Thesis for the Completion of Masters of Science

In Applied Environmental Measurement Techniques

Platinum Group Elements and Their Distribution in Accra, Ghana

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Abstract

Over the past few decades there have been increasing amounts of platinum group elements (PGE) mobilised in the environment. It has been proven that these metals are being emitted from the exhaust systems of vehicles equipped with catalytic converters. Recent findings suggest that PGE are being transported globally. A loose network of researchers has begun to try and assess the validity of this hypothesis. This project takes a first look at PGE levels in the developing world.

Samples were collected in Accra, Ghana. Aerosol, road sediment, soil and grass samples were taken from five sites that differed in traffic density. Samples were put into solution by microwave digestion and than analysed using ICP-MS. Concentrations were then corrected mathematically. Only platinum concentrations could be determined. Aerosol concentrations were deemed inaccurate.

Despite the fact that the car fleet in Ghana is old, approximately 70% of the car fleet is equipped with catalytic converters. In general Pt concentrations increased with increasing traffic density, indicating a vehicular source. Pt concentrations decreased along environmental compartments. Pt in road sediments ranged between 1.30 and 39.56 ng g^{-1}. Pt in soils ranged between 1.09 and 15.80 ng g^{-1}. These levels are comparable to those found in Europe. There is some indication that the soil character together with several environmental factors special to Ghana may render Pt more soluble. This was reflected in grass Pt concentrations which ranged from 0.50 and 15.28 ng g^{-1}. These values are higher than those found in Europe. This could be a significant issue in the future as food is a major pathway for PGE into humans.

Leaded petrol is still in use in Ghana. Environmental lead levels showed the same concentration variations as Pt across sites for the analysed media. This indicates that Pt and Pb both have a vehicular source. It is unclear if there is an association between Pt and Pb.

Evidence found here suggests that the PGE problem is as advanced in Ghana as it is in Europe. This problem could be augmented by the use of leaded petrol.

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Abbreviations and Acronyms

AAS	Atomic Absorption Spectrometry
AECC	Association for Emissions Control by Catalyst
AFR	Air to Fuel Ratio
cpsi	cells per square inch
CSV	Cathodic Stripping Voltammetry
DC	Direct Current
E_{50}	Median Effect Concentration
ETV	Electrothermal Vaporisation
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
	LA- Laser Ablation
	HR- High Resolution
	LR- Low Resolution
IR	Infra Red
LDT	Long Distance Transport
LEAFS	Laser-Excited Atomic Fluorescence Spectrometry
m/z	mass to charge ratio
NAA	Neutron Activation Analysis
ppb	Parts Per Billion
PGE	Platinum Group Elements (specifically Pt, Pd and Rh)
PM	Particulate Matter
RF	Radio Frequency
SIMS	Secondary Ion Mass Spectrometry
TWC	Three-Way Catalyst
USN	Ultrasonic Nebuliser
UV	Ultra Violet
XRF	X-Ray Fluorescence

Project Overview

The installation of catalytic converters on automobiles in Europe, Japan and North America has been rising since the late 1970's. Today, catalytic converters are mandatory on all new vehicles manufactured in these locations. Concurrently, there has been a growing research focus placed on the platinum group elements (PGE). This occurrence is not coincidental. These noble metals, specifically platinum (Pt), palladium (Pd) and rhodium (Rh) have been increasingly mobilized in the environment and it has been proven that these metals are emitted from the exhaust systems of catalytically equipped cars. While the background and current levels are low, the full implication of these potentially allergenic and toxic metals accumulating in various environmental compartments is not known. Part of the uncertainty surrounding PGE research lies in the fact that they exist in such low concentrations and are difficult to determine accurately. They have been assayed in a variety of different media from tree bark to soils to aquatic macroinvertebrates to atmospheric aerosols, demonstrating the fact that PGE are able to disperse widely. If PGE are indeed found to be a threat, the implications are great.

Recently PGE have been discovered in polar and alpine regions (Barbante et al., 2001). This was a landmark finding in PGE studies as manufacturers have disputed the claim that catalytic metals are transported away from the vicinity of traffic areas. The PGE levels in Greenland indicate that these metals are being circulated globally, an event partially attributable to their inert character. In response a loose network of researchers the world over has begun to try and increase the validity of what has been termed the *global PGE particle distribution theory*. Locations for this work include Sweden, Australia, France, South Africa, United States, Greenland and Ghana. This thesis presents findings from research carried out in Ghana.

Yet, finding PGE in Ghana does not prove that these metals are transported to this equatorial region solely from catalytically equipped nations. In this country all vehicles are imported, the vast majority of them coming from Europe. Therefore it is by chance that the car fleet in Ghana has quite a few catalytically equipped vehicles, all of which may emit PGE to the environment. This issue is further complicated by the fact that the only petrol that is available in this country, and many of those surrounding, is leaded. Leaded petrol poisons catalytic converters and in many developed countries this had prompted the phase out of this fuel type. There is little research about what type of PGE emissions are produced when a catalytic converter is used with leaded petrol.

While proving or disproving the global PGE particle distribution theory is beyond the scope of this project, it does serve as a starting point for PGE monitoring in Ghana and may one day be able to aid in accepting or rejecting this idea. The above in mind the objectives of this project are:

1. Determine PGE concentrations in various media in Ghana at both urban and rural sites.
2. Understand the movement of PGE in and between different environmental compartments.
3. Lay the groundwork for future PGE monitoring in Ghana.
4. Explore what type of PGE emission, if any, arise from cars equipped with catalytic converters employing leaded petrol.

Background Information

1. Platinum Group Metals

The platinum group elements (PGE) are a metal group comprised of iridium, osmium, platinum, palladium, ruthenium and rhodium. These metals have similar advantageous properties such as high melting points, low vapour pressures and resistance to chemical attack. They are best known for their outstanding catalytic properties. The automotive industry, in attempts to decrease harmful gaseous emissions from cars, has used platinum in catalytic converters since they were first developed; later palladium and rhodium were also included. As PGE emissions from catalytic converters are the focus of this research the abbreviation PGE will henceforth only refer to Pt, Pd and Rh.

1.1 Production and Consumption

The automotive industry has been the single largest consumer of PGE since 1979, accounting for nearly 50% of the world-wide consumption in the year 2000 (Hilliard, 2000). In general a single catalytic converter contains just 1.4 to 5.8 g of PGE (Petrucci et al., 2000). PGE are also used in electrical equipment, jewellery, chemical, glass and petroleum applications (Table 1).

Table 1. World-wide PGE demand by industrial sector (modified from Cowley and Hankin, 2001).

Application	*Demand for PGE (in tons)*					
	2000			2001		
	Pt	Pd	Rh	Pt	Pd	Rh
Autocatalyst (gross)[a]	53.6	159.9	22.5	66.9	137.2	15.5
Autocatalyst (recovery)[b]	13.3	6.5	2.2	14.5	8.2	2.6
Chemical	8.1	7.2	0.99	8.1	6.9	1.2
Electrical/Electronic	12.8	61.2	0.19	10.8	29.8	0.17
Glass	7.2	-	1.2	8.2	-	1.2
Jewellery	80.2	7.2	-	71.4	6.8	-
Petroleum	3.0	-	-	3.7	-	-
Other	14.6	24.9	0.31	13.8	21.4	0.31

a- Autocatalyst gross demand is purchases of PGE by the automotive industry for manufacture of catalytic converters.
b- Autocatalyst recovery refers to the PGE recovered from used catalytic converters.

PGE in the earth's crust are not very abundant. The Spaniards first mined platinum in the 1700's but at the time it was considered an impurity in silver mining. There are very specific geological conditions required in order for PGE mining to be economically profitable and it was not until the mid 1960's that techniques for determining ppb levels in geological materials were developed (Hilliard, 2000). PGE can be found in primary deposits in which they are associated with other elements and often mined as by-products (*e.g.* with copper, iron or silver)(Rao and Reddi, 2000). PGE can also be found in secondary deposits formed by the erosion and accumulation of PGE in a pure metallic form (Hilliard, 2000; Rauch and Morrison, 2001).

PGE mining is concentrated to a few countries (Table 2). Data from 1997 to present indicate that for nearly every year and each metal, the demand for these metals was higher than the supply; therefore PGE prospecting is increasing yearly. This is especially true for platinum and rhodium as their use is expected to increase in the next years due to the higher market price of palladium, the stricter emissions standards being enacted in many countries and the increasing demand for diesel engine catalysts (Hilliard, 2000; Cowley and Hankin, 2001).

Table 2. Regions producing PGE world-wide (modified from Cowley and Hankin, 2001).

Producing Region	*Supply of PGE (in tons)*					
	2000			2001		
	Pt	Pd	Rh	Pt	Pd	Rh
South Africa	107.7	52.7	13.0	115.7	56.7	12.5
North America	8.1	18.0	0.45	9.6	23.1	0.62
Russia	31.2	147.4	6.5	29.8	130.4	2.8
Others[a]	3.0	3.0	0.085	3.1	9.8	0.11

a- Other producing countries are Australia, Serbia and Montenegro, Colombia, Finland, Japan and Zimbabwe (Hilliard, 2000).

There is still little known about the behavior of PGE, such as their bioavailability, speciation behavior and environmental transformations. These unknowns are further compounded by the analytical difficulties that are inherent to PGE determination. Among the three catalytic PGE, platinum is the best studied. Owing to lack of quality assurance in Pd analysis and the lack of information available on the environmental behavior of rhodium, larger knowledge gaps exist with regard to these metals.

1.2 Platinum, Palladium and Rhodium and Human Risk

South Americans have used platinum in jewellery for several centuries and this practice still continues today. Modern applications began in the 19th century when platinum was first used in dentistry and the electrical and chemical engineering fields. In the 1940's platinum was used as a catalyst in the large-scale production of fertiliser. It also served a catalytic function in the petrochemical industry. In the 1960's the medical field started exploring the use of platinum based drugs against forms of cancer as it was shown to inhibit cell division (Rauch and Morrison, 2001). Perhaps the most significant platinum use to be developed in terms of increasing the environmental levels however, was the introduction of the first catalytic converters in 1975 in the US (Heck and Farrauto, 1996).

The effects of platinum in terms of adverse health impacts are as yet unclear. In humans, the use of platinum based drugs in medicine has shed some light on the potential effects. Platinum reacts with DNA to slow tumour growth but side effects include nephrotoxicity and the inhibition of bone marrow formation. Platinum is known to bind to blood proteins that serve as transport vehicles to the liver and kidneys where it resides before it is excreted. This excretion occurs over a long time period as was monitored in cancer patients taking cisplatin, a platinum based drug (Rauch and Morrison, 2001).

Studies on platinum intake by individuals have produced mixed results. Evidence points to the fact that the platinum species in question is of central importance. Metallic Pt has proven to be innocuous in toxicity tests and there are few, if any, reports of it being an occupational hazard (Merget and Rosner, 2001). There is some question though, as to whether or not the same can be said for finely dispersed metallic Pt particles, as there are few studies on this topic. In model experiments performed by Artelt et al. (1999a), Pt(0) was deposited on aluminium oxide particles in order to mimic those emitted from catalytic converters. These particles were then used in inhalation studies on rats. Their findings suggested that Pt was indeed bioavailable. In body tissues and fluids over 90% of this bioavailable platinum was bound to proteins.

Emissions from catalytic converters are thought to be almost exclusively in the relatively inert metallic form. Indeed, highway workers exposed to vehicle emissions did not show significantly higher platinum concentrations in their urine as compared to non-exposed individuals (Begerow et al., 1997). Despite this, one cannot exclude the possibility that Pt salts are emitted or that they are not formed from Pt particles once liberated in the environment. Platinum salts are soluble and in general become more deleterious with increasing solubility. Halogenated Pt salts are proven harmful causing respiratory sensitisation and allergenic reactions. There are many cases of occupational exposure in Pt refineries and catalyst production plants. In two of these cases the level was below the occupational threshold limit value (Merget and Rosner, 2001).

Like platinum, palladium is used in dentistry and electrical applications. It has seen an increasingly important role in catalytic converters acting as a compliment or a substitute to platinum (Rauch and Morrison, 2001). Future projections see a decrease in the use of this metal due to its currently high market price. Conversely, Rh use is expected to increase in the near future to meet the stricter emissions standards being implemented in various countries (Cowley and Hankin, 2001). It has only been in the last twenty years that the use of rhodium has begun but its ability to reduce nitrogen oxides has been realised and they are included with platinum and palladium in the latest catalytic converter models (Heck and Farrauto, 1996).

Metallic Pd, unlike Pt, can cause contact dermatitis. Halogenated Pd and Rh salts have caused increased tumour incidences in one study but the study itself was questioned for its validity[1]. Their cytogenic and mutagenic effects have proven to be less than that of platinum (Merget and Rosner, 2001). What is of concern however is the fact that though Pd and Rh are found in lower concentrations in the environment than Pt, these two metals show higher blood and urine levels in humans (Begerow et al., 1997; Krachler et al., 1998). This is probably due to their different mobility and uptake mechanisms in the environment, which highlights the need to further study these two PGE.

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[1] For further reading see Schroeder, H.A. and M. Mitchner. Scandium, chromium (VI), gallium, yttrium, rhodium, palladium, indium in mice: effects on growth and life span. J Nutr 101:1431-1438.

2. Catalytic Converters and Platinum Group Metals

If cars burned fuel with perfect efficiency, the only by-products would be carbon dioxide and water, which are relatively harmless. In reality this is not the case and those hydrocarbon (HC) molecules in fuel that are not burned to completion leave the vehicular exhaust system either intact or as carbon monoxide (CO). In addition to this, atmospheric nitrogen is often oxidised during combustion creating nitrogen oxides (NO_x) (web ref. 1). Carbon monoxide is a dangerous gas that can be fatal at high levels and cause heart problems at lower ones. NO_x alone can cause respiratory complications, but when able to react with HCs in the air, forms ozone. Ozone can also cause respiratory complications but more importantly it is a component of smog, an air quality problem that plagues most cities (Warneck, 2000).

