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# Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters

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## Abstract

A health risk assessment of platinum (Pt) emitted from automotive catalytic converters is presented. Following a stepwise approach, the relevant literature is discussed in order to characterize Pt emissions as well as the toxic potential of Pt and its compounds. In an exposure assessment, ambient Pt concentrations in air are predicted to range from approximately 4 pg/m<sup>3</sup> (street canyon, typical conditions) up to approximately 112 pg/m<sup>3</sup> (express motorway, severe conditions). These values agree well with the few measured concentrations, which are also in the low pg/m<sup>3</sup> range. Pt is emitted from catalytic converters in very small amounts (ng/km range), mainly in the (0)-oxidation state (elemental Pt). The nanocrystalline Pt particles are attached to μm-sized aluminum oxide particles. Whether free ultrafine Pt particles may be emitted and result in biological effects has not been studied sufficiently. Hence, risk assessment can only be based on the respiratory sensitizing potential of halogenated Pt salts. The presence of such compounds in automotive Pt emissions cannot definitely be excluded. From recent occupational studies conducted in catalytic converter production, a conservative no-effect level (NOEL) of 1.5 ng/m<sup>3</sup> can be derived for the sensitizing effect of halogenated Pt salts. In a (reasonable) worst case approach, it is assumed that such compounds comprise 1% (0.1%) of the total Pt emissions. Applying a safety factor of 10 to account for interindividual variability, a guidance value of 15 (150) ng/m<sup>3</sup> is derived for catalyst-borne Pt. The exposure to Pt in ambient air as measured or predicted is at least two orders of magnitude below this guidance range. Rhodium is also contained in automotive catalysts, palladium has increasingly substituted Pt, and iridium-based catalysts have recently been introduced. Although the database on these platinum group metals is rather small, there is no evidence that they pose a health risk to the general population. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Automotive catalytic converter; Platinum; Palladium; Iridium; Rhodium; Health effects; Respiratory sensitization; Risk assessment

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## 1. Introduction

Halogenated platinum (Pt) compounds (Pt salts) are highly potent sensitizing substances causing asthma, rhinoconjunctivitis and contact urticaria in a significant number of occupationally exposed workers in precious metal refineries and catalyst productions (Calverley et al., 1995; Merget et al., 1999). The introduction of Pt-containing automotive catalytic converters approximately 20 years ago in the US, and more than 10 years ago in Europe, gave cause for concern that emission from car catalysts might become a new environmental allergen. Thus, the establishment of the dose–response relationship of Pt salt allergy and the quantitative and qualitative analysis of catalyst emissions was considered important for risk assessment.

Based on emission data available from the older pellet-type catalysts, dispersion models predicted ambient Pt air concentrations in the range 1–70 ng/m<sup>3</sup> (Rosner and Hertel, 1986; Rosner and Merget, 1990). At that time it was still assumed that, according to the engine test bench studies of Hill and Mayer (1977), approximately 10% of the total Pt emissions were water-soluble, possibly containing halogenated Pt salts.

New qualitative and quantitative data on emissions and data on the dose–effect relationships in occupational settings have become available, and prompted us to reevaluate the health risks of Pt emitted from automotive catalysts. Our risk assessment is based on the respiratory sensitizing effect of halogenated Pt salts. In a worst case

approach, the emission of these compounds from automotive catalysts is assumed. There is no evidence that other end-points than sensitization could be of concern. In addition, we briefly discuss the relevance of further catalyst-borne platinum group metals, i.e. palladium (Pd), rhodium (Rh) and iridium (Ir).

## 2. Characterization of Pt emissions

### 2.1. Emission factors derived from engine test bench experiments<sup>2</sup>

During the early catalyst years pellet-type catalysts were used in the USA and Japan. In Europe usually monolith catalysts have been brought on the market, in which the platinum group metals, Pt and/or Pd and Rh, are supported on a ceramic or metallic honeycomb monolith. In driving and dynamometer experiments, Hill and Mayer (1977) measured Pt emissions from the older pellet-type catalyst of up to 2000 ng/km. The Fraunhofer Institute of Toxicology and Aerosol Research in Hanover, Germany, conducted a series of test bench experiments with three-way monolith-type catalysts (König et al., 1992; Artelt et al., 1999a). Depending on test conditions and catalyst age, Artelt et al. (1999a) found emission

<sup>2</sup>Emission factors (ng/km) are used here to quantify the amount of automotive platinum emissions per kilometer travelled. The term emission rate is sometimes used synonymously.

