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Platingruppenelemente in Straßenstäuben

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EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre an Eides statt, dass ich die vorliegende Masterarbeit selbständig und ohne fremde Hilfe verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche erkenntlich gemacht habe.

Kurzfassung

Platingruppenelemente in Straßenstäuben

Bestimmung der anthropogenen Verteilung und des Transports der PGE in der Umwelt entlang österreichischer Straßen

Automobil-Katalysatoren werden in Österreich seit 1987 angewandt, und somit wurden Schadstoffemission wie Kohlenmonoxid, Kohlenwasserstoffe und Stickoxiden deutlich reduziert. Allerdings hat die Emission von Platingruppenelementen (PGE) aus Kfz-Katalysatoren einen raschen Anstieg der Pt-, Pd- und Rh-Konzentrationen in die Straßemedien, wie z.B. Boden, Wasser, Pflanzen und Klärschlamm, zu verzeichnen. Durch die Untersuchung der PGE-Konzentrationen in diesen Medien sowie den Vergleich von PGE-Konzentrationen und PGE- Verhältnisse in den verschiedenen Medien bei gleichem Standort, kann man nicht nur die Verteilung der PGE, sondern auch die Umwandlung und den Transport von PGE in der Umwelt erkennen.

Eine Studie von Fritsche (2003) die schon am Lehrstuhl Allgemeine und Analytische Chemie durchgeführt wurde hat sich nur auf die Verteilung der PGE in den straßennahen Böden der österreichischen Autobahnen und Bundesstraßen konzentriert. Um einen Überblick über die PGE in anderen Umweltkompartimenten zu bekommen, wurden 31 Proben von verschiedenen Standorten und Medien, wie beispielsweise straßennahen Böden, straßennahem Schnee, Straßenkehrichte und Schlamm aus Absetzbecken und Gully für diese Studie gezogen und auf PGE und Schwermetalle untersucht.

Erstmalig wurden Schneeproben untersucht um den anthropogenen Eintrag möglichst genau zu definieren. Für die Gehaltsbestimmungen wurden die aufbereiteten Proben in einem Mikrowellen-Aufschluss-System aufgeschlossen und die Lösungen mittels ICP-MS mit der Methode der Isotopenverdünnung untersucht. Die Konzentrationen der PGE wurden durch die Online-Kopplung einer Kationentauschersäule an das ICP-MS ermittelt. Diese chromatographische Kopplung ermöglicht es, interferierende Matrixelemente abzutrennen

An allen Standorten wird eine eindeutige Akkumulation aller bestimmten PGE in den verschiedenen Medien der Straße festgestellt. Die Konzentrationen von Pt und Pd liegen deutlich über dem zu erwarteten Hintergrundwert. Aus der Untersuchung der Beziehung zwischen der PGE-Konzentration im straßenahen Schnee und der Verkehrsdichte wurde keine gradlinige Beziehung der beiden Faktoren gefunden. Durch die Berechnung der Pt/Pd-Verhältnisse und Element-Korrelationen der Proben, können jedoch gute lineare Beziehung zwischen den beiden Elementen dargestellt werden die eindeutig auf einen anthropogenen Einfluss hinweisen.

Abstract

The Platinum group elements in road dust

Determination of PGE anthropogenic distribution and transport in environment along Austrian motorways

The automobile catalytic converters have been in use in Austria since 1987, and therefore the emission of the pollutant such as carbon monoxide, hydrocarbons and nitric oxides has been significantly reduced. However, the emission of platinum group elements (PGE) from automobile catalytic converters has led to a rapid increase in Pt, Pd and Rh concentrations in roadside media, which include soils, water, plants and sludge from sediments. Through the investigation of PGE concentration in such media and the comparison of the PGE-concentrations and PGE-ratios in the different media at the same site, one can study not only the distribution of PGE, but also the transformation and transport of PGE in the environment.

Already a study by Fritsche (2003) which concentrated on soil was carried out to determinate the distribution of the PGE in the roadside soil of the Austrian motorways. In this work the study is extended to roadside soils, roadside snow, street sweepings and sludge in the infiltration basin and roadside drain and 31 samples were taken from different sample sites.

Snow samples were studied for the first time in Austria in order to better distinguish between geogenic and anthropogenic PGE sources. All the samples were digested by microwave digestion system and analyzed by ICP-MS with the isotope dilution method. To separate the interfering matrix constituents all samples were measured through online-coupling of a chromatographic column with the ICP-MS system.

At all the sample sites the accumulation of the PGE was clearly observed in different roadside media, the concentrations of Pd and Pt significantly exceeds the to expected natural background value. No straightforward relationship between the PGE-concentration in the roadside snow and traffic density was found. Through the calculation of the Pt/Pd-ratios and correlation, the samples show the good linear relationship between the Pd and Pt which points to a purely anthropogenic source.

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1 General introduction

Research on exhaust emissions from motor vehicles has received considerable attention and their identification as a significant source of environmental hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_X) and other pollutants led to the introduction and progressive tightening of exhaust gas emission standards. The principal technology through the control and limitation of these pollutants is the catalytic converter. Automotive catalytic converters were initially developed to meet the emission regulations introduced in the United States in the 1970s.

In the 1980s central Europe (e.g. Germany, Austria) and Australia followed suit, soon followed by the rest of Europe in order to comply with the introduction of EU emissions regulations (Whiteley, 2004). To achieve emission reductions converters utilize the catalytic properties of platinum (Pt), palladium (Pd) and Rhodium (Rh), to transform HC, CO and NO_X into the more innocuous carbon dioxide (CO_2), nitrogen (N_2) and water The environmental benefit of this introduction has been obvious with the removal of about 90% of CO, unburned HC, and NO_X from the exhaust (Barefoot, 1997; Artelt et al., 1998; Zereini et al., 2001a) resulting in significant decreases in urban air pollution for these species.

As catalytic converters require the use of unleaded petrol an additional benefit has been the reduction of vehicle derived environmental lead pollution. There is however, growing evidence that the ever increasing use of this technology is leading to the widespread dispersion and accumulation of Platinum Group Elements (PGE) in the environment. While the detailed mechanisms remain unclear, the numbers of studies that have demonstrated increasing concentrations of PGE in roadside environments since catalytic converter introduction provide compelling evidence for the vehicle catalyst as the predominant source. This emission of PGE into the urban environment, which in all probability will increase in coming years, has led to concern for both environmental and human health (Whitely, 2004).

So far, there are still only few data about the distribution of the PGE in Austria. Johannes Fritsche (2003) has investigated the distribution of PGE along the highway in Austria, but he took only the samples from the roadside soil. To get more information, the object which is investigated in this thesis includes not only roadside soil but also the roadside snow with dust, as well as sweepings from urban streets and the sludge from the roadside drain. By analyzing the data, the distribution, transform and transport of the PGE in the environment can be established. Furthermore this information is also crucial for the basics about the estimation of the risk for the human health and environment.

As the beginning of the thesis some theoretical foundations about the PGE is introduced, and then the usual determination methods related with the PGE is the overviewed. In latter chapters one can see some basic knowledge of the platinum group elements and the principle of equipments which are applied in the experiments for PGE measurement. This thesis configuration is described as below. The experimental part comes after the theory parts which are mainly about the strategy of sampling, the detailed process of the experiments and the method of the data evaluation. The last two chapters are the results discussions and the conclusions, respectively.

In this work the range of the investigation extends to the roadside soils, roadside snow, street sweepings and sludge in the infiltration basin and roadside drain. Snow samples were studied for the first time in Austria in order to better distinguish between geogenic and anthropogenic PGE sources. All the samples were digested by microwave digestion system and the completeness of digestion was also studied. Except rhodium the concentration of the PGE was determined after the isotope dilution method by ICP-MS. This method was applied to all the samples in this thesis and maybe it can be used as the procedure for the investigation of low concentration environmental samples in the future.

2 Foundations of the theory

2.1 Introduction

The elements referred to as the platinum group elements (PGE) in the periodic table consist of a family of six grayish to silver-white metals, with close chemical and physical affinities. These may be subdivided, according to their relative densities, into three heavier metals-platinum (Pt), iridium (Ir) and osmium (Os), with the density about 22g/cm^3; and the lighter metals-palladium (Pd), rhodium (Rh) and ruthenium (Ru), with the density about 12g/cm^3.

2.1.1 Occurrence of the PGE

The platinum group elements are amongst the 90 or so elements that comprise less than 2% by weight of the earth’s crust or 10 mile thick outer layer of the earth. Their concentrations are estimated to be (Römpp, 1997):

Ru	0.10[ng/g]	Rh	0.06[ng/g]	Pd	0.40[ng/g]
Os	0.05[ng/g]	Ir	0.05[ng/g]	Pt	0.40[ng/g]

The major producers of platinum group metals are South Africa (Merensky Reef) and Russia (Norilsk). Canada (Sudbury) is the medium producer, whilst Columbia (Choco), China (Jinchang) and West Australia are all minor producer. USA in Alaska and Montana is a potential producer (Hartley, 1991).

2.1.2 Properties of the PGE

All six of the platinum group metals are silvery white lustrous metals, although osmium has a slightly blue tinge. They are all sufficiently ductile and malleable to be drawn into wires, rolled into sheet or formed by spinning and stamping. All the metals have high melting point. The main physical properties of the platinum group elements are shown in the Table 1 (Hartley, 1991).

The platinum group elements are all noble metals as a consequence of their high sublimation energies and high ionization potentials. The relative ease of attack of oxygen lies in the order Os<Ru<Ir<Rh<Pd<Pt (Hartley, 1991). Thus osmium is oxidizable at room temperature in its powdered form; in bulk it is not oxidized below 400℃. Oxidation yields the volatile tetroxide, which can be detected by its characteristic odour when finely powdered Osmium is exposed to air. Ruthenium requires about 600℃ to promote oxygen attack leading to a protective dioxide film which prevents further oxidation until much higher temperatures are reached. Rhodium is somewhat more resistant to aerial oxidation even at red heat whilst palladium is oxidized to palladium (II) oxide in air at 700℃ but above 875℃ the oxide dissociates back to the free metal and oxygen.

Table 1: Main chemical and physical properties of the PGE

properties	***units***	***Ru***	***Rh***	***Pd***	***Os***	***Ir***	***Pt***
atomic number		44	45	45	76	77	78
atomic mass		101.07	102.90	106.40	190.20	192.22	195.09
density at 25□	g/cm^3	12.45	12.41	12.02	22.61	22.65	21.45
melting point	□	2310	1960	1554	3050	2443	1769
boiling point	□	3900	3730	3125	5500	4500	3825
ionization potential-1st	eV	7.36	7.46	8.33	8.7	9.6	9.0
specific heat at 0□	J/K/mole	24.095	24.941	25.929	-	25.121	25.958
thermal conductivity 0-100□	Watt/m/□	105	150	76	87	148	73
Electrical resistively	μΩ•cm	6.80	4.33	9.33	8.12	4.71	9.85
Hardness (annealed-Vicker Hardness number)		220	101	41	>250	220	41

Source: Hartley, 1991

Fluorine and chlorine attack osmium at about 100□ to give mixtures of fluorides and chlorides respectively. Similar reactions on ruthenium require about 300□ whilst iridium is not attacked below red heat. Rhodium is even more resistant to halogen attack, particularly attack by fluorine. In contrast palladium is attacked by moist halogens at room temperature and even platinum is attacked slowly under these conditions.

Osmium is barely affected by aqua regia, oxidizing acids, hydrochloric or sulphuric acid, but does dissolve in molten alkalis and oxidizing fluxes. Ruthenium is insoluble in all acids including aqua regia, although if potassium chlorate is added to the aqua regia ruthenium is oxidized explosively. Palladium even in the bulk state is attacked by hot concentrated nitric and sulphuric acids particularly in the presence of oxygen and oxides of nitrogen. In powder form, palladium dissolves slowly in hydrochloric acid in the presence of oxygen. Platinum is unaffected by acids except for aqua regia in which it readily dissolves whereas iridium and rhodium are unaffected even by aqua regia. Palladium reacts slowly with molten alkalis at 800□, platinum in molten caustic potash at 500□ and rhodium can be dissolved in a potassium bisulphate melt, a property used in extraction, but iridium is inert to alkali fusion (Hartley, 1991).

2.1.3 Applications of the PGE

The principal applications of PGE depend on either their nobility or their catalytic properties. Because of the catalytic properties are the platinum, palladium and rhodium applied mostly as the catalyst in the exhaust system of automobile or in the chemical industries. The nobility of PGE and their low electrical resistance are responsible for the use in the electrical industries and the protection against corrosion. They have been also widely used in the glass making industry, jewelry factory, pharmaceutical industry and so on (Figure 1). Concrete applications of each PGE are shown in the following table

Table 2: The applications of PGEs

Elements	**Applications**
Platinum	-auto catalyst -jewelry -catalyst in oxidation of ammonia to nitric acid -temperature measurement -sensor of gas detection -optical data storage -glass making -corrosion protection -reaction vessels in chemical analysis -Anti-cancer drugs(cis-[$Pt(NH_3)_2Cl_2$])
Palladium	-auto catalyst -jewelry -dentistry -electrical application -nitric acid production
Rhodium	-auto catalyst -hydroformylation of olefine and carbonylation of methanol to yield acetic acid -nitric acid production -glass making
Ruthenium	-electrical applications -chemical catalyst
Iridium	-Electrochemical industries -chemical catalyst -petroleum
Osmium	-Osmium alloys as very hard materials - fingerprint detection (OsO_4)

Source: Hartley, 1991

2.1.3.1 PGE in the automobile catalysts

The decline of urban air qualities in many US and European cities in the 1960s due to both industrial sources and the increasing emissions of vehicle derived hydrocarbons, nitrogen oxides and carbon monoxide became a serious problem. In order to achieve compliance with newly developed emissions standards the predominant strategy adopted by the automotive industry was to equip new cars with noble metal catalytic converters The early forms of catalytic converters (1976-1979), known as pellet-type catalysts, normally consisted of Pt and Pd, in a ratio of around 5:2, dispersed on the surfaces of γ-alumina (Barefoot, 1997). Such `two-way' designs catalytically reduced HC and CO emissions. The reduction of NO_X was achieved through the addition of Rh in the early 1980s thus giving rise to the three-way catalytic converter.

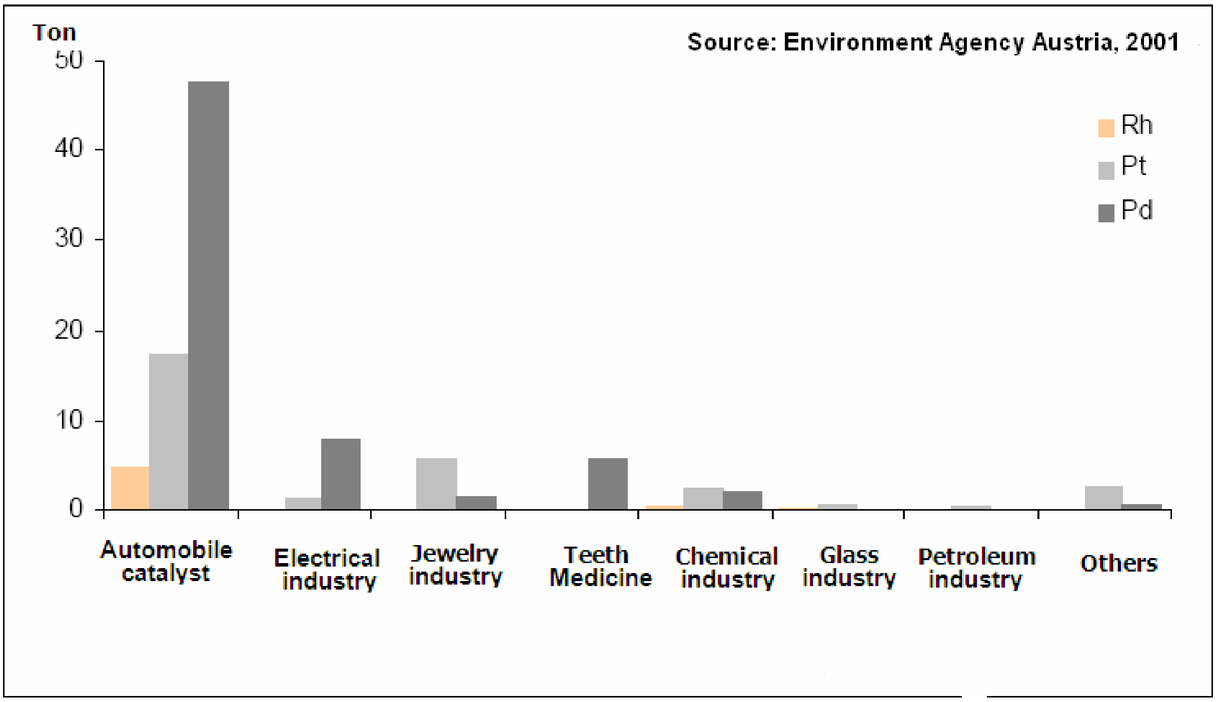
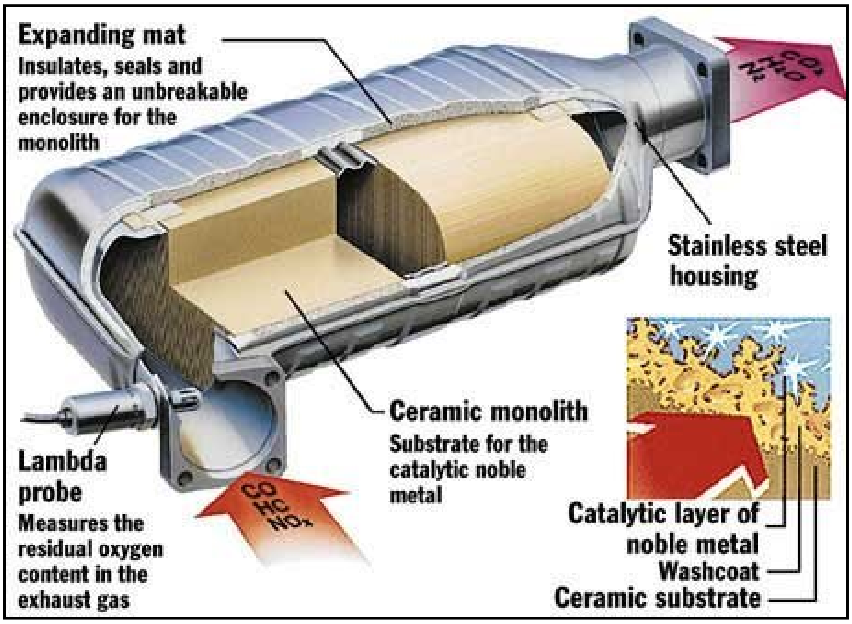


Figure 1: Consumption of PGE in the west Europe countries

The replacement of PGE coated spheres of γ-alumina in the mid 1980s with monolithic substrates resulted in the modern three-way catalyst. Modern designs utilize a ceramic honeycomb or monolith substrate of cordierite ($Mg_2Fe_2Al_3(Si_5AlO_{18})$) to which a surface coating of γ-alumina along with various other rare earths (e.g. Ce), and/or alkaline earths, and other metal oxides is applied. Pt, Pd and Rh are fixed into the washcoat surface by impregnation or by coating from a solution of hexachloroplatinic(IV)acid, palladium chloride or rhodium chloride salt. The monolith is then encased in a metal can be suitable for attachment to the exhaust system (Whiteley, 2004). The composition and relative proportions of PGE contained in a catalyst are dependent on engine size and manufacturer and the exact composition is generally under patent, but typical converters contain 0.10-0.15% m/m PGE, which generally equates to around 1.75 g PGE for an average sized family car (Barefoot, 1997).

Between 1984 and 1992 the vast majority of converters were of the Pt / Rh type, with the ratio of these metals being relatively constant at 5:1 (Wei and Morrison, 1994a; Zereini et al.). However, since 1992 the development of more efficient catalysts based on Pd-Rh, Pd alone or Pt-Pd-Rh have seen widespread introduction. This technology has been successful in meeting the gradually tightening emissions regulations. However the development was likely a response to the rapid increase in world Pt prices. The 1991 demand for platinum and palladium for use in catalytic converters were estimated at 47 ton and 11 ton respectively. Pt usage peaked in 1996 at 58 ton falling to 56 ton in the year 2000, whereas automotive Pd demand has increased more than 15 fold over the same period (Johnson Matthey, 2001). This shift towards Pd usage in automobile catalysts may well be reflected in increasing or altering ratios of PGE determined in road dusts and roadside sediment. Further uncertainty regarding the use of PGE ratios as future indicators of source is created as catalyst manufacturers may be forced to move back to platinum as the major active component of catalysts. This prediction is due to the palladium price more than doubling during 2000 culminating at over US $20 per g (Johnson Matthey, 2001). Thus a new degree of caution is required during the interpretation of contaminated environments, especially in the context of the greater solubility of catalyst derived Pd.



Source: (UMICORE, 2009)

Figure 2: A three-way catalytic converter

To review, catalytic converter technology is continually evolving and four main generations of catalytic exhaust pipes have been identified. Firstly, two-way catalysts, secondly, three-way catalysts containing Pt, Pd and Rhodium (Rh), thirdly, second generation three-way catalysts better suited to the high operating temperatures of modern engines, and finally a new generation of three-way Pd rich catalysts introduced to meet even stricter European emissions legislation.

During operation pollutant exhaust gases that are a direct product of fuel combustion are directed through the catalyst and converted, through a variety of reactions into less harmful components.

Oxidation reactions:

$$\begin{aligned} CO+\frac{1}{2}O_2 &\longrightarrow CO_2 \\ H_2+\frac{1}{2}O_2 &\longrightarrow H_2O \\ C_xH_y+(x+\frac{y}{4})O_2 &\longrightarrow xCO_2+\frac{y}{2}H_2O \end{aligned}$$

Steam-reforming:

$$C_xH_y+xH_2O \longrightarrow xCO+(x+\frac{y}{2})H_2$$

NO_X Reduction:

$$\begin{aligned} 2CO+2NO &\longrightarrow 2CO_2+N_2 \\ H_2+NO &\longrightarrow H_2O+\frac{1}{2}N_2 \\ C_xH_y+(2x+\frac{y}{2})NO &\longrightarrow xCO_2+\frac{y}{2}H_2O+(x+\frac{y}{4})N_2 \end{aligned}$$

Water-gas shift:

$$CO+H_2O \longrightarrow CO_2+H_2$$

The main reaction types occurring in a three-way catalyst illustrate the mechanisms by which CO, HC and NO_X are converted into CO_2, H_2O and N_2. A number of mechanisms that affect catalyst performance and may lead to PGE release occur during catalyst aging. These can be characterized as deterioration due to chemical poisoning, sintering, thermal and mechanical erosion (Palacios et al., 2000b). Chemical poisoning may be due to sulfur compounds, lead, zinc or phosphorus, all of which may be found in fuels. The deterioration is manifested as irreversible adsorption, or reaction changes in the catalyst surface. Sintering is triggered by the axial and radial temperature gradients generated by exothermic catalytic reactions. Thermal erosion is essentially metal volatilization, and although the PGE are relatively thermally stable, under oxidizing conditions losses of Pt and Rh may occur at temperatures above 900□, which may be attained on catalyst surfaces during operation (Palacios et al., 2000b). Finally, losses of catalyst support material and cracking of the washcoat layer have associated losses of PGE bearing catalyst material. These processes are promoted by vibration and impact, and it has been reported as not uncommon for catalysts to be partly demolished due to mechanical impacts (Artelt et al., 1999b). Mechanical and thermal erosion processes are declared as the principal mechanisms of PGE release into the environment.

In the early 1990s the diesel engine manufacturers, being aware of the successes of the catalytic converter for the gasoline engine, considered a catalyzed flow-through monolith for controlling emissions from their engines. The exhaust, however, comprises particulates composed of solid dry carbon or soot, and liquid fuel and oil called the soluble organic fraction or SOF. Furthermore, the gaseous exhaust contained significant amounts of SO_2 which, over most oxidation catalysts, would be converted to SO_3 (H_2SO_4) which is obviously an unfavorable secondary emission and indeed contributes to the total particulates. The general idea was for the catalyst to oxidize the liquid or SOF component of the particulates to CO_2 and H_2O (Farrauto and Heck, 1999). Diesel engines operate lean and therefore are much cooler than modern stoichiometrically operated gasoline engines. The catalyst would therefore have to function at much lower temperatures than in the gasoline counterpart and would be required to treat liquids rather than gases. For those low temperature conditions, the high surface area washcoat would have to act as a sponge for the liquids and effectively store them until the exhaust temperature increased sufficiently to initiate catalytic oxidation.

