Series: Platinum Group Elements in the Environment – Anthropogenic Impact

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Series Editors: [1]Eckard Helmers, [2]Klaus Kümmerer
[1] Prof. Dr. Eckard Helmers, Chemisches Institut im Amt für Umweltschutz (EPA), Stafflenbergstraße 81, D-70184 Stuttgart, Germany
[2] Dr. Klaus Kümmerer, Institute of Environmental Medicine and Hospital Epidemiology, University, Hugstetterstr. 55, D-79016 Freiburg, Germany

Anthropogenic Platinum Fluxes: Quantification of Sources and Sinks, and Outlook

[1]Eckard Helmers, [2]Klaus Kümmerer

[1] FH Trier, University of Applied Sciences, environmental campus Birkenfeld, P.O. Box 30 13 80, D-55761 Birkenfeld, Germany
[2] Institute of Environmental Medicine and Hospital Epidemiology, University of Freiburg, Hugstetterstr. 55, D-79016 Freiburg, Germany

Corresponding author: Prof. Dr. Eckard Helmers

Abstract

Employing the data available to date, anthropogenic Pt fluxes are calculated for Germany with special emphasis on the Pt emitted by cars equipped with catalytic converters. Pt fluxes are quantified using five different methods (street deposition, automobile emission rate, sewage sludges, atmospheric load, industrial consumption). During the first and the second methods, approx. 100 kg of emitted Pt are seen to result for both for the mid 1990's. Up to the year 2018, a total of 2100 kg of Pt will be emitted by cars equipped with catalytic converters. The diffuse atmospheric Pt deposition amounts to 0.73 - 4.4 µg/m^{2}y or 260 kg Pt/year. Industrial sources emitting Pt into the atmosphere are likely but difficult to quantify. The enrichment of Pt in soils during agriculture fertilization with sewage sludges and during diffuse atmospheric deposition result in a level of 46 - 460 ng/kg up to the year 2018. Although this is slightly below the geogenic background, a comparison with the pollution history of Pb implies that forthcoming environmental Pt enrichment should not be neglected.

Keywords: Atmospheric load; automobile emissions; environmental enrichment; industrial consumption; lead; platinum fluxes; palladium; Pb; Pd; PGE; platinum group element; Pt; sewage sludges; sinks; street deposition

1 Introduction

Contributions in this series have considered several environmental and analytical aspects of platinum group elements (PGE) emitted by automobiles with catalytic converters (e.g. Helmers, 1997a) as well as by industrial sources (Zereini et al., 1998). As a synopsis, the strength of fluxes as they can be estimated up to now, and the different sources and sinks for anthropogenically emitted platinum, are discussed in this concluding contribution.

The assessment of sources and sinks constitutes a logical step localized at the end of an analytical strategy. Analytical strategy in this case starts with the development of analytical methods suitable for the reproducible determination of – in this case – ultratrace levels. As the next step, there should be analytical quality assurance followed then by the collection of field data. Since analytical methods are continuously developing, the data should be assessed and summarized from time to time (e.g. as done by Lustig et al., 1997 and Hees et al., 1998). Prior to the quantification of sources and sinks, spatial and particularly time trends of the investigated elemental parameter are to be identified. These trends are clearly indicating sources and sinks within an emission situation.

It should be achieved to quantify sources and sinks of all the three PGE emitted by cars equipped with catalytic converters (Pt, Pd, Rh). However, there is still not enough experience (Hees et al., 1998) to reliably investigate the Pd and Rh fluxes. There is a lack of quality assurance particularly during Pd analysis (Helmers et al., 1998). Also, there is only little environmental data on Rh (Helmers and Mergel, 1998). Additionally, further sources emitting Pd and Rh should be quantified to enable a comparison with automobile emissions. In the case of Pt, an anthropogenic source other than the automobile has already been assessed and quantified: hospital effluents (Kümmerer and Helmers, 1997; Kümmerer et al., 1998).

Pt fluxes are calculated here using different methods: first, analytical data obtained for specific environmental matrices was extrapolated with respect to the corresponding nationwide fluxes in Germany (Pt deposition onto the streets, atmospheric Pt fluxes). Secondly, Pt emissions of two individual sources have been extrapolated (Pt emissions of automobile catalytic converters, Pt fluxes as transported by sewage sludges and the freshwater system). As there may be temporal and site-specific variations, results of the second attempt are only extrapolated with respect to future Pt levels. In a third attempt, Pt consumption by different industrial sectors is considered.