Catalytic converters were introduced in the US in 1975 in response to new legislation, the Clean Air Act of 1970, which raised concerns over automobile emissions. A catalytic converter is a device which is mounted directly onto the exhaust system of a car. The converter catalyses the conversion of HC and CO to water and CO_2 and NO_x to N_2 thereby reducing the harmful impacts of vehicle exhaust. Catalytic converters were proven effective and in 1976 both Canada and Japan followed the US's example and began their use. They have been required on all new vehicles manufactured in the United States since 1977 and in Europe since 1993 (Rauch and Morrison, 2001).

Catalytic converters are a commercial, but still developing technology, and much research goes into improving their performance. With the projected increase in world-wide car use their role could be essential.

2.1 Catalytic Converter Reactions

The first catalytic converters focused on the oxidation of CO and HC and employed Pt and Pd in a ratio of 2.5:1. These metals were chosen because of their resistance to poisoning from the sulphur contained in fuels, something other metals like copper, chromium and nickel could not offer. These converters were termed Oxidation or Two-Way Converters and are still used today on diesel engine vehicles. The second wave of catalytic converters, the Three-Way Converters (TWC), were introduced in 1979. These differed from their predecessor in that they were able to reduce NO_x by including a third catalytic metal, rhodium (Heck and Farrauto, 1996). The equations for these oxidation and reduction reactions, promoted by the heat contained in exhaust, are given in the following reactions (2.1-2.5):

Oxidation of CO

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ (2.1)

Oxidation of Hydrocarbons

$C_xH_y + (x + y/4)\ O_2 \rightarrow xCO_2 + y/2H_2O$ (2.2)

Reduction of NO_x

$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$ (2.3)

$NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O$ (2.4)

$(2 + y/2)\ NO + C_xH_y \rightarrow (1 + y/4)\ N_2 + xCO_2 + y/H_2O$ (2.5)

2.2 Catalytic Converter Structure

Initially, small alumina pellets through which the exhaust passed supported the catalytic metals. This particulate support was replaced shortly after its introduction by monolithic support that involves a ceramic honeycomb structure coated with catalytic metals (Figure 1). Generally the ceramic used is cordierite, which is strong, resistant to thermal shock and does not expand at higher temperatures

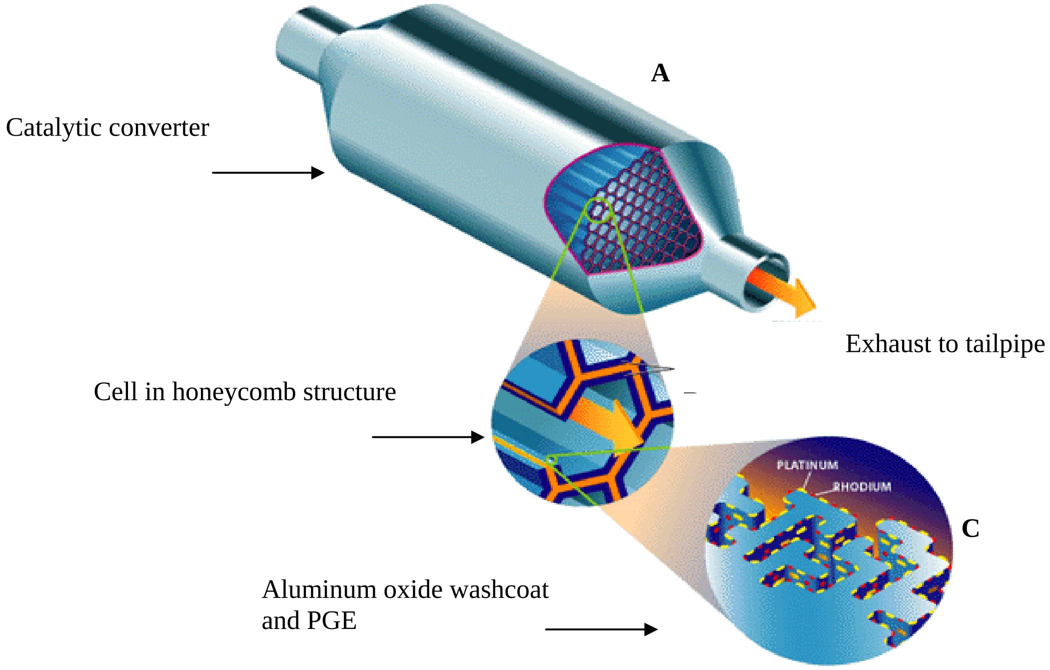

Figure 1. A monolith catalytic converter at different levels of magnification. (A) The catalytic converter is fitted on the exhaust system of the car, ideally close to the engine. (B) It is composed of cells in a ceramic honeycomb structure that is packed in a wire mesh. It is through these channels that the exhaust flows and meets the reaction surface. (C) The reaction surface is made up of an aluminum oxide washcoat that has PGE metals absorbed to it in the desired ratios (modified from web ref. 1).

(Palacios et al., 2000). Early honeycomb designs were clumsy with cell densities of 200 cells per square inch (cpsi) and wall thicknesses of 0.305 mm. Today manufacturers have produced honeycombs with 400, 600 and even 900 cpsi and wall thicknesses of 0.05 mm. This increases the surface area within the catalyst and thus the available reaction surfaces, improving the efficiency of the converter (web ref. 2). The honeycomb is coated with a porous aluminum oxide washcoat to which the desired PGE metals are absorbed. Ultrafine PGE particles are used with diameters in the nanometer range (1-10 nm)(Artelt et al., 1999b). There may be one or two washcoats, with double coats enhancing specific reactions and increasing durability. The washcoats are designed to provide the least amount of diffusion resistance thereby allowing gases to reach reaction sites readily (Heck and Farrauto, 1996).

TWC require a strict air-to-fuel ratio (AFR). This is controlled by exhaust-gas oxygen sensors, which make simultaneous oxidation and reduction reactions possible. The optimal AFR is between 14.4 and 14.7 for gasoline engines. The exhaust system operates between slightly rich and slightly lean but there is a time lag in adjusting the AFR to these variations. This would decrease conversion if not for washcoat additives that ‘store’ oxygen during the lean part of exhaust fluctuations. The most commonly used additive is CeO_2. Other washcoat additives include barium, nickel, titanium, lanthanum and zirconium oxides; these act mostly as stabilising agents (Heck and Farrauto, 1996; Rauch, 2001).

2.3 Catalytic Converter Ageing and PGE Emissions

Many of the problems that first affected the performance of catalytic converters have been overcome. For example, the time to 'light off' when adequate temperatures have been reached for catalytic reactions to begin has been reduced from 2 minutes to less than 20 seconds. Improving the positioning and increasing the depth of converters has achieved this (web ref. 2). Currently, the most pressing issues to understand are catalytic ageing and the loss of PGE from the converter itself. The latter has a recently realised, important environmental aspect.

In converters Pt may be found alone or in combination with various amounts of Pd and Rh, depending on the manufacturer. In a fresh catalyst platinum can be present as an oxide, chloride and/or bound to hydrocarbons. The chloride is most likely a remnant of chloroplatinic acid, which is used in converter fabrication. Rhodium in fresh catalyst is found in its metallic form or as an oxide (Rauch and Morrison, 2001). In fresh catalysts there is a relatively low soluble PGE fraction estimated at 5%. This soluble fraction in the fresh catalytic converter may be a result of washcoat preparation rather than PGE transformation (Palacios et al., 2000).

A fresh catalytic converter has the ability to remove 90% of pollutant gases (Barefoot, 1999). However, additives and impurities in fuel and other vehicular fluids can coat catalytic surfaces decreasing its effectiveness, even if 'clean' fuels are used. Good examples of this are the sulphur contained naturally in fuels and elements in lubricating oils (*i.e.* P, Ca and Zn)(Rauch and Morrison, 2001). This fouling, as well as mechanical deterioration and thermal and chemical processes can cause catalytic ageing. Any PGE species found in an aged catalyst that differ from fresh catalysts may be the result of reactions between catalyst components (*e.g.* Pt forming alloys with Rh) or sintering. The movement of atoms or smaller crystallites towards larger crystallites creates sintering. In this movement some of the PGE particles may leave the catalyst surface (Palacios et al., 2000). A fresh TWC would have particles averaging in diameter between 3-4 nm while aged catalytic particles may grow from 10 nm to several microns in diameter due to sintering action (Bertil et al., 1990). The high temperatures found within the converter and the nanocrystalline structure of catalytic PGE aids in such transformations (Rauch and Morrison, 2001).

Releases of PGE to the environment from catalytic converters can be attributed to evaporation, thermal sintering or mechanical and thermal erosion. Evaporation of PGE decreases the surface area available for reactions and is known to occur, despite the thermal stability of PGE, under oxidising conditions at temperatures above 900°C. Both of these conditions can be satisfied during vehicle operation. Studies by Palacios et al. (2000) and Moldovan, et al. (2002) have found that there are differential PGE release mechanisms for diesel and gasoline engine catalytic converters. In comparing old and new gasoline engine catalysts, PGE loses were greatest in the front portion of the converter indicating that mechanical abrasion is the most probable contributor to PGE release to the environment. PGE emissions based on exhaust fumes found that gasoline converters had decreased emissions with age. This is explained by the presence of weakly adsorbed PGE on the washcoat surface, which are expelled during the first stages of use. Bench tests performed by Artelt et al. (1999b) also found decreased platinum emissions with age. Conversely, PGE emissions from diesel engine catalysts were found to be more dependent on age than gasoline engine catalysts. Their PGE loss was spatially more constant than that found with the gasoline converter which indicates that there is a different mechanism for PGE loss, possibly as a result of sintering or fouling processes (Palacios et al., 2000; Moldovan et al., 2002).

3. Analytical Techniques

A major stumbling block for PGE studies is their determination. They are trace metals and though increasing in the environment, remain in low concentrations. There are several methods used in PGE determination: cathodic stripping voltammetry (CSV), neutron activation analysis (NAA), secondary ion mass spectrometry (SIMS), X-ray fluorescence (XRF), inductively coupled plasma-mass spectrometry (ICP-MS) and laser-excited atomic fluorescence spectrometry (LEAFS). Of these, ICP-MS has become the most commonly used instrument for PGE detection. It is advantageous in that it has a multi-element capability, low sample consumption, detection limits of ng l^{-1} and even pg l^{-1}, a wide dynamic range, high speed and the ability to measure isotopic ratios (Barbante et al., 1999). It is occasionally paired with laser ablation (LA) techniques for the analysis of solids.

3.1 Working Principle of ICP-MS

ICP-MS can be broken down into 5 main processes: sample introduction, sample ionization, ICP-MS interface, mass discrimination and detection (Figure 2).

1. Sample Introduction

   ICP-MS is capable of accepting gas, solid or liquid samples. Before reaching the plasma however, particles or droplets must be small enough in size. Gases require no pre-step before reaching the plasma. Solid samples are converted into micrometer-sized particles or vaporised. This can be done by, for example, laser ablation. If a liquid sample is introduced a nebuliser must be used in order to convert the sample into droplets. The nebuliser aspirates the sample with a flow of high velocity argon, which forms an aerosol. This fine mist must pass through a spray chamber, which removes particles larger than 4 μm.

2. Sample Ionization

   The sample is carried to the torch through an axial tunnel. It is in the torch that the plasma is located. The plasma itself is a highly ionized gas at elevated temperature. ICP-MS usually utilizes an argon plasma with temperatures between 6 000 and 10 000 K. Such is the case with the instrument used in this study but argon/nitrogen plasmas are also used. There are three concentric Ar gas flows into the torch. One supplies the nebuliser, which presents the sample to the plasma and one controls the position of the plasma within the torch. The main gas flow provides Ar to the plasma. The plasma is ignited by an electric discharge and maintained by a fine copper tube, the coupling or load coil. This produces a radio frequency, which creates an electromagnetic field. It is in this electromagnetic field that electrons are accelerated and collide with Ar atoms, thus forming the plasma. In the plasma the sample is vaporised, atomised and then ionised.

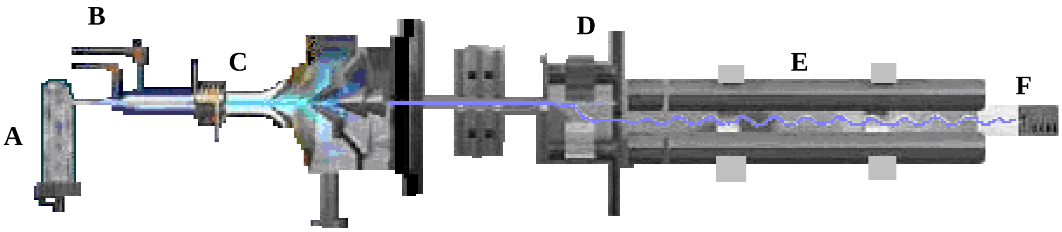

Figure 2. Cross-section of an ICP-MS instrument. The sample is introduced into the spray chamber (A) by the nebuliser. From there it flows into the torch (B) which has auxiliary and plasma gas inflows. The plasma (C) is maintained by the load coil just before the interface. The ion lenses (D) focus the ion beam. This beam passes through to the quadropole mass filter (E) in a vacuum chamber. Those species selected for will reach the detector (F) (modified from web ref. 3).

3. ICP-MS Interface

This is a most crucial part of the sample movement in this instrument. The atomization and ionization step occurs at high temperatures and atmospheric pressure. Ions are then fed into the MS component, which functions at room temperature under vacuum. Ions flow from the plasma through two successive cones, the sample and skimmer cones, having orifices of approximately 1 mm in diameter, into a pumped vacuum system. Here a supersonic jet forms and the ions are passed to the MS at high speeds. These vacuum conditions are required so that ions are free to move without the possibility of colliding with air molecules (Jarvis et al., 1992; Rauch, 2001).

4. Mass Discrimination

After the interface, ions are focuses into a beam by ion lenses and isotopes are separated based on their mass-to-charge ratio (m/z). The most commonly used mass filter is the quadropole mass filter. It is made up of four metal rods aligned in parallel with opposite rods paired together. Direct current (DC) and radio frequency (RF) potentials are applied to each pair. The ions pass through the central axis of the four rods and depending on the voltage values only one particular m/z will be selected for. If an ion does not have the m/z selected for its trajectory will be such that it does not make it through the quadropole to the detector (Rao and Reddi, 2000).