The design of the catalyst had to include hydrocarbon adsorption and storage by an organophilic surface with the proper pore size to promote condensation. Another very important catalytic property was that it must have a low activity for the oxidation of the gaseous SO_2 to SO_3; the latter quickly forms sulfate particles, adding to the particulate load. Catalyst formulations comprised of bulk CeO_2 admixed with Al_2O_3 are now used for the effective oxidation of the liquid portion of the particulates (the SOF) without generation of SO_3 particulates (Farrauto and Heck, 1999). Since 1996, diesel passenger cars in Europe have to abate CO and HC emissions and the preferred catalyst consists of a small amount of Pt supported on Al_2O_3 with additions of bulk CeO_2 and a zeolite (Farrauto and Voss, 1996). The zeolite effectively stores the unburned HCs during cold conditions and releases them to the Pt for light-off as the temperature increases in the exhaust. All of these formulations are deposited on ceramic monoliths.

2.2 Anthropogenic PGE Emissions

PGE emissions might occur during PGE production, manufacture of PGE-containing products, and use and disposal of these products. At present, the only documented anthropogenic PGE sources are metal production, automobile exhaust catalysts and medical applications (Rauch and Morrision, 2008). Although additional sources of PGE to the environment may exist, they have not been characterized or reported to date.

2.2.1 Emissions of PGE from automobile catalysts

The quantification of PGE emissions from catalytic converters has principally taken one of two approaches. Firstly, those that directly sample exhaust emissions under operating conditions. Secondly, that which determine anthropogenic PGE in relevant environmental media (e.g. road dusts, soils etc.) at regular intervals and thereby measure actual environmental levels which when modeled along with traffic statistics enables estimations of emissions rates.

2.2.1.1 Direct sampling

A common approach has been the use of an engine dynamometer operated under laboratory conditions. In order to simulate real driving conditions as closely as possible, tests have been performed with the engines running both isokinetic and through standardized, computer controlled cycles of fluctuating speeds,

Significantly, many of the studies performed using dynamometers have found that emission rate is strongly related to engine speed and tenfold increases in emissions rates with doubling engine speeds (e.g. from 100 to 200 km/h) have been demonstrated (Whiteley,2004). Another general conclusion that may be drawn from the literature is that the simulated urban driving cycles result in higher PGE emission rates than constant 80km/h tests indicating a correlation between emissions and the harsher stop / start type driving typical of urban areas. Exhaust temperature is directly related to engine speed and may be one of the important mechanistic factors controlling emission rate increase.

From some studies we can also see that the emissions from gasoline catalysts are expected to be in the low nanogramm per traveled kilometer range, whereas 10-100-fold higher Pt emissions have been measured for diesel catalysts (Moldovan et al, 2002).

2.2.1.2 Estimation of emissions based on concentrations in the environment

Indirect determinations of PGE emission rates are based on models which combine anthropogenic PGE levels in environmental media with traffic statistics. Environmental media from which emissions estimates have been made include soils, waters, plants and sludge. Estimates from such approaches are variable and generally considerably higher than those from dynamometer experiments.

At present, the limited amount of research that enables emission rate calculation from environmental sampling, and the disparity of the results obtained, raises the question of whether accurate estimations can be made using indirect methods. Further research is needed to provide a sufficient framework within which consensus can be obtained, especially that which includes greater quantification of influences such as meteorological conditions.

2.2.2 Other sources of anthropogenic PGE in the environment

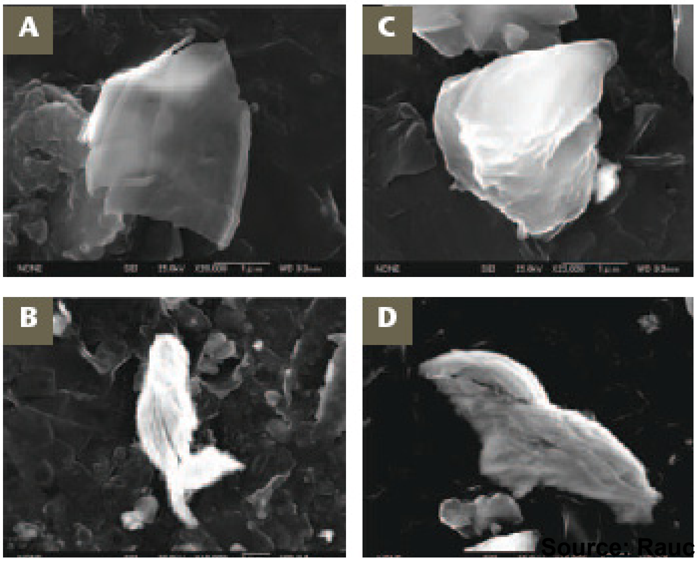
The research presented in this thesis is focused on roadside environments and delineated catchments receiving road runoff, therefore contributions from other sources to reported concentrations are extremely unlikely. However, for completeness, some other sources are briefly discussed.

A number of sources other than catalytic converters can be responsible for increased environmental levels of PGE and can create difficulty in the interpretation of results. Identified contributions have been shown to derive from PGE processing industries and automobile catalyst manufacture (Zereini et al., 1998), jewelry manufacture (Lottermoser, 1994; Laschka and Nachtwey, 1997) and medical and dental use (Kummerer and Helmers, 1997; Kummerer et al., 1999). Further emissions are likely to result from other industrial and chemical uses such as during petroleum refining, ammonia oxidation, glass manufacture and electronic industries though very few data are available on emissions from such sources (WHO, 1991). The chemical form and hence solubility / toxicity etc. of PGE derived from medical and industrial sources differ from automobile catalyst emissions.

2.3 The Forms and Transformation of PGE in the Environment

2.3.1 Physicochemical Forms

The chemical form of PGE in the environment depends on the forms in which PGE are emitted and on subsequent transformations. In the environment, PGE are generally associated with the particle phase as a result of their emission as particle or their interaction with environmental components (figure 3).



Source: Rauch and Morrison, 2008

Figure 3: Field-emission scanning electron microscope images of PGE-containing particles in urban air in Göteborg, Sweden.

PGE are present as finely dispersed nanoparticles in catalysts and are likely to be emitted in the form of PGE nanoparticles or as PGE attached to washcoat particles of γ-Al_2O_3. Sintering may also result in the emission of PGE particles in the micrometer range(Rauch and Morrison, 2008). In addition, soluble PGE species have been found in automobile exhaust and hospital emissions. In the automobile emissions the metallic PGE are the predominant forms.

Particle size and especially the occurrence of PGE as nanoparticles may also play a major role in the presence and formation of soluble PGE species. Fine particle have relatively large surface areas and offer more possibility for reactions with environmental substances. Larger particles are likely to be composed of catalyst washcoat and PGE nanoparticles may be released under conditions that promote the dissolution of γ-Al_2O_3.

The emission of PGE is mainly in a metallic form bound to aluminum oxide particles together with Ce, and the diameter of the PGE particles range from submicrometers to several micrometers (Alt et al., 1993; Gómez et al., 2001). However, platinum in fresh automobile catalysts is not only present in the metallic state, but also in the form of oxides, chlorides and bound to hydrocarbons. Rhodium is also present in the form of oxides. The soluble fraction of Pt represents about 10% and for Pd and Rh it is close to 50% of the total Pt, Pd and Rh, respectively, released from automobile catalysts (Moldovan et al., 2002). Sulfur in the fuel might bind to PGE, which could increase the solubility of PGE (Rauch and Morrison, 2001; Moldovan et al., 2003) and, therefore, emission might follow different mechanisms for gasoline and diesel catalysts (Moldovan et al., 1999; Palacios et al., 2000a).

2.3.2 Environmental transport, distribution and transformation

PGE particles emitted from automobile catalysts deposit on the road surface or in the roadside environment. The soluble fraction of Pt has been reported to be about 10% of the total amount of Pt in exhaust fumes of gasoline and diesel catalysts, but for Pd and Rh, the soluble fraction was in the same order of magnitude as the particulate fraction (Moldovan et al., 2002). This implies that the effects of Pd and Rh emissions could have a more adverse effect on the environment than Pt emissions. The concentration of PGE in soil decreases with increasing distance from the road, as well as with increasing soil depth (Fritsche and Meisel, 2004; Schäfer and Puchelt, 1998; Müller and Heumann, 2000). The deposited particles can then be washed into rivers and water bodies during rain events, where they accumulate in sediments; levels in water are very low (Rauch, 2001). It was suggested that the predominant inorganic form of Pd in freshwater may be the neutral hydroxide species. The transport way of PGE from the automobile catalyst in the urban environment is shown in the following figure 4. In seawater, the predominant form is $PdCl_4^{2-}$ (Melber et al., 2002). Pd (II) can be complexed by amino acids and it has been shown that $PdCl_2$ complexed with glycine is more stable than all known inorganic Pd(II) complexes (Melber et al., 2002).

From the literature, it is clear that the concentration of PGEs has been increased significantly in the environment. Moreover, Barbante et al. (1999, 2001) showed that the spread of PGEs in the environment is rather a global process, despite some works asserting the low transportability of these pollutants. Therefore, it is important to study how these PGE species may become chemically/biochemically active and mobile in interactions with various environmental matrices under the changing weather conditions, in order to give a prediction on the possible hazards of PGEs for human health.

Scanning laser ablation of road and river sediments revealed a coincidence of PGE and Ce peaks, indicating direct transport of PGE containing catalyst particles into the river. Although total PGE concentrations are low in sediments, PGE containing particles are concentrated in a few sediment particles where they have relatively high concentrations (Rauch et al., 2002). In river sediments, PGE remain associated to Ce particles, but part of the particulate PGE might be released from the Ce particle through formation of soluble PGE species or breakdown of the particle (Rauch et al., 2002). Fritsche (2003) has also found the Ce-anomalies in soil along the motorways in Austria.

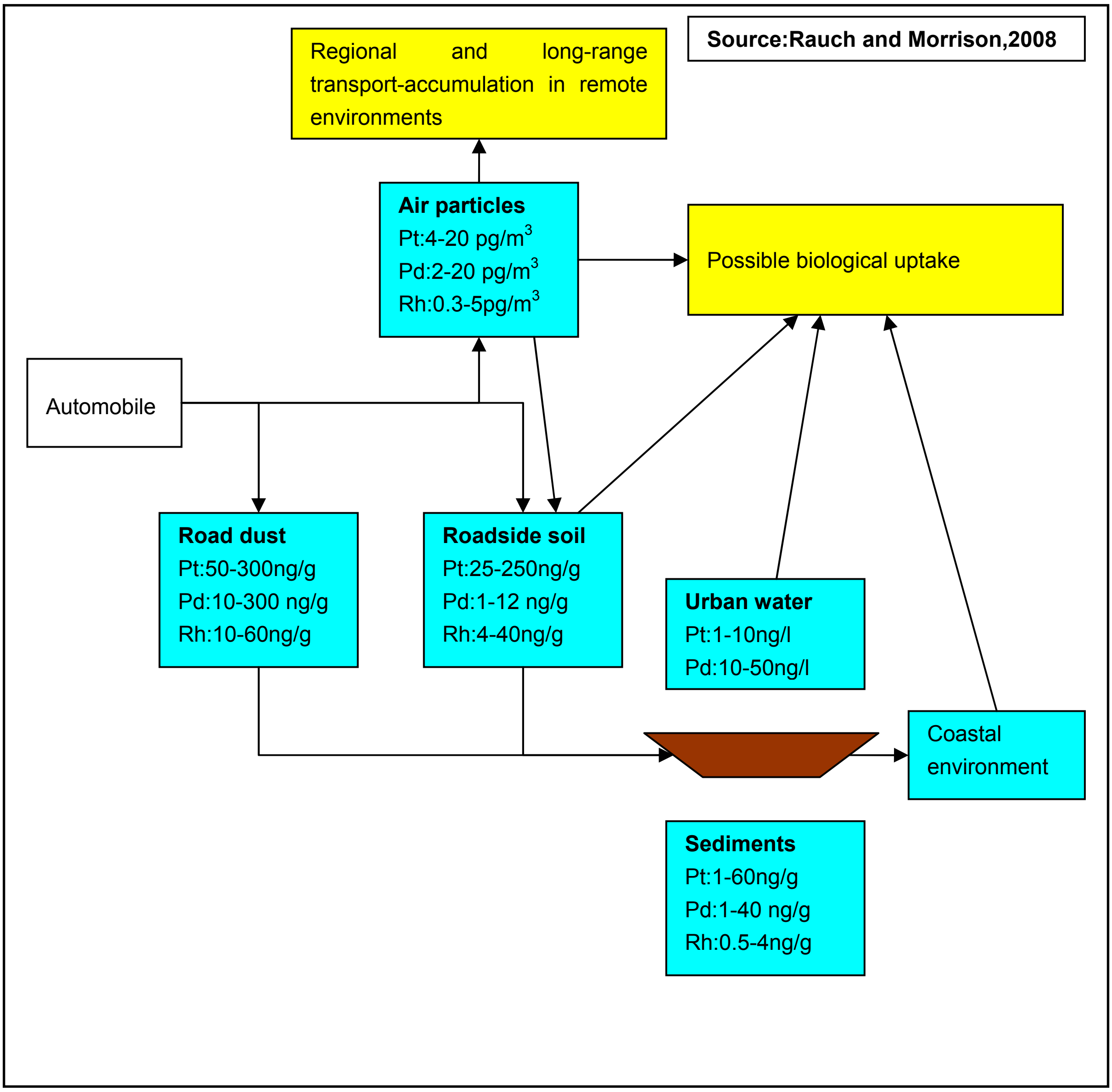

Source:Rauch and Morrison,2008

Figure 4: The distribution of PGEs in the environment.

The water-soluble fraction of Pt in tunnel dust was 3.9% and the fraction soluble in organic solvents was 3.1%, while no platinum was soluble in organic solvents for tested platinum compounds (Pt-black, K_2PtCl_4, $Na_2PtCl_6 \cdot 6H_2O$). This indicates that the soluble species of Pt in tunnel dust are of an organic character (Kristine et al., 2004). The solubility of Pt in tunnel dust was 52% and 25% in EDTA and thiourea, respectively; much higher than the solubility for tested platinum compounds. This means that 52% of the original metallic Pt in tunnel dust is mobile and oxidized in the soil (Rauch and Morrison, 2004). The oxidation is most probably caused by the presence of humic soil, which contains S-attached complexones that oxidize platinum, forming insoluble compounds. The reason why Pt in tunnel dust is oxidized so efficiently may be related to its nanocrystalline particle size (0.1–20 µm) and its ultrafine dispersion (Lustig et al., 1996).

Pt-black and Pt-containing tunnel dust can be solubilized in water by natural complexing agents, which can result in potentially bioavailable platinum species. The ligand that had the greatest effect on the dissolution of metallic platinum was L-methionine. Tunnel dust platinum was generally dissolved to a higher extent than Pt-black, which is probably because of the smaller particle size (nanometer) and the ultrafine dispersion of tunnel dust Pt compared to Pt-black. Metallic Pt was first oxidized and then a complexing agent removed the Pt oxide formed. However, in the absence of a complexing agent, the surface of metallic Pt was rapidly saturated with the oxide, inhibiting further oxidation. It was suggested that metallic Pt in tunnel dust is oxidized in the soil and that the majority of the Pt species formed in the oxidation are immobilized; these compounds could be humic acid complexes of Pt, Pt-black and hydrocomplexes, on the other hand, were transformed into inorganic Pt species (Lustig et al., 1998). The amount of soluble Pt in airborne dust was 30–43%, while it was only 2.5–6.9% in tunnel dust (Alt et al., 1993). It was suggested that this might be due to the different origin of the platinum, traffic being the origin of road dust while airborne dust represents more environmentally occurring Pt.

In Boston harbour sediments, Pt concentrations showed a high variability within the mixed layer, indicating remobilization of Pt within these layers on a short time scale. It was suggested that Pt is associated with organic matter and then remobilized due to organic matter oxidation. For Pd, on the other hand, there was no clear evidence of remobilization once it was fixed in the anoxic layer (Tuit et al., 2000). Pt, Pd and Rh, in the form of complexes of chloride and nitrate, were dissolved in rain water (pH 4–5) rich in natural organic matter (NOM) under controlled laboratory conditions. Solutions were shaken in plastic containers for a week and it was shown that roughly one half of the Pt, Pd and Rh present were complexed with NOM. This shows that PGE can be efficiently mobilized by NOM, contributing to their redistribution in the environment (Menzel et al., 2001).

In conclusion, PGE can be transformed into soluble species in soil by complexation with NOM, such as humic acids, through oxidation by sulfur-attached complexones. Catalyst-emitted PGE is nanocrystalline-sized and ultrafine dispersed, which allows more efficient oxidation.

2.3.3 PGE in the roadside compartments

Road dusts, roadside soils and roadside vegetation represent the principal media that have been utilized in the examination of environmental PGE. In many cases, due to the analytical difficulties surrounding Pd determination, and the relatively recent increase in Pd use in automobile catalysts, only Pt and Rh are reported.

2.3.3.1 Road dust

The major constituents of road dust in Europe have been reported as soil, organic matter derived from adjacent vegetation and input from traffic, plus seasonal or local inputs such as road construction materials, vehicle collision fragments, salt and grit and general waste (Jarvis et al., 2001).

As metals in road dusts may be removed in solution, by particulate wash-off or blow-off or by street sweeping, they can only be considered to reflect short term inputs of PGE. Concentrations of road dust PGE are also affected by driving style, and a number of studies have found the highest concentrations of PGE at heavily frequented crossings or in close proximity to traffic lights (Whiteley, 2001). Additionally, although Schäfer and Puchelt (1998) found a direct correlation between traffic intensity and PGE concentrations in road dusts, the sampling site near Stuttgart revealed concentrations about 75% higher than the maximum values found at the sampling site near Heidelberg even though the traffic density is only approximately 20% higher. Thus, even though the correlation between traffic volume and PGE concentrations in road dusts is qualitatively simple, factors such as precipitation, wind and road structure can exert significant influences.

2.3.3.2 Tunnel dust

Tunnel dusts may be considered as a special case of road dusts, as meteorological influences are minimized. This enables sampling of vehicle derived PGE in a similar chemical form and matrix to that in which they were emitted (Lustig et al., 2000).

The reduced potential for mobilization and removal of PGE bearing dusts through aeolian and fluvial mechanisms in road tunnels appears to have resulted in high concentrations of catalyst derived PGE.

A significant finding of research on tunnel dusts is that when compared to road dusts, although the Pt/Rh ratio remains relatively constant, Pt/Pd ratios in road dusts are both higher and more variable. These observations are only apparent when compared to tunnel dusts that are not exposed to rain, and indicate that Pd may be more susceptible to removal in solution than Pt and Rh (Schäfer et al., 1999).

Correlations between tunnel traffic volume and PGE levels are less clear than for road dusts, roadside soils or roadside grasses. The reasons for this are uncertain, but are likely to be a function of differing dilution of PGE bearing particles by quartz, soot or other road-dust components.

2.3.3.3 Roadside soils

Roadside soils represent an environmental media that are also becoming contaminated with automobile catalyst derived PGE. As for road dusts, traffic volume and concentration in roadside soils are in general positively correlated (Ely et al., 2001; Morton et al., 2001), Though the heterogeneous distribution of PGE in soils along motorways makes quantitative relationships difficult to elucidate (Zereini et al., 2000). Based on the relationship between

PGE concentrations and proximity to exits and accelerating junctions, Zereini et al. (2000) advocate a dependency on engine capacity and driving characteristic, suggesting that PGE emission rate is correlated with speed and acceleration.

In addition to providing information about levels of contamination, the sampling of roadside soils enables investigation of the spatial distribution of PGE emitted from catalyst-equipped vehicles. The majority of studies that have sampled roadside soils have considered the lateral distribution of PGE contamination by sampling at specific intervals perpendicular to the roadside. In most cases, a pattern of rapidly decreasing concentration with distance is seen. Furthermore, the relatively constant Pt/Rh ratios suggest that even at distances greater than 10m from the roadside the catalyst is the principal source. The examination of relationships between PGE and common vehicle derived contaminants (e.g. Pb, Cd, Cu, Zn etc.) shows that lateral PGE distribution is highly correlated to that of other traffic derived metals (Schäfer and Puchelt, 1998).

In comparison to the lateral distribution of PGE in roadside soils, vertical profiles have received less attention. PGE were found to be restricted to the top 20 cm of cores taken adjacent to motorways in Germany, with maximum values in the uppermost (0-4cm) region (Schäfer and Puchelt, 1998; Zereini et al., 2000).

2.3.3.4 Roadside vegetation

Investigations into the use of plant species as biogeochemical exploration tools have demonstrated that PGE are accumulated by a number of vegetation types growing over platiniferous zones. However, most pertinent to this thesis are those that attempt to monitor the accumulation of PGE using grass as the sampling medium.

Due to the degree of elevation of PGE concentrations in both road dusts and roadside soils, the determination of catalyst derived Pt and Rh has been possible since the early 1990s. However, the elucidation of a clear time trend utilising these media is complicated as removal from road dusts is likely to be highly variable and soils represent an accumulating matrix (Helmers, 2000). In contrast, the enrichment of PGE bearing dust by vegetation types such as common grass, when sampled over one growing season (i.e. several months) in successive years enables the discrimination of time trends. Great care was taken to reproduce sampling and analytical methodologies during each collection period, the only variation being a slight difference in sampling date. Priority was given to comparability of antecedent weather conditions as previous research had determined that heavy rain showers may reduce Pt concentrations in vegetation by as much as 40% (Helmers and Mergel, 1998). In agreement with the spatial and temporal trends found in roadside soils, results illustrate rapidly declining PGE levels with increasing distance from the carriageway, and a yearly increase that is strongly correlated with the percentage of catalyst-equipped vehicles. Between 1992 and 1997, platinum contamination in grass sampled at a 20 cm distance from the highway had increased from 3 to 10.6ng/g. Data for rhodium are only available between 1994 and 1997; the equivalent increase is from 0.65 to 1.54 ng/g (Whiteley,2004).

2.4 Biological availability of PGE

Generally, PGEs are referred to behave in an inert manner and to be immobile. However, there is an evidence of spread and bioaccumulation of these elements in the environment. Platinum content of road dusts can be soluble. Consequently it enters the waters, sediments, soil and finally, the food chain.

A number of approaches to determine the plant uptake of catalyst derived PGE have been attempted. Earlier studies demonstrating the potential for Pt uptake generally used high doses and/or nutrient solutions containing water-soluble Pt compounds (Messerschmidt et al., 1994; Ballach and Wittig, 1996). While useful as first attempts, such studies do not adequately simulate natural conditions (Schäfer et al., 1998; Lustig and Schramel, 2000). Although some proportion of PGE in road dusts and soils has been shown to be soluble, the extrapolation of results to natural systems where little is known about the speciation of traffic derived PGE is tenuous.

PGE have been found in roadside vegetation, yet how representative this is of actual uptake is not clear. Based on the differences in Pt concentration of grass samples prepared with and without prior washing, the results of Helmers (1996) indicate that a significant proportion of the Pt content of roadside vegetation results from deposition on the plant surface. However, Ely et al. (2001) found no difference between the Pt abundance of washed and unwashed grasses collected in the USA reporting that Pt adhering to grass leaves and stems is insignificant and that Pt is taken up by grass. It seems likely that PGE from roadside vegetation will reflect both uptake and deposition and the relative contribution of each will be dependent on climatic, biological and pedological factors.

To overcome these issues, research on plant uptake has adopted approaches that more accurately simulate interactions between plant roots and the rhizosphere. These have generally involved growing plants under controlled conditions in mixtures of soil and road or tunnel dust (Schäfer et al., 1998; Lustig and Schramel, 2000), or applying Pt containing nutrient solutions to soils at environmentally relevant concentrations (Verstraete et al., 1998). Results from these studies suggest a small, but measurable uptake of PGE by plants. Transfer coefficients (the ratio of the concentration of a metal in the plant and the concentration of the same metal in the soil) provide a classification method by which the relative biological availability of metals can be compared (Schäfer et al., 1998). The classification of some common heavy metals based on calculated transfer coefficients are given below:

- Extremely immobile elements (Pb, Cr)
- Moderately mobile elements (Cu, Ni)
- Mobile, plant available elements (Zn, Cd)

Schäfer et al. (1998), growing some plants on contaminated soils collected from the side of a highway and uncontaminated soils (sandy and claylike) found that Pt and Rh transfer coefficients for all plants grown on contaminated soil were similar to moderately mobile Cu.

Pd transfer coefficients were generally found to be higher than for Pt and Rh, in some cases as high as Zn and in all cases the order of uptake rates was Pd > Pt ¸ Rh.