Sources and sinks, however, are closely connected within biogeochemical cycles: The atmosphere constitutes a primary sink since aerosols possess a residence time of only several days (BUAT-MÉNARD, 1983). International exchange of Pt via the atmosphere is not considered here. In another view, the atmosphere acts as a diffuse source for Pt polluting soils as the secondary and permanent sink. Also, freshwater as well as the seas are receiving Pt from diffuse (atmospheric input) or point sources (dumping) in the function of a primary sink. The anthropogenic input of metals into freshwater and seawater (e.g. Pb, see HELMERS et al., 1990) is then followed, for example, by scavenging and generating polluted sediments as a secondary sink.

2 Sources and Fluxes

2.1 Pt deposition onto the streets

An extended study (LASCHKA et al., 1996) is supplying information about the Pt deposition on the streets emitted by cars equipped with catalytic converters: the investigated street (16,000 cars/day) is located in a southeastern German city revealing a deposition rate of 14 ng Pt/(m^2 d). This number allows an independent assessment of the Pt flux derived from automobile catalysts in a realistic situation. Up to now, this flux was calculated solely by extrapolating the Pt emission rate of an individual car (KÜMMERER et al., 1998).

First of all, it has been checked whether the published flux of 14 ng Pt/m^{2}d is representative: with the reviewed Pt emission rate of 0.5 - 0.8 µg/km (HELMERS, 1997a), a minimum of 8 µg Pt will be emitted by 16,000 cars/day, most of it being deposited on approx. 6 m^2 resulting in a deposition of 1.3 µg Pt/m^2, a value which is 100 times higher than that measured by LASCHKA et al. (1996). This leads to two conclusions: first, the flux of overall Pt emissions calculated by the emission rate should be refined considering the actual speeds driven (→ *Chapter 2.2*).

Secondly, the deposition rate of 14 ng Pt/(m^2 d) is very low, caused by the fact that a speed of only 50 km/h was driven here (LASCHKA, personal communication). Investigations of KÖNIG et al. (1992) clearly revealed that the Pt load of exhausts strongly increase in relationship to the speed of a car. This increase has been considered during the calculation below of a nationwide Pt flux: for example, the deposition rate on highways will be ten times higher than on the city street investigated by LASCHKA et al. (1996).

Accordingly, surfaces of the three street categories (highways, federal and national streets, district and city streets) are multiplied with specified deposition rates resulting in a nationwide Pt deposition from automobile catalysts of 33 kg/y. In the next step, Pt deposition of all the three street categories are adapted to the individual traffic intensities: for example, only 2% of the streets are highways, but 30% of all traffic occurs here. This is the manner in which an overall deposition of 130 kg results. The magnitude of this deposition corresponds fairly well with the flux calculation by emission rate (→ *Chapter 2.2* and *Fig. 1*).

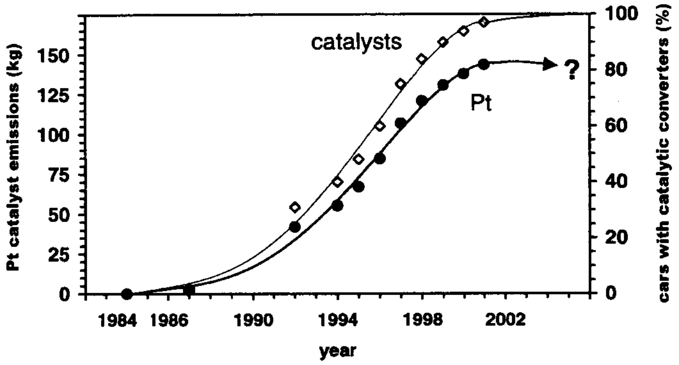

Fig. 1: Pt emission of catalytic converters and share of cars equipped with catalytic converters in Germany extrapolated up to the year 2001

2.2 Pt emissions of automobile catalysts as suggested by the emission rate

Up to now, the nationwide Pt emissions have been calculated (e.g. KÜMMERER and HELMERS, 1997) by employing the reviewed emission rate of 0.5 - 0.8 (mean: 0.65) µg of Pt/km for an individual car (HELMERS, 1997a). However, a quantification of the Pt deposition onto the streets (→ *Chapter 2.1*) suggests that the emission decreases during lower speeds, as also published by KÖNIG et al. (1992). In a very careful attempt leading to low fluxes, the overall Pt flux as emitted by cars has been recalculated here: an emission rate of 0.65 µg/km (HELMERS, 1997a) was assumed for highways (mean speed of cars in Germany > 130 km/h, see Helmers, 1997a). According to the lower Pt discharge at decreasing speeds as reported by KÖNIG et al. (1992), an emission rate of 0.18 µg/km was adapted in this calculation to federal and national streets (100 km/h), while an emission rate of 0.065 µg/km was assumed for district and city streets, the latter nevertheless demonstrating higher speed limits in part of up to 100 km/h.

