dicotyledonous plants, whilst lead accumulated mainly in the root of monocotyledonous but in the shoots of dicotyledonous plants. Keller & Deuel (1957) suggested that the difference in metal accumulation between monocotyledonous and dicotyledonous plant species is due to the number of negatively charged sites located in the cell walls, which is higher in dicotyledonous than in monocotyledonous plants.

According to Warren et al. (2003), the arsenic concentration of crop plants increased in the approximate order: potato (*Solanum tuberosum*) < spinach (*Spinacea oleracea*) < cauliflower (*Brassica oleracea*) < lettuce (*Lactuca sativa*) < beetroot (*Beta vulgaris*) < radish (*Rhapanus*

sativus). A comparison may be made with the order for arsenic concentration in crops grown on arsenic contaminated estuary sediments in the Netherlands which was wheat < potato < carrot < lettuce < grass < radisch (Smilde et al. 1982). In the present study, platinum and palladium concentrations (total average) increased as follows: lettuce < potato at the low-level (300 µg/l) and potato < barley at the high-level (2000 µg/l) treatment which is not in agreement with the previously mentioned experiments. By only considering platinum and palladium concentrations in the shoots (**Figure 16 and 22**), the order of increase at low- and high-level treatments was: lettuce < potato (for platinum) and potato < lettuce (for palladium), and barley < potato (for both metals), respectively. This indicates that the uptake of noble metals into shoots, to some extent, depends not only on plant species but also on metal species applied (compare platinum with palladium concentration in **Figure 50 and 51**). Furthermore, the platinum and palladium concentrations in the shoots and the roots of potato plants increased with increasing concentration of the two metals in the hydroponic medium (**Figure 50 and 51**). However, the recovery of platinum and palladium from the hydroponic medium depends on plant species, metal species, and noble metal concentration in the nutrient medium.

Potato, lettuce, and barley treated with 300 µg/l and 2000 µg/l platinum and palladium in the nutrient solution, respectively, accumulated platinum and palladium levels that were higher than platinum and palladium supplied in the nutrient solution. This suggests that potato, lettuce, and barley accumulate platinum and palladium against the concentration gradient. It has been reported by Verma & Dubey (2003) and Shah et al. (2001) that rice plants (*Oryza sativa* L.) accumulated heavy metals (Cd and Pb) against the concentration gradient since Pb concentration found in rice shoots and roots after 20 days of treatment with $Pb(NO_3)_2$ were far higher than the amount added to the nutrient medium.

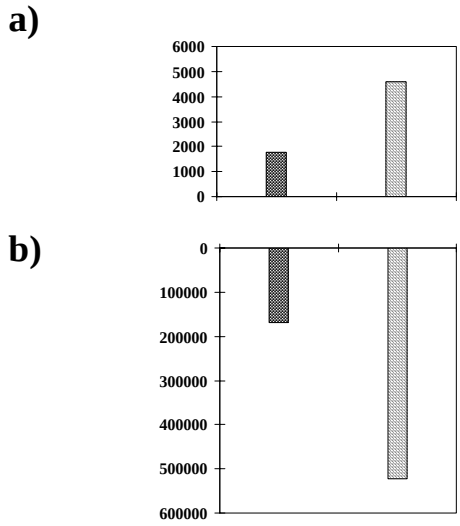

Figure (50): The increase of platinum concentration in shoots (dark) and roots (light) of potato plants. (a = Pt concentration in low-level and b) Pt concentration in high-level treated plants.

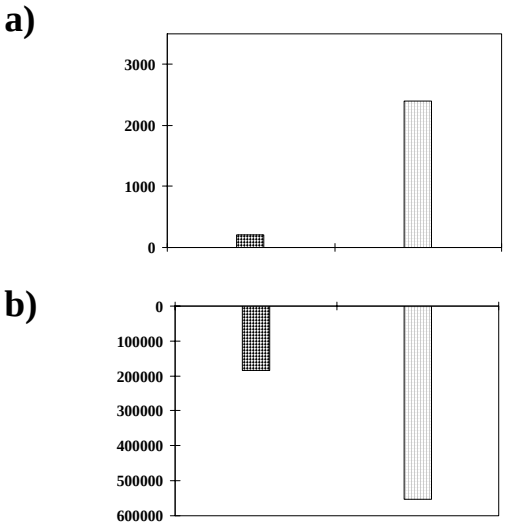

Figure (51): The increase of palladium concentration in shoots (dark) and roots (light) of potato plants. (a = Pd concentration in low-level and b) Pd concentration in high-level treated plants.

5.5 Distribution of Platinum and Palladium in Greenhouse Plants

Accumulation, Transport, Mobility, and Binding of PGE by Crop Plants

5.5.1 Retention of Platinum and Palladium in Plant Roots

Heavy metal accumulation in plants differs greatly among plant species and also among organs or tissues in the same plant (Ramos et al. 2002). Platinum and palladium were mainly found in the roots of potato, lettuce, and barley. According to Davies (1980), this pattern (i.e. higher metal concentration in roots than shoots) was observed in grasses and lettuce, whereby 65-90% and only 50% of the total Cd content found in the two plants, respectively, was located in the roots. However, higher Cd concentrations in leaves than in roots of spinach and lettuce were observed by Kabata-Pendias & Pendias (1992). Lettuce, endives, and other similar horticultural plants tend to accumulate Cd in the above-ground parts, since they have a relatively

high potential for Cd uptake and translocation (FAO 1983). Moreover, the transport of platinum and to a lesser extent palladium to the tops of tomato (*Lycopersicon esculentum* L.), bean (*Phaseolus vulgaris*), and corn (*Zea mays* L.) has been shown by Farago et al. (1979).

The roots of plant species (potato, lettuce, and barley) examined in the present study contained higher platinum and palladium contents compared to the other plant organs such as shoots or tubers (**Figure 16, 18, 19, 20, 21, 22, 23, 24, 25, and 26**). Since metals, after their uptake, are transported either apoplastic (in cell walls) or symplastic (from cell to cell or membrane transport) (Greger 1999; Wittke 2002) from roots to shoots, it is suggested that the roots of potato, barley, and lettuce acted as a barrier against transport of platinum and palladium into the upper plant organs. The root system barrier was more effective against palladium than platinum, which led to restricted palladium transport into the plant shoots (**Figure 16 and 22**). However, barley at the high-level treatment showed the most effective barrier against platinum and palladium uptake. Barley uptake was stronger than lettuce and potato indicated by the higher concentration of platinum and palladium in barley roots than potato and lettuce roots (**Table 14B, 15B, 16B, and 17B; Appendix B**). At both treatment levels, potato seems to have developed poor effective exclusion mechanism(s) against platinum and palladium uptake from the hydroponic medium. This is because the concentrations of platinum and palladium in potato shoots and roots increased with increase of noble metal concentration in the hydroponic medium, which is well illustrated in **Figures 50** and **51**.

However, the lower amounts of palladium taken up into the shoots of potato, lettuce, and barley, compared to platinum could have several reasons. The cell wall plays an important role in the binding of metal species. Farago & Parsons (1994) concluded that most of the platinum taken up by water hyacinth (*Eichhornia crassipes*) was bound to α-cellulose of the cell walls.

The cell wall binding could fully saturate at such palladium but not platinum concentration in the hydroponic medium. Similar results have been shown for bread (*Triticum aestivum* L.) and durum wheat (*Triticum turgidum* L.) plants at Cd^{+2} concentration of 90 µM in the nutrient solution (Hart et al. 1998). Moreover, saturable time-dependent Cd accumulation was reported in barley (Cutler & Rains 1974). According to Dunbar et al. (2003), the concentrations of Cd in the roots greatly exceed that of the other potato tissues suggesting that most Cd in roots should have been symplastic due to binding in the cell wall. Moreover, Wagner (1993) and other authors showed that Cd binds to cell walls and its translocation to shoot was limited.

The retention of palladium in roots reduces its transport to the aerial parts, which could be due to one of the exclusion mechanisms excreted by plants against palladium phytotoxicity. Phytotoxic symptoms of palladium on crop plants are shown in **Figure 43, 46, and 49**. The large differences between platinum and palladium concentration in shoots and roots of potato and lettuce indicate an important restriction to the internal transport of those metals from the roots towards aerial parts (leaves, leaf stalks, and stems). Immobilization of platinum and also palladium (to a greater extent in root systems) as emphasized by the shoot : root ratio quotient <<1 is related to an exclusion strategy. However, metal tolerance depends on plant species and may result from two main strategies which according to Baker (1981) are metal exclusion and metal accumulation. Dahmani-Muller et al. (2000) suggested an exclusion mechanism by immobilization of Pb and Cu in plant roots.

It has been demonstrated that plant roots contained the highest Cd concentrations of all organs (Florjin & Van Beusichem 1993; Guo et al. 1995; Hart et al. 1998). Furthermore, studies conducted by Farago et al. (1979) and Farago & Parsons (1986a; 1994) with PGE soluble salts applied at different concentrations to water hyacinth showed similar results. In uptake experiments with poplar cuttings, Ballach (1995; 1999), Ballach & Wittig (1996) and Ballach et al. (2000) showed that platinum (IV) was accumulated, to a great extent, in the roots than the shoots. In the present study, PGE were mainly accumulated in roots of crop plants and translocation to the shoots is demonstrated.

5.5.2 Distribution of Platinum and Palladium in Potato Tubers

Based on calculations of metal ratios in the different organs of plants, the concentrations of platinum and palladium in potato tubers may be influenced by one or several physiological factors, including different uptake mechanisms of both elements from nutrient solution, translocation from roots to shoots via xylem, sequestration in subcellular compartments, and re-translocation from source (mature leaves) to sink organs (tuber, younger leaves) via phloem.

The lower palladium than platinum concentration in the tubers of potato plants treated with 300 µg/l palladium and platinum chloride salts, was a result of the toxic effect of palladium (as shown in **Figures 43 and 46**) which led to a reduced uptake of palladium from the nutrient medium and its re-translocation from leaves to tubers. This suggestion is supported by the higher leaf : tuber metal ratios of platinum than palladium (**Figure 29**). Reid et al. (2003), using short-

term experiments with Cd^{109}, showed that rapid exchange of Cd between stem and phloem was possible and Cd in leaves could be rapidly transferred to tubers. It remains unclear if the early death of palladium treated potato plants resulted in severe phytotoxic symptoms of this metal that led to rapid tuber bulking and thus transport of this metal into tubers. However, leaf : tuber ratios of platinum and palladium concentration, were generally higher than other ratios calculated for other plant organs (**Figure 29 and Table 23B; Appendix B**). This indicates that the noble metals were accumulated mainly by leaves and transported into tubers via phloem. Platinum and palladium concentrations in tubers were lowest among plant shoots and roots indicating that the noble metals were not accumulated mainly in the tubers, but rather in the root systems and aerial parts.

Platinum concentration in the shoots (5227 µg/kg DW) of the high-level (2000 µg/l) treated potato plants was approximately 3-times higher than in shoots (1791 µg/kg DW) of the low-level (300 µg/l) treated plants. The increase of platinum concentrations in the nutrient medium led to an increase of the platinum concentration in shoots by a factor of 6 (high-level treatments) and by a factor of 3 (low-level treatments) than tubers. The increase of palladium concentration in the nutrient medium from 300 to 2000 µg/l led to an increase of its concentration in shoots (204 and 2403 µg/kg DW, respectively) by approximately a factor of 12. Consequently, palladium content in the tubers (1204 µg/kg DW) of plants treated with 2000 µg/l was 6-times higher than in the tubers (184 µg/kg DW) of plants treated with 300 µg/l palladium chloride. However, the platinum and palladium concentrations in potato shoots and tubers correlate positively with each other and with their concentration in the nutrient medium.

Currently, no data are available on PGE mobility in phloem and their transport from shoots to tubers. The same amount of platinum and palladium was added separately to the nutrient solution. Even by calculating their concentration as µmol/kg DW (**Table 18B and 19B; Appendix B**), the low palladium and high platinum concentration in tubers indicate that a direct uptake across the tuber periderm or via stolon and tuber roots was negligible, if not excluded. Although the periderm of the tuber accumulated high concentration of Cd, a direct penetration of the metal into the tuber itself was limited (Reid et al. 2003). The latter also added that the phloem has a dominant role in supplying nutrients to the tubers. However, under the current experimental conditions, phloem is suggested to play an important role in transport of platinum and palladium into potato tubers.

Radiotracer experiments on the uptake of ^{45}Ca by potato plants conducted by Davies & Millard (1985) showed that the periderm was the area of highest ^{45}Ca activity. The periderm clearly had the highest and the medulla the lowest Ca concentration. Furthermore, calcium requirements of the sprout will be met by root uptake and xylem transport. However, three movement pathways of Ca were suggested by Davies & Millard (1985): (1) Movement in the xylem (apoplast) as a consequence of evapotranspiration from the sprout surface; (2) Movement by mass flow in the phloem, and (3) Movement in the symplasm in response to gradients in osmotic potential. Unfortunately, comparable data on the transport mechanisms of PGE within plants are not available. Nevertheless, comparing PGE with Ca, an element with a relative immobility in the symplasm (Davies & Millard 1985), it seems that PGE could be transported by all these pathways. However, platinum has been shown to displace calcium in grass treated with platinum and the Ca deficit in the plant was assumed to be a reaction to platinum stress (Klueppel et al. 1998)

The ratio of metal concentrations in leaves to their concentrations in tubers may be indicative of the ability of solutes to be mobilized from leaves into phloem. This assumes that the tuber does not access significant Cd through the tuber skin or stolon roots (Reid et al. 2003). Certainly, in the case of PGE, metal ratios of platinum and palladium concentrations in potato organs might explain their transport pathways. However, platinum and palladium ratios of leaf : tuber were mostly higher than leaf stalk : tuber and stem : tuber, which were nearly similar (**Figure 35, 38, and 39**). These patterns of metal ratios strongly support the view that phloem is the major pathway for loading platinum and palladium into tubers. In both hydroponic experiments with potato, palladium concentrations in the stems were higher than in leaf stalks. This supports the hypothesis that the phloem plays an important role in transport of PGE, especially palladium transport from leaves to tubers. The high palladium concentrations of potato roots compared to other organs (**Figure 18, 19, 23, and 24**) might indicate a certain defence mechanism against the phytotoxic Pd^{+2}, perhaps by a mechanism involving sequestration or decreased xylem loading of palladium.

Based on the noble metal concentrations and ratios in potato organs, it seems reasonable to conclude that the most likely pathway for platinum and palladium movement into tubers is from the hydroponic medium to the basal roots to shoots in the xylem, then back down to tubers in the phloem. Here exists the xylem connection between roots and leaves indicated by the concentration of platinum and palladium in aerial parts. Furthermore, the phloem connection between leaves and tubers is indicated by the considerable concentration of the two noble metals

in potato tubers as well as the high leaf : tuber metal ratios. In the future, radiotracer experiments with PGE are necessary to exactly define whether PGE are a subject to direct uptake into potato tubers across the periderm.

5.5.3 Translocation of Platinum and Palladium within Crop Plants

The plant species examined in the present study showed great variation in the uptake of platinum and palladium via roots. The higher platinum concentrations in all plant organs (except roots) than the palladium are possibly a result of variations in both metals uptake via roots and in transport from root to shoot. This is well illustrated by variations of both metal concentrations and their ratios in the different plant organs (**Figures 18, 19, 20, 21, 23, 24, 25, 26, 27, 28, 29, 30, 31, and 32**). The higher platinum than palladium concentrations in the shoots and the higher palladium than platinum concentrations in the roots of potato (**Figure 18, 19, 23, and 24**) reflect differential distribution of platinum and palladium between roots and shoots. Figures **27, 31, 33, and 36** illustrate the shoot : root ratio in all plants, which indicate that these ratios were mostly higher for platinum than palladium. This implies that a higher proportion of platinum than palladium will be transported from the nutrient medium via roots into shoots. Retention of palladium in plant roots was higher than platinum, which is demonstrated by the lower root : shoot ratios of the latter than the former (**Figure 28, 32, 34, and 37**). This pattern is more clearly illustrated when platinum and palladium concentrations in all plants and plant organs (except barley) are expressed in µmol/kg DW (**Table 18B, 19B, 20B, and 21B; Apendix B**). Barley shoots showed higher platinum concentrations (expressed as µg/kg DW) than palladium and barley roots were of similar platinum and palladium concentrations (**Figure 25 and 26**). When taking platinum and palladium concentrations, expressed in µmol/kg DW, into account, palladium concentrations in the shoots were slightly higher than platinum, whilst palladium concentrations in the roots were twice higher than platinum (**Figure 52 and 53**). Palladium concentrations of lettuce roots, expressed in µmol/kg DW were higher than platinum (**Figure 54**).

By taking the leaf : stem (L : Sm) ratios of potato (**Figure 29**) and lettuce (**Figure 30**), both at the low-level-treatments, as well as leaf : leaf stalk (L : LS) ratios of potato (**Figure 29**) into account, it is clear that palladium is more mobile than platinum and will translocate more into leaves implying its high xylem mobility than platinum.

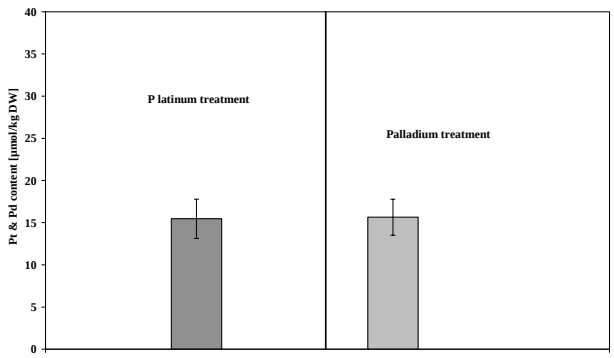

Figure (52): Platinum and palladium concentration, expressed in µmol/kg DW, in barley shoots. Both noble metals show similar concentration in barley shoots.

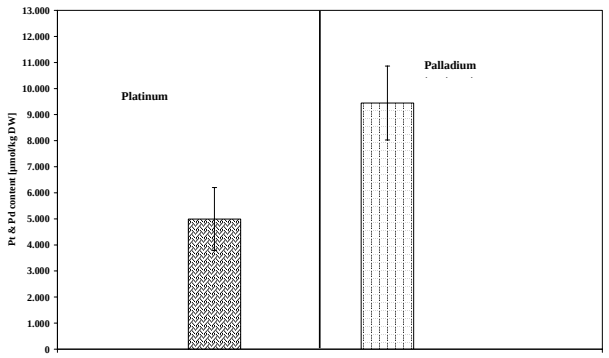

Figure (53): Platinum and palladium concentration, expressed in µmol/kg DW, in barley roots. Palladium concentration is higher than platinum in roots.

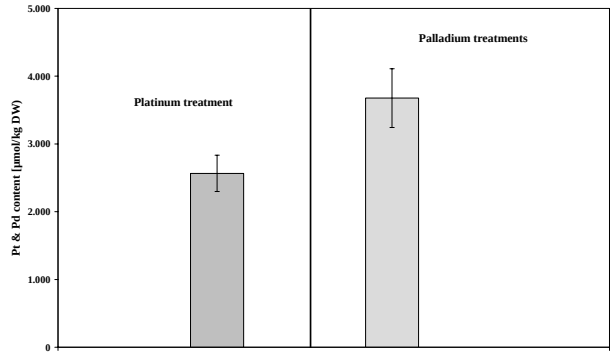

Figure (54): Palladium shows higher concentration (expressed in µmol/kg DW) than platinum in lettuce roots.

Irrespective of plant species, higher amounts of platinum than palladium were found in the shoots, whereas higher amounts of palladium than platinum were found in the roots. There were differences in the translocation of both metals from the roots to the shoots of potato and lettuce. The restricted translocation of palladium from the roots to the shoots reduces consequently its transport via xylem and re-translocation via phloem into sink organs such as tubers and younger leaves. Cadmium, a non-essential metal like PGE, showed high mobility in both xylem and phloem (Reid et al. 2003). In their long-term experiments with ^{109}Cd, it has been demonstrated that Cd concentrations in the stems were actually lower than in the leaves. In short-term experiments, Cd was rapidly sequestered by stems, which was the case in stems of palladium treated potato plants. Furthermore, stems quite possibly act as a major interchange site for transfer of solutes between xylem and phloem. Reid et al. (2003) suggested that stems may act as a transitional storage pool that turns over rapidly, and from which Cd and other nutrient elements

are redistributed to leaves and tubers of potato plants. However, potato, especially at the low-level treatments, showed higher palladium content in stems than leaf stalks. This can be explained by the sequestering of palladium in the stem, which was not the case for platinum. Moreover, accumulation of palladium in potato and lettuce stems might be desirable, not only because it alleviates palladium injury in plants, but also because it reduces palladium entry into the human food chain.

Ballach & Wittig (1996) pointed out that the root : shoot (R : S) and especially the root : leaf (R : L) ratios showed a strong correlation to platinum content in roots of poplar cuttings (*Populus maximowiczii* L.). Furthermore, platinum was accumulated in roots but not translocated to aerial organs of water hyacinth (Farago & Parsons 1994), tomato and bean plants (Farago et. al. 1979), South African grass (Farago & Parsons 1986b), cucumber (Verstraete et al. 1998), and grass (Klueppel et al. 1998).

Since plants treated with platinum and palladium were fed with the same nutrient solution containing the same inorganic nutrients (**Table 3**), the high platinum and low palladium concentration can not be referred to as a deficiency of some elements such as Cu, Fe, and Zn. Graham et al. (1992) and Cakmak et al. (1998) pointed out that higher Cd accumulation in grains of wheat may be related to their higher sensitivity to Zn deficiency. Nevertheless, a relationship between the applied platinum concentration and the uptake of Fe and Zn has been reported by Farago & Parsons (1986b). Hart et al. (1998) mentioned that Cd uptake appears to occur via a carrier mediated system, since Cd is not known to be an essential plant mirconutrient. Studies conducted by Cataldo et al. (1983) and Costa & Morel (1993) showed that Zn competitively inhibits Cd uptake in plant roots, suggesting that Cd is transported across the plasma membrane via a native Zn-transport system. Transport systems, in which PGE are involved, are not known at present.

A plant must have the ability to translocate an element from roots to shoots at high rates. Normally, Zn, Cd, or Ni concentrations in roots are 10 or more times higher than in shoots. In hyperaccumulators, metal concentration in the shoot can exceed that in root (Chaney et al. 1997 and references therein). The higher concentration of platinum in aerial organs of lettuce (**Figure 20**) and potato (**Figure 18 and 23**) compared to palladium, suggests that the uptake and transport of platinum in lettuce and potato does not underlie an exclusion strategy as for palladium. A diffusion mechanism may allow platinum to be more transported with sap than palladium to stems and leaves.

The noble metals shoot : root ratios in potato (**Figure 27 and 33**) and lettuce (**Figure 31**) were higher for platinum than palladium suggesting that palladium was more immobilized in the roots of potato and lettuce than in platinum. Interestingly, these ratios for platinum (0.003) were similar to that calculated for palladium (0.002) in barley indicating common uptake, translocation, and accumulation mechanisms in this monocotyledonous plant. Furthermore, the similar shoot : root ratios calculated for platinum in potato plants from the two hydroponic experiments (0.010 - 0.011), which were higher than lettuce (0.003), imply the uptake variations between the two dicotyledonous plants. The shoot : root ratio for palladium (0.004) in the 2000 µg/l treated potato plants was higher than that (0.001) of the low-level treatments (300 µg/l), indicating that palladium was taken up rapidly depending on the metal concentrations in the hydroponic medium. However, palladium shoot : root ratios in potato and lettuce (300 µg/l treatments) were similar (0.001) but lower than potato (0.004) and barley (0.002) treated with 2000 µg/l. This indicates similar uptake mechanisms in potato and lettuce as well as plant species dependence of palladium uptake.

Presently, no data exists on the importance of cell wall binding of platinum and palladium and the limitation of the translocation into shoots via xylem. Klueppel et al. (1998) concluded that a major proportion of platinum taken up was not metabolized but deposited or stored in the phloem and xylem of grass or precipitated in the vacuoles, similar to Cd (Vögeli-Lange & Wagner 1990). At present, no data concerning the chemical species and transport mechanisms of PGE movement in the phloem sap are available.

5.5.4 The Role of Xylem and Phloem in the Transport of Platinum and Palladium

The considerable amounts of platinum and palladium found in potato tubers indicate their high mobility in the phloem. However, palladium is suggested to be more mobile in the phloem than platinum in potato and lettuce plants. The main function of the phloem is the transport of photoassimilates (mainly sucrose, Riesmeier et al. 1993; Kühn et al. 1999) from “source” tissue (actively photosynthesizing leaves) to “sink” tissue (immature leaves, growing root tips, and developing flowers, fruit, tuber, and seed) (Eckardt 2001). The transport of materials through phloem sieve tubes is passive, nonselective, and driven entirely by pressure gradients that are maintained by active loading of photosynthate in source tissue and unloading of materials in sink tissue (for a review see Riesmeier et al. 1993; Kühn et al. 1999; Eckardt 2001). Potato has been

suggested to represent an excellent system in which to explore how Cd moves around plants because of the dominant role of phloem in supplying nutrients to the tubers (Reid et al. 2003). Although a lesser amount of palladium than platinum was taken up by lettuce roots into stems and leaves (**Figure 20 and 21**), palladium was transported more into the leaves than platinum was, which is well demonstrated by the leaf : stem (L : Sm) ratios shown in **Figure (30)**.

The total platinum concentrations in shoots were higher than palladium (**Figure 16**). Higher proportion of the latter than the former was translocated into leaves indicating its high mobility within plants. More platinum was translocated to shoots of lettuce and more palladium was translocated to leaves as indicated by the higher platinum shoot : root ratio than palladium (**Figure 31**) and the higher palladium leaf : stem ratio than platinum (**Figure 30**). These indicate that palladium within shoots (phloem) had higher mobility than platinum, and higher platinum amounts than palladium were retained in the stems of lettuce. The noble metal concentration ratios of potato organs displayed the greatest differences (**Figure 29**) suggesting the mobility of both metals in the phloem. Palladium might be removed from the transpiration stream by rapid transport into potato tubers to coupe its toxic effect. Removal of Cd from the transpiration stream suggests that Cd may have been transported to the grain of durum wheat primarily by the phloem (Harris & Taylor 2001).

The processes involved in PGE movement in plants are unknown. However, the re-translocation of platinum and palladium into potato tubers appears likely to occur by loading via phloem. This is well illustrated by the considerable amounts of platinum and palladium in stems and leaf stalks of potato (**Figure 18 and 23**).

In the present study, palladium was applied as Pd^{+2} and platinum as Pt^{+4} chloride salts. Krüger et al. (2001) suggested that divalent metals are transported as complexes of metal-binding proteins within the phloem. Unfortunately, there is no equivalent information available for palladium and platinum. Therefore, it is difficult to make any meaningful comments about its likely speciation in phloem. From cancer therapies, it is known that platinum binds to proteins and inhibits cell division. There have only been a few studies conducted by Bournique et al. (1976), Ivanov et al. (1976), Pauw-Gillet et al. (1979), and Dubrovsky (1993) on how *cis*-platin affects plant cell division. Platinum also has an affinity to form strong chloride complexes. Therefore, PGE chloride complexes could be abundantly present in the phloem, where Cl, according to Reid et al. (2003), is abundant in the phloem.

5.5.5 Binding, Exclusion, and Tolerance of Crop Plant to Platinum and Palladium

According to Sanita di Toppi & Gabrielli (1999), plant tolerance to heavy metals can be achieved by different strategies: selective exclusion of metals during uptake, metal excertion, metal retention in roots, immobilization by means of cell walls and extracellular carbohydrates, complexation by metal-binding to low-molecular weight proteins (phytochelatins = PCs), and specific tolerance of enzymatic systems to a metal.

Generally, a possible tolerance of potato, barley, and lettuce to PGE could be by metal retention in roots, immobilization by binding onto cell walls, and complexation by PGE-binding low-molecular phytochelatins (PCs). Messerschmidt et al. (1994) and Weber et al. (1998) reported that PGE were found in the low-molecular weight fraction. At present, there are no data available on the tolerance of plants to PGE. Nevertheless, Cd tolerance has been shown to be related to the ability to synthesize phytochelatins (Rauser 1990; Cobbett 2000). Furthermore, phytochelatins stimulated vacuolar storage of Cd in roots and prevented xylem transport of Cd from roots into shoots (Cakmak et al. 2000). PGE as well as Cd have high affinity to bind to sulfhydryl groups. Zhang et al. (1998) concluded that Zn and Cd were replaced by Pt in metallothioneins (MTs) from rabbits treated with platinum and that platinum can be bound strongly by MTs. Bao et al. (1997) demonstrated the affinity of platinum to rabbit liver MTs, which was higher than Zn and Cd. Unfortunately, no data exits on the binding of PGE to phytochelatins in plant species.

Platinum has been found to bind completely to protein of high molecular mass fraction (> 100 kDa) in untreated grass, whereas in treated cultivars, 90% of total platinum appeared in several fractions of low molecular mass fraction (Klueppel et al. 1998; Messerschmidt et al. 1994, 1995). Alt et al. (1998) also concluded that platinum binding ligands in grass, treated with tetramine platinum(II)nitrate, were carbohydrates and not peptides as shown by Klueppel et al. (1998) and Messerschmidt et al. (1994, 1995). Recently, platinum, palladium, and rhodium were assumed to bind to proteins of a wide range of molecular masses as well as carbohydrates in the low molecular mass range in grass studied by Lesniewska et al. (2004b) and in lettuce studied by Weber et al. (2004). Klueppel et al. (1998) couldn't definitively identify phytochelatins (PCs) in

platinum treated grass. However, cadmium has been suggested to be move into vacuole by two main routes, either by complexation with phytochelatins (PCs) followed by active transport of the PC-Cd complex across tonoplast (Vögeli-Lange & Wagner 1990; Ortiz et al. 1995; Salt & Rauser 1995), or by H^+/Cd^{2+} antiport (Salt & Wagner 1993). The induction of phytochelatin synthesis in lettuce at different levels of Cd concentrations is well demonstrated by Maier et al. (2003), who added that phytochelatins were present in lettuce and probably an important component of metal detoxification. Phytochelatins (PCs) are low molecular mass (1.5-3 kDa) peptides (Lesniewska et al. 2004b) which bind heavy metals in plants. Based on data from the above mentioned studies, it is assumed that PGE might induced phytochelatin synthesis in crop plants examined here as a metal detoxification mechanism, although phytochelatins were not determined in the present study.

Although barley accumulated considerable amounts of PGE, no severe phototoxic symptoms n barley were observed. This might indicate the binding of noble metals in the vacuole. Uptake studies using Zn^{65} with barley leaves showed that a rapid compartmentation of Zn into the vacuole was an important mechanism dealing with high levels of Zn (Brune et al. 1994). Further studied on barley leaves showed that Cd, Zn, and Mo were found mainly in the vacuole (Brune et al. 1994, 1995).

By comparing the shoot : root (S : R) ratios of platinum and palladium concentration within a species such as potato (**Figure 27 and 33**), the high tuber platinum or palladium accumulators had the highest ratios. This suggests that the high tuber platinum and/or palladium accumulation is associated with an increased shoot : root platinum and/or palladium ratio. Florijn & van Beusichem (1993) indicated the existence of two groups of lines – "shoot Cd excluders" containing a relatively high Cd concentrations in the root with a low concentration in the shoot (a shoot : root ratio of approximately 0.02), and "non-shoot Cd excluders" exhibiting a much higher translocation of Cd to the shoot (a shoot : root ratio of approximately 0.8) – both having a similar total Cd uptake. However, barley and lettuce showed shoot : root ratios for platinum (mean = 0.003, **Table 24B and 25B; Appendix B**) and palladium (mean = 0.002 and 0.001, respectively) imply that both plants are "shoot platinum and palladium excluders". Furthermore, potato showed shoot : root ratios that were higher for platinum (mean = 0.01 at both treatments, **Table 22B and 23B; Appendix B**) than for palladium (mean = 0.001 and 0.004, at low- and high-level treatments, respectively), indicating that potato; compared to barley and lettuce, is a "non-shoot platinum, but a palladium excluder". The lower shoot : root metal ratios for palladium than for

platinum could be due to the phytotoxic effect of palladium that led to lower palladium uptake by potatoes. Based on these results, an exclusion strategy and restriction of palladium uptake by the three plants which was higher in the case of barley but lower in lettuce and potato, is suggested.

Since platinum and palladium concentrations in shoots were far lower than in roots, potato, lettuce, and barley can not be considered as hyperaccumulators of PGE in the present study. Baghour et al. (2002) mentioned that field grown potato is a hyperaccumulator of platinum under different root zone temperatures, whereby platinum concentrations in shoots were higher than in roots. Therefore, further short-term experiments must be conducted to shed more light on this point.

The results of the current experiments suggest that lettuce and barley are able to retain more platinum and palladium in their root systems than potato. They would also be more tolerant to platinum and palladium than potato and would survive with higher platinum and palladium concentrations in their shoots without severe symptoms of toxicity. Cultivars of *Lactuca species* (i.e. lettuce and endives) have been considered as Cd accumulating species with relatively high potential for Cd uptake and translocation (Ramos et al. 2002).

5.6 Phytotoxicity of PGE on Crop Plants

A little amount of palladium taken up was far more toxic compared to platinum (**Figure 41 to 46**). Moreover, platinum to a greater extent than palladium was transported to leaves reconcile the continued need for xylem input in order to replace transpirational losses of water. Palladium was retained at a higher proportion than platinum in potato roots which is explained by the toxic effect of palladium leading to earlier death of the plants which reduced the uptake. Comparing the elemental composition in each plant organ, platinum was generally higher than palladium (except for roots) as shown in **Figure 18, 20, 23, and 25**. This suggests that palladium is preferentially sequestered either by physical compartments such as the vacuole or into chemical complexes.

The high platinum and palladium concentrations in leaves compared to stems, leaf stalks, and tubers of potato plants (**Figure 18 and 23**) might indicate that both elements are interfering with the photosynthetic processes since stems, leaf stalks, and tubers are organs with low

transpiration. High platinum and low palladium concentrations in potato and lettuce leaves (**Figure 18, 20, and 23**) indicate that palladium is more phytotoxic and affecting the photosynthetic processes.

As mentioned previously in chapter (IV), the main visible symptoms of phytotoxicity resulting from the addition of platinum and palladium to the hydroponic medium were chlorosis, brown patches on tips of leaves (**Figure 41, Picture 5 and 6; Appendix A**), and that upper leaves were visibly smaller compared to control plants. These symptoms were very clear in the case of potato plants at both treatment levels. The leaves were clearly yellow, the upper leaves were smaller than the middle and lower ones of the same plant and smaller than upper leaves of control plants. Roots of PGE treated plants were darker than roots of control ones. These phototoxic effects were more intensive in the case of palladium than platinum treated plants.

The stunted growth and small leaves of these plants were similar to the symptoms of PGE exposure described by Michenfelder et al. (1988) and Farago & Parsons (1983c; 1994). Roots of palladium treated potato, lettuce, and barley appeared generally darker than the roots of control plants. This was perhaps due to root death in the case of potato, or accumulation of platinum and palladium in case of lettuce and barley. Similar symptoms were observed in palladium treated plants but to a lower extent.

It has been shown by Farrago et al. (1979; 1983a; 1983b; 1983c) that PGE at low concentrations in the hydroponic medium were not phytotoxic to corn, tomato, and grass, whereas the growth of Kentucky blue grass was stimulated by small amounts of palladium (II) chloride which was phytotoxic at higher levels (Sarwar et al. 1970). In the present study, the two treatment levels were neither severely toxic nor had tonic effects on barley and lettuce but, were very toxic to potato.