Studies of Pt speciation in plants indicate that when grass was grown under experimental conditions constraining root uptake as the only accumulation mechanism, almost all of the Pt is bound to low molecular weight species (Messerschmidt et al., 1994; Alt et al., 1998). However, under natural conditions, Pt in plants was found in high molecular weight proteins (Klueppell et al., 1998). Thus, the different speciation appears related to uptake mechanism (i.e. accumulation through root uptake vs. a surface mechanism). Pt bound to proteins may be significant in terms of toxicity and transport as proteins are known to be important in term of metal metabolism and transport in humans and animals (Weber et al., 2000; Rauch, 2001).

The bioavailability of finely dispersed elemental Pt on larger aluminum oxide particles has been investigated following intratracheal instillation and inhalation by laboratory rats (Artelt et al., 1998, 1999a). Pt was found in the blood, urine, faeces and all examined organs above detection limits. Bioavailability was defined as the Pt found in body fluids and all organs except the lung divided by the amount of Pt retained in the lung. Using this approach, following intratracheal instillation up to 16%, and after 90 days inhalation, up to 30% of the Pt was considered bioavailable. It should be noted that only small amounts (»1%) were deposited in the lung and almost 99% was found in the faeces. However, an intravenous study by the same authors indicates that part of the Pt deposited in the lung may resorbed and hence bioavailable, contributing to that found in the faeces. Of the bioavailable portion, ¸90% was bound to high molecular weight compounds, most probably proteins (Artelt and Levsen, 2000). Given the differences in results obtained during solubility experiments using synthetic and real samples, and as noted by Artelt et al. (1999a), a greater proportion of PGE may be bioavailable than estimated using model substances.

2.5 The toxicity and the healthy risk of PGEs

The toxicity of the PGE, as for many other metals, is dependent on speciation (Farago et al., 1998). The acute toxicity of PGE compounds depends on their solubility. In animal experiments the soluble Pt salts are considerably more toxic than metallic Pt or compounds such as PtO, PtO_2 or $PtCl_2$ (Merget and Rosner, 2001). The most toxic Pt species, which are acutely nephrotoxic and cause tubule damage, are those where Pt is found in a chemically bonded complex (chloroplatinates and amines). The LD_{50} of these species ranges from 20-200mg/kg body weight in rats (Gebel, 2000). Pd salts have also been shown to be of low acute oral toxicity (LD_{50} >1g/kg body weight in rats) observed effects being nephrotoxicity, cardiotoxicity and convulsion. The Microtox test that determines the EC_{50} of the marine bacterium Photobacterium phosphorem when exposed to platinum chloride was found to be about 25g/l, lower than that of common stormwater contaminants such as copper, lead or zinc (Wei and Morrison, 1994b).

Although the toxic potential of Pt, and to a lesser extent Pd and Rh have been demonstrated using soluble compounds, there is no available evidence to indicate that current environmental concentrations have an obvious effect on either public or ecosystem health. Until recently, PGE were thought to remain inert under environmental conditions and therefore have a low environmental impact. However, the recently demonstrated bioavailability and uptake of PGE, especially of Pd by both flora and aquatic fauna may represent an ecological risk.

In terms of human health, almost no data are available regarding the toxicology of finely dispersed Pt particles (Merget and Rosner, 2001), thus the only relevant end point regarding PGE toxicity is the allergenic and sensitizing effect of halogenated Pt compounds. Metallic Pd can cause contact dermatitis, however does not appear to cause respiratory sensitization and only a limited cross-reactivity between Pt and Pd salts in refinery workers (Rosner and Merget, 2000). Occupational exposure to soluble platinum salts can be responsible for the development of platinosis, a syndrome characterized by respiratory and cutaneous hypersensitivity (Vaughan and Florence, 1992). Symptoms include wheezing and breathlessness (asthma), runny nose and sneezing (rhinitis), burning and itching eyes (conjunctivitis), eczematous and urticarial skin lesions (contact urticaria) and signs of mucous membrane inflammation (Farago et al., 1998; Merget, 2000).

Increasing levels of PGE in the environment have generated growing concern about potentially hazardous effects for humans and other living organisms. The uptake of PGE by organisms living or growing in environments contaminated by PGE emitted from catalytic converters is of some concern. Soils and sediments represent the principal sinks for traffic derived PGE and levels approaching those of ore deposits have been reported (Schäfer et al., 1999). Recent evidence suggests a greater solubility and mobility of PGE than had previously been thought. Furthermore, a portion is bioavailable either as emitted or following species transformation of automobile catalyst-derived PGE in the environment. The implications for the detrimental impact on ecosystems of bioaccumulation, biomagnification and translocation in the food chain have not been established. In terms of ecosystem risk assessment, further research, especially on the solubility, transformation and ecotoxicology of Pt, Pd and Rh under various environmental conditions is required.

3 Determination of platinum group elements

The growing interest in anthropogenically derived PGE in the environment has driven the development of analytical techniques for their determination. PGE emissions from catalytic converters have led to observable, and in some cases extremely rapid increases in the concentrations of these metals in the environment, however, environmental PGE concentrations rarely exceed a few hundred ng/g, and are frequently much lower. Highly sensitive and increasingly sophisticated sample preparation and analytical methods are required to overcome the combination of low environmental levels, complex and variable matrices and interferences during analysis. Although significant advances have been made, the accurate quantification of Pt, Rh and especially Pd remains an analytical challenge. The difficulties associated with the determination of trace levels of PGE in often complex matrices can be of sufficient severity to make early attempts at their quantification questionable.

3.1 Preparations of the samples

3.1.1 Storage of the samples

Sampling processes, the handling of samples, and the dissolution/digestion procedures have a substantial influence on the accuracy and precision of the analytical procedures used for the ultra-trace analysis of PGEs. Special precaution is required for the purification of the decomposition agents and the vessels employed to achieve appropriately low blank levels. The proper choice of vessels for the storage of samples has been verified in the case of Pd, as hydrolysis/adsorption occurs for weak acidic conditions on long standing. Similar sorption losses of Pt were observed when utilizing PTFE vessels for digestion. However, quartz vessels are advantageous for opening up samples and, additionally, they also provide better storage properties and lower blank values, particularly after thiourea plus HCl cleaning pre-treatment. For solutions stored in polyethylene bottles, the Pt concentration showed a drastic fall on standing, whereas this was not detected in polystyrene flasks (Bencs et al., 2003).

3.1.2 Digestion Method

Several methods have been offered for digestion of PGEs, such as acidic dissolution, fusion methods, the application of chlorination and fire assay (i.e. fusion and collection of PGEs on a metal sulfide – usually NiS – button, also referred to as ‘docimasy’) procedures (Heinrich et al.,1996; Frago,1998; Zischka,2000). The most common decomposition method is the acidic dissolution, based on the application of aqua regia plus hydrofluoric acid (HF), the latter used only in the presence of silicate matrix constituents. Microwave ovens, high-pressure PTFE bombs and high-pressure ashers (HPAs) are used to decompose a variety of matrices, e.g. road dust, soil, airborne particulate and biological materials. Accurate analytical results were also obtained without the application of HF for ‘difficult’ silicate- containing matrices (e.g. road dust) particularly via aqua regia leaching under high-pressure and -temperature conditions (Müller, 2000). Despite this, in some cases, Pd has been reported to be strongly bound to silicate matrices compared to other PGEs, which demands efficient HF digestion procedures. Vaporization of the excess HF can be avoided by addition of boric acid (Boch, 2002). For biological materials, such as blood samples, mineralization or decomposition by UV photolysis is highly recommended (Begerow, 1997), whereas urine can be measured without decomposition of the samples by GFAAS (Begerow, 2002) or with UV photolysis by ICP-MS (Begerow, 1997).

3.1.3 Pre-concentration and matrix separation methods

In environmental samples, the low concentration of PGEs (below microgram per gram levels) together with the high concentration of interfering matrix components often requires a pre-concentration/enrichment step combined with a matrix separation. The usual methods of pre-concentration are for example fire-assay procedure, extraction and ion exchange etc.

Ion exchange-Chromatographic Separations

Chromatographic separations of mixtures of various compounds are based on their distribution between a stationary and a mobile phase, which are present in a chromatographic column. The mobile phase moves across the column, in effect washing (eluting) compounds at a different rate. These differences are based in properties such as the boiling point, the polarity, the electric charge (for ionic compounds), the size of the molecule, and so forth. If at the column outlet there is a system for detecting and measuring the quantity of each component, then a quantitative determination of the separated components is achieved.

The movement of substance A through a chromatographic column can be considered as a movement through successive equilibration chambers called theoretical plates. A theoretical plate is the volume of the column required for a complete equilibration between stationary (S) and mobile (M) phases, described by the distribution ratio or distribution coefficient

$$D_A = \frac{(C_A)_S}{(C_A)_M}$$

For a given chromatographic column with a particular type of stationary phase the number of theoretical plates is not a fixed number (as the number of tubes in a Craig apparatus) but depends on a number of factors, most important of them being the nature and the velocity of the mobile phase, kinetic factors involved in the distribution equilibrium and everything which can affect it (e.g. temperature, column packing) and the nature of A itself.

The ion-exchange is based on the reversible exchange between a stationary phase, synthetic resin, mobile phase, and the solution of the sample. Through the column which is filled with resin, the different ion from the sample can be separated, because they have the different affinity with the resin.

After the digestion the PGEs will be in the state of chloro-complexes, and the on–line separation of these complexes permits highly selective determination of concentration via isotope dilution. Through monitoring the transient signal it is possible to select only interference free sections of the peak and hence select a plateau for ratio averaging. Through the measurement of three isotopes (Pd, Ru and Pt) it is possible to calculate concentrations via more than one isotope ratio, thus allowing to test for undetected interferences if concentrations do not agree (Meisel, 2001)

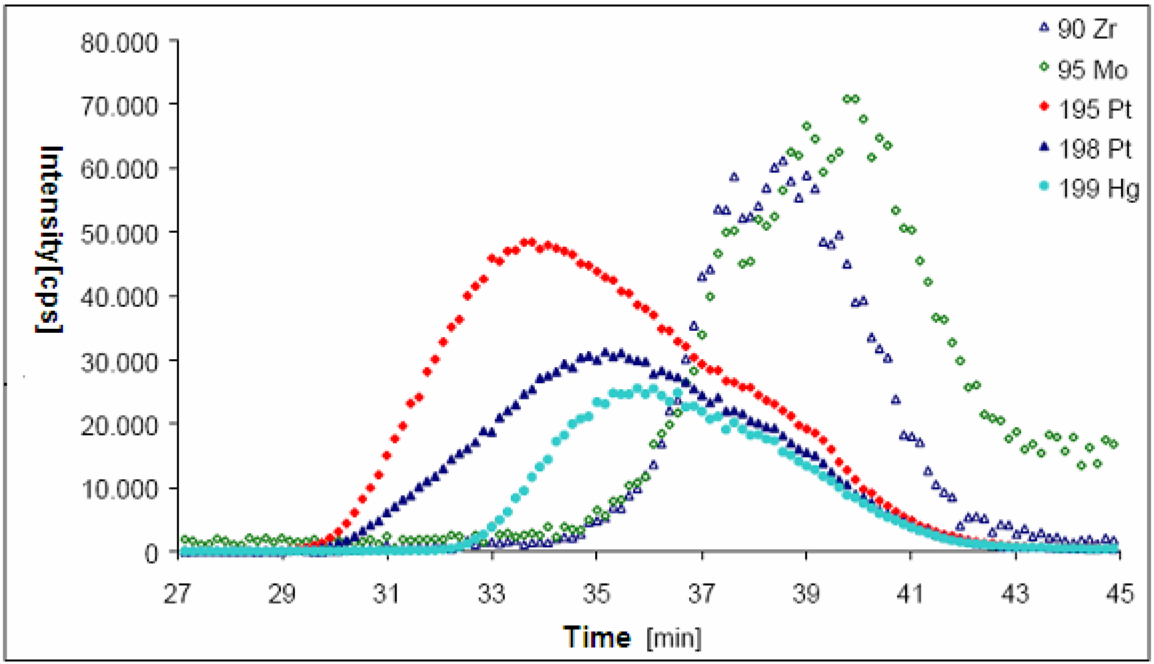


Figure 5: The comparison of different isotopes after chromatographic separation

3.2 Detection methods of the platinum group elements

A number of analytical methods have been used for the determination of the platinum group elements. Among them, the most sensitive apparatuses include inductively coupled plasma mass spectrometry (ICP-MS) , inductively coupled plasma atomic emission spectrometry (ICP-AES) electrothermal atomic absorption spectrophotometry (ETAAS), cathodic stripping voltammetry (CSV), neutron activation analysis (NAA) and laser-excited atomic activation analysis (LEAFS).

3.2.1 Inductively coupled plasma-mass spectrometry

3.2.1.1 General

ICP-MS is an acronym for Inductively Coupled Plasma - Mass Spectrometry: a fast, precise, accurate, and extremely sensitive multielement analytical technique for the determination of trace elements in a variety of liquid and solid sample materials. Chemical analysis with inductively coupled plasma (a state of the matter containing electrons and ionized atoms) is based on the principles of vaporization, dissociation, and ionization of chemical elements when introduced into the hot plasma. These ions can be then separated according to their mass/charge ratios by a high resolution magnetic sector mass analyzer and detected, multiplied, and counted using fast digital electronics.

ICP-MS was first developed in the early 80's and now is increasingly becoming the analytical tool of choice over such techniques as Atomic Absorption Spectrometry (AAS), ICP-Atomic Emission Spectrometry (ICP-AES) and Neutron Activation Analysis (NAA). ICP-MS is a successful, state-of-the-art hybrid of the two classical analytical techniques: ICP and MS. It surpasses most heavy metals detection techniques that are commercially available in terms of:

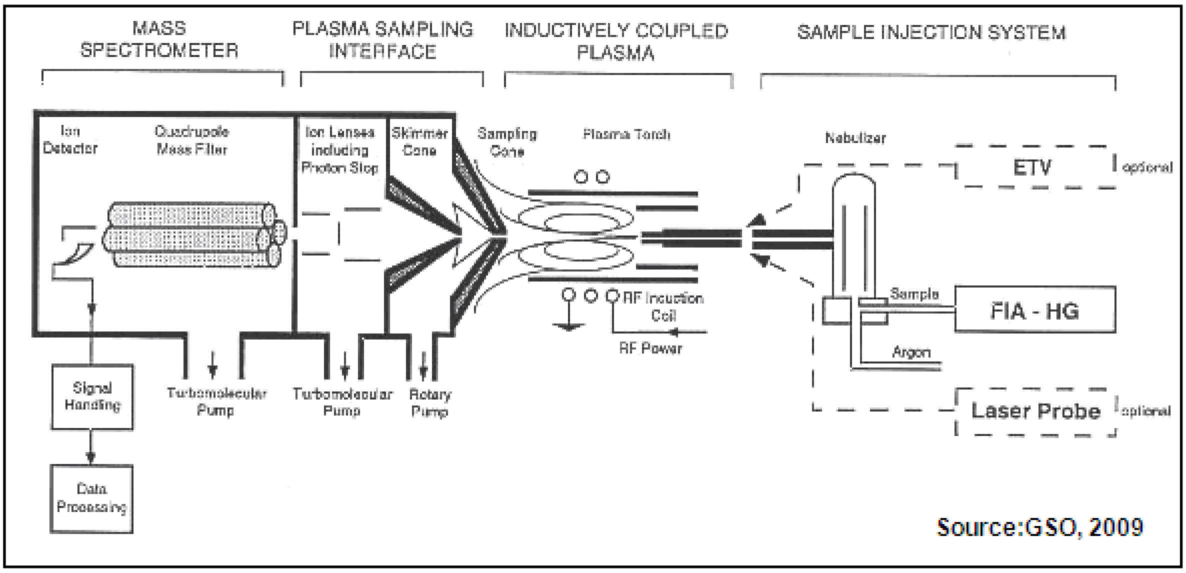
- sensitivity
- speed of analysis
- versatility
- simplicity of operation

In ICP-MS, elemental abundances or isotopic ratios are determined by the mass spectrometry (MS) of ions generated in inductively coupled Ar plasma (ICP).

As shown on the figure 6, the ICP-Mass Spectrometer consists of several integrated components:

- sample injection system,
- inductively coupled plasma,
- plasma sampling interface,
- mass analyzer,
- detector,
- computer.

Using a stream of Ar carrier gas, liquid or solid sample from sample injection systems is introduced into hot plasma which serves as an efficient source of positively charged analyte ions. The Ar plasma is generated and maintained at the end of the glass torch located inside the loops of a water cooled copper load coil. A radio frequency (RF) potential applied to the coil produces an electromagnetic field in the part of the torch located within its loops. A short electric discharge from a wire inside the torch provides the electrons to ignite the plasma. In the electromagnetic field of the load coil these electrons are accelerated and collide with Ar atoms in the Ar gas flowing through the torch producing Ar^+ ions and free electrons. Further collisions cause an increasing number of Ar atoms to be ionized and result in the formation of plasma. The plasma-forming process rapidly becomes self-sustaining and may be maintained as long as Ar gas continues to flow through the torch.



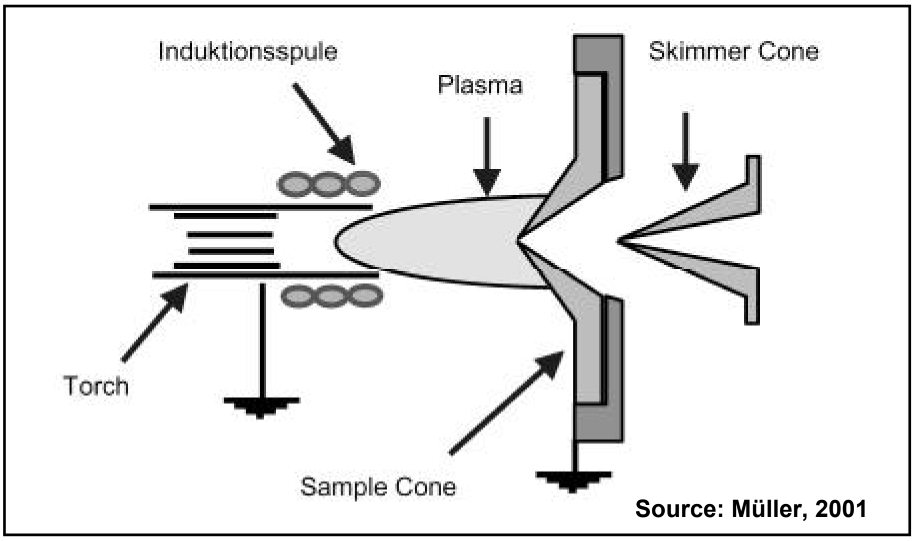
Source:GSO, 2009

Figure 6: The integrated components of the ICP-MS

The development of the interface region was crucial in the development of ICP-MS instruments. The main problem lies in the fact that the ions have to be extracted from the high temperature (~ 6000K or more), atmospheric pressure ($1.013*10^5$Pa) environment of often chemically corrosive Ar plasma into a mass spectrometer operating in a high vacuum ($1.34*10^{-3}$ Pa) at room temperature. The interface region contains two successive Ni cones with millimeter-sized orifices through which the ions in the center of the plasma may be sampled. The ions are first extracted trough the orifice of the sample cone into the region between two cones held at a pressure of about 130-400Pa by a large capacity rotary vacuum pump. At this stage, most of the Ar atoms are removed by a vacuum pump. The ion beam is further extracted through the orifice of the skimmer cone into the front section of the mass spectrometer chamber that is maintained at a pressure of about 0.13-0.013 Pa by a large turbo molecular vacuum pump.

Focused by an ion lens system, analyte isotopes are separated according to their mass/charge ratio by either a quadrupole or magnetic sector mass analyzer. Ions with specific m/z ratios are transmitted sequentially to the ion detection system. Ions with lower or higher mass/charge ratios have different trajectories and are lost ("filtered").

The ion detection and counting system consists of an electron multiplier used in a dual-gain pulse counting mode or low gain analog mode depending on the ion-beam intensity. The most commonly used type of detector in ICP-MS is an electron multiplier. The signal intensity is measured simultaneously at two different points in the detector. In the upper, analog stage of the detector, the signal is measured as a current which is subsequently converted into a count per second (cps) equivalent. This stage is responsible for measuring high intensity signals. The lower, pulse stage of the detector measures low intensity signals as cps. To prevent detector damage and prolong its life span, signals of exceedingly high intensities are prevented from entering the detector.



Source: Müller, 2001

Figure 7: The schematic map for the interface of ICP-MS

The ICP-MS instrument is computer controlled. The computer controls various hardware components as well as acquisition, storage, display and processing of the data

3.2.1.2 Interference effects and their elimination

Although ICP-MS is rapidly becoming the analytical technique of choice for the determination of PGE, a large number of principally spectroscopic interferences present major problems in their accurate determination (Table 3). The degree of interference is enhanced due to typical concentrations of interference forming elements in road dusts, river sediments and airborne particulates often being several orders of magnitude higher than those of the PGE (Rauch et al., 2000b). To overcome these problems a number of approaches have been attempted including modified sample introduction systems, instrument optimization, the use of high resolution ICP-MS (HR-ICP-MS), mathematical corrections, both off and on-line matrix separation and using dynamic reaction or collision cells.

The main sources of spectral interferences in ICP-MS are:

- Direct overlap from a different element with an isotope at the same nominal mass known as an isobaric interference, e.g. ^{114}Sn overlap on ^{114}Cd
- Overlap from a polyatomic ion formed from the combination of species derived from the plasma gas, sample solvent and/or sample matrix e.g. $^{40}Ca^{16}O$ overlap on ^{56}Fe
- Doubly-charged species resulting from ions created by the loss of two electrons instead of just one. Because the quadrupole separates ions based on m/z (mass over charge ratio), a doubly-charged ion (M^{2+}) will appear at mass M/2. An example of a doubly-charged interference would be the $^{136}Ba^{2+}$ overlap on $^{68}Zn^{+}$.

There are many ways to remove or correct for spectral interferences. The easiest way to avoid a direct isobaric overlap is to choose another (interference free) isotope of the element of interest, if available. Oxides (MO^{+}) and doubly charged species (M^{2+}) can be significantly reduced through proper tuning of the plasma and torch conditions, and by good plasma design.

Table 3: Possible spectral interference of the PGEs

Isotope	Possible interference	Isotope	Possible interference
^{99}Ru	^{83}Kr^{16}O, ^{82}Kr^{17}O , ^{82}Se^{17}O ^{59}Co^{40}Ar, ^{61}Ni^{38}Ar ^{64}Ni^{35}Cl, ^{64}Zn^{35}Cl ^{98}Mo^{1}H , ^{98}Ru^{1}H ^{49}Ti^{50}Ti	^{108}Pd	^{92}Zr^{16}O, ^{90}Zr^{18}O, ^{92}Mo^{16}O ^{68}Zn^{40}Ar, ^{70}Zn^{38}Ar ^{71}Ga^{37}Cl, ^{73}Ge^{35}Cl ^{107}Ag^{1}H ^{54}Cr^{54}Cr, ^{54}Fe^{54}Fe
^{101}Ru	^{83}Kr^{18}O, ^{85}Rb^{16}O ^{61}Ni^{40}Ar ^{63}Cu^{38}Ar ^{66}Zn^{35}Cl, ^{64}Zn^{37}Cl, ^{64}Ni^{37}Cl ^{100}Mo^{1}H, ^{100}Ru^{1}H ^{50}V^{51}V ^{84}Sr^{16}O^{1}H	^{191}Ir	^{175}Lu^{16}O, ^{173}Yb^{17}O, ^{173}Yb^{18}O ^{155}Gd^{36}Ar ^{156}Gd^{35}Cl, ^{154}Gd^{37}Cl, ^{156}Dy^{35}Cl, ^{154}Sm^{37}Cl ^{190}Pt^{1}H, ^{190}Os^{1}H ^{97}Mo^{94}Mo
^{102}Ru	^{86}Sr^{16}O ^{62}Ni^{40}Ar ^{154}Sm^{40}Ar, ^{65}Cu^{37}Cl ^{85}Sr^{16}O^{1}H	^{193}Ir	^{177}Hf^{16}O, ^{176}Hf^{17}O, ^{176}Lu^{17}O, ^{175}Lu^{18}O, ^{176}Yb^{17}O ^{155}Gd^{38}Ar ^{156}Gd^{37}Cl, ^{156}Dy^{37}Cl, ^{158}Dy^{35}Cl ^{192}Pt^{1}H, ^{192}Os^{1}H ^{98}Mo^{95}Mo, ^{96}Mo^{97}Mo
^{103}Rh	^{87}Rb^{16}O, ^{87}Sr^{16}O ^{66}Zn^{37}Ar, ^{67}Zn^{36}Ar, ^{63}Cu^{40}Ar, ^{65}Cu^{38}Ar ^{68}Zn^{35}Cl ^{102}Pd^{1}H, ^{102}Ru^{1}H ^{51}Cr^{52}Cr ^{86}Sr^{16}O^{1}H	^{194}Pt	^{178}Hf^{16}O, ^{177}Hf^{17}O, ^{176}Hf^{18}O, ^{176}Yb^{18}O, ^{176}Lu^{18}O ^{154}Gd^{40}Ar, ^{156}Gd^{38}Ar, ^{158}Gd^{36}Ar ^{157}Gd^{37}Cl, ^{159}Tb^{35}Cl ^{193}Ir^{1}H ^{100}Mo^{94}Mo, ^{98}Mo^{96}Mo
^{105}Pd	^{87}Rb^{18}O, ^{87}Sr^{18}O, ^{88}Sr^{17}O, ^{89}Y^{16}O ^{65}Cu^{40}Ar ^{70}Zn^{35}Cl, ^{68}Zn^{37}Cl ^{104}Ru^{1}H, ^{104}Pd^{1}H ^{52}Cr^{53}Cr ^{88}Sr^{16}O^{1}H	^{195}Pt	^{179}Hf^{16}O, ^{178}Hf^{17}O, ^{177}Hf^{18}O ^{155}Gd^{40}Ar, ^{157}Gd^{38}Ar, ^{159}Tb^{36}Ar ^{160}Gd^{35}Cl, ^{160}Dy^{35}Cl, ^{158}Dy^{37}Cl ^{194}Pt^{1}H ^{98}Mo^{97}Mo
^{106}Pd	^{90}Zr^{16}O, ^{88}Sr^{18}O, ^{89}Y^{17}O ^{66}Zn^{40}Ar	^{198}Pt	^{182}W^{16}O ^{198}Hg

Source: Zischka, 1998

Interference equations

Interference equations are mathematical equations used to correct elemental, polyatomic and doubly charged isobaric interferences in ICP-MS analysis. They are based on the fact that the relative abundances of the naturally occurring isotopes of almost all elements are fixed in nature and are not changed through any sample preparation or analysis techniques.