Table 1  
Emission factors (ng Pt/km) for new automotive catalysts under different operating conditions (adapted from Artelt et al., 1999a)<sup>a</sup>

Operating conditions	Geometric mean	Arithmetic mean	Lower quartile	Upper quartile
US72 cycle	29	37	14	57
80 km/h constant	7	12	2	20
US72-EUDC cycle	19	19	8	40
130 km/h constant	75	90	41	136

<sup>a</sup>Values used for the exposure calculations are in italics.

factors ranging from 2 to 120 ng/km. With respect to the number of catalysts investigated and the number of repetitions, the emission data on new catalysts can be considered reliable. Engine test bench experiments cannot simulate all possible factors influencing the operating conditions of catalytic converters and hence the emission of Pt. We therefore based our exposure calculations on the upper quartiles of emission factors obtained in the dynamometer studies (Table 1). The following emission factors were used for the different exposure scenarios (see below):

- City: 60 ng/km (US 72 cycle)
- Street tunnel: 20 ng/km (constant speed 80 km/h)
- Highway: 140 ng/km (constant speed 130 km/h)

## 2.2. Calculated versus measured Pt emissions

Emission rates derived from Pt concentrations in plants and soils near German motorways were claimed to give better estimates of the average Pt emission factors. However, as further discussed by Rosner and Merget (1999), emission values calculated from environmental levels and traffic data have to be interpreted with caution, as they are based on several imprecisely defined factors and assumptions. This pertains in particular to emission rates of up to 9700 ng/km calculated by Helmers et al. (1994). These values were reconsidered by Helmers (1997), and emission factors ranging from 500 to 800 ng Pt/km are now suggested.

Factors such as engine malfunction, severe driving conditions and improper car maintenance cannot usually be simulated in dynamometer studies. These factors can cause partial or complete destruction of catalysts. Although there are no reliable statistical data on the % of broken automotive catalysts, reports from the recycling industry (Hagelüken, 1995) and unpublished information from the catalyst and automotive industry are indicative of a considerable amount of demolished catalysts. This was especially true for

the first generation of catalytic converters. Thus, the relatively high Pt levels found in environmental samples are likely to result from the emission of larger particles or whole catalyst pieces that are deposited within a very short distance from roads and are, due to their size, probably not of toxicological relevance. Two findings support our theory. Firstly, all measured ambient Pt air concentrations are only in the low pg/m<sup>3</sup> range (see below). Secondly, biomonitoring studies by Philippeit and Angerer (1999) and Begerow and Dunemann (1999) indicate that significantly elevated Pt levels in body fluids most probably result from dental prostheses, while the uptake of Pt via inhalation is thought to be of minor relevance.

## 2.3. Particle size and chemical speciation

Pt is emitted from automotive catalytic converters in particulate form, mainly in the (0) oxidation state (elemental Pt). The nanocrystalline Pt particles are attached to  $\mu\text{m}$ -sized aluminum oxide particles. The largest fraction comprises Pt-loaded particles with sizes of  $> 10.2 \mu\text{m}$ . Between 11 and 36% of the particles were found to be  $< 3.14 \mu\text{m}$  (Artelt et al., 1999a). For comparison, particles with aerodynamic diameters  $> 10 \mu\text{m}$  are inhalable, but are mainly deposited in the upper respiratory tract. Particles  $\leq 10 \mu\text{m}$  reach the tracheobronchial region with a likelihood of  $\geq 50\%$ , whereas particles  $\leq 4 \mu\text{m}$  are mainly respirable, i.e. deposit in the alveolar region of the human lung (DFG, 1999).