At the two treatment levels, platinum and palladium did not adversely affect growth and viability of lettuce and barley, respectively. Platinum and palladium could be sequestered in vacuoles of lettuce and barley and thus, making those potentially toxic metals unavailable for interaction with metabolically active cellular compartments. Platinum and palladium are not essential nutrients, but they have been shown to be toxic to potato plants. It is curious as to what drives their movement between plant tissues, and in which physiological processes they are involved.

The platinum and palladium concentrations added at two different levels (i.e. 300 µg/l for lettuce and 2000 µg/l for barley) are considered to be at non-growth-inhibition concentrations, but for potato it was severely phytotoxic. According to Michenfelder et al. (1988), visible phytotoxic symptoms were observed at platinum levels higher than 2500 µg/l in the nutrient medium. Therefore, our results are in agreement with Michenfelder et al. (1988), but only for lettuce and barley, whilst potato was in disagreement with their conclusions.

Since PGE are oxido-reducing metals, they could induce oxidative stress in plants. The toxicity of palladium could be due to higher production of H_2O_2 mainly in chloroplasts (Verma & Dubey 2003) and other cell organelles leading to rapid cell death and consequently the whole plant, which resulted in lower uptake and accumulation of palladium in plant shoots.

Chapter VI

Summary, Conclusions, and Recommendations

VI Summary, Conclusions, and Recommendations

From field experiments conducted in the present study it has been demonstrated that the PGE emitted from automobile catalytic converters are subject to uptake by aerial parts of lettuce. The PGE, which were added as catalyst's powders to the soils were taken up by lettuce roots into aerial organs. The catalyst's powders contained PGE as metallic species, were added to the soil during the experiments with barley. Eighteen months later, experiments with lettuce were conducted in the same pots. The uptake of PGE by field grown lettuce, indicate that the PGE were bioavailable for plants. This suggests that PGE had undergone reactions with the soil components, such as humic matter or bacteria. The concentrations of palladium and platinum in the catalyst' powders were similar, though palladium was taken up by plant roots to a higher extent than platinum. It has been demonstrated that palladium is more bioavailable than platinum and rhodium for uptake and thus more mobile in the environment than platinum and rhodium.

Greenhouse experiments were conducted under controlled conditions and the PGE uptake was made exclusively via plant roots. The crop plants were treated with two different concentration levels of platinum and palladium chloride salts that were separately added to the nutrient solution. Two dicotyledonous (potato and lettuce) and one monocotyledonous (barley) plant species were examined in the present study. Platinum and palladium were mainly retained in the roots of potato, lettuce, and barley. Nevertheless, the noble metals were transported from the plant roots to the shoots. The crop plants accumulated higher platinum in their shoots than palladium, but lower platinum in their roots than palladium. However, palladium was more translocated into leaves than palladium. The dicotyledonous plants, which were grown in the greenhouse, accumulated higher platinum and palladium in their shoots, but lower in their roots than the monocotyledonous plant species. From the two experiments with potato plants, it has been shown that the PGE concentration in the plant organs depend on the PGE concentration in the nutrient media. It can be concluded that the uptake of noble metals depends on the plant species, the noble metal species applied, and the noble metal concentration in the nutrient medium.

In potato and lettuce aerial organs, platinum and palladium were mainly accumulated in the leaves indicating the mobility of the two metals within the two plant species. At present, no data are available on PGE mobility in the phloem and their transport from leaves into

potato tubers. However, results from the current experiments with potato plants, demonstrated that the phloem play an important role in the transport of platinum and palladium into potato tubers. Furthermore, palladium is suggested to be more mobile than platinum in plants and will translocate more into leaves implying its higher xylem mobility than platinum.

However, from the noble metal concentrations and ratios in the different potato organs, it seems reasonable to conclude that the most likely pathway for platinum and palladium movement into tubers is from the nutrient solution to the plant roots to shoots via the xylem then back down from leaves to tubers via the phloem. The current study presents a first approach to the transport of PGE within plant species since there are no comparable data and the processes involved in PGE movement in plants and transport systems, in which PGE are involved, are not known.

Lettuce and barley were able to retain more platinum and palladium in their root systems than potato. This suggests that the two plant species are more tolerant to platinum and palladium than potato and would survive with high platinum and palladium concentrations in their shoots without severe visible phototoxic symptoms. Nevertheless, a little amount of palladium taken up was far more toxic to potato compared to platinum.

The photosynthetic machinery is known to be extremely sensitive to some heavy metals and PGE are oxido-reducing metals. The high platinum and palladium concentrations in the leaves compared to other aerial parts and tubers of potato plants might indicate that both elements are interfering with the photosynthetic processes since stems, leaf stalks, and tubers are organs with low transpiration.

The two concentration levels of platinum and palladium were neither severely toxic nor had tonic effects on barley and lettuce but, were very toxic to potato and are considered to be at growth-inhibition concentrations for potato. The main visible symptoms of phytotoxicity were chlorosis, brown patches on tips of leaves, smaller upper leaves, and dark root systems compared to control plants. These phototoxic effects were more intensive in the case of palladium than platinum treated plants.

Recommendations based on this study are as follows:

1. Field experiments under natural conditions with other plant species, that might treated with PGE-containing dust or autocatalyst's powder are necessary.
2. Short-term experiments to study the phytotoxicity of PGE on further plant species are recommended.
3. Radiotracer experiments with PGE are necessary to exactly define whether PGE are a subject to direct uptake into the tuber across the periderm and their transport from leaves into tubers.
4. Greenhouse experiments are necessary to study the species and the transport mechanisms of PGE within the different plant species.
5. Phytochelatins (PCs) were not examined in the present study. Studies on PCs induction in plants by PGE are needed.
6. Biochemical and genetic studies are necessary to clear the role of phytochelatins in PGE detoxification.
7. Since PGE are used in catalytic reactions, it is recommended to conduct experiments to explain oxidative stress induced by PGE in plant species.
8. Study of superoxide dismutase (SOD) activities in mycorrhizal roots of PGE treated plants is also recommended.
9. Microscopic examination of plant roots treated with PGE to determine the role of root cell walls in binding of PGE.
10. The PGE concentrations in future hydroponic experiments with plants must be adapted to the estimated PGE emissions from catalytic converters into the environment.

VII References

VI References

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Appendices

Appendix A:

Plate 1: Some photographs from the field experiments.

Picture (1): Homogenization and filling of the soil in pots at the highway site for field experiments.

Picture (2): Filling soil from the barley field into the plastic pots (Mr. Bacher, Mr. Bacher Jr., and Simone Gießler.

Picture (3): Barley grown at the highway site.

Picture (4): A lettuce plant grown at the botanical garden site.

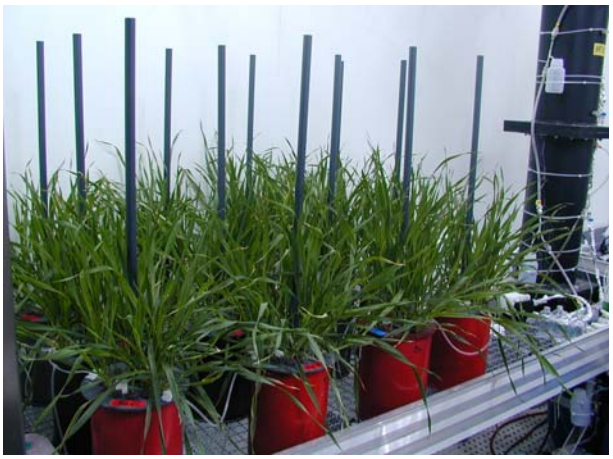
Plate 2: Some photographs showing the phytotoxic symptoms of platinum and palladium treated plants grown in the growth chamber.

Picture (5): Phytotoxic symptoms (chlorosis) of a potato leaf from the growth chamber experiments.

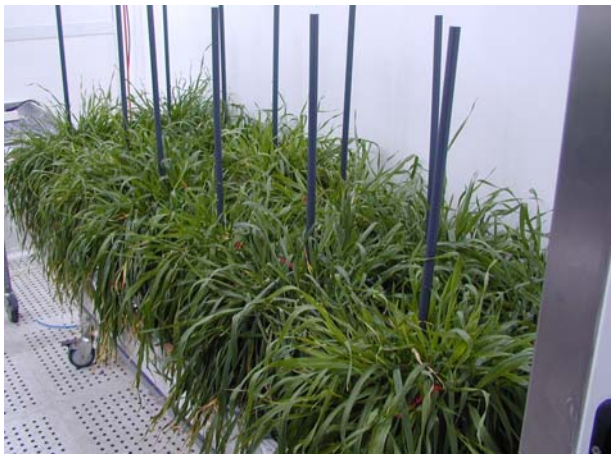
Picture (6): Phytotoxic symptoms: chlorosis and brown leaf edges of potato leaves treated with platinum.

Picture (7): Control potato plants in the growth chamber at the end of the experiment.

Picture (8): Early death of palladium treated plants (compare to picture 7 of control plants).



Picture (9): Barley plants grown in the growth chamber before treatment.



Picture (10): Barley plants showing no phytotoxic symptoms after treatment with platinum and palladium chloride salts.

Plate 3: Some photographs showing the phytotoxic symptoms of low-level (300 µg/l) platinum and palladium treated potato plants grown in the growth chamber.

Picture (11): A palladium treated potato plant showing dark roots and foam (oxidative stress?).

Picture (12): A palladium treated potato plant showing dark roots and more tuber yield than controls (compare to picture 14).

Picture (13): A platinum treated potato plant showing dark roots and more tuber yield than controls (picture 14).

Picture (14): A control potato plant showing white roots and lower tuber yield than platinum and palladium treated plants (pictures 11, 12, and 13).

Appendix B:

Table 1B: Loss on ignition [wt.%] of field grown lettuce plants.

Sample	Field Lettuce		
HW-C-1	87	*Sample*	
HW-C-2	89	**BG-C-1**	86
HW-C-3	88	**BG-C-2**	86
HW-C-4	89	**BG-C-3**	88
HW-C-5	87	**BG-C-4**	83
HW-Pt-1	87	**BG-Pt-1**	84
HW-Pt-2	89	**BG-Pt-2**	86
HW-Pt-3	90	**BG-Pt-3**	87
HW-Pt-4	89	**BG-Pt-4**	84
HW-Pt-5	89	**BG-Pt-5**	88
HW-Pd-1	88	**BG-Pd-1**	85
HW-Pd-2	86	**BG-Pd-2**	81
HW-Pd-3	89	**BG-Pd-3**	85
HW-Pd-4	88	**BG-Pd-4**	84
HW-Pd-5	88	**BG-Pd-5**	86

Table 2B: Loss on ignition [wt.%] of barley plants grown in the growth chamber.

Treatment	Barley	
	shoot	root
BT-1	86	94
BT-2	86	94
BT-3	86	94
BT-4	85	95
BD-1	86	94
BD-2	86	96
BD-3	87	94
BD-4	86	95

Table 3B: Loss on ignition [wt.%] of lettuce plants grown in the growth chamber.

Treatment	Lettuce		
	L	Sm	R
LT-1	85	93	90
LT-2	85	93	90
LT-3	91	95	90
LT-4	86	94	89
LD-1	85	93	89
LD-2	85	93	90
LD-3	85	92	90
LD-4	84	94	89

Table 4B: Loss on ignition [wt.%] of potato (I) plants grown in the growth chamber.

Treatment	Potato I				
	L	LS	Sm	T	R
P-I-T-1	87	76	86	93	92
P-I-T-2	86	74	82		92
P-I-D-1	89	79	87	93	91
P-I-D-2	89	76	85		91

Table 5B: Loss on ignition [wt.%] of potato (II) plants grown in the growth chamber.

Treatment	Potato II				
	L	LS	Sm	T	R
P-II-T-1	85	73	79	95	91
P-II-T-2	84	75	84	95	92
P-II-T-3	87	73	84	95	92
P-II-T-4	87	73	80	95	91
P-II-D-1	86	73	82	95	93
P-II-D-2	89	75	82	95	93
P-II-D-3	87	73	84	95	91
P-II-D-4	88	73	84	96	90

Table 6B: Concentration of rhodium, palladium, and platinum in the procedural blanks taken during the ICP-MS measurements of PGE.

	Rh	Pd	Pt
Blank 1	0.005	0.16	0.08
Blank 2	0.004	0.14	0.17
Blank 3	0.009	0.22	0.03
Blank 4	0.004	0.25	0.14
Blank 5	0.005	0.09	0.20
Blank 6	0.004	0.18	0.23
Blank 7	0.015	0.1	0.2
Blank 8	0.005	0.2	0.5
Blank 9	0.003	0.2	0.2
Blank 10	0.002	0.1	0.2
Blank 11	0.002	0.0	0.2
Blank 12	0.001	0.1	0.2
Blank 13	0.021	0.26	0.09
Blank 14	0.015	0.14	0.13
Blank 15	0.013	0.27	0.08
Blank 16	0.013	0.32	0.07
Blank 17	0.013	0.70	0.26

Table 7B: Limit of detection (LOD) for rhodium, palladium, and platinum calculated from the procedural blanks (Table 6B) as 3* ∑.

Mean	**Rh**	**Pd**	**Pt**
(n=17)	**0.01**	**0.20**	**0.18**
SD	**0.01**	**0.15**	**0.12**
3*∑	**0.02**	**0.44**	**0.35**

Table 8B: Concentration [ng/g] of platinum, palladium, and rhodium in a replicate potato sample measured at ISAS and IMG.

Sample	Platinum [ng/g]		Palladium [ng/g]		Rhodium [ng/g]	
	ISAS	IMG	ISAS	IMG	ISAS	IMG
1	4.8	5.3	4.0	4.4	0.2	0.5
2	2.2	0.3	14.0	12.6	1.1	0.1
3	nd	nd	34.7	43.0	nd	nd
4	58.2	56.2	37.0	55.5	10.6	7.5
5	4.8	4.8	nd	nd	0.3	0.7

nd = not determined

Table 9B: Concentration [µg/kg DW] of rhodium, palladium, and platinum measured in duplicate potato samples (X-D = duplicate, whereby X = element).

Controls	**Rh**	**Rh-D**	**Pd**	**Pd-D**	**Pt**	**Pt-D**
Sample 1C	0.1	0.0	0.4	0.4	0.5	0.6
Sample 2C	0.2	0.2	1.7	1.4	2.5	1.9
Sample 3C	0.1	0.3	1.0	1.2	1.4	1.3
Sample 4C	0.0	0.0	0.1	0.1	0.1	0.1
Pt-treatment						
Sample 1Pt	0.2	0.1	1.0	0.9	1.5	1.6
Sample 2Pt	0.1	0.1	0.5	0.6	5.6	5.2
Sample 3Pt	1.3	1.1	0.1	0.1	6.3	6.1
Sample 4Pt	0.2	0.2	0.5	0.8	1.5	1.2
Sample 5Pt	0.2	0.1	0.7	0.8	11.8	11.8
Sample 6Pt	nd	nd	nd	nd	4.2	4.8
Sample 7Pt	nd	nd	1.6	1.3	1.9	2.7
Sample 8Pt	nd	nd	1.2	0.9	1.7	2.6
Sample 9Pt	0.0	0.0	0.6	0.2	0.0	0.1
Pd-treatment						
Sample 1Pd	0.1	0.1	2.3	3.1	1.4	0.8
Sample 2Pd	0.9	0.9	4.8	3.8	0.7	0.3
Sample 3Pd	0.0	0.0	0.2	0.2	0.2	0.1
Sample 4Pd	0.0	0.0	0.3	0.2	0.2	0.1
nd = not determined						

Table 10B: Concentration [ng/g] of platinum in grass samples determined by voltammetry and ICP-MS (Data from Klueppel et al. 1998).

treated grass samples	detection method	
	voltammetry	ICP- MS
	Concentration [ng/g]	
1st harvest	-	-
2nd harvest	86	74
3rd harvest	1700	-
4th harvest	3390	3260
5th harvest	8220	6790
treated roots	67200	59600

Table 11B: Descriptive statistic on rhodium, palladium, and platinum concentrations [µg/kg DW] in lettuce plants grown at the highway and botanical garden sites.

BG	Min.			Max.			Mean			SD		
	Rh	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt
Controls	0.2	17	7	2	42	32	1	29	15	1	10	11
Pt-treatment	9	4	40	35	9	104	24	7	77	11	3	23
Pd-treatment	5	42	2	44	269	12	23	140	7	16	95	4

HW	Min.			Max.			Mean			SD		
	Rh	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt
Controls	0.0	6	2	2	21	21	0	13	8	1	6	8
Pt-treatment	10	12	34	27	62	90	18	39	68	6	25	21
Pd-treatment	17	74	3	21	127	9	20	94	5	2	20	2

Table 12B: Concentrations [µg/kg DW] of rhodium, palladium, and platinum in the field grown lettuce plants. BG-C: Control plants grown at the Botanical Garden site, BG-Pt : Platinum treated plants grown at the Botanical Garden site, BG-Pd : Palladium treated plants grown at the Botanical Garden site, HW-C: Control plants grown at the highway site, HW-Pt : Platinum treated plants grown at the highway site, HW-Pd : Palladium treated plants grown at the highway site. The Pt/Rh and Pd/Rh ratios are also listed.

Botanical Garden Site					
Sample	**Conc. [µg/kg DW]**			**Ratio**	
	Rh	**Pd**	**Pt**	**Pt/Rh**	**Pd/Rh**
BG-C-1	0.3	26	8	29	93
BG-C-2	0.2	17	7	46	106
BG-C-3	0.2	31	14	60	128
BG-C-4	2.1	42	32	15	20
BG-Pt-1	35	9	82	2	0
BG-Pt-2	35	5	104	3	0
BG-Pt-3	21	4	77	4	0
BG-Pt-4	21	9	80	4	0
BG-Pt-5	9	9	40	4	1
BG-Pd-1	14	89	7	0	6
BG-Pd-2	16	88	7	0	6
BG-Pd-3	5	42	2	0	9
BG-Pd-4	34	269	6	0	8
BG-Pd-5	44	209	12	0	5

Highway Site					
Sample	**Conc. [µg/kg DW]**			**Ratio**	
	Rh	**Pd**	**Pt**	**Pt/Rh**	**Pd/Rh**
HW-C-1	1.5	6	3	2	4
HW-C-2	0.0	21	10	756	1581
HW-C-3	0.6	13	2	3	21
HW-C-4	0.0	15	21	1636	1143
HW-C-5	0.0	8	3	222	513
HW-Pt-1	17.8	56	67	4	3
HW-Pt-2	16.6	52	70	4	3
HW-Pt-3	9.8	62	34	3	6
HW-Pt-4	20.8	13	90	4	1
HW-Pt-5	27.2	12	79	3	0
HW-Pd-1	21.1	85	9	0	4
HW-Pd-2	20.6	127	5	0	6
HW-Pd-3	17.5	74	3	0	4
HW-Pd-4	21.5	95	3	0	4
HW-Pd-5	19.4	90	3	0	5

Table 13B: Mean and standard deviation (SD) of the Pt/Rh and Pd/Rh ratios, found in field grown lettuce plants.

	Mean	SD
Pt/Rh BG	3	0.8
Pt/Rh HW	4	0.6
Pd/Rh BG	7	1.6
Pd/Rh HW	5	0.8
Pt/Rh	4	0.7
Pd/Rh	6	1.6

Table 14B: Platinum and palladium concentrations in potato (II) plants treated with 300 µg/l PGE chloride salts and grown in the growth chamber. P-II-T : Pt-treated, P-II-D : Pd-treated. Shaded fields were excluded from the statistical analysis.

Platinum treatments	Conc. [µg Pt/kg DW]						
	leaf	leaf stalk	stem	tuber	root	shoot	average
P-II-T-1*	4,273	2,251	2,434	449	188,119	2,986	39,505
P-II-T-2	2,552	1,420	1,426	681	162,925	1,799	33,801
P-II-T-3	2,515	1,491	1,247	443	209,158	1,751	42,971
P-II-T-4	2,627	1,405	1,433	555	132,215	1,821	27,647
mean*	2,565	1,439	1,369	560	168,099	1,791	34,806
SD	57	46	106	119	38,731	36	7,711
min.	2,515	1,405	1,247	443	132,215	1,751	27,647
max.	2,627	1,491	1,433	681	209,158	1,821	42,971

Palladium treatments	Conc. [µg Pd/kg DW]						
	leaf	leaf stalk	stem	tuber	root	shoot	average
P-II-D-1	260	86	94	175	198,724	147	39,868
P-II-D-2*	194	69	97	151	350,367	120	70,175
P-II-D-3	523	181	270	235	180,761	324	36,394
P-II-D-4	339	109	229	175	176,134	226	35,397
mean*	329	111	172	184	185,206	204	45,459
SD	142	49	91	36	11,933	92	16,589
min.	194	69	94	151	176,134	36	7,711
max.	523	181	270	235	198,724	324	70,175

Table 15B: Platinum and palladium concentrations in potato (I) plants treated with 2000 µg/l PGE chloride salts and grown in the growth chamber. P-I-T : Pt-treated, P-I-D : Pd-treated. Shaded fields were excluded from the statistical analysis.

Platinum treatments	Conc. [µg Pt/kg DW]						
	leaf	leaf stalk	stem	root	tuber	shoot	average
P-I-T-1	8,606	4,381	3,822	491,629	751	5,603	
P-I-T-2	8,145	3,390	3,022	553,255		4,852	
mean	8,375	3,885	3,422	522,442	751	5,227	119,667
SD	325	701	566	43,576		2,484	228,884
min	8,145	3,390	3,022	491,629		3,022	751
max.	8,606	4,381	3,822	553,255		8,606	553,255

Palladium treatments	Conc. [µg Pd/kg DW]						
	leaf	leaf stalk	stem	root	tuber	shoot	average
P-I-D-1	3,529	1,642	2,559	432,562	1,204	2,577	
P-I-D-2	3,320	1,447	1,923	673,074		2,230	
mean	3,425	1,544	2,241	552,818	1,204	2,403	124,584
SD	148	138	450	170,067		878	250,122
min	3,320	1,447	1,923	432,562		1,447	1,204
max.	3,529	1,642	2,559	673,074		3,529	673,074

Table 16B: Platinum and palladium concentrations in lettuce plants treated with 300 µg/l PGE chloride salts and grown in the growth chamber. LT : Pt-treated, LD: Pd-treated. Shaded fields were excluded from the statistical analysis.

Platinum treatments	Conc. [µg Pt/kg DW]				
	leaf	stem	root	shoot	average
LT-1	1,329	1,614	537,730	1,472	180,224
LT-2	1,368	1,545	522,468	1,457	175,127
LT-3	1,022	806	440,395	914	147,408
LT-4*	571	385	1,563,981	478	521,646
mean*	1,240	1,322	500,198	1,281	167,586
SD	190	448	52,349	318	17,660
min.	1,022	806	440,395	914	147,408
max.	1,368	1,614	537,730	1,472	180,224

Palladium treatments	Conc. [µg Pd/kg DW]				
	leaf	stem	root	shoot	average
LD-1	329	327	449,023	328	149,893
LD-2	290	335	402,321	313	134,315
LD-3	485	214	348,511	349	116,403
LD-4	301	173	358,561	237	119,679
mean	351	262	389,604	307	130,073
SD	90	81	45,988	49	15,338
min.	290	173	348,511	237	116,403
max.	485	335	449,023	349	149,893

Table 17B: Platinum and palladium concentration in barley plants treated with 2000 µg/l PGE chloride salts and grown in the growth chamber. BT : Pt-treated, BD: Pd-treated. Shaded fields were excluded from the statistical analysis.

Platinum treatments	Conc. [µg Pt/kg DW]		
	shoot	root	average
BT-1	2,764	777,076	389,920
BT-2	3,537	765,378	384,457
BT-3*	*5,688*	1,153,242	579,465
BT-4	2,741	1,201,060	601,900
mean*	3,014	974,189	488,936
SD	453	235,220	117,865
min	2,741	765,378	384,457
max.	3,537	1,201,060	601,900

Palladium treatments	Conc. [µg Pd/kg DW]		
	shoot	root	average
BD-1*	1,766	*515,349*	*258,558*
BD-2	1,889	1,156,083	578,986
BD-3	1,363	992,270	496,817
BD-4	1,615	855,753	428,684
mean*	1,658	1,001,369	501,496
SD	227	272,265	75,260
min	1,363	515,349	428,684
max.	1,889	1,156,083	578,986

Table 18B: Platinum and palladium concentrations calculated as [µmol/kg DW] in potato (I) plants treated with 2000 µg/l PGE chloride salts and grown in the growth chamber. P-I-T : Pt-treated, P-I-D : Pd-treated.

Platinum	Conc. [µmol Pt/kg DW]						
treatments	leaf	leaf stalk	stem	root	tuber	shoot	average
P-I-T-1	44	22	20	2,521	0	29	
P-I-T-2	42	17	15	2,837		25	
mean	43	20	18	2,679	0	27	614
SD	2	4	3	223		13	1,174
min	42	17	15	2,521		15	4
max.	44	22	20	2,837		44	2,837

Palladium	Conc. [µmol Pd/kg DW]						
treatments	leaf	leaf stalk	stem	root	tuber	shoot	average
P-I-D-1	33	15	24	4,081	0		
P-I-D-2	31	14	18	6,350			
mean	32	15	21	5,215	0	23	1,175
SD	1	1	4	1,604		8	2,360
min	31	14	18	4,081		14	11
max.	33	15	24	6,350		33	6,350

Table 19B: Platinum and palladium concentrations calculated as [µmol/kg DW] in potato (II) plants treated with 300 µg/l PGE chloride salts and grown in the growth chamber. P-II-T : Pt-treated, P-II-D : Pd-treated. Shaded fields were excluded from the statistical analysis.

Platinum	Conc. [µmol Pt/kg DW]						
treatments	leaf	leaf stalk	stem	tuber	root	shoot	average
P-II-T-1*	22	12	12	2	965	15	203
P-II-T-2	13	7	7	3	836	9	173
P-II-T-3	13	8	6	2	1,073	9	220
P-II-T-4	13	7	7	3	678	9	142
mean*	13	7	7	3	862	9	178
SD	0	0	1	1	199	0	40
min.	13	7	6	2	678	9	142
max.	13	8	7	3	1,073	9	220

Palladium	Conc. [µmol Pd/kg DW]						
treatments	leaf	leaf stalk	stem	tuber	root	shoot	average
P-II-D-1	2	1	1	2	1,875	1	376
P-II-D-2*	2	1	1	1	3,305	1	662
P-II-D-3	5	2	3	2	1,705	3	343
P-II-D-4	3	1	2	2	1,662	2	334
mean*	3	1	2	2	1,747	2	429
SD	1	0	1	0	113	1	156
min.	2	1	1	1	1,662	1	334
max.	5	2	3	2	1,875	3	662

Table 20B: Platinum and palladium concentrations calculated as [µmol/kg DW] in lettuce plants treated with 300 µg/l PGE chloride salts and grown in the growth chamber. LT : Pt-treated, LD: Pd-treated. Shaded fields were excluded from the statistical analysis.

Platinum	Conc. [µmol Pt/kg DW]				
treatments	leaf	stem	root	shoot	average
LT-1	7	8	2,758	8	924
LT-2	7	8	2,679	7	898
LT-3	5	4	2,258	5	756
LT-4*	3	2	8,020	2	2,675
mean*	6	7	2,565	7	859
SD	1	2	268	2	91
min.	5	4	2,258	5	756
max.	7	8	2,758	8	924

Palladium	Conc. [µmol Pd/kg DW]				
treatments	leaf	stem	root	shoot	average
LD-1	3	3	4,236	3	1,414
LD-2	3	3	3,795	3	1,267
LD-3	5	2	3,288	3	1,098
LD-4	3	2	3,383	2	1,129
mean	3	2	3,676	3	1,227
SD	1	1	434	0	145
min.	3	2	3,288	2	1,098
max.	5	3	4,236	3	1,414

Table 21B: Platinum and palladium concentrations calculated as [µmol/kg DW] in barley plants treated with 2000 µg/l PGE chloride salts and grown in the growth chamber. BT : Pt-treated, BD: Pd-treated.

Platinum	Conc. [µmol Pt/kg DW]		
treatments	shoot	root	average
BT-1	14	3,985	2,000
BT-2	18	3,925	1,972
BT-3	29	5,914	2,972
BT-4	14	6,159	3,087
mean*	15	4,996	2,507
SD	2	1,206	604
min	14	3,925	1,972
max.	18	6,159	3,087

Palladium	Conc. [µmol Pd/kg DW]		
treatments	shoot	root	average
BD-1	17	4,862	2,439
BD-2	18	10,906	5,462
BD-3	13	9,361	4,687
BD-4	15	8,073	4,044
mean	16	9,447	4,731
SD	2	2,569	710
min	13	4,862	4,044
max.	18	10,906	5,462

Table 22B: Metal ratios in potato (I) treated with 2000 µg/l PGE chloride salts. P-I-T : Pt-treated, P-I-D : Pd-treated. L : Leaf, LS : Leaf Stalk, T : Tuber, Sm : Stem, S : Shoot, R : Root. Values in bold font were used for the graphical representation.

Platinum treatments	L/LS	L/Sm	L/T	LS/Sm	LS/T	Sm/T	S/R	R/S
	ratio							
P-I-T-1	2	2	11	1	6	5	0.011	88
P-I-T-2	2	3	11	1	5	4	0.009	114
mean	2	2	11	1	5	5	**0.010**	**100**
SD	0	0	0	0	1	0.8	0.002	19

Palladium treatments	L/LS	L/Sm	L/T	LS/Sm	LS/T	Sm/T	S/R	R/S
	ratio							
P-I-D-1	2	1	3	1	1	2	0.006	168
P-I-D-2	2	2	3	1	1	2	0.003	302
mean	2	2	3	1	1	2	**0.004**	**230**
SD	0	0	0	0	0	0.4	0.002	95

Table 23B: Metal ratios in potato (II) treated with 300 µg/l PGE chloride salts. P-II-T : Pt-treated, P-II-D : Pd-treated. L : Leaf, LS : Leaf Stalk, T : Tuber, Sm : Stem, S : Shoot, R : Root. Shaded fields were excluded from the statistical analysis. Shaded fields were excluded from the statistical analysis.

Platinum treatments	L/LS	L/Sm	L/T	LS/Sm	LS/T	Sm/T	S/R	R/S
	ratio							
P-II-T-1*	*1.9*	*1.8*	*9.5*	*0.9*	*5.0*	*5.4*	*0.016*	*63*
P-II-T-2	1.8	1.8	3.7	1.0	2.1	2.1	0.011	91
P-II-T-3	1.7	2.0	5.7	1.2	3.4	2.8	0.008	119
P-II-T-4	1.9	1.8	4.7	1.0	2.5	2.6	0.014	73
mean*	1.8	1.9	4.7	1.1	2.7	2.5	0.011	94
SD*	0.1	0.1	1.0	0.1	0.6	0.4	0.003	24

Palladium treatments	L/LS	L/Sm	L/T	LS/Sm	LS/T	Sm/T	S/R	R/S
	ratio							
P-II-D-1	3.0	2.8	1.5	0.9	0.5	0.5	0.001	1354
P-II-D-2*	2.8	2.0	1.3	0.7	0.5	0.6	*0.000*	*2923*
P-II-D-3	2.9	1.9	2.2	0.7	0.8	1.1	0.002	557
P-II-D-4	3.1	1.5	1.9	0.5	0.6	1.3	0.001	780
mean*	3.0	2.0	1.7	0.7	0.6	0.9	0.001	897
SD	0.1	0.5	0.4	0.2	0.1	0.4	0.001	411

Table 24B: Metal ratios in lettuce treated with 300 µg/l PGE chloride salts. LT : Pt-treated, LD : Pd-treated. L : Leaf, Sm : Stem, S : Shoot, R : Root. Shaded fields were excluded from the statistical analysis.

Platinum treatments	L/Sm	R/S ratio	S/R
LT-1	0.8	365	0.003
LT-2	0.9	359	0.003
LT-3	1.3	482	0.002
*LT-4**	*1.5*	*3,271*	*0.000*
mean*	1.0	402	0.003
SD	0.2	69	0.000

Palladium treatments	L/Sm	R/S ratio	S/R
LD-1	1.0	1,368	0.001
LD-2	0.9	1,287	0.001
LD-3	2.3	997	0.001
LD-4	1.7	1,511	0.001
mean	1.5	1,291	0.001
SD	0.7	216	0.000

Table 25B: Metal ratios in barley treated with 2000 µg/l PGE chloride salts. BT : Pt-treated, BD : Pd-treated. S : Shoot, R : Root. Shaded fields were excluded from the statistical analysis.

Platinum treatments	S/R	R/S ratio
BT-1	0.004	281
BT-2	0.005	216
BT-3*	*0.005*	*203*
BT-4	0.002	438
mean*	0.003	187
SD	0.001	189

Palladium treatments	S/R	R/S ratio
BD-1*	*0.003*	*292*
BD-2	0.002	612
BD-3	0.001	728
BD-4	0.002	530
mean*	0.002	623
SD	0.001	185

Appendix C:
Data of physiological parameters determined for the greenhouse plants.

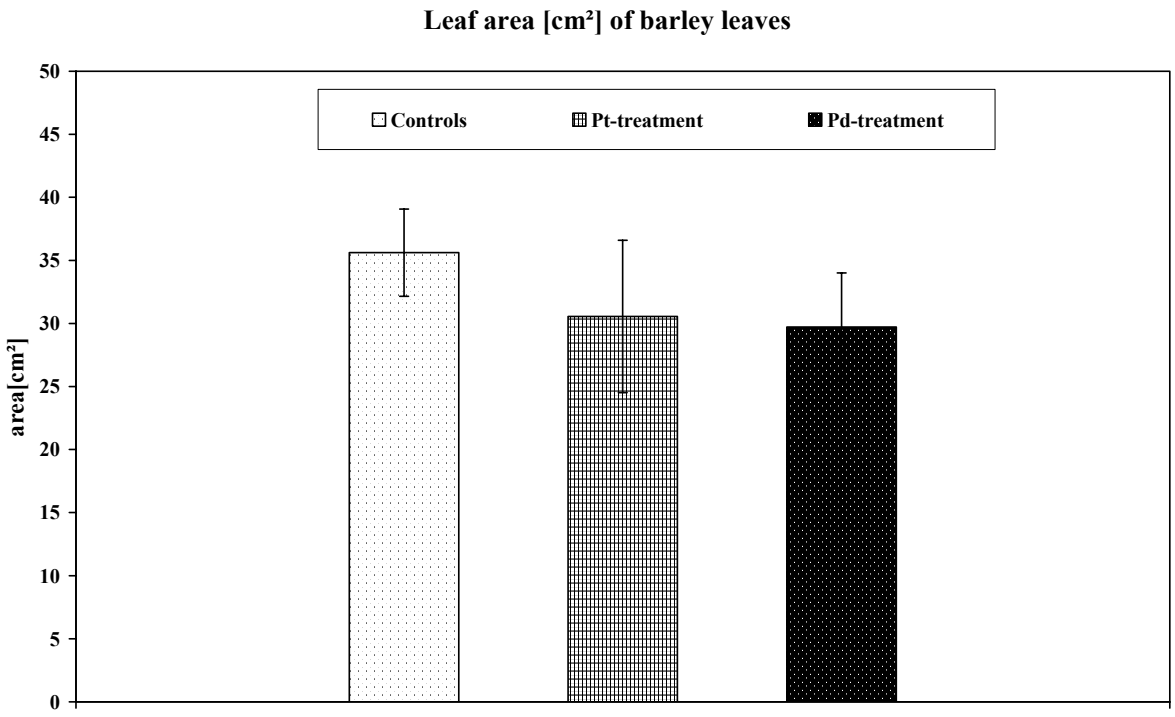


Figure (1C): Lower leaf area of the palladium and platinum treated barley compared to the control plants.