Because natural isotopic abundances are known and constant, isobaric overlaps are predictable and, where an alternative, uninterfered isotope is either unavailable or too small in abundance, mathematical correction can be used to correct for isobaric spectral overlaps.

Although this type of correction can also be used for polyatomic interferences, the intensity of polyatomic species can vary with tuning, and many corrections need to go through more than one level of measurement and calculation to obtain a concentration value for the target element, leading to a level of uncertainty in the result.

The most serious limitation of this type of correction equation is that it cannot deal with the common situation where interferences appear at one of the intermediate masses used in the calculation.

Collision/Reaction Cell (CRC) ICP-MS

The CRC devices in commercial ICP-MS instruments have been designed to remove polyatomic species, and were developed either through the need to find an alternative to cool plasma for the semiconductor industry or, in the case of Agilent, to extend the application of ICP-MS to the most complex and difficult sample types. Since the introduction of CRC ICP-MS in the late 1990s, the CRC configuration has become the standard in ICP-MS, such that the vast majority of all ICP-MS currently shipped are CRC systems.

Some CRC designs utilize very specific, single-element conditions to selectively and efficiently remove a single interfering species, using highly reactive gases and complex but theoretically predictable reaction pathways. Such instruments were developed as an alternative to cool plasma in the semiconductor industry, where the sample matrix is low, predictable and constant and the analyte concentrations are typically also very low. Other approaches use less reactive gases but more generic interference removal methods. The latter approach has proved suitable for the measurement of multiple analytical elements in complex and variable sample matrices, where the source and level of potential interferences cannot easily be predicted in advance.

3.2.1.3 Isotope dilution

Isotope dilution was used to quantify amounts of chemical compounds, first by applying radioactive isotopes and later by using stable isotopes. This powerful technique has now been applied many times, for different purposes and using different instrumental methods to quantify the isotope ratios. Primarily, the latter has been achieved using mass spectrometry (IDMS), although other isotope-specific techniques can be used (e.g. gamma ray spectrometry in combination with neutron activation). There have been two significant driving forces in the development of isotope dilution: the need for reliable measurements in the areas of geochronology and nuclear chemistry (Vanhaecke, 1999).

Contrary to many other approaches in analytical chemistry, isotope dilution makes full use of the existence of isotopes. Therefore, from a first principles point of view, quantifying chemicals via this route offers some quite unique advantages, especially for providing reference measurements.

By inducing a deliberate change in a chosen isotope ratio of an element, it is possible to measure the amount or the concentration of a particular chemical compound in the sample studied. For this purpose, an amount of this chemical is add to the sample (the spiking process). The isotope composition of the element in this spike or trace needs to be sufficiently different from the one in the sample.

For example, for measuring of the concentration of platinum in a sample via addition of the spike solution, the following equation holds (Moser, 2004):

$$\left[\frac{{}^{194}\mathrm{Pt}}{{}^{195}\mathrm{Pt}}\right]_{\mathrm{dilution}}=\frac{{}^{194}\mathrm{Pt}_{\mathrm{sample}}+{}^{194}\mathrm{Pt}_{\mathrm{spike}}}{{}^{195}\mathrm{Pt}_{\mathrm{sample}}+{}^{195}\mathrm{Pt}_{\mathrm{spike}}}=\frac{{}^{194}\mathrm{a}_{\mathrm{sample}}.\mathrm{N}_{\mathrm{Pt,sample}}+{}^{194}\mathrm{a}_{\mathrm{spike}}.\mathrm{N}_{\mathrm{Pt,spike}}}{{}^{195}\mathrm{a}_{\mathrm{sample}}.\mathrm{N}_{\mathrm{Pt,sample}}+{}^{195}\mathrm{a}_{\mathrm{spike}}.\mathrm{N}_{\mathrm{Pt,spike}}} \quad (1)$$

$\mathrm{Pt}_{\mathrm{sample}}$, $\mathrm{Pt}_{\mathrm{spike}}$: Amount of the platinum from the sample and spike

$\mathrm{a}_{\mathrm{sample}}$, $\mathrm{a}_{\mathrm{spike}}$: Part of the platinum in the sample and spike

$\mathrm{N}_{\mathrm{Pt,sample}}$, $\mathrm{N}_{\mathrm{Pt,spike}}$: Amount of the platinum in the sample and spike

$$\mathrm{N}_{\mathrm{Pt,sample}}=\mathrm{N}_{\mathrm{Pt,spike}}\cdot\frac{{}^{194}\mathrm{a}_{\mathrm{spike}}-{}^{195}\mathrm{a}_{\mathrm{spike}}\cdot\left[\frac{{}^{194}\mathrm{Pt}}{{}^{195}\mathrm{Pt}}\right]_{\mathrm{dilution}}}{{}^{195}\mathrm{a}_{\mathrm{sample}}\cdot\left[\frac{{}^{194}\mathrm{Pt}}{{}^{195}\mathrm{Pt}}\right]_{\mathrm{dilution}}-{}^{194}\mathrm{a}_{\mathrm{sample}}} \quad (2)$$

$$\mathrm{N}_{\mathrm{Pt,spike}}=\frac{m_{\mathrm{spike}}}{AM_{\mathrm{Pt,spike}}}.c_{\mathrm{Pt,spike}} \quad (3)$$

$C_{\mathrm{Pt,spike}}$: the concentration of the platinum in the spike

The concentration of the platinum in the original sample is:

$$[\mathrm{Pt}]_{\mathrm{sample}}=\frac{\mathrm{N}_{\mathrm{Pt,sample}}.AM_{\mathrm{Pt,sample}}}{m_{\mathrm{sample}}} \quad (4)$$

Through the combination of the equation (2), (3) and (4), the concentration of the platinum is:

$$[\mathrm{Pt}]_{\mathrm{sample}} = c_{\mathrm{Pt,spike}} \cdot \frac{m_{\mathrm{spike}} . AM_{\mathrm{Pt,sample}}}{m_{\mathrm{sample}} . AM_{\mathrm{Pt,spike}}} \cdot \frac{{}^{194}\mathrm{a}_{\mathrm{spike}} - {}^{195}\mathrm{a}_{\mathrm{spike}} \cdot \left[\frac{{}^{194}\mathrm{Pt}}{{}^{195}\mathrm{Pt}}\right]_{\mathrm{dilution}}}{{}^{195}\mathrm{a}_{\mathrm{sample}} \cdot \left[\frac{{}^{194}\mathrm{Pt}}{{}^{195}\mathrm{Pt}}\right]_{\mathrm{dilution}} - {}^{194}\mathrm{a}_{\mathrm{sample}}}$$

(5)

$\mathrm{AM}_{\mathrm{sample}}$, $\mathrm{AM}_{\mathrm{spike}}$: Atomic mass of the platinum

$\mathrm{m}_{\mathrm{sample}}$, $\mathrm{m}_{\mathrm{spike}}$: the weight of the sample and spike

Compare to other calibration method reveals isotope dilution following advantage:

- Not susceptible to temporal changes in sensitivity or to matrix-induced changes in sensitivity.
- Isotope ratios can be measured reproducibly, isotope dilution results in a small uncertainty on the assay.
- In the blend are the isotope ratios always constant after isotopic equilibration, so that it is not affected by further sample treatment or the loss of the sample.

3.2.2 Atomic absorption spectrometry (AAS-GFAAS)

In GFAAS analysis, usually a small volume (typically 20 ml) of the sample solution, or solid sample (0.1–1.0 mg) is dispensed into a graphite atomizer mounted in the optical path of an absorption spectrometer. Using electrothermal heating of the graphite atomizer, the sample is pre-treated (dried, pyrolyzed) for the removal of the matrix constituents, and then atomized to produce free atomic vapour of the analyte. Graphite atomizers provide nearly a 100 to 1000-fold increase in the residence time of the sample vapors in the optical path compared to flame and ICP excitation–atomization sources. Certainly, a lower dilution of the sample vapor prevails for the analyte, as well as for the matrix constituents, which entails greater gas–phase (chemical) interferences.

The GFAAS determination of PGEs required high atomization temperature due to the high vaporization temperature of the PGE compounds. It is to be noted here that for small sample amounts, i.e., below the microgram mass-range, the vaporization of the sample constituents take place around their melting points rather than their boiling points. Several matrix constituents especially chloride salts of transition metals, have been reported to cause interference effects with GFAAS measurements (Bencs, 2006)

3.2.3 Voltammetry

The development of adsorptive voltammetric techniques for the determination of Pt in the late 1980s and early 1990s made it possible to measure ultra-trace levels of platinum in biological and environmental samples. The method is most commonly based on the pre-concentration of a platinum-formazone (a condensation product of formaldehyde and hydrazine) complex at the surface of a hanging mercury drop electrode (HMDE) in a sulphuric acid medium, followed by cathodic stripping voltammetry. The electrochemically active complex formed at the surface of the HMDE serves as a catalyst for the reduction of protons. This lowers the hydrogen overpotential at the electrode and produces a very sensitive current at a potential of ~ -0.85V that is measured in differential pulse mode (Whiteley, 2004).

3.2.4 Total reflection X-ray fluorescence

For the accurate analysis of PGE common analytical techniques face a number of difficulties. Applying wavelength XRF, the sample preparation is often complicated, the number of certified reference standards is limited and the detection limits are not sufficient in many cases. Atomic spectroscopy strictly requires digestion of the sample material. Additionally, there is always the risk of long system down-times after a concentrated sample was introduced accidentally.

In contrast TXRF is an ideal technique for PGE analysis due to the ability to process solid and liquid samples. Major benefits are the quantification, based only on internal standardization, and a broad analytical range, which allows the accurate analysis from low ppb up to % concentrations.

A low-power benchtop TXRF spectrometer was used for the analysis of different sample types including Pt-bearing ores, catalysts, wash-coats, bloods and docimastic digestion solutions. The results clearly indicate the suitability of this technique for an accurate PGE analysis in different sample types (Stosnach, 2009).

3.2.5 Neutron activation analysis (NAA)

Neutron Activation Analysis (NAA) is a quantitative and qualitative method of high efficiency for the precise determination of a number of main-components and trace elements in different types of samples. NAA, based on the nuclear reaction between neutrons and target nuclei, is a useful method for the simultaneous determination of about 25-30 major, minor and trace elements of geological, environmental, biological samples in ppb-ppm range without or with chemical separation.

In NAA, samples are activated by neutrons. During irradiation the naturally occurring stable isotopes of most elements that constitute the rock or mineral samples, biological materials are transformed into radioactive isotopes by neutron capture. Then the activated nucleus decays according to a characteristic half-life; some nuclides emit particles only, but most nuclides emit gamma-quanta, too, with specific energies. The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma-ray lines in the spectra.

The indisputable advantage of the method is its sensitivity and accuracy especially in respect of some trace elements. The method is of a multielement character, i.e. it enables the simultaneous determination of many elements without chemical separation. In the case of instrumental determination, the preparation of samples involves only the preparation of representative samples, i.e. pulverization or homogenization in most cases, and this reduces the danger of contamination to a minimum and accelerates the whole analytical process (Monar, 2009).

4 Sampling

For the research of the distribution of PGE in Austria 31 samples will be taken from 15 sample sites in Styria and Tyrol, and most of these are located in the edge of the highway or near the highway. The coordinate of each sample site are shown in the supplement with satellite images or the maps. There are also some samples from non-polluted area, for example, in the forest. They were investigated as the reference of the PGE measurement for the aim of the comparison with the roadside samples.

Table 4: The list of all the samples

Sample Nr.	Sort of the sample	Sample site
BP01	roadside soil	Etschmayerstreet, Leoben
BP02	roadside soil	Etschmayerstreet, Leoben
BP03	roadside soil	Etschmayerstreet, Leoben
BP04	roadside soil	Highway A2,Bridge 32
BP05	roadside soil	Highway A2,Bridge 32
SLP01	Sludge from infiltration basin	Etschmayerstreet, Leoben
SLP02	Sludge from infiltration basin	Highway A2,Bridge 45
SLP03	Sludge from infiltration basin	Highway A2,Bridge 45
SLP04	Sludge from infiltration basin	Highway A2,Bridge 45
SLP05	Sludge from infiltration basin	Highway A2,Bridge 45
SLP06	Sludge from infiltration basin	Highway A2,Bridge 32
SNP01	roadside snow	Highway A13, Garberbach
SNP02	roadside snow	Highway A12, Vomp
SNP03	roadside snow	Achensee national road B181
SNP04	roadside snow	Tuxer Landesstreet L6
SNP05	roadside snow	Gerlos national road B165
SNP06	roadside snow	Zillertal national road B169
SNP07	roadside snow	Zillergrund
KGP01	street sweeping	Etschmayer crossing, Leoben
KGP02	street sweeping	Etschmayer crossing, Leoben
KGP03	street sweeping	Annaberger crossing, Leoben
KGP04	street sweeping	Annaberger crossing, Leoben
KGP05	street sweeping	Jakobi crossing, Leoben
KGP06	street sweeping	Jakobi crossing, Leoben
KGP07	street sweeping	Tivoli crossing, Leoben
KGP08	street sweeping	Tivoli crossing, Leoben
KGP09	street sweeping	Prettachfeld, Leoben
KGP10	street sweeping	Sludge from the sewage treatment plant of the street sweepings
KGP11	street sweeping	Highway A2, Bridge 40
WP01	road runoff	Etschmayerstreet, Leoben

The sorts of the sample are not only roadside soil, but also roadside snow with the dust and the sludge from roadside drain as well as the urban street sweepings. For each sort of the sample there is a different samplings strategy. The followings are the complete introduction for all sample collection and the sampling sites.

4.1 Roadside soil

The soil is usually not homogeneous, so we always took as large amount of soil as possible. To ensure the representativeness of the sample, we collected a lot of subsamples from one area and then mixed all the samples together.

4.1.1 Sample collection

The first two soil samples (BP01 and BP02) along the edge of the bridge on the S6 road over the Etschmayer Street were collected with the prick cylinder (Figure 8) in two depth levels The first level is 0-5cm and the second is 5-10cm. 15 subsamples were collected into the polyethylene-bags and the distance between each sampling spot is 30cm (see figure 9).

Figure 8: prick cylinder and plastic spoon

The third sample (BP03) was the road dust which was flushed by the rainwater from the bridge to the underneath. It was also collected as described above.

The other two samples (BP04 and BP05) were the soil under the bridge 32 from highway A2. 15 subsamples were collected with prick cylinder and the depth level was 0-5cm. The distance between each sampling spot is 50cm.

4.1.2 Sample site

To choose the sampling sites, it is important to know the traffic density and the type of the vehicle on the road. In this thesis, the sampling sites were chosen near the major urban roads and their intersections.

Figure 9: Sample site of the soil sample (BP01 and BP02)

4.1.2.1 Etschmayer S6

The bridge 32 is located on the highway S6 and over the Etschmayer Street. Highway S6 is the entrance of Leoben, the traffic density on it is about 6000 vehicles/day (ASFINAG, 2009). During the raining time, the road dust is always flushed by the rainwater to the underneath part. Therefore there is the accumulation of the road dust in the soil not only from air but also from water. The soil here is humus with a lot of organic substance.

4.1.2.2 Highway A2

The bridge 32 is located on the highway A2. The Highway A2 is the longest highway in Austria. It connects the capital Vienna with Kärnten, and crosses 5 Austrian states. It is also the main route to the south of Europe. In the summer a lots of Austrian drive through the A2 to Italy and Croatia. On the other hand it connects Vienna and Graz, and also an important way for economy and transport. Therefore the traffic density on this highway is relative high, about 14000-16000 vehicles/day (ASFINAG, 2009). The soil under the bridge 32 is loamy and easy to be sampled.

4.2 Roadside snow

Usually the roadside soil are taken as the sample to investigate the PGE distribution, but the soil samples have some shortcomings, such as the disturbance of the nature abundance, heterogeneity, long time for sample preparing and so on. Therefore it is important to search other sample sources. In winter, the dust flies from road onto the roadside snow and accumulates in the snow. If the snow which is staying beside the road for a long time is collected, one can obtain the pure road dust by separating the molten snow with filter. The snow samples have less interference than the soil samples and the preparation is also easy to operate.

4.2.1 Sample collection

All the snow samples were collected with prick cylinder in depth level 0-10cm and stored in plastic boxes. Overall there are 20 subsamples from each sample site. The distance from the sampling spot to the road is about 1m, and the distance between each sampling spot is 50cm (see figure 10). The detailed information of the each sample will be described in the table 5.

Figure 10: Sample site and sampling spot of the snow sample (SNP01, beside Highway A13)

4.2.2 Sample sites

All the snow samples were collected in Tyrol, which is famous because of the tourism and perfect place to ski. There is plenty snow in the winter and the snow remains for long periods of fine because of low temperature. The snow, from which the sample were collected, is very old snow, and remained beside the road at least for three weeks even over one month. The other reason to choose Tyrol is the high traffic density (see figure 11) in the winter, because a lot of people drive to ski in Tyrol. Table 5 gives informations on the 7 sample sites.

4.3 Street sweepings

Besides the roadside snow the urban street sweeping is also an ideal source, although it contains interference from external environment. Usually, it consists of complex fractions. The street sweeping includes many different substances such as gravel, leaves, rubbish and so on. But through sieving and drying one can get the fine fraction as the sample to analyze. Moreover if one collects the leaves in the autumn, it is very helpful for the investigation of the PGE distribution in the plants (see figure 12).

Figure 11: High traffic density on the Zillertal national road

Table 5: The sample sites of the roadside snow

Sample Nr. and site	Traffic density	Comment
SNP01, Highway A13, Garberbach	22000vehicle/day[1)]	Important route between Germany and Italy, from Kufstein to Brennerpass,
SNP02, Highway A12, Vomp	21000vehicle/day[1)]	Important route between Austria and Germany
SNP03, Achensee national road B181	High	The way to the famous lake, Achen Lake
SNP04, Tuxer local road L6	Normal	The route to the ski resort, high traffic density in the winter
SNP05, Gerlos national road B165	Normal	Mountain road to the Tyrol, also a important route to the east Austria and Germany
SNP06, Zillertal national road B169	Very high	The way, which connect many tourist city and ski resort, in the winter have a very high traffic load.
SNP07, Zillergrund	Almost null	The spot in the forest near the Ziller river, it has very low traffic density, the snow is white and clean

1) Data from the website of ASFINAG, 2009

Figure 12: The collected sample from Street sweeping (KGP08, Tivoli crossing)

4.3.1 Sample collection

The cleaning department of the city Leoben has swept the main urban street in April 2009. The street sweeping was collected by sweep machine from four crossings and stored in the plastic tub. From each crossing two samples were collected. One was the sweepings from street (KGP 01, 03, 05, 07, 09); the other is the sweepings from the drain under the grate beside the roads (KGP 02, 04, 06, 08). Moreover the sample was also collected from the sewage plant of sweepings (KGP10).

The last sample (KGP11) of street sweeping was collected from the heap of the street sweeping near the Herzogberg tunnel (see figure 13), which was swept from bridge 40 on the highway A2. The sweep area is about 400m^2 (width: 1m, length: 400m). Ten subsamples were collected with prick cylinder on the heap and stored in polyethylene bags.

4.3.2 Sample sites

The four crossings are all the crossings of the main urban streets in Leoben, which have a relative high traffic density. The following are the introduction of each sample site:

Etschmayer Crossing (KGP01 and KGP02): it is an important collection between the highway from Vienna and Graz to Leoben and street in Leoben. It is also near the logistic center of Leoben, and therefore it has a very high traffic density.

Annaberg Crossing (KGP03 and KGP04): it is the district between Donawitz and Leoben, and consequently an industrial zone. The crossing is near the Donawitz steel plant, and the traffic density is normal.

Jakobi Crossing (KGP05 and KGP06): is near the center of Leoben, because of this reason it has a high density of the passed vehicles.

Tivoli Crossing (KGP07 and KGP08): it links the two major streets in Leoben together. Almost all the autos in Leoben pass through this crossing.

Prettachfeld (KGP09): it is an important water runoff collection of the roads in west of Leoben.

Bridge 40, A2 (KGP11): the bridge 40 is located on the highway A2. Information about highway A2 is given in chapter 4.1.2.2

Figure 13: The street sweepings from highway A2 (KGP11)

4.4 Sludge in the infiltration basin and roadside drain

Similar to the roadside soil, the sludge, which is in the infiltration basin and roadside drain, is also an important sample to study the PGE distribution. A number of the studies show the urban road runoff is becoming contaminated by the vehicle derived platinum group elements. Of all of these, the highest levels of PGE were found in the sediments of infiltration or catch-basin (Whiteley and Murray, 2004).

Through the examination of the PGE distribution in the sludge, one can assess the degree and spatial pattern of PGE contamination in urban environments receiving road runoff. Additionally by comparing PGE ratios and concentrations of PGE in infiltration basin and roadside with those obtained from road dusts collected at nearby locations, is to determine whether PGE fractionation is occurring during transport.

4.4.1 Sample collection

Overall six sludge samples were collected from three sample sites. The first sample (SLP01) was collected from the runoff pipe (see figure 14) with the plastic spoon and stored in polyethylene bags

Figure 14: The roadside drain beside S6 and the sludge in the runoff pipe (SLP01)

The second and third sample (SLP02 and SLP03) were collected from sediments of the infiltrations basin under the bridge 45 on the highway A2 (see figure 15). Meanwhile, fourth and fifth sample (SLP04 and SLP05) were collected from runoff pipe beside the basin. All the samples were collected in polyethylene bags.

Figure 15: The infiltration basin under the bridge 45 (SLP 02, 03, 04, 05)

The last sample (SLP06) was collected with prick cylinder from infiltration basin under the bridge 32 on highway A2, and the sample were also collected in the polyethylene bags.

4.4.2 Sample sites

The samples were collected from the range of the highway A2 and S6, the information about these two principal roads can be read in chapter 4.1.2.

5 Sample preparation and analysis

All the samples were measured by ICP-MS after the isotope dilution method and digestion of acid. To ensure the low blind value the application of the chemical agents and the steps of the operation were as less as possible. The spectral interference was reduced through the connection of online-ion exchanger to the ICP-MS. This method was developed by Thomas Meisel (Meisel et al., 2003) and it will be described in the following chapter. Additional measurement was applied using the XRF which is described as the complement at last.

5.1 Sample preparation

5.1.1 Preparation of the soil and street sweeping

The sample was dried at first in the air at ambient temperature for about two weeks, and then reduced in gramm size in an agate bowl. After this the sample was sieved to the fine fraction <2mm. The sieved sample was collected and separated into smaller aliquots (about 50-80g) by the sample splitter. One part of the sample was milled to the fraction <0.02mm, and the fine sample was collected in plastic tube and stored in cool and dark condition.

