

Deposition modelling of Russian smelter derived PGE at Summit, Central Greenland

Master's Thesis in the International Master's Programme Applied Environmental Measurement Techniques

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ABSTRACT

The atmospheric dispersion model software HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) was used to simulate the dispersion and deposition of airborne particulate PGE (Platinum Group Elements) emissions from two major Russian production facilities. Proxy data was used to establish two emission scenarios and the short range deposition output from the model was found to agree well with previously published data for Pt and Pd in snow pack samples. 100 days of emission, dispersion and deposition simulations were used to calculate a yearly deposition rate of PGE at the Summit, central Greenland. Russian PGE production contributes approximately 90 and 380 kg to the annual global flux of Pt and Pd respectively making it a smaller emitter than automotive catalytic converters, but still significant source. Most of the deposition of Russian smelter derived Pt and Pd emissions were found to occur locally. The smelter derived deposition on Greenland was found to be up to 0.008% (Platinum) and 0.034% (Palladium) of the total deposition of PGE, if all production is assumed to occur in Monchegorsk and 0.5 μm particles. For the Taymir scenario this share is less (0.3 ppm and 0.4 respectively, 5 μm particles).

Modellering av deposition på Summit, Grönland, av Platina-gruppmetaller från ryska smältverk

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SAMMANFATTNING

En programvara för modellering av dispersion och deposition av atmosfäriska föroreningar, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory), användes för att beräkna och uppskatta spridning och transport av luftburna partiklar innehållande Platina-gruppmetaller (PGM) emitterade från två viktiga ryska smältverk. Relaterade data användes för att etablera två utsläppsscenarier och vid tillämpning av dessa för lokal deposition beräknad från HYSPLIT, visade resultaten god överensstämmelse med tidigare publicerade koncentrationer av platina och palladium i snöprover. Vidare simulerades 100-200 dagars emissioner, spridning och transport av fina partiklar och med hjälp av depositionen av dessa på Summit, Grönland beräknades årlig deposition. Den ryska produktionen av PGM befanns bidra med 90 och 380 kg av Pt och Pd årligen, till det globala massflödet. Detta är mindre än vad som beräknas emitteras från bilkatalysatorer, men det är fortfarande en signifikant mängd. Största delen av de från smältverken emitterade partiklarna deponeras lokalt. Smältverket i Monchegorsk och dess bidrag till deposition av PGM på Grönland beräknades vara upp till 0.008% (Platina) and 0.034% (Palladium) av den totala, uppmätta depositionen, antagande att all produktion sker där, och att de emitterade partiklarna var 0.5 μm . För smältverket i Taymir var motsvarande andel 0.3 och 0.4 ppm för Pt och Pd, under antagandet att de emitterade partiklarna var 5 μm .

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1 Introduction

Platinum group elements (PGE), their pathways and environmental relevance have recently received increased interest and attention, mostly because of the gradual introduction of automobile catalytic converters from the 1970s and onward. Research indicates that automobile catalytic converters is a significant contributor to the elevated concentrations of PGE's found in environmental samples collected in such diverse locations as urban roadsides (Gomez et al., 2002; Ely et al., 2001; Jarvis et al, 2001) and the isolated Summit, central Greenland (Barbante, Cozzi et al. 1999; Motelica-Heino, Rauch et al. 2001). This widespread distribution suggests mobility and a trans-boundary character of these elements, and thus highlights the importance of understanding their environmental transport pathways. While automotive emissions of PGE's have been thoroughly studied over the last couple of decades (Palacios, Gomez et al. 2000; Moldovan, Rauch et al. 2003), there are only few studies made on the contributions from other anthropogenic and natural sources, including wastewater effluents from hospitals (Kummerer, Helmers et al. 1999) and input from cosmic dust (Gabrielli, Barbante et al. 2004).

A possible source of PGE emissions which has been little investigated is the mining and smelter operation associated with non-ferrous metal production. Although the PGE concentrations in the majority of ore processed is very low, the sheer volume of the world wide mining and smelter operations may accumulate to a significant contributor to the global PGE flux. Investigations of metal fluxes, including those from mining and smelting have been performed by Pacyna and Pacyna (2001), though it excluded the platinum group elements. Initial investigations on global fluxes of PGE's have been attempted by Rauch et al (2005), but the share of mining and smelter operations of this flux is yet to be assessed.