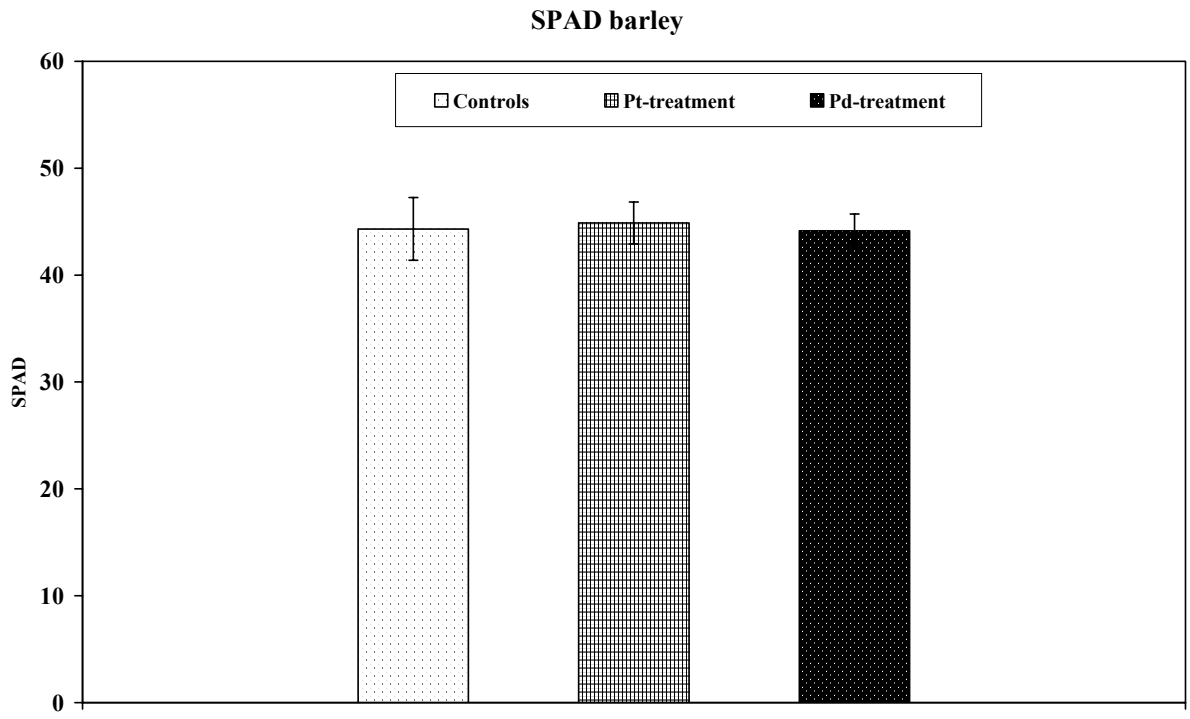


Figure (2C): SPAD units determined on barley leaves indicating lower chlorophyll content of the palladium treated plants than the controls.

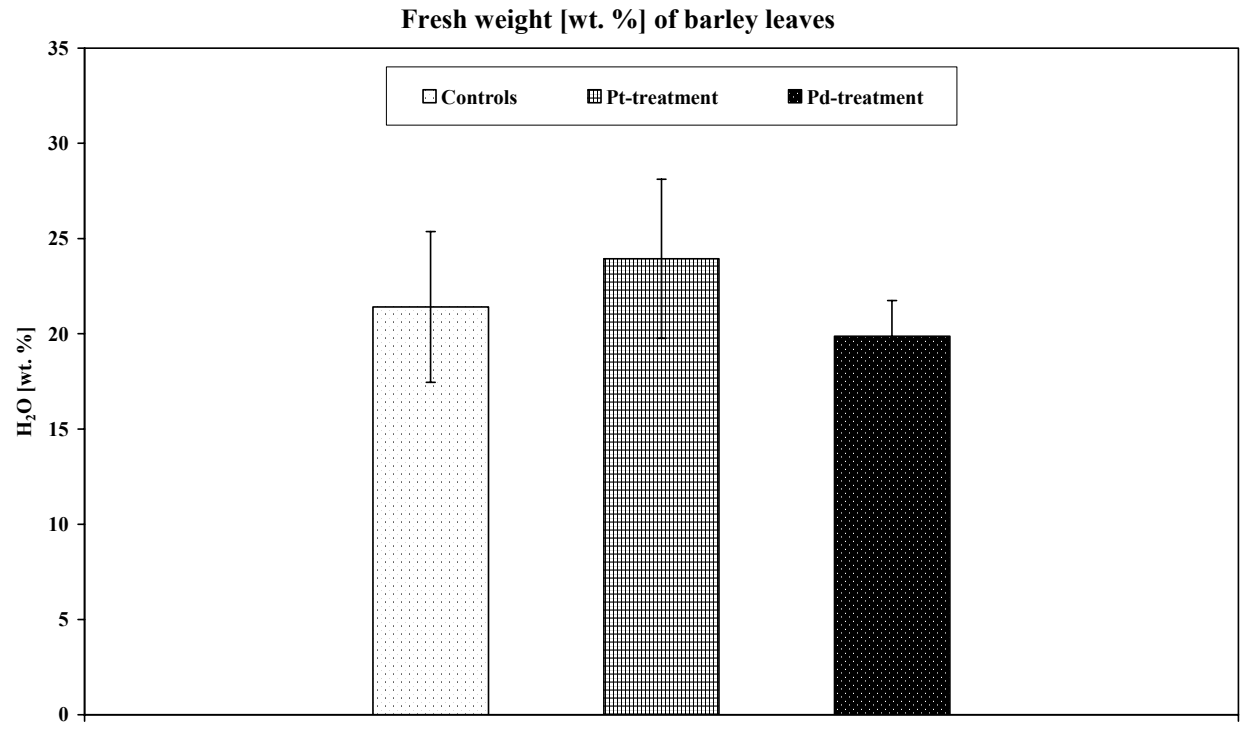


Figure (3C): Palladium treated barley plants showed lower fresh weight than the control and platinum treated plants.

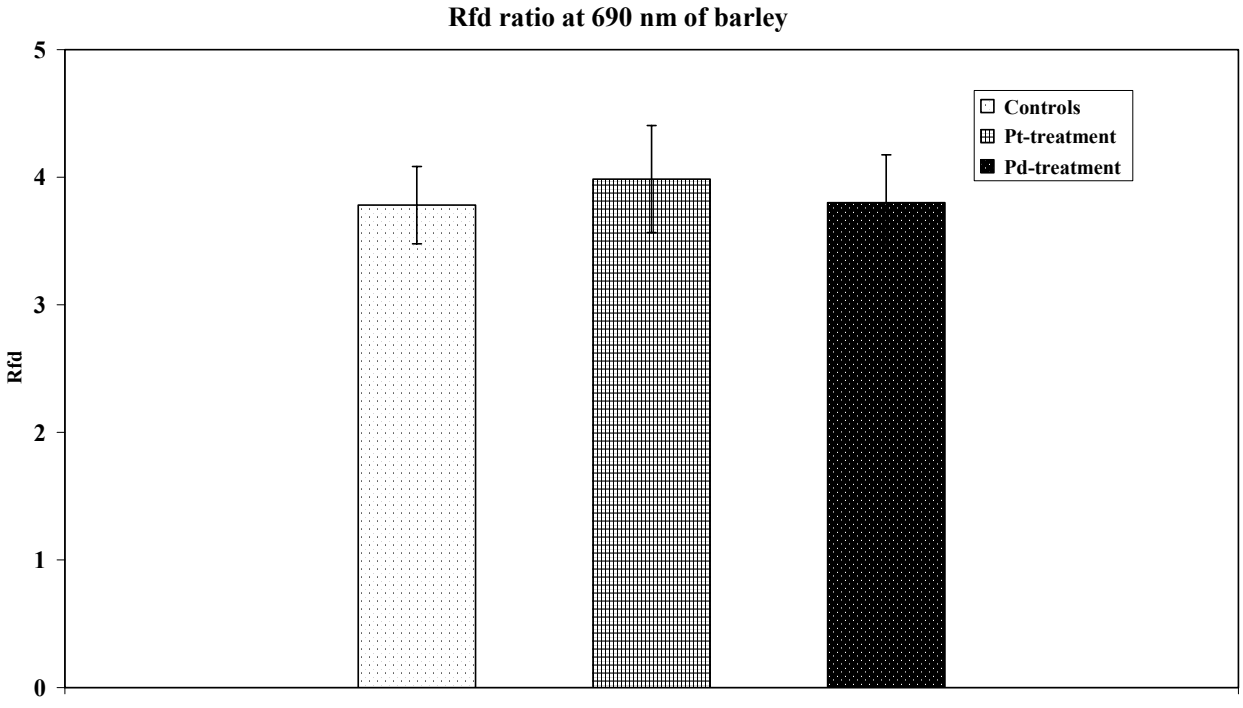


Figure (4C): ratio fluorescence decrease (Rfd) at 690 nm showed no difference between the control and treated barley plants.

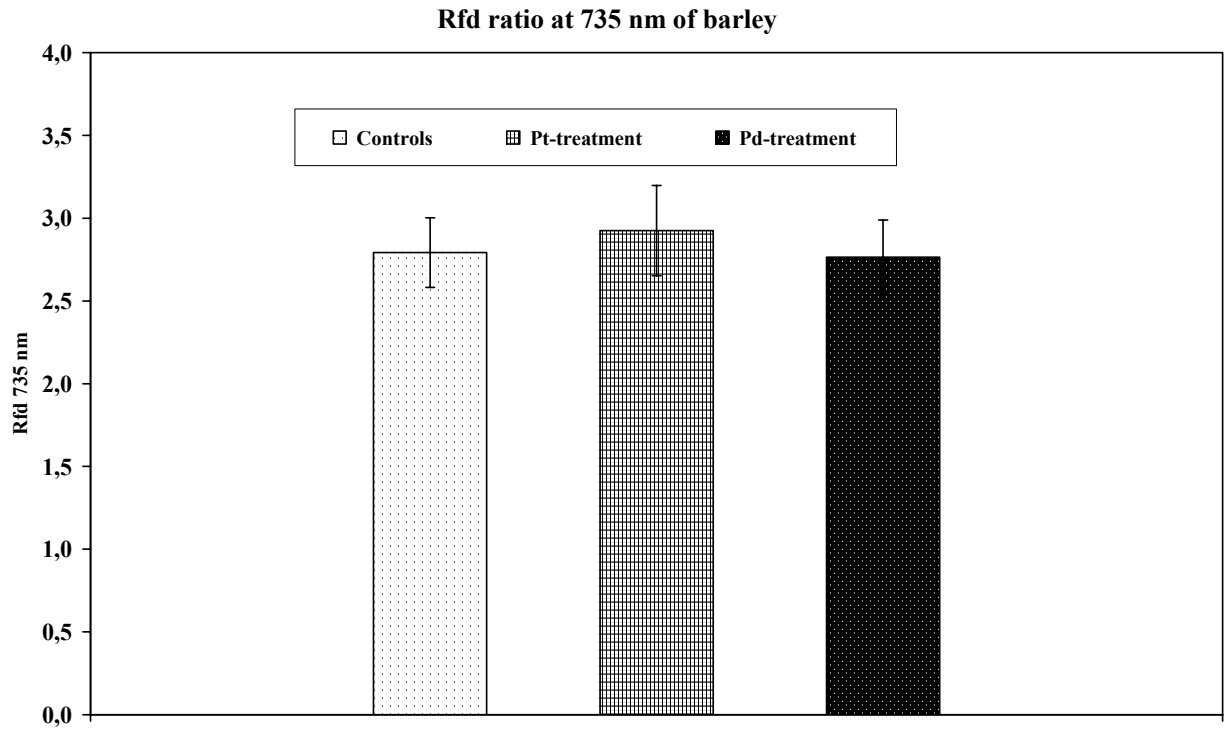


Figure (5C): Ratio fluorescence decrease (Rfd) at 735 nm showed no difference between the control and treated barley plants.

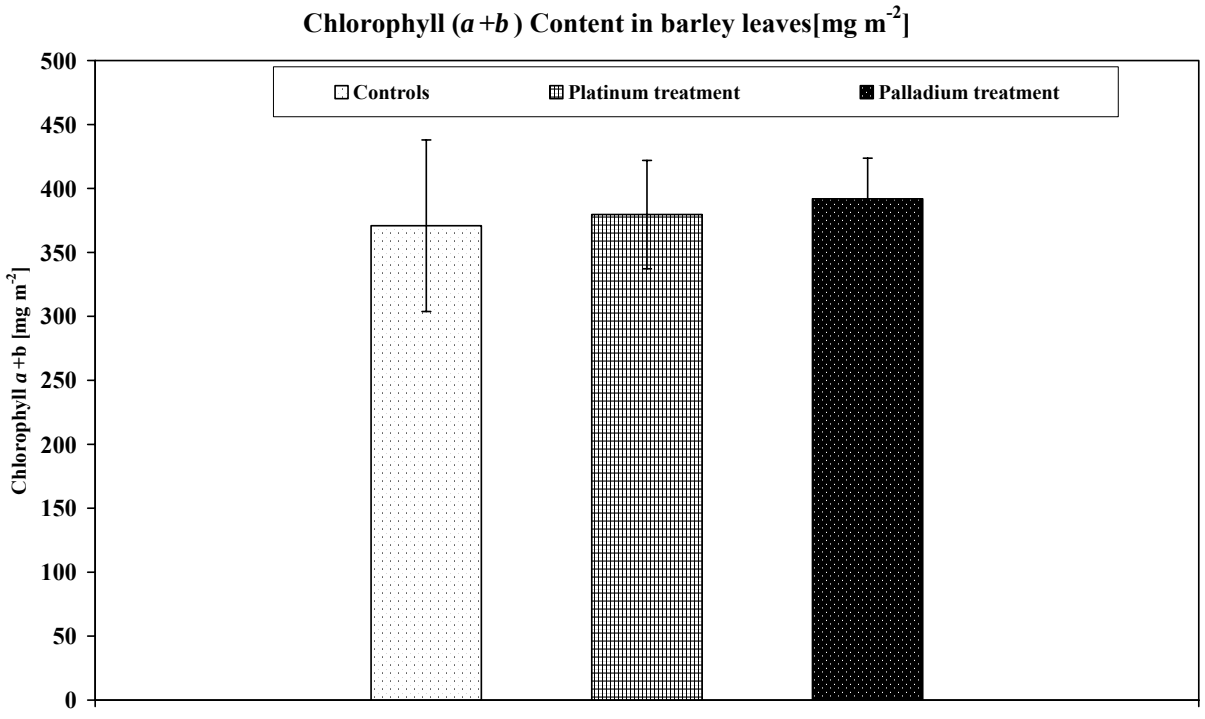


Figure (6C): Total chlorophyll (*a* + *b*) content of barley treated with platinum and palladium showed no difference compared to the control plants.

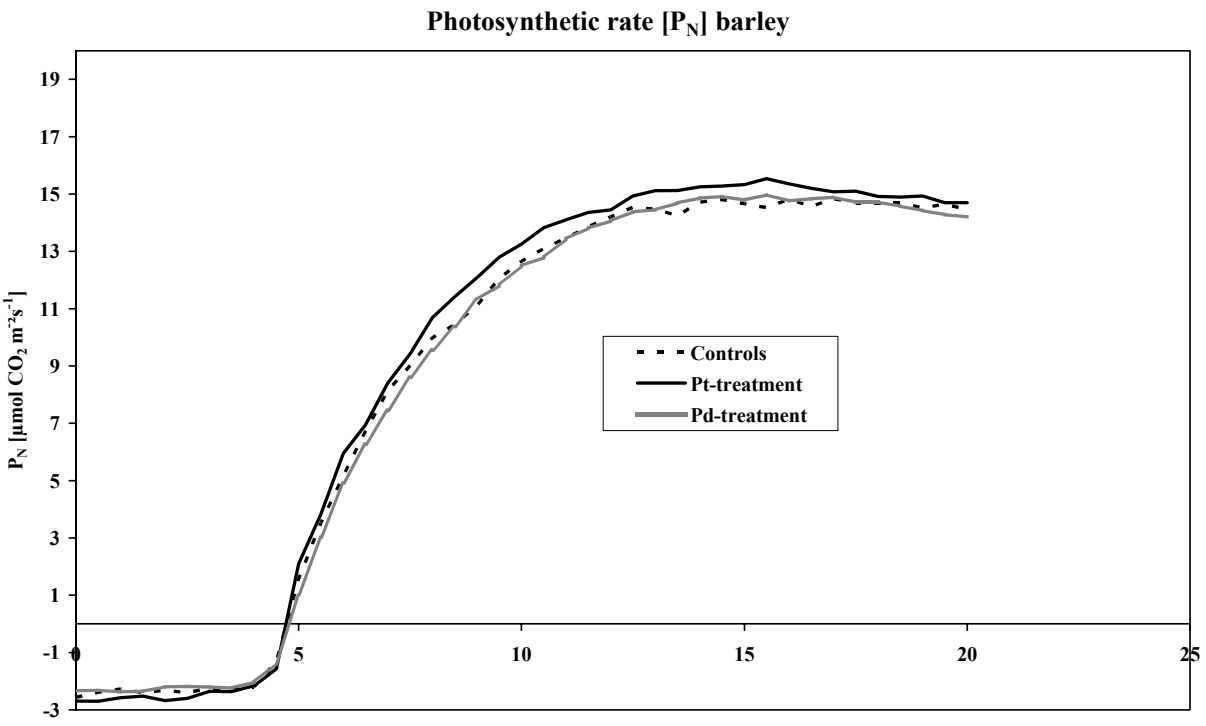


Figure (7C): The photosynthetic rate (P_N) determined for the treated as well as control barley plants, was nearly similar. The platinum treated plants showed slightly higher P_N than controls and palladium treated plants.

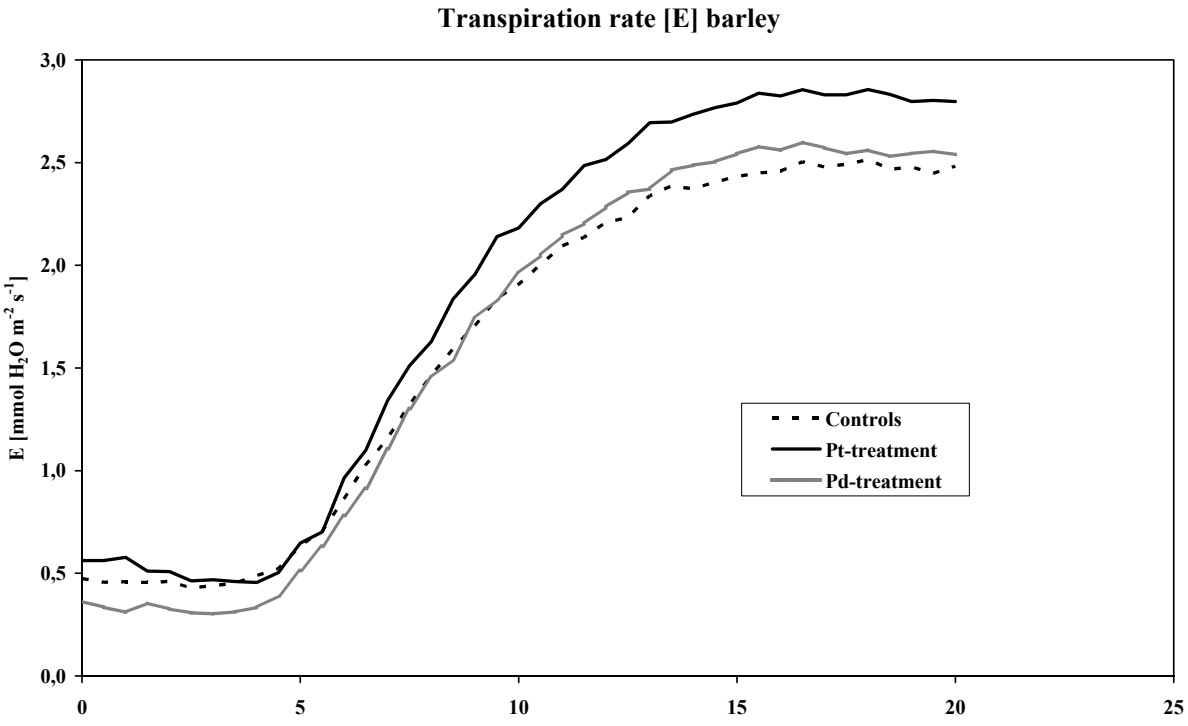


Figure (8C): The transpiration rate (E) determined for platinum treated plants, was higher than the controls and the palladium treated plants which indicate opening stomata and hence higher P_N rate.

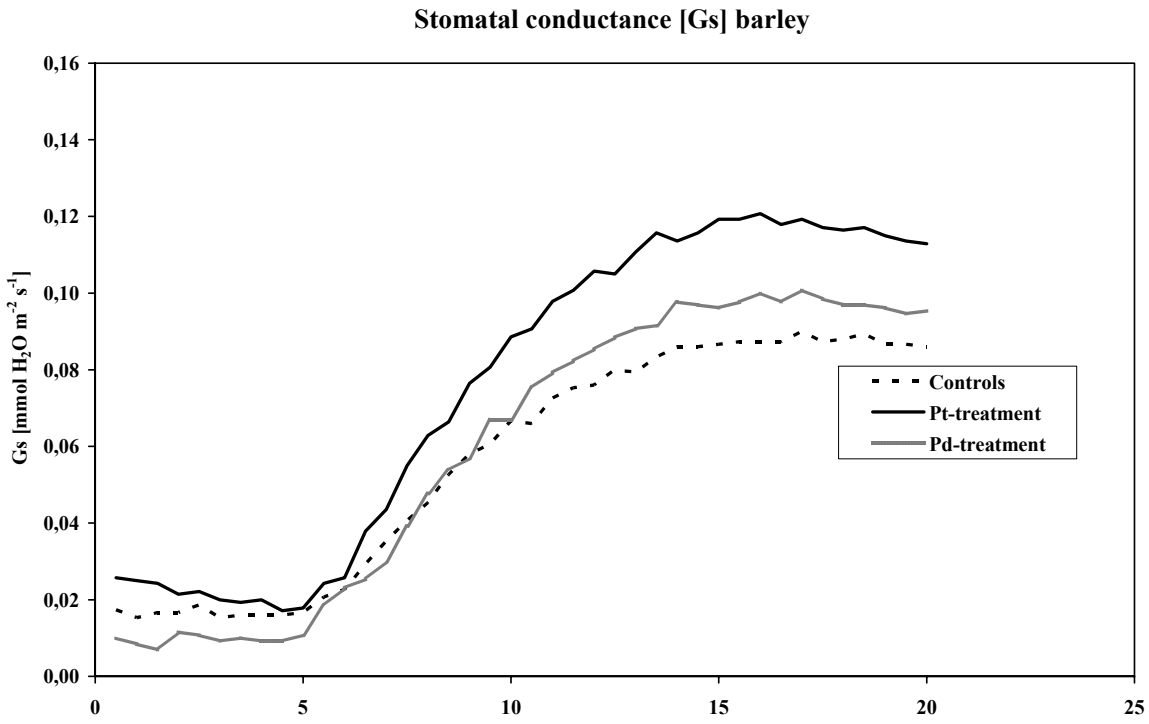


Figure (9C): The stomatal conductance (Gs) determined for platinum treated plants, was higher than controls and palladium treated plants. This indicates opening stomata and higher P_N rate of platinum than palladium treated plants as well as controls.

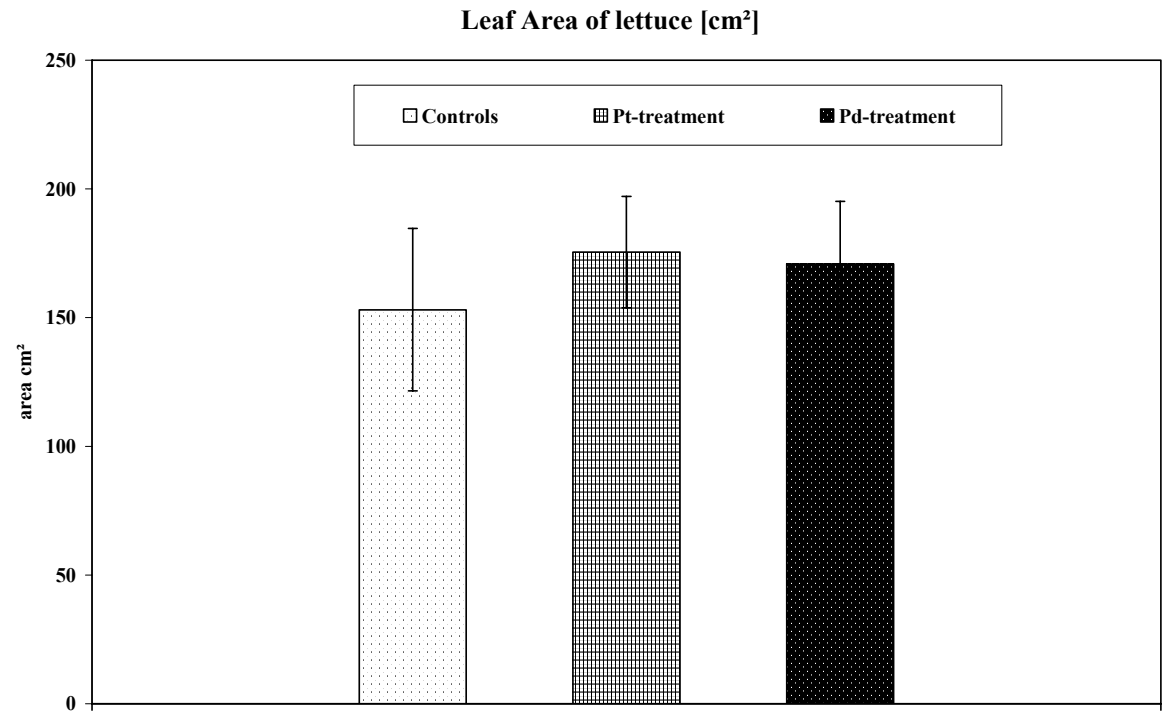


Figure (10C): Leaf area of treated lettuce plants showed no difference between the treated and control plants.

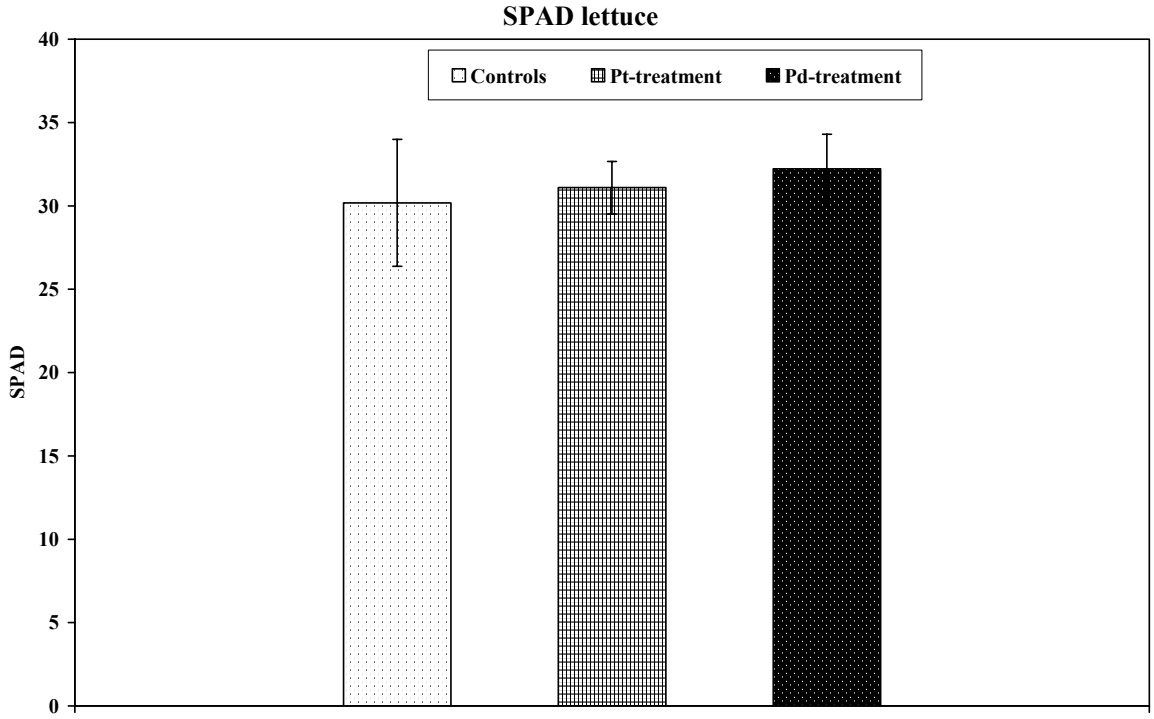


Figure (11C): SPAD units of the treated lettuce plants were similar to those of the controls.

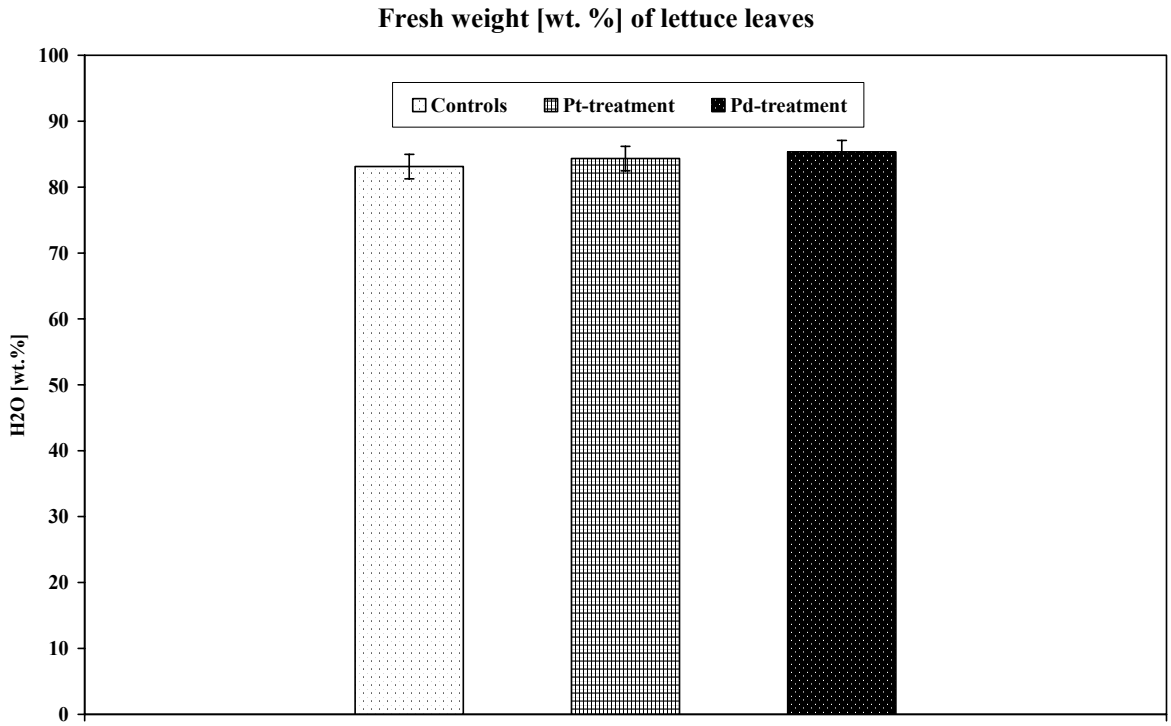


Figure (12C): Fresh weights of the treated lettuce plants were similar to the controls.

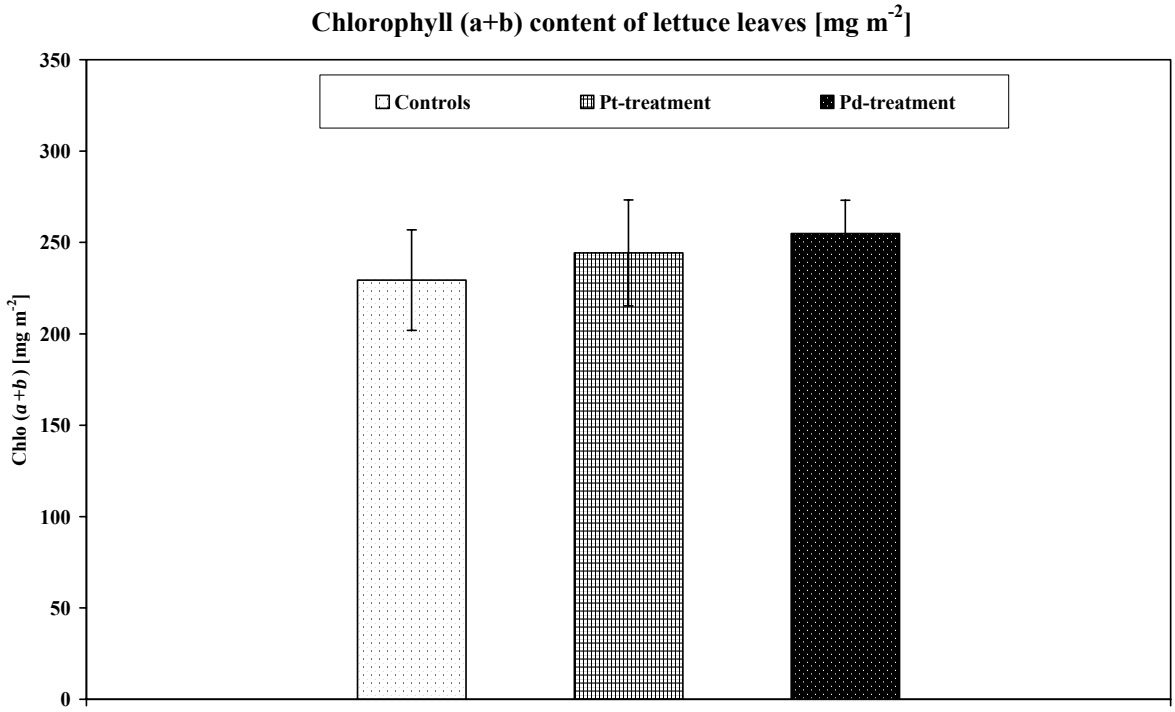


Figure (13C): Chlorophyll content (*a* + *b*) of palladium treated lettuce plants was slightly higher than controls.