5. Detection

In an ICP-MS system, the most common type of ion detector found is an electron multiplier. When an ion strikes the surface of the cone shaped detector it causes electrons to leave and strike the surface further on, causing a cascade of electrons. These incoming electrons are converted to an electrical signal, which is interpreted by a computer (Jarvis et al., 1992; Rauch, 2001).

3.2 Interference in ICP-MS

When using ICP-MS to analyse PGE the results are subject to interference. These interferences can be broadly categorised into two groups: non-spectral and spectral. Non-spectral interference or matrix affects are complicated and not that well understood. It is more severe for the lighter mass elements and can be caused by suppression and enhancement effects and physical effects caused by high total dissolved solids (Rao and Reddi, 2000). This type of interference can however be overcome by using an internal standard that closely resembles the analyte.

Spectral interference occurs when several isotopes have the same or similar m/z so the mass filter has difficulty separating their signals. Spectral interference can be further sub-divided into three types: isobaric overlap, polyatomic ions and double charged ions. Isobaric overlap occurs when two different isotopes have essentially the same mass. This issue be can solved by using the isotopic pattern of the interfering element and the signal of one of its isotopes. Both polyatomic ions and double charged ions can be formed in the plasma and in ion extraction. Because samples are generally prepared in solution and Ar is the carrier gas there exists Ar, O, N and, depending on the sample preparation, Cl and other solvent components available to combine with each other or other available elements. These polyatomic ions may have the same m/z as the element being determined, causing spectral overlap. It is not the norm for the plasma to produce doubly charged ions. However, if the second ionization energy of an element is lower than the first ionization energy of argon, a doubly charged ion may form which will have half the m/z of a single charged ion. This will naturally lead to complications in the mass filtering of ions.

There are a number of methods for resolving these interferences. Changes can be made in the mode of sample introduction such as desolvation or LA to reduce oxide formation in the plasma (Rauch at al., 2000b; Barefoot, 1997). The easiest approach is to estimate the amount of interference and correct mathematically.

3.3 PGE Determination

As mentioned previously, PGE determination by ICP-MS has become an accepted and well-used technique. As such there is a great deal of experience in dealing with interferences in PGE determination (Krachler et al., 1998; Barbante et al., 1999; Rauch et al., 2000b). Argides, oxides and doubly charged ions overlap with PGE isotopes. The interfering species of each of the most abundant and analytically simple PGE isotopes are given in Table 3 together with the resolution required to deal with each.

Table 3. Interfering species and minimum resolution required to separate interferent and analyte masses (modified from Rauch et al., 2000b).

Element	*Interfering Species*	*Minimum Resolution Required ($\Delta m/m$)*
^{103} Rh	$ArCu^+$	8 040
	$ArZn^+$	10 100
	Pb^{2+}	1 248
	SrO^+	102 900
	RbO^+	147 000
^{105} Pd	$ArCu^+$	700
	YO^+	27 600
	SrO^+	1 000 000
	RbO^+	28 400
^{195} Pt	HfO^+	8 100

Rauch et al. (2000b) found that the only interfering species affecting Pt, HfO^+, can be eliminated by the use of high resolution (HR) ICP-MS. The same technique was also able to remove some of the interferences affecting Rh but no such results were obtained with Pd. Pd remains an analytical challenge and previous findings are subject to some speculation. Pt results with low resolution (LR) ICP-MS were found to be similar to those results using HR; Rh levels were slightly higher with LR than HR.

Here, interferences can be corrected mathematically by estimating the contribution of the interfering species to PGE signals through the analysis of standard solutions. The formulas used in corrections are given below (3.1-3.3):

$$I_{Pt} = I_{Pt,s} - (I_{Hf,s} * R_{HfO/Hf}) \tag{3.1}$$

$$I_{Pd} = I_{Pd,s} - (I_{Cu,s} * R_{ArCu/Cu} + I_{Y,s} * R_{YO/Y} + I_{Sr,s} * R_{SrO/Sr} + I_{Rb,s} *x\ R_{RbO/Rb}) \tag{3.2}$$

$$I_{Rh} = I_{Rh,s} - (I_{Cu,s} * R_{ArCu/Cu} + I_{Pb,s} * R_{Pb^{2+}/Pb} + I_{Sr.s} * R_{SrO/Sr} + I_{Rb,s} * R_{RbO/Rb}) \tag{3.3}$$

Where I_{PGE} is the corrected intensity, $I_{X,s}$ is the apparent intensity of the species and $R_{A,B}$ is the ratio of A^+ to B^+ determined previously in standard solutions containing the selected species (Rauch et al., 2001).

3.4 Laser Ablation-ICP-MS

Laser ablation is a sample introduction system for ICP-MS that has been increasingly used to investigate solid samples. Lasers concentrate a large amount of energy into light and when focused on a sample have the ability to vaporise the material if various parameters like the wavelength and absorption characteristics of the material are correct. LA-ICP-MS takes this ability to ablate materials and uses it to introduce the sample into the ICP-MS. Both infrared (IR) and ultraviolet (UV) lasers have been used but UV lasers have been found more effective as there is less melting around the craters that are formed on the surface of ablated materials. This allows for the ablation of smaller, well-defined areas. The ablated material is swept by a carrier gas flow to the ICP-MS for analysis (Rauch, 2001).

LA-ICP-MS has several advantages. Firstly, there is no sample preparation required. Sample preparation can be lengthy, potentially cause contamination and for biological samples, dissolution may not be complete. Secondly, as it is a dry sample, the interferences caused by polyatomic species are reduced because there are no water or acid species to interact with the Ar in the plasma. Its spatial resolution is also high and can be controlled. This means that gradients across samples can be examined. On the other hand, calibration of LA-ICP-MS is challenging. This requires a very close matrix-matched calibration standard. Additionally this technique suffers from the fact that due to sample heterogeneity and small spatial resolution, results may be misleading.

These drawbacks aside it has proven effective in determining PGE concentrations. New methods using scanning LA-ICP-MS are being developed to identify and track individual PGE particles emitted from catalytic converters. Presently Rauch et al. (2002) have been able to use this technique to identify from which type of catalyst a particle comes from. It is hoped that eventually particles may be tracked to catalytic manufacturers and even the car producer.

4. Platinum Group Metals in the Environment

The accumulation of PGE in the environment is an emerging issue and there is no long-term information database available. No direct effects of PGE on ecosystem or human health have been proven. Evidence to date is however suggestive of damaging effects.

4.1 Natural PGE

The natural background values of PGE are low (Table 4). Prior to any anthropogenic inputs the natural levels of PGE were in the range of ~0.01 pg g^{-1} for Pt and Pd and 0.0007 pg g^{-1} for Rh (Barbante et al., 2001). Among the three PGE discussed here, Pt is the most abundant. The geochemical frequency of Pt lies in the 5-10 ppb range and it holds the 72nd position in the elemental frequency table (Alt et al., 1997).

Table 4. Crustal concentrations of PGE.

Location	*PGE*	*Concentration (ng g^{-1})*	*Reference*
Earth crust	Pt	0.4	Wedepohl, 1995
	Pd	0.4	
	Rh	0.06	

4. 2 Anthropogenic PGE

There are 500 million cars equipped with catalytic converters world-wide with an average yearly mileage of 15 000 km. Based on the most recent reliable estimates this equates to 0.5-1.4 tons of Pt being emitted into the environment in one year (Barbante et al., 2001). These emitted PGE have entered all environmental compartments having been measured in the atmosphere, the hydrosphere, the geosphere and the biosphere. In this study aerosol, soil, road sediment and vegetation samples were taken. As such the following review will look specifically at these media.

4.2.1 PGE Emissions from Catalytic Converters

It has become an accepted fact within the scientific community that the increasing environmental PGE levels are caused by emissions from catalytic converters. The calculation of Pt/Rh ratios from environmental samples has been a good evidence for this, as this ratio is known for particles emitted from catalytic converters to be 5 or 6 (Gomez et al, 2001; Zereini et al., 1997). Rauch et al. (2001) found agreement with this ratio in their assay of airborne materials in Gothenburg, Sweden. However, some ratios were much higher than expected. This was attributed to catalytic ageing; Pt particles grow in size within the catalyst while Rh remains finely dispersed, thus increasing the ratio. Gomez et al.

(2001) also used associations with other known car pollutants (Pb, Ce, Zr and Hf) to establish that PGE emissions are indeed from vehicles.

Test stands have estimated PGE emissions to be in the area of 2-40 ng of Pt per km driven (König et al., 1992). Artelt et al. (1999b) found mean platinum emissions of ~90 ng of Pt per km occurred in test stands with new converters. Increased simulated speeds increased the platinum release from the exhaust system. Studies simulating stop-and-go city traffic found that emissions were two to three times higher than at a constant speed (Zereini et al., 1997).

It is believed that PGE emissions under real driving conditions are even higher. Schäfer et al. (1999) estimated emissions of 270 ng per km per vehicle based on a combination of traffic density and soil Pt level data in Germany. Helmers (1997) suggested an even higher figure of 500-800 ng Pt per km based on test stand experiments and plant and soil samples. The substantial difference in emissions between simulated and true releases can be attributed to the fact that working conditions in reality are rarely optimal (*e.g.* temperature, waste gas composition) thereby reducing waste gas conversion and increasing PGE emissions. Today's monolithic converters however, have emission rates two orders of magnitude lower than older pelleted catalysts (Barefoot, 1997).

It should be noted that not all environmental PGE is accounted for by catalytic emissions. This is especially true for Pd and Rh. It is possible that an amount of Pd and Rh are released from other vehicular sources (*e.g.* fuel, oil, spark plugs) or from industrial alloys. It is also possible that these two metals have higher nobilities than Pt, thus persist longer (Palacios et al., 2000). Kummerer and Helmers (1997) found that hospital effluents contain a high amount of platinum and contribute to the elevated levels in sewage sludge.

4.2.2 Characteristics of PGE in the Environment

Much effort has been directed towards understanding PGE behaviour once released from an exhaust system. The main oxidation states of Pt are 0, +2 and +4. It is reportedly emitted in its metallic form. PGE are emitted attached to particles of aluminium oxide and is often found associated with Ce, which can be sourced back to the catalytic converter washcoat. Elemental fingerprinting by LA-ICP-MS shows that aside from Pt-Rh, PGE have a low association within particles indicating that they are emitted separately (Rauch et al., 2000a).

Past studies have found that there was a small amount of altered Pt, possibly in an oxidised form, liberated from converters (Barefoot, 1997). König et al. (1992) detected no water-soluble Pt species in PGE emissions tests. Artelt et al. (1999b) suggest that the emitted soluble Pt fraction is less than 1% of the total emissions, therefore most of the emitted Pt is not readily available for uptake by biota. However, past studies that have found Pt in biological samples are numerous: roadside vegetation (Alt et al., 1997; Helmers, 1997), macroinvertebrates (Rauch and Morrison, 1999) and trees

(Becker et al., 2000) to name but a few. This indicates that there is some process rendering the Pt bioavailable. This process probably occurs in the media surrounding the plant or animal (*i.e.* aquatic sediment, soil or road sediments) but the specifics remain unclear. Studies of roadside catch basins found no dissolved platinum in solution in undisturbed basins. Disturbed basins showed dissolved Pt concentrations of 1.7 to 3.8 ng l^{-1}. There is a possibility that this is due to bacteria in the sediments that are able to release organically bound water-soluble species (Wei and Morrison and, 1994a). There is a suggestion that humic materials in soils may act to transform Pt as well.

Alt et al. (1993) found that Pt had different solubility (in 0.07 M HCl) depending on which size fraction was examined. Smaller airborne particles showed higher solubility (30-43%) than tunnel dust (2.5-6.9%). The finely dispersed form of catalytic metals in the environment does make them more likely to be soluble due to differences in reaction surface area compared to bulk PGE. Zereini et al. (1997) examined PGE solubility under various environmental conditions. They found that low pH and the presence of sulphur increased the solubility of catalytic PGE. They state that only a relatively small fraction of Pt and Rh is soluble under different environmental conditions

Studies of Pt binding capacity to proteins has shown that it is capable of binding to both low and high molecular weight proteins. This is important in terms of their pathway through biological materials. The oxidation state of Pt species has been shown to influence binding behaviour. For example, Pt(II) can form many more bonds than Pt(IV). There is some suggestion that the binding behaviour of platinum is dependent on which biotic species one is examining. Under laboratory conditions the methylation of platinum has been performed. Methylation of metals in general leads to more toxic species. It is as yet unclear if methylation of platinum occurs *in vivo* (Rauch and Morrison, 1999).

4.3 PGE in Different Environmental Compartments

4.3.1 Soils and Sediments

Important to the dispersion of PGE in the environment is the formation of road sediments from the wearing of vehicles and their emissions. It is in this environmental compartment that most PGE first resides after emission. From this point it may be taken away as airborne particulate matter, transported by water to enter aquatic biota and river sediments or deposited on nearby soils were it can enter into terrestrial biotic pathways (Schäfer et al., 1999). Road dusts are known to exhibit spatial and temporal variability in their content and rain and wind patterns as well as traffic conditions influence distribution. No seasonal differences have been reported (Gomez et al., 2001).

Several authors have reported rising concentrations of PGE in road dust over the past years. Schäfer et al. (1999) found values two and three times higher for Rh and Pt between the years of 1990 and 1997 along various motorways in Germany. Wei and Morrison (1994b) found that in three different size fractions, <63 μm, 63-125 μm and 125-1 000 μm, Pt increased from 3.0 to 8.9 ng g^{-1}, 1.5 to 3.6 ng g^{-1} and <0.5 to 2.8 ng g^{-1} respectively between the years of 1984 and 1991. Table 5 gives an overview of concentrations found in recent publications.

Table 5. Concentrations of PGE in various soil and road sediment studies.