2 Aims and objectives

The aim of this work is to provide an indicative assessment of the contributions from Russian mining and smelter operations to the global platinum group element flux, and the atmospheric dispersion and deposition patterns of particulate emissions from two smelter plants in Russia. This will be attained by using PGE production data together with smelter operation emission factors applied from literature data in conjunction with the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) software to simulate dispersion and deposition. The resulting deposition rates for PGE's in central Greenland will be compared to those determined from ice core and snow pack samples (Barbante, Veysseyre et al. 2001), and an overall assessment of the significance of Russian PGE production to the global flux of PGE's.

3 Platinum group elements

The platinum group elements (*here: Pt, Pd and Rh*) belong to group VIII in the periodic table. Other elements in the group, which are not discussed here, are Ir, Os and Ru.

3.1.1 Properties

Platinum is a relatively inert, soft and ductile metal of silvery color. Platinum has the atomic number 78 and three isotopes (relative occurrence in brackets) ^{194}Pt (32.8%), ^{195}Pt (33.7%) and ^{196}Pt (25.4%). Above 450 °C Platinum will slowly lose weight because a volatile oxide (PtO_2) is formed. The principal oxidation states are +2, +4 and 0, of which the first is the most common and the highest oxidation number possible is +6 (e.g PtF_6). Platinum and its oxides are insoluble in water, while the complex salts potassium hexachloroplatinate and ammonium hexachloroplatinate exhibit a limited solubility. The tetrachloroplatinate salts are more easily soluble in water than the corresponding hexachloroplatinates (Rosner, König et al. 1991; Lindell 1997).

Rhodium is found in the earth's crust predominantly in its metallic form, often together with Nickel and Copper. There are very few minerals containing Rhodium. At room temperature Rhodium is a silvery metal with a melting point of 1963 C. It is a relatively inert metal, reacting with oxygen under heating to form Rh_2O_3 . It does not react with water and is inert to aqua regia. Its main uses are as an industrial catalyst, in jewellery, as an alloy and in automobile catalytic converters (source: <http://www.webelements.com/webelements/elements/text/Rh/uses.html>).

Palladium is the lowest melting and least dense of the platinum group elements. It is a steel-white metal that is inert in air. It reacts with oxygen when heated to form palladium oxide, PdO . It melts at 1828 C. Palladium is commonly found in its metallic form, associated with platinum, nickel and copper deposits. Common uses for palladium is to make fine instruments, electrical contacts, to purify hydrogen gas, in jewellery and in automobile catalytic converters (source: <http://www.webelements.com/webelements/elements/text/Pd/key.html>).

3.1.2 Occurrence

The average crustal concentration of Pt and Pd in 16 samples from 3 continents are 506 and 518 pg g^{-1} respectively (Peucker-Ehrenbrink and Jahn 2001) and the Rh concentration has been reported to 60 pg g^{-1} (Wedepohl 1995).

3.1.3 *Environmental and human health risk*

The toxicity of Pt depends greatly on solubility of the species, thus highly soluble salts of Pt like $\text{H}_2[\text{PtCl}_6]$ and other halogenated forms are of far more concern than insoluble species like PtO.

The environmental toxicity has been studied for platinum in various organisms, including *Daphnia Magna* (Biesinger and Christensen, 1972), *Lumbriculus variegatus* (Veltz et al., 1996) and *Asellus aquaticus* (Rauch and Morrison, 1999). There is no published data on the toxicity of Pd and Rh. PGEs (Pt, Pd and Rh) was found to bioaccumulate in *Asellus aquaticus* (Moldovan, Rauch et al. 2001; Moldovan, Palacios et al. 2002), a bottom feeding detritivore, and can thus potentially accumulate in the food chain although no such evidence has yet been presented .

In human health studies it has been concluded that present levels of Pt in urban environment is approximately six orders of magnitude below the estimated levels for human health concern ($15\text{-}150 \text{ ng m}^{-3}$) as reported by Merget and Rosner (Merget and Rosner 2001). The health effect in humans concerns mainly sensitizing of airways and allergenic reactions that increase in catalyst manufacturing workers with high level and long term exposure (Cristaudo, Sera et al. 2005). The health effects of Pd and Rh is less known but is generally regarded as being of less concern than Pt (Gomez, Palacios et al. 2002).