According to the X-ray photoelectron spectroscopy studies by Schlögl et al. (1987), the presence of small amounts of oxidic Pt, probably located on the surface of metallic Pt particles, cannot be excluded. Recent studies by this group indicate that the fraction of oxidic Pt is less than 5% of the total Pt emitted. The definitive presence of Pt oxides could neither be proved nor disproved (Rühle et al., 1997).

As will be discussed below, only soluble Pt compounds are of possible toxicological relevance. Monolith catalysts seem to emit only very low amounts of soluble Pt. In the engine test bench studies by Artelt et al. (1999a), this fraction was approximately 1%. However, these studies

Table 2  
Measurements of ambient Pt air concentrations (dust samples)

Location (year)	Traffic condition	Pt concentration (pg/m <sup>3</sup> )			Reference
		Min.	Max.	Mean	
San Diego, USA (1974)	Free-way before the introduction of catalysts	—	< 0.05	—	Johnson et al. (1975, 1976)
Germany (1989)	Rural area	≤ 0.6	1.8	Not given	Tölg and Alt (1990)
Frankfurt/Main, Germany (1989)	Close to city roads shortly before the introduction of catalysts	≤ 1	13	Not given	Tölg and Alt (1990)
Dortmund, Germany (1991/92)	City with no direct traffic load	0.02	5.1	Not given	Alt et al. (1993)
Munich, Germany (1996)	Inside city buses and street cars	0	43.1	7.3	Schierl and Fruhmann (1996)
Munich, Germany (1995/96)	City, high traffic volume	4.4	42.4	13.6 (median)	Dietl et al. (1999)

were performed with laboratory-aged catalysts. It cannot be excluded that new catalysts emit more soluble Pt. On the other hand, the method used could not distinguish between soluble Pt emitted with the exhaust stream and Pt salts secondarily formed from particles due to acidic ultrasonic treatment, which was part of the analytical procedure. In laboratory experiments using a model substance consisting of aluminum oxide particles loaded with nanocrystalline Pt particles, tetra- and hexachloroplatinate was formed in physiological saline solution (Nachtigall et al., 1996; Nachtigall, 1997). It was also shown that smaller sized Pt particles (3–5 nm in diameter) were much more soluble (up to 22%) in saline solution than larger particles (15–25 nm, solubility 1.4%), as they are more typical of aged catalysts (Rühle et al., 1997).

Table 3  
Estimated ambient air concentrations of Pt at different exposure conditions based on dispersion models of Ingalls and Garbe (1982) and emission factors of Artelt et al. (1999a)

Scenario	Traffic volume	Emission factor (ng/km)	Ambient Pt concentration (pg/m <sup>3</sup> )
(1a) Street canyon (side walk), typical	800 vehicles/h at 8 km/h 1600 vehicles/h at 32 km/h	60 60	4 9
(1b) Street canyon (side walk), severe	1200 vehicles/h at 8 km/h 2400 vehicles/h at 32 km/h	60 60	14 28
(2a) Roadway tunnel, typical	25 vehicles travelling at 72 km/h at all times	20	36
(2b) Roadway tunnel, severe	165 vehicles traveling at 40 km/h at all times	20	92
(3a) On express-way, typical	28 000 vehicles/day	140	51
(3b) On express-way, severe	200 000 vehicles/day	140	112

### 3. Exposure assessment

#### 3.1. Ambient air concentrations

Due to the extremely sophisticated methodology required to analyze ultratrace Pt, only a few measurements of ambient air concentrations have been reported (Table 2). Concentrations of up to 2 pg/m<sup>3</sup> can be assumed as a background level in Germany. In the close vicinity of city roads, Pt concentrations are in the low pg/m<sup>3</sup> range.