Location	*Size fraction*	*PGE*	*Concentration* [a] *(ng* g^{-1}*)*	*Medium*	*Reference*
Dortmund, Germany	-	Pt	0.14	Background soil	Alt et al., 1997
			20.9	Highway soil	
Ascot, UK	-	Pt	<0.21	Background soil	Jarvis et al., 2001
		Pd	<0.45		
		Rh	<0.16		
Sheffield, UK	<63μm	Pt	58	Urban road dust	Gomez et al., 2002
London, UK		Pt	53		
Munich, Germany		Pt	179		
		Rh	74		
Rome, Italy	<63μm	Pt	14.4-62.2	Urban road dust	Petrucci et al., 2000
		Pd	102-504		
		Rh	1.9-11.1		
Madrid, Spain	<63 μm	Pt	220	Urban road dust	Gomez et al., 2001
		Rh	74		
		Pt	<1.6	Background dust	
		Rh	<0.2		
Göteborg, Sweden	<63 μm	Pt	157	Urban road dust from 1998	Rauch et al., 2000b
		Rh	60.4		
		Pt	<0.15	Urban road dust from 1984	
		Rh	2.82		

a- Values with <x indicate values below given detection limit, single values are means, while two values represent a range.

Zereini et al. (1997) found a Pt/Rh ratio of between 4.6 and 5.6 in soil. They use this as evidence for the inert and immobile nature of PGE in soils. PGE were left for 5 months in soils of various pH and they report the greatest solubility of PGE was under acid conditions (pH 1-3). Naturally soils vary in pH between 5 and 8 thus anthropogenic influence is likely to be required to reach such conditions. NaCl concentrations were found to have little effect on Pt and Rh solubility in soil. Of most interest was the finding for sulphur: increasing sulphur levels in soil increased the solubility of Pt and the solubility increased with residence time. Sulphur, a catalytic poison, is contained in fuels and is known to lower the redox potential of Pt to allow for oxidation. It is possible then that Pt is emitted on particles containing sulphur and Pt may be increasingly mobilised with time. Moreover, sulphur-containing complexones are common in humic soils where Pt particles may be oxidised.

Lustig et al. (1996) point out that for PGE to enter into the food chain the nature of the soil growing the vegetation is of key importance. Transformation reactions in the soil may oxidise Pt creating a more reactive species and thus increase chances that Pt is bioavailable. Bioavailability may however decrease depending on the sorption-capacity of the specific soil; those high in clay or organic materials are known to absorb heavy metals. By comparing different Pt compounds with tunnel dust on a clay-like humic soil, it was also demonstrated that the particle size is important for Pt transformations. The tunnel dust was oxidised to a larger extent than the comparable Pt compounds which was attributed to its nanocrystalline size. Zereini et al. (1997) found that small but significant amounts of Pt and Rh are absorbed in soils. Their findings also suggest the importance of the chemical (*e.g*. oxidation state) and physical (*e.g.* particle size) nature of a PGE particle in understanding its behaviour.

4.3.2 Air

The presence of PGE in airborne matter is important in terms of human health risk as particles may be small enough to be respirable and able to descend into the alveoli of the lung. Artelt et al. (1999b) found that 43-74% of emitted PGE containing particles had aerodynamic diameters greater than 10 μm and are as such non-inhalable. The respirable fraction, defined as those particles being less than 3.14 μm in this study, accounted for 11-36% of the emitted PGE depending on engine size. The size of this particular fraction increased with age.

Since airborne concentrations are quite low, in the pg m^{-3} range, their analysis is a challenge (Table 6). The measured airborne values have been found to increase with disruptive traffic flow (Zereini et al, 1997), traffic density and driving speed (Gomez et al., 2001). The distribution of PGE in airborne particles is not homogeneous and is associated with a wide range of particle diameters. Gomez et al. (2001) used a cascade impactor (size range from 65.3 to <0.39 μm) to sample atmospheric aerosols in Madrid and while no definite trend for Pt content and size fraction could be established, in most cases the Pt content was highest in the <0.39 fraction. Past methods for analysis have involved the digestion of filter samples which does not reflect particle distribution. Rauch et al. (2001) used scanning LA-ICP-MS and a parallel sampling scheme and found that there were relatively few particles of PGE but that they were found in multi-PGE complexes in high concentrations.

Table 6. Concentrations of PGE in various atmospheric aerosol studies.

Location	*Size fraction*	*PGE*	*Concentration* [a] *(pg m^{-3})*	*Site Type*	*Reference*
Munich, Germany	PM 10	Pt	33.0 3.0	Bus high traffic route Bus suburban route	Schierl and Fruhmann, 1996
Rome, Italy	PM 10	Pt Pd Rh	7.8-38.8 21.2-85.7 2.2-5.8	Urban roadside	Petrucci et al., 2000
Gothenburg, Sweden	PM 10	Pt Pd Rh	<0.2-907 <0.9-151 <0.2-73	High traffic urban roadside	Rauch et al., 2001
		Pt Pd Rh	<0.2-2.3 <0.9-1.7 <0.2-0.8	Background	
Madrid, Spain	PM 10	Pt Rh	<0.1-57.1 <0.2-12.2	Urban roadsides	Gomez et al., 2001
		Pt Rh	<0.1 <0.2	Background	

a- Values with <x indicate values below given detection limit, single values are means, while two values represent a range.

4.3.3 Flora and Fauna

The research pertaining to PGE in fauna and flora is not as extensive as that available for other environmental compartments. There was some indication even before the full-scale introduction of catalytic converters that PGE had the potential to cause harm to organisms. The E_{50} of platinum chloride to *Photobacterium phosphorum* was determined in 1975 by Brubaker et al. and was found to be much lower than that of copper, being 25 μg l^{-1} and 200 μg l^{-1} respectively (Wei and Morrison, 1994b). There have been several animal species besides humans studied. These include rats (Artelt et al., 1999a), eels (Sures at al., 2001) and macroinvertebrates (Moldovan et al., 2001).

Studies of PGE in plant species are more common. Vegetation is thought to be a route for PGE entry into humans. Incorporation into plant tissue may occur through absorption by the roots or by the above ground parts through deposition of dust and/or absorption of airborne particles. As airborne PGE are more soluble the latter is more probable (Rauch and Morrison, 2000).

Schäfer et al. (1998) used different plant species and grew them on PGE containing soils. Uptake of PGE by the plants was calculated using transfer coefficients (ratio of concentration in the plant and the concentration of the element in the soil) and a gradient of Pd > Pt ≥ Rh was found, making palladium the most mobile of the PGE. Most interestingly, they found that plants grown on contaminated soils had transfer coefficients for Pt and Rh that were about the same as the value for copper, an essential nutrient. These values were one order of magnitude higher than those for lead. Another important finding was that PGE uptake by plants was similar across species. This finding is supported by work done by Lustig et al. (1997). This same study by Lustig et al. (1997) used several different plant species grown on both natural and spiked clay-like soils and found that plants growing on untreated soils took up less than 1% of the platinum naturally occurring in the soil. Those plants that were grown on soils treated with tunnel dust took up only slightly more platinum than the control plants. This study was only carried out over one vegetative season and thus does not take into account accumulation of noble metals in tissues over several years.

Platinum is known to affect vegetative success. Exposure of plants to soluble Pt(IV) resulted in decreased nutrient uptake and plant growth (Ballach and Wittig, 1996). Several studies have found that Pt concentrations are greatest in the roots (Verstraete et al. , 1998; Alt et al., 1997), which may affect these processes. In general, authors have found that platinum was located in the vegetative rather then the regenerative portions of plants (Lustig et al., 1997). This may have implications in exposure of humans to platinum as food is one of the suggested pathways into man (Alt et al., 1997).

Table 7. Concentrations of PGE in various vegetation studies.

Location	*Vegetative Sample Type*	*PGE*	*Concentration* [a] *(ng g^{-1})*	*Site Type*	*Reference*
UK	Bark	Pt	0.07-5.4	Various urban and non-urban sites	Becker et al., 2000
San Francisco, USA Tokyo, Japan	Bark	Pt	13.0 12.8	Near major roadway	Ma et al., 2001
Germany	Plant (spinach, cress, phacelia, stinging nettle)	Pt Pd Rh	8.6 1.9 1	Grown on highway contaminated soils in greenhouse	Schäfer et al., 1998
Germany	Grass	Pt	0,14 0,29	Removed from roadway	Alt et al., 1997

a- Single values are means, while two values represent a range.

5. Sources of PGE in Ghana

Research for this project was carried out in Ghana. Ghana is one of the most densely populated countries in West Africa. It has a population of 18.8 million people and Accra, the capital city, is home to 1.3 million of them. Ghana is located just 5 degrees and 36 minutes north of the equator and 10 minutes east of the Greenwich meridian. It covers an area of 238 537 km^2. It is bordered by the Gulf of Guinea to the south and Cote D'Ivoire, Burkina Faso and Togo to the west, north and east respectively (Figure 3). The climate is tropical and there are two distinct rainy seasons: May-June and September-October. The average humidity is ±80% the year through and temperatures range between 25°C and 29°C. The country is made up of wooded hill ranges, wide valleys, low-lying coastal plains and pockets of thick rainforest. The coastal zone sees only light rains even in the rainy season (web ref. 4).

Figure 3. Map of Ghana and its location in Africa (web ref. 4).

Ghana is a developing country. While it is rich in natural resources, namely cocoa, timber and gold, years of political unrest and corruption have lead to a weak GDP and a large national debt. The minimum wage is 5 500 cedis a day, equivalent to less than US$0.80. The infrastructure is poor with roads (even within the capital city) being in bad condition. Life expectancy is just under 56 years. However, in West Africa it is the country that shows the most promising prospects for the future under the new president, John Kufour. Since 1983 economic reforms and substantial international assistance has reduced inflation and privatization is increasing (web ref. 4).

In Ghana environmental issues are of lower priority than in developed countries; without adequate finances to tackle these problems they fall by the wayside. While there exists no formal environmental policy for air quality in Ghana, the government has banned the import of vehicles older than 10 years of age since 1998. There is a possibility that environmental initiatives such as the mandatory installation of catalytic converters could be a reality in the distant future. The phase out of leaded fuel has already been called for in 25 sub-Saharan nations in the World Bank's Clean Air Initiative, 2001.

There are several possible sources of PGE in Ghana. It is likely that any PGE found in this study is the result of one or more of these sources.

1. Direct emissions from gasoline or diesel vehicles equipped with catalytic converters in Ghana.
2. Long distance transport (LDT) from mining and smelting locations in South Africa and Zimbabwe.
3. LDT from countries (mainly Europe but North America and Japan) that are emitting PGE from catalytically equipped vehicles.

Establishing which of these is the actual contributor is challenging and would require a greater temporal resolution than that found here. However, discussion of these ideas remains important.

5.1 Direct Emissions from Catalytic Converters in Ghana

The majority of vehicles in Ghana are imported from Europe so by happenstance there are quite a few catalytically equipped cars in this country. As vehicle registration and importation information is at the moment recorded manually, there is a large amount of data that is incomplete and hard to sort through. Figuring the actual number of catalytically equipped vehicles in a location is thus difficult. The vehicle fleet is much older than that found in developed countries. Vehicles must deal with tougher driving conditions in terms of road quality and vehicle loads. Since vehicle condition is poorer, optimum functioning of catalytic converters is unlikely. The use of leaded petrol in gasoline engines renders their installation somewhat useless due to poisoning.

The phase out of leaded petrol that started in the 1980's in developed countries was advantageous for two reasons. Firstly, unleaded fuel did not poison catalytic converters so air quality standards could be achieved in the respective countries where such legislation existed. Secondly, the deleterious impacts of lead emissions to the environment became more obvious in terms of human health and ecosystem damage (Kaysi et al., 2000). There was not much resistance to the phase out of leaded fuel in developed countries despite the economic complications. As such there have been few, if any, publications made about the type of PGE emissions from gasoline engines equipped with catalytic converters using leaded petrol. Studies made after the phase out of lead/introduction of catalytic converters found that concurrent to the decrease in environmental lead concentrations, there was an increase in the levels of PGE (Wei and Morrison, 1994b).

Some research does exist about catalytic converter poisoning by the trace amounts of lead contained in unleaded fuels used in developed countries. Lead compounds (as oxides and sulphides) are known to form a coating on catalytic surfaces, decreasing the amount of available active sites. This deactivation would lead to increased emissions of gaseous pollutants as well as toxic lead compounds. It has also been suggested that lead can form non-catalytic alloys with PGE at high temperatures

(Searles, pers. comm.). Studies by Moldovan et al. (2002) found that Pb levels increased the most relative to other catalytic contaminants (namely P, S, Zn and Cu) with ageing of catalytic converters. Scanning along the channels of gasoline engine catalysts using LA-ICP-MS revealed that lead is deposited in the front brick of the converter and decreases along the channels. This may be a result of lead's higher affinity or solubility for the catalyst washcoat causing it to be absorbed preferentially. In road dust, lead was found to associate with Fe/Mn and Ca/Mg/Sr phases while PGE had no association with any particular phases (Rauch et al., 2000a). Lead poisoning is of course not a problem for diesel engine catalysts since there is no lead additive for this fuel.

5.2 Transport of PGE from Catalytic Converters in Developed Countries

With technological advances man is exploiting greater and increasingly varied amounts of natural resources. Invariably wastes are created in this process. Some of these wastes are released as small particles into the air. It is important to understand the behavior of these particles and their movement because of the fact that often natural processes do not release the same type of particles to the atmosphere as anthropogenic activities do. Therefore there may be no natural mechanism to deal with the anthropogenic release. PGE are an example of this: they are found in low concentration in the environment but because of human activities their levels and distribution is increasing globally.

5.2.1 Particulate Matter Theory

The term aerosol refers to an assembly of gas and suspended particles whether they be solid, liquid or a mixture of both. Aerosols are ubiquitous in the atmosphere and can influence different earth processes (*e.g*. radiation budgets, hydrological cycles, *etc*.). Understanding aerosols and the particulate matter portion of them is important in terms of how far a particular pollutant may be spread. The most important aspect of this is the size of the airborne particles as it is this that determines the length of time they remain in the air and thus the distance that they are transported.

The size of a particle is usually based on its aerodynamic diameter due to the fact that solid particles often vary in shape. The term particulate matter generally means particles smaller in size than 10 μm. It is most often divided into a coarse fraction which is all particles less than 10 μm (PM 10) and a fine fraction which is all particles less than 2.5 μm (PM 2.5) in aerodynamic diameter. PM 10 is the inhalable fraction, which means that it is able to enter into the respiratory system but it is not necessarily able to reach gas exchange surfaces. Those particles that can, called the respirable fraction, are smaller in size, usually referred to as the fine fraction. Aerosols may be natural or anthropogenic in source. Larger particles tend to be formed by natural mechanical processes like erosion of crustal elements. Fine particles are formed by anthropogenic activities such as combustion. Once emitted, particle size and chemical composition are all subject to change.