4 Environmental occurrence of PGE

4.1 Urban and roadside environments

Some of the highest environmental concentrations of PGEs have been found in urban roadside areas. The occurrence in these locales has been well documented the last 20 years and generally an increase has been observed with the introduction of automobile catalytic converters (see Table 1). Environmental pathways for PGEs in these compartments are well understood and investigated.

Table 1. PGE concentrations in various environmental compartments as reported in the literature.

	Location	Year	Concentration (pg m ⁻³)			Note	Ref.
			Pt	Pd	Rh		
Background	Germany	1998-1999	<1		0.47	Background site	(Gomez, Palacios et al. 2002)
	Germany	2001-2002	5	3	1	Background site	(Zereini, Alt et al. 2005)
	Italy	1998-1999	<1	3.6	<1	Background site	(Gomez, Palacios et al. 2002)
	Spain	1998-1999	<1		0.5	Background site	(Gomez, Palacios et al. 2002)
	Sweden	1999	2.7	5.2	0.9	Background site, low traffic	(Gomez, Palacios et al. 2002)
	US (California)	1975	<0.05			year of catalyst introduction	(Johnson and Tillery 1975)
Urban sites	Austria (Vienna)	2002	4.3	2.6	0.4	PM10, heavy traffic, stop and go	(Kanitsar, Koellensperger et al. 2003)
	Austria (Klagenfurt)	2001		3.9		PM10, urban	(Limbeck, Rendl et al. 2004)
	Austria (Salzburg)	2001		16.5		PM10, urban	(Limbeck, Rendl et al. 2004)
	Germany (Dortmund)	1991-1992	1.3			PM10, urban	(Alt, Bambauer et al. 1993)
	Germany (Munich)	1998-2000	4.1		0.3	PM10, urban	(Gomez, Palacios et al. 2002)
	Germany (Frankfurt)	2001-2002	23	15	4	PM10, urban, high traffic	(Zereini, Alt et al. 2005)
	Italy (Rome)	1998-1999	10.5	51.4	2.6	PM10, urban	(Gomez, Palacios et al. 2002)
	Japan (Tokyo)	2003	2.1	0.8	0.5	PM7, urban	(Mukai, Ambe et al. 1990)

Spain (Madrid)	1998-1999	15.6	4.2	PM10, urban	(Gomez, Palacios et al. 2002)
Sweden (Göteborg)	1999	14.1	4.9	2.9	PM10, urban (Rauch, Lu et al. 2001)
Sweden (Göteborg)	1999	5.4	1.5	1.6	PM2.5, urban (Rauch, Lu et al. 2001)
US (Boston)	2002-2003	6.9	8.1	1.5	PM10, urban (Rauch, Hemond et al. 2005)

4.2 Remote environments

4.2.1 The Kola and Taymir Peninsula

The Kola and Taymir peninsulas are both characterized by heavy industry and industrial pollution, and the associated environmental degradation. The severe condition of the environment have attracted much attention and a large part of the Kola peninsula geochemistry has been mapped in a large project involving Norwegian, Finnish and Russian researchers (Gregurek et al. 1999). The Taymir peninsula is less investigated, probably because of its inaccessibility, as it is situated in a remote part of the Siberian polar region and can only be reached by boat or air.

In an investigation Gregurek et al (1999) concluded that PGE's found in snow pack samples collection in proximity to the Nikel, Monchegorsk and Zapoljarnij smelters at the Kola Peninsula in the north-western part of the Russian federation contained elevated levels of precious metals. The authors suggested that the source could be indicated by the ratio between Pt, Pd, Rh and Au, as it gives a distinct fingerprint reflective on the relative ratios in the ore (Gregurek, Melcher et al. 1999).

4.2.2 Greenland

Crustal enrichment factors (EF_c) for Pt, Rh and Pd of $>10^4$ relative Al have been reported by Barbante et al (2003), which suggests that a significant proportion of the PGE in Greenland snow is of anthropogenic origin (Barbante, Boutron et al. 2003).

Table 2. PGE levels found in environmental samples at various locations and temporal records.