#### 3.2. Estimation of ambient air concentrations using dispersion models

Rosner and Hertel (1986) estimated ambient air Pt concentrations for different scenarios based

on dispersion models described by Ingalls and Garbe (1982). As shown by Bärtsch and Schlatter (1988), who compared measured sulfate and lead concentrations with calculated values, these dispersion models are valid. Because of the weak database regarding analytical measurements, the model calculations have been updated using emission values obtained from the engine-test bench experiments with monolith catalysts by Artelt et al. (1999a), as described above. As shown in Table 3, a selection of different traffic scenarios has been chosen, taking into consideration that on, or close to, city roads and motorways the highest exposure can be expected.

The predicted Pt concentrations in street canyons (4–28  $\mu\text{g}/\text{m}^3$ ) are in the same order of magnitude as the measured concentrations. The highest concentrations can be expected on, or very close to, highly frequented motorways. This is in agreement with Pt concentrations found in roadside dust samples, in which a decreasing tendency was found in the following order: close to motorways (308  $\mu\text{g}/\text{kg}$ ); city sites (257  $\mu\text{g}/\text{kg}$ ); parking garages (189  $\mu\text{g}/\text{kg}$ ); and roadway tunnels (141  $\mu\text{g}/\text{kg}$ ) (Zereini et al., 1997). These data suggest the predicted Pt load in roadway tunnels to be an overestimate. For the scenarios of parking and personal garages, no emission data are available. However, there is evidence that Pt emission is negligible at idling or very low speed conditions (König et al., 1992), which is principally confirmed by the findings of Zereini et al. (1997).

#### 4. Health effects and dose–response assessment

For an assessment of the health effects of Pt, a clear distinction needs to be made between elemental, i.e. metallic Pt, and halogenated Pt compounds. Pt metal has been considered as virtually biologically inert. However, concerning the toxicology of finely dispersed Pt particles, almost no data are available. There is epidemiologic evidence that the sensitizing potential of Pt compounds is restricted to halogenated compounds (Linnett et al., 1999). The medical use of the

anticancer drug cisplatin {*cis*-diamminedichloroplatinum(II), *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]} and its analogues and their toxic effects are beyond the scope of this manuscript. However, it should be kept in mind that the pharmacodynamic as well as the toxic properties of cisplatin are, due to its specific planary structure, exceptional compared to other Pt compounds. This is particularly true for nephro-, myelo- and ototoxic side effects observed in patients treated with therapeutic doses, and mutagenic and carcinogenic effects observed in experimental animal studies (WHO, 1991).

##### 4.1. Toxicity of metallic Pt

Relatively few data on the effects of metallic Pt are available. The acute oral toxicity of 1–5- $\mu\text{m}$  Pt particles was reported as very low in rats (WHO, 1991). In the mouse popliteal lymph-node assay, finely dispersed Pt, and the compounds PtO<sub>2</sub> and PtCl<sub>2</sub>, did not induce an immune response (Schuppe et al., 1993). No clear allergic reaction has been reported from workplaces with exposure to metallic Pt, or as a result of Pt use in dental prostheses or jewelry. One alleged contact dermatitis from a ‘platinum ring’ was reported (Sheard, 1955), but has never been confirmed. Thus, metallic Pt appears to be non-allergenic. This is in contrast to metallic Pd, which can cause contact dermatitis. Workers in the Pt industry who were highly sensitive to tetra- and hexachloroplatinates were skin-prick tested with extracts of particulate exhaust samples and no positive responses were observed (Cleare, 1977). However, these extracts were from a pellet-type catalyst and the filter used collected mainly particles > 500 nm. Thus, false negative results cannot be fully excluded.

In model experiments, Artelt et al. (1999b) found that Pt(0) particles  $\geq 4$  nm deposited on aluminum oxide particles  $\leq 5$   $\mu\text{m}$  were bioavailable to some degree. The model substance closely resembled particles emitted from catalytic converters. After intratracheal instillation to rats up to 16% and after 90 days inhalation, up to 30% of finely dispersed Pt was considered bioavailable. However, these figures refer to Pt determined in

body fluids and all organs, except the lung and feces, relative to the Pt retained in the lung. Only very small amounts of Pt were deposited in the lung, e.g. only approximately 1% of the total Pt recovered (1390  $\mu\text{g}$ ) after 90-day inhalation. Almost 99% was found in the feces. From intravenous studies with soluble Pt salts (Moore et al., 1975; Artelt et al., 1999b), there is evidence that part of the Pt found in the feces originates from bioavailable Pt resorbed by the lung