When looking at the size distribution of aerosol particles in terms of particle transport and residence time, the fine fraction is further divided into the nucleation mode (particles from size <0.1 μm) and the accumulation mode (0.1-0.2 μm) (Figure 4). The nucleation mode is the PM that are emitted from very high temperature processes, have just undergone gas to particle conversion or can act as condensation nuclei. The accumulation mode consists of particles that have grown from the nucleation mode by coagulation or condensation of vapors. Depending on which range a particle falls into its residence time will be shorter or longer.

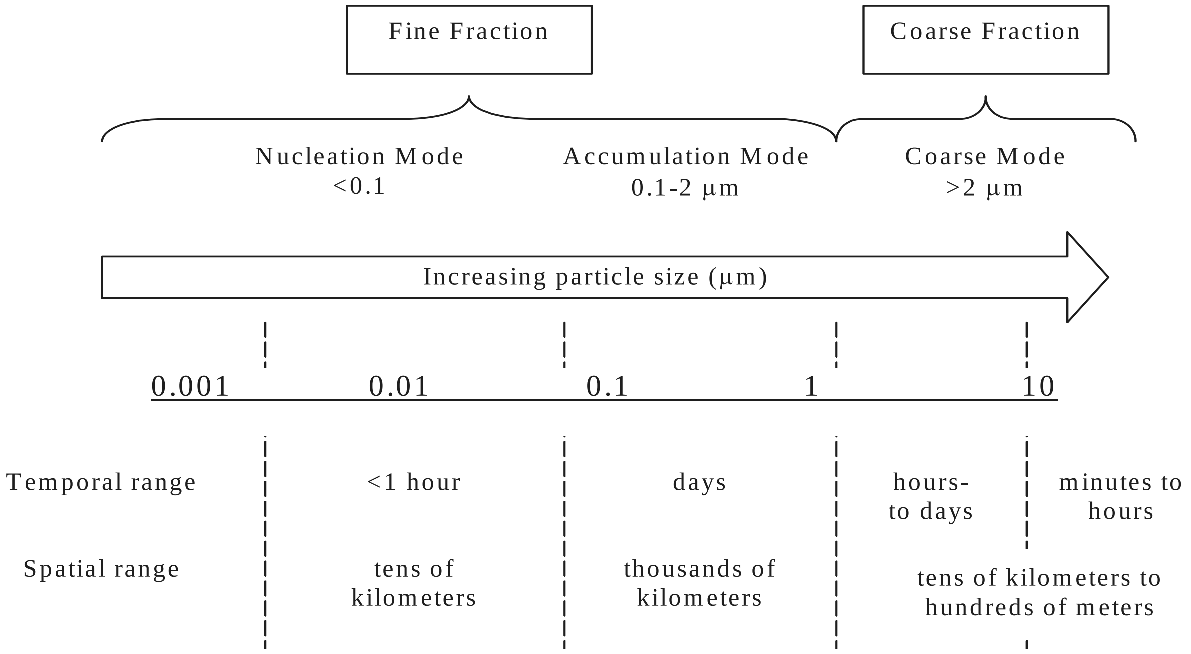

Figure 4. Relationship between different size ranges, residence time and range of transport for particulate matter (modified from Chimidza, 2001 and Warneck, 2000).

Smaller particles are able to travel great distances. This is called LDT. It is estimated that particles emitted in one hemisphere will take 1 to 2 months to be distributed throughout that hemisphere and it takes 1 year for a pollutant to be circulated in both hemispheres (Hallquist, pers. comm.).

5.2.2 Evidence of LDT of PGE from Developed Countries

The PGE global dispersion theory was inspired by groundbreaking work done by Barbante et al. (2001) using snow and ancient ice from Greenland. This research made comparisons between the PGE levels from 3 different time frames. Natural levels are represented by data from ice cores dating 7 000 years back, pre-catalytic converter PGE levels are gleaned from snow dating from 1969 to 1975 and changes since autocatalyst introduction are derived from snow samples from 1976 to date. It was found that natural PGE levels 7 000 years ago were ~6, 15 and 45 times lower than the levels found in pre-autocatalyst times for Pt, Pd and Rh respectively. This was attributed to the mining and smelting of PGE and various industrial activities. Since 1976 however there has been a significant increase in PGE levels in Greenland snow. Compared to 7 000 years ago there was a 40, 80 and 120 fold increase for Pt, Pd and Rh respectively. These findings are attributed to the introduction of catalytic converters and are further supported by exploration of the various PGE ratios over the sampled time frame.

Advocates for catalytic converters dispute the possibility that PGE are able to move away from traffic areas. They suggest that Barbante's findings are the result of mining activities and the overall increase in PGE use in the past years (Searles, 2001). Many researchers disagree and believe that finding PGE in Greenland means that these metals are in fact circulated globally. In order for global circulation to occur however the particles must be small enough in size to be transported in aerosols. It is therefore those particles which are in the size range of ~0.1 to 2 μm that are of greatest interest. Past research has focused mostly on determining environmental concentrations, so few publications on size fractions exist. In the literature available, there are contradictory findings as to which size fraction is largest. There is an inherent difficulty in measuring smaller particles, which may explain some of the variations. Gomez et al. (2001) used a seven stage impactor measuring particles from <0.39-10 μm; roughly 75% of the collected Pt particles were below 2.1 μm. Alt et al., (1993) used a 5 stage impactor and found that the lowest concentration were observed for larger particles (>8μm). Conversely, in test stands performed by Artelt et al. (1999b) the fraction below 3.14 μm accounted for just 13% of the total. The largest contribution to the PM in this case was found to be from particles over 10.2 μm. It should be noted for the latter study, that real and simulated driving conditions are quite different.

5.3 Transport of PGE from Metallurgical Operations in Southern Africa

Southern Africa is the location of much of the world's PGE mining operations. In the year 2000, South Africa was responsible for 55% of the world's total PGE production while Zimbabwe accounted for 0.06 % (Hilliard, 2000). These levels are expected to increase in the coming years. Much of the opposition that the automotive catalyst industry has to the sourcing of PGE to converters is the fact that mining operations are responsible for PGE emissions as well. Barbante et al. (2001) found that this is indeed possible as concentrations of PGE in ice cores taken from Greenland were higher than natural concentrations even before the introduction of catalytic converters.

Some work has been carried out on the Kola Peninsula in Northwest Russia to determine if metallurgical activities, primarily Ni-Cu production, of which PGE is a by-product, are causing an enrichment of heavy and noble metals in the area. Two separate publications found that there was indeed such an enrichment. Boyd et al. (1997) studied topsoils in various catchments and found that those catchments closer to industrial plants were higher in metal concentration than those further away. Additionally the pattern of PGE concentrations was similar to that known for the ores used at the given processing plants. The authors feel that this indicates that PGE bearing emissions consist mainly of ore dust and are thus transportable. Gregurek et al. (1999) worked in the same area and used snow samples instead. They found that the concentrations of PGE decreased away from industrial sources of smoke and dust following the prevailing wind direction. This study also used known ore composition to determine that PGE found in samples was indeed from local smelters.

Both of the above mentioned studies highlighted the fact that the plants in operation were in great need of modernisation and that much of the emitted PGE could be saved with such improvements. One might assume, given the prominence of PGE mining in South Africa and the recent and projected improvements contained in Cowley and Hankin (2001) that the metallurgical establishments in South Africa do not suffer from the same problems as the Russian establishments. The same is not likely to be true for Zimbabwe’s PGE activities but their output is rather low so their emissions not likely to be as significant.

Experimental Methodology

1. Sampling Locations

Sampling took place in Ghana during the months of September and October 2001. There were 5 sampling sites located in the Central and Greater Accra Regions (Figure 5). Background values and low traffic samples were measured in the village of Atakwa at a site back from the road (Site A) and on the main road (Site B) respectively. The former was an isolated living area about 200 m from the road on a rise behind some dwellings; it was well exposed to daily activities like open fire cooking and housekeeping work. The latter saw less than 200 cars a day passing continuously. A residential site (Site D) was selected within Accra to reflect a lower traffic intensity site. At this site less than 500 cars a day passed and the traffic was continuous. Two sites were selected to represent high traffic locations. These were positioned along the Cape Coast Highway (Site C) and at Kotoka International Airport in Accra (Site E). On the highway approximately 4 000 cars passed in a day continuously. The traffic at the airport was on average 5 000 cars a day but this traffic came in dense fluxes associated with aeroplane arrivals and was very stop-and-go in nature.

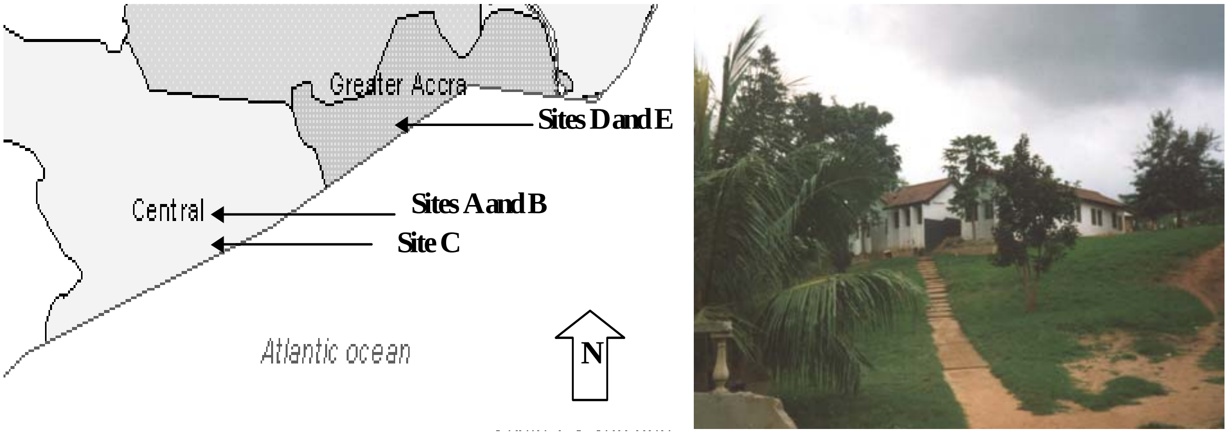

Figure 5. Map location of the 5 sampling sites in the Greater Accra and Central Regions in Ghana (web ref. 6) and a photo of the Background site from the road.

2. Sampling Methodology

As this project was a first assay at PGE analysis done in Ghana a wide array of media were selected for study. Road sediments, soil, vegetation and air samples were all taken from the various sites in Ghana back to Sweden for analysis.

Air samples were collected using home-made low flow samplers. These are not 100% efficient in their sampling and they do not select for a definite size fraction. The construction consisted of an inverted funnel with an intake diameter of 0.5 cm, a stem internal diameter of 0.07 cm and a height of 3.5 cm. Positioned behind the funnel was a casing holding a cellulose acetate filter, which captured particles as the air was pumped by PVC tubing towards the pumps. Six samplers were run in parallel as their functioning allowed. They were run for 7 successive days. The placement of air samplers was a particularly difficult logistical problem as power availability, traffic intensity and security were all issues to consider. Air samplers were only placed at two sites: Site A in Atakwa and at Site E at Kotoka International Airport. Previous studies found that height has no bearing on PGE collection so all intakes were placed at roughly 2 m from the ground as supporting structures would allow.

Road sediment samples were taken in the proximity of air samplers as well as at the other three sites using a brush and a fashioned spatula. A 1 m long strip was taken approximately 20 cm from the roadside, where gutters permitted, and placed into plastic containers.

Plants were removed at the root using a garden implement at the same locations as road sediment samples were taken. Two additional samples were taken at the Accra sampling sites because of obstructions in the sampling areas. When able, soil samples were included with the plants. Soil samples were taken from the top 5 cm of the soil.

3. Sample Preparation

Samples were to be used in both ICP-MS and in LA-ICP-MS. Those samples used for ICP-MS required sample preparation while those used in LA-ICP-MS did not. Filters selected for ICP-MS were first mineralised. This was done by placing samples in sealed PTFE vessels (HP500) together with 8 ml of *aqua regia* (6 ml 30% HCl and 2 ml 65% HNO_3). The samples were then digested in a CEM Mars5 (CEM, Mattheus, USA) microwave digestion system that increased temperature and pressure in the stepwise fashion given in Table 8. After microwave digestion, samples were heated to dryness in a glass beaker and the residue then dissolved in 5 ml of 2% HCl. This solution was placed in ICP-MS tubes and frozen until analysis.

Table 8. Time, temperature and pressure settings used in microwave digestion of samples.

Stage	*Power (W)*	*Attempting temperature (℃)*	*Maximum pressure (psi)*	*Ramp (min)*	*Holding (min)*
1	600	110	50	5	2
2	600	140	100	5	2
3	1200	170	200	5	2
4	1200	200	300	5	6

Soil and road sediment samples were dried at 100°C for approximately 24 hours and sieved into two size fractions: <63 μm and >63μm. Only the smaller fraction was used in analysis so as to be able to make comparisons with past studies. The digestion of 250 mg aliquots of soil and road sediment samples adheres to the sample procedure as given above for filter digestion.

Grass samples were cut into approximately two halves and one half of each was washed in nanopure water. All samples were then dried at 60°C for 24 hours. 250 mg of plant sample and 8 ml of *aqua regia* was used in the microwave phase of the preparation. The microwave was not run on the same program as that employed for other samples. Rather it stayed at 100% power for 10 minutes, reaching 150 psi and 210°C in that time. After microwave digestion, the procedure also adheres to that given above.

Just prior to analysis samples were defrosted and where required, decanted. For a fixed volume of 5 ml of sample, 50 μl of internal standard was added to each sample. The internal standard used in this case was a 1 ppm solution of In and Ir.