Location	time period	sample matrix	PGE concentrations		
			Pt ($\mu\text{g g}^{-1}$)	Pd ($\mu\text{g g}^{-1}$)	Rh ($\mu\text{g g}^{-1}$)
Greenland	<i>Summit</i> 7260-7760 BP	Icecore samples ^a	0.01	0.01	7×10^{-4}
	1969-1988	Snowcore samples ^a	0.17	0.44	0.04
	1991-1995	Snowpit samples ^a	0.37	0.93	0.05
Kola					

<i>Monchegorsk</i>	1996	Snowpack samples ^b (2.5-8 km from smelter)	11-650	33-2770	0.5-19
<i>Monchegorsk</i>	1996?	Topsoil samples ^c	4.3-167 $\times 10^3$	39-682 $\times 10^3$	0.4-5 $\times 10^3$

^a Barbante et. al (2001)

^b Gregurek et al. (1999)

^c Boyd et al. (1997)

Deposition rates of PGE are sparingly reported in the literature. Rauch et al (2005) suggest that the catalyst derived deposition rate in remote environments (Summit used as a proxy) to be 0.02-0.06 g km⁻¹ year⁻¹. Using concentrations of Pt and Pd in snowpack samples as reported by Gregurek et al (1999) and an estimated deposition period of 5 months (pers. comm. Dr. Reimann Clemens) the deposition rate near the Monchegorsk plant ranges from 4-232 and 12-989 g km⁻¹ year⁻¹ for Pt and Pd respectively.

In an attempt to identify contributing sources to PGE deposition in Greenland Rauch et al (2005) investigated the elemental ratios found in Greenland ice and snow and compared those ratios to ratios found in urban airborne particles, road dust and road side soil, Russian ores and production, snow and soil near Russian smelters, continental crust and automobile catalytic converter composition (see Figure 1). Rauch et al. argues that the elemental composition found in Greenland ice and snow samples suggests multiple sources (i.e. emissions from automobile catalytic converters and Russian smelters, even though correlation with Russian PGE production, air mass trajectory and PGE demand for catalysts are absent (Rauch, Hemond et al. 2005).

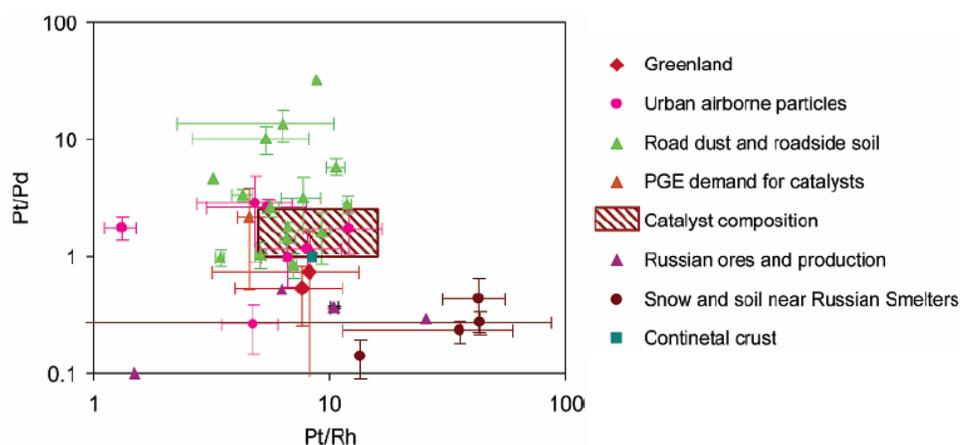


Figure 1. Plot of elemental ratios for a range of environmental samples and potential sources (Rauch, Hemond et al. 2005).

In a slightly different treatment it can be seen that while crustal elemental composition ratios corresponds rather well with Summit ice-core samples (7260-7760 Before present), ratios in more recent (1969-1995) Summit samples deviate from that of the natural crust (see Figure 2). This suggests an anthropogenic input with a relative increase in the Platinum and Rhodium deposition.

A closer look at the elemental ratios found in snow and topsoil samples on the Kola peninsula in close proximity to the Monchegorsk smelters indicates a significantly higher Pt/Rh ratio than what has been observed in recent snow samples on the Summit (see Figure 2).