During a previous calculation, the number of cars in Germany has been multiplied with a yearly mean of 15,000 km per car, resulting in a flux of 152 kg for 1994 (KÜMMERER et al., 1998). Here, the number of total km has been taken from traffic statistic data supplied by the German federal environmental agency (UBA, 1994) being multiplied with the emission rates as specified for each street category. Of course, the flux is smaller with this method and results, for instance, in 55.2 kg Pt for 1994 (→ *Fig. 1*). Pt emission has been extrapolated: while only 2% of the cars were equipped with catalytic converters in 1987, three years after the introduction of this technology in Germany, a share of 97% is to be expected for the year 2001 (→ *Fig. 1*). The corresponding Pt emission is less easy to predict: first, there will be an increase of up to 145 kg Pt by the year 2002, more than three times higher than in 1992. However, since the early 1990's, new cars have been equipped with advanced types of catalytic converters other than Pt/Rh-version, but mainly based on Pd as a catalytically active component (HELMERS et al., 1998). Consequently, the Pt emission from this source should decrease in relationship. However, during the next years, this effect may be compensated by the fact that the aging of catalytic converters together with the cars will increase overall Pt emissions (HELMERS, 1997a). However, the time series (→ *Fig. 1*) reveals that over 16 years are required until more than 95% of the cars are equipped with a new technology. Consequently, if all new cars are equipped with Pd-catalytic converters from the year 2000 on, some 15 years or more will be required until the Pt emissions from this source fall below 10 kg/year.

This scenario allows to summarize the overall Pt emissions as being predictable for the lifetime of the Pt/Rh-catalytic converter technology (up to the year 2018): the emissions displayed in **Figure 1** are doubled also considering a continuous traffic increase of 1%/y. In this way, 2100 kg of Pt will be emitted altogether by cars in Germany equipped with Pt/Rh-catalytic converters from 1985 to the year 2018.

2.3 Pt fluxes as transported by sewage sludges

In a unique time series of Pt measured in archived sewage sludge ashes back to the year 1972 (sampled in Stuttgart, Germany), a continuous increase has been observed since 1984 which was traced back to automobile releases (HELMERS et al., 1994). The equivalent excess Pt amounted to 500 mg Pt/kg ash corresponding to approx. 250 mg Pt/kg sewage sludge. If this is extrapolated to 5 x 10^{10} kg of sewage sludges resulting in Germany at the beginning of the 1990s (HELMERS and WIPPLER, submitted), 12,500 kg of Pt result. This is two orders of magnitude higher than the Pt flux emitted by the traffic as reported in Chapter 2.2. Obviously, excess Pt in Stuttgart's sewage sludges cannot be extrapolated on a national scale. In fact, with a mean of 35 mg/kg, much lower Pt concentrations have been observed in other (smaller) German purification plants (reviewed in Helmers et al., 1998). Moreover, in another study, it has been concluded that the Pt content of Munich's sewage sludges is not primarily affected by traffic releases (LASCHKA and NACHTWEY, 1997).

Consequently, Pt fluxes transported via the German sewage systems must be calculated employing the source data:

First, we assume that 50% of the Pt emitted by cars is received by the sewage systems. This share will not be reached along smaller streets in the countryside. However, most traffic occurs on the highways and city streets which are connected to the local sewage systems. Secondly, Pt is emitted from hospitals (KÜMMERER and HELMERS, 1997; KÜMMERER et al., 1998) being completely received by the sewerage systems. Pt received from the two sources above can be summed up to 42.9 kg in 1994 and 56.4 kg in 1996. We have not considered the additional input in the order of possibly 10 kg/y emitted from industrial sources (→ *Chapter 2.5*) since this flux is even more difficult to quantify. Within the purification plants, Pt is eliminated to an extent of 72% (LASCHKA and NACHTWEY, 1997). Accordingly, the remaining 28% is emitted into the freshwater (→ *Table 1*). In Germany, 30% of the sewage sludges are used as fertilizers in agriculture. The remaining 70% of Pt is deposited directly (→ Table 1) as sewage sludges or, after incineration, as sewage sludge ashes (HELMERS and WIPPLER, submitted). However, we do not know whether a relevant portion is emitted into the atmosphere during incineration.