4. Sample Analysis

4.1 ICP-MS

The instrument at Chalmers is a Perkin Elmer Sciex Elan 6000. It is in a clean room and has an autosampler to allow for sample selection by computer. The autosampler extracted solution at a rate of 1 ml min^{-1}. This particular ICP-MS instrument employs a quadropole mass filter. Aerosols are created by a cross-flow nebuliser and introduced to the plasma in a Fazel-Scott spray chamber. Two slightly different settings were used for the analysis of the prepared samples and these are given in Table 9.

Table 9. ICP-MS settings used in sample analysis.

Sample Introduction	
Carrier Gas	Soil and Road Sediment Samples: Ar at a flow rate of 0.86 1 min $^{-1}$ Filter and Grass Samples: Ar at a flow rate of 0.90 1 min $^{-1}$
ICP	
Plasma Gas	Ar at a flow rate of 16 1 min $^{-1}$
Auxiliary Gas	Ar at a flow rate of 0.9 1 min $^{-1}$
Rf Power	Soil and Road Sediment Samples: 1000 Watt Filter and Grass Samples: 1175 Watt
Acquisition	
Data acquisition	Peak hopping
Dwell time	100
Sweeps per reading	10
Peak width	6

In order to make interference calculations for PGE and calibrate the instrument several sets of standards were run prior to the analysis of samples. These are given in Table 10.

Table 10. Standard concentrations used for calibration in ICP-MS analysis.

Element	*Concentration (ppb)*					
	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
Cu	1000	100	10	1		
Hf	100	10	1	0.1		
Pb	1000	100	10	1	0.1	
Y	100	10	1	0.1	0.01	
Sr	1000	100	10	1	0.1	
Rb	1000	100	10	1	0.1	
PGE	1	0.5	0.1	0.05	0.01	0.005

The real concentrations of the chosen analytes were calculated using mathematical corrections based on the apparent concentrations and true and apparent intensities of specific analytes (the formulas used for this are given in the Background Information Section 3.3).

4.2 LA-ICP-MS

The laser system at Chalmers is a Cetac LSX-200 LA system. It is equipped with a Nd:YAG laser. The settings in Table 11 were used for sediment analysis. Sediments were adhered to a piece of tape and then shot with a laser at the given scan speed.

Table 11. Settings for LA-ICP-MS analysis.

Parameter	*Setting*
Wavelength	UV 226 nm
Operating mode	Q-switch
Carrier gas	Argon
Spot size	50 μm
Energy	3 (0.4 mJ)
Repetition rate	20 Hz
Scan speed	10 μm s^{-1}

Results and Discussion

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1. The Car Fleet

To get a better idea about PGE emissions in Accra and to aid in future investigations it was necessary to gather data on the car fleet. This proved to be a difficult task as records are not as yet computerised and those that exist are often incomplete. Data was gathered by three different methods: (i) open interviews, (ii) standard questionnaire interviews and (iii) tabulations of data taken by the Driver and Vehicle Licensing Authority (DVLA) in Accra (all these data are presented in the Appendix). The first two methods proved useful in gaining background information on the car fleet. Nearly all cars come from Europe through private sales or commercial operations. In Accra, the capital city, cars are usually imported at the age of 8 years. In 1998 the importation of cars older than 10 years was completely banned. The average car age is estimated to be 13 years.

Data taken from the DVLA was useful in that it gave the total number of vehicles registered in the Greater Accra Region. The relevant data are in Table 12 and the numbers given are the total cars presently registered on the roads in Accra.

Table 12. Total number of vehicles in a given category as tabulated by the DVLA, Greater Accra Region up to the year 2000.

Vehicle Type	*Total No.*
Motor vehicle up to 2000 cc	314 733
Buses and Coaches	83 614
Trucks up to 24 tons	51 954
Total vehicles in Accra	450 301

In attempts to estimate the number of catalytically equipped cars and the number of diesel engines in and around Accra, registry books from 2001 were used. The registry books did not include the year of make so many assumptions were made in order to come to any conclusions (these are also included in the Appendix). Best estimates place the number of catalytically equipped vehicles in Accra at an upper end figure of 71.2% and the number of diesel vehicles at 19.7% based on a sample number of 4 285. Rounding down, these percentages translate to approximately 300 000 catalytically equipped vehicles and 90 000 diesel engine vehicles on the roads in Accra. The number of catalytically equipped cars will undoubtedly increase in the future.

2. ICP-MS Performance

The determination of PGE concentrations is hampered by interference from various species. While this study set out to analyse all three catalytic PGE, only trustworthy results were generated for platinum. This was due to the fact that there were such high levels of copper and lead in the samples. These are interferents to palladium and rhodium respectively. Interference plots for platinum showing the interference/real Pt concentration vs. the real Pt concentration were constructed. As soils and sediments were run on slightly different ICP-MS settings than those for grass and filters, they were plotted separately. All ratios under 1 indicate that interference generates half the signal while Pt produces the other half of the signal. Ratios higher than 3 should be considered carefully (Rauch et al., 2001).

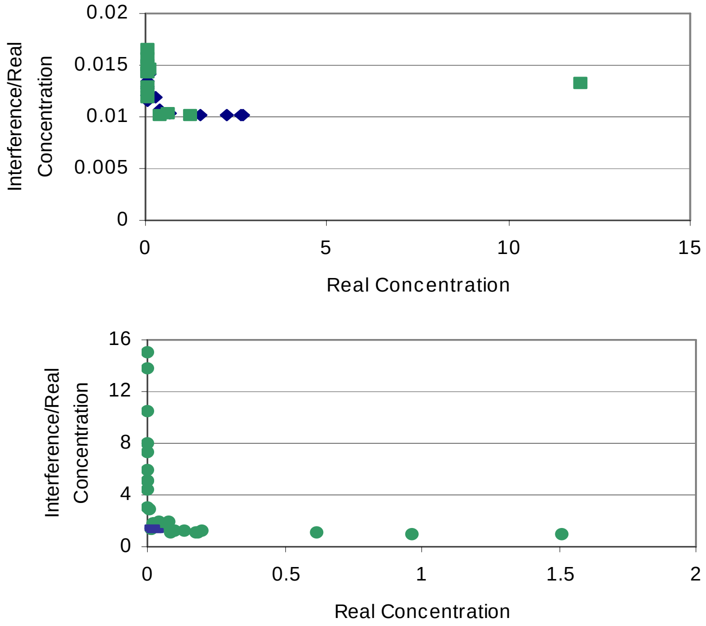

Figure 6. (A) Depicts the ratios obtained for soils (green squares) and sediments (blue diamonds) for interference/real concentration vs. real concentration; (B) depicts the same for grass (green circles) and filter (blue dashes) samples.

The ratios obtained for soils (n=17) and sediments (n=11) (Figure 6A) show that all concentration values calculated can be considered accurate as all ratios were under 0.02. Such accuracy was not obtained with the grass results (n=35). Though the majority of the calculated ratios were between 1.0 and 1.8 (Figure 6B) the data had considerable spread. Two extreme outliers were removed from the preliminary analysis; these were very low concentration values. The unreliability in the determined vegetation Pt concentrations may be attributable to matrix effects and variability in the biological make-up of the analysed samples. While only grass species were selected for sampling it is possible that the specimens taken differed in age, cellular density, plant part used, *etc.* which may have caused variations in the amounts of interference. The higher interference/real concentration ratios were found at low concentrations and low ratios were found at high concentrations, thus there is more uncertainty at low concentrations. Samples with interference/real concentration ratios higher than 3 were eliminated from analysis; this affected low traffic sites only. The air samples (n=6) all showed acceptable ratios except for one value, which was removed from further analysis.

3. Aerosol Samples

Concentrations of Pt in aerosols are low and difficult to determine accurately. The results obtained here from the analysis of the acquired air particles were not of good quality due to equipment malfunction and will only be mentioned briefly. The first pumping station established showed good working of pumps but the same cannot be said for the second pumping station; pump rates were below the detection limit of the flow meter for all days running. The pumps may have failed for any number of reasons such as wear caused by fluctuations in the electrical supply or the constant high humidity.

The mean concentration found at the background site was 7.35 ± 0.92 ng m^{-3} while the high traffic site had a mean concentration of 21.27 ± 21.43 ng m^{-3}. These results are not considered accurate.

4. Platinum in Road Sediments and Soils

Road sediments are a primary starting point for the dispersion of PGE into the environment and their importance cannot be overlooked. The sampling sites used in this study all differed in the level of traffic experienced at each. The traffic density increased between sites as follows: background site at village of Atakwa < road site at village of Atakwa < residential site in Accra < Cape Coast Highway < Kotoka International Airport in Accra (these are denoted as Background, Village, Residential, Highway and Airport for future reference). Accordingly the platinum concentrations in road dust found at each of these sites increased with increasing traffic indicating a vehicular source (Figure 7).

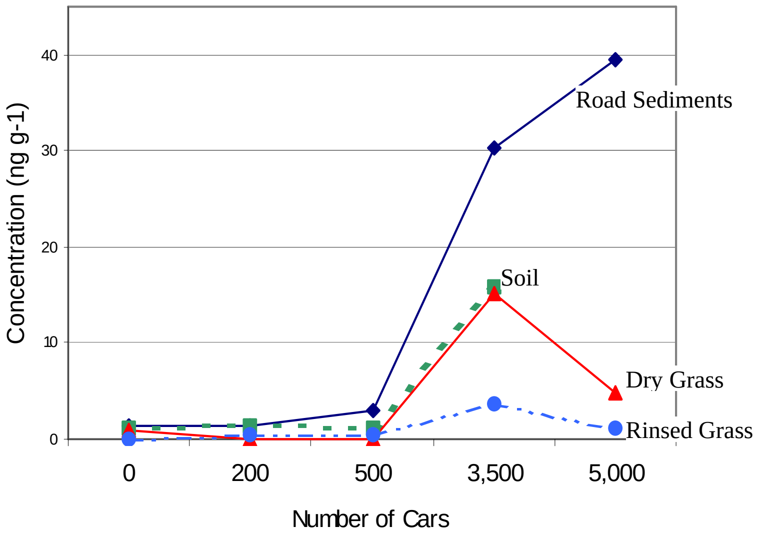

Figure 7. Plot of mean PGE concentrations at each site for the four sample media.

The background levels for both road sediment and soil measured in this study were slightly higher than those found in other studies having mean background values of 1.31 ng g^{-1} and 1.23 ng g^{-1} respectively. Gomez et al. (2001) found background levels below the detection limit of 1.6 ng g^{-1} for road dusts. Studies by Farago et al. (1996) assumed a background level in the area of 1 ng g^{-1} for the same media. Both Jarvis et al. (2001) and Alt et al. (1997) found soil Pt levels an order of magnitude lower than those found at the background site used here. There is a strong possibility that the levels of Pt in Ghana are naturally high. This is supported firstly by the location of the background sampling site. Its distance large from the road, its topographic character and the presence of buildings make the possibility of wind born transport of Pt from local traffic to the established concentrations dubious. A crustal origin is likely. Secondly, mining activities in Ghana include gold and, to a lesser extent, copper, both of which are known to be geologically associated with PGE to some degree. The background value in this study is trusted based on the low interference/real concentration ratio and the similarity in soil and road sediment values as they were essentially the same sample.

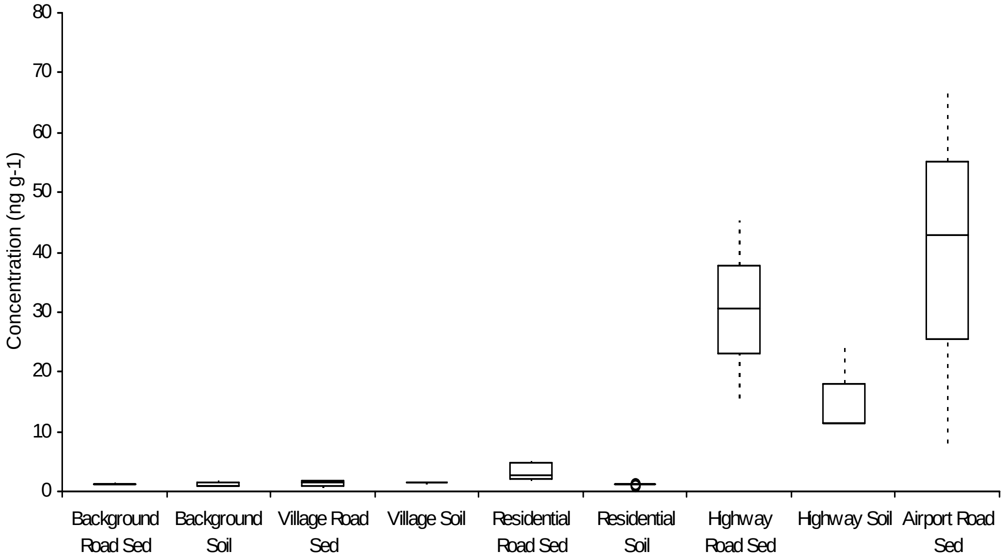

Figure 8. Box plots of road sediments and soils at the different sampling sites showing the spread of data and the higher values of road sediments compared to soil samples at each site.

In general, the values found for road sediments were higher than expected. This expectation was based on the idea that present PGE levels in developed countries are the result of catalytic converters having been efficiently employed for the past two to three decades. In Ghana catalytic converters are not mandatory and if present they are deactivated by leaded fuel. Current Pt levels in road dusts in and around Accra agree with recent study results from Europe. Petrucci et al. (2000) found a range of 14.4 to 62.2 ng g^{-1} Pt at high traffic sites. Farago et al. (1996) found concentrations of 0.42 to 29.8 ng g^{-1} in road dust in the UK. Jarvis et al. (2001) found a range of 10-100 ng g^{-1} at a roadway experiencing roughly 17 000 cars a day. The highest traffic density in this study was found at Kotoka International Airport with approximately 5 000 cars a day and a mean Pt value of 39.5 ng g^{-1}.