Rural and urban soil and road dust samples show a relatively higher Rhodium and lower Palladium concentration. It should be noted that the elemental ratios for rural locations were calculated using only two data points.

From the elemental ratio patterns there is no clear indication on the origin of the PGE deposits in Greenland ice and snow, no single source can be appointed nor excluded based on this treatment.

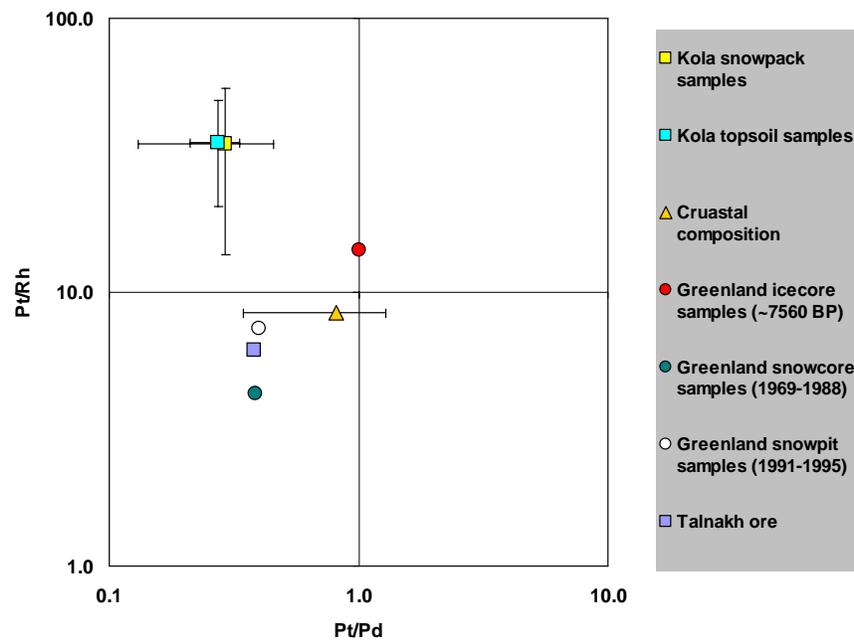


Figure 2. Elemental ratios calculated from observed concentrations in samples from Kola peninsula and Summit, urban and rural sites, as well as crustal composition and average concentrations in Talnakh ore (Johnson and Tillery 1975; Wedepohl 1995; Boyd, Niskavaara et al. 1997; Gregurek, Melcher et al. 1999; Barbante, Vesyseyre et al. 2001; Peucker-Ehrenbrink and Jahn 2001; Zereini, Alt et al. 2005).

4.2.3 *Historic trend*

The deposition of PGE has been observed to increase significantly in different environmental compartments during recent years. For example, the PGE levels in urban lake sediments reveal 6-16 times higher deposition rates for Pt, Pd and Rh between 1992-2002 than before the introduction of automotive catalytic converters (Rauch, Hemond et al. 2004). Sediment records showed little variation in input of platinum 1870-1975, raised sharply to reach a plateau in the 1990's about 9 times higher than pre-introduction of catalytic converters (Rauch and Hemond 2003).

The trend of increasing PGE concentrations in various environmental records after introduction of the automotive catalytic converters is confirmed also by Zereini et al (1997) who found temporally increasing Pt and Rh concentrations post 1987 in drainage basin sediment in Germany (Zereini, Skerstupp et al. 1997).

Greenland ice core records show that PGE concentrations in this remote location have increased since the beginning of the industrialization by 6, 15 and 45 times for Pt, Pd and Rh respectively. Further, post ~1976 the elemental ratios of the anthropogenic PGE have dramatically changed, indicating input from a new anthropogenic source. Because of the timing of the shift in elemental ratio and the actual ratio the automotive catalytic converters are a likely candidate source (Barbante, Veysseyre et al. 2001).

Natural variations in PGE deposition in remote areas do occur, as observed during the last glacial period. However, the increased flux of PGE during this period is believed to originate from high input of terrestrial dust. This is confirmed also by studies of the elemental ratios of Pt/Al and Ir/Al (Gabrielli, Barbante et al. 2004; Gabrielli, Varga et al. 2004).