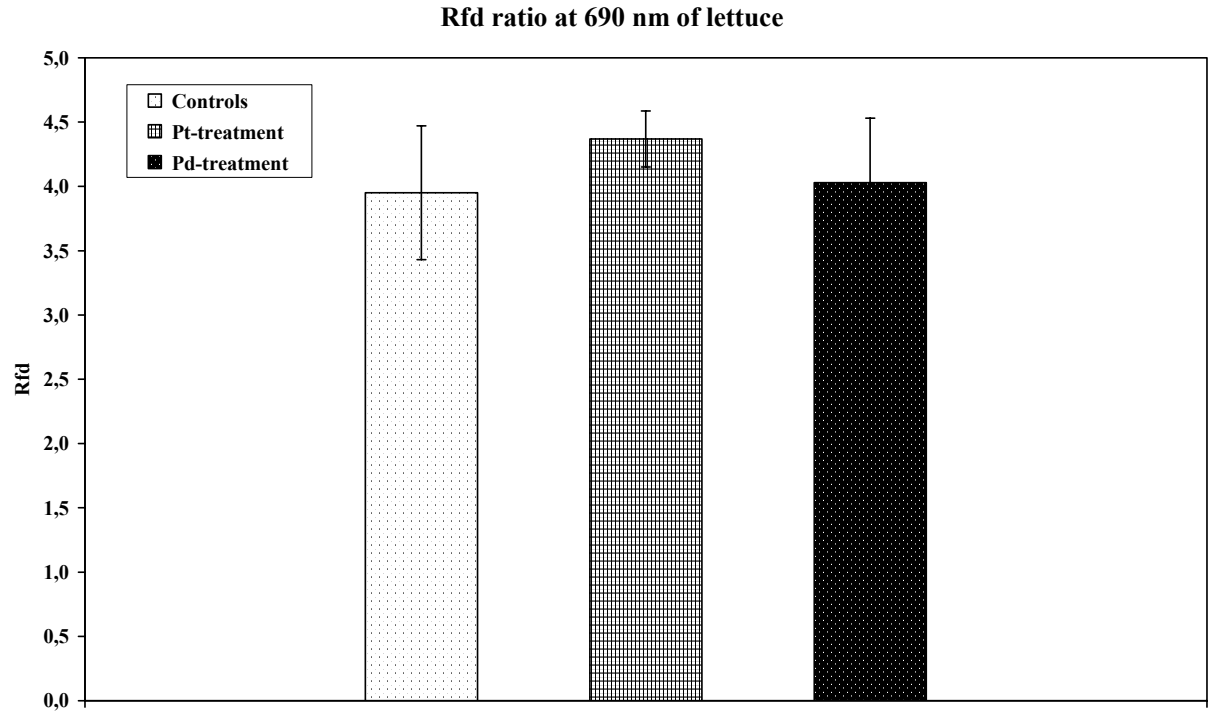


Figure (14C): Rfd of platinum and palladium treated plants was similar to the controls and was slightly higher for platinum than palladium treated lettuce plants.

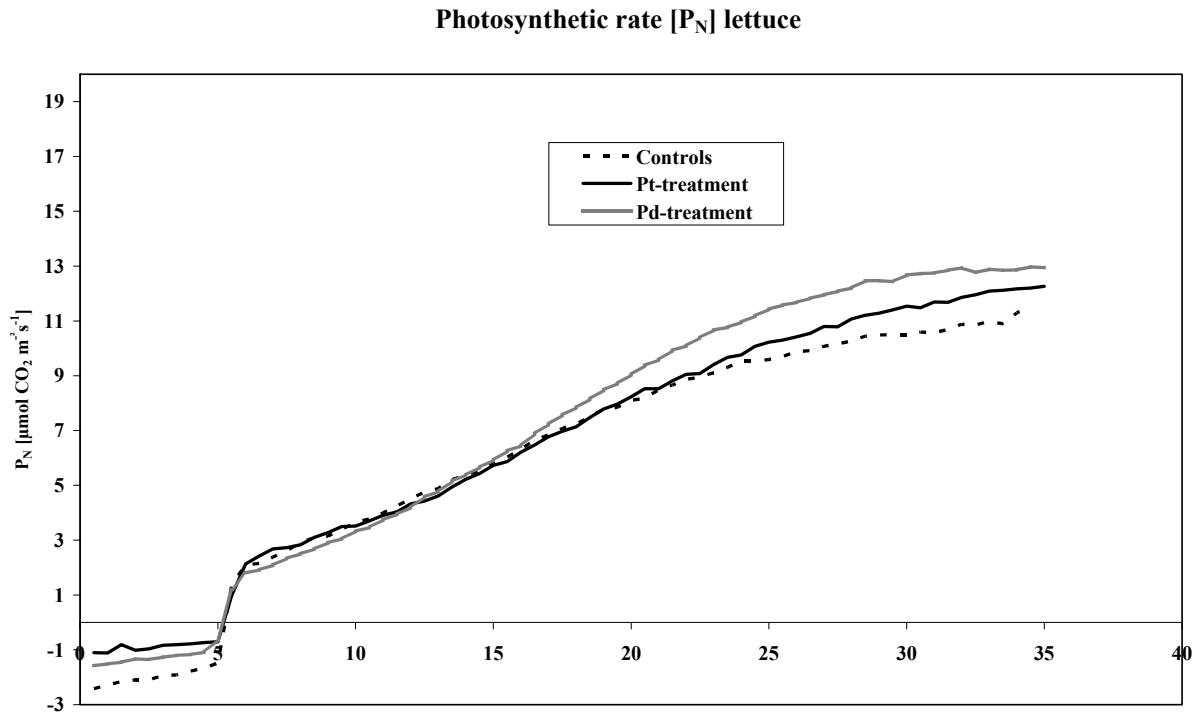


Figure (15C): Palladium treated lettuce plants showed higher P_N than the controls and platinum treated ones.

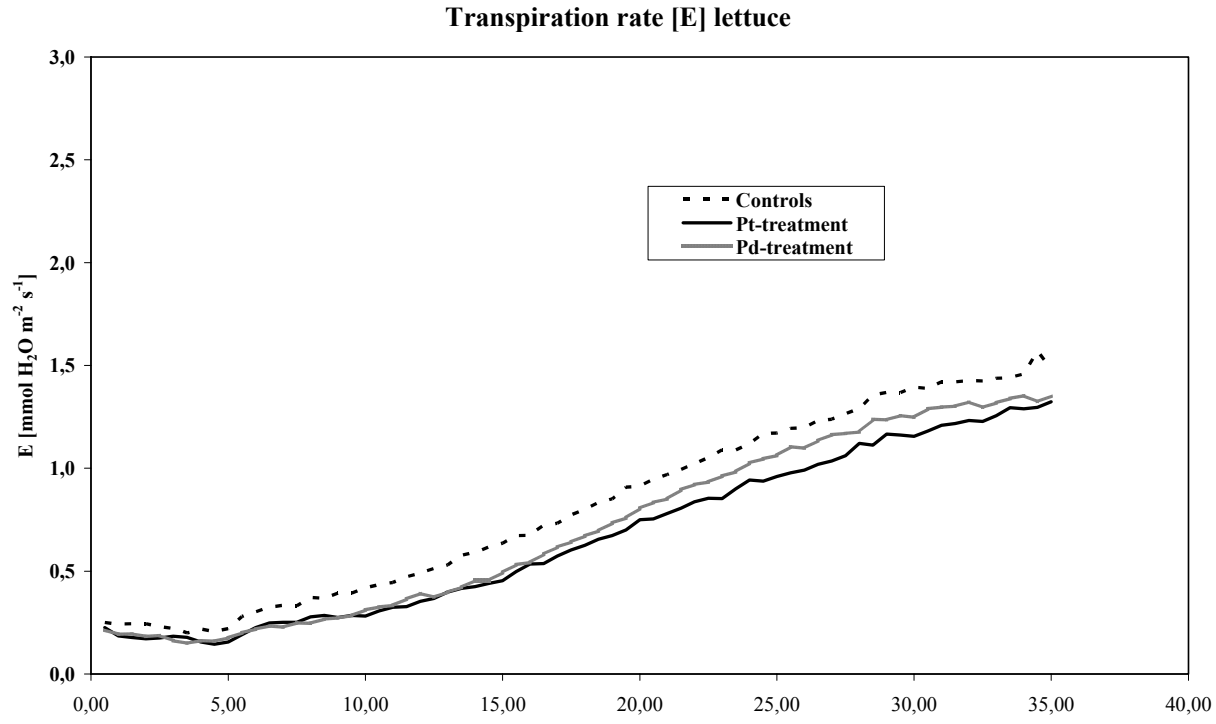


Figure (16C): Control lettuce plants showed higher E than the platinum and palladium treated ones.

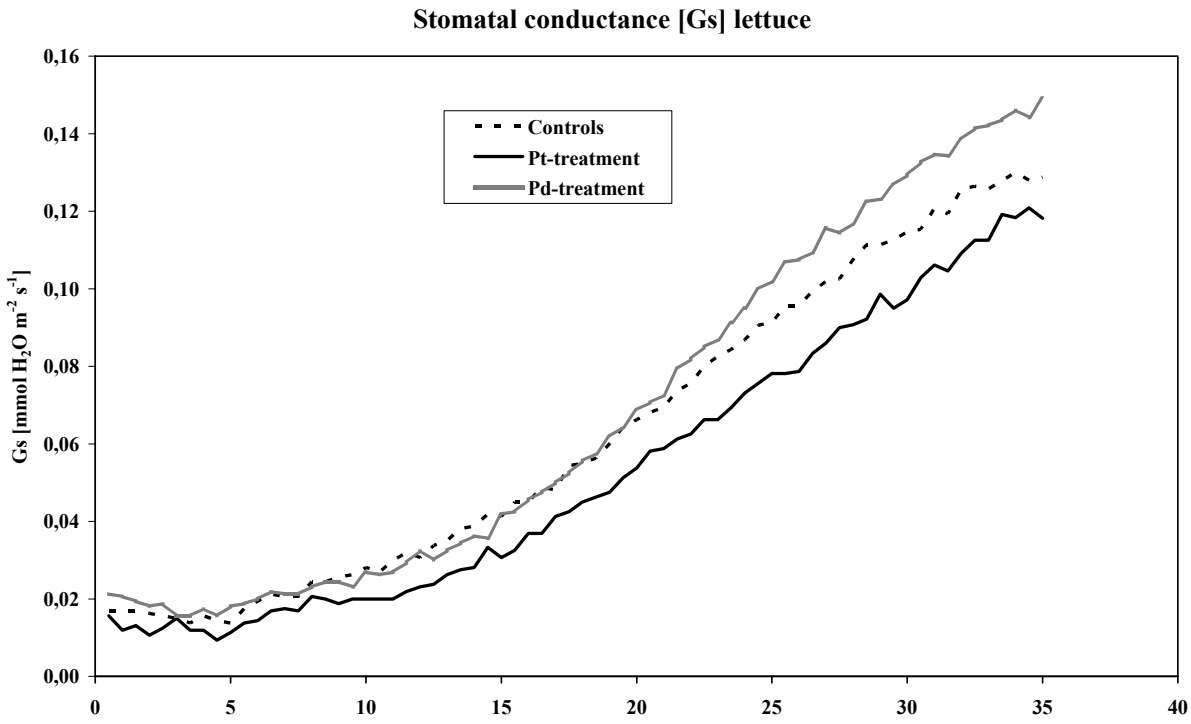


Figure (17C): Palladium treated lettuce showed higher Gs than platinum treated and control ones indicating opening stomata.

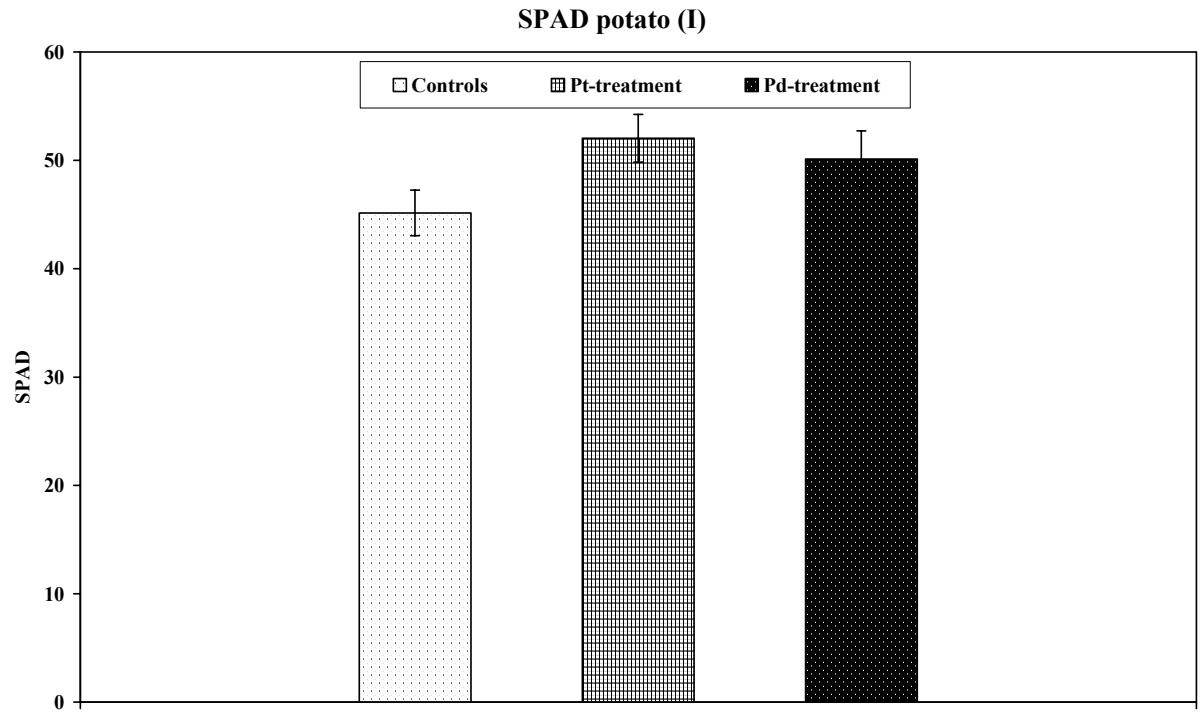


Figure (18C): Potato (I) treated with 2000 µg/l soluble PGE salts showed higher SPAD value than controls.

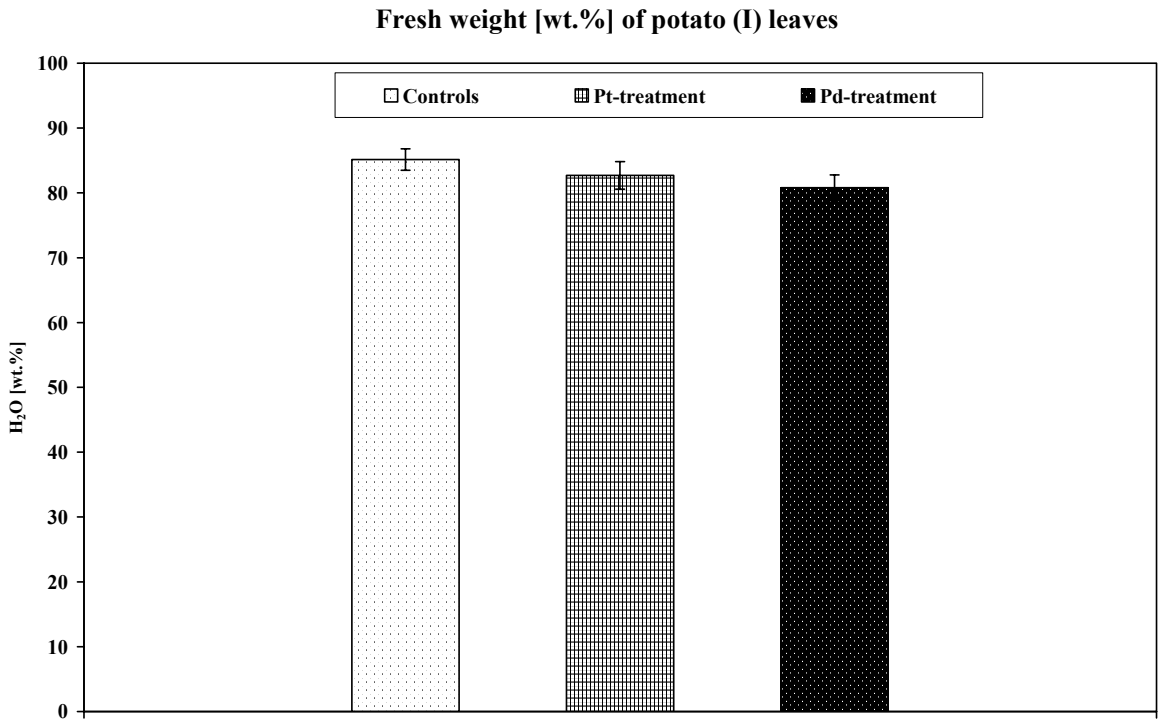


Figure (19C): Potato (I) treated with 2000 µg/l soluble PGE salts showed lower fresh weight than the controls

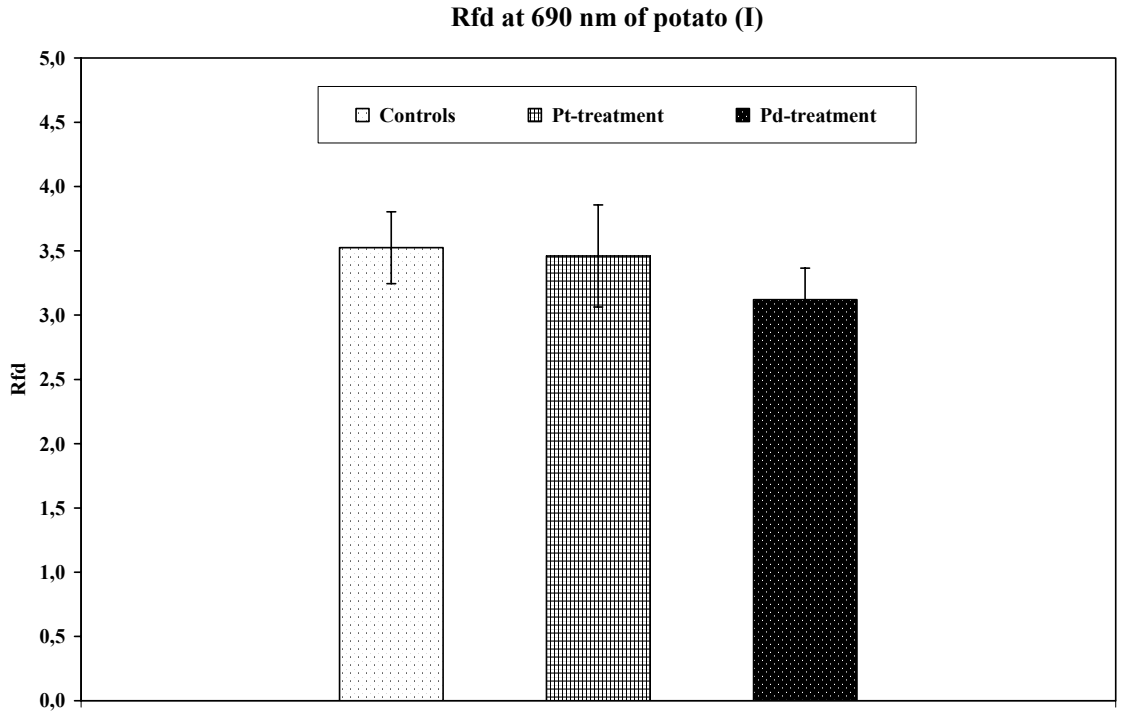


Figure (20C): Palladium treated potato (I) showed lower Rfd than the controls and platinum treated plants, which indicates the involving of palladium in the photosynthetic processes.

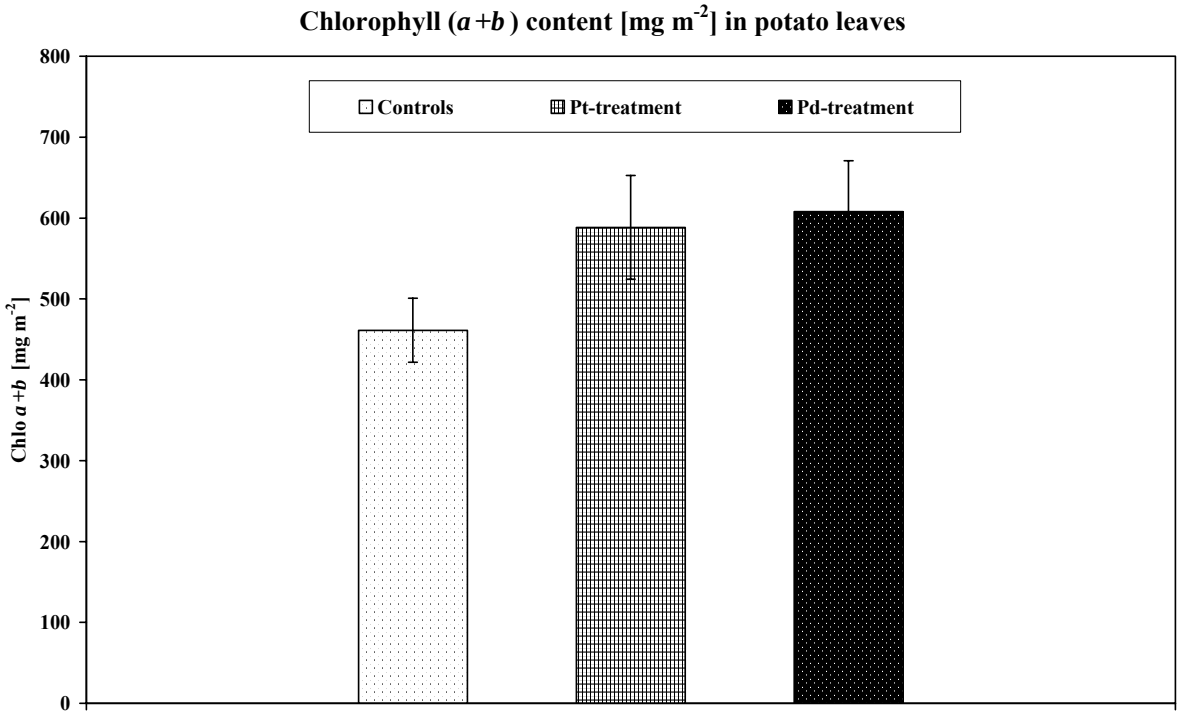


Figure (21C): The potato (I) treated with 2000 µg/l soluble PGE salts showed higher chlorophyll content than the controls.

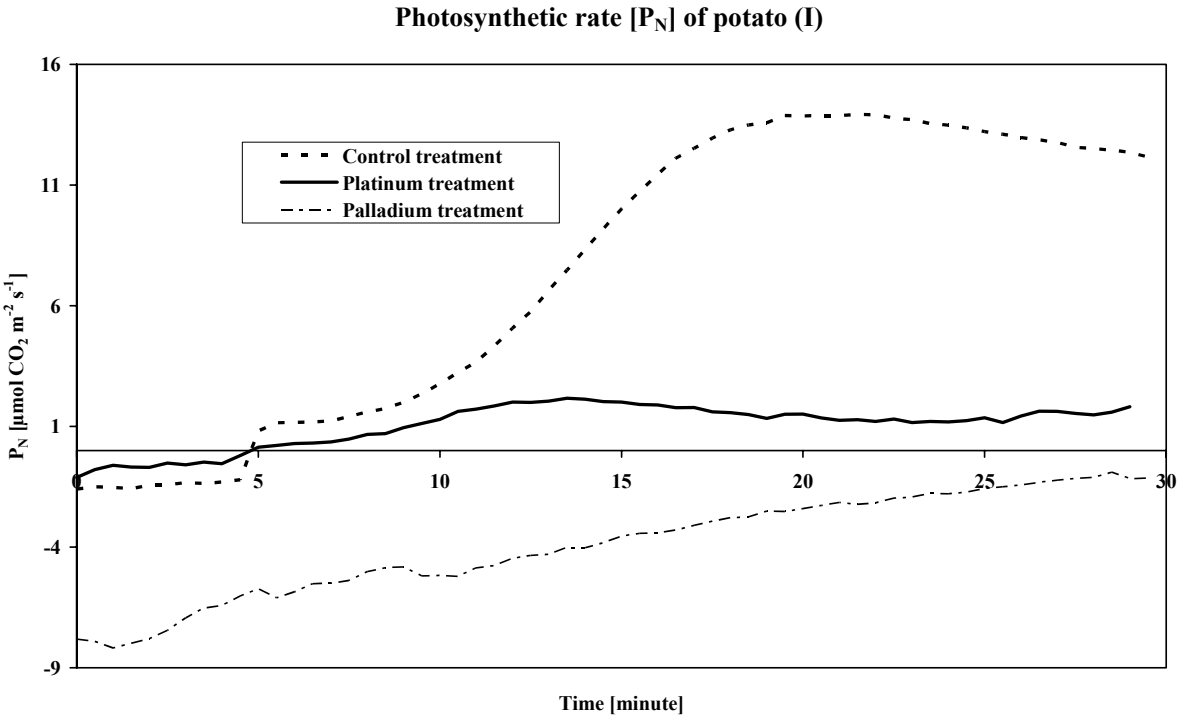


Figure (22C): The P_N measured for PGE treated potato (2000 µg/l) was far lower than the control plants, that indicates the interfering of PGE with photosynthetic processes.

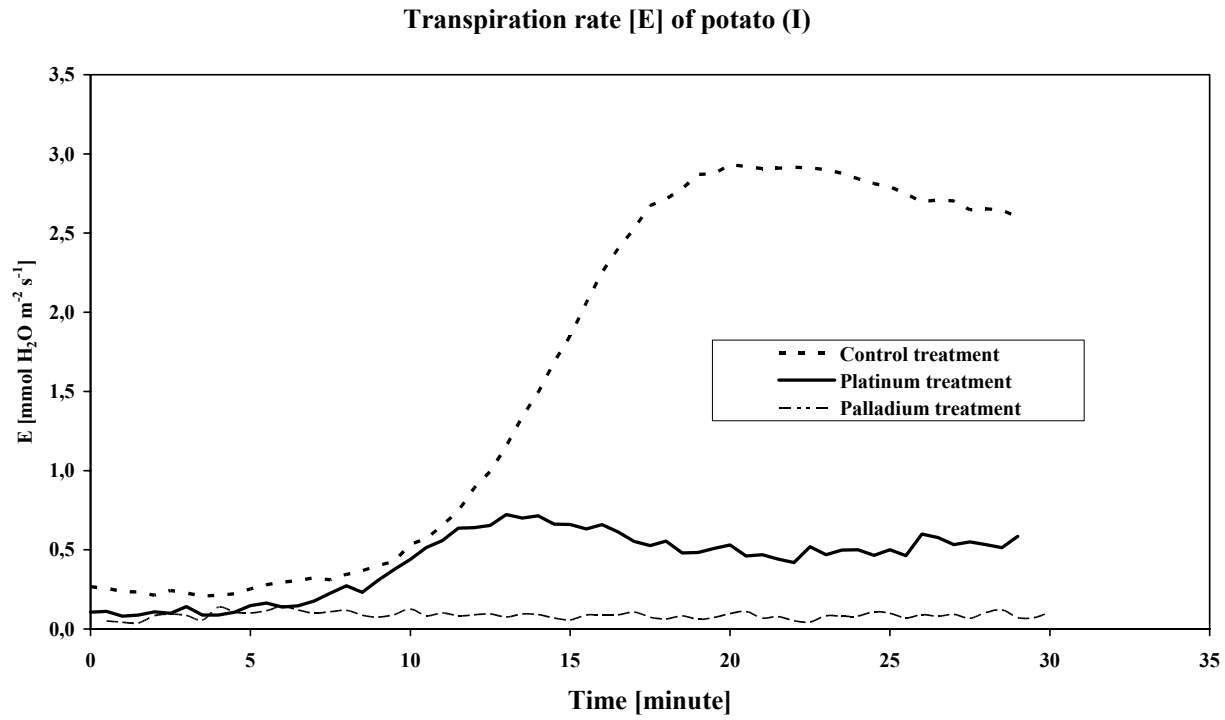


Figure (23C): The E measured for the PGE treated potato (2000 µg/l) was far lower than the control plants. Palladium phytotoxicity was more severe than platinum.

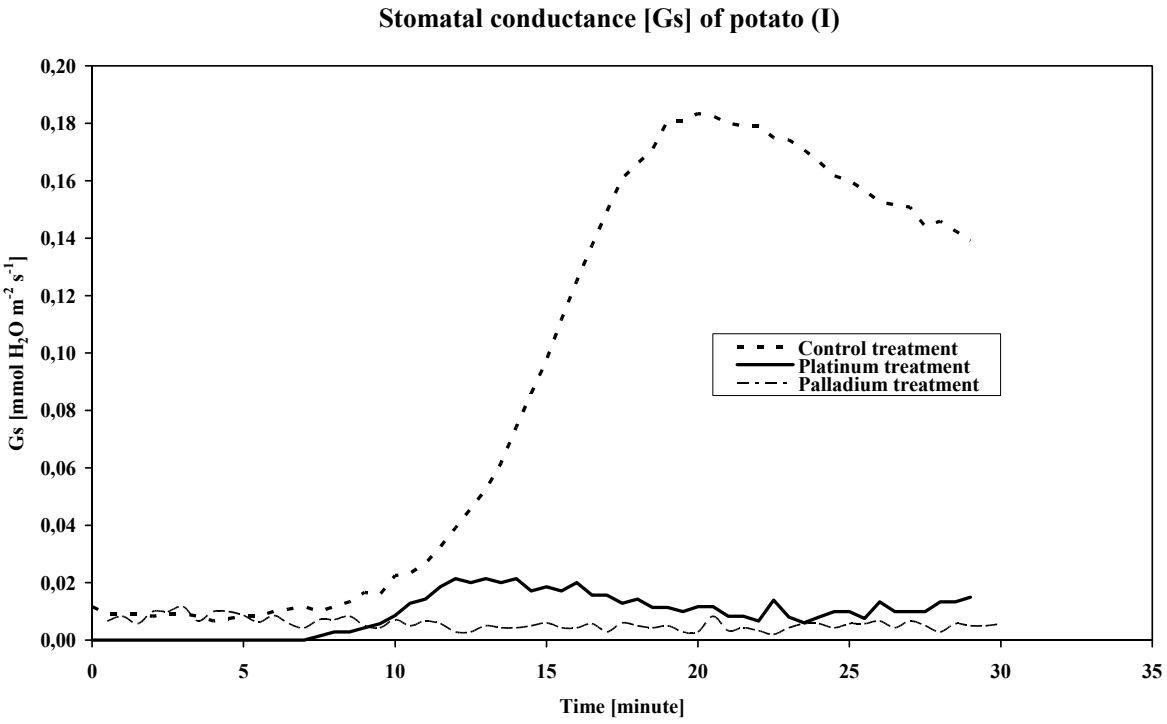


Figure (24C): The Gs measured for PGE treated potato (2000 µg/l) was far lower than the control plants, also indicting the interfering of PGE with photosynthetic processes.

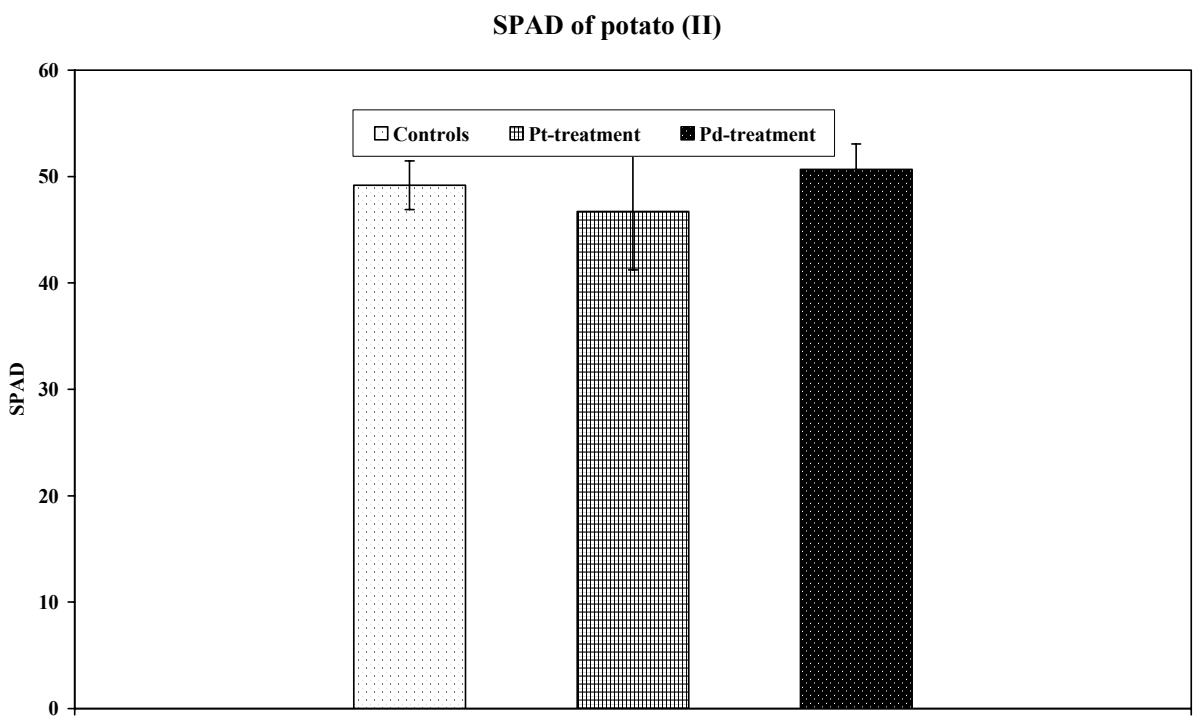


Figure (25C): SPAD units determined for potato (II) treated with soluble PGE salts were similar to the controls.

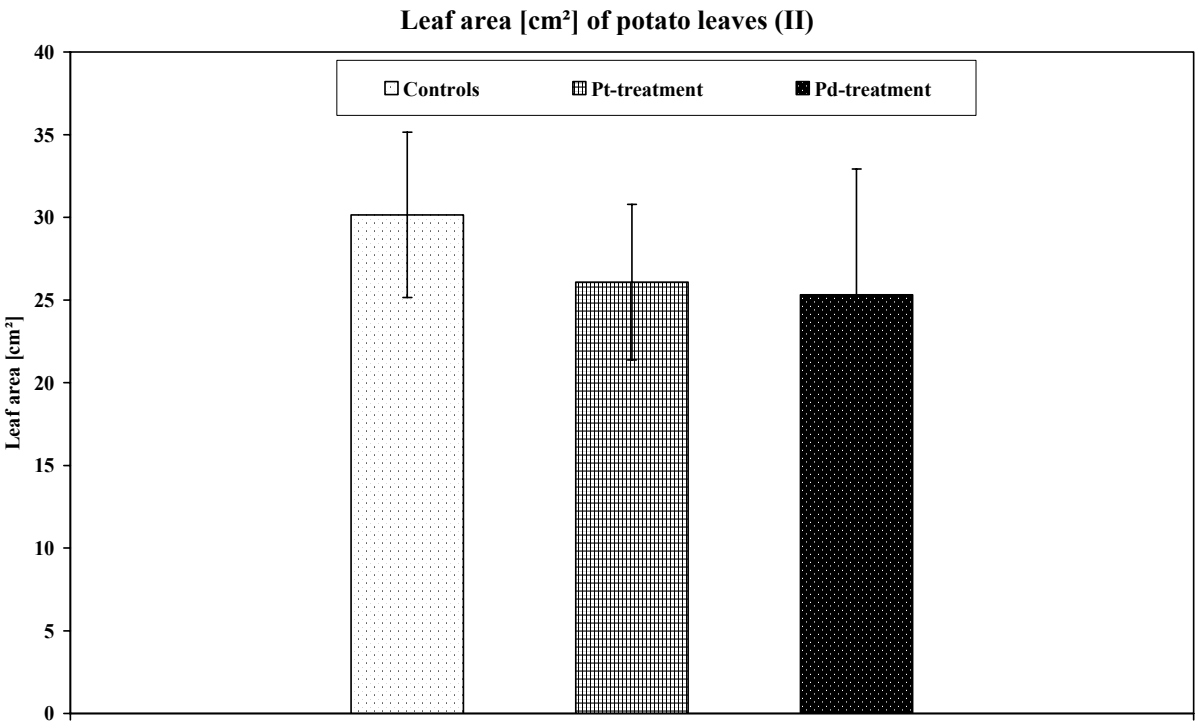


Figure (26C): Leaf areas of PGE treated potato (II) plants were lower than the controls.