There are several explanations and implications of such levels of Pt in the road dust from Accra. Part of the elevated Pt levels are attributable to higher natural levels. Another contributing factor has to do with the age of the car fleet. Cars in Ghana are usually 8 years in age at the time of importation and are not driven much past 20 years in age. This is important for two reasons. Firstly, there is probably a greater number of cars equipped with pelleted catalysts which are known to emit two orders of magnitude more PGE than the modern monolithic converters. Secondly, and probably less significant, has to do with catalytic ageing. Moldovan et al. (2002) studied catalytic ageing and found during 80 000 km driven (equivalent to approximately 5 and a half years of driving) gasoline engine catalysts emitted decreasing amounts of PGE while diesel engine catalysts showed increasing PGE emissions. This is placed into context when looking at consumer behavior in developing and developed nations. There is a high turnover of vehicles in developed countries relative to developing countries thus they receive greater amounts of fresh gasoline catalytic PGE emissions in the former. In Accra there is a large dependence on mass transport as the economic situation in this country prevents most people from having personal vehicles. Based on vehicle registry data for the Greater Accra Region and assuming that all vans, buses, coaches and trucks are powered by diesel engines, roughly 20% of the car fleet is diesel powered (this estimate does not include those cars that are diesel so this figure is probably even higher). A small number of these are probably catalytically equipped; it is not until the past few years that diesel engine catalysts have come into use in developed countries. Diesel engine catalysts are not subject to the same lead poisoning problem as gasoline engine catalysts are and their PGE emissions would be similar to diesel vehicles in all countries. The relevance of this theory could be validated if Pt/Rh ratios were available; diesel engine catalysts are largely composed of Pt while gasoline engine catalysts are known to emit particles that have a Pt/Rh ratio between 5 and 6. A last aspect relevant to the car fleet is the driving conditions in Ghana; they are far from the optimal conditions used in test stands. The cars are old, using poor quality fuel and experience much greater wear and tear in terms of road condition, traffic flow and vehicle loads; this will increase Pt emissions.

The phase out of leaded fuel was prompted by the hope that catalytic converters might solve air pollution problems in developed countries. The only petrol available in Ghana is leaded and this must undoubtedly affect Pt emissions. Lead coats catalytic surfaces but there could be cracking of catalytic channels that exposes more reaction surfaces, especially in light of the advanced age of the converters present and the rigorous driving conditions in Accra. Platinum and lead could be emitted in some sort of association. Emissions may be enhanced by mechanical abrasions within the converter caused by the relatively lower quality fuel sold in Ghana. This study could not establish if this was indeed true. Analysis of lead concentrations in samples revealed similar concentration variations between Pt and Pb. This result can prove little more than the fact that both Pb and Pt come from vehicular sources.

A last, simpler explanation of the results acquired may have to do with the outlay of the individual sites. Of the four sites exposed to traffic, all of them had some type of barrier present, whether it be vegetation or fencing. It is possible that the dispersion of Pt from the roadside may be lower than that found at sites that lack physical obstructions and allow for wind to move PGE particles away.

In comparing road sediment and soil Pt concentrations (refer back to Figure 8), higher levels were found in road dust except for one site where the concentration was quite low all together. This finding is accurate with other studies (Farago et al., 1996) and logical as Pt is dispersed from road dust to other environmental compartments. Between sites, Pt concentrations generally adhere to trends in traffic density. Samples were taken from the top 5 cm of soil and at a distance no further than 1 m from the road. Past studies have found that it is at this depth and distance that the greatest PGE concentrations are detected (Jarvis et al., 2001; Schäfer et al., 1999). Concentration ranges in this study were similar for equivalent sites in other publications with mean values between 1.1 and 1.4 ng g^{-1} for the more remote sites and 15.8 ng g^{-1} for the high traffic site. Farago et al. (1996) found concentrations ranging from 0.35 to 4.26 ng g^{-1} and 11.2 to 23.7 ng g^{-1} for comparable locations. Alt et al. (1997) analyzed cultivated and roadside soils and found ranges of 0.15 to 3.9 and 15.6 to 31.7 ng g^{-1} respectively. Zereini et al. (1997) found concentrations in soils in Germany along major motorways to be in the range of 23 to 112 ng g^{-1}.

While it is important to ascertain the concentration of platinum in a soil, as it is the crucial link between road dust and terrestrial biota, it is the amount of soluble platinum that is paramount. The determination of the latter is beyond the scope of this study but some factors affecting the solubility and thus the bioavailability of platinum should be highlighted. It is feasible that the solubility of platinum in Ghanaian soils may be higher than that found in other soil types because of both soil character (*i.e.* acidity, porosity, sorption capacity, humic content) and environmental variables (*i.e.* other anthropogenic additives, climate).

Generally speaking, the soils in Ghana are classified as Ferralsols in the French system, which equates roughly to Oxisols in the English system. This soil type is typical of moist tropical climates. The litter layer is thin and is rapidly and completely broken down. The upper horizon is sandy and has poor water retention. Consequently, the soil is low in organic content and nutrients; humic materials formed from the modification of materials released by the decay of plant, animal and microbial tissues are washed away due to the porous nature of the soil. While the clay content of Ferralsols increases with depth it still experiences strong leaching at lower horizons. In contrast to soils found in temperate and continental climates like those in Europe, nutrients and other essential building blocks are stored in biotic materials rather than in soils. These soils are acid with a pH in the area of 5.0 at the surface. This pH value decreases with depth and there are few base cations available for exchange (Gerrard, 2000; Ahn, 1970).

Present evidence indicates that the humic content and the sorption capacity of a soil plays a role in platinum's ability to move into biotic materials. Lustig et al. (1996) suggest that humic substances oxidize Pt(0) and may form complexes with this new species. These complexes may be immobilized by soil through absorption to soil minerals, in particular to clay-like elements. The soils in Ghana however, are poor in organic content and clay elements. It is possible that Pt is oxidized on the surface of the soil. Then, due to the high porosity and leaching rate of Ferrasols and the persistent humidity and high rainfall in this climate, Pt compounds are easily dispersed within the soil. If vegetation or soil fauna do not take the platinum species available up, ground and surface waters move them to aquatic sediments where they are either immobilized or incorporated into aquatic food webs. Additionally, Zereini et al. (1997) found increasing Pt solubility with decreasing pH. Ferrasols are acidic in nature and soils in West Africa have been found to be at risk to further acidification caused by anthropogenic activities like agriculture (Pieri, 1985). Sulfur has also been found to increase the solubility of Pt in soils (Zereini et al., 1997). The fuels used in Ghana are likely to be high in sulfur. This sulfur would be emitted to the environment at the same time as any PGE, reaching the same environmental compartments. Lastly, catalytic converters emit smaller sized particles with age (Artelt et al., 1999b). It has been shown that there was a greater amount of soluble Pt in soils when Pt compounds that had smaller particle sizes were used (Lustig et al., 1996).

From the above discussion it can be seen that there is evidence supporting the idea that Pt in soils in Ghana may be more soluble than in areas previously studied. Hence there may be greater uptake by terrestrial biota and/or quick movements of Pt from soils into aquatic systems. If this is in fact found to be true in future investigations, a large population of people may be at risk. Soil acidification caused by agricultural activities is a realistic threat to a country made up of roughly 90% subsistence farmers creating a greater risk for exposure to platinum through food crops.

5. Platinum in Grass

The plant selected for Pt analysis here was grass. Grass has the advantage in that it is ubiquitous along roadsides. Many publications to date have utilized grass to study Pt bioavailability as it has a proven ability to take up the Pt present in soils. It should be noted however that monocotyledons, like grass, are known to accumulate less metals than dicotyledons (Verstraete et al., 1998). Therefore faunal comparisons between studies should be made with care.

Mean concentrations of Pt in vegetation samples were lower than both those found in road sediments and soils at the same sites. As Pt moves along a given biotic pathway, decreasing concentrations are expected, so these findings are reasonable. However, mean concentrations within sites did not show increasing Pt levels with increasing traffic density (Table 13).

Table 13. Mean and standard deviation for Pt concentrations in grass at each site.

Site	*Treatment*	*n*	*Concentration (ng g^{-1})*
Background	Rinsed	1	0.83
	Dry	1	0.056
Village	Rinsed	1	0.54
Residential	Rinsed	4	0.50 ± 0.202
Highway	Rinsed	2	3.74 ± 1.53
	Dry	4	15.28 ± 16.09
Airport	Rinsed	4	1.05 ± 0.891
	Dry	6	4.81 ± 6.87

The background site, as well as village and residential sites showed low concentrations. As discussed previously, the grass samples demonstrated greater problems with interference than the other media used in this project. The removal of samples from the data set because of their large interference/real concentration ratio weakens the statistical strength of the results, with some groups represented by one (background dry and rinsed and village rinsed) or no points (village dry and residential dry). The interference was greatest at lower concentrations thus more faith can be placed in the higher concentration sites (Highway and Airport), which have ample replicates. According to these results, the Airport has lower grass Pt concentrations then the Highway despite experiencing higher traffic. Grass samples at the former were taken from a traffic median, as little suitable vegetation was available in the proximity of the air and road sediment sample location. This would create lower platinum concentrations compared to the Highway site as particles would be more subject to dispersion by the wind.

Past researchers have argued the importance of deposition versus uptake by the roots in terms of platinum movement into plant tissues. Many experimental methods that decreased the chance of Pt deposition on plant surfaces have been implemented. While these studies do pose an essential question they exclude an important intake mechanism in plants: their above-ground surfaces. In this study half of the plants from a given site were rinsed in nanopure water before analysis. For the available sites, the platinum concentrations in dry specimens were higher than those found for rinsed specimens. This is a sound finding and in looking closer we can see that deposited platinum makes up a substantial portion of the total platinum in the dry samples.

The results acquired for both dry and rinsed grass samples from Accra are generally higher than those found in other research. Low traffic sites in this study ranged between 0.50 and 0.83 ng g^{-1} for available samples. The two higher traffic sites on the Highway and at the Airport showed mean concentrations of 15.2 and 4.81 ng g^{-1} respectively for dry grass. Alt et al. (1997) found background levels of 0.14 and 0.29 ng g^{-1} for dry grass in Germany. Another German study found platinum concentrations in grass at sites close to roadways in the range of 0.8 to 2.9 ng g^{-1}. The same study found a range 0.17 to 0.51 ng g^{-1} at more removed sites (Becker, 2000).

There are several alternative ideas as to why grass samples from Accra show higher Pt levels than that found elsewhere. The fact that the natural Pt background is high is a primary starting point. It is also questionable if studies from Europe are comparable to the work done here because of the vast difference in environmental variables. Most importantly among these variables is climate, which influences the level of bacterial activity, vegetation and soil type.

Southern Ghana is a tropical climate; temperatures remain over 20°C and the relative humidity hovers around 80% the year round (web ref. 6). There is no distinct growing season and plants flourish continually. Klueppel et al. (1998) found that in grass grown on contaminated soil concentrations of platinum increased the longer a plant was allowed to grow. Grass samples taken in European studies do not enjoy an unrestricted growing season like those taken in Ghana; therefore platinum from the soil would be able to accumulate to higher concentrations in tropical vegetation. A publication by Lustig et al. (1997) mentions this weakness in their experimental design. It was found that, independent of plant type, only 0.02-0.6% of the total Pt in the study soil was taken up over one growing season. This study was also performed using clay-like soils, rather than sand-like soils. This is the case with many European studies and it creates problems in terms of trying to make comparisons with Ghana.

The soil, as described previously, encourages Pt solubility and has a lower ability to immobilize metal pollutants than soil types commonly found in Europe (*e.g.* podzols). This would allow for easier uptake of platinum into vegetative tissues and explain the higher concentrations found in Ghana. Nutrients and other essential substances can be stored in soils in temperate and continental forests. Conversely, tropical forests tend to use vegetative tissues as a storage media because of the weakness of their soils. Therefore the trapping of platinum in vegetative tissues may occur during the high turnover faunal materials. The shallow, fibrous root structure associated with tropical plants means that there is more plant/soil interaction near the soil surface where platinum concentrations have been found to be the greatest (Schäfer et al., 1999) increasing the chance for Pt uptake. This association may be enhanced by greater bacterial activity, which has been suggested to play a part in the speciation of platinum (Wei and Morrison, 1994a).

Food has been indicated as the main pathway into man (Alt et al., 1997) and evidence points to platinum entering tropical vegetation with greater ease than in colder climates.

6. Environmental Lead Concentrations

Ghana is one of the many developing countries in the world that still employs leaded petrol. In fact unleaded petrol is not even available in this country. The determination of Pb by ICP-MS is not as complicated as for PGE but the high levels found at some sites in this study required dilutions of 100 and 1 000 times. It was hoped in this research to establish some relationship between PGE levels and leaded petrol. With the current data no tight link could be made between Pb and Pt except that both are derived from traffic.

Wei and Morrison (1994b) measured both Pt and Pb levels in Gothenburg, Sweden one and eight years after the complete ban of leaded petrol. In this time the concentrations fell from 326 to 182 $\mu g\ g^{-1}$. Mean concentrations for the lead levels in the various media from Ghana are given in Table 14. The levels found at comparable sites are much higher than the 1984 values in Sweden, which is expected because of the prolonged and full use of leaded fuels.

The concentrations of lead were proportional to traffic density. The platinum levels showed the same tendency. To confirm this, correlation analysis was performed between lead and platinum concentrations. The findings are given in Figure 9. The road sediments and soils were positively correlated having r-values of 0.86 and 0.89 respectively. The relationship between lead and platinum in the grass samples was not as clear. Dry grass concentrations of these two metals had a low value at r =0.47. Rinsed grass samples however showed good correlation with r =0.87.

Table 14. Mean and standard deviation for lead concentrations in sampled media at each site.