2.4 Atmospheric Pt fluxes

There is still only little data available on the atmospheric Pt concentrations: SCHIERL and FRUHMANN (1996) reported airborne Pt concentrations of around 500 µg Pt/kg sampled in city buses. However, these numbers cannot be extrapolated on a nationwide scale. ALT et al. (1993) measured a mean of 34 µg Pt/kg in urban airborne particulate matter in 1992. HELMERS and MERGEL (1998) reported 68 µg Pt/kg after open Bergerhoff-sampling. This is far above the local geogenic background (< 0.4 µg Pt/kg soil; CUBELIC et al., 1997), thus implying that Pt is enriched anthropogenically. This is little, although homogenous data, so that it may serve as a basis for the following calculations employing a corresponding air load of 2 pg Pt/m³.

Table 1: Partition of anthropogenic Pt fluxes (in kg) within the German sewerage system. Calculation see Chapter 2.3

year	received by the sewerage systems	remaining in sewage sludges	disposal with sludges or ashes	deposited agriculturally with sludges	released into freshwater
1994	42.9	30.9	21.6	9.3	12
1996	56.4	40.6	28.4	12.2	15.8

Data is missing on the atmospheric transport dynamics of aerosols contaminated by Pt. We have to assume that, similar to the well-investigated Pb, a negligible portion of 15% is attributed to "far fall out" and "airborne input", as concluded for Stuttgart in 1992 (HELMERS et al., 1995). There are only two results of Pt analysis in rain revealing 0.08 - 0.17 ng/l (ALT et al., 1997). However, since this is very close to the detection limit and risk of contamination is high in this concentration range, we should not extrapolate this on a national scale. In comparison with the atmospheric Pb load, a present rain concentration of 0.1 - 1 ng Pt/l has nevertheless been proposed (HELMERS et al., 1998).

The diffuse atmospheric Pt deposition is calculated using two different methods: from the comparison with Pb and, secondly, utilizing the atmospheric sedimentation rate.

Depending on the date of sampling, there is a relatively constant Pb/Pt-ratio in matrices polluted by traffic releases. In grass sampled during 1992 along a German highway, this relation amounted to 2400 : 1 (HELMERS et al., 1994). Due to the phasing out of Pb and the simultaneous increase of Pt emissions, this relation is continuously seen to be decreasing. In other countries with a different history in traffic policies, there are specific Pb/Pt-ratios. For example, the ratio was 8600 : 1 in California in the year 1985 (HODGE and STALLARD, 1986).

Data published on Pb concentrations in urban aerosols vary from 10 to 9,000 ng/m^3 (reviewed in SCHÜÜRMANN et al., 1994). Another study reveals 200 - 800 ng Pb/m^3 for European and American cities, accompanied by 50 - 300 ng/m^3 for rural areas (OECD, 1993). Since these numbers are approx. ten years old, only the lower range (10 - 50 ng Pb/m^3) will presently be valid. This results in a 10,000 time higher Pb enrichment in the atmosphere compared with Pt (2 pg/m^3). Considering the decrease of Pb releases within the past 10 years (e.g. HELMERS et al., 1995), this Pb/Pt-relationship should be realistic for the early 1990's.

Accordingly, Pb deposition data may be utilized to estimate the Pt deposition: SCHÜÜRMANN et al. (1994) reviewed German Pb deposition rates varying from 7 to 103 (mean: 44.3) mg Pb/m^{2}y. In rural areas, Pb deposition was 30.6 mg/m^{2}y, while 58 mg Pb/m^{2}y was deposited in an urban area investigated (all mean values, data from the 1980s).

The above attempt results in a Pt deposition of 4.4 µg Pt/m^{2}y, valid for the early 1990's.

In another, possibly more precise attempt, the atmospheric Pt deposition is calculated via the atmospheric sedimentation rate. Outside of dust production areas and along the continental margins, the sedimentation is normally between 0.1 and 1 g/m^{2}y (DUCE et al., 1991). In Florida, for example, a mean annual sedimentation of 1.3 g/m^{2}y was measured (PROSPERO, 1990). Due to a lack of representative information, the atmospheric sedimentation may also be concluded from Al-deposition data based on an Al concentration in soils of 8% (PROSPERO, 1990). In this way, the mean annual Al deposition into the North Sea (KRIEWS, 1992) leads to a sedimentation rate of 2.8 g/m^{2}y. ULRICH (1984) published an Al-deposition rate for the Solling (a forest in central Germany) resulting in a sedimentation rate of 2.8 - 3.5 g/m^{2}y. The sedimentation in urban areas should be higher due to industrial activities and the traffic. Actually, during the past 10 years, a mean annual sedimentation of 25.6 g/m^2 was measured in the city of Stuttgart (R. REUTER, personal communication, 1998). Thus, a mean atmospheric sedimentation rate for Germany of 14.3 g/m^{2}y results in a deposition of 0.73 µg Pt/m^{2}y. However, the magnitude of industrial Pt consumption (→ *Chapter 2.5*) as well as investigations performed in the vicinity of a producer of automobile catalytic converters (ZEREINI et al., 1998) both imply that Pt deposition will probably be higher locally.