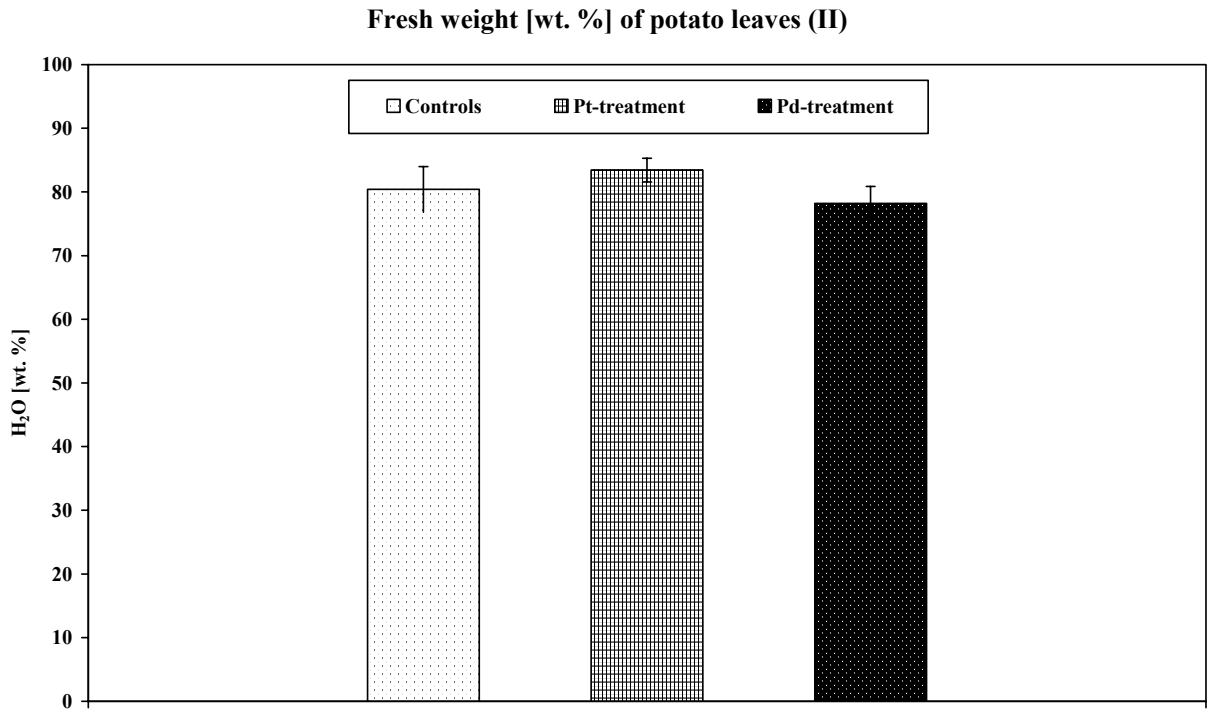


Figure (27C): The fresh weights calculated for palladium treated potato plants were lower than the controls.

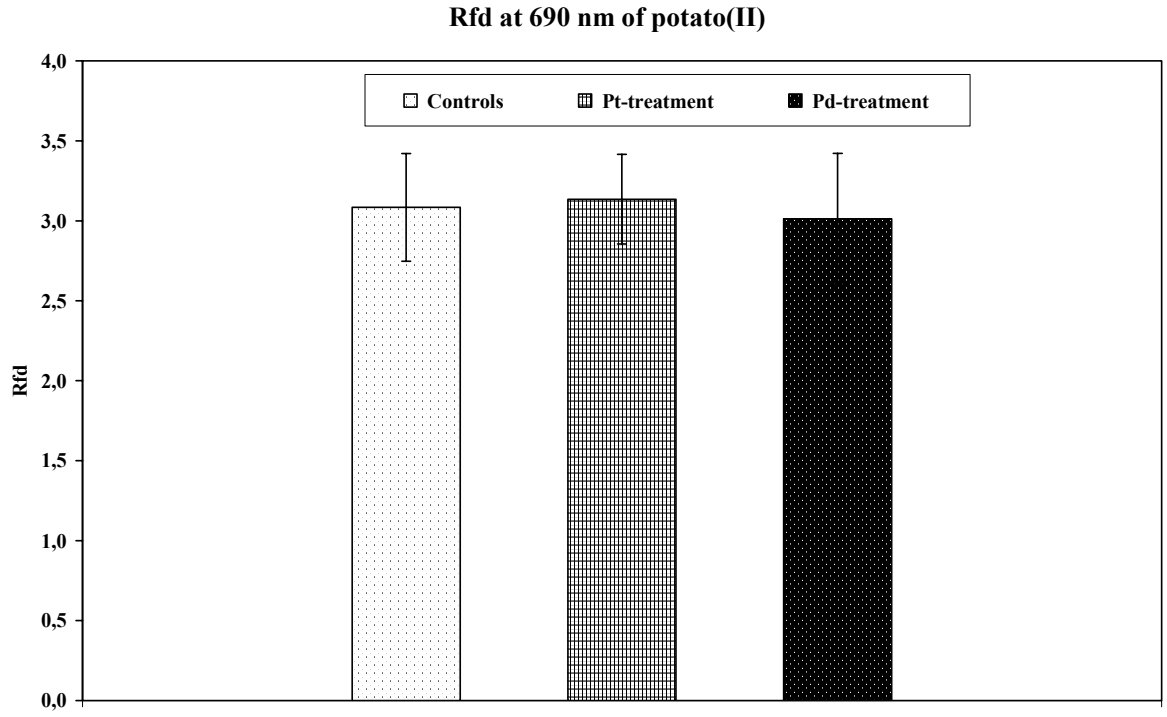


Figure (28C): The Rfd ratios of treated potatoes (300 µg/l) were similar to the controls.

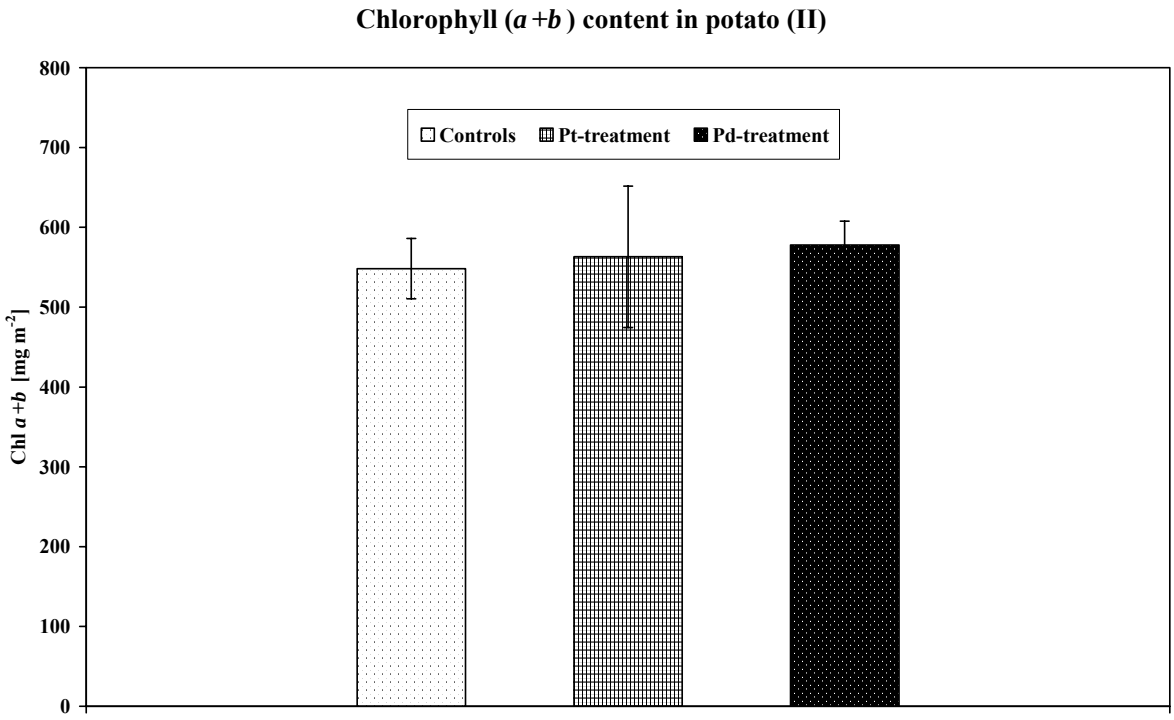


Figure (29C): Total chlorophyll content of palladium treated potato (II) plants was slightly higher than the controls.

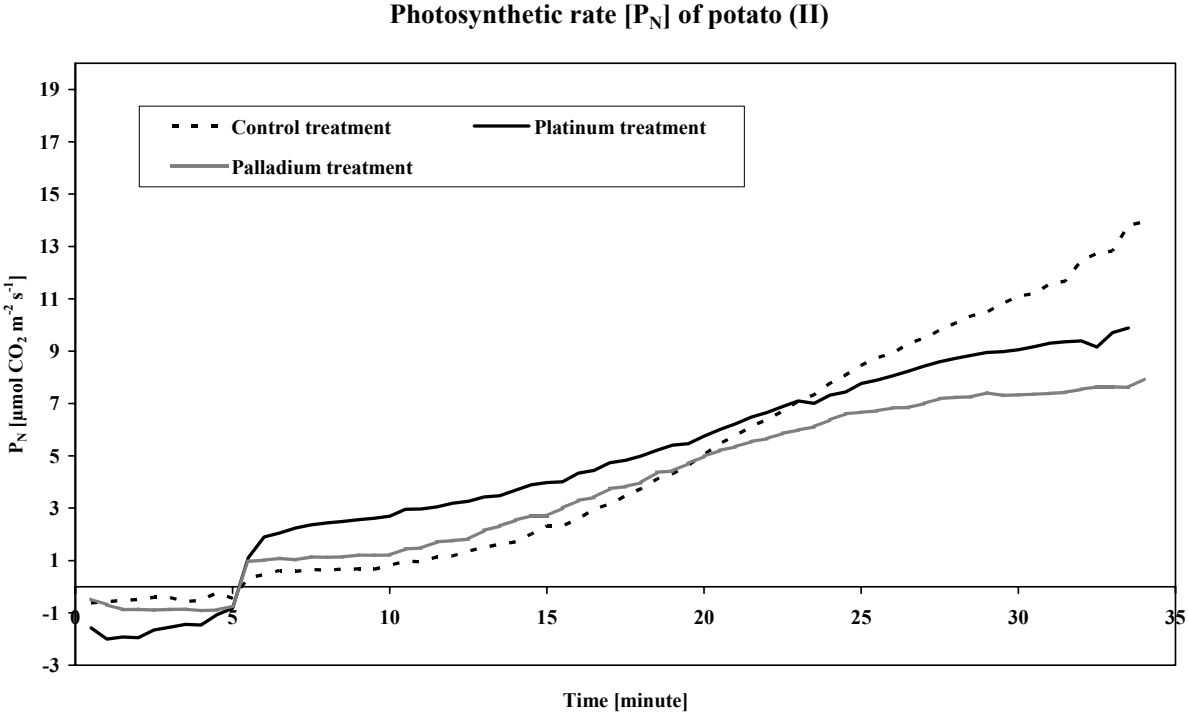


Figure (30C): The photosynthetic rate [P_N] of the PGE treated potato (II) was lower than the controls.

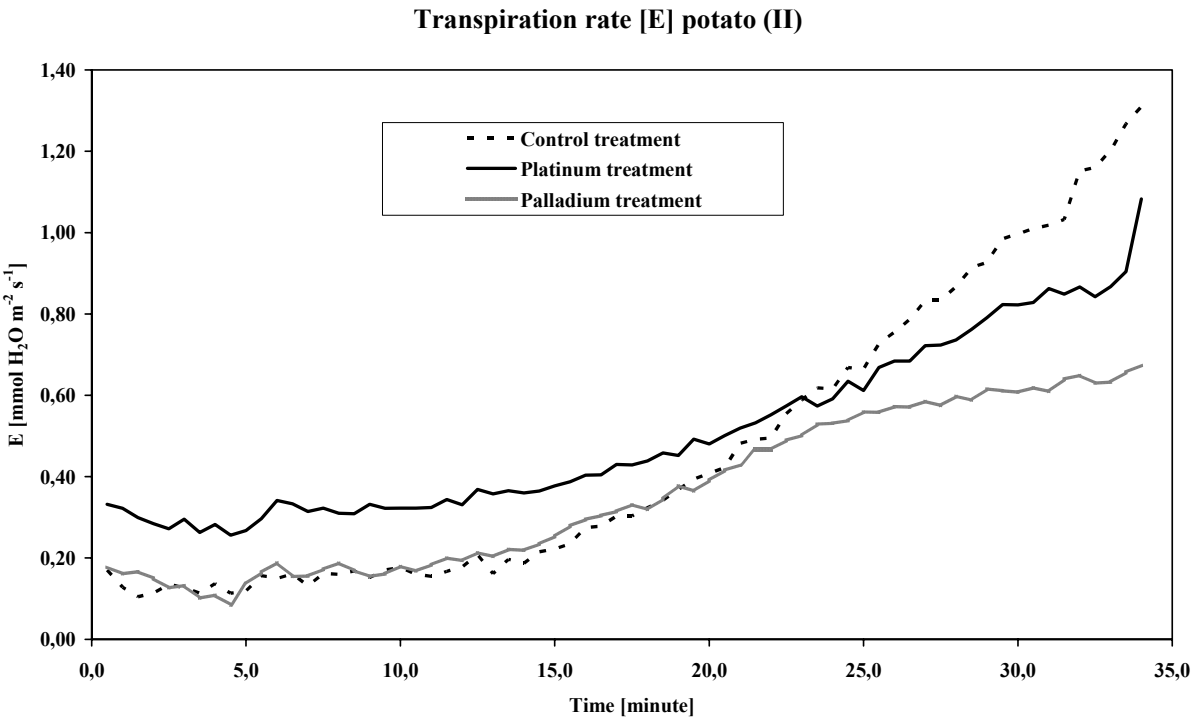


Figure (31C): The transpiration rate [E] of the PGE treated potato (II) was lower than the controls.

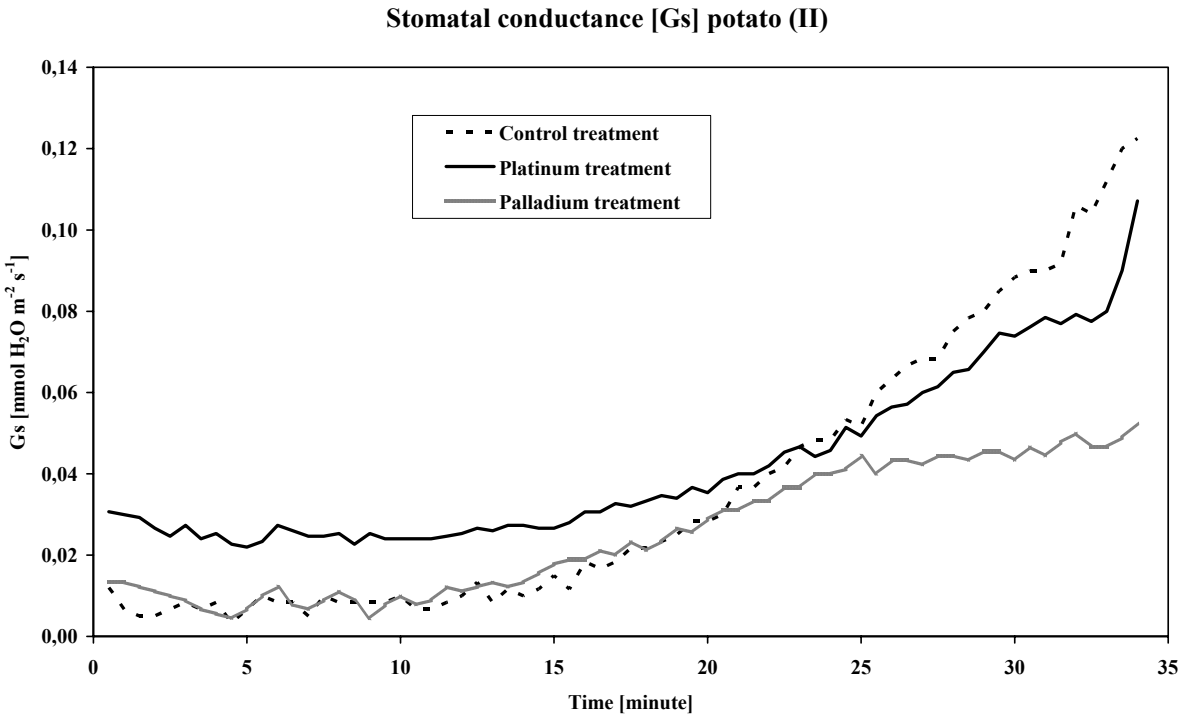


Figure (32C): The stomatal conductance [Gs] of PGE treated potato (II) was lower than the controls.

Appendix D:

Table 1D: SPAD units measured for greenhouse plants.

SPAD-Barley	Mean	SD	**SPAD-Potato I**	Mean	SD
Controls	44.3	2.9	Controls	66	28
Pt-treatment	44.9	2.0	Pt-treatment	64	29
Pd-treatment	44.2	1.6	Pd-treatment	83	1
SPAD-Lettuce	Mean	SD	**SPAD-Potato II**	Mean	SD
Controls	30.2	3.8	Controls	49	2
Pt-treatment	31.1	1.6	Pt-treatment	47	5
Pd-treatment	32.2	2.1	Pd-treatment	51	2

Table 2D: Leaf area of greenhouse grown crop plants.

Barley	Mean	SD	Median	Min.	Max.
Controls	35.6	3.5	37.0	29.2	39.5
Pt- treatment	30.6	6.0	30.1	20.7	40.3
Pd- treatment	29.7	4.3	29.9	22.3	37.7
Lettuce	Mean	SD	Median	Min.	Max.
Controls	153.1	31.5	152.4	108.0	209.4
Pt- treatment	175.5	21.7	172.5	143.7	220.7
Pd- treatment	170.9	24.3	169.8	132.1	221.0
Potato II	Mean	SD	Median	Min.	Max.
Controls	30	5	31	22	41
Pt- treatment	26	5	25	19	34
Pd- treatment	25	8	24	16	39

Table 3D: Fresh and dry weight of greenhouse grown plants.

Barley

Fresh weight	Mean	SD	Median	Min.	Max.
Controls	21	4	21	16	27
Pt- treatment	24	4	23	18	33
Pd- treatment	20	2	20	17	24
Dry weight	Mean	SD	Median	Min.	Max.
Controls	79	4	79	73	84
Pt- treatment	76	4	77	67	82
Pd- treatment	80	2	80	76	83

Potato I

Fresh weight	Mean	SD	Median	Min.	Max.
Controls	85	2	85	82	88
Pt- treatment	83	2	84	79	85
Pd- treatment	81	2	81	78	84
Dry weight	Mean	SD	Median	Min.	Max.
Controls	15	2	15	12	18
Pt- treatment	17	2	16	15	21
Pd- treatment	19	2	19	16	22

Lettuce

Fresh weight	Mean	SD	Median	Min.	Max.
Controls	83	2	84	79	86
Pt- treatment	84	2	85	81	87
Pd- treatment	85	2	85	82	89
Dry weight	Mean	SD	Median	Min.	Max.
Controls	17	2	16	14	21
Pt- treatment	16	2	15	13	19
Pd- treatment	15	2	15	11	18

Potato II

Fresh weight	Mean	SD	Median	Min.	Max.
Controls	80	4	80	74	85
Pt- treatment	83	2	83	80	86
Pd- treatment	78	3	78	76	83
Dry weight	Mean	SD	Median	Min.	Max.
Controls	20	4	20	15	26
Pt- treatment	17	2	17	14	20
Pd- treatment	22	3	22	17	24

Table 4D: Results of fluorescence measurements conducted on barley plants.

RFD Barley

WL 690	Mean			Standard Deviation (SD)		
	Controls	Pt- treatment	Pd- treatment	Controls	Pt- treatment	Pd- treatment
Fo	0.9	1.0	0.9	0.10	0.19	0.13
I	2.4	2.5	2.3	0.33	0.32	0.29
Fp	3.1	3.2	2.9	0.22	0.39	0.34
Fs	0.6	0.6	0.6	0.06	0.08	0.10
Fv	2.1	2.2	2.0	0.16	0.21	0.25
Fd	2.4	2.6	2.3	0.19	0.33	0.26
T1/2	0.0	0.0	0.0	0.00	0.00	0.00
TI	0.0	0.0	0.0	0.06	0.01	0.00
Tp	0.4	0.4	0.5	0.06	0.06	0.07
T50	10	10	10	2	2	1
T90	37	46	50	10	21	19
Fv/Fo	2.3	2.3	2.3	0.22	0.21	0.33
Fv/Fp	0.7	0.7	0.7	0.02	0.02	0.03
Rfd	3.8	4.0	3.8	0.30	0.42	0.37

WL 735	Mean Rfd			Standard Deviation (SD)		
	Controls	Pt- treatment	Pd- treatment	Controls	Pt- treatment	Pd- treatment
Fo	1.5	1.6	1.5	0.13	0.18	0.18
I	3.8	3.9	3.6	0.44	0.49	0.42
Fp	5.1	5.2	4.9	0.33	0.35	0.48
Fs	1.3	1.3	1.3	0.07	0.11	0.18
Fv	3.6	3.6	3.4	0.27	0.21	0.35
Fd	3.7	3.9	3.6	0.29	0.31	0.33
T1/2	0.0	0.0	0.0	0.00	0.00	0.00
TI	0.0	0.1	0.0	0.06	0.08	0.00
Tp	0.5	0.5	0.6	0.07	0.06	0.10
T50	10	11	11	2	2	1
T90	37	46	50	10	20	19
Fv/Fo	2.3	2.3	2.3	0.22	0.19	0.23
Fv/Fp	0.7	0.7	0.7	0.02	0.02	0.02
Rfd	2.8	2.9	2.8	0.21	0.27	0.23

Table 5D: Results of fluorescence measurements conducted on the lettuce.

RFD lettuce

WL690 nm	Mean			Standard Deviation (SD)		
	Controls	Pt- treatment	Pd- treatment	Controls	Pt- treatment	Pd- treatment
Fo	0.6	0.5	0.5	0.09	0.10	0.12
I	1.6	1.6	1.5	0.17	0.22	0.28
Fp	2.3	2.2	2.3	0.19	0.27	0.26
Fs	0.5	0.4	0.5	0.06	0.04	0.06
Fv	1.7	1.7	1.8	0.16	0.19	0.14
Fd	1.8	1.8	1.8	0.18	0.23	0.23
T1/2	0.0	0.0	0.0	0.01	0.01	0.01
TI	0.0	0.0	0.0	0.01	0.01	0.01
Tp	0.8	0.8	0.9	0.14	0.09	0.25
T50	19	17	23	7	3	10
T90	70	50	76	36	9	31
Fv/Fo	2.9	3.3	3.5	0.51	0.51	0.53
Fv/Fp	0.7	0.8	0.8	0.04	0.03	0.03
Rfd	4.0	4.4	4.0	0.52	0.22	0.50

WL735 nm	Mean			Standard Deviation (SD)		
	Controls	Pt- treatment	Pd- treatment	Controls	Pt- treatment	Pd- treatment
Fo	0.8	0.8	0.8	0.10	0.13	0.13
I	2.3	2.4	2.3	0.19	0.23	0.31
Fp	3.3	3.4	3.4	0.24	0.23	0.30
Fs	0.8	0.7	0.8	0.08	0.05	0.08
Fv	2.5	2.6	2.6	0.21	0.14	0.20
Fd	2.6	2.7	2.6	0.21	0.19	0.27
T1/2	0.0	0.0	0.0	0.01	0.01	0.02
TI	0.0	0.0	0.0	0.01	0.01	0.01
Tp	0.9	0.8	0.9	0.13	0.09	0.11
T50	19	18	24	6	2	10
T90	68	49	73	35	7	30
Fv/Fo	3.0	3.4	3.4	0.42	0.45	0.39
Fv/Fp	0.7	0.8	0.8	0.03	0.02	0.02
Rfd	3.3	3.6	3.4	0.37	0.17	0.36

Table 6D: Results of fluorescence measurements conducted on the potato I.

WL690	Mean			Standard Deviation (SD)		
	Controls	Pt-treatment	Pd-treatment	Controls	Pt-treatment	Pd-treatment
Fo	0.77	0.66	0.62	0.14	0.05	0.06
I	1.71	1.59	1.71	0.21	0.13	0.37
Fp	2.48	2.14	2.03	0.21	0.14	0.20
Fs	0.55	0.48	0.49	0.07	0.05	0.04
Fv	1.71	1.48	1.40	0.12	0.17	0.21
Fd	1.93	1.66	1.53	0.16	0.12	0.17
T1/2	0.01	0.01	0.01	0.01	0.00	0.00
TI	0.03	0.03	0.12	0.00	0.01	0.13
Tp	0.56	0.58	0.67	0.09	0.11	0.16
T50	13	14	14	2	4	3
T90	42	46	40	10	20	11
Fv/Fo	2.26	2.28	2.27	0.35	0.39	0.46
Fv/Fp	0.69	0.69	0.69	0.04	0.04	0.05
Rfd	3.52	3.46	3.12	0.28	0.40	0.25

WL735	Mean			Standard Deviation (SD)		
	Controls	Pt-treatment	Pd-treatment	Controls	Pt-treatment	Pd-treatment
Fo	1.47	1.33	1.33	0.19	0.12	0.14
I	3.45	3.68	4.19	0.35	0.69	0.78
Fp	5.19	4.73	4.63	0.31	0.31	0.38
Fs	1.37	1.28	1.33	0.12	0.13	0.07
Fv	3.72	3.39	3.30	0.18	0.32	0.39
Fd	3.82	3.45	3.30	0.22	0.24	0.32
T1/2	0.02	0.01	0.01	0.01	0.00	0.00
TI	0.03	0.09	0.22	0.01	0.11	0.14
Tp	0.69	0.68	0.74	0.08	0.09	0.07
T50	13	14	16	2	4	3
T90	44	50	45	9	23	13
Fv/Fo	2.57	2.56	2.50	0.31	0.35	0.43
Fv/Fp	0.72	0.72	0.71	0.03	0.03	0.04
Rfd	2.80	2.72	2.47	0.17	0.26	0.16

Table 7D: Results of fluorescence measurements conducted on the potato II.

WL690 nm	Mean			Standard Deviation (SD)		
	Controls	Pt-treatment	Pd-treatment	Controls	Pt-treatment	Pd-treatment
Fo	0.38	0.34	0.37	0.08	0.07	0.06
Fp	1.42	1.40	1.36	0.15	0.08	0.12
Fs	0.35	0.34	0.34	0.03	0.03	0.05
Fv	1.04	1.05	0.99	0.15	0.05	0.12
Fd	1.07	1.06	1.02	0.14	0.07	0.09
T1/2	0.01	0.01	0.01	0.00	0.00	0.01
Tp	0.71	0.68	0.69	0.17	0.14	0.11
T50	12	15	10	2	4	4
T90	35	46	30	12	15	12
Fv/Fo	2.86	3.17	2.72	0.71	0.59	0.56
Fv/Fp	0.73	0.76	0.73	0.05	0.04	0.04
Rfd	3.08	3.14	3.01	0.34	0.28	0.41

WL735 nm	Mean			Standard Deviation (SD)		
	Controls	Pt-treatment	Pd-treatment	Controls	Pt-treatment	Pd-treatment
Fo	0.81	0.73	0.78	0.13	0.09	0.08
Fp	3.10	2.99	2.93	0.24	0.16	0.23
Fs	0.89	0.86	0.87	0.05	0.05	0.10
Fv	2.28	2.26	2.15	0.23	0.15	0.23
Fd	2.21	2.13	2.06	0.22	0.14	0.15
T1/2	0.02	0.02	0.02	0.01	0.01	0.01
Tp	0.71	0.74	0.63	0.11	0.09	0.04
T50	13	16	11	3	4	4
T90	38	49	30	13	16	12
Fv/Fo	2.88	3.12	2.77	0.55	0.43	0.43
Fv/Fp	0.74	0.75	0.73	0.04	0.03	0.03
Rfd	2.48	2.46	2.40	0.24	0.19	0.24

Table 8D: Pigments contents of barley and lettuce grown in greenhouse.

Barley

Controls

	Mean	SD	Median	Min.	Max.
Chl a	286.0	49.3	290.8	221.3	353.5
Chl b	84.8	18.4	80.3	59.2	110.5
x+c	44.6	9.1	43.6	31.6	61.4
a+b	**370.8**	**67.0**	**374.6**	**280.5**	**460.0**
a/b	3.4	0.2	3.4	3.0	3.7
a+b/x	8.4	0.8	8.5	7.3	9.9

Pt-treatment

Chl a	294.5	35.0	292.4	247.1	352.2
Chl b	85.1	7.5	84.0	74.6	98.4
x+c	48.9	8.7	48.3	36.4	60.9
a+b	**379.6**	**42.4**	**374.5**	**321.7**	**450.6**
a/b	3.5	0.1	3.4	3.3	3.7
a+b/x	7.9	0.7	7.8	6.9	9.2

Pd-treatment

Chl a	305.6	26.3	306.2	254.2	342.8
Chl b	86.3	9.6	83.4	69.7	106.8
x+c	50.9	8.5	51.8	36.3	62.1
a+b	**391.9**	**31.8**	**399.6**	**323.8**	**438.5**
a/b	3.6	0.4	3.6	3.0	4.1
a+b/x	7.8	1.1	7.9	6.4	9.9

Lettuce

Controls

	Mean	SD	Median	Min.	Max.
Chl a	180.8	21.5	180.3	135.6	223.6
Chl b	48.6	6.1	48.8	34.8	60.2
x+c	49.3	5.8	49.2	39.9	60.2
a+b	229.4	27.5	229.1	170.5	283.8
a/b	3.7	0.1	3.7	3.5	3.9
a+b/x+c	4.7	0.2	4.7	4.3	5.0

Pt-treatment

Chl a	193.3	23.9	189.8	151.6	229.4
Chl b	51.0	5.3	50.3	41.3	59.8
x+c	51.4	5.7	50.7	42.5	62.3
a+b	244.3	29.0	240.4	192.9	286.6
a/b	3.8	0.2	3.8	3.6	4.1
a+b/x+c	4.8	0.2	4.6	4.5	5.1

Pd-treatment

Chl a	200.9	14.8	201.1	178.7	225.4
Chl b	54.0	3.8	53.8	47.0	61.8
x+c	53.3	3.3	53.4	49.1	59.0
a+b	254.9	18.3	254.9	227.7	283.0
a/b	3.7	0.1	3.7	3.5	3.9
a+b/x+c	4.8	0.2	4.8	4.4	5.2

Table 9D: Contents of pigments in potato I and potato II plants.

Potato I

Controls	Mean	SD	Median	Min.	Max.
Chl a	364	32	359	312	408
Chl b	97	8	100	85	113
x+c	73	9	72	62	88
a+b	**461**	40	447	397	516
a/b	4	0.2	4	3	4
a+b/x+c	6	0.4	6	6	7

Pt- treatment

Chl a	459	52	450	389	541
Chl b	130	12	125	112	148
x+c	89	13	86	75	110
a+b	**589**	64	579	501	689
a/b	4	0.1	3	3	4
a+b/x+c	7	0.4	6	6	7

Pd- treatment

Chl a	473	49	473	385	560
Chl b	135	14	134	108	162
x+c	99	12	100	80	125
a+b	**608**	63	607	493	722
a/b	4	0.1	3	3	4
a+b/x+c	6	0.3	6	6	7

Potato II

Controls	Mean	SD	Median	Min.	Max.
Chl a	422	30	422	370	478
Chl b	127	8	129	109	136
x+c	90	13	92	70	109
a+b	**548**	**38**	**551**	**479**	**615**
a/b	3	0.1	3	3	4
a+b/x+c	6	0.7	6	5	7

Pt-treatment

Chl a	433	71	428	311	568
Chl b	130	18	126	101	162
x+c	91	13	86	77	119
a+b	**563**	**89**	**554**	**421**	**730**
a/b	3	0	3	3	4
a+b/x+c	6	1	6	5	7

Pd-treatment

Chl a	442	22	437	408	475
Chl b	135	9	136	123	148
x+c	97	7	98	88	110
a+b	**578**	**30**	**572**	**531**	**613**
a/b	3	0.1	3	3	3
a+b/x+c	6	0.5	6	5	7

Figure 10D: Photosynthetic rate [P_N] measured for barely.

Time	Photosynthetic rate [µmol CO_2 m^{-2} s^{-1}] for barley														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	-2.6	0.8	-2.3	-4.6	-1.7	-2.7	0.8	-2.5	-4.6	-1.7	-2.3	0.6	-2.5	-3.1	-1.2
1.0	-2.4	0.8	-2.2	-4.6	-1.6	-2.7	0.8	-2.3	-4.4	-1.9	-2.3	0.5	-2.3	-3.0	-1.1
1.5	-2.3	0.4	-2.2	-3.1	-1.7	-2.6	0.8	-2.3	-4.7	-1.8	-2.4	0.6	-2.7	-3.0	-1.1
2.0	-2.4	0.5	-2.4	-3.2	-1.4	-2.5	0.8	-2.2	-4.4	-1.7	-2.4	0.6	-2.3	-3.5	-1.1
2.5	-2.3	0.5	-2.3	-3.1	-1.2	-2.7	1.0	-2.4	-4.4	-1.4	-2.2	0.6	-2.2	-3.0	-0.8
3.0	-2.4	0.7	-2.5	-3.8	-1.6	-2.6	0.9	-2.4	-4.7	-1.5	-2.2	0.6	-2.1	-3.3	-1.2
3.5	-2.2	0.7	-2.3	-3.9	-1.3	-2.4	0.7	-2.3	-4.0	-1.1	-2.2	0.5	-2.2	-2.9	-1.0
4.0	-2.2	0.5	-2.1	-3.1	-1.6	-2.4	0.9	-2.2	-4.3	-0.9	-2.2	0.4	-2.2	-3.1	-1.3
4.5	-2.2	0.4	-2.2	-2.9	-1.5	-2.2	0.8	-2.1	-3.7	-0.7	-2.0	0.6	-2.2	-3.0	-1.0
5.0	-1.3	0.6	-1.2	-2.7	-0.2	-1.6	0.9	-1.5	-3.6	0.0	-1.4	0.9	-1.7	-2.5	-0.1
5.5	1.6	1.0	1.3	0.2	4.2	2.1	2.1	1.3	0.3	8.5	1.0	1.0	0.6	0.0	3.3
6.0	3.5	2.1	3.2	0.8	8.1	3.8	2.2	3.4	1.0	9.9	3.0	1.3	3.1	0.9	5.0
6.5	5.2	1.8	5.1	1.5	7.9	5.9	2.4	6.1	1.7	11.4	4.9	2.1	4.9	1.1	8.8
7.0	6.7	2.3	6.5	3.0	9.6	6.9	2.2	7.4	3.4	11.4	6.3	2.3	6.5	1.9	10.5
7.5	8.1	2.6	8.0	3.8	13.2	8.4	2.2	8.4	4.5	12.9	7.4	2.7	6.8	2.5	12.6
8.0	9.0	2.7	8.3	4.4	14.4	9.4	2.1	9.4	5.5	13.0	8.6	2.7	8.4	3.6	13.3
8.5	10.0	2.4	9.4	6.2	14.7	10.7	1.9	10.9	7.7	14.5	9.6	2.7	9.7	4.5	14.4
9.0	10.4	2.4	10.9	6.2	14.6	11.4	2.0	11.5	8.4	14.4	10.4	2.8	10.5	5.4	14.7
9.5	11.1	2.3	11.3	7.7	15.4	12.1	1.5	12.2	9.4	14.7	11.3	2.8	11.6	6.5	16.0
10.0	12.1	2.6	11.8	8.0	17.0	12.8	1.8	12.5	9.6	15.3	11.8	2.9	12.1	7.1	17.3
10.5	12.7	2.9	12.8	8.6	17.6	13.3	1.7	13.3	10.1	15.9	12.5	2.7	13.0	8.5	17.5
11.0	13.1	2.7	13.5	8.9	18.0	13.8	1.8	13.9	10.6	16.1	12.8	3.0	12.9	8.7	18.4
11.5	13.5	2.9	13.3	9.0	18.8	14.1	1.8	14.1	10.9	16.3	13.4	2.7	13.6	9.4	18.2
12.0	13.9	2.7	14.1	9.8	18.4	14.4	1.5	14.9	11.4	16.0	13.8	2.8	14.0	9.4	19.0
12.5	14.2	2.8	14.2	9.6	19.3	14.4	1.8	14.9	11.7	16.8	14.1	2.6	14.1	10.1	19.0
13.0	14.5	2.8	14.4	10.3	19.4	14.9	1.6	15.5	11.8	16.6	14.4	2.7	14.4	10.2	18.7
13.5	14.5	2.8	15.0	9.3	18.8	15.1	1.6	15.5	12.0	17.1	14.4	2.5	14.3	10.6	18.3
14.0	14.2	2.7	14.2	10.1	19.5	15.1	1.5	15.3	12.0	17.0	14.7	2.5	14.7	10.5	19.0
14.5	14.7	2.8	15.2	9.9	19.2	15.3	1.6	15.9	11.9	17.2	14.9	2.3	14.8	11.1	19.2
15.0	14.8	3.1	15.0	9.9	20.2	15.3	1.6	16.0	12.0	16.8	14.9	2.3	14.6	10.8	19.0
15.5	14.7	3.0	14.9	9.6	19.6	15.3	1.4	15.6	12.8	17.3	14.8	2.3	14.7	11.3	19.3
16.0	14.5	2.7	14.6	10.5	19.4	15.5	1.4	15.8	12.6	17.2	15.0	2.4	14.5	11.3	19.5
16.5	14.8	3.2	15.1	9.9	20.2	15.4	1.4	16.0	12.6	16.8	14.8	2.2	14.6	11.2	18.5
17.0	14.6	2.7	14.7	10.6	19.3	15.2	1.5	15.6	12.4	16.9	14.8	2.3	14.5	10.8	19.2
17.5	14.8	3.2	15.5	10.3	20.3	15.1	1.3	15.5	12.5	16.6	14.9	2.1	14.8	11.6	18.8
18.0	14.7	3.2	14.9	10.1	20.0	15.1	1.4	15.6	12.4	16.9	14.7	2.1	14.6	11.5	18.3
18.5	14.7	3.3	15.0	10.0	20.5	14.9	1.4	15.4	12.1	16.9	14.7	2.3	14.5	11.3	18.3
19.0	14.7	3.2	15.2	10.0	19.9	14.9	1.5	15.2	11.9	17.3	14.6	2.1	14.7	11.7	18.7
19.5	14.5	3.4	15.0	9.8	20.0	14.9	1.4	14.8	12.1	16.5	14.4	2.2	14.0	11.5	18.3
20.0	14.6	3.5	14.8	9.6	20.2	14.7	1.3	15.1	12.2	16.4	14.3	2.3	13.8	11.2	18.2

Table 11D: Transpiration rate [E] measured for barley.