#### 4.2. Toxicity of Pt compounds

The acute toxicity of Pt compounds depends mainly on their solubility. Soluble Pt salts are much more toxic in animal experiments than compounds with a low solubility, such as PtO, PtO<sub>2</sub> and PtCl<sub>2</sub>. Several soluble Pt compounds showed mutagenic effects in bacterial systems (WHO, 1991; Bünger, 1997; Gebel et al., 1997) as well as in mammalian cells, but not in vivo in *Drosophila* or in a mouse micronucleus test (WHO, 1991). In comparative mutagenicity studies, cisplatin was several times more effective than other Pt salts. Except for cisplatin, no experimental data relevant to risk assessment are available for the effects on reproduction, embryotoxicity, teratogenicity and carcinogenicity of Pt compounds.

The relevant end-point for humans is the sensitizing effect of some halogenated Pt compounds. There are no scientific reports on any health effects related to non-occupational exposure to allergenic Pt compounds. In several occupational cases and epidemiological studies, it was proven that exposure to halogenated Pt salts can cause respiratory sensitization. The prevalence and incidence of allergic reactions resulting from Pt salt exposure in Pt refineries and catalyst productions are still high, although exposure was reported below the occupational threshold limit value (TLV) for soluble Pt in two refineries. Based on epidemiological studies by Merget et al. (1988) and Bolm-Audorff et al. (1992) in these plants, exposure to soluble Pt of approximately 0.1  $\mu\text{g}/\text{m}^3$  does not exclude sensitization.

#### 4.3. Dose–response assessment for the sensitizing effect of Pt salts

A recent longitudinal study in a catalyst production site provided more data on the degree of occupational exposure (Merget et al., 1999). Halogenated Pt salts are used in the production of automotive catalytic converters. Due to technical control measures, the workplace concentrations were generally low. For example, samples from production areas ranged between 8 and 41  $\text{ng}/\text{m}^3$  in 1992 and between 12 and 64  $\text{ng}/\text{m}^3$  in 1993 for soluble Pt, which is approximately 30–250 times lower than the former MAK value. However, personal samples revealed maximal concentrations of up to 3.7  $\mu\text{g}/\text{m}^3$ . Due to the high variability of Pt concentrations in production areas (with cases of sensitization), a valid threshold for sensitization could not be established. Thus, the German MAK value of 2  $\mu\text{g}/\text{m}^3$ , set as an 8-h time-weighted average, was abolished. Instead, this value was recommended as a ceiling value, which should not be exceeded (DFG, 1995). This is in line with a recommendation given by WHO (1991). The authors suggested that the NOEL be based on the maximum concentrations of soluble Pt measured in low exposure areas (with no sensitizations). These were 8.6 and 1.5  $\text{ng}/\text{m}^3$  in 1992 and 1993, respectively (Merget, 1999).

### 5. Risk assessment for catalyst-borne Pt in ambient air

The available emission data suggest that Pt emitted from monolith catalysts is almost exclusively in the metallic form. However, it cannot be completely excluded that halogenated Pt salts are emitted, or are secondarily formed from nanocrystalline Pt particles under physiological conditions. In addition, due to the insufficient database regarding other end-points, risk assessment can at present be based only on the sensitizing potential of halogenated Pt salts. We suggest a worst-case approach in assuming that the ‘soluble’ Pt fraction determined in engine-test bench

experiments is approximately 1% of the total Pt emission and theoretically has a sensitizing potential. As a 'reasonable' worst case, we suggest that sensitizing Pt salts comprise a fraction of 0.1%.