5.1.2 Preparation of the sludge

The sludge contains more water than the soil, and therefore the sludge was put into drying oven and dried at 50 □ for about one day. Then it was dried in the air for about one week. The rest sample treatments were the same as that of soil.

5.1.3 Preparation of the snow

The molten snow water was filtered with cellulose membrane filter (0.45µm) at first to separate the road dust. The filter paper with road dust was dried in exsiccator and then was stored in a clean small plastic box. Before the storage of filtrate, 2ml concentrated nitric acid (65% subboiled) was added into the filtrate and then the filtrate was stored in closed polypropylene boxes and bottles. These containers were kept in the refrigerator.

All the molten snow water was dried in PFA vials (50ml) to remove the water, and the residue was prepared for the digestion.

5.2 Reference materials and reagents

5.2.1 Reference materials

Overall three well characterized reference materials were applied to evaluate the result in this experiment. They were OKUM (GEO LABS, Ontario), BRC-723 (IRMM, Geel) and TDB-1 (CCRMP-CANMET, Ottawa).

OKUM is an ultramafic komatiite collected at Serpentine Mountain in McArthur Township, 25 km south of Timmins, Ontario. The sample consists of black massive rocks composed of randomly oriented spinifex blades 5-10 cm long.

The reference material BCR-723 is the tunnel dust from Tanzenberg tunnel in Styria. It was chosen because the content of the Pt, Pd and Rh in the dust was similar to the concentration in the investigated samples.

TDB-1 was obtained from Tremblay Lake, Saskatchewan, Canada. This diabase rock is composed of a siliceous matrix containing numerous small masses, aggregates and discrete grains of titaniferous magnetite and ilmenite intimately associated with ferroan titanite.

The following table shows the certified PGE-concentration in the reference materials

Table 6: The certified PGE-concentration in the reference materials

	OKUM1)		**BCR-7232)**		**TDB-13)**	
	Concentration	Uncentainty	Concentration	Uncentainty	Concentration	Uncentainty
Rh	1.44	—	12.8	±1.2	0.4714)	—
Pd	12.00	—	6.0	±1.8	22.4	±1.4
Pt	11.19	—	81.3	±3.3	5.8	±1.1

Values in ng/g,

1) Data from GEO LABS in Canada.
2) Data from IRMM, Geel, Belgium.
3) Data from CCRMP-CANMET-MMSL, Ottawa, Canada
4) Data from the work of Meisel et al, 2004, not certified values

5.2.2 Reagents

Commercially available acids (suprapur Merck) were used throughout this study. Water (18 MΩ/cm) was purified with a reverse osmosis MilliQ system (Millipore). Quartz glass and PFA vials and vessels were employed during digestion and sample treatment.

5.2.3 Spike

An ideal spike has the following characteristics (Meisel et al., 2003):

- freedom of isobaric and molecular interference,
- highest possible enrichment of one isotope that has a low abundance in the natural element,
- minimized total uncertainty of the concentration determination.

The table 7 shows the PGE-concentration as well as Re-concentration in the spike, which was applied in the experiment, and the isotope abundance are shown in the table 8.

5.2.4 Standard solution

The standard solution (5 ng/g) of PGE was prepared from the standard solution (10µg/ml) of Ru, Rh, Re, Pd, Ir, and Pt. From this standard solution, 500µl solution was taken from each solution and then it was diluted using the 0.1 mol/l HCl in the1000ml volumetric flask.

Table 7: The concentration of PGE and Rhenium in the spike

	Ru	**Pd**	**Ir**	**Pt**	**Re**
Concentration(ng/g)	13.20	21.79	21.53	18.97	20.93

Table 8: The isotope abundance in the spike

Ru Isotope	**abundance**		**Pt Isotope**	**abundance**		**Pd Isotope**	**abundance**	
	Nature	spike		Nature	spike		Nature	spike
96	5.54	0.51	198	7.163	95.75	108	26.46	93.45
98	1.87	0.19	195	33.832	1.21	105	22.33	0.20
99	12.76	95.55	190	0.014	0.0008	102	1.02	0.00
100	12.60	1.09	192	0.782	0.01	104	11.14	0.06
101	17.06	0.58	194	32.97	0.82	106	27.33	5.68
102	31.55	0.71	196	25.242	2.21	110	11.72	0.61
104	18.62	0.32						
Ir Isotope	**abundance**		**Re Isotope**	**abundance**				
	Nature	spike		Nature	spike			
191	37.272	98.14	185	37.40	97.4			
193	62.728	1.86	187	62.60	2.6			

5.3 Digestion and preconcentration

5.3.1 Instruments

Microwave sample preparations system from Anton Paar (Company in Graz, Austria):

- Multiwave (Anton Paar Physica) with 3×50ml quartz vessels
- Anton Paar Multiwave 3000 with 4×100ml quartz vessels and 4×100ml PTFE vessels

5.3.2 Procedure

Precise results throughout the entire concentration range were analyzed by use of a novel analytical procedure described by Meisel et al. (2003). This procedure, which was originally developed for the analysis of geological materials, requires only a few sample preparation steps: Firstly, a corresponding amount of the multi-element spike solution was added to the sample (about 1g); Secondly, the samples in quartz glass vessels were then mixed with 2 ml conc. HCl and 5 ml conc. HNO_3; Thirdly, it was sealed and digested in the microwave preparation system.

The digestion in the Multiwave was separated in three steps:

- Preheating(0-800W, 15 min):
- Heating(800W, 60min)
- Cooling(0W,20min)

In the digestion procedure the temperature reaches about 250℃ and the highest pressure 80 bar. The following figure shows the whole process of the microwave digestion.

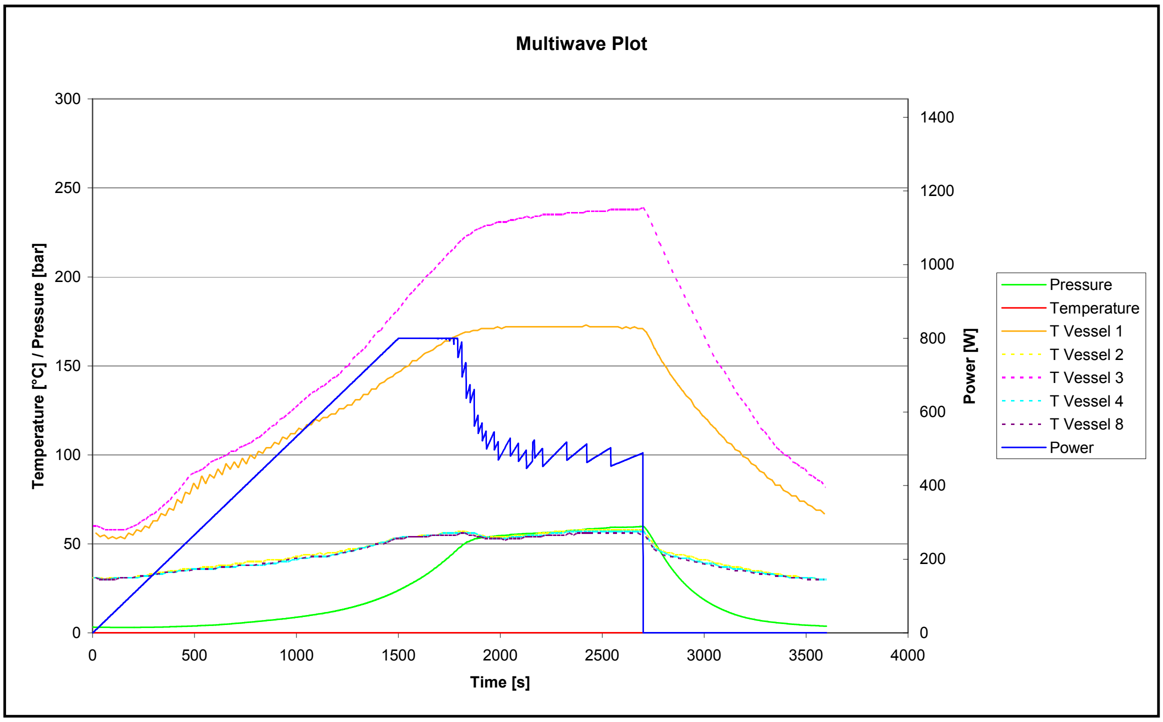


Figure 16: The tendency of power and temperature during the microwave digestion

In the following steps, undigested material was removed by centrifugation and the sample was dried in PFA vials (about 60℃) to remove most of the concentrated acid. The residue was then dissolved in approximately 2 ml of 0.1mol/l HCl and the resulting sample solution was separated from any solids using a syringe filter (0.45 µm). Finally, the samples were fed into a cation exchange column, which was directly coupled to the ICP-MS. Thus, the PGEs and Re were separated on-line from other matrix constituents and the measurement could be monitored for any interfering species of these constituents.

5.4 Chromatographic separation of the PGE

The analytical set up is shown in Figure 17 below. Luer low pressure fittings (PE or PC) were used for all connections of this set up. The chromatographic column consists of a PFA tube with the dimensions of 6.0 mm in outer diameter, 4.2 mm in inner diameter and 1 m in length, where the inner diameter is most important since it needs to fit the male luer of the 3-way stopcock (2 female luer to male luer; MPL-Sarstedt) and the 0.45 mm syringe filter tightly. (The filter is used mainly to keep the resin in the column and is preferred over a frit, since it can be removed easily.) The tube has a volume of approximately 13 ml and was filled (through gravitation) with the cation-exchange resin. The filter part of the column is connected via a male luer to the tubing of the peristaltic pump. The other part of the column is connected via a 3-way stopcock (2 female luer to male luer), a sample loop plus another 3-way stopcock (2 female luer to male luer) to a 53 ml Glass column (1.5×30 cm Econo-colum, Bio-Rad Laboratories) used as a 0.1 mol/l HCl eluent reservoir. Nitrogen gas with 2 bar pressure was applied onto the reservoir to push the mobile phase through the column whereas the flow rate was determined by the speed of the peristaltic pump of the sample introduction system (approx. 0.4 ml/min).

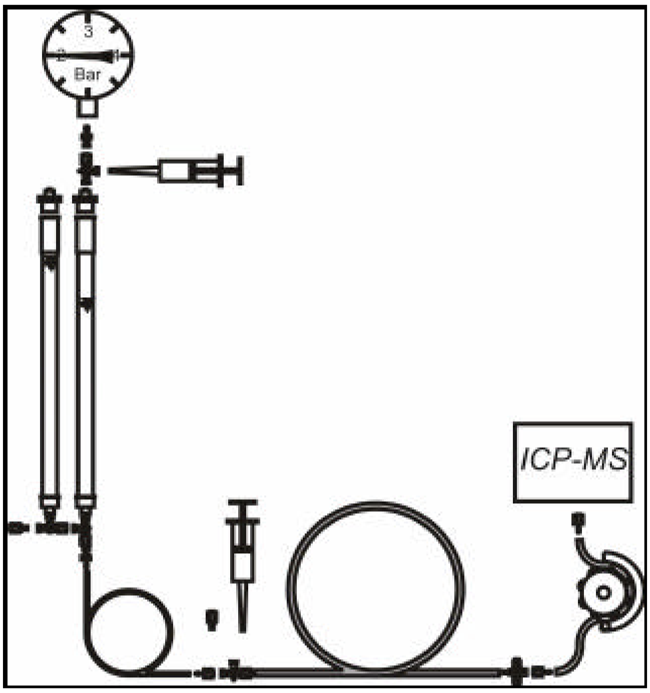


Figure 17: Schematics of the on-line chromatographic set up

The column was cleaned off-line to remove matrix cations and remaining PGEs with 50 ml HCl 1+1 and re-equilibrated with 0.1mol/l HCl (ca. 50 ml). During rinsing the resin shrinks and does not re-expand to the former volume after passing through dilute acid. Through shrinking the resistance is increased and the flow rate is reduced significantly. Flushing the column with 0.1 mol/l HCl with a syringe from the exit side helps the resin to expand to the original volume. After cleaning with the described procedure the columns were reused randomly. All column blanks were always tested prior to sample loading and were as good as freshly prepared columns.

5.5 Measurement of the PGE

5.5.1 Instrumentation

A HP4500 quadrupole ICP-MS in a standard configuration with a savillex nebulizer was used for the PGE measurements and the following table shows the standard configuration of the ICP-MS.

Table 9: The operation configuration of ICP-MS

Instrument	**HP4500 Agilent Technologies**
RF-Power	1500W
Carrier gas	0.89 l/min
Makeup gas	0.1 l/min
Nebulizer	Savillex
Measurement mode	Time resolve

5.5.2 Measurement of ruthenium, palladium, iridium, platinum and rhenium

The measurements of the PGE were executed in the following steps (see figure 18):

- Before the measurement the equipment parameters were optimized by the tuning solution (Solution contains ^{7}Li, ^{89}Y, ^{205}Tl) to get an ideal sensitivity and background signal.

- The whole system was washed with 0.1mol/l HCl, until the intensity sank to the background value.

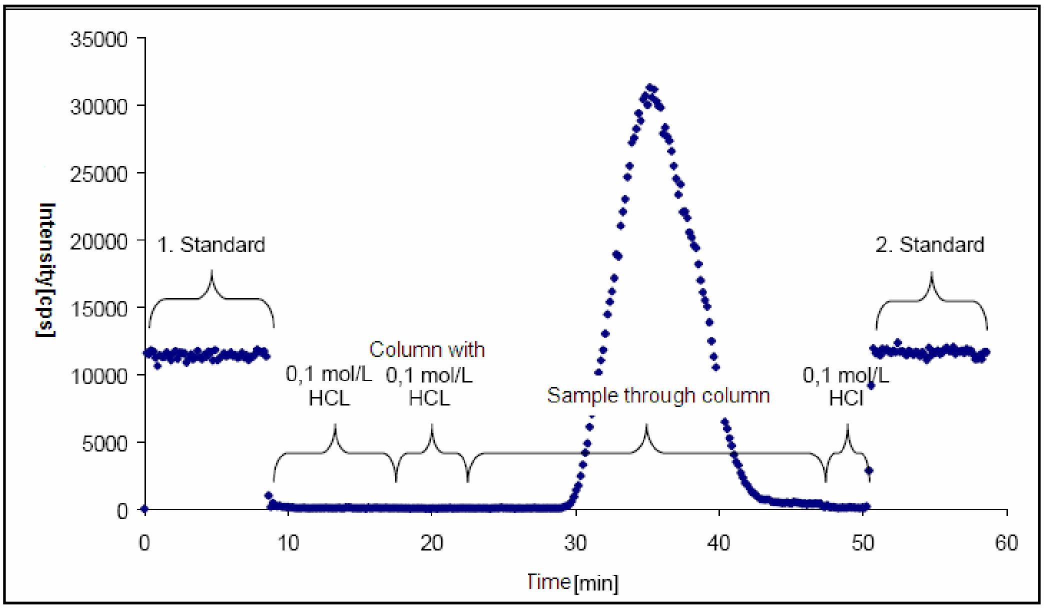


Figure 18: The chromatogram for platinum measurement

- Without the connection of the chromatographic column the intensity of the standard solution (see chapter 5.2.4) was measured for about 5 min.

- The system was washed once more with the 0.1mol/l HCl.

- The chromatographic column was connected with the sample loop and they were also washed with 0.1mol/l HCl, and then the column background value was monitored (usually below 100 counts per second). Thereby one can confirm whether there are contaminations in the column or sample loop.

- If the intensity corresponded to the background value, the sample solution (1-2ml) was added by pipette and sucked into the sample loop (see figure 17). Care was taken to ensure that a small air bubble separate the sample from the 0.1 mol/l HCl of the reservoir. After reconnecting the sample loop with the column, the elution of the PGE chloro-complexes and ReO_4^- takes about 30 minutes. Additionally, some isotopes of the interfered elements were measured too, and the following table 10 shows the integration time of all the isotopes.

- After the measurement of the sample the system was washed again with the 0.1mol/l HCl ,

- At last the standard solution was measured again. With the both measurements of standard solution one can control the mass bias. .

Table 10: The integration times of all the isotopes

Isotope	Integration time(s)	Isotope	Integration time(s)
^{57}Fe	0.0001	^{105}Pd	0.8
^{60}Ni	0.01	^{106}Pd	0.5
^{63}Cu	0.005	^{108}Pd	0.3
^{68}Zn	0.005	^{111}Cd	0.5
^{75}As	0.5	^{179}Hf	0.01
^{85}Rb	0.01	^{182}W	0.01
^{86}Sr	0.005	^{185}Re	0.5
^{89}Y	0.005	^{191}Ir	0.3
^{90}Zr	0.005	^{193}Ir	0.8
^{95}Mo	0.01	^{194}Pt	0.5
^{99}Ru	0.3	^{195}Pt	0.5
^{101}Ru	0.8	^{198}Pt	0.5
^{102}Ru	0.8	^{199}Hg	0.5
^{103}Rh	0.5		

-Data from thesis of Fritsche, 2003

5.6 Calculations

The concentrations were calculated off-line directly from the intensities in a self-made spread sheet. Background count rates present the average background over two minutes prior to the chromatographic peak. The count rate of each data point of the peaks of interest was at first dead time corrected. After background and isobaric interference corrections the isotope ratios were calculated. ^{102}Ru, ^{106}Pd, ^{108}Pd and ^{198}Pt were corrected for isobaric interferences.

The mass bias corrections and mass bias drift were done with linear interpolation of the measured ratio of the natural standard solution before and after the sample. Mass bias drift corrections were up to 2% relative. After having applied all the corrections, plotting the calculated isotope ratios versus time should result in plateaus that ideally coincide with the time interval of the peak (see figure 19). This was always the case for Re, Ir and Pt. In some cases for Pd and particularly for ^{101}Ru/^{99}Ru the plateaus were narrower due to in-growing interfering peaks. For this reason the time interval for the isotope ratios had to be selected manually for all elements. The selected isotope ratios were averaged to give the measured data. Details on the laborious calculation procedure are laid out in Moser et al.(Meisel et al., 2003) Concentrations were calculated from more than one isotope ratio where possible to test for unknown interferences: ^{101}Ru/^{99}Ru and ^{102}Ru/^{99}Ru and ^{105}Pd/^{108}Pd, ^{106}Pd/^{108}Pd and ^{105}Pd/^{106}Pd, ^{194}Pt/^{198}Pt and ^{195}Pt/^{198}Pt. In addition known interferences can be identified by monitoring the elements, which cause the interferences (Meisel et al., 2003).

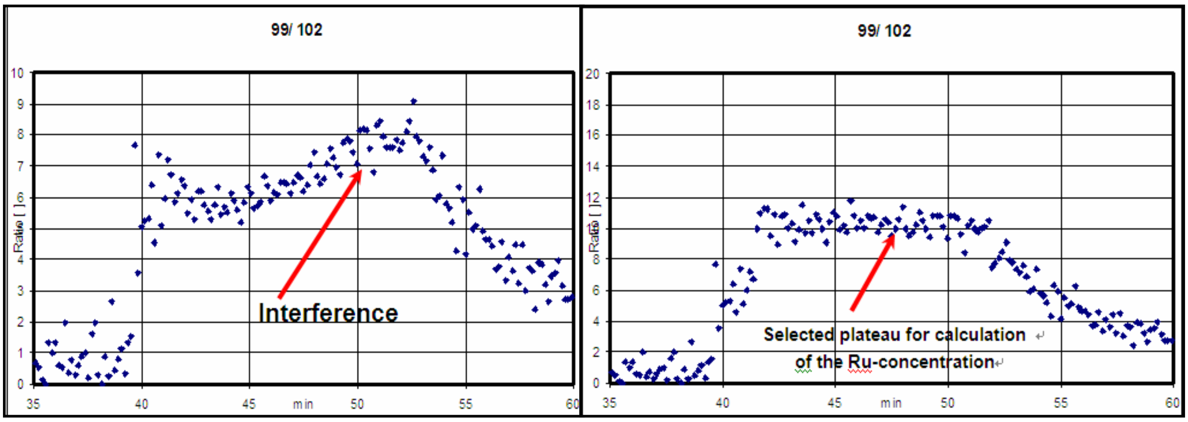


Figure 19: ^{99}Ru/^{102}Ru – ratios of samples affected and unaffected by the interference

Rhodium is monoisotopic, therefore it cannot be measured with IDMS and an alternative approach had to be found. Here instead of ratios the count rates (corrected for dead time, background and isobaric interferences) are used to calculate the rhodium concentrations. Because all the PGEs show a similar chemical behaviour on the chromatographic column they can act as ideal internal standards for the concentration calculation of Rh. However, the count rate of each PGE isotope cannot be directly related to its concentration, since all PGE amounts of substances other than Rh are enriched through the spike addition.

The natural isotope ratio standards for mass bias correction are also used as intensity standards. Since these standards have a defined concentration the amount of substance ratio between rhodium and the other PGE isotopes $n_{Rh,standard}/n_{PGE,standard}$ can be calculated. The amount of substance for one PGE isotope in the blend $n_{PGE,blend}$ is composed of the amount of substance from the sample (from IDMS) plus the amount of substance contributed from the spike (from concentration and isotopic composition) for the isotope. The amount of substance of rhodium in the blend $n_{Rh,blend}$ can be calculated as follows:

$$n_{Rh,blend} = n_{PGE,blend} \times \frac{n_{Rh,standard}}{n_{PGE.standard}} \times \frac{c_{Rh,blend}}{c_{PGE,blend}} \times \frac{c_{PGE,standard}}{c_{Rh,standard}}$$

Where $C_{Rh,blend}$ and $C_{PGE,blend}$ are the integrated count rates of Rh and of the PGE isotope in the blend, respectively. $C_{PGE,standard}$ and $C_{Rh,standard}$ are the sum of the integrated count rates of Rh and one PGE isotope, which are in the standard before and after the sample peak, respectively. Here it is necessary to select time windows of similar width for the integration of the standard before and after the sample. It is necessary to use the same integration window for Rh and for the other PGE isotope of the sample peak to avoid problems with the transient nature of the signal. One of the advantages of this approach is the possibility to eliminate spectral interferences through the selection of an undisturbed integration window of the sample peak (see figure 20).

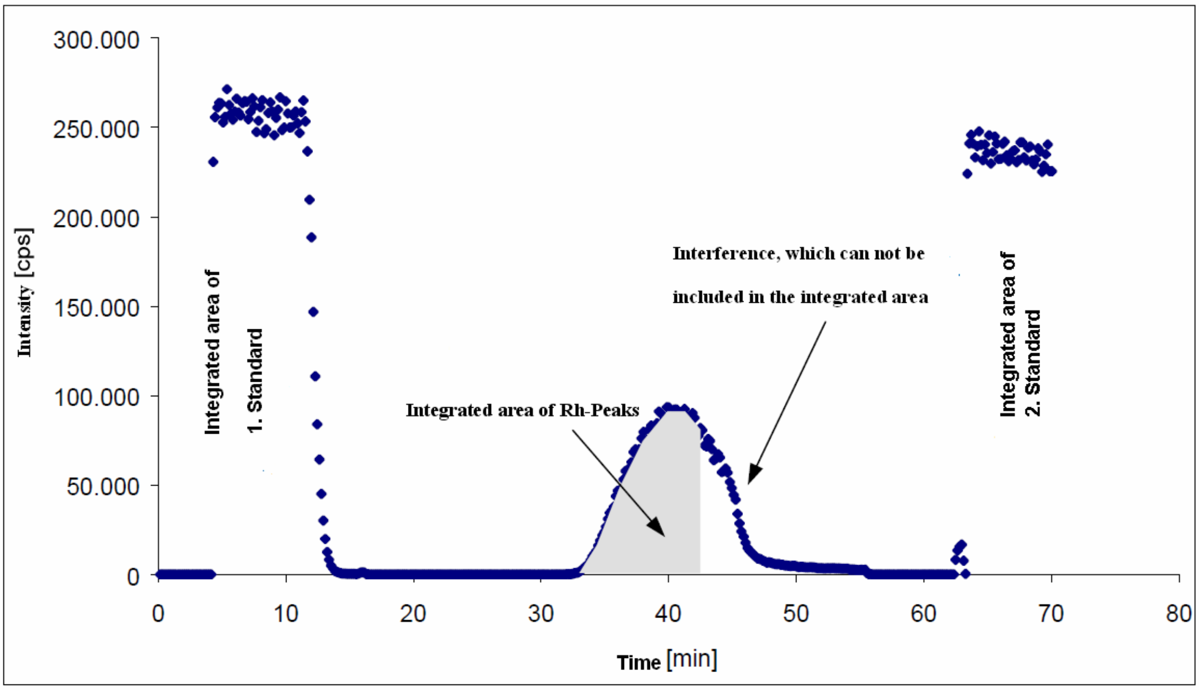


Figure 20: Chromatogram of Rh-measurement

5.7 Interference in the PGE analysis

The on-line coupling of the cationic exchange column to the ICP-MS proved to be a very selective and sensitive method. However, as in any other analytical method, interferences from matrix constituents occurred and had to be identified and corrected if possible. Isobaric and polyatomic interferences were detected frequently on Ru, Pd, Ir and Pt but were not systematic in any way.