2.5 Industrial Pt consumption

In an independent attempt, it is interesting to discuss the Pt consumption by different industrial sectors (→ *Table 2*). Around 65% of Pt on the European market is consumed by the automobile catalytic converter industry. Surely, a distinct proportion of these 18,800 kg Pt yearly is emitted during the production process either into the atmosphere or into waste water. There is no data concerning the industrial emission rate, despite the 92 kg of Pt which is emitted yearly via ammonia production (BECK et al., 1995). However, a considerable emission of Pd was already measured near an industrial plant producing automobile catalytic converters (ZEREINI et al., 1998). Assuming a loss of 1%, 180 kg of Pt will be emitted on a European scale. According to the national concentration of producers of automobile catalysts, some 90 kg may apply to Germany. European-wide, further industrial sectors (jewelry sector and the unspecified "others" not considered, → *Table 2*) are emitting some further 39.8 kg at an assumed loss of 1%. A 20% German share accounts for another 8 kg, summing up to 98 kg a year for Germany.

Table 2: European Pt demand in 1994 (published by the Johnson Matthey company, 1996)

Sector	demand (kg)
Car catalytic converters industry	gross: 18,000 recovery: 900
Chemical	1,500
Electrical	775
Glass	930
Jewellery	3,100
Petroleum	775
Other (not specified)	2,015

This seems to be high with respect to only 55.2 kg of Pt calculated for 1994 (→ *Fig. 1*) when employing the automobile Pt emission rates. However, calculation of the overall atmospheric fluxes also results in 260 kg of Pt per year (→ *Chapter 3.2*). Moreover, 130 kg of Pt resulted for the nationwide Pt street deposition (→ *Chapter 2.1*). Altogether, there are probably industrial point sources emitting Pt which cannot presently be quantified precisely.

3 Sinks

3.1 Soil: Pt input from the deposition of sewage sludges

Similar to Pb (PUCHELT et al., 1993), anthropogenically deposited Pt exhibits an immobile behavior in soil (CUBELIC et al., 1997). Assuming that sewage sludges are dumped onto 50% of the agriculture area in Germany, an enrichment of Pt within the upper soil horizon (15 cm) may be calculated. Pt fluxes of 1994 and 1996 as reported in **Table 1** then cause a soil concentration of 0.7 - 0.92 ng Pt/kg soil. After a linear enrichment of 10 years, concentrations may reach 10 ng Pt/kg soil. Higher values of up to 50 ng/kg result if the Pt from this source is enriched on only 5% of the agriculture area over 10 years. However, all these concentrations are below the geogenic background of 140 ng Pt/kg (in comparison: cultivated soils exhibited 1.1 μg Pt/kg, both data taken from ALT et al., 1997).

It is even possible to extrapolate the overall fluxes towards a future situation (year 2018) when the Pt/Rh-technique has been probably completely displaced by catalysts based on alternative active components.

The Pt emissions by automobile releases have been extrapolated (→ *Chapter 2.2*) assuming a maximum output in the year 2002 (→ *Fig. 1*) followed by a continuous decrease mirroring the present increase. We also assume that emissions from further anthropogenic sources (hospital, industry) will remain at the present level. Accordingly, agriculture fertilization transports some 609 kg of Pt onto the fields up to the year 2018. Depending on the area of enrichment (5 - 50% of agriculture area available), 46 up to 460 ng Pt/kg soil are yielded (→ *Table 3*). This is not significantly above the present background (→ *Table 3*). Atmospheric deposition of the Pt flux linearly extrapolated to the year 2018 causes a similar, additional Pt enrichment (→ *Table 3*).

3.2 Soil: Pt input from atmospheric deposition

Aside from sewage sludges, diffuse atmospheric input is also adding Pt to the soil. The assessment of atmospheric fluxes (→ *Chapter 2.4*) yields a yearly deposition of 0.73 (- 4.4) μg Pt/m^{2}y. A nationwide extrapolation results in a yearly deposition of 260 (- 1600) kg Pt/y attributed to the mid 1990's, since it is based on airborne dust Pt concentrations determined from 1992 to 1997.