It is well established that the PGE concentrations in several independent environmental compartments has increased as a result of anthropogenic activity. In some instances a sharp increase has been observed with the introduction of catalytic converters on cars. Even in remote locations like the Summit, the effect of PGE emissions from catalytic converters has been observed, further strengthening the trend of increased environmental concentrations.

4.2.4 *Global PGE flux and deposition rates*

The global flux of PGE's is not very well investigated. There are estimates on the annual emissions from automobile catalytic converters and annual influx from cosmic dust and meteorites, reported by Barbante et. al. (2001) (see Table 3). It has been estimated that the influx of cosmic dust contributed 13, 7 and 29% to the deposition on Greenland of Pt, Pd and Rh respectively from natural sources (Barbante, Veysseyre et al. 2001). However there are several other significant contributors to the global PGE flux, but there are very little data

available. Comprehensive inventories of global anthropogenic emissions of trace metals have been performed by Pacyna and Pacyna (2001), though this inventory does not include any platinum group elements (Pacyna and Pacyna 2001).

Other contributors to the global PGE flux includes emissions from hospitals and PGE containing drugs, mining and extraction, emissions from mining and refining of PGE's, volcanic aerosols, erosion of rocks and resuspension of dust, and forest fires. Estimates for annual fluxes are presented in Table 3.

Table 3. Global fluxes of PGE from natural and anthropogenic sources.

Source	Flux	Reference
<i>Anthropogenic sources</i>		
Annual global emissions of Pt from automobile catalytic converters	0.5-1.4 ton y ⁻¹	Barbante et al. (2001)
Emissions from mining and smelting of PGM containing ore	n.a.	
Hospital emissions from drugs containing platinum	16.5-172 kg y ⁻¹	Adopted from (Kummerer, Helmers et al. 1999) ^a
Mining and extraction	184.3 ton y ⁻¹ Pt 216.0 ton y ⁻¹ Pd 20.6 ton y ⁻¹ Rh	Supply of PGE in 2004 (Johnson Matthey, 2005)
<i>Natural sources</i>		
Cosmic dust	149 kg y ⁻¹ Pt 84 kg y ⁻¹ Pd 20 kg y ⁻¹ Rh	Barbante et al. (2001)
Rock and soil dust	n.a.	
Volcanic aerosols	n.a.	
Forest fires	n.a.	

^a The emission values were calculated by combining the estimate reported by Kummerer et al (1999) and the estimate on total Pt catalytic converter emissions reported by Barbante et al (2001).

5 Russian PGE production

5.1 Process description

The PGE in the Norilsk-Talnakh area is mined from different types of ores containing very high, but widely varying, concentrations of PGE, averaging on around 10-11 ppm (g tonne⁻¹). The three main types of ore are:

Massive sulphide ore: occurs in lens-shaped deposits 1-40 m wide containing extremely high concentrations of Nickel, and occasionally as much as 100 ppm, or more PGE, though the typical concentration is more likely around 12-14 ppm. The Pd-Pt ratio in this ore is typically between 3:1-4:1.

Copper-rich ore: forms boundary layers around the sulphide ore, containing higher concentrations of copper while nickel levels are lower than that of the massive sulphide ore. The PGE levels are about the same as in the sulphide ore.

Disseminated ore¹: Occurs in wide zones of up to 50 meters thickness. This ore is less rich in base and precious metals and the PGE concentration ranges between 5-15 ppm (Kendall 2004).

After mining the ore is treated in a multi-stage process that is schematically described in Figure 15 and Figure 16 in the appendix.

5.2 Production volume

Russia (mainly Norilsk Nickel) accounts for more than 40 per cent of annual global palladium production, and approximately 15 per cent of the platinum production (Kendall 2004). The Russian PGE production is located at five main sites, Norilsk, Kola Peninsula, Kondyor, Koryak and Central Urals. Kondyor and Koryak are situated in the far east of Russia and the mining operations there are mainly alluvial, and the relatively simple subsequent processing by hydraulic breaking up of and washing the ore in what is essentially industrial panning.