Cadmium and Hg were responsible for the most important isobaric interferences on Pd and Pt. As isotopes of these elements were eluted towards the end of the PGE-peaks (Figure 25 gives an example), their effect on the PGE-ratios was minor. Moreover, isobaric interferences from Cd and Hg were corrected by measuring the abundance of ^{111}Cd and ^{199}Hg.

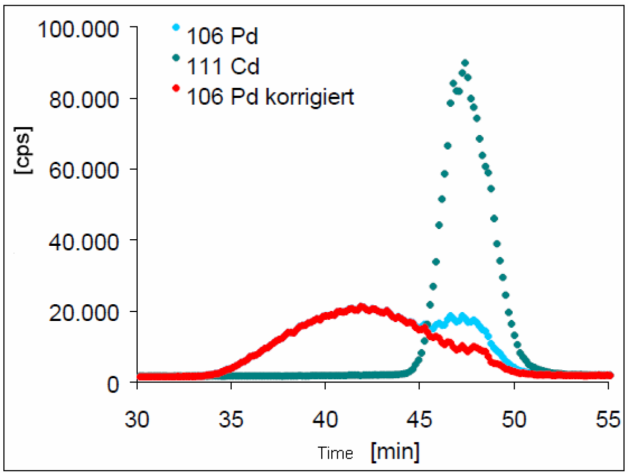


Figure 21: Chromatographic diagram of ^{106}Pd

More challenging appeared the occurrence of polyatomic interferences. Species of Zr, Y and Sr interfered primarily with Pd by affecting the plateaus of the calculated Pd-ratios. Figure 26 compares the $^{106}Pd/^{105}Pd$-ratio of a sample seriously affected by the $^{88}Sr^{16}OH$-interference with another sample free of such interference. The $^{88}Sr^{16}OH$-interference in this example has altered the Pd-ratio to such an extent, that the calculation of the Pd-concentration was not possible. However, through the determination of three isotope ratios and correction of the aforementioned interferences by their formation rates, accurate results could be obtained.

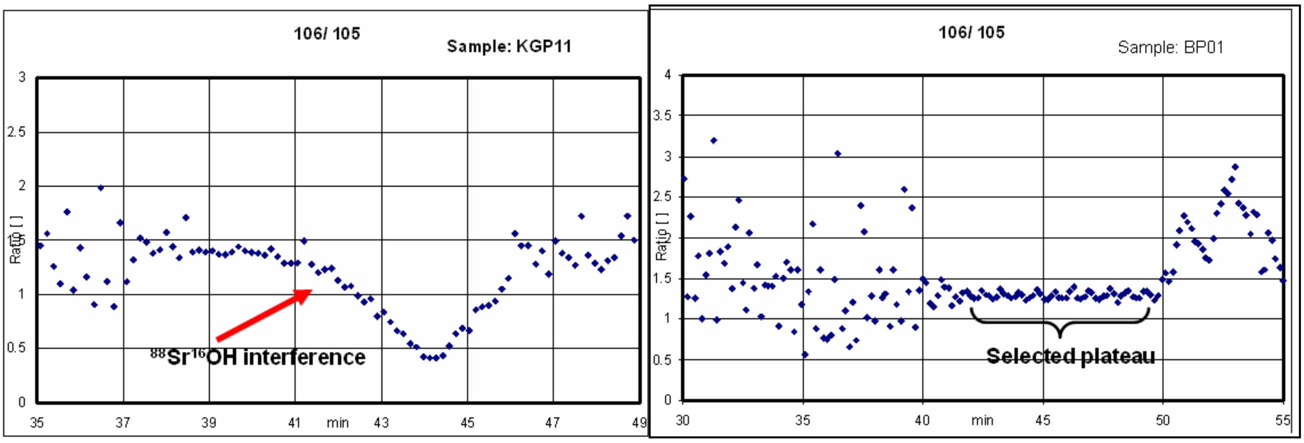


Figure 22: The $^{106}Pd/^{105}Pd$-ratio of a sample seriously affected by the $^{88}Sr^{16}OH$-interference and the sample free of such an interference.

5.8 Measurement of XRF

In the experiment the samples were prepared for the XRF-measurement after the fusion method or the pressing method. The both methods are described in the following section:

Fusion method: the fine milled samples (about 2g) were weighed in platinum crucible, and dried in drying closet at 106□ until the weight was constant. Then the samples were heated in the oven (at 500□ for 1 hour; at 1000□ for 3 hours). To calculate the loss on ignition the samples were weighed again. The ignited samples (about 1g) were weighed and mixed homogenously with dilithium tetraborate (about 8g $Li_2B_4O_7$) in platinum crucible, and then the crucible was heated in the fusion machine for about 15min. After fusion the molten samples were poured into the platinum mould. At last the molten samples were cooled and became the flat glass discs. The discs were measured in the x-ray fluorescence spectrometer with the calibration of GEO27 and GEOWSU.

Pressing method: the fine samples were dried in the drying closet at 106□, until the weight was constant. Then the dry samples (about 1g) were weighted and mixed homogenously with wax (about 4g) in PE vessels. The samples and wax were pressed by a hydraulic press to pellet, which can be analyzed in the x-ray fluorescence spectrometer with the calibration of ProTraceGeo.

6 Result

6.1 Platinum group elements

6.1.1 Total procedure blanks

The total blank concentrate is mainly dependent on the pureness of the reagents and cleanness of the reaction vessels. For each set (3-4 samples) of digestions total procedure blanks (TPB) were determined. As the reference the some special procedure blanks were determined too. These special procedures included the filter of the molten snow water (digestion of clean membrane filter) and the drying of the snow water (drying of MilliQ water in the clean PFA vial). The absolute concentration in the blind samples and the detection (3s of TPB) as well as determination limits (10s of TPB) are shown in the table 11.

Table 11: The absolute amount of total procedure blanks

	Ru (ng)	**Rh (ng)**	**Pd (ng)**	**Re (ng)**	**Ir (ng)**	**Pt (ng)**
Blank01	0.001	0.023	0.026	0.003	-0.003	0.392
Blank02	0.008	0.017	-0.078	0.001	0.012	0.412
Blank03	0.014	0.166	0.320	0.002	-0.002	0.326
Blank04	0.009	0.043	0.150	0.006	-0.002	0.224
Blank05	0.009	0.010	0.170	-0.004	-0.004	0.239
Blank06	0.005	0.005	0.003	0.005	-0.006	0.043
Blank-Membrane	0.009	0.021	0.035	0.011	-0.004	0.396
Blank-PFA	0.01	-0.004	-0.004	0.004	-0.007	0.244
Average	**0.008**	**0.041**	**0.078**	**0.004**	**-0.002**	**0.269**
SD	0.004	0.057	0.127	0.004	0.006	0.166
RSD%	46	138	163	123	296	61
Detection limit	0.013	0.210	0.460	0.016	0.016	0.768
Determination limit	0.023	0.606	1.351	0.047	0.057	1.932

6.1.2 Reference materials

Three reference materials were determined after microwave digestion. The results for reference materials OKUM, BCR-723 and TDB-1 along the standard deviation are presented in the table 12. The values of palladium in BCR-723 and OKUM are indistinguishable and within the uncertainties quote, but the value of platinum is problematic. They are higher than the certified value perhaps because of heterogeneity of the reference materials. The first and second concentration of the Ru and Ir in OKUM are very high, this may be due to the lower test portion size and systematic error.

Table 12: Concentration of PGEs in the reference materials

OKUM(test portion size of RM:0.1g)						
	Ru (ng/g)	**Rh (ng/g)**	**Pd (ng/g)**	**Re (ng/g)**	**Ir (ng/g)**	**Pt (ng/g)**
1	10.2	1.56	13.4	0.79	4.31	32.8
2	8.54	1.33	9.74	0.59	4.03	24.4
3	3.86	1.30	11.7	0.52	0.90	23.9
4	3.91	1.21	9.60	0.48	1.04	31.7
5	3.82	1.33	10.6	0.48	1.00	31.8
6	4.68	1.70	14.1	0.49	1.68	15.2
Average	**5.83**	**1.41**	**11.0**	**0.56**	**2.16**	**26.6**
SD	0.40	0.19	1.9	0.13	1.6	4.40
RSD%	14	13	17	23	73	15
Certified value	4.59[5)]	1.44[1)]	12.0[1)]	0.57[5)]	1.04[5)]	11.2[1)]
BCR-723(test portion size of RM:0.1g)						
	Ru (ng/g)	**Rh (ng/g)**	**Pd (ng/g)**	**Re (ng/g)**	**Ir (ng/g)**	**Pt (ng/g)**
1	7.87	8.07	5.94	7.17	1.30	96.8
2	7.54	10.1	7.51	7.83	1.59	142
3	4.64	12.7	5.98	6.86	1.47	104
4	4.30	12.1	36.1	7.22	1.56	136
5	0.87	13.2	5.26	6.34	0.94	113
6	0.72	13.5	3.88	6.21	0.28	86.8
Average	**4.32**	**11.6**	**5.71**	**6.94**	**1.19**	**113**
SD	3.10	2.12	1.32	0.60	0.50	22
RSD%	71	18	23	8.7	42	19
Certified value	0.85[3)]	12.8[2)]	6.0[2)]	6.65[3)]	0.53[3)]	81.3[2)]
uncertainty		±1.2	±1.8			±3.3
TDB-1(test portion size of RM:0.1g)						
1	0.41	0.69	21.7	0.65	0.04	4.52
2	0.73	0.55	18.9	0.64	0.09	4.91
Average	**0.57**	**0.62**	**20.3**	**0.65**	**0.06**	**4.72**
SD	0.22	0.10	1.93	0.007	0.04	0.27
RSD%	40	16	9.5	1.03	59	5.8
Certified value	0.198[3)]	0.471[3)]	22.4[4)]	0.794[3)]	0.075[3)]	5.8[4)]
uncertainty		-	±1.2			±1.1

1) Data from GEO LABS in Canada.

2) Data from IRMM, Geel, Belgium.

3) Data from the work of Meisel et al, 2004, not certified values

4) Data from CCRMP-CANMET-MMSL, Ottawa, Canada

5) Meisel, 2010, personal communication.

6.1.3 Roadside soils

The background values of the PGEs in the soil are usually very low. Fritsche investigated the soil samples from Vienna city park, Graz city park and Lungau (cleaning land in the valley), and the following values were found: Rh 0.04-0.15 ng/g. Pd: 0.32-1.12 ng/g. Pt 0.28-2.56 ng/g. The analytical results of the roadside soil samples are shown in the table 13. Compared to the background value it is easy to find the accumulation of the PGE in the roadside soil beside the motorway S6 (BP01, 02, 03), and also it is clear that the concentrations in the deeper level are lower than the flat level (see figure 23). The values of the soil under the bridge 40 on the highway A2 (BP04 and BP05) are almost same as those of the unpolluted soil. These values can be used as the reference for the analysis of the sludge from the highway A2.

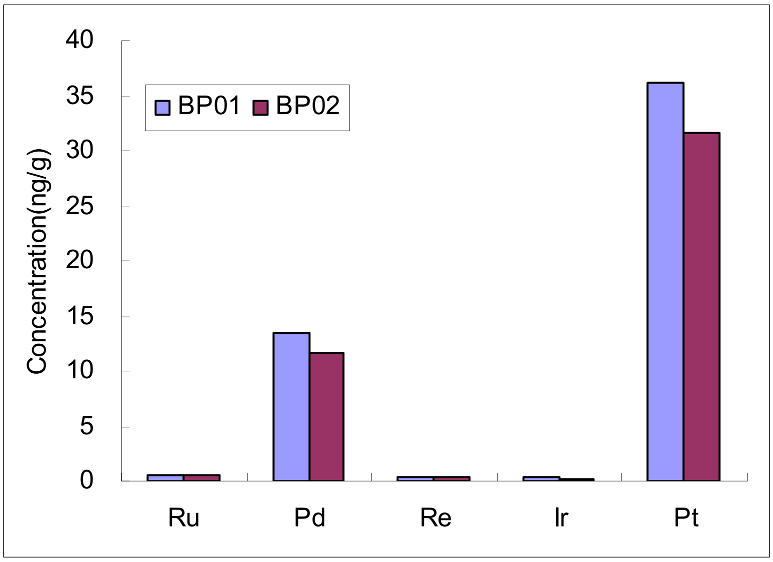


Figure 23: The compare of the PGE and Re-concentration in the different depth levels

Table 13: The PGE and Re-concentration in the roadside soil

	Ru	Rh	Pd	Re	Ir	Pt	Pt/Pd
BP01	0.64	4.66	13.4	0.44	0.30	36.1	2.70
BP02	0.56	1.64	11.6	0.38	0.27	31.6	2.72
BP03	0.68	1.38	5.14	0.89	0.42	20.7	4.02
BP04	0.45	0.06	0.74	0.27	0.06	4.60	6.18
BP05	0.41	0.11	0.71	0.11	0.11	3.83	5.41

Values in ng/g

6.1.4 Roadside snow

To investigate the background value of PGE in the snow, the snow samples were taken from Zillergrund (in the forest) and the following data were found: Pt: 4.1 pg/g; Pd: 0.4 pg/g. All the snow samples along the traffic routes show high concentration of PGE and exceed the background value about 5-25 fold. The concentrations of PGE and Rhenium (SNP-S) are listed in the table 14. The values in the table 14 are very low (in pg/g), because they were calculated based on the filtered mass. This means for the calculations of them the weight of snow (about 300-500g) was taken instead of the weight of the filtered dust (about 0.01-0.6g). The highest concentration of palladium was found in the highway A13 sample (SNP-S01) and of platinum was found in the national road B169 samples (SNP-S03), which are both important tourist routes in the winter season. The high concentrations could also be due to the long accumulation period on the snow.

Table 14: The PGE and Re-concentration in the roadside snow

	Ru	Rh	Pd	Re	Ir	Pt	Pt/Pd
SNP-S01	0.61	1.02	18.0	1.75	0.17	48.2	2.68
SNP-S02	0.10	2.04	4.34	0.59	0.10	24.0	5.53
SNP-S03	0.06	8.27	13.0	0.21	0.067	74.0	5.69
SNP-S04	0.18	3.29	8.96	2.89	1.51	40.5	4.52
SNP-S05	0.031	0.60	3.39	0.11	0.76	-	-
SNP-S06	0.08	7.86	8.50	0.45	0.63	118	13.9
SNP-S07	0.05	0.070	0.30	0.0081	0.77	4.14	13.8

Values in pg/g

The analysis of snow sample includes not only the investigation of the PGE-concentration in the snow, but also in the filtered road dust from snow and in the filtrate of molten snow. Because the amount of the dust in the SNP05 and SNP07 is very small (<0.01g) and the concentrations of PGE and Rhenium in it are not high enough for a correct measurement, the values are ignored and only the other five samples are listed in the table 15. The concentrations in the filtered dust are very high (Pd: max. 95.8ng/g; Pt: max. 607ng/g). These high concentrations can be attributed to the high traffic density of the motorway in the winter of Tyrol.

Table 15: The PGE and Re-concentration in the filtered dust from roadside snow

	Ru	Rh	Pd	Re	Ir	Pt	Pt/Pd
SNP-F01	1.32	1.71	38.4	3.74	0.36	103	2.58
SNP-F02	0.70	29.8	36.9	5.02	0.88	203	5.53
SNP-F03	0.48	92.4	95.8	1.56	0.50	547	5.69
SNP-F04	0.09	1.52	4.70	1.52	0.79	21.2	4.52
SNP-F06	0.44	36.4	43.9	2.32	3.28	607	13.8

Values in ng/g

The PGE and Re-concentrations in the filtrate of the molten snow (SNP-W) are listed in the table 16, the values were measured in the residue after drying, but for the calculation the weight of the filtrate was taken instead of weight of the residue. So the values are very low (in pg/g) similar to the SNP-S samples.

Table 16: The PGE and Re-concentration in the filtrate

	Ru	Rh	Pd	Re	Ir	Pt	residue%	Pt/Pd
SNP-W01	0.34	0.30	1.66	0.47	0.072	1.81	0.076	1.09
SNP-W02	0.12	0.15	1.48	0.21	0.056	1.85	0.060	1.25
SNP-W03	0.11	0.036	1.05	0.18	0.052	1.58	0.055	1.50
SNP-W04	1.45	0.10	0.90	0.49	0.17	1.27	0.19	1.41
SNP-W05	0.057	0.084	0.24	0.076	0.0030	1.32	0.006	5.50
SNP-W06	0.16	0.084	0.40	0.24	0.050	1.03	0.040	2.58
SNP-W07	0.0024	0.020	0.14	0.057	0.0018	0.42	0.0003	3.02

values in pg/g

Note: residue% is the mass percent of the residue, equal to the mass of residue divide the mass of filtrate

6.1.5 Street sweepings

Table17 summarizes the PGE and Rhenium concentrations in the fine fraction of street sweeping. Most samples show relative high concentrations. The highest values were observed in the Annaberg crossing (KGP04), which is located in the industrial section. Compared to the other crossings, its traffic density is highest in Leoben (about 3500 vehicles per day). Therefore it has a higher concentration of PGE. The sample from the sewage plant (KGP10) has a normal concentration of PGE and Rhenium.

Table 17: The PGE and Re-concentration in the street sweeping

	Ru	Rh	Pd	Re	Ir	Pt	Pt/Pd
KGP01	0.98	25.9	56.9	3.68	0.35	119	2.09
KGP02	1.25	1.26	5.54	0.58	0.34	9.06	1.63
KGP03	5.25	22.1	65.4	2.96	0.56	123	1.88
KGP04	1.15	25.6	106	3.91	0.65	280	2.64
KGP05	2.07	6.41	31.0	2.61	0.80	36.6	1.18
KGP06	1.49	16.3	24.0	1.58	0.82	124	5.20
KGP07	1.71	39.7	61.8	3.94	0.63	60.4	0.98
KGP08	1.25	11.3	30.0	2.96	0.64	131	4.37
KGP09	0.59	0.92	4.43	0.44	0.28	16.9	3.82
KGP10	3.21	2.88	19.8	0.87	0.73	17.8	0.90
KGP11	0.63	2.89	6.33	1.16	0.18	44.4	7.02

Values in ng/g

6.1.6 Sludge in the infiltration basin and roadside drain

The PGE and Rhenium concentrations are summarized in the table 18, the concentrations of the samples from infiltration basin (SLP02, SLP03) and samples from the runoff pipe (SLP04, SLP05), which were taken from same sites(under bridge 45, A2), are not identical. This may be due to the heterogeneity of the sediment. But it is interesting that the Pt/Pd ratios are same at same site. The sludge sample under the bridge 32 on A2 highway (SLP06) has the similar values to the soil sample (BP04, BP05) at same site, so it is not polluted and not representative sample for the sludge analysis.

6.2 Accompanying heavy metals

Concomitantly some important heavy metals were measured by X-ray fluorescence spectrometer. They are Vanadium (V), Chromium (Cr), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Mercury (Hg) and Lead (Pb), which may be produced through the rubbing off of the tyre and the brake liners or by the automobile exhaust.

The concentration of these heavy metals were measured with three calibrations (GeoWSU, Geo27 and ProTraceGeo), the detailed data are listed in the table 19, 20 and 21. The average concentration of these metals in the upper earth's crust is also shown in the table 20. Compared to the average value the accumulation of the Cr, Ni and Zn is very apparent, but the concentrations of the Hg and Pb are not high. The values, which were obtained with the calibration GeoWSU and Geo27, are very consistent for the same element, but they are quite different to the value from ProTraceGeo. This should be due to heterogeneity of the press rings or the different measurement ranges of the different routes. On the other hand, the concentrations are quite inconsistent in different sample type (soil, sweeping and sludge samples). The highest values of Cr (KGP10, 2263µg/g) and Ni (KGP10, 1160µg/g) are observed in the street sweeping. It is very interesting that the ratios of the Cr and Ni are very linear, and the relation is very clear if the ratios are plotted (see figure 24). A possible source of the chromium is the street gravel from the Kraubath source (Preg quarry), which is ultramafic rock with a lot of chromium in chromite.

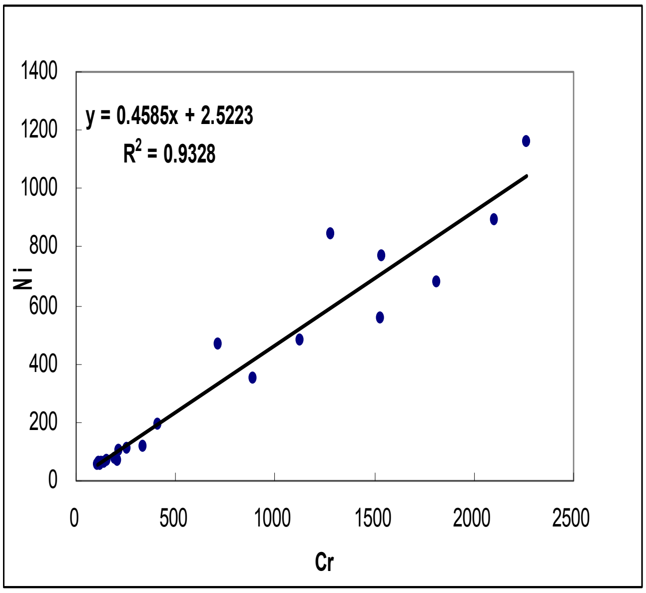


Figure 24: The tendency of the Cr/Ni ratios in all the measured samples

Table 18: The PGE and Re-concentration in the sludge from infiltration basin and drain

	Ru	Rh	Pd	Re	Ir	Pt	Pt/Pd
SLP01	0.78	3.27	8.57	1.47	0.34	23.0	2.69
SLP02	0.23	10.2	26.0	1.82	0.11	45.6	1.76
SLP03	0.22	8.82	42.5	1.06	0.08	64.4	1.52
SLP04	1.72	0.92	5.24	1.99	0.51	21.5	4.10
SLP05	1.27	1.27	7.28	0.93	0.22	32.1	4.42
SLP06	1.11	0.90	3.54	0.52	0.13	17.4	4.93

Values in ng/g

Table 19: The concentration of heavy metal in the samples (with calibration GeoWSU)

Sample Nr.	V	Cr	Co	Ni	Cu	Zn	Pb
BP01	105	208	93	16	46	304	42
BP02	108	264	104	19	102	385	46
BP03	89	381	193	19	67	416	64
BP04	16	167	123	26	60	53	75
BP05	17	146	107	22	60	48	59
KGP01	61	839	24	333	297	351	20
KGP02	37	731	25	464	36	137	15
KGP03	64	1537	42	549	198	338	50
KGP04	72	1147	34	476	213	467	53
KGP05	105	2103	43	983	106	207	22
KGP06	78	1309	52	834	135	511	113
KGP07	79	1780	37	675	193	228	37
KGP08	64	1526	47	768	140	368	44
KGP09	103	117	20	63	36	220	31
KGP10	59	2317	65	1143	35	118	11
KGP11	77	338	11	115	162	2232	35
SLP01	420	173	22	76	385	71	15
SLP02	83	204	13	71	84	3523	35
SLP03	76	142	12	60	71	2431	38
SLP04	138	201	20	71	34	495	11
SLP05	110	157	16	63	54	1794	18
SLP06	155	124	23	62	61	425	37

Values in µg/g

Table 20: The concentration of heavy metal in the samples (with calibration Geo27)

Sample Nr.	V	Cr	Ni	Co	Cu	Zn	Cr/Ni
BP01	109	214	105	-	54	351	2.03
BP02	108	258	108	-	97	399	2.38
BP03	91	411	195	-	62	411	2.11
BP04	165	119	58	23	61	141	2.06
BP05	140	108	58	21	55	111	1.86
KGP01	62	889	347	25	311	341	2.56
KGP02	37	715	464	25	47	136	1.54
KGP03	64	1527	554	41	206	331	2.76
KGP04	68	1125	481	35	215	458	2.34
KGP05	98	2102	891	40	160	207	2.36
KGP06	78	1279	845	54	134	503	1.51
KGP07	80	1814	680	39	201	223	2.67
KGP08	66	1534	766	45	148	363	2.00
KGP09	105	114	60	13	54	217	1.90
KGP10	61	2264	1161	61	44	120	1.95
KGP11	74	336	115	11	117	2208	2.92
SLP02	82	207	72	14	8	3489	2.90
SLP03	74	139	60	12	20	2413	2.32
SLP04	136	197	73	20	31	495	2.71
SLP05	110	153	67	17	21	1751	2.28
SLP06	153	125	60	21	68	424	2.07

Values in µg/g

Table 21: The concentration of heavy metal and arsenic in the samples (with calibration ProTraceGeo)

Sample Nr	V	Cr	Co	Ni	Cu	Zn	As	Hg	Pb
BP01	120	163	18	77	35	287	23	<2	33
BP02	101	173	17	85	46	345	21	<2	39
BP03	102	312	20	182	43	404	11	<2	59
BP04	174	128	21	54	43	146	4	<2	33
BP05	151	109	22	54	37	108	4	<2	33
KGP01	63	701	23	330	221	369	3	<2	17
KGP02	67	650	21	333	290	362	2	<2	19
KGP03	61	1015	36	521	145	335	5	<2	49
KGP04	80	938	39	493	193	584	7	<2	60
KGP05	70	980	37	620	81	258	4	<2	21
KGP06	82	957	48	764	122	540	4	<2	116
KGP07	66	894	40	654	183	285	1	<2	32
KGP08	74	957	42	691	141	398	4	<2	47
KGP09	113	123	13	55	43	223	6	<2	46
KGP10	46	1038	58	990	30	102	5	<2	20
KGP11	67	158	10	46	25	2106	1	<2	28
SLP01	128	350	19	158	93	403	20	<2	46
SLP02	77	154	12	51	57	3983	1	<2	32
SLP03	78	106	10	45	66	2385	5	<2	26
SLP04	121	129	20	57	25	503	4	<2	9
SLP05	97	144	16	54	30	1823	0	<2	14
SLP06	160	120	23	53	53	411	3	<2	35
Average value in the earth's crust[1)]									
	V	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Hg**	**Pb**
	53	35	11.6	18.6	14.3	52	-	0.056	17

Values in µg/g

1) Wedepohl, 1995

7 Discussion

7.1 PGE abundance vs. traffic density

Some workers have advocated a direct relationship between PGE levels and traffic volume in roadside environments (Schäfer and Puchelt, 1998; Ely et al., 2001; Zereini et al., 2001b). However, other studies have demonstrated that driving style and topography may exert more significant influences. Whiteley and Murray (2003) have investigated relationship of PGE-concentration in the road dust and traffic volume in Australia, but no straightforward relationship was found.