Time	Transpiration rate [mmol H_2O m^{-2} s^{-1}] for barley														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	0.5	0.4	0.5	0.0	1.4	0.6	0.4	0.5	0.1	1.9	0.4	0.2	0.3	0.1	0.6
1.0	0.5	0.3	0.5	0.1	1.0	0.6	0.4	0.5	0.1	1.9	0.3	0.2	0.3	0.0	0.6
1.5	0.5	0.3	0.5	0.1	1.1	0.6	0.4	0.5	0.1	1.8	0.3	0.2	0.3	0.1	0.6
2.0	0.5	0.3	0.4	0.1	1.3	0.5	0.5	0.4	0.1	1.8	0.4	0.1	0.4	0.1	0.6
2.5	0.5	0.3	0.4	0.1	1.2	0.5	0.4	0.4	0.2	1.9	0.3	0.2	0.4	0.1	0.5
3.0	0.4	0.3	0.4	0.1	1.2	0.5	0.4	0.4	0.0	1.6	0.3	0.2	0.3	0.1	0.6
3.5	0.4	0.3	0.4	0.1	1.2	0.5	0.3	0.4	0.1	1.4	0.3	0.2	0.3	0.1	0.5
4.0	0.5	0.3	0.5	0.1	1.2	0.5	0.4	0.4	0.1	1.7	0.3	0.2	0.3	0.1	0.6
4.5	0.5	0.3	0.5	0.1	1.1	0.5	0.4	0.3	0.1	1.5	0.3	0.2	0.4	0.0	0.6
5.0	0.5	0.3	0.5	0.1	1.4	0.5	0.4	0.4	0.1	1.7	0.4	0.2	0.4	0.1	0.7
5.5	0.6	0.4	0.6	0.1	1.5	0.6	0.4	0.5	0.3	1.9	0.5	0.2	0.6	0.1	0.8
6.0	0.7	0.4	0.6	0.3	1.5	0.7	0.4	0.6	0.3	1.9	0.6	0.3	0.6	0.2	1.1
6.5	0.9	0.3	0.8	0.4	1.5	1.0	0.5	0.8	0.4	2.3	0.8	0.3	0.8	0.3	1.2
7.0	1.0	0.4	1.0	0.5	1.8	1.1	0.5	0.9	0.4	2.4	0.9	0.2	0.9	0.4	1.4
7.5	1.2	0.3	1.2	0.6	1.8	1.3	0.6	1.1	0.5	2.8	1.1	0.4	1.2	0.4	1.7
8.0	1.3	0.4	1.3	0.7	2.0	1.5	0.7	1.2	0.6	3.0	1.3	0.4	1.3	0.4	1.8
8.5	1.5	0.4	1.6	0.9	2.2	1.6	0.6	1.3	0.8	2.7	1.5	0.5	1.3	0.5	2.4
9.0	1.6	0.4	1.7	1.0	2.2	1.8	0.8	1.5	1.0	3.3	1.5	0.4	1.5	0.6	2.2
9.5	1.7	0.4	1.8	1.1	2.4	2.0	0.7	1.7	1.1	3.2	1.7	0.5	1.8	0.6	2.7
10.0	1.8	0.4	1.9	1.1	2.3	2.1	0.8	1.9	1.2	3.7	1.8	0.5	1.9	0.8	2.5
10.5	1.9	0.4	2.0	1.3	2.5	2.2	0.7	1.9	1.2	3.5	2.0	0.5	2.0	0.9	3.0
11.0	2.0	0.4	1.9	1.3	2.6	2.3	0.8	2.1	1.3	3.6	2.0	0.5	2.1	0.9	3.0
11.5	2.1	0.5	1.9	1.3	2.8	2.4	0.8	2.1	1.4	3.9	2.1	0.5	2.2	1.0	3.2
12.0	2.1	0.5	2.0	1.4	2.9	2.5	0.8	2.3	1.4	3.9	2.2	0.6	2.2	1.2	3.4
12.5	2.2	0.5	2.2	1.3	3.1	2.5	0.9	2.4	1.5	4.0	2.3	0.6	2.3	1.3	3.4
13.0	2.2	0.5	2.3	1.4	3.0	2.6	0.9	2.4	1.5	4.2	2.4	0.6	2.4	1.2	3.5
13.5	2.3	0.5	2.4	1.4	3.1	2.7	0.9	2.6	1.6	4.3	2.4	0.6	2.5	1.3	3.4
14.0	2.4	0.6	2.4	1.5	3.6	2.7	0.9	2.5	1.6	4.3	2.5	0.7	2.6	1.3	3.6
14.5	2.4	0.5	2.5	1.5	3.3	2.7	0.9	2.5	1.5	4.3	2.5	0.6	2.6	1.4	3.5
15.0	2.4	0.6	2.4	1.5	3.3	2.8	0.9	2.6	1.6	4.5	2.5	0.6	2.5	1.5	3.6
15.5	2.4	0.6	2.5	1.4	3.5	2.8	0.9	2.7	1.7	4.4	2.5	0.6	2.7	1.5	3.7
16.0	2.5	0.6	2.4	1.5	3.6	2.8	0.9	2.7	1.6	4.4	2.6	0.5	2.7	1.7	3.7
16.5	2.5	0.7	2.5	1.5	3.7	2.8	0.9	2.6	1.7	4.3	2.6	0.6	2.6	1.7	3.6
17.0	2.5	0.7	2.5	1.6	3.8	2.9	0.9	2.7	1.6	4.5	2.6	0.6	2.7	1.6	3.9
17.5	2.5	0.6	2.6	1.5	3.6	2.8	0.9	2.5	1.6	4.6	2.6	0.6	2.6	1.6	3.7
18.0	2.5	0.7	2.3	1.6	3.8	2.8	0.9	2.7	1.7	4.4	2.5	0.5	2.5	1.7	3.5
18.5	2.5	0.7	2.4	1.5	3.9	2.9	0.9	2.6	1.7	4.5	2.6	0.5	2.5	1.8	3.5
19.0	2.5	0.7	2.3	1.6	3.7	2.8	0.9	2.6	1.8	4.5	2.5	0.6	2.5	1.7	3.8
19.5	2.5	0.7	2.3	1.5	4.1	2.8	0.9	2.7	1.7	4.5	2.5	0.5	2.6	1.7	3.7
20.0	2.4	0.7	2.3	1.5	3.9	2.8	0.9	2.6	1.8	4.3	2.6	0.5	2.5	1.7	3.6

Table 12d: Stomatal conductance measured for barley.

Time	Stomatal conductance [mmol H_2O m^{-2} s^{-1}] for barley														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	media	min.	max.	mean	SD	media	min.	max.	mean	SD	media	min.	max.
0.5	0.02	0.02	0.01	0.00	0.08	0.03	0.03	0.02	0.00	0.12	0.01	0.01	0.01	0.00	0.02
1.0	0.02	0.02	0.01	0.00	0.06	0.03	0.03	0.02	0.00	0.12	0.01	0.01	0.01	0.00	0.03
1.5	0.02	0.02	0.02	0.00	0.06	0.02	0.03	0.02	0.00	0.11	0.01	0.01	0.01	0.00	0.02
2.0	0.02	0.02	0.01	0.00	0.07	0.02	0.03	0.02	0.00	0.12	0.01	0.01	0.01	0.00	0.03
2.5	0.02	0.02	0.02	0.00	0.07	0.02	0.03	0.01	0.00	0.12	0.01	0.01	0.01	0.00	0.03
3.0	0.02	0.02	0.01	0.00	0.07	0.02	0.03	0.01	0.00	0.10	0.01	0.01	0.01	0.00	0.02
3.5	0.02	0.02	0.01	0.00	0.07	0.02	0.02	0.02	0.00	0.09	0.01	0.01	0.01	0.00	0.03
4.0	0.02	0.02	0.01	0.00	0.07	0.02	0.03	0.02	0.00	0.11	0.01	0.01	0.01	0.00	0.03
4.5	0.02	0.02	0.01	0.00	0.06	0.02	0.02	0.02	0.00	0.08	0.01	0.01	0.01	0.00	0.03
5.0	0.02	0.02	0.01	0.00	0.07	0.02	0.02	0.01	0.00	0.09	0.01	0.01	0.01	0.00	0.03
5.5	0.02	0.02	0.02	0.00	0.07	0.02	0.03	0.02	0.00	0.10	0.02	0.01	0.02	0.00	0.04
6.0	0.02	0.02	0.02	0.00	0.07	0.03	0.02	0.02	0.00	0.09	0.02	0.01	0.02	0.00	0.05
6.5	0.03	0.02	0.03	0.01	0.07	0.04	0.03	0.03	0.00	0.12	0.03	0.01	0.03	0.00	0.05
7.0	0.04	0.02	0.03	0.01	0.09	0.04	0.03	0.04	0.00	0.13	0.03	0.01	0.03	0.01	0.05
7.5	0.04	0.02	0.04	0.02	0.09	0.06	0.04	0.04	0.01	0.15	0.04	0.02	0.04	0.01	0.06
8.0	0.05	0.02	0.04	0.02	0.09	0.06	0.04	0.05	0.02	0.16	0.05	0.02	0.05	0.01	0.09
8.5	0.05	0.02	0.05	0.03	0.09	0.07	0.04	0.06	0.02	0.14	0.05	0.03	0.05	0.01	0.12
9.0	0.06	0.02	0.06	0.03	0.09	0.08	0.05	0.06	0.02	0.18	0.06	0.02	0.05	0.02	0.11
9.5	0.06	0.02	0.06	0.03	0.10	0.08	0.05	0.07	0.03	0.17	0.07	0.03	0.06	0.02	0.14
10.0	0.07	0.02	0.06	0.03	0.11	0.09	0.06	0.08	0.03	0.20	0.07	0.03	0.07	0.02	0.13
10.5	0.07	0.03	0.06	0.03	0.12	0.09	0.05	0.09	0.03	0.19	0.08	0.04	0.06	0.03	0.16
11.0	0.07	0.03	0.07	0.04	0.13	0.10	0.06	0.09	0.04	0.20	0.08	0.04	0.07	0.03	0.16
11.5	0.08	0.03	0.07	0.03	0.13	0.10	0.06	0.09	0.04	0.22	0.08	0.04	0.07	0.03	0.17
12.0	0.08	0.03	0.07	0.04	0.14	0.11	0.06	0.09	0.04	0.22	0.09	0.04	0.07	0.03	0.18
12.5	0.08	0.03	0.07	0.04	0.14	0.11	0.07	0.09	0.04	0.23	0.09	0.04	0.08	0.04	0.18
13.0	0.08	0.03	0.07	0.04	0.14	0.11	0.07	0.09	0.04	0.23	0.09	0.05	0.07	0.03	0.20
13.5	0.08	0.03	0.08	0.04	0.16	0.12	0.07	0.10	0.05	0.26	0.09	0.04	0.08	0.04	0.19
14.0	0.09	0.04	0.08	0.04	0.16	0.11	0.07	0.09	0.05	0.25	0.10	0.05	0.08	0.04	0.20
14.5	0.09	0.04	0.08	0.04	0.17	0.12	0.07	0.10	0.04	0.25	0.10	0.05	0.08	0.04	0.19
15.0	0.09	0.04	0.08	0.04	0.17	0.12	0.08	0.10	0.05	0.27	0.10	0.05	0.08	0.04	0.20
15.5	0.09	0.04	0.08	0.04	0.19	0.12	0.07	0.09	0.05	0.26	0.10	0.05	0.08	0.04	0.20
16.0	0.09	0.04	0.08	0.04	0.19	0.12	0.07	0.10	0.05	0.26	0.10	0.05	0.08	0.05	0.20
16.5	0.09	0.04	0.08	0.04	0.20	0.12	0.07	0.10	0.05	0.24	0.10	0.05	0.08	0.05	0.19
17.0	0.09	0.04	0.08	0.04	0.21	0.12	0.07	0.10	0.05	0.25	0.10	0.05	0.08	0.05	0.21
17.5	0.09	0.04	0.08	0.04	0.19	0.12	0.07	0.10	0.05	0.26	0.10	0.05	0.08	0.05	0.20
18.0	0.09	0.04	0.08	0.04	0.21	0.12	0.07	0.10	0.05	0.24	0.10	0.04	0.08	0.05	0.19
18.5	0.09	0.04	0.08	0.04	0.21	0.12	0.07	0.10	0.05	0.25	0.10	0.05	0.08	0.05	0.19
19.0	0.09	0.04	0.08	0.04	0.20	0.12	0.07	0.10	0.05	0.25	0.10	0.05	0.07	0.05	0.20
19.5	0.09	0.05	0.08	0.04	0.22	0.11	0.06	0.10	0.05	0.24	0.09	0.04	0.08	0.05	0.19
20.0	0.09	0.04	0.08	0.04	0.21	0.11	0.06	0.10	0.05	0.23	0.10	0.04	0.08	0.05	0.18

Table 13D: Photosynthetic rate measured for lettuce.

Time	Photosynthetic rate [µmol CO_2 m^{-2} s^{-1}] for lettuce														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	-2.4	1.0	-2.4	-4.8	-1.1	-1.1	0.6	-1.2	-2.4	-0.3	-1.6	0.9	-1.4	-3.6	-0.1
1.0	-2.3	1.1	-2.4	-4.8	-0.6	-1.1	0.5	-1.2	-1.8	-0.3	-1.5	0.9	-1.4	-3.1	-0.3
1.5	-2.2	1.0	-2.4	-4.2	-0.8	-0.8	0.4	-0.8	-1.5	-0.2	-1.5	0.9	-1.3	-3.2	-0.4
2.0	-2.1	1.0	-2.0	-4.7	-0.7	-1.0	0.4	-1.2	-1.5	-0.2	-1.3	1.0	-1.3	-3.2	0.2
2.5	-2.1	0.9	-2.1	-4.3	-0.9	-1.0	0.3	-1.0	-1.4	-0.3	-1.4	0.8	-1.1	-3.3	-0.5
3.0	-1.9	1.0	-1.9	-4.2	-0.9	-0.8	0.3	-0.9	-1.4	-0.4	-1.3	0.7	-1.1	-3.0	-0.4
3.5	-1.9	0.9	-1.9	-4.3	-0.8	-0.8	0.4	-0.8	-1.3	-0.1	-1.2	0.9	-1.0	-3.3	-0.3
4.0	-1.8	1.0	-1.7	-4.4	-0.5	-0.8	0.4	-0.8	-1.4	-0.3	-1.2	0.9	-0.9	-3.0	-0.1
4.5	-1.7	1.0	-1.6	-4.1	-0.4	-0.7	0.4	-0.6	-1.7	-0.2	-1.1	0.8	-1.0	-2.9	-0.2
5.0	-1.5	1.0	-1.0	-3.7	-0.2	-0.7	0.3	-0.8	-1.0	-0.3	-0.6	0.6	-0.5	-2.1	0.0
5.5	1.4	1.0	0.8	0.5	3.2	1.0	1.3	0.4	-0.6	3.7	1.2	0.7	1.1	0.4	2.6
6.0	2.1	1.0	2.2	0.4	3.4	2.1	1.5	2.0	0.6	5.1	1.8	0.7	1.8	0.6	2.8
6.5	2.2	0.9	2.0	0.6	3.4	2.4	1.4	2.4	0.5	5.2	1.9	0.6	2.0	0.8	2.7
7.0	2.4	1.0	2.3	0.8	3.7	2.7	1.3	2.6	1.1	5.4	2.1	0.6	2.1	1.0	3.1
7.5	2.6	1.0	2.3	1.2	4.3	2.7	1.4	2.6	1.1	5.3	2.3	0.6	2.5	0.9	3.4
8.0	2.9	1.2	2.6	1.2	4.6	2.8	1.4	2.7	1.1	5.4	2.5	0.5	2.6	1.3	3.4
8.5	3.1	1.1	2.9	1.4	4.8	3.1	1.4	3.0	1.4	5.8	2.7	0.6	2.8	1.2	3.8
9.0	3.2	1.2	3.0	1.4	5.0	3.3	1.4	3.2	1.7	5.8	2.9	0.6	3.0	1.6	3.7
9.5	3.4	1.1	3.4	1.9	5.3	3.5	1.6	3.3	1.6	6.7	3.1	0.7	3.0	1.8	4.2
10.0	3.6	1.1	3.5	2.0	5.3	3.5	1.6	3.2	1.7	6.7	3.3	0.7	3.3	2.0	4.2
10.5	3.8	1.1	3.5	2.4	5.5	3.7	1.6	3.5	2.0	7.1	3.5	0.7	3.5	2.1	4.4
11.0	4.0	1.2	4.1	2.2	5.9	3.9	1.7	3.5	1.7	7.2	3.7	0.8	3.8	2.1	4.8
11.5	4.3	1.2	4.2	2.7	6.1	4.0	1.8	3.7	2.0	7.4	3.9	0.8	3.8	2.6	5.1
12.0	4.5	1.2	4.4	2.6	6.1	4.3	1.6	4.1	1.9	7.4	4.2	0.9	4.3	2.6	5.4
12.5	4.8	1.2	5.0	2.8	6.3	4.4	1.8	4.0	2.3	7.7	4.6	0.8	4.7	3.4	5.7
13.0	4.9	1.2	5.0	3.1	6.3	4.6	1.8	4.3	2.2	8.1	4.8	0.9	4.7	3.4	6.0
13.5	5.2	1.2	5.4	3.2	6.7	4.9	1.8	4.4	2.4	8.3	5.2	1.0	5.3	3.6	6.5
14.0	5.4	1.2	5.5	3.3	6.8	5.2	2.0	4.7	2.3	9.0	5.4	1.1	5.4	3.8	6.9
14.5	5.5	1.2	5.6	3.6	7.0	5.4	2.0	5.1	2.4	8.9	5.7	1.1	5.7	4.0	7.2
15.0	5.8	1.3	5.8	3.7	7.6	5.7	2.0	5.5	2.7	9.1	5.9	1.2	5.9	4.0	7.6
15.5	6.0	1.5	6.2	3.6	7.8	5.9	2.0	5.8	2.8	9.0	6.3	1.2	6.3	4.3	8.2
16.0	6.3	1.4	6.7	4.2	8.2	6.2	2.1	6.2	2.7	9.2	6.4	1.2	6.6	4.7	8.2
16.5	6.7	1.4	6.9	4.3	8.4	6.5	2.3	6.1	2.7	9.8	6.9	1.2	7.0	5.2	8.8
17.0	6.8	1.5	7.2	4.4	8.6	6.8	2.2	6.6	3.0	10.1	7.2	1.2	7.5	5.3	9.1
17.5	7.1	1.4	7.6	4.9	8.9	7.0	2.2	6.9	3.3	10.0	7.6	1.3	7.6	5.4	9.8
18.0	7.2	1.5	7.8	4.6	9.1	7.1	2.2	6.9	3.3	10.4	7.8	1.4	7.6	6.0	10.0
18.5	7.5	1.4	8.0	5.4	9.5	7.5	2.2	7.5	3.5	10.3	8.1	1.3	8.2	6.2	10.4
19.0	7.8	1.4	8.3	5.5	9.7	7.8	2.2	8.0	3.6	10.6	8.5	1.4	8.3	6.3	10.9
19.5	7.8	1.4	8.2	5.4	10.1	8.0	2.3	7.9	4.0	11.3	8.7	1.3	8.9	6.9	11.1
20.0	8.1	1.5	8.6	6.0	10.3	8.2	2.3	8.1	3.9	11.8	9.0	1.4	8.9	6.8	11.2
20.5	8.2	1.5	8.9	6.0	10.3	8.5	2.2	8.4	4.3	11.7	9.4	1.3	9.3	7.5	11.6
21.0	8.5	1.4	8.9	6.6	10.4	8.5	2.2	8.6	4.3	11.6	9.6	1.3	9.5	7.3	11.8
21.5	8.7	1.5	8.6	6.7	10.6	8.8	2.3	8.9	4.3	11.9	9.9	1.4	9.7	7.7	12.3
22.0	8.9	1.5	8.9	6.7	11.2	9.1	2.1	9.3	4.8	12.1	10.1	1.4	9.6	8.3	12.8
22.5	8.9	1.3	8.9	7.0	11.1	9.1	2.0	9.1	5.0	11.9	10.4	1.5	10.0	8.4	13.3
23.0	9.1	1.4	9.2	7.0	11.6	9.4	2.0	9.5	5.1	12.1	10.7	1.4	10.4	8.7	13.5
23.5	9.3	1.5	9.2	7.1	11.8	9.7	2.0	9.8	5.3	12.2	10.8	1.3	10.5	8.9	13.2
24.0	9.5	1.5	9.5	7.3	11.9	9.8	2.0	9.8	5.5	12.9	11.0	1.4	10.6	9.0	13.4
24.5	9.5	1.5	9.7	7.4	11.8	10.1	1.9	10.4	5.8	12.7	11.2	1.3	11.0	9.1	13.5
25.0	9.6	1.6	9.8	7.5	12.0	10.2	1.7	10.3	6.3	12.7	11.4	1.4	11.2	9.2	13.8
25.5	9.7	1.5	10.2	7.8	11.8	10.3	1.8	10.3	6.3	12.7	11.6	1.3	11.4	9.5	14.3
26.0	9.9	1.6	10.2	7.8	12.3	10.4	1.5	10.7	7.1	12.7	11.7	1.2	11.5	10.0	13.9
26.5	9.9	1.5	10.2	7.8	12.1	10.5	1.7	10.8	6.6	13.0	11.8	1.4	11.7	9.9	14.6
27.0	10.1	1.6	10.6	7.9	12.6	10.8	1.5	10.9	7.5	13.0	12.0	1.3	11.8	10.2	14.3
27.5	10.2	1.6	10.7	7.8	12.7	10.8	1.5	11.1	7.3	13.0	12.1	1.3	12.1	10.3	14.3
28.0	10.3	1.5	10.7	8.0	12.7	11.1	1.6	11.3	7.3	13.3	12.2	1.3	12.3	10.4	14.4
28.5	10.4	1.6	11.0	7.8	12.8	11.2	1.5	11.6	7.8	13.2	12.5	1.3	12.3	10.7	14.9
29.0	10.5	1.7	10.9	7.6	12.7	11.3	1.5	11.6	7.9	13.7	12.5	1.3	12.4	10.6	14.8
29.5	10.5	1.7	10.9	7.7	12.8	11.4	1.3	11.5	8.5	13.4	12.4	1.3	12.5	10.4	14.4
30.0	10.5	1.7	10.8	7.9	12.8	11.5	1.4	11.8	8.4	13.3	12.7	1.3	12.7	10.7	14.7
30.5	10.6	1.7	11.0	7.6	12.8	11.5	1.1	11.6	9.1	13.1	12.7	1.4	13.0	10.6	15.0
31.0	10.6	1.8	11.0	7.8	13.1	11.7	1.1	11.9	9.2	13.4	12.8	1.3	12.9	10.6	14.9
31.5	10.7	1.8	11.0	7.9	13.1	11.7	1.0	11.7	9.4	13.2	12.8	1.3	12.9	11.2	15.1
32.0	10.9	1.8	11.1	7.9	13.6	11.9	1.1	12.0	9.5	13.6	12.9	1.3	13.0	11.0	14.9
32.5	10.9	1.8	11.2	8.1	13.2	12.0	1.0	12.0	9.7	13.5	12.8	1.4	12.9	11.0	14.8
33.0	11.0	1.7	11.1	8.0	13.2	12.1	1.0	12.2	10.0	13.4	12.9	1.5	13.2	10.9	15.2
33.5	10.9	1.7	10.9	8.0	13.3	12.1	0.9	12.1	10.5	13.5	12.8	1.5	13.0	10.9	15.2
34.0	11.3	1.5	11.4	9.0	13.3	12.2	0.7	12.1	10.7	13.2	12.9	1.6	12.7	10.9	15.4
34.5	11.5	1.8	12.0	9.3	13.3	12.2	0.8	12.3	10.8	13.5	13.0	1.6	12.7	10.9	15.7
35.0	11.2	1.9	11.7	9.1	13.3	12.3	0.8	12.4	10.7	13.3	12.9	1.6	12.7	10.8	15.6

Table 14D: Transpiration rate measured for lettuce.

Time	Transpiration rate [mmol H_2O m^{-2} s^{-1}] for lettuce														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	0.3	0.1	0.3	0.1	0.5	0.2	0.1	0.2	0.1	0.5	0.2	0.1	0.2	0.1	0.4
1.0	0.2	0.1	0.2	0.1	0.5	0.2	0.1	0.2	0.0	0.4	0.2	0.1	0.2	0.0	0.4
1.5	0.2	0.1	0.2	0.1	0.5	0.2	0.1	0.2	0.0	0.4	0.2	0.1	0.2	0.0	0.4
2.0	0.2	0.1	0.2	0.1	0.4	0.2	0.1	0.2	0.0	0.4	0.2	0.1	0.2	0.0	0.4
2.5	0.2	0.1	0.3	0.1	0.4	0.2	0.1	0.2	0.0	0.4	0.2	0.1	0.2	0.0	0.4
3.0	0.2	0.1	0.2	0.1	0.4	0.2	0.1	0.2	0.0	0.4	0.2	0.1	0.2	0.1	0.3
3.5	0.2	0.1	0.2	0.1	0.4	0.2	0.1	0.2	0.1	0.4	0.1	0.1	0.2	0.0	0.2
4.0	0.2	0.1	0.3	0.1	0.3	0.2	0.1	0.1	0.0	0.4	0.2	0.1	0.2	0.0	0.3
4.5	0.2	0.1	0.2	0.0	0.4	0.1	0.1	0.1	0.0	0.3	0.2	0.1	0.2	0.0	0.3
5.0	0.2	0.1	0.2	0.1	0.3	0.2	0.1	0.1	0.0	0.4	0.2	0.1	0.2	0.0	0.3
5.5	0.3	0.1	0.3	0.1	0.5	0.2	0.1	0.1	0.0	0.5	0.2	0.1	0.2	0.1	0.4
6.0	0.3	0.1	0.3	0.1	0.5	0.2	0.2	0.2	0.1	0.6	0.2	0.1	0.2	0.1	0.4
6.5	0.3	0.1	0.3	0.2	0.5	0.2	0.2	0.2	0.1	0.5	0.2	0.1	0.2	0.1	0.5
7.0	0.3	0.1	0.3	0.2	0.6	0.3	0.1	0.2	0.1	0.5	0.2	0.1	0.2	0.1	0.4
7.5	0.3	0.1	0.4	0.1	0.5	0.3	0.1	0.2	0.2	0.6	0.2	0.1	0.2	0.2	0.5
8.0	0.4	0.2	0.4	0.1	0.7	0.3	0.2	0.2	0.1	0.6	0.2	0.1	0.2	0.2	0.4
8.5	0.4	0.1	0.3	0.2	0.6	0.3	0.1	0.2	0.2	0.7	0.3	0.1	0.2	0.2	0.5
9.0	0.4	0.1	0.4	0.2	0.6	0.3	0.2	0.2	0.1	0.7	0.3	0.1	0.2	0.2	0.5
9.5	0.4	0.1	0.4	0.2	0.7	0.3	0.2	0.2	0.1	0.7	0.3	0.1	0.3	0.2	0.5
10.0	0.4	0.2	0.4	0.2	0.7	0.3	0.2	0.2	0.1	0.7	0.3	0.1	0.3	0.2	0.5
10.5	0.4	0.2	0.4	0.1	0.7	0.3	0.2	0.2	0.1	0.7	0.3	0.1	0.3	0.2	0.5
11.0	0.4	0.2	0.4	0.2	0.8	0.3	0.2	0.2	0.2	0.8	0.3	0.1	0.3	0.2	0.5
11.5	0.5	0.2	0.5	0.2	0.8	0.3	0.2	0.3	0.1	0.8	0.4	0.1	0.3	0.2	0.6
12.0	0.5	0.2	0.5	0.3	0.8	0.4	0.2	0.3	0.1	0.8	0.4	0.1	0.4	0.3	0.6
12.5	0.5	0.2	0.5	0.2	0.8	0.4	0.2	0.3	0.1	0.8	0.4	0.1	0.3	0.2	0.6
13.0	0.5	0.2	0.5	0.2	0.8	0.4	0.2	0.3	0.2	0.9	0.4	0.1	0.4	0.3	0.6
13.5	0.6	0.2	0.5	0.2	0.8	0.4	0.2	0.4	0.1	0.9	0.4	0.1	0.4	0.2	0.6
14.0	0.6	0.2	0.6	0.2	0.9	0.4	0.2	0.3	0.2	0.9	0.5	0.1	0.4	0.3	0.7
14.5	0.6	0.2	0.6	0.3	0.9	0.4	0.2	0.4	0.1	1.0	0.5	0.1	0.4	0.3	0.7
15.0	0.6	0.2	0.6	0.3	1.0	0.5	0.3	0.4	0.2	1.0	0.5	0.1	0.5	0.3	0.7
15.5	0.7	0.2	0.7	0.3	1.1	0.5	0.3	0.4	0.2	1.0	0.5	0.1	0.5	0.3	0.8
16.0	0.7	0.2	0.7	0.3	1.0	0.5	0.3	0.4	0.2	1.1	0.5	0.2	0.6	0.3	0.8
16.5	0.7	0.2	0.8	0.3	1.0	0.5	0.3	0.5	0.2	1.0	0.6	0.2	0.6	0.4	0.9
17.0	0.7	0.2	0.8	0.3	1.1	0.6	0.3	0.5	0.2	1.1	0.6	0.2	0.6	0.4	0.9
17.5	0.8	0.2	0.8	0.3	1.1	0.6	0.3	0.5	0.2	1.2	0.6	0.2	0.7	0.4	1.0
18.0	0.8	0.2	0.9	0.4	1.1	0.6	0.3	0.6	0.2	1.1	0.7	0.2	0.6	0.4	1.0
18.5	0.8	0.3	0.9	0.4	1.2	0.7	0.3	0.6	0.2	1.2	0.7	0.2	0.7	0.4	1.1
19.0	0.9	0.3	0.9	0.4	1.2	0.7	0.3	0.6	0.2	1.3	0.7	0.2	0.7	0.5	1.1
19.5	0.9	0.3	0.9	0.4	1.2	0.7	0.3	0.6	0.3	1.3	0.8	0.2	0.7	0.5	1.2
20.0	0.9	0.3	1.0	0.4	1.3	0.8	0.3	0.7	0.3	1.3	0.8	0.2	0.8	0.5	1.2
20.5	0.9	0.3	1.0	0.5	1.4	0.8	0.3	0.7	0.3	1.4	0.8	0.2	0.8	0.6	1.3
21.0	1.0	0.3	1.0	0.4	1.3	0.8	0.4	0.7	0.3	1.4	0.9	0.2	0.8	0.6	1.3
21.5	1.0	0.3	1.1	0.4	1.4	0.8	0.4	0.7	0.3	1.4	0.9	0.3	0.9	0.6	1.3
22.0	1.0	0.3	1.1	0.4	1.4	0.8	0.4	0.7	0.3	1.4	0.9	0.3	0.9	0.6	1.4
22.5	1.1	0.3	1.1	0.5	1.5	0.9	0.3	0.8	0.3	1.4	0.9	0.2	0.9	0.6	1.4
23.0	1.1	0.3	1.1	0.5	1.5	0.9	0.4	0.8	0.3	1.5	1.0	0.3	0.9	0.6	1.5
23.5	1.1	0.3	1.1	0.5	1.5	0.9	0.4	0.8	0.3	1.5	1.0	0.3	0.9	0.7	1.5
24.0	1.1	0.3	1.2	0.5	1.6	0.9	0.3	0.9	0.4	1.5	1.0	0.3	1.0	0.6	1.5
24.5	1.2	0.3	1.2	0.5	1.7	0.9	0.3	0.8	0.4	1.5	1.0	0.2	1.0	0.8	1.5
25.0	1.2	0.3	1.2	0.6	1.6	1.0	0.4	0.9	0.4	1.6	1.1	0.3	1.0	0.7	1.6
25.5	1.2	0.3	1.3	0.6	1.7	1.0	0.4	0.9	0.4	1.6	1.1	0.3	1.1	0.8	1.6
26.0	1.2	0.3	1.3	0.5	1.7	1.0	0.3	0.9	0.4	1.6	1.1	0.3	1.0	0.8	1.6
26.5	1.2	0.3	1.3	0.7	1.7	1.0	0.3	0.9	0.5	1.6	1.1	0.3	1.1	0.7	1.6
27.0	1.2	0.3	1.3	0.5	1.8	1.0	0.4	0.9	0.5	1.7	1.2	0.3	1.1	0.8	1.6
27.5	1.3	0.3	1.3	0.6	1.7	1.1	0.3	1.0	0.4	1.6	1.2	0.3	1.1	0.9	1.7
28.0	1.3	0.3	1.4	0.6	1.8	1.1	0.3	1.1	0.5	1.7	1.2	0.3	1.2	0.8	1.6
28.5	1.4	0.2	1.4	1.0	1.8	1.1	0.4	1.1	0.5	1.7	1.2	0.3	1.2	0.9	1.7
29.0	1.4	0.2	1.4	1.0	1.8	1.2	0.3	1.1	0.6	1.7	1.2	0.3	1.2	0.9	1.7
29.5	1.4	0.2	1.4	1.0	1.8	1.2	0.3	1.1	0.6	1.6	1.3	0.3	1.3	0.8	1.8
30.0	1.4	0.2	1.4	1.0	1.8	1.2	0.3	1.1	0.7	1.7	1.2	0.3	1.2	0.9	1.7
30.5	1.4	0.3	1.4	1.0	1.9	1.2	0.3	1.1	0.7	1.7	1.3	0.3	1.3	0.9	1.8
31.0	1.4	0.3	1.4	1.0	1.9	1.2	0.3	1.1	0.7	1.8	1.3	0.3	1.3	0.9	1.8
31.5	1.4	0.3	1.4	0.9	1.9	1.2	0.3	1.2	0.7	1.7	1.3	0.3	1.3	1.0	1.8
32.0	1.4	0.3	1.4	1.0	1.9	1.2	0.3	1.2	0.8	1.7	1.3	0.3	1.3	0.9	1.8
32.5	1.4	0.3	1.4	1.0	1.9	1.2	0.3	1.2	0.8	1.7	1.3	0.3	1.3	0.9	1.8
33.0	1.4	0.3	1.4	1.0	1.9	1.3	0.3	1.3	0.8	1.7	1.3	0.3	1.3	1.0	1.8
33.5	1.4	0.3	1.4	1.0	1.9	1.3	0.3	1.3	0.8	1.8	1.3	0.3	1.3	1.0	1.8
34.0	1.5	0.3	1.5	1.0	1.9	1.3	0.3	1.3	0.9	1.8	1.4	0.3	1.4	1.0	1.8
34.5	1.6	0.3	1.5	1.1	2.0	1.3	0.3	1.2	0.9	1.8	1.3	0.3	1.4	0.8	1.8
35.0	1.5	0.3	1.5	1.0	1.9	1.3	0.3	1.3	1.0	1.8	1.4	0.3	1.4	1.0	1.8

Table 15D: Stomatal conductance measured for lettuce.