As automobile catalytic converters have been calculated to supply only a mean of 67 kg/y over this period (→ *Fig. 1*), this constitutes an indication for further sources emitting Pt into the atmosphere (→ *Chapter 2.5*). However, we must stress that these estimations are reliable only with respect to the order of magnitude.

A deposition of 260 kg of Pt onto the German soil will cause a soil concentration of 2.4 ng Pt/kg within the upper 30 cm. If this input continues over 10 years, 24 ng Pt/kg are reached far below the geogenic background.

3.3 Pt input into freshwater and seawater

In order to get a rough estimation of Pt levels in freshwater, the releases of purification plants (→ *Table 1*) are related to the German rivers Rhein, Ems, Weser and Elbe, which all flow into the North Sea. Resulting freshwater concentration is only up to 0.16 ng Pt/l (→ *Table 3*). Interestingly, this very rough estimation is in good accordance with investigations of LASCHKA (1996): She investigated the Pt concentration in the Bavarian Isar river which exhibited concentrations from < 0.05 to 0.8 ng Pt/l. Discharges of Munich's purification plant into the river yielded an increase of 0.5 ng/l. Moreover, LASCHKA (1996) calculated a increase of 1.1 ng Pt/l caused by the mean Pt freight of the purification plant. Annually, 1.3 kg of Pt is discharged into the river water alone by the Munich purification plant (LASCHKA, 1996). A nationwide extrapolation results in approx. 52 kg Pt/year discharged into the rivers, nearly four times higher than that calculated by extrapolating automobile emissions (→ *Chapter 2.3* and *Table 1*). Accordingly, the theoretically expected river concentrations will be on the order of 0.5 ng/l.

Another portion is supplied by the diffuse atmospheric input summing up to 26 - 160 kg Pt/y, since the sealed area is

Table 3: Sinks: predicted background Pt levels in polluted matrices (*extrapolated to the year 2018, **open ocean value)

	fertilization with sewage sludges	diffuse atmospheric deposition	discharges of purification plants	in comparison: present background
soil* (ng/kg)	46 - 460	48		140 - 1,100
river water (ng/l)			0.1 - 0.5	< 0.05 - 0.1
North Sea (ng/l)			0.01	0.1**

around 10% on a nationwide scale (→ *Chapter 3.2*). However, we neglect this portion since we do not know how much of this run-off is received and correspondingly retained by the sewage systems.

There is a new European guideline standardizing the quantification of pharmaceuticals in surface waters (EU, 1995). This guideline operates with the input flux of a substance, a mean waste water volume of 150 l/inhabitant, the number of inhabitants on a national scale, and a dilution factor relative to the freshwater. Application of this formula (EU, 1995) leads to Pt concentrations in freshwater which are two orders of magnitude higher than those calculated above (→ *Table 3*).

Rivers are discharging their freights into the Seas. We can calculate the resulting Pt concentration in the North Sea (losses during scavenging, sedimentation, and mixing not considered) by employing an attempt of Kriews (1992) who reported atmospheric Pb input into the North Sea and the corresponding Pb concentration in the seawater (→ *Appendix*). A yearly German river discharge of 40 kg Pb is assumed and extrapolated to 100 kg as released by the nations surrounding the North Sea. In a very rough estimation, considering the German nationwide atmospheric Pt deposition (→ *Chapter 3.2*), another 100 kg should be deposited from air into the North Sea. The sum of 200 kg Pt/year then results in a seawater concentration of 0.01 ng Pt/l, which is below the background surface seawater level of 0.1 ng Pt/l (Goldberg and Koide, 1990).

4 Comparison of Pt Pollution with the Pb Emission History

As mentioned in **Chapter 2.2**, emissions of automobile catalysts will sum up to 2,100 kg of Pt from the year 1985 to 2018 in Germany. It is interesting to compare this flux with the Pb emitted by automobile exhausts up to now: Since the 1950's, some 2 x 10^9 kg of Pb has been emitted by the combustion of leaded gasoline in Germany (Bliefert, 1994). This resulted in a deposition of 1 g Pb/m^2 (Bliefert, 1994) or, refering to a soil depth of 15 cm, 6 mg Pb/kg. This is below the local geogenic background of approx. 15 mg Pb/kg (Puchelt et al., 1993). However, many sites along the streets have been heavily polluted with Pb (e.g. Puchelt et al., 1993), much more than implied by the above calculation of the mean.