In the samples for this study the snow samples are the best samples to investigate the relationship between the traffic density and PGE-concentration. The figure 25 shows the PGE-concentration in five different sample sites. There is no clear linear relationship to be observed. It may be due to the other influence factors, such as driving style and the topography.

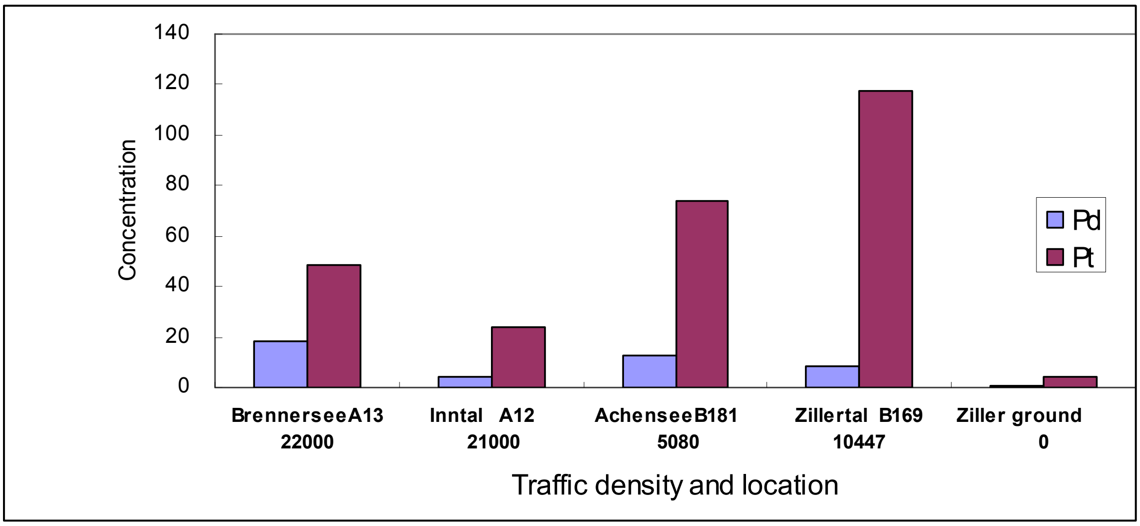


Figure 25: The PGE-concentration and traffic density in different locations

7.2 PGE ratios and correlations

The most common method used to attribute elevated levels of environmental PGE to emissions from automobile catalysts is through the use of PGE ratios (Wei and Morrison, 1994a; Zereini et al., 1997; Schäfer and Puchelt, 1998; Ely et al., 2001). Previously defined ranges are Pt/Rh 5–16 and Pt/Pd 1–2.5 and Pd/Rh 4–9 (Ely et al., 2001). Average Pt/Rh and Pt/Pd ratios from all infiltration basin sediments are within these ranges being Pt/Rh–6.7 (range 5.6–8.6) and Pt/ Pd–1.8 (range 1.5–2.3). However, some Pd/Rh ratios fall outside the previously defined range and the average ratio is 3.8 (range 2.7–5.0) (Whiteley and Murray, 2003).

In this study the PGE-ratios of soil samples, sludge samples and sweeping are calculated and listed in table 13, 16 and 17. The following average Pt/Pd ratios are found: soil sample, 4.3; sludge sample 3.2; sweeping: 2.5. The Pt/Pd ratios of sweepings fall inside the defined range from the literature. The figure 26 shows the Pt-Pd plots in the aforementioned samples. It is easy to see the linear relationship between the concentration of Pt and Pd. The correlations of Pt and Pd are also calculated, they are: soil 0.99; sludge, 0.98; sweeping, 0.83, which means that the correlations are very good. The Pt/Pd ratios in the roadside snow are very inconsistent, and therefore no linear relationship can be found in them. That may be because of the complexity and instability of the snow sample and the lower PGE-concentration in the snow.

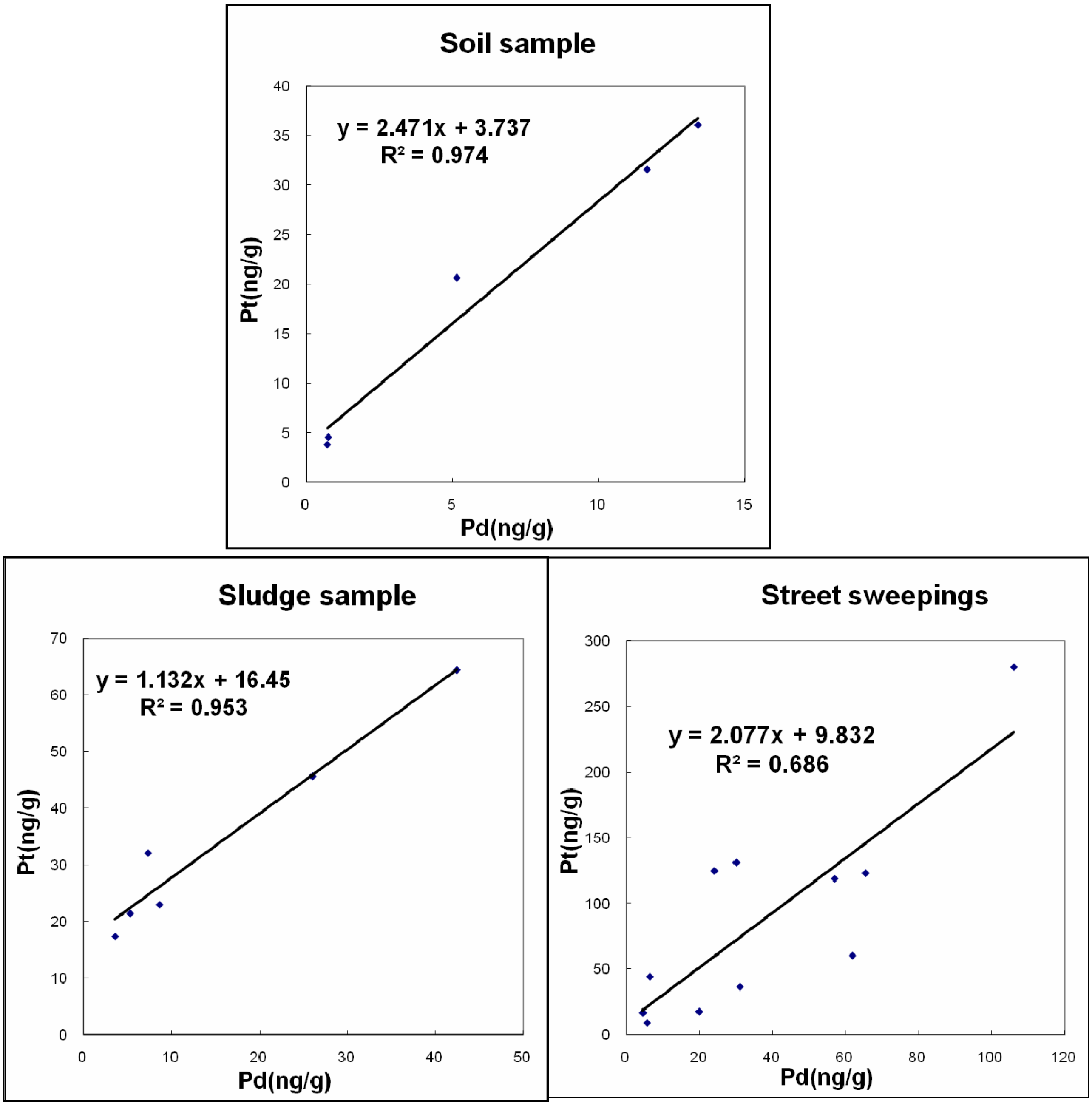


Figure 26: The Pt-Pd plots in the soil, sludge and sweeping

As the reference the PGE-correlations are all calculated and listed in the following table, it is very helpful to find the relationship among the elements.

Table 22: The PGE-correlations in the different samples

<table>
<tr><th colspan="6">All the samples</th></tr>
<tr><th></th><th>Ru</th><th>Pd</th><th>Re</th><th>Ir</th><th>Pt</th></tr>
<tr><td>Ru</td><td>1.00</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Pd</td><td>0.36</td><td>1.00</td><td></td><td></td><td></td></tr>
<tr><td>Re</td><td>0.38</td><td>0.84</td><td>1.00</td><td></td><td></td></tr>
<tr><td>Ir</td><td>0.59</td><td>0.45</td><td>0.59</td><td>1.00</td><td></td></tr>
<tr><td>Pt</td><td>0.22</td><td>0.87</td><td>0.73</td><td>0.46</td><td>1.00</td></tr>
<tr><th colspan="6">Soil samples</th></tr>
<tr><th></th><th>Ru</th><th>Pd</th><th>Re</th><th>Ir</th><th>Pt</th></tr>
<tr><td>Ru</td><td>1.00</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Pd</td><td>0.66</td><td>1.00</td><td></td><td></td><td></td></tr>
<tr><td>Re</td><td>0.89</td><td>0.28</td><td>1.00</td><td></td><td></td></tr>
<tr><td>Ir</td><td>0.96</td><td>0.60</td><td>0.88</td><td>1.00</td><td></td></tr>
<tr><td>Pt</td><td>0.77</td><td>0.99</td><td>0.43</td><td>0.72</td><td>1.00</td></tr>
<tr><th colspan="6">Street sweepings</th></tr>
<tr><th></th><th>Ru</th><th>Pd</th><th>Re</th><th>Ir</th><th>Pt</th></tr>
<tr><td>Ru</td><td>1.00</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Pd</td><td>0.25</td><td>1.00</td><td></td><td></td><td></td></tr>
<tr><td>Re</td><td>0.13</td><td>0.87</td><td>1.00</td><td></td><td></td></tr>
<tr><td>Ir</td><td>0.29</td><td>0.33</td><td>0.33</td><td>1.00</td><td></td></tr>
<tr><td>Pt</td><td>0.01</td><td>0.83</td><td>0.68</td><td>0.29</td><td>1.00</td></tr>
<tr><th colspan="6">Sludge samples</th></tr>
<tr><th></th><th>Ru</th><th>Pd</th><th>Re</th><th>Ir</th><th>Pt</th></tr>
<tr><td>Ru</td><td>1.00</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Pd</td><td>-0.83</td><td>1.00</td><td></td><td></td><td></td></tr>
<tr><td>Re</td><td>0.03</td><td>0.07</td><td>1.00</td><td></td><td></td></tr>
<tr><td>Ir</td><td>0.75</td><td>-0.60</td><td>0.57</td><td>1.00</td><td></td></tr>
<tr><td>Pt</td><td>-0.78</td><td>0.98</td><td>0.04</td><td>-0.61</td><td>1.00</td></tr>
</table>

7.3 PGE transport in the environment

Road dusts and possibly roadside soils represent the source material that is being transported and ultimately deposited in infiltration basin sediments. This combination presents the opportunity to examine whether PGE ratios vary from source to deposition.

From road S6 and Highway A2 the roadside soil and sludge were both taken. Although the amount of samples is insufficient to give a systematic pattern to show the transport route, some interesting relationships between the soil and sludge samples were found. The Pt/Pd ratios of the soil sample (BP01 and BP02, national road S6) and sludge sample from runoff pipe (SLP01, national road S6) are almost same (see figure 27). This can imply that the PGE in the sludge have the same source of the PGE in the soil. On the other hand a negative shift of the Pt/Pd-ratios is observed from soil to the infiltration basin sediment. The reason of this shift may be the different solubility of the Palladium and Platinum in the road runoff. Through the calculation of the correlation a good linear relationship between the Pt and Pd from soil to sediment is also found (see figure 27).

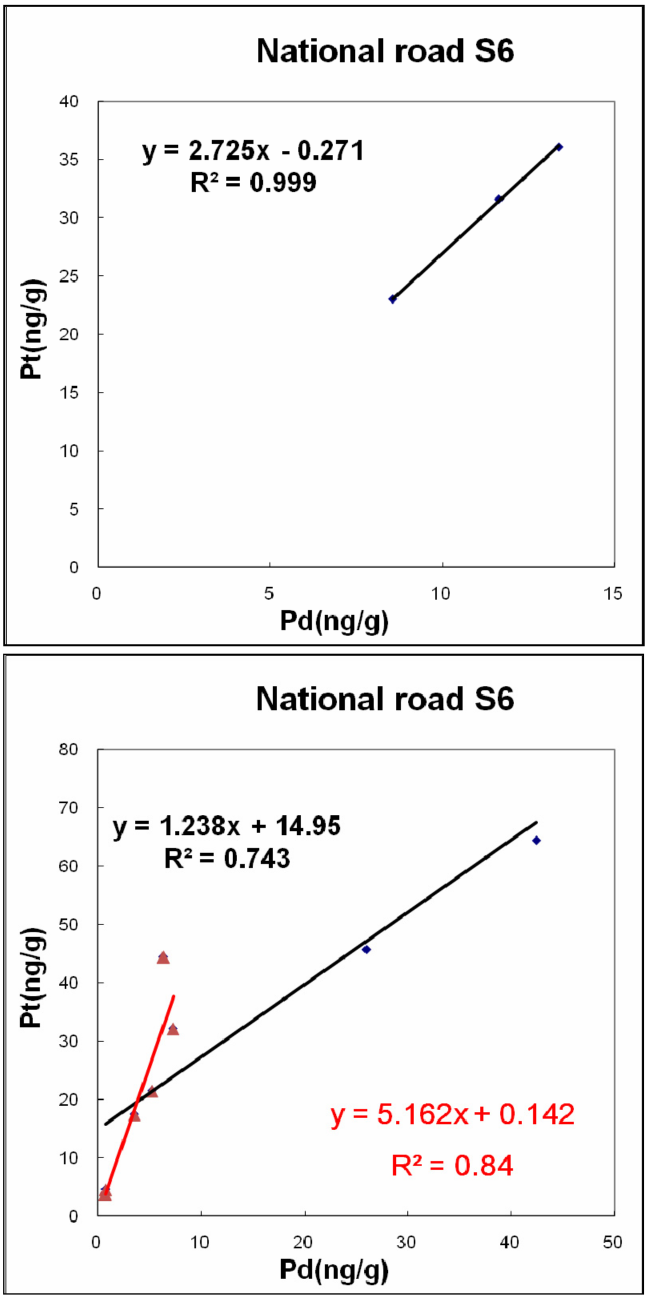


Figure 27: The Pt-Pd plots in the samples from national road S6 and highway A2

7.4 Investigation for the anthropogenic source of the rhenium

An anthropogenic enhancement Re might be expected on the basis of the high concentrations of these metals in fossil fuels (Miller et al., 2009). Re is also found in fuel processing catalysts (Chang, 1998), and the use of Re in brake liners is thought to be the source for high concentrations of Re (up to 10 ng g−1) in road dusts (Meisel and Stotter, 2007).

Because of the good ductility rhenium is added to the tungsten and molybdenum-based alloys to increase the ductility at higher temperature. Rhenium has also good wear resistance, so it can be applied as the material of brake lining. The material of the brake lining is always the copper-based alloy with iron, titanium on similar.

From results of the rhenium measurement a good correlation value (0.87) between rhenium and palladium was observed in the street sweepings, this means the high concentration of the anthropogenic rhenium in these samples. A possible source of the rhenium can be the brake lining. In order to prove deduction the concentrations of cooper were also studied and it shows also a higher value than the values in other media (see table19, 20 and 21). Lower value of the rhenium was found in the soil samples and sludge samples, which may be due to the high solubility of rhenium compound.

7.5 Completeness of the microwave digestion

All the samples were digested by the microwave digestion system. In order to get an optimized digestion conditions several processes of digestion were studied. To get a higher temperature of the reaction different reagents were added in the vessels, the maximal temperature and press in the digestion are listed in the table 23, and in this table the digestion effects with HCl and HF are also compared.

Table 23: The digestion parameter of microwave digestion with different reagents

	Reagents	**T_{max} □□□**	**P_{max}□bar□**	**Rh**	**Pd**	**Pt**
A	water	160	16.5	-	-	-
B	6ml HNO_3	220	80	-	-	-
C	4ml HNO_3+2mlHCl	180-200	80	-	-	-
D	5ml HNO_3+2mlHCl	200-210	80	1.45	11.5	28.6
E	3ml HNO_3+2mlHCl+2mlHF	220	60	1.37	11.2	28.0

Note: the concentrations in the table are the PGE-concentrations in the RM (OKUM), values in ng/g
A, B, C, D….. Microwave program XQ80-4; power 800W; p-Limit: 80bar, T-Limit: 280□
E…………….. Microwave program XF100-4; power 800W; p-Limit: 60bar, T-Limit: 260□

The maximal temperature was rising if there is more nitric acid in the vessels, but on the other hand hydrochloric acid is also important for the digestion because of the complexing reaction. After the test of aqua regia with difference ratio of HNO_3 and HCl, the ratio 5:2 shows a better digestion effect than others. The digestion effect of the hydrofluoric acid is similar to the effect of the hydrochloric acid (see table 23), the reason may be that the compounds of the PGE are not in the form of silicate, which can dissolve very good in the hydrofluoric acid.

To investigate the completeness of the microwave digestion the results of measurement in this thesis and some results from literature are listed in the table 24. The PGE-concentration in the reference materials BCR-723 and TDB-1 are used to compare. As the reference the certified values are also listed in the table.

Table 24: Comparison of the PGE-concentration after the HPA and microwave digestion

Method	RM	Ru	Rh	Re	Pd	Pt	n
A	BCR-723	4.32	11.6	6.94	5.71	113	6
B	BCR-723	0.85	11.8	6.65	4.52	82.4	5
C	BCR-723	-	13.1	-	5.86	81.0	6
D	BCR-723	0.62	13.1	6.98	5.27	80.7	3
Certified value	BCR-723	-	12.8	-	6.0	81.3	
A	TDB-1	0.57	0.62	0.79	20.3	4.72	2
E	TDB-1	0.198	0.471	0.794	24.3	5.01	7
Certified value	TDB-1	-	-	-	22.4	5.8	

Note: the certified values of BCR-723 are from IRMM, and values of TDB-1 from CCRMP-CANMET-MMSL

A……microwave digestion in this thesis

B……HPA digestion, Meisel, 2003

C……HPA digestion, Whitely and Murray, 2003

D……microwave digestion, Fritsche, 2003

E……HPA digestion, Meisel et al., 2004

From the table one can see that the values from the microwave digestion normally lower than the values from the HPA digestion. That means the completeness of the microwave digestion may be less than the HPA digestion, but the values are satisfying if they are compared with the certified values. Moreover the microwave digestion only need about 90min (HPA need 180-360min) times and the operations of the digestion are also easier than the HPA digestion. As a fast and easy digestion method microwave is still an ideal selection.

8 Conclusion and outlook

At all the sample sites an evidence accumulation of the PGE was observed in different roadside media. The concentrations in different types of sample are also quite different too, because of their different characteristic of them. The highest concentration was found in the filtered dust from the roadside snow.

To investigate the relationship between the PGE-concentration and traffic volume, the PGE-concentration in the roadside snow and the corresponding traffic volume were plotted, but a straightforward relationship was not found between them because of the influence from other factor such as driving style and topography. To obtain the convictive results the samples should be collected in the similar topography condition and correlated with the driving style.

The Pt/Pd-ratios were also calculated for an assessment of mobility, besides the snow sample the ratios are relative stable and the correlation between the Pt and Pd were also very good. It showed the linear tendency of the Pt/Pd in the diagram.

In this study the PGE distribution was also considered from the soil to the sediments. There was a negative shift of Pt/Pd-ratios from soil to the sediment beside the highway A2. To show systematic changes in the transport process, the number of samples in this study was not sufficient.

For the further investigation in the future the different sample sorts should be collected in the same sites, because it is better to study the transport and transform of PGE in the environment through the comparison of the PGE-concentration in different roadside media. On the other hand, the sample should be collected at the same site in different times in order to show the seasonal changes. Moreover after the good investigation of the PGE-distribution in the environment one could also find the methods to reduce contamination, even find the methods to refine them from road dust and sludge again.

In the European Union emission standards (EURO 5 is valid from 2008, set out in the EU Directive 99/96/EC) more stringent emission limits were set for both petrol and diesel cars as well as for trucks (Lang, 2003). The desire for more efficient fuel usage and lower greenhouse gas emissions - mainly CO_2 - predicts predicted an increasing demand for diesel vehicles around the world. The development of catalyst technology to reduce the NO_X for cars and trucks are very important. The California Air Resources Board (CARB) has already developed the zero-emission vehicles (Rear and Farrauto, 2001). All these developments will require larger amounts of platinum group elements with specific catalyst technologies. In this context, the fuel cell should be mentioned, which will be worked in the automotive sector with great zeal. According to current development a vehicle powered by fuel cells need 10 grams of platinum for the catalytic reaction of hydrogen and oxygen into water (Amatayakul and Ramnas, 2001). In view of these developments and the increasing of the automobile catalyst as well as the expansionary traffic density the increasing PGE-concentration will be found in many environmental compartments.