Based on the results of the longitudinal study by Merget et al. (1999), Pt concentrations below 10 ng/m<sup>3</sup> soluble Pt or below 100 ng/m<sup>3</sup> total Pt may be defined as safe. In a more conservative approach, we assume a NOEL of 1.5 ng/m<sup>3</sup> for soluble Pt, as derived from that workplace study. Hence, for automotive Pt emissions with halogenated Pt salts, presumably comprising only 1 or 0.1%, NOELs of 150 and 1500 ng/m<sup>3</sup> of total Pt would result. Applying an safety factor of 10 to account for the potentially higher susceptibility of sensitive groups, we derive guidance values of 15 and 150 ng/m<sup>3</sup> of total catalyst-borne Pt, respectively.

#### **6. Other platinum group metals: palladium, rhodium and iridium**

Rh is contained in catalysts in much smaller quantities than Pt. Pd has increasingly substituted Pt in automotive catalysts, and Ir has recently been introduced in Japan in so-called DeNO<sub>x</sub> catalysts which have been developed to reduce the emission of nitrogen oxides in the exhaust of lean-burn engines. The database for these platinum group metals with respect to emissions from catalytic converters is much smaller than that for Pt, thus precluding a quantitative risk assessment.

For both PdCl<sub>2</sub> and RhCl<sub>3</sub>, increased tumor incidences were observed in a life-time drinking water carcinogenicity study with mice (Schroeder and Mitchener, 1971). However, due to major methodological deficiencies (e.g. only one dose applied; higher longevity in treated as compared to control group; number of tumors pooled despite sex-specific differences) the validity of this study is questioned.

With regard to the sensitizing potential, there is no evidence that other platinum group metals show a higher potency than Pt salts. There is a striking difference between Pt and Pd, since metallic Pd can cause contact dermatitis. However, this potential cannot be projected to the

respiratory sensitizing potential of Pd and its salts. Murdoch and Pepys (1987) described immediate-type sensitizations to Pd only in refinery workers sensitized to Pt, and limited cross-reactivity between both metals. Their study showed a low prevalence of sensitizations to platinum group metals other than Pt. Bergman et al. (1995) reported one case of an occupational Ir salt immediate-type allergy without Pt salt allergy.

#### **7. Discussion and conclusion**

The exposure to Pt in traffic-related ambient air as measured or predicted is at least two orders of magnitude below the guidance range of 15–150 ng/m<sup>3</sup>. Even if considerably higher emission factors were used, estimated ambient air concentrations would not pose any health risk with regard to the sensitizing effect of Pt salts.

There are still information gaps, e.g. the biological relevance of ultrafine Pt particles, or the qualitative and quantitative assessment of exposure (Rosner et al., 1998). On the other hand, the derivation of our NOEL is rather conservative, thus arriving at a relatively low 'critical' range of 15–150 ng/m<sup>3</sup>. Therefore, it may be assumed that there is also sufficient protection from other potential effects, for which, however, no scientific substantiation has been given so far. Although current knowledge indicates that Pt emitted from automotive catalysts does not present a health risk to the general population, it is wise to minimize the release of substances that can accumulate in the environment. Thus, technical improvements aimed at optimizing the conversion efficacy of the catalyst may, as a positive side effect, also result in a reduced emission of platinum group metals. For instance, on-board diagnostic (OBD) devices, which are already in use in the USA and will be mandatory for new cars in Germany by the year 2000, are supposed to substantially reduce malfunctions of the engine and protect catalysts from damage (Glöckler and Mezger 1994). There are also industrial efforts to improve the production engineering of catalytic converters, aiming to enhance the embedding of the noble metal particles and thus, the long-term

stability of catalysts. In addition, any further reduction in the loss of platinum group metals would enhance the economics of recycling catalytic converters, and thus reduce the environmental pollution due to mining and refining of platinum-group metals (Hochfeld and Jenseit, 1999).

Although the database is rather small to evaluate the health risk potential of emissions of Rh, Pd and Ir, there is no evidence that they pose a health risk to the general population. If Ir catalysts should be used in the future, the health-risk potential of automotive Ir emissions should be assessed, since, due to its relatively high volatility, the release of Ir can be assumed to be considerably higher than that of Pt or Pd.

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