The present situation may be enlightened by comparing the pollution situations of Pb and Pt: In **Figure 2**, concentration levels of highly polluted sites have been collected and compared. Principally, the Pb concentration levels are three orders of magnitude higher as compared with Pt. This is related to the much higher geogenic background of Pb as well as the higher magnitude of emissions (see above). However, the magnitudinal increase of Pt at polluted sites is partly higher compared with Pb: Pt in highly polluted soil and dust is approximately 1000 fold the background, while Pb levels of soil and dust are only 10 - 100 times higher than the background. As already mentioned and also indicated in **Figure 2**, Pb pollution is continuously decreasing. The highest Pb enrichment occurs in the polluted atmosphere (enrichment of up to four orders of magnitude). Background atmospheric Pt data is missing. The Pb concentration of polluted freshwater is also extraordinarily increased in comparison to unaffected freswater, possibly due to additional industrial releases (→ *Fig. 2*).

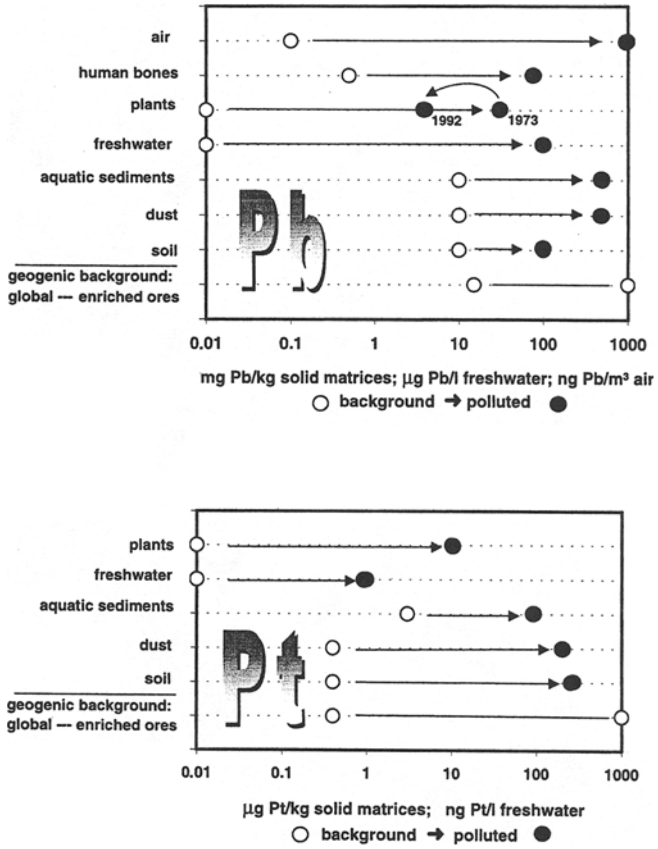

Fig. 2: Pollution situations of Pb and Pt: comparison. Highly polluted matrices sampled immediately near a highway, mostly in southwestern Germany (plants, soil, dust). The curved arrow, as an example, indicates the decrease in Pb pollution.
Geogenic background data from Wedepohl (1995), Pt ore data from Helmers and Mergel (1998), Pt and Pb soil and dust data from Cubelic et al. (1997), Pb sediment data obtained from lake sediments (Renberg et al., 1994), Pt sediment data obtained from a drainage basin near a highway (Zereini et al., 1997), Pb freshwater data from Helmers (1997b) and UBA (1994), Pt freshwater data from Laschka (1996), Pt plant data from Helmers and Mergel (1998), Pb plant data from Helmers et al. (1995), Pb human bones data from Grupe (1991), background Pb in air taken from Ewers and Schlipköter (1994), Pb in polluted air reviewed by Schüürmann et al. (1991).

In conclusion, the overall increase of the concentrational magnitudes of Pb and Pt is comparable. This is astonishing considering that Pt was emitted in relevant quantities since then years only, while Pb is already emitted in high quantities since about 40 years.

The toxic effects caused by the long-term Pb pollution even in densely populated areas are well known. Analysis of ancient bones exhibiting considerably lower Pb concentrations compared with recent ones (→ *Fig.* 2) allows one to obtain a "physiological zero point" for this metal (GRUPE, 1991). With respect to the physiological zero point (DRASCH, 1982), the Pt enrichment, as obvious in **Figure 2**, may also be of toxicological relevance, although resulting concentrations are very low with respect to the absolute magnitude. However, this does not mean that these two metals possess a comparable toxicology.