9 Index

9.1 References

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9.2 Table of the Abbreviations

°C	Grad Celsius
CCRMP	Canadian Certified Reference Materials Project
e.g.	for example
etc.	et cetera
GFAAS	Graphite furnace atomic absorption spectrometry
GOS	Graduate school of Oceangraphy
ICP-MS	Inductively coupled plasma mass spectrometry
i.e.	Id est
Ir	Iridium
IRMM	Institute for Reference Materials and Measurements
NAA	Neutron atomic analysis
Os	Osmium
Pd	Palladium
Pt	Platinum
Re	Rhenium
Rh	Rhodium
Ru	Ruthenium
TXRF	Total reflection X-ray fluorescence

Zn	Zinc

9.3 Tables

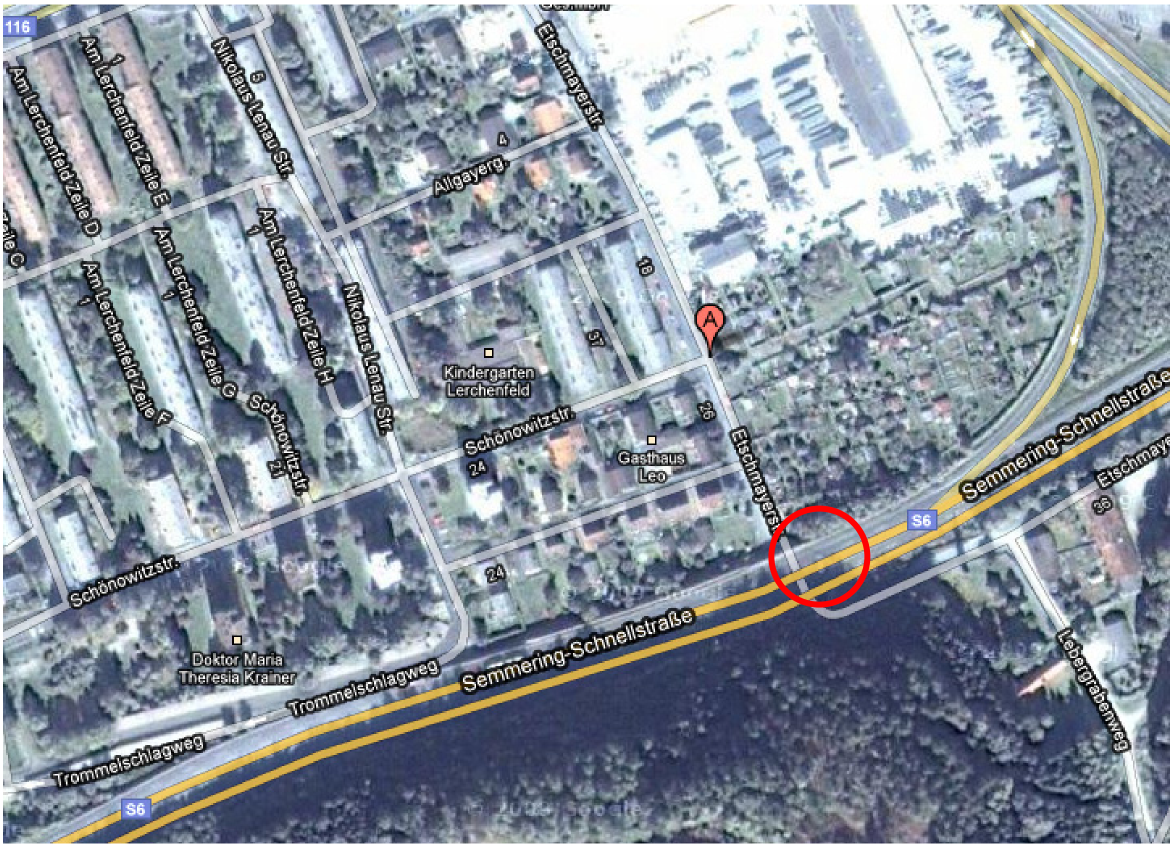
9.4 Figures

Supplement

S.1 Sample Sites

National road S6 in Leoben

Sample site of the soil samples (BP01, BP02 and BP03) and sludge sample (SLP01)



Coordinate: North latitude 47°22′55″; East longitude: 15°27′18″

Highway A2

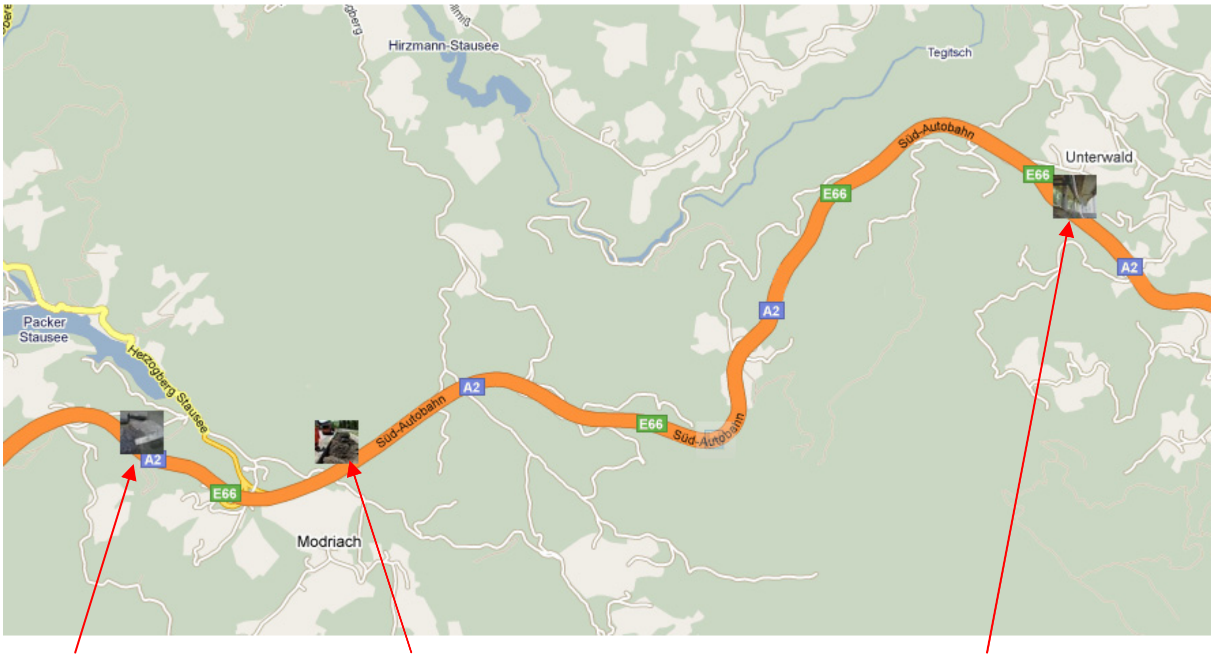
Infiltration basin (SLP02, SLP03), under bridge 45, Highway A2 (left);

Runoff pipe at the infiltration basin (SLP04, SLP05), under bridge 45, Highway A2 (middle);

Infiltration basin (SLP06), under bridge 32, Highway A2 (right);

Collection of the soil sample (BP04, BP05), under bridge 32, Highway A2 (left);

Street sweeping (KGP11) from bridge 40, Highway A2 (right);



Bridge 45 (SLP02-05) Sweeping (KGP11) Bridge 32(SLP06, BP04, 05)

Coordinate:

Bridge 45: North latitude 46°57′57″; East longitude: 15°2′11″

Sweeping: North latitude 46°57′53″; East longitude: 15°3′40″

Bridge 32: North latitude 46°59′40″; East longitude: 15°9′15″

Crossings in Leoben

The traffic density at each crossing in Leoben

Sample sites and sample numbers:

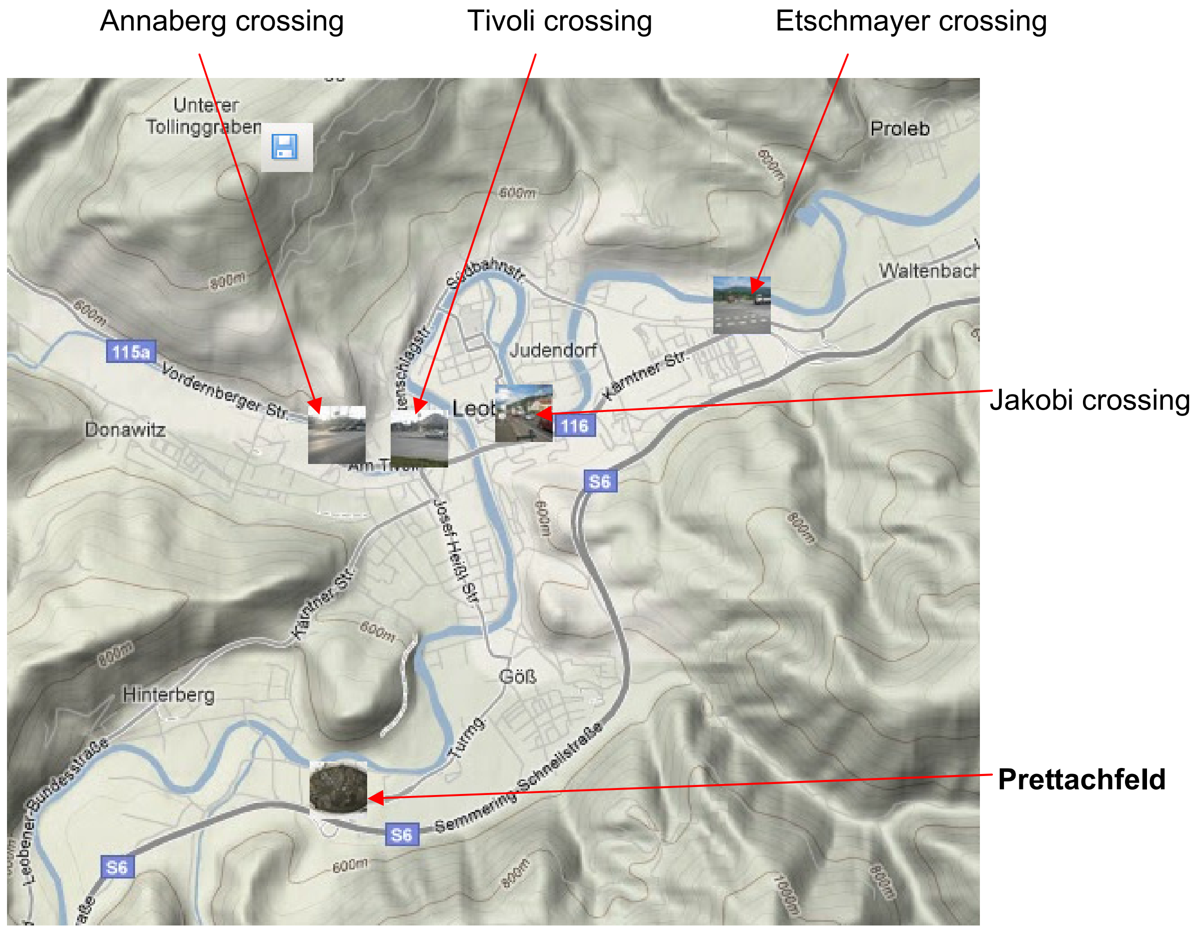
Etschmayer crossing: KGP01 and KGP02

Annaberg crossing: KGP03 and KGP04

Jakobi crossing: KGP05 and KGP06

Tivoli crossing: KGP07 and KGP08

Prettachfeld: KGP09



Annaberg crossing

Tivoli crossing

Etschmayer crossing

Jakobi crossing

Prettachfeld

Coordinate:

Etschmayer Crossing: North latitude 47°23′5″; East longitude: 15°7′9″

Annaberg Crossing: North latitude 47°22′35″; East longitude: 15°4′50″

Jakobi Crossing: North latitude 47°22′40″; East longitude: 15°5′54″

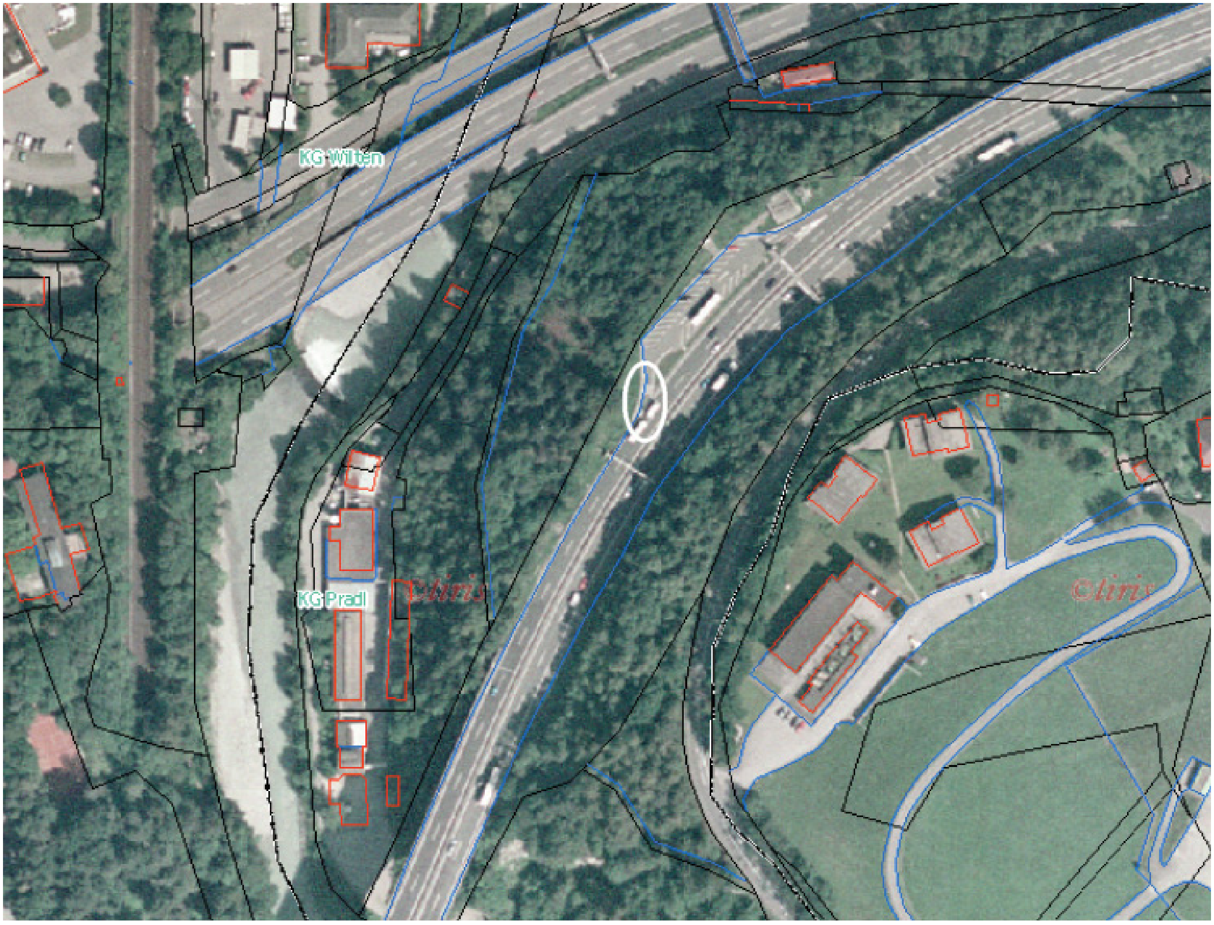
Tivoli Crossing: North latitude 47°22′34″; East longitude: 15°5′19″

Prettachfeld: North latitude 47°21′12″; East longitude: 15°4′51″

Sample sites for snow sample

Highway A13

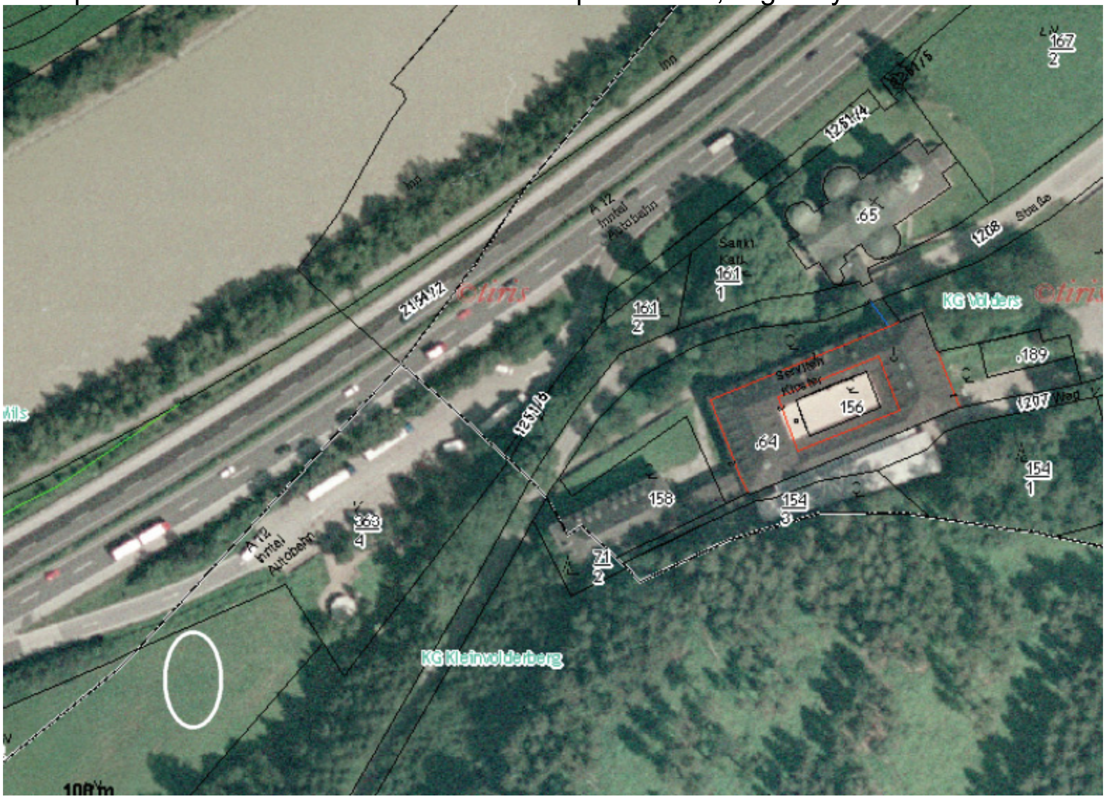
Sample site and collection of the snow sample SNP01, Highway A13



Coordinate: North latitude 47°15′5″; East longitude: 11°24′24″

Highway A12

Sample site and collection of the snow sample SNP02, Highway A12



Coordinate: North latitude 47°16′58″; East longitude: 11°33′10″

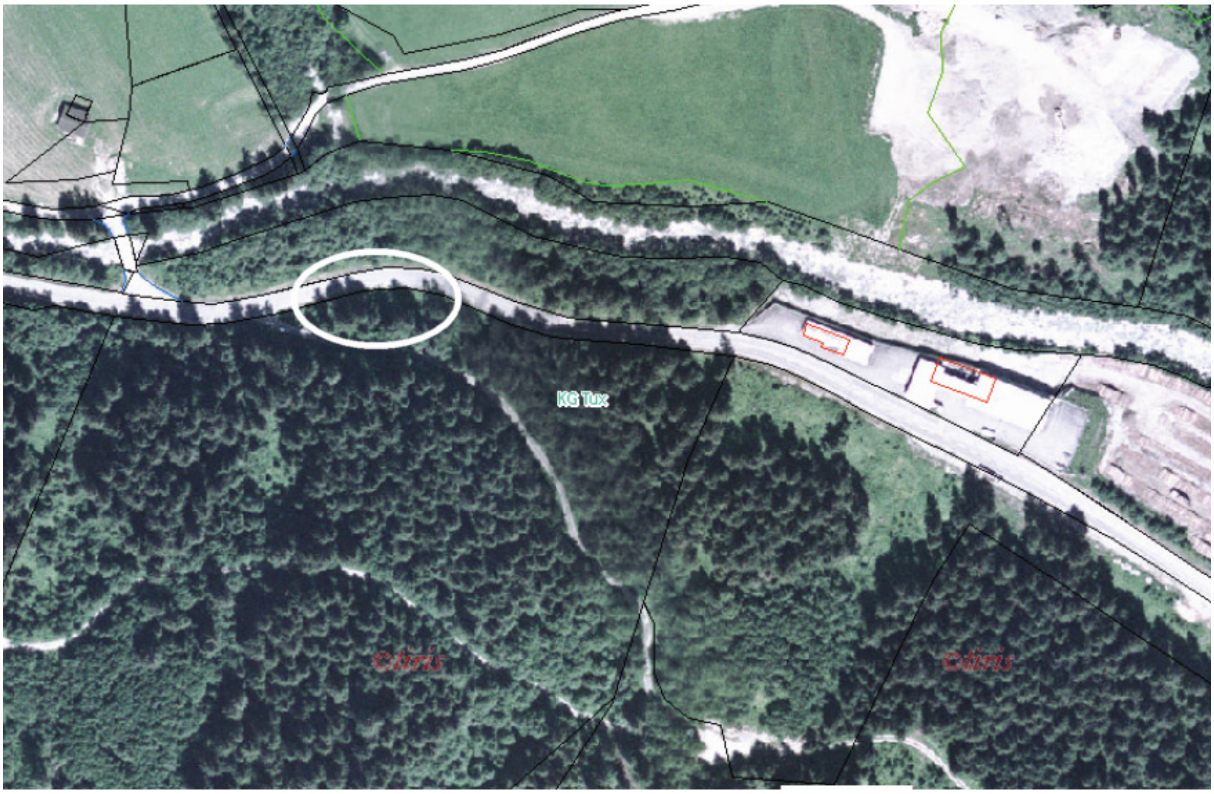
National road B181

Sample site and collection of the snow sample SNP03, National road B181

Coordinate: North latitude 47°24′25″; East longitude: 11°47′8″

Tuxer local road L6

Sample site and collection of the snow sample SNP04, Tuxer local road L6



Coordinate: North latitude 47°9′34″; East longitude: 11°45′25″

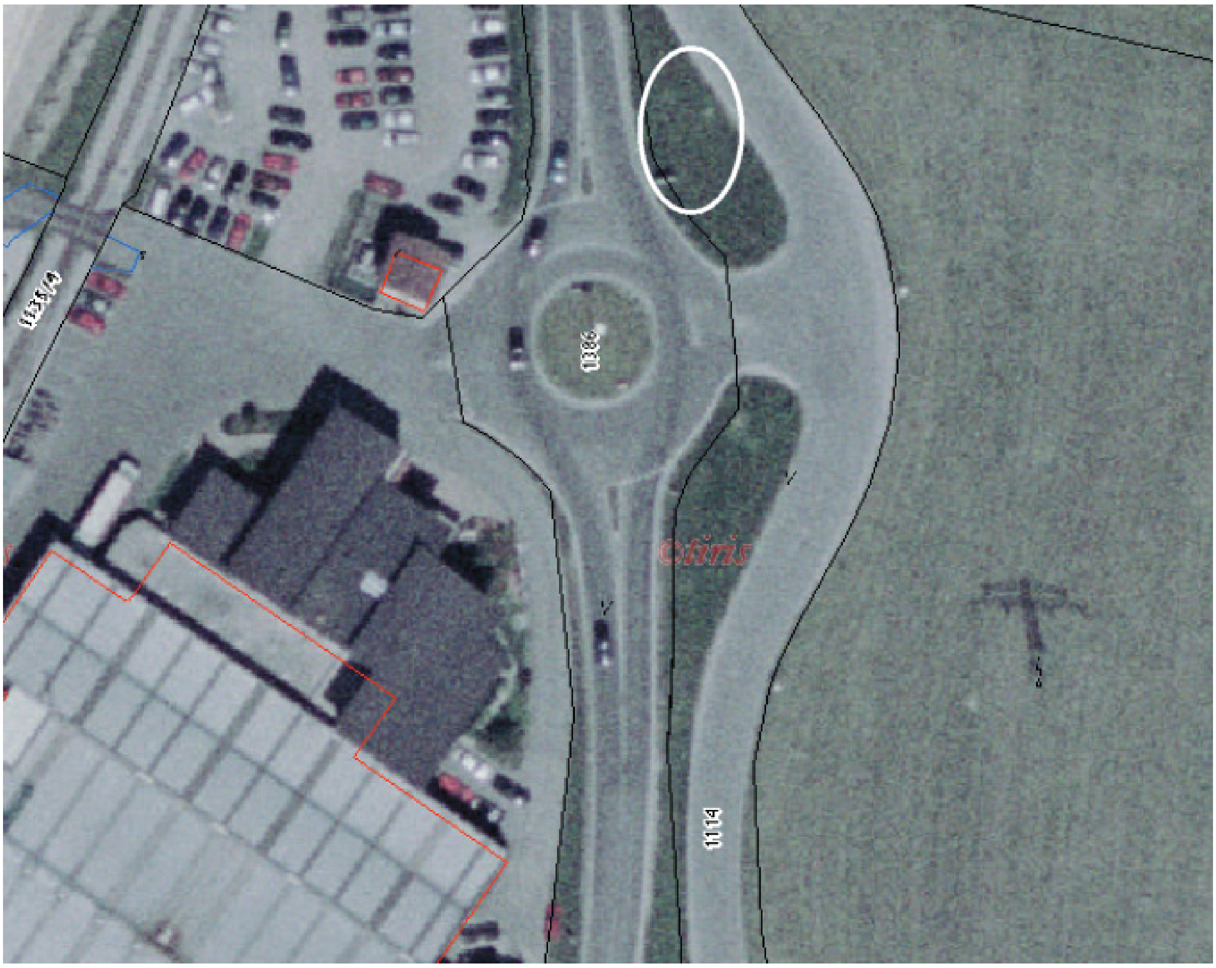
National road B165

Sample site and collection of the snow sample SNP05, National road B165

Coordinate: North latitude 47°12′46″; East longitude: 11°55′46″

National road B169

Sample site of the snow sample SNP06, National road B169



Coordinate: North latitude 47°11′36″; East longitude: 11°52′15″

Zillergrund

Sample site and collection of the snow sample SNP07, Zillergrund

Coordinate: North latitude 47°9′50″; East longitude: 11°54′12″