Time	Stomatal conductance [mmol H_2O m^{-2} s^{-1}] for lettuce														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	0.02	0.01	0.02	0.01	0.04	0.02	0.02	0.02	0.00	0.05	0.02	0.01	0.02	0.01	0.03
1.0	0.02	0.01	0.02	0.01	0.04	0.02	0.01	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.04
1.5	0.02	0.01	0.02	0.01	0.04	0.02	0.02	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.04
2.0	0.02	0.01	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.04
2.5	0.02	0.01	0.02	0.01	0.03	0.02	0.02	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.04
3.0	0.02	0.01	0.02	0.00	0.03	0.02	0.01	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.03
3.5	0.02	0.01	0.02	0.00	0.04	0.02	0.02	0.02	0.00	0.04	0.01	0.01	0.02	0.00	0.02
4.0	0.02	0.01	0.02	0.01	0.03	0.02	0.01	0.02	0.00	0.04	0.02	0.01	0.02	0.00	0.03
4.5	0.02	0.01	0.02	0.00	0.04	0.01	0.01	0.02	0.00	0.03	0.01	0.01	0.02	0.00	0.03
5.0	0.02	0.01	0.02	0.00	0.03	0.01	0.01	0.01	0.00	0.04	0.02	0.01	0.02	0.00	0.03
5.5	0.02	0.01	0.02	0.01	0.04	0.02	0.02	0.01	0.00	0.05	0.02	0.01	0.02	0.01	0.04
6.0	0.02	0.01	0.02	0.01	0.05	0.02	0.02	0.02	0.00	0.05	0.02	0.01	0.02	0.01	0.04
6.5	0.03	0.01	0.02	0.02	0.05	0.02	0.02	0.02	0.00	0.05	0.02	0.01	0.02	0.01	0.05
7.0	0.03	0.01	0.02	0.01	0.05	0.02	0.01	0.02	0.01	0.05	0.02	0.01	0.02	0.01	0.04
7.5	0.03	0.01	0.03	0.01	0.05	0.02	0.01	0.02	0.01	0.05	0.02	0.01	0.02	0.01	0.05
8.0	0.03	0.02	0.03	0.01	0.06	0.03	0.02	0.02	0.01	0.06	0.02	0.01	0.02	0.02	0.04
8.5	0.03	0.01	0.03	0.01	0.05	0.03	0.01	0.02	0.01	0.06	0.02	0.01	0.02	0.01	0.04
9.0	0.03	0.01	0.03	0.01	0.05	0.03	0.02	0.02	0.01	0.06	0.02	0.01	0.02	0.01	0.05
9.5	0.03	0.01	0.03	0.02	0.06	0.03	0.02	0.02	0.01	0.06	0.02	0.01	0.02	0.01	0.04
10.0	0.03	0.02	0.03	0.02	0.06	0.03	0.02	0.02	0.01	0.06	0.03	0.01	0.02	0.02	0.05
10.5	0.04	0.02	0.03	0.01	0.06	0.03	0.01	0.02	0.02	0.06	0.03	0.01	0.03	0.02	0.05
11.0	0.04	0.02	0.03	0.02	0.07	0.03	0.02	0.02	0.01	0.07	0.03	0.01	0.03	0.02	0.05
11.5	0.04	0.02	0.04	0.02	0.07	0.03	0.02	0.02	0.02	0.07	0.03	0.01	0.03	0.02	0.06
12.0	0.04	0.02	0.03	0.02	0.07	0.03	0.02	0.02	0.01	0.07	0.03	0.01	0.03	0.02	0.06
12.5	0.04	0.02	0.04	0.01	0.07	0.03	0.02	0.03	0.02	0.07	0.03	0.01	0.03	0.02	0.05
13.0	0.04	0.02	0.04	0.02	0.07	0.04	0.02	0.03	0.01	0.08	0.03	0.01	0.03	0.02	0.05
13.5	0.05	0.02	0.04	0.02	0.07	0.04	0.02	0.03	0.02	0.08	0.04	0.01	0.03	0.02	0.06
14.0	0.05	0.02	0.05	0.02	0.08	0.04	0.02	0.03	0.02	0.08	0.04	0.01	0.04	0.02	0.07
14.5	0.05	0.02	0.05	0.03	0.08	0.04	0.02	0.03	0.02	0.09	0.04	0.01	0.03	0.02	0.06
15.0	0.05	0.02	0.05	0.02	0.08	0.04	0.03	0.03	0.02	0.09	0.04	0.01	0.05	0.03	0.07
15.5	0.06	0.02	0.06	0.02	0.10	0.05	0.02	0.04	0.02	0.09	0.05	0.01	0.05	0.03	0.07
16.0	0.06	0.02	0.06	0.02	0.09	0.05	0.03	0.04	0.02	0.09	0.05	0.01	0.05	0.03	0.07
16.5	0.06	0.02	0.07	0.03	0.09	0.05	0.03	0.04	0.02	0.09	0.05	0.02	0.05	0.03	0.08
17.0	0.06	0.02	0.07	0.03	0.09	0.06	0.03	0.05	0.02	0.11	0.06	0.02	0.05	0.03	0.09
17.5	0.07	0.02	0.07	0.03	0.10	0.06	0.03	0.05	0.02	0.11	0.06	0.02	0.06	0.03	0.09
18.0	0.07	0.02	0.08	0.03	0.10	0.06	0.03	0.06	0.02	0.11	0.06	0.02	0.06	0.04	0.09
18.5	0.07	0.02	0.08	0.03	0.10	0.06	0.03	0.06	0.02	0.12	0.06	0.02	0.06	0.04	0.09
19.0	0.07	0.03	0.08	0.03	0.11	0.06	0.03	0.06	0.02	0.12	0.07	0.02	0.07	0.04	0.10
19.5	0.08	0.03	0.09	0.04	0.11	0.07	0.03	0.06	0.02	0.12	0.07	0.02	0.07	0.04	0.11
20.0	0.08	0.03	0.09	0.03	0.11	0.07	0.03	0.07	0.03	0.13	0.08	0.02	0.07	0.05	0.11
20.5	0.08	0.03	0.09	0.04	0.11	0.08	0.04	0.07	0.03	0.14	0.08	0.02	0.07	0.05	0.12
21.0	0.08	0.03	0.10	0.03	0.11	0.08	0.04	0.07	0.03	0.15	0.08	0.03	0.08	0.05	0.13
21.5	0.09	0.03	0.10	0.04	0.12	0.08	0.04	0.07	0.03	0.14	0.09	0.03	0.08	0.05	0.13
22.0	0.09	0.03	0.11	0.04	0.12	0.08	0.04	0.08	0.03	0.15	0.09	0.03	0.09	0.05	0.14
22.5	0.09	0.03	0.11	0.04	0.12	0.09	0.04	0.08	0.03	0.15	0.09	0.03	0.09	0.06	0.14
23.0	0.10	0.03	0.11	0.04	0.13	0.09	0.04	0.08	0.03	0.14	0.09	0.03	0.09	0.06	0.15
23.5	0.10	0.03	0.11	0.04	0.12	0.09	0.04	0.08	0.03	0.16	0.10	0.03	0.10	0.06	0.16
24.0	0.10	0.03	0.11	0.05	0.13	0.10	0.04	0.09	0.04	0.15	0.10	0.03	0.10	0.07	0.15
24.5	0.11	0.03	0.12	0.05	0.14	0.10	0.04	0.09	0.04	0.16	0.11	0.03	0.10	0.07	0.16
25.0	0.11	0.03	0.12	0.05	0.14	0.10	0.04	0.09	0.04	0.17	0.11	0.03	0.11	0.07	0.17
25.5	0.11	0.03	0.12	0.06	0.14	0.10	0.04	0.09	0.04	0.17	0.11	0.03	0.11	0.08	0.17
26.0	0.11	0.03	0.12	0.05	0.14	0.10	0.04	0.09	0.04	0.17	0.11	0.03	0.10	0.08	0.17
26.5	0.11	0.02	0.12	0.07	0.14	0.11	0.04	0.09	0.04	0.16	0.12	0.03	0.12	0.08	0.18
27.0	0.12	0.03	0.13	0.05	0.15	0.11	0.04	0.09	0.06	0.18	0.12	0.03	0.12	0.09	0.18
27.5	0.12	0.03	0.13	0.06	0.15	0.11	0.04	0.10	0.05	0.18	0.12	0.03	0.11	0.08	0.18
28.0	0.12	0.03	0.13	0.06	0.16	0.12	0.04	0.10	0.05	0.17	0.12	0.03	0.12	0.08	0.17
28.5	0.13	0.02	0.13	0.07	0.15	0.12	0.04	0.11	0.05	0.17	0.13	0.03	0.12	0.09	0.19
29.0	0.13	0.02	0.13	0.07	0.15	0.12	0.03	0.12	0.06	0.17	0.13	0.03	0.13	0.09	0.20
29.5	0.13	0.02	0.13	0.07	0.16	0.12	0.04	0.11	0.06	0.19	0.14	0.03	0.12	0.09	0.20
30.0	0.13	0.03	0.13	0.07	0.16	0.12	0.03	0.11	0.07	0.17	0.13	0.03	0.12	0.09	0.19
30.5	0.13	0.02	0.13	0.07	0.16	0.13	0.03	0.11	0.08	0.19	0.14	0.03	0.13	0.10	0.19
31.0	0.14	0.02	0.14	0.08	0.17	0.13	0.03	0.12	0.08	0.18	0.14	0.03	0.13	0.10	0.20
31.5	0.13	0.02	0.14	0.07	0.16	0.13	0.03	0.12	0.08	0.18	0.14	0.03	0.14	0.10	0.19
32.0	0.14	0.02	0.14	0.08	0.17	0.13	0.03	0.13	0.08	0.19	0.15	0.03	0.14	0.11	0.19
32.5	0.14	0.02	0.14	0.08	0.16	0.14	0.03	0.13	0.09	0.18	0.14	0.03	0.14	0.11	0.20
33.0	0.14	0.02	0.14	0.08	0.17	0.14	0.03	0.13	0.09	0.18	0.15	0.03	0.14	0.11	0.21
33.5	0.14	0.02	0.14	0.08	0.17	0.14	0.03	0.13	0.09	0.19	0.15	0.02	0.14	0.11	0.19
34.0	0.13	0.05	0.14	0.00	0.17	0.14	0.02	0.14	0.10	0.18	0.15	0.03	0.15	0.12	0.21
34.5	0.11	0.07	0.15	0.00	0.17	0.14	0.02	0.13	0.11	0.18	0.15	0.03	0.14	0.11	0.19
35.0	0.14	0.04	0.15	0.08	0.17	0.14	0.03	0.14	0.11	0.18	0.15	0.03	0.15	0.12	0.20

Table 16D: Photosynthetic rate measured for potato (I).

Time	Photosynthetic rate [µmol CO_2 m^{-2} s^{-1}] for potato (I)														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	-1.6	0.4	-1.6	-2.2	-0.8	-1.1	1.2	-0.9	-3.2	-0.2	-7.8	7.7	-5.0	-19.5	-0.8
1.0	-1.5	0.3	-1.6	-1.9	-0.9	-0.8	1.1	-0.3	-2.9	-0.1	-7.9	8.1	-4.9	-20.1	-0.3
1.5	-1.5	0.2	-1.5	-1.7	-1.2	-0.6	1.1	-0.1	-2.7	0.1	-8.2	8.9	-4.6	-23.3	-0.1
2.0	-1.6	0.3	-1.6	-2.0	-1.2	-0.7	1.1	-0.1	-2.7	0.0	-8.0	8.9	-4.3	-24.2	-0.3
2.5	-1.4	0.3	-1.4	-2.1	-1.0	-0.7	1.0	-0.2	-2.7	-0.1	-7.8	9.2	-3.5	-25.1	-0.1
3.0	-1.4	0.4	-1.5	-1.9	-0.2	-0.5	0.9	-0.1	-2.5	0.0	-7.5	9.1	-3.5	-25.7	0.1
3.5	-1.3	0.4	-1.4	-1.7	-0.3	-0.6	0.9	-0.3	-2.7	-0.2	-6.9	8.7	-3.1	-24.3	-0.1
4.0	-1.4	0.3	-1.4	-1.7	-0.9	-0.5	0.9	-0.2	-2.5	0.0	-6.5	8.4	-2.9	-24.3	-0.2
4.5	-1.3	0.2	-1.3	-1.7	-1.0	-0.5	0.8	-0.3	-2.4	-0.1	-6.4	8.3	-2.7	-23.5	0.1
5.0	-1.2	0.4	-1.3	-1.6	-0.1	-0.2	0.3	-0.1	-0.9	0.0	-6.0	8.0	-2.3	-22.7	-0.1
5.5	0.8	0.7	0.5	0.1	1.9	0.1	0.1	0.1	0.0	0.3	-5.7	7.8	-2.0	-22.1	0.0
6.0	1.2	0.6	1.0	0.4	2.4	0.2	0.2	0.3	0.0	0.6	-6.1	7.7	-3.6	-21.3	-0.1
6.5	1.2	0.8	0.9	0.1	3.1	0.3	0.3	0.2	0.0	0.9	-5.8	7.4	-3.4	-20.7	-0.2
7.0	1.2	0.6	0.9	0.3	2.2	0.3	0.3	0.3	0.1	0.9	-5.5	7.2	-3.2	-19.8	-0.1
7.5	1.2	0.8	0.9	0.3	3.2	0.4	0.5	0.1	0.0	1.5	-5.5	7.4	-3.1	-20.5	0.0
8.0	1.4	0.9	1.1	0.4	3.7	0.5	0.6	0.3	0.1	1.7	-5.4	7.1	-2.7	-19.7	-0.1
8.5	1.6	0.9	1.4	0.4	3.8	0.7	0.8	0.4	0.1	2.5	-5.0	6.9	-2.7	-19.2	-0.1
9.0	1.7	0.9	1.6	0.3	3.9	0.7	1.0	0.4	0.0	2.9	-4.9	7.0	-2.4	-19.6	0.0
9.5	2.0	1.0	2.0	0.3	4.2	1.0	1.2	0.4	0.3	3.6	-4.8	7.3	-2.3	-20.5	-0.1
10.0	2.3	1.3	2.3	0.3	5.2	1.1	1.6	0.5	0.3	4.7	-5.2	8.3	-2.0	-23.2	0.0
10.5	2.8	1.6	2.7	0.3	6.3	1.3	1.9	0.5	0.1	5.6	-5.2	8.5	-2.2	-23.8	-0.1
11.0	3.2	1.6	3.3	0.4	6.1	1.6	2.4	0.7	0.3	6.9	-5.2	9.1	-1.9	-25.1	0.0
11.5	3.7	1.8	3.8	0.4	6.5	1.7	2.6	0.5	0.2	7.4	-4.9	8.4	-1.8	-23.5	-0.1
12.0	4.3	2.1	4.5	0.5	7.6	1.9	2.9	0.6	0.2	8.2	-4.8	8.2	-1.8	-22.7	0.1
12.5	5.1	2.4	5.5	0.6	8.5	2.0	3.1	0.6	0.3	8.9	-4.5	7.7	-1.6	-21.5	0.0
13.0	5.7	2.7	6.2	0.4	9.2	2.0	3.0	0.7	0.2	8.7	-4.3	7.5	-1.3	-20.9	-0.1
13.5	6.6	3.0	7.3	0.6	10.1	2.1	3.1	0.8	0.2	8.8	-4.3	7.4	-1.5	-20.5	0.0
14.0	7.5	3.3	8.3	0.7	11.5	2.2	3.0	0.7	0.3	8.8	-4.0	7.0	-1.2	-19.3	0.0
14.5	8.3	3.7	9.1	0.6	12.8	2.1	2.9	0.9	0.1	8.4	-4.0	7.0	-1.4	-19.3	0.1
15.0	9.2	3.8	10.3	1.1	14.4	2.0	2.9	0.7	0.2	8.2	-3.8	6.8	-1.5	-18.8	0.1
15.5	10.0	4.0	11.6	1.1	14.3	2.0	2.7	0.6	0.3	7.9	-3.5	6.5	-1.3	-17.8	0.2
16.0	10.7	4.1	12.3	1.2	15.5	1.9	2.7	0.8	0.2	7.6	-3.4	6.3	-1.2	-17.3	0.3
16.5	11.5	4.2	12.8	1.5	16.2	1.9	2.5	0.7	0.3	7.3	-3.4	6.3	-1.3	-17.2	0.1
17.0	12.1	4.3	13.5	1.5	16.6	1.8	2.4	0.6	0.3	6.9	-3.3	6.0	-0.9	-16.6	0.0
17.5	12.5	4.2	13.9	2.1	17.3	1.8	2.3	0.8	0.2	6.9	-3.1	5.8	-0.7	-16.0	0.1
18.0	12.9	4.2	14.5	2.1	17.4	1.6	2.2	0.7	0.1	6.5	-2.9	5.6	-0.8	-15.3	0.1
18.5	13.3	4.1	15.0	2.5	17.4	1.6	2.0	0.9	0.1	6.0	-2.8	5.3	-0.7	-14.5	0.2
19.0	13.5	4.0	15.1	3.2	17.9	1.5	2.1	0.6	0.2	6.0	-2.7	5.2	-0.9	-14.2	0.2
19.5	13.6	3.9	14.9	3.6	17.4	1.3	1.9	0.5	0.2	5.6	-2.5	5.1	-0.5	-14.0	0.2
20.0	13.9	3.7	15.3	4.4	17.7	1.5	2.0	0.8	0.2	5.4	-2.5	4.9	-0.6	-13.5	-0.1
20.5	13.9	3.7	15.2	4.4	17.4	1.5	1.8	0.9	0.3	5.1	-2.4	4.7	-0.7	-13.0	-0.1
21.0	13.9	3.5	15.1	4.7	17.2	1.4	1.8	0.6	0.2	5.1	-2.3	4.5	-0.4	-12.4	0.0
21.5	13.9	3.3	14.8	5.7	17.4	1.3	1.7	0.7	0.1	4.7	-2.1	4.4	-0.6	-12.0	0.2
22.0	13.9	3.2	14.7	6.0	16.8	1.3	1.5	0.7	0.3	4.3	-2.2	4.4	-0.6	-12.2	0.1
22.5	13.9	3.0	14.4	6.8	17.0	1.2	1.5	0.7	0.2	4.2	-2.2	4.2	-0.6	-11.6	-0.1
23.0	13.8	2.9	14.0	7.5	17.0	1.3	1.7	0.7	0.2	4.2	-2.0	4.1	-0.3	-11.2	-0.1
23.5	13.7	2.7	13.5	8.2	16.9	1.2	1.6	0.5	0.2	3.9	-1.9	4.1	-0.4	-11.3	0.1
24.0	13.6	2.6	13.2	8.7	17.0	1.2	1.6	0.5	0.2	3.9	-1.8	3.8	-0.3	-10.3	-0.2
24.5	13.5	2.5	12.9	9.6	17.0	1.2	1.4	0.5	0.2	3.6	-1.8	3.8	-0.3	-10.3	-0.2
25.0	13.4	2.5	12.8	9.7	16.9	1.2	1.5	0.6	0.2	3.5	-1.7	3.6	-0.4	-9.9	-0.2
25.5	13.2	2.4	12.5	10.2	16.9	1.4	1.4	0.8	0.3	3.4	-1.6	3.5	-0.3	-9.5	-0.1
26.0	13.1	2.4	12.4	9.7	16.6	1.2	1.5	0.7	-0.1	3.4	-1.5	3.4	-0.3	-9.1	-0.1
26.5	13.0	2.5	12.2	9.6	16.5	1.4	1.7	0.9	0.1	3.3	-1.4	3.3	-0.2	-8.9	0.0
27.0	12.9	2.5	12.2	9.4	16.6	1.6	1.7	1.1	0.2	3.6	-1.3	3.2	-0.1	-8.6	0.2
27.5	12.8	2.5	12.5	9.0	16.4	1.6	1.7	1.1	0.2	3.6	-1.2	2.8	-0.3	-7.5	0.2
28.0	12.6	2.5	12.4	8.7	16.6	1.5	1.6	1.0	0.2	3.4	-1.2	2.8	-0.2	-7.6	0.2
28.5	12.5	2.6	12.6	8.4	16.3	1.5	1.5	0.9	0.4	3.1	-1.1	2.7	-0.3	-7.2	0.9
29.0	12.4	2.7	12.7	8.0	16.6	1.6	1.6	1.1	0.3	3.4	-0.9	2.6	-0.1	-6.7	0.9
29.5	12.4	2.7	12.8	7.7	16.3	1.8	2.1	1.8	0.3	3.3	-1.2	3.0	-0.3	-7.8	1.0
30.0	12.2	2.8	12.6	7.5	16.2	0.3	0.0	0.3	0.3	0.3	-1.1	3.2	-0.1	-8.4	1.0

Table 17D: Transpiration rate measured for potato (I).

Time	Transpiration rate [mmol H_2O m^{-2} s^{-1}] for potato (I)														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	0.27	0.18	0.23	0.07	0.62	0.11	0.04	0.11	0.07	0.14	0.05	0.06	0.05	-0.03	0.17
1.0	0.26	0.12	0.23	0.13	0.46	0.11	0.07	0.11	0.01	0.21	0.04	0.07	0.05	-0.09	0.16
1.5	0.24	0.13	0.20	0.06	0.53	0.08	0.07	0.06	0.01	0.20	0.04	0.09	0.05	-0.15	0.15
2.0	0.23	0.14	0.23	0.05	0.54	0.09	0.07	0.09	0.01	0.16	0.09	0.10	0.08	-0.09	0.27
2.5	0.21	0.10	0.22	0.05	0.42	0.11	0.04	0.12	0.05	0.15	0.09	0.09	0.09	-0.01	0.21
3.0	0.24	0.10	0.25	0.12	0.44	0.10	0.05	0.09	0.02	0.19	0.09	0.10	0.10	-0.06	0.23
3.5	0.23	0.10	0.22	0.05	0.44	0.14	0.05	0.13	0.08	0.21	0.06	0.07	0.04	-0.05	0.18
4.0	0.21	0.10	0.23	0.06	0.43	0.09	0.04	0.10	0.02	0.12	0.14	0.08	0.15	0.03	0.26
4.5	0.22	0.07	0.22	0.09	0.32	0.09	0.07	0.09	0.02	0.21	0.11	0.09	0.14	-0.02	0.25
5.0	0.22	0.10	0.21	0.10	0.38	0.11	0.05	0.09	0.08	0.22	0.10	0.10	0.09	0.00	0.22
5.5	0.25	0.09	0.23	0.14	0.38	0.15	0.04	0.16	0.10	0.20	0.12	0.07	0.12	0.03	0.20
6.0	0.28	0.12	0.26	0.12	0.56	0.16	0.03	0.17	0.12	0.20	0.14	0.10	0.12	0.03	0.30
6.5	0.30	0.11	0.27	0.15	0.49	0.14	0.07	0.17	0.03	0.24	0.12	0.08	0.09	0.02	0.24
7.0	0.31	0.11	0.30	0.15	0.51	0.15	0.08	0.13	0.05	0.28	0.10	0.06	0.10	0.02	0.18
7.5	0.32	0.13	0.31	0.17	0.63	0.18	0.07	0.17	0.07	0.31	0.11	0.05	0.10	0.04	0.18
8.0	0.31	0.12	0.28	0.14	0.58	0.23	0.14	0.16	0.10	0.50	0.12	0.07	0.12	0.03	0.21
8.5	0.35	0.11	0.37	0.18	0.51	0.27	0.16	0.23	0.15	0.62	0.09	0.08	0.05	-0.02	0.19
9.0	0.37	0.12	0.35	0.19	0.60	0.23	0.18	0.17	0.13	0.63	0.08	0.08	0.04	-0.04	0.18
9.5	0.40	0.13	0.39	0.16	0.59	0.31	0.30	0.21	0.10	0.98	0.09	0.07	0.08	0.01	0.19
10.0	0.43	0.16	0.41	0.19	0.64	0.38	0.40	0.25	0.12	1.28	0.13	0.07	0.13	0.02	0.23
10.5	0.54	0.19	0.52	0.21	0.84	0.44	0.52	0.23	0.17	1.62	0.08	0.06	0.08	0.00	0.19
11.0	0.57	0.20	0.58	0.22	0.82	0.51	0.68	0.25	0.19	2.05	0.10	0.07	0.11	0.00	0.18
11.5	0.65	0.24	0.68	0.27	1.00	0.56	0.77	0.27	0.15	2.29	0.08	0.06	0.05	0.03	0.17
12.0	0.74	0.28	0.79	0.20	1.06	0.64	0.80	0.32	0.15	2.43	0.09	0.05	0.08	0.02	0.16
12.5	0.89	0.32	0.90	0.32	1.35	0.64	0.90	0.40	0.08	2.66	0.09	0.03	0.11	0.02	0.12
13.0	0.99	0.41	1.02	0.24	1.58	0.65	0.90	0.33	0.13	2.66	0.08	0.07	0.05	0.00	0.19
13.5	1.15	0.49	1.13	0.31	1.91	0.72	0.93	0.32	0.26	2.80	0.09	0.07	0.09	0.01	0.17
14.0	1.34	0.57	1.33	0.28	2.27	0.70	0.84	0.35	0.22	2.55	0.09	0.06	0.11	0.02	0.17
14.5	1.49	0.64	1.50	0.29	2.58	0.72	0.87	0.39	0.10	2.64	0.07	0.08	0.07	-0.03	0.21
15.0	1.68	0.70	1.79	0.30	2.66	0.66	0.84	0.32	0.11	2.49	0.06	0.10	0.02	-0.07	0.20
15.5	1.85	0.77	1.98	0.31	2.97	0.66	0.79	0.37	0.21	2.42	0.09	0.05	0.09	0.02	0.17
16.0	2.06	0.79	2.16	0.35	3.09	0.63	0.76	0.32	0.09	2.27	0.09	0.06	0.11	0.02	0.18
16.5	2.25	0.82	2.33	0.40	3.30	0.66	0.68	0.37	0.29	2.16	0.09	0.07	0.07	0.02	0.21
17.0	2.40	0.86	2.52	0.34	3.36	0.61	0.71	0.30	0.23	2.16	0.11	0.05	0.11	0.02	0.16
17.5	2.53	0.85	2.65	0.47	3.43	0.55	0.65	0.25	0.17	1.99	0.07	0.08	0.08	-0.02	0.19
18.0	2.67	0.84	2.83	0.55	3.50	0.53	0.59	0.34	0.12	1.81	0.06	0.09	0.04	-0.04	0.21
18.5	2.72	0.83	2.81	0.56	3.56	0.56	0.56	0.35	0.14	1.80	0.08	0.07	0.07	0.02	0.23
19.0	2.78	0.83	2.92	0.58	3.68	0.48	0.57	0.27	0.13	1.77	0.06	0.05	0.05	0.00	0.16
19.5	2.87	0.80	3.00	0.71	3.75	0.48	0.55	0.32	0.09	1.71	0.07	0.03	0.08	0.02	0.11
20.0	2.87	0.79	3.02	0.70	3.81	0.51	0.55	0.32	0.13	1.59	0.10	0.05	0.11	0.02	0.15
20.5	2.93	0.76	3.08	0.88	3.83	0.53	0.51	0.37	0.21	1.55	0.11	0.11	0.07	-0.04	0.25
21.0	2.92	0.72	3.04	0.97	3.91	0.46	0.49	0.26	0.17	1.44	0.07	0.07	0.07	-0.03	0.17
21.5	2.91	0.70	2.97	1.04	3.85	0.47	0.46	0.27	0.21	1.38	0.08	0.05	0.07	0.02	0.17
22.0	2.91	0.68	2.93	1.11	3.81	0.44	0.45	0.28	0.16	1.34	0.05	0.09	0.05	-0.10	0.18
22.5	2.92	0.61	2.83	1.39	3.83	0.42	0.45	0.28	0.11	1.33	0.04	0.07	0.04	-0.04	0.16
23.0	2.91	0.58	2.88	1.50	3.73	0.52	0.40	0.41	0.19	1.22	0.08	0.05	0.07	0.02	0.16
23.5	2.90	0.55	2.78	1.70	3.77	0.47	0.37	0.35	0.18	1.11	0.08	0.10	0.04	0.01	0.29
24.0	2.88	0.52	2.75	1.93	3.89	0.50	0.38	0.37	0.25	1.17	0.08	0.07	0.06	0.02	0.24
24.5	2.84	0.54	2.69	2.02	3.79	0.50	0.38	0.36	0.22	1.17	0.11	0.10	0.10	0.01	0.31
25.0	2.81	0.51	2.75	2.03	3.79	0.47	0.46	0.29	0.15	1.14	0.10	0.08	0.09	0.02	0.24
25.5	2.79	0.53	2.70	2.07	3.80	0.50	0.37	0.38	0.20	1.04	0.07	0.11	0.03	0.02	0.31
26.0	2.75	0.55	2.69	2.02	3.77	0.46	0.41	0.30	0.18	1.07	0.09	0.10	0.06	0.00	0.29
26.5	2.70	0.52	2.65	1.89	3.68	0.60	0.38	0.41	0.35	1.04	0.08	0.10	0.04	0.01	0.27
27.0	2.71	0.53	2.72	1.91	3.69	0.58	0.45	0.35	0.29	1.09	0.09	0.09	0.07	0.00	0.26
27.5	2.70	0.56	2.72	1.79	3.71	0.53	0.40	0.31	0.30	0.99	0.07	0.07	0.05	0.00	0.20
28.0	2.65	0.60	2.74	1.65	3.74	0.55	0.38	0.36	0.30	0.99	0.10	0.08	0.11	0.00	0.26
28.5	2.65	0.61	2.75	1.62	3.78	0.53	0.41	0.38	0.22	1.00	0.12	0.12	0.10	0.02	0.38
29.0	2.64	0.62	2.74	1.62	3.70	0.51	0.36	0.38	0.24	0.92	0.07	0.11	0.04	0.00	0.31
29.5	2.60	0.67	2.75	1.47	3.70	0.59	0.54	0.59	0.20	0.97	0.07	0.08	0.03	0.00	0.23
30.0	2.57	0.65	2.73	1.48	3.50	0.33	0.00	0.33	0.33	0.33	0.10	0.10	0.09	0.02	0.31

Table 18D: Stomatal conductance measured for potato (I).