5 Concluding Synopsis

There is a relative wealth of data which allows to quantify and to assess fluxes of anthropogenically emitted Pt. However, the discussed fluxes constitute only a part of the whole biogeochemical cycling of Pt, which seems to be considerably affected by automobile releases in the populated environment. Since the natural background level of Pt is one of the lowest of all elements and, on the other hand, since very sensitive analytical methods allow to detect even small amounts of excess Pt, the spreading of automobile catalytic converter technology is relatively easy to observe in environmental matrices. Pt levels as predicted here for the future (soil, water) seem to be on the order of the geogenic background or even below. However – a comparison with the pollution history of lead clearly exhibited that considerably elevated Pt levels result at heavily polluted sites and in receiving matrices (along the streets, sewage sludges). In contrast to Pb, this occurred quickly after automobile catalytic converters had been introduced in the 1980's.

However, an assessment of the toxicological relevance remains difficult and must be done after further research (speciation, behavior in soils, etc.). Scientific results published in this series, particularly concerning fluxes, sources and sinks of anthropogenically emitted Pt, constitute a precondition for risk assessment. It should be stressed again that the reported fluxes are reliable only with respect to the order of magnitude or even less (see above). It is seriously necessary to obtain more data since some of the calculations are still based on few, partly regional investigations in order to enable a continuous revision and improvement of precision of the flux calculations in the future.

Although this report specifically quantifies the German national situation, results may be extrapolated for the other European countries with respect to their individual traffic density and history of catalytic converter policy (KÜMMERER et al., 1998). However, since there is no highway speed limit in Germany, highway Pt emissions of other countries may be halved in comparison with the German situation (HELMERS, 1997a).

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Appendix: Basic Data for Calculations

Pt deposition onto streets
Surface of German streets (after UBA, 1994): highways (1.32 x 10^8 m^2), federal streets and national streets (7.64 x 10^8 m^2), district and city streets (3.01 x 10^9 m^2). Increase of Pt-load in aerosols emitted by cars equipped with catalytic converters (60 km/h = 1): 100 km/h (2.8); 140 km/h (10.1), after König et al., 1992. Traffic as attributed to street categories: 30% (highways), 40% (federal and national streets), 30% (district and city streets). Pt deposition rate: 141 ng Pt/(m^2 d) on highways (10.1 times the basic result), 39.2 ng Pt/(m^2 d) on federal and national streets (2.8 times the basic result), 14 ng Pt/(m^2 d) on district and city streets as calculated from the data published by Laschka et al. (1996).

Pt emission of automobile catalysts by emission rate
km driven by cars in Germany in 1992: 4.71 x 10^{11} km. Traffic increase per year: 1% (UBA, 1994). 1993: 3.89 x 10^7 cars in Germany

Pt fluxes as transported by sewage sludges
Pt emissions from catalytic converters in Germany (→ *Fig. 1*): 55.2 kg in 1994; 84.4 kg in 1996. Pt emission by German hospitals (Kümmerer et al., 1998): 15.3 kg in 1994; 14.2 kg in 1996.

Soil: Pt input from the deposition of sewage sludges
50% of the surface in Germany (3.52 10^5 km^2) is used agriculturally (UBA, 1994).

Atmospheric Pt fluxes
In Germany, tropospheric air contains around 40 µg of particulate material per m^3 (UBA, 1994). Mean Pt concentration of atmospheric particulate material: 51 µg/kg.

Pt input into freshwater and seawater
Draining rate of the German rivers Rhein, Ems, Weser and Elbe: 3.28 10^3 m^3/s. A deposition of 3.5 10^6 kg Pb/year results in a mean concentration of 200 ng Pb/l in the North Sea (Kriews, 1992).

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Platinum Emission Rate of Automobiles with Catalytic Converters
by E. Helmers, in: *ESPR 4 (2) 100-103 (1997)*

Influence of Micro-Organisms on the Dissolution of Metallic Platinum Emitted by Automobile Catalytic Converters
by S. Lustig, S. Zang, W. Beck, P. Schramel,
in: *ESPR 4 (3) 141-145 (1997)*

Comparison of Palladium and Platinum in Environmental Matrices by E. Helmers, M. Schwarzer, M. Schuster,
in: *ESPR 5 (1) 44-50 (1998)*

Distribution of Platinum Group Elements (Pt, Rd, Rh) in Environmental and Clinical Matrices by T. Hees,
B. Wenclawiak, S. Lustig, P. Schramel, M. Schwarzer,
M. Schuster, D. Verstraete, R. Dams, E. Helmers,
in: *ESPR 5 (2) 105-111 (1998)*

Sources of Anthropogenic Platinum-Group Elements (PGE)
by F. Zereini, F. Dirksen, B. Skerstupp, H. Urban,
in: *ESPR 5 (4) 223-230 (1998)*

Anthropogenic Platinum Fluxes by E. Helmers, K. Kümmerer,
in: *ESPR 6 (1) 29-36 (1999)*