Medium	*n*	*Site*	*Concentration* ($\mu g\ g^{-1}$)
Road Sediment	3	Background	22.20 ± 0.44
	3	Village	31.91 ± 0.81
	3	Residential	67.55 ± 6.62
	3	Highway	425.12 ± 30.93
	3	Airport	504.01 ± 59.98
Soil	3	Background	22.50 ± 2.18
	3	Village	21.60 ± 17.53
	2	Residential	17.54 ± 2.32
	3	Highway	315.58 ± 1.37
Dry Grass	1	Background	3.14
	2	Village	2.85 ± 0.41
	3	Residential	3.02 ± 0.78
	4	Highway	146.52 ± 32.21
	6	Airport	29.01 ± 20.70
Rinsed Grass	1	Background	1.77
	4	Village	2.49 ± 0.22
	2	Residential	6.55 ± 5.18
	8	Highway	140.89 ± 2.33
	4	Airport	9.58 ± 1.35

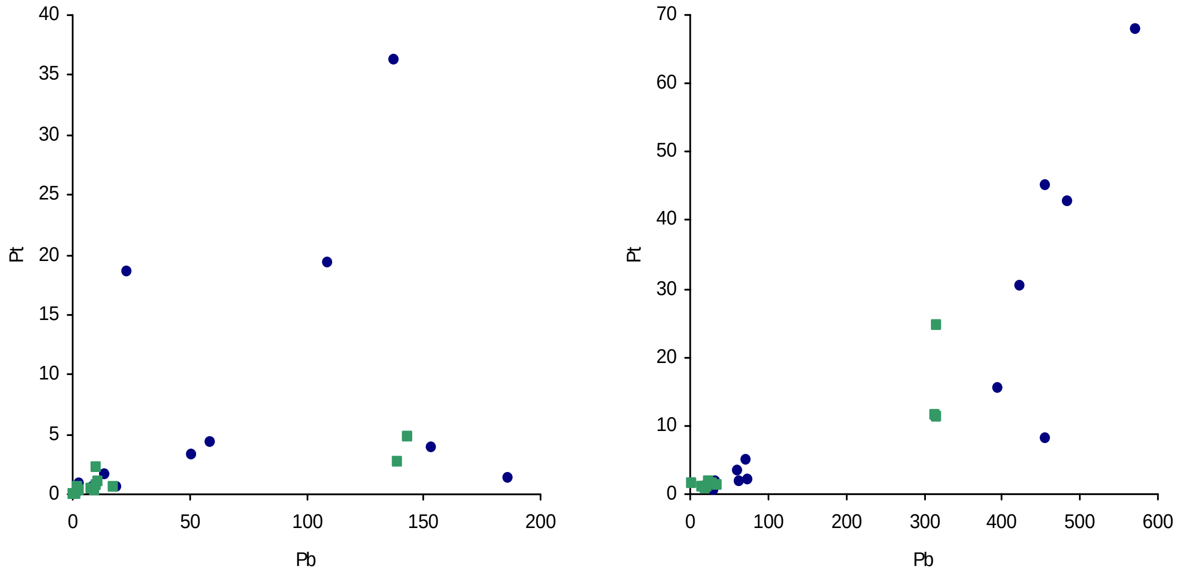

Figure 9. Correlation analysis for Pt and lead concentrations in (A) soils (squares) and road sediments (circles) and (B) rinsed (squares) and dry (circles) grass samples.

The reason for the weak correlation in dry grass samples may have to do with differential intake mechanisms for lead and platinum through plant surfaces or differential abilities to adhere to plant surfaces. Lead is known to be a 'sticky' metal and is found in the environment in a wide range of species, most of them bioavailable. It is likely that lead enters through plant surfaces whereas platinum, biologically inert in most cases, merely stays on surfaces. Data comparing plant Pt concentrations in this study show that a significant amount of Pt is deposited on plant surfaces compared to that Pt which is found in the tissue (Refer back to Table 13). The correlation for rinsed grass samples was good between Pt and Pb indicating perhaps that Pt in vegetation comes primarily from uptake by the roots.

7. Future Recommendations

This project is a starting point for future PGE monitoring in Ghana. Much can be done to expand the scope of this study; it can serve as a tool in mapping the changes in PGE levels in a developing country. Given below is a list of suggestions that could be considered for PGE projects in Ghana in the years to come.

i. A major priority in any future research in Ghana is to determine the environmental concentrations of Rh and Pd. These levels can be used to calculate ratios between PGE. These ratios would help determine what the exact sources of environmental PGE in Ghana are. Tell tale ratios would source present PGE to gasoline or diesel engine catalysts or to an external source like mining in Southern Africa, which has specific PGE ratios in its ores.

ii. This research was inspired by the desire to explore the PGE particle global distribution theory. Two major data were missing in terms of this theory. Firstly, the determination of Pd and Rh concentrations would be, as discussed previously, incredibly useful. Secondly, aerosol size fraction information would help. It could then be assessed if airborne particles were indeed transportable over long distances and thus explainable by anthropogenic activities. If the majority of airborne PGE fall into larger size fractions their presence is more explainable by natural processes. Developments in LA-ICP-MS could eventually track PGE particles to catalytic converter brands and possibly even car manufacturer; in this way PGE from Europe and elsewhere could be tracked.

iii. It would be of value to establish sampling sites that had different traffic densities as this would give a smoother data range, rather than having only high and low sites, which ended up being the case in this study.

iv. It would be useful to have a better idea of lead/platinum associations. Laser-ablation of road sediment samples was attempted in this study to explore this aspect but with no success. The reasons for this failure are unclear and further work on this needs to be done. If it could be shown that both PGE and Pb are released on wash coat particles some form of concentration tracking could be done. It is important to find out whether or not such emissions act in a synergistic fashion or if the two metals act independently of one another.

v. There have been many attempts in past research to determine the exact transformation and solubility behavior of PGE. Most studies have been based on European and North American conditions and this may be hindering the development of ideas. The use of model substances is a good tool for outlining solubility but perhaps more focus should be placed on using materials and parameters that are closer to reality (*e.g.* tunnel dust). If a wider variety of soils are used with known pedological character, the movement of PGE out of soils into vegetation and, on a greater scale, humans can be clarified. Explorations about uptake by vegetation, whether through roots or surfaces would fit well with this.

vi. In Ghana it would be of interest to explore PGE in the aquatic sphere. In particular, PGE concentrations in aquatic sediments could shed light on the movement and sinks of PGE in a country where the environmental parameters are so different from those studied previously.

vii. A more detailed assessment of the actual natural and anthropogenic levels of PGE in Ghana would be important in terms of comparisons between developed and developing nations. This could be done by geological survey or the use of pollutant tracers, for example, lead isotopes.

Conclusions

This study demonstrates that increasing PGE levels in the environment is not just a problem special to the developed world. In fact the PGE issue is at a much more advanced stage than expected. Many developing countries rely on importation to supply vehicular demands. Accra was estimated to have, as an upper estimate, 70% of its car fleet catalytically equipped. This number will undoubtedly increase in coming years.

This study used ICP-MS effectively to determine the Pt concentrations in various media in Accra. Road sediments showed the highest Pt concentrations. Soils, dry grass and rinsed grass showed decreasing concentrations of Pt, which agrees with its dispersion in successive environmental compartments. In general the sample media also showed increasing Pt levels with increasing traffic; this is another evidence supporting the sourcing of Pt to catalytically equipped vehicles.

Road sediment and soil Pt levels suggest that Ghana may have a background level naturally higher than that found in Europe. The differences in the Ghanaian car fleet in terms of its older age and lower turnover compared to Europe have resulted in nearly equivalent environmental Pt levels in both locations. It is likely that the soils in Ghana is have characteristics that when taken into consideration with external environmental variables, increase the solubility of Pt in the environment. This is an issue that should be monitored in the future as diet is a main pathway of PGE into man.

Grass samples were subject to analytical difficulties. Dry samples were higher in Pt concentration than rinsed samples. Levels were higher than those found in comparable studies in Europe which may be due to the fact that tropical climates give rise to different vegetation types, nutrient cycling systems, growing seasons and plant structures.

Lead concentrations in all media varied proportionally to traffic densities. Correlation analysis showed that lead and Pt had similar variations in concentrations in most media. Dry grass was the exception; this was attributed to the fact that samples from one of the sites was in a windblown area thus decreased deposition on plant surfaces occurred.

This study was the first time that Pt research was done in a developing country. The findings here highlight the fact that PGE emissions are an issue and require further exploration outside of the developed world.

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Appendix- Car Data

Car data was collected by standard question interviews, open interviews and from the Driver and Licensing Authority (DVLA) for the Greater Accra Region. The results are given below.

1. Standard Question Interview

Appendix Table 1. Standard Question Interview Results

Make and Model	*Year*	*Age upon arrival in Ghana (year)*	*Time in Ghana (year)*	*Private (P) or Commercial (C)*
Toyota Trecel	1987	4	10	C
Renault 19	1990	1	10	C
Mazda 626	1981	5	15	C
BMW 318	1993	8	1	P
Opel Kadett	1988	10	3	C
Opel Kadett	1986	9	6	P
Opel Vectra	1990	10	<1	P
Daewoo Family	1983	10	8	C
Peugot 505	1970	10	18	P
Merc Benz 190E	1980	14	16	P
Kia Pride	1990	8	3	P
Kia Sephia	1999	1	1	P
Merc Benz C280	1997	3	1	P
Daewoo Tico	1986	13	2	C
Ford Escort	1988	3	10	C
Opel Kadett	1991	8	2	C
VW Golf	1996	2	3	P
Nissan Sentra	1990	7	3	C
Peugot 504	1971	4	16	C
Toyota Trecel	1987	8	4	C
Hyundai Excel	1994	2	5	C

From this data it was estimated that the age of cars imported in Ghana was 8 years and that the average vehicle age is 13 years.

2. Open Interviews

Interview Notes from G. Obery- UST graduate student

- Cars generally 8 to 10 years old when imported
- Cars used for 5 years then get an engine/body overhaul and get used for 5 years
- Cars that are 1-5 years old more expensive but have lower import tax
- Cars 6-10 years old cheaper but have higher import tax
- Cars over 10 years old cannot be imported
- 3 import scenarios
    - bring car in from Europe themselves
    - have people send a car in
    - use dealers who have contacts and sellers adds

Interview Notes from EK Quartey- Chief Executive Driver and Vehicle Licensing Authority, Accra

- DVLA has existed since 1995
- All regional capitals have an office but Accra has the biggest
- Sample books surveyed are all from 2001
- Prior to 1995 police handled all vehicle registration
- When DVLA took over in 1995 all pre-registered vehicles had to re-register in 1996 therefore there is a large number of cars registered in that year
- Books include all vehicles

Interview Notes from A. Ama- Black Market Licensor

- Average car age on import is 8 year
- No cars over 10 years allowed to be imported
- Cars usually 1990+
- Cars usually no older than 12-15 years

Interview Notes from Professor K. Andam- Head of Engineering, UST

- Ban on importing cars older than 10 years, legislation in 1998
- Vehicles must pass inspections every few years
- Standards for strictness increasing
- Generation of revenue
- Most cars come from Europe

3. DVLA Data

DVLA authorities gave data on the total number of vehicles registered at this particular branch. Record books were also examined. Only the make of the car and the number of each of a particular make were available from these books. In order to estimate the number of catalytic converters in the Accra region a lot of assumptions had to be made.

Assumptions

- Cars were considered to have or not have catalytic converters based on their average and maximum possible age (20 years) or known production dates and the manufacturer's home country. As most cars were imported from Europe this was felt to be a safe assumption. Based on information from the AECC the following years were given:
    - Japan:1975
    - USA:1977
    - South Korea: 1978
    - Australia: 1986
    - Sweden: 1988
    - Germany: 1985
    - Rest of EU: 1993
- When available information on individual car manufacturers was also used.
- All buses, truck and vans were assumed to be non-catalytically equipped and diesel. It was felt that this type of assumption would balance with those diesel cars that could not be gleaned due to insufficient data. If it was known for certain however, it was recorded.
- If in doubt it was assumed that a car was not catalytically equipped.

Appendix Table 2. Sample of populations with estimated catalytically equipped cars and the number of diesel vehicles.

Make	*Cats*	*Diesel*	*Total*	*Make*	*Cats*	*Diesel*	*Total*
Toyota	347	144	491	MB	54	104	167
Susuki	33	2	35	Audi	67	0	67
VW	121	26	147	Opel	848	6	858
Ford	61	54	115	Chevrolet	2	1	3
Volvo	32	1	33	Chrysler	2	0	2
Lexus	3	0	3	Peugot	0	4	45
Aston M	0	0	5	Subaru	7	3	10
Mitsubishi	54	31	85	Misc	13	22	80
Honda	37	0	37	Pontiac	4	0	4
Kia	211	0	211	BMW	0	0	125
Mazda	42	48	90	Land Rover	0	21	21
Skoda	0	0	13	Isuzu	9	83	92
Hyundai	609	91	700	Asia	0	7	7
Nissan	192	159	351	Lada	0	0	5
Dodge	1	12	13	Geo	47	0	47
Diahatsu	23	0	23	Renault	0	16	79
Fiat	0	0	55	Seat	0	8	33
Daewoo	233	0	233	**Total**	**3052**	**843**	**4285**

Using this data the percentage of catalytically equipped cars was put at 71.2%, non-catalytically equipped cars at 9.1% the number of diesel engine vehicles at 19.7%.

Appendix Table 3. Total number of cars registered at the Greater Accra Region DVLA up to the year 2000.

Vehicle Type	*Total Number of Vehicles Registered Per Year*						
	1995	1996[a]	1997	1998	1999	2000	Total
Private motor vehicle up to 2000cc	17471	111991	23400	22448	28075	20770	224155
Commercial motor vehicle up to 2000cc	2941	36475	5676	4869	8023	11885	69869
Motor vehicle above 2000cc	2775	2154	1946	2049	6574	5211	20709
Buses and Coaches	7619	42367	8838	9463	9858	5469	83614
Trucks up to 16 tons	5134	13794	2793	3769	3454	1428	30372
Trucks from 16-22 tons	995	4073	1070	1169	590	395	8292
Trucks above 22 tons	498	2037	535	585	292	229	4176
Articulated trucks up to 24 tons	686	2243	619	394	196	120	4258
Articulated trucks up between 24-32 tons	176	1403	416	319	291	305	2910
Articulated trucks between 32 tons	3	988	315	252	262	126	1946
Total	38298	217525	45608	45317	57615	45938	450301

a- The number for this year is high do to a shift in administrative roles. The police department had formerly registered cars and in 1995 this responsibility was moved to the DVLA. All cars had to be reregistered at the DVLA in this year.

Projecting based on these tabulations 315 n 210 vehicles in Accra are catalytically equipped and 90 060 are diesel powered. To account for the fact that the data books used were from 2001 these numbers are rounded down to 300 000 and 90 000.