Time	Stomatal conductance [mmol H_2O m^{-2} s^{-1}] for potato (I)														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	0.01	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.03
1.0	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.04
1.5	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.03
2.0	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.04
2.5	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.03
3.0	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.04
3.5	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.03
4.0	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.03
4.5	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.03
5.0	0.01	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.03
5.5	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.03
6.0	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.03
6.5	0.01	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.02
7.0	0.01	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02
7.5	0.01	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.04
8.0	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.03
8.5	0.01	0.01	0.01	0.00	0.03	0.00	0.01	0.00	0.00	0.02	0.01	0.01	0.01	0.00	0.02
9.0	0.01	0.01	0.01	0.00	0.03	0.00	0.01	0.00	0.00	0.02	0.01	0.01	0.00	0.00	0.02
9.5	0.02	0.01	0.02	0.00	0.04	0.00	0.01	0.00	0.00	0.03	0.00	0.01	0.00	0.00	0.02
10.0	0.02	0.01	0.02	0.00	0.04	0.01	0.02	0.00	0.00	0.04	0.01	0.01	0.00	0.00	0.02
10.5	0.02	0.01	0.02	0.00	0.05	0.01	0.02	0.00	0.00	0.05	0.01	0.01	0.00	0.00	0.02
11.0	0.02	0.01	0.02	0.00	0.05	0.01	0.03	0.00	0.00	0.07	0.01	0.01	0.00	0.00	0.03
11.5	0.03	0.01	0.03	0.01	0.05	0.01	0.03	0.00	0.00	0.08	0.01	0.01	0.00	0.00	0.03
12.0	0.03	0.02	0.04	0.00	0.06	0.02	0.03	0.00	0.00	0.09	0.00	0.01	0.00	0.00	0.02
12.5	0.04	0.02	0.04	0.01	0.06	0.02	0.04	0.01	0.00	0.10	0.00	0.01	0.00	0.00	0.02
13.0	0.05	0.02	0.05	0.00	0.08	0.02	0.04	0.00	0.00	0.10	0.01	0.01	0.00	0.00	0.02
13.5	0.05	0.03	0.05	0.01	0.09	0.02	0.04	0.00	0.00	0.11	0.00	0.01	0.00	0.00	0.02
14.0	0.06	0.03	0.07	0.01	0.11	0.02	0.04	0.00	0.00	0.10	0.00	0.01	0.00	0.00	0.02
14.5	0.07	0.04	0.08	0.01	0.13	0.02	0.04	0.01	0.00	0.10	0.01	0.01	0.00	0.00	0.02
15.0	0.09	0.04	0.10	0.01	0.15	0.02	0.03	0.00	0.00	0.09	0.01	0.01	0.00	0.00	0.02
15.5	0.10	0.05	0.11	0.01	0.16	0.02	0.03	0.00	0.00	0.09	0.00	0.01	0.00	0.00	0.02
16.0	0.11	0.05	0.13	0.01	0.19	0.02	0.03	0.00	0.00	0.08	0.00	0.01	0.00	0.00	0.02
16.5	0.13	0.06	0.15	0.01	0.20	0.02	0.03	0.01	0.00	0.08	0.01	0.01	0.00	0.00	0.02
17.0	0.14	0.06	0.16	0.01	0.22	0.02	0.03	0.00	0.00	0.08	0.00	0.01	0.00	0.00	0.02
17.5	0.15	0.06	0.17	0.02	0.24	0.02	0.03	0.00	0.00	0.07	0.01	0.01	0.00	0.00	0.02
18.0	0.16	0.06	0.18	0.02	0.25	0.01	0.02	0.00	0.00	0.06	0.01	0.01	0.00	0.00	0.02
18.5	0.17	0.07	0.18	0.02	0.26	0.01	0.02	0.01	0.00	0.06	0.00	0.01	0.00	0.00	0.02
19.0	0.17	0.07	0.19	0.02	0.27	0.01	0.02	0.00	0.00	0.06	0.01	0.01	0.00	0.00	0.02
19.5	0.18	0.07	0.20	0.03	0.27	0.01	0.02	0.00	0.00	0.06	0.00	0.01	0.00	0.00	0.02
20.0	0.18	0.07	0.20	0.03	0.27	0.01	0.02	0.00	0.00	0.05	0.00	0.01	0.00	0.00	0.02
20.5	0.18	0.07	0.20	0.03	0.27	0.01	0.02	0.01	0.00	0.05	0.01	0.01	0.01	0.00	0.02
21.0	0.18	0.07	0.19	0.04	0.26	0.01	0.02	0.01	0.00	0.05	0.00	0.00	0.00	0.00	0.01
21.5	0.18	0.07	0.19	0.04	0.27	0.01	0.02	0.00	0.00	0.04	0.00	0.01	0.00	0.00	0.02
22.0	0.18	0.07	0.18	0.04	0.27	0.01	0.02	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.01
22.5	0.18	0.07	0.17	0.06	0.26	0.01	0.02	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.01
23.0	0.18	0.07	0.17	0.06	0.27	0.01	0.02	0.01	0.00	0.04	0.00	0.01	0.00	0.00	0.02
23.5	0.17	0.07	0.17	0.07	0.28	0.01	0.01	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.02
24.0	0.17	0.06	0.16	0.08	0.27	0.01	0.01	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.02
24.5	0.17	0.06	0.15	0.09	0.26	0.01	0.01	0.00	0.00	0.03	0.00	0.01	0.00	0.00	0.02
25.0	0.16	0.06	0.15	0.09	0.26	0.01	0.01	0.01	0.00	0.03	0.01	0.01	0.00	0.00	0.02
25.5	0.16	0.06	0.14	0.10	0.25	0.01	0.01	0.01	0.00	0.03	0.01	0.01	0.00	0.00	0.02
26.0	0.16	0.06	0.14	0.09	0.25	0.01	0.02	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.02
26.5	0.15	0.05	0.14	0.09	0.24	0.01	0.02	0.01	0.00	0.03	0.00	0.01	0.00	0.00	0.02
27.0	0.15	0.05	0.13	0.09	0.24	0.01	0.02	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.02
27.5	0.15	0.06	0.14	0.09	0.24	0.01	0.02	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.02
28.0	0.14	0.05	0.14	0.08	0.23	0.01	0.02	0.00	0.00	0.03	0.00	0.01	0.00	0.00	0.02
28.5	0.15	0.06	0.14	0.08	0.24	0.01	0.02	0.01	0.00	0.03	0.01	0.01	0.00	0.00	0.02
29.0	0.14	0.05	0.14	0.08	0.23	0.01	0.02	0.01	0.00	0.03	0.01	0.01	0.00	0.00	0.02
29.5	0.14	0.05	0.14	0.07	0.23	0.02	0.02	0.02	0.00	0.03	0.01	0.01	0.00	0.00	0.02
30.0	0.14	0.05	0.14	0.07	0.21	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.02

Table 19D: Photosynthetic rate measured for potato (II).

Time	Photosynthetic rate [µmol CO_2 m^{-2} s^{-1}] for potato (II)														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	-0.6	0.2	-0.6	-0.8	-0.4	-1.6	1.8	-1.5	-5.9	2.6	-0.5	0.8	-0.5	-1.4	1.2
1.0	-0.6	0.3	-0.5	-1.0	-0.3	-2.0	1.4	-1.5	-5.1	-0.2	-0.7	0.4	-0.8	-1.3	0.1
1.5	-0.5	0.3	-0.4	-1.1	-0.1	-1.9	1.1	-1.6	-4.3	-0.7	-0.9	0.3	-0.9	-1.3	-0.5
2.0	-0.5	0.4	-0.4	-0.9	-0.1	-1.9	1.1	-1.7	-3.9	-0.8	-0.9	0.4	-0.8	-1.5	-0.3
2.5	-0.4	0.3	-0.4	-0.9	-0.1	-1.7	0.9	-1.3	-3.4	-0.3	-0.9	0.3	-0.9	-1.4	-0.5
3.0	-0.4	0.4	-0.4	-0.9	0.1	-1.6	0.9	-1.4	-3.8	-0.3	-0.9	0.3	-0.8	-1.3	-0.4
3.5	-0.6	0.4	-0.6	-1.2	-0.1	-1.4	0.7	-1.4	-3.1	-0.2	-0.9	0.4	-0.9	-1.5	-0.4
4.0	-0.5	0.3	-0.6	-0.9	-0.2	-1.5	0.7	-1.3	-3.2	-0.1	-0.9	0.3	-0.9	-1.5	-0.3
4.5	-0.2	0.4	-0.4	-0.7	0.4	-1.1	0.6	-1.1	-2.1	-0.1	-0.9	0.4	-0.8	-1.5	-0.4
5.0	-0.4	0.3	-0.3	-0.9	-0.2	-0.8	0.7	-0.6	-2.5	-0.1	-0.7	0.5	-0.8	-1.7	0.0
5.5	0.3	0.2	0.3	0.0	0.6	1.1	1.4	0.6	0.0	5.6	1.0	0.5	1.2	0.1	1.5
6.0	0.5	0.3	0.4	0.1	1.0	1.9	1.7	1.5	0.4	5.9	1.0	0.6	1.2	0.0	1.9
6.5	0.6	0.3	0.7	0.2	1.0	2.1	1.8	1.6	0.2	6.1	1.1	0.7	1.2	0.2	1.9
7.0	0.6	0.3	0.7	0.2	0.9	2.2	1.8	1.9	0.2	6.2	1.0	0.7	1.2	0.0	2.0
7.5	0.7	0.3	0.8	0.3	1.0	2.4	1.6	2.2	0.3	6.3	1.1	0.7	1.4	0.2	1.9
8.0	0.6	0.2	0.7	0.3	0.9	2.4	1.5	2.3	0.5	6.0	1.1	0.7	1.4	-0.1	1.8
8.5	0.7	0.2	0.6	0.5	1.1	2.5	1.5	2.2	0.7	6.2	1.1	0.6	1.4	0.3	1.8
9.0	0.7	0.3	0.7	0.3	1.2	2.6	1.5	2.2	0.8	6.4	1.2	0.6	1.4	0.2	2.1
9.5	0.7	0.2	0.7	0.4	1.1	2.6	1.5	2.3	1.0	6.3	1.2	0.7	1.3	0.1	2.0
10.0	0.8	0.4	0.8	0.4	1.4	2.7	1.5	2.2	1.3	5.9	1.2	0.7	1.5	0.2	2.0
10.5	1.0	0.4	0.9	0.5	1.6	3.0	1.6	2.4	1.4	6.2	1.4	0.8	1.6	0.3	2.6
11.0	1.0	0.5	0.8	0.4	1.5	3.0	1.5	2.5	1.4	6.3	1.5	0.7	1.5	0.5	2.6
11.5	1.1	0.5	1.2	0.3	1.7	3.1	1.6	2.2	1.4	6.5	1.7	0.6	1.8	0.7	2.5
12.0	1.2	0.5	1.1	0.4	1.8	3.2	1.6	2.6	1.6	6.6	1.8	0.7	1.9	0.7	2.8
12.5	1.4	0.7	1.4	0.3	2.0	3.3	1.6	2.6	1.6	6.8	1.8	0.8	1.5	0.7	3.4
13.0	1.5	0.7	1.5	0.5	2.3	3.4	1.7	2.7	1.4	6.7	2.1	0.8	1.9	1.2	3.9
13.5	1.6	0.8	1.7	0.3	2.6	3.5	1.7	2.7	1.5	6.4	2.3	0.9	2.1	1.3	4.1
14.0	1.7	0.8	1.7	0.5	2.8	3.7	1.8	3.0	1.7	7.0	2.5	0.9	2.2	1.6	4.5
14.5	2.0	1.1	2.1	0.5	3.5	3.9	1.9	3.0	1.7	7.2	2.7	1.1	2.5	1.7	5.0
15.0	2.3	1.3	2.3	0.6	4.0	4.0	2.0	3.6	1.8	7.2	2.7	1.2	2.3	1.2	5.0
15.5	2.3	1.5	2.0	0.5	4.6	4.0	2.0	3.7	1.7	7.3	3.0	1.1	2.9	1.6	4.9
16.0	2.6	1.7	2.2	0.7	5.3	4.3	2.1	4.3	1.8	7.6	3.3	1.4	3.0	1.6	5.8
16.5	3.0	1.9	2.5	0.9	6.0	4.4	2.2	4.3	1.9	7.9	3.4	1.3	2.9	2.0	5.7
17.0	3.2	2.1	2.6	0.9	6.8	4.7	2.2	4.9	1.9	8.2	3.8	1.6	3.5	2.2	6.8
17.5	3.5	2.3	2.9	1.2	7.5	4.8	2.4	5.3	2.0	8.9	3.8	1.5	3.4	2.1	6.7
18.0	3.7	2.3	3.2	1.3	7.8	5.0	2.5	5.4	1.8	9.2	4.0	1.7	3.7	2.1	7.4
18.5	4.1	2.6	3.2	1.7	8.7	5.2	2.6	5.8	1.8	9.6	4.4	1.8	4.2	2.2	8.0
19.0	4.3	2.9	3.4	1.5	9.5	5.4	2.8	6.1	2.0	10.3	4.4	1.9	4.4	1.7	8.0
19.5	4.6	3.2	3.5	1.7	10.4	5.5	2.8	6.5	2.0	10.0	4.7	2.1	4.8	2.4	8.5
20.0	5.0	3.5	3.9	1.8	11.1	5.7	2.8	6.6	1.9	10.5	5.0	2.1	5.1	2.7	9.1
20.5	5.5	3.6	4.2	2.2	11.7	6.0	3.0	7.1	2.0	11.0	5.2	2.3	5.2	2.5	9.6
21.0	5.8	4.0	4.2	2.3	12.9	6.2	3.1	7.3	2.1	11.7	5.4	2.5	5.2	2.5	10.1
21.5	6.1	3.9	4.4	2.9	13.0	6.5	3.3	7.5	2.3	12.0	5.5	2.6	5.1	2.5	10.5
22.0	6.4	3.9	4.9	2.9	13.0	6.7	3.6	7.4	2.2	12.7	5.7	2.6	5.4	2.6	10.8
22.5	6.7	4.1	5.1	3.0	13.7	6.9	3.6	8.1	2.4	13.4	5.9	2.8	5.8	2.7	11.5
23.0	7.1	4.4	5.1	3.1	14.6	7.1	3.9	8.2	2.1	13.6	6.0	2.6	5.7	3.0	10.9
23.5	7.3	4.5	5.3	3.5	14.6	7.0	4.0	7.5	2.3	13.7	6.1	2.8	5.8	2.6	11.2
24.0	7.8	4.7	5.7	3.9	15.4	7.3	4.1	7.7	2.5	14.3	6.4	2.7	6.3	2.8	11.2
24.5	8.1	4.8	6.0	3.9	15.7	7.4	4.3	7.8	2.3	14.7	6.6	2.8	6.0	3.3	11.4
25.0	8.5	4.7	6.5	4.6	16.1	7.8	4.5	8.1	2.3	15.8	6.7	3.0	6.1	2.8	11.6
25.5	8.7	4.7	6.9	4.8	16.4	7.9	4.6	8.2	2.5	16.0	6.7	3.0	6.0	3.0	11.7
26.0	8.9	4.7	6.7	5.1	16.2	8.1	4.8	8.4	2.5	16.5	6.8	2.9	6.0	3.1	11.4
26.5	9.3	4.7	7.1	5.4	16.7	8.2	4.9	8.5	2.6	16.7	6.8	2.9	6.0	3.0	11.3
27.0	9.5	4.7	7.4	5.6	16.8	8.4	5.0	8.7	2.3	17.3	7.0	2.9	5.7	2.9	11.2
27.5	9.8	4.7	7.8	6.0	16.7	8.6	5.1	8.8	2.5	17.5	7.2	3.0	5.8	3.3	11.3
28.0	10.1	4.9	7.9	6.1	17.4	8.7	5.2	9.0	2.3	18.1	7.2	3.1	5.5	3.3	11.7
28.5	10.3	4.8	8.1	6.3	17.6	8.8	5.4	9.2	2.4	18.3	7.3	3.1	5.5	3.2	12.0
29.0	10.5	4.6	8.2	6.8	17.4	9.0	5.6	8.7	2.7	18.3	7.4	3.0	5.9	3.5	11.8
29.5	10.8	4.6	8.6	6.9	17.8	9.0	5.7	9.0	2.7	18.3	7.3	3.1	6.2	3.3	12.2
30.0	11.1	4.5	9.0	7.1	17.7	9.1	5.8	8.9	2.5	18.2	7.3	3.1	6.1	3.3	12.2
30.5	11.2	4.4	9.1	7.6	17.9	9.2	5.8	9.3	2.6	18.4	7.4	3.0	6.3	3.5	12.2
31.0	11.6	4.5	9.6	7.5	18.0	9.3	5.9	9.7	2.6	18.3	7.4	3.1	6.0	3.4	12.5
31.5	11.7	4.4	9.3	8.2	18.1	9.4	5.8	10.0	2.4	18.3	7.4	3.0	6.3	3.7	12.4
32.0	12.5	4.7	9.4	8.7	18.5	9.4	5.9	9.8	2.4	18.3	7.5	3.2	6.3	3.9	13.3
32.5	12.7	4.6	10.1	8.8	18.8	9.2	6.1	9.1	2.8	18.4	7.6	3.2	6.5	3.8	13.5
33.0	12.8	4.3	10.2	9.4	18.5	9.7	6.0	9.6	2.8	18.4	7.6	3.3	6.5	3.9	13.6
33.5	13.8	4.4	13.6	9.4	18.5	9.9	6.8	10.1	3.0	18.6	7.6	3.2	6.8	3.8	13.6
34.0	13.9	4.1	13.8	9.9	18.3	11.8	6.7	12.5	2.7	18.9	7.9	3.2	6.8	4.0	13.5
34.5	13.2	4.5	11.5	9.7	18.3	10.8	6.6	11.5	3.0	18.7	8.2	3.6	7.1	3.7	14.0
35.0	10.7	1.6	10.7	9.6	11.8	11.5	6.7	12.5	3.3	18.8	5.3	1.4	5.4	4.0	6.7

Table 20D: Transpiration rate measured for potato (II).

Time	Transpiration rate [mmol H_2O m^{-2} s^{-1}] for potato (II)															
	Control treatment					Platinum treatment					Palladium treatment					
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.	
0.5	0.17	0.09	0.14	0.10	0.33	0.33	0.16	0.27	0.16	0.71	0.18	0.08	0.22	0.04	0.26	
1.0	0.13	0.09	0.12	0.03	0.29	0.32	0.14	0.29	0.15	0.61	0.16	0.08	0.20	0.03	0.27	
1.5	0.11	0.09	0.08	0.02	0.27	0.30	0.15	0.24	0.17	0.64	0.17	0.06	0.17	0.06	0.26	
2.0	0.11	0.09	0.10	0.01	0.29	0.28	0.16	0.23	0.05	0.64	0.15	0.07	0.12	0.04	0.24	
2.5	0.14	0.09	0.11	0.03	0.29	0.27	0.17	0.20	0.00	0.67	0.13	0.09	0.11	0.00	0.27	
3.0	0.13	0.06	0.14	0.02	0.21	0.30	0.14	0.25	0.11	0.66	0.13	0.10	0.10	0.03	0.29	
3.5	0.11	0.07	0.12	0.03	0.23	0.26	0.14	0.22	0.05	0.55	0.10	0.07	0.09	0.02	0.24	
4.0	0.14	0.07	0.14	0.05	0.24	0.28	0.13	0.25	0.11	0.59	0.11	0.07	0.10	0.02	0.22	
4.5	0.11	0.07	0.09	0.07	0.25	0.26	0.11	0.23	0.12	0.52	0.08	0.07	0.06	0.02	0.23	
5.0	0.12	0.07	0.13	0.03	0.20	0.27	0.13	0.21	0.12	0.60	0.14	0.05	0.12	0.07	0.21	
5.5	0.16	0.05	0.15	0.08	0.23	0.30	0.11	0.26	0.16	0.56	0.16	0.05	0.14	0.10	0.25	
6.0	0.15	0.06	0.15	0.09	0.25	0.34	0.09	0.34	0.22	0.57	0.19	0.06	0.18	0.11	0.33	
6.5	0.16	0.09	0.15	0.05	0.32	0.33	0.12	0.30	0.19	0.61	0.15	0.08	0.13	0.05	0.29	
7.0	0.13	0.10	0.10	0.06	0.33	0.31	0.13	0.27	0.17	0.68	0.16	0.05	0.14	0.10	0.28	
7.5	0.16	0.07	0.15	0.08	0.25	0.32	0.12	0.33	0.16	0.55	0.17	0.07	0.16	0.11	0.30	
8.0	0.16	0.07	0.17	0.08	0.26	0.31	0.11	0.30	0.19	0.53	0.19	0.08	0.19	0.03	0.32	
8.5	0.17	0.09	0.15	0.07	0.33	0.31	0.12	0.29	0.19	0.51	0.17	0.09	0.16	0.07	0.31	
9.0	0.15	0.07	0.16	0.04	0.24	0.33	0.11	0.29	0.21	0.56	0.15	0.07	0.12	0.08	0.29	
9.5	0.17	0.06	0.15	0.12	0.28	0.32	0.09	0.31	0.20	0.53	0.16	0.09	0.15	0.06	0.31	
10.0	0.18	0.06	0.16	0.12	0.27	0.32	0.11	0.29	0.15	0.53	0.18	0.06	0.17	0.10	0.24	
10.5	0.16	0.10	0.11	0.08	0.30	0.32	0.11	0.29	0.20	0.55	0.17	0.08	0.14	0.07	0.29	
11.0	0.16	0.07	0.14	0.08	0.28	0.32	0.09	0.29	0.21	0.50	0.18	0.09	0.14	0.05	0.32	
11.5	0.17	0.06	0.16	0.09	0.25	0.34	0.11	0.32	0.21	0.62	0.20	0.04	0.19	0.14	0.27	
12.0	0.18	0.06	0.15	0.12	0.28	0.33	0.11	0.31	0.13	0.57	0.19	0.08	0.17	0.06	0.30	
12.5	0.21	0.07	0.22	0.13	0.29	0.37	0.10	0.35	0.24	0.55	0.21	0.07	0.21	0.12	0.35	
13.0	0.16	0.10	0.17	0.02	0.29	0.36	0.12	0.35	0.18	0.60	0.20	0.07	0.19	0.10	0.29	
13.5	0.20	0.09	0.17	0.08	0.35	0.37	0.12	0.33	0.20	0.60	0.22	0.05	0.23	0.16	0.30	
14.0	0.19	0.12	0.18	0.03	0.39	0.36	0.13	0.32	0.20	0.62	0.22	0.05	0.20	0.16	0.27	
14.5	0.22	0.09	0.22	0.12	0.33	0.36	0.12	0.35	0.21	0.60	0.23	0.05	0.23	0.15	0.31	
15.0	0.22	0.11	0.21	0.07	0.41	0.38	0.10	0.37	0.24	0.56	0.25	0.05	0.24	0.20	0.35	
15.5	0.24	0.14	0.19	0.11	0.46	0.39	0.12	0.36	0.24	0.69	0.28	0.06	0.28	0.17	0.36	
16.0	0.28	0.13	0.25	0.14	0.48	0.40	0.13	0.36	0.22	0.66	0.29	0.07	0.31	0.19	0.39	
16.5	0.28	0.14	0.22	0.15	0.52	0.40	0.13	0.38	0.21	0.65	0.30	0.07	0.32	0.16	0.40	
17.0	0.30	0.17	0.28	0.14	0.60	0.43	0.14	0.41	0.26	0.76	0.31	0.07	0.32	0.21	0.44	
17.5	0.30	0.14	0.25	0.17	0.55	0.43	0.14	0.41	0.24	0.76	0.33	0.08	0.32	0.23	0.49	
18.0	0.32	0.18	0.26	0.18	0.65	0.44	0.14	0.41	0.27	0.76	0.32	0.05	0.30	0.25	0.43	
18.5	0.34	0.23	0.25	0.15	0.75	0.46	0.15	0.45	0.27	0.76	0.35	0.09	0.32	0.17	0.44	
19.0	0.37	0.20	0.31	0.20	0.70	0.45	0.14	0.43	0.28	0.73	0.38	0.08	0.36	0.27	0.52	
19.5	0.39	0.28	0.28	0.17	0.83	0.49	0.16	0.48	0.25	0.83	0.36	0.09	0.35	0.27	0.56	
20.0	0.41	0.26	0.31	0.18	0.85	0.48	0.18	0.50	0.22	0.87	0.39	0.09	0.40	0.26	0.51	
20.5	0.42	0.30	0.29	0.17	0.93	0.50	0.17	0.48	0.27	0.83	0.42	0.10	0.42	0.28	0.61	
21.0	0.48	0.29	0.39	0.23	1.01	0.52	0.19	0.52	0.24	0.90	0.43	0.11	0.43	0.30	0.65	
21.5	0.49	0.32	0.39	0.18	1.03	0.53	0.21	0.46	0.21	0.90	0.47	0.13	0.45	0.28	0.72	
22.0	0.50	0.35	0.33	0.24	1.10	0.55	0.23	0.58	0.26	0.99	0.47	0.15	0.48	0.30	0.82	
22.5	0.56	0.32	0.43	0.28	1.11	0.57	0.24	0.51	0.25	0.98	0.49	0.14	0.44	0.31	0.79	
23.0	0.59	0.37	0.45	0.23	1.19	0.60	0.22	0.53	0.25	0.96	0.50	0.16	0.48	0.31	0.79	
23.5	0.62	0.38	0.45	0.31	1.19	0.57	0.23	0.55	0.22	0.93	0.53	0.16	0.47	0.39	0.88	
24.0	0.62	0.42	0.45	0.26	1.24	0.59	0.24	0.57	0.27	1.03	0.53	0.17	0.48	0.36	0.89	
24.5	0.67	0.45	0.49	0.29	1.38	0.63	0.27	0.67	0.23	1.14	0.54	0.18	0.50	0.37	0.91	
25.0	0.67	0.41	0.48	0.32	1.27	0.61	0.30	0.61	0.19	1.15	0.56	0.18	0.51	0.33	0.87	
25.5	0.73	0.45	0.51	0.38	1.40	0.67	0.32	0.71	0.26	1.26	0.56	0.16	0.51	0.38	0.92	
26.0	0.76	0.44	0.58	0.38	1.37	0.68	0.33	0.69	0.28	1.30	0.57	0.17	0.49	0.35	0.89	
26.5	0.79	0.47	0.56	0.41	1.44	0.68	0.37	0.68	0.21	1.39	0.57	0.17	0.53	0.39	0.87	
27.0	0.83	0.45	0.63	0.46	1.42	0.72	0.38	0.70	0.28	1.48	0.59	0.15	0.52	0.39	0.83	
27.5	0.83	0.49	0.60	0.42	1.46	0.72	0.37	0.71	0.28	1.46	0.57	0.15	0.52	0.40	0.80	
28.0	0.87	0.53	0.59	0.46	1.58	0.74	0.41	0.77	0.25	1.47	0.60	0.16	0.53	0.41	0.81	
28.5	0.91	0.52	0.68	0.50	1.59	0.76	0.41	0.81	0.28	1.51	0.59	0.17	0.53	0.39	0.88	
29.0	0.93	0.50	0.67	0.54	1.58	0.79	0.43	0.81	0.23	1.59	0.62	0.19	0.56	0.35	0.88	
29.5	0.99	0.51	0.74	0.55	1.66	0.82	0.46	0.82	0.29	1.62	0.61	0.18	0.56	0.37	0.92	
30.0	1.00	0.50	0.76	0.60	1.63	0.82	0.46	0.80	0.27	1.59	0.61	0.14	0.55	0.47	0.88	
30.5	1.01	0.50	0.78	0.59	1.65	0.83	0.47	0.78	0.27	1.58	0.62	0.17	0.56	0.40	0.92	
31.0	1.02	0.49	0.80	0.57	1.68	0.86	0.48	0.82	0.32	1.72	0.61	0.17	0.59	0.41	0.87	
31.5	1.03	0.49	0.78	0.66	1.67	0.85	0.47	0.89	0.31	1.56	0.64	0.20	0.60	0.39	0.99	
32.0	1.15	0.54	0.88	0.70	1.77	0.87	0.47	0.87	0.30	1.64	0.65	0.16	0.60	0.50	1.00	
32.5	1.16	0.55	0.95	0.67	1.84	0.84	0.50	0.79	0.32	1.64	0.63	0.16	0.59	0.44	0.89	
33.0	1.20	0.49	0.98	0.79	1.78	0.87	0.47	0.86	0.29	1.63	0.63	0.21	0.57	0.43	1.02	
33.5	1.27	0.57	1.33	0.65	1.76	0.90	0.59	1.00	0.26	1.80	0.66	0.18	0.60	0.48	0.98	
34.0	1.31	0.48	1.31	0.86	1.76	1.08	0.52	1.15	0.34	1.71	0.67	0.22	0.58	0.46	1.02	
34.5	1.18	0.52	0.92	0.83	1.78	0.99	0.55	1.12	0.24	1.70	0.68	0.20	0.59	0.50	0.99	
35.0	0.88	0.06	0.88	0.83	0.92	0.95	0.62	1.09	0.20	1.72	0.50	0.20	0.54	0.24	0.69	

Table 21D: Stomatal conductance measured for potato (II).

Time	Stomatal conductance [mmol H_2O m^{-2} s^{-1}] for potato (II)														
	Control treatment					Platinum treatment					Palladium treatment				
[minute]	mean	SD	median	min.	max.	mean	SD	median	min.	max.	mean	SD	median	min.	max.
0.5	0.01	0.01	0.01	0.00	0.03	0.03	0.02	0.02	0.01	0.08	0.01	0.01	0.02	0.00	0.02
1.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.03	0.01	0.06	0.01	0.01	0.02	0.00	0.02
1.5	0.01	0.01	0.00	0.00	0.02	0.03	0.02	0.02	0.02	0.07	0.01	0.01	0.01	0.00	0.02
2.0	0.01	0.01	0.00	0.00	0.02	0.03	0.02	0.02	0.00	0.07	0.01	0.01	0.01	0.00	0.02
2.5	0.01	0.01	0.00	0.00	0.02	0.02	0.02	0.02	0.00	0.07	0.01	0.01	0.01	0.00	0.02
3.0	0.01	0.01	0.01	0.00	0.02	0.03	0.02	0.02	0.01	0.07	0.01	0.01	0.00	0.00	0.02
3.5	0.01	0.01	0.01	0.00	0.02	0.02	0.02	0.02	0.00	0.06	0.01	0.01	0.00	0.00	0.02
4.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.01	0.06	0.01	0.01	0.00	0.00	0.02
4.5	0.00	0.01	0.00	0.00	0.02	0.02	0.01	0.02	0.01	0.06	0.00	0.01	0.00	0.00	0.02
5.0	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.06	0.01	0.01	0.00	0.00	0.02
5.5	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.05	0.01	0.01	0.01	0.00	0.02
6.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.03	0.01	0.05	0.01	0.01	0.01	0.00	0.02
6.5	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.01	0.05	0.01	0.01	0.01	0.00	0.02
7.0	0.01	0.01	0.00	0.00	0.02	0.02	0.01	0.02	0.01	0.06	0.01	0.01	0.01	0.00	0.02
7.5	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.05	0.01	0.01	0.01	0.00	0.02
8.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.01	0.05	0.01	0.01	0.01	0.00	0.02
8.5	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.04	0.01	0.01	0.01	0.00	0.02
9.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.01	0.05	0.00	0.01	0.00	0.00	0.02
9.5	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.04	0.01	0.01	0.01	0.00	0.02
10.0	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.04	0.01	0.01	0.01	0.00	0.02
10.5	0.01	0.01	0.00	0.00	0.02	0.02	0.01	0.02	0.01	0.04	0.01	0.01	0.01	0.00	0.02
11.0	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.04	0.01	0.01	0.00	0.00	0.02
11.5	0.01	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.01	0.05	0.01	0.01	0.01	0.00	0.02
12.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.00	0.05	0.01	0.01	0.01	0.00	0.02
12.5	0.01	0.01	0.02	0.00	0.02	0.03	0.01	0.02	0.02	0.04	0.01	0.01	0.01	0.00	0.02
13.0	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.01	0.04	0.01	0.01	0.01	0.00	0.02
13.5	0.01	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.02	0.05	0.01	0.01	0.01	0.00	0.02
14.0	0.01	0.01	0.01	0.00	0.03	0.03	0.01	0.03	0.01	0.05	0.01	0.01	0.01	0.01	0.02
14.5	0.01	0.01	0.02	0.00	0.02	0.03	0.01	0.02	0.01	0.05	0.02	0.01	0.02	0.00	0.02
15.0	0.02	0.01	0.02	0.00	0.03	0.03	0.01	0.03	0.02	0.04	0.02	0.00	0.02	0.01	0.02
15.5	0.01	0.01	0.01	0.00	0.03	0.03	0.01	0.03	0.02	0.05	0.02	0.01	0.02	0.01	0.03
16.0	0.02	0.01	0.02	0.00	0.03	0.03	0.01	0.03	0.02	0.05	0.02	0.01	0.02	0.01	0.03
16.5	0.02	0.01	0.02	0.00	0.04	0.03	0.01	0.03	0.02	0.05	0.02	0.01	0.02	0.01	0.03
17.0	0.02	0.01	0.02	0.00	0.04	0.03	0.01	0.03	0.02	0.06	0.02	0.01	0.02	0.01	0.03
17.5	0.02	0.01	0.02	0.01	0.04	0.03	0.01	0.03	0.02	0.06	0.02	0.01	0.02	0.01	0.04
18.0	0.02	0.02	0.02	0.01	0.05	0.03	0.01	0.03	0.02	0.06	0.02	0.01	0.02	0.01	0.03
18.5	0.02	0.02	0.02	0.00	0.06	0.03	0.01	0.03	0.02	0.06	0.02	0.01	0.02	0.01	0.03
19.0	0.03	0.02	0.03	0.01	0.05	0.03	0.01	0.03	0.02	0.06	0.03	0.01	0.02	0.02	0.04
19.5	0.03	0.02	0.02	0.01	0.07	0.04	0.01	0.03	0.02	0.07	0.03	0.01	0.02	0.01	0.05
20.0	0.03	0.02	0.02	0.01	0.07	0.04	0.02	0.03	0.01	0.07	0.03	0.01	0.03	0.01	0.04
20.5	0.03	0.03	0.02	0.01	0.08	0.04	0.02	0.04	0.02	0.07	0.03	0.01	0.03	0.02	0.05
21.0	0.04	0.03	0.03	0.02	0.09	0.04	0.02	0.04	0.02	0.07	0.03	0.01	0.03	0.02	0.05
21.5	0.04	0.03	0.03	0.01	0.09	0.04	0.02	0.04	0.02	0.07	0.03	0.01	0.03	0.02	0.06
22.0	0.04	0.03	0.03	0.02	0.10	0.04	0.02	0.04	0.02	0.08	0.03	0.02	0.03	0.02	0.07
22.5	0.04	0.03	0.03	0.02	0.10	0.05	0.02	0.04	0.02	0.08	0.04	0.02	0.03	0.02	0.07
23.0	0.05	0.03	0.04	0.02	0.11	0.05	0.02	0.04	0.02	0.08	0.04	0.02	0.04	0.02	0.07
23.5	0.05	0.04	0.04	0.02	0.11	0.04	0.02	0.04	0.02	0.08	0.04	0.02	0.03	0.02	0.08
24.0	0.05	0.04	0.03	0.02	0.12	0.05	0.02	0.04	0.02	0.09	0.04	0.02	0.04	0.02	0.08
24.5	0.05	0.04	0.04	0.02	0.13	0.05	0.03	0.05	0.01	0.10	0.04	0.02	0.04	0.02	0.08
25.0	0.05	0.04	0.04	0.02	0.12	0.05	0.03	0.05	0.01	0.11	0.04	0.02	0.04	0.02	0.08
25.5	0.06	0.05	0.04	0.03	0.14	0.05	0.03	0.06	0.02	0.12	0.04	0.02	0.03	0.02	0.08
26.0	0.06	0.05	0.04	0.03	0.14	0.06	0.03	0.06	0.02	0.13	0.04	0.02	0.04	0.02	0.08
26.5	0.07	0.05	0.04	0.03	0.15	0.06	0.04	0.05	0.02	0.13	0.04	0.02	0.04	0.02	0.08
27.0	0.07	0.05	0.05	0.03	0.14	0.06	0.04	0.05	0.02	0.15	0.04	0.02	0.04	0.02	0.07
27.5	0.07	0.05	0.04	0.03	0.15	0.06	0.04	0.06	0.02	0.14	0.04	0.02	0.04	0.02	0.07
28.0	0.08	0.06	0.05	0.03	0.17	0.07	0.05	0.06	0.02	0.16	0.04	0.02	0.04	0.02	0.07
28.5	0.08	0.06	0.05	0.03	0.16	0.07	0.05	0.07	0.02	0.17	0.04	0.02	0.04	0.02	0.07
29.0	0.08	0.05	0.05	0.04	0.16	0.07	0.05	0.06	0.01	0.17	0.05	0.02	0.04	0.02	0.08
29.5	0.09	0.06	0.06	0.04	0.18	0.07	0.06	0.06	0.02	0.19	0.05	0.02	0.04	0.02	0.07
30.0	0.09	0.06	0.06	0.04	0.18	0.07	0.05	0.06	0.02	0.18	0.04	0.02	0.04	0.02	0.07
30.5	0.09	0.06	0.06	0.04	0.18	0.08	0.05	0.06	0.02	0.18	0.05	0.02	0.04	0.03	0.07
31.0	0.09	0.06	0.06	0.04	0.18	0.08	0.06	0.06	0.02	0.19	0.04	0.02	0.04	0.02	0.08
31.5	0.09	0.06	0.06	0.05	0.18	0.08	0.06	0.07	0.02	0.18	0.05	0.02	0.04	0.02	0.08
32.0	0.11	0.06	0.07	0.05	0.19	0.08	0.06	0.07	0.02	0.18	0.05	0.02	0.04	0.03	0.08
32.5	0.10	0.07	0.07	0.05	0.18	0.08	0.06	0.06	0.02	0.20	0.05	0.02	0.04	0.02	0.08
33.0	0.11	0.06	0.08	0.06	0.19	0.08	0.06	0.07	0.02	0.20	0.05	0.02	0.04	0.02	0.09
33.5	0.12	0.07	0.12	0.05	0.20	0.09	0.08	0.09	0.02	0.23	0.05	0.02	0.04	0.03	0.09
34.0	0.12	0.06	0.12	0.07	0.19	0.11	0.07	0.10	0.02	0.21	0.05	0.03	0.05	0.02	0.10
34.5	0.11	0.08	0.07	0.07	0.20	0.10	0.07	0.10	0.02	0.21	0.05	0.02	0.04	0.03	0.09
35.0	0.07	0.00	0.07	0.07	0.07	0.10	0.08	0.10	0.02	0.22	0.03	0.02	0.03	0.02	0.05