Norilsk has by far the largest production of PGE. Although the Russian authorities classify the production data the estimated total platinum and palladium production in 2003 was 24948

¹ Ore in which small particles of valuable minerals are spread more or less uniformly through the deposit. (This is distinct from 'massive' wherein the valuable minerals occur in almost solid form with very little waste matter included).

kg (24.9 ton) and 76544 kg (76.5 ton) respectively, of which the Norilsk combine accounts for 74 and 100 per cent respectively (Kendall 2004). The preliminary production figures for 2005 for Norilsk Nickel alone were 97.4 ton of Pd and 23.4 ton of platinum, which represent a significant increase for Palladium. Projected figures for 2006 was estimated to 90-92 and 22-21 ton of palladium and platinum respectively (NorilskNickel 2006).

Table 4. PGE mining for Russian mining operations at the Kola and Taymir peninsula (Kendall 2004)

	Process type	Estimated production 2003	
		Pt (ton)	Pd (ton)
Kola Peninsula <i>Nikel</i> <i>Monchegorsk</i>	Smelters	<0.6 ^a	-
Taymir peninsula <i>Norilsk</i>	Smelters	18.4	76.5
Kondyor	Panning	3.69	-
Koryak	Panning	2.55	-
Central Urals	Panning	0.28	-

^a The number for the Kola Peninsula mining includes all PGM's.

5.3 Emissions from smelter operation

There is very limited data available on smelter stack emissions, as this information is most likely considered confidential and is not published, and thus difficult to obtain. However there is some data on emissions rates readily available in the literature. These are listed in elemental composition and size distribution

Table 5. Smelter stack emission rates reported in the literature.

Smelter	Emission rate (kg hr ⁻¹)					
	Fe	Cr	Zn	Ni	Cu	Co
Mongechorsk ^a				185	107	9
ZIMASCO ^b	2.423	6.217	0.042		0.006	
Sudbury ^b	128	4	7		37	

^a Boyd et al. (1997)

^b Pumure (2002)

Other data are available in the form of emission factors (ϵ), which are expressed as amount of emitted metal (gram) per amount of produced metal (ton). Emission factors for smelter operations has been reported by Skaeff et al (1997) and Pacyna et al (2001), though values for PGE's are not reported. Emission factors reported for metals that are the primary product ranges from 200 g_{Pb} t⁻¹_{Pb} (ϵ for Pb primary production in Europe) and 10,000 g_{Zn} t⁻¹_{Zn} (ϵ for Zn b primary production in Africa, Asia and South Africa).

Table 6. Emission factors (in gram per ton produced metal) from smelters for a number of metals.

	As	Cd	Cu	Emission factor ϵ (g t ⁻¹)				Sb	Se	Zn
				Hg	Mn	Ni	Pb			
(Skeaff and Dubreuil 1997)										
<i>Canada</i>	91.2	56.7	781	5.58	0.18	631	827	1.5	3.7	316
(Pacyna and Pacyna 2001)										
				<i>Primary product Cu</i>						
<i>Europe, N.A.^a, Australia</i>	100	50	300	5.6	1	150	300	10	10	200
<i>Africa, Asia, S.A.^b</i>	500	200	3000	10	10	1500	1000	50	50	500
				<i>Primary product Pb</i>						
<i>Europe, N.A.^a, Australia</i>	3	10	5	3	-	5	200	20	10	20
<i>Africa, Asia, S.A.^b</i>	10	15	10	3	-	10	2000	75	35	80
				<i>Primary product Zn</i>						
<i>Europe, N.A.^a, Australia</i>	26	49	6	7.6	-	-	380	13	10	1466
<i>Africa, Asia, S.A.^b</i>	50	200	50	20	-	-	500	15	15	10000

^a North America

^b South Africa.

6 Aerosols (airborne particles)

In air pollution particles are often classified according to their size since this is one of the most important parameter for a range of aspects, including health and mobility. Particles are categorized into *coarse* ($>2.5\mu\text{m}$), *fine* ($<2.5-0.1\mu\text{m}$) with the subcategories *accumulation mode* ($1-0.1\mu\text{m}$) and *ultra-fine* ($<100\text{nm}$) particles (is $<100\text{nm}$ a subcategory of fine?). Sometimes the term *Aitken mode* size fraction is also used, referring to particles between $0.1-0.01\mu\text{m}$ (Hemond and Fechner-Levy 2000). When measuring air quality, methods often refer to PM10 and PM2.5, which represents size fractions less than $10\mu\text{m}$, and less than $2.5\mu\text{m}$ respectively. The PM10 fraction is considered to be *inhaleable*, and the PM2.5 is considered *respirable*, meaning that they will end up in different places in the human respiratory system.

Table 7. Classification of aerosols with regard to their size. Adopted from Hemond (2000).

Particle classification	Size range	Main formation mechanisms
Coarse	$>2.5\mu\text{m}$	Wind blown dust, sea spray, abrasion generated particles
Fine	$<2.5\mu\text{m}$	Condensation and aggregation of low volatility vapours (e.g. SO _x , NO _x , and NH ₃)
Accumulation mode	$1-0.1\mu\text{m}$	
ultrafine	$<0.1\mu\text{m}$	Condensation of hot vapours from combustion
Aitken mode ^a	$0.1-0.01\mu\text{m}$	

^aAitken mode particles are a subcategory of the ultrafine particle size range

Particles can be measured and expressed as number of particles, mass of particles or surface area of particles. Each way of expressing the result will give emphasize on different size fractions. The ultra-fine particles dominate in numbers, but have little impact on mass, while accumulation mode is significant in both mass and numbers, and coarse particles are most significant by mass.

6.1 Fate of aerosol particles

Removal of particles from the air can happen through either deposition or evaporation. Deposition can happen in different ways depending on particle composition and size. Relevant for atmospheric conditions are sedimentation, interception, impaction and diffusion.

6.1.1 Dry deposition

6.1.1.1 Gravitational sedimentation

Gravitational sedimentation affects primarily particles larger than 1 μm , for which settling is a significant removal mechanism. The deposition rate for a steady state particle in a fluid medium can be determined using Stokes law, which expresses the settling velocity (ω) as a function of particle radius (r), density (ρ) and the fluid viscosity (η). See Equation 6.1.

$$\omega_f = \frac{2 g \left(\frac{\rho_s}{\rho_f} - 1 \right) r^2}{9 \eta_f} \quad \text{Equation 6.1}$$

where ρ_f is the density of the fluid and g is the gravitational acceleration. However, in air the density of the fluid is often negligible as compared to the particle density, hence Equation 6.1 can be reduced to

$$\omega_f = \frac{2 g \rho_s r^2}{9 \eta_f} \quad \text{Equation 6.2}$$

Stokes law applies only to spherical particles, but is still valid if the empirical aerodynamic particle radius is used for r (Hemond and Fechner-Levy 2000).

Sub micrometer particles have sedimentation velocities less than 0.04 mm s^{-1} . The upper limit for aerosols is around 100 μm when the sedimentation velocity reaches 0.25 m s^{-1} . Larger particles aren't considered to be airborne because of the high sedimentation rate.

6.1.1.2 Other dry deposition mechanisms

There are other mechanisms for dry deposition of particles affecting mainly particles that are so small that gravitation settling becomes less significant.

Impaction is a mechanism that takes place for a particle with so much inertia that it cannot follow sudden direction changes in the air stream as it flows over a surface, and hence the particle is impacted on the surface. *Interception* takes place as a particle following the air stream close to a surface is deposited on the surface due to the larger size of the particle compared to the molecules in the air stream.

Diffusion affects only very fine particles that can be subject to Brownian motion that occur as molecules in the air collides with the particle, resulting in a net transport of particles to volumes of lower concentrations (*ie.* close to surfaces) where the particle might sediment by impaction.

It is difficult to accurately describe the rates of which the aforementioned mechanisms takes place due to the large variability of the environment, with complex surfaces and a diverse

spectrum of atmospheric particles, but an estimate for long term deposition on vegetation surfaces can be made using

$$J = V_a - C_a \quad \text{Equation 6.3}$$

Where J is the flux density of particles and V_a is the deposition velocity and C_a is the average particle concentration in the air (Hemond and Fechner-Levy 2000).

6.1.2 Wet deposition

Deposition of particles may take place when there is atmospheric precipitation, either by *washout*, as raindrops are colliding with particles and removing them from the atmosphere (below-cloud-scavenging), or by *rainout*, when rain is formed by condensation around the actual particle and then wet deposited with the precipitate (in-cloud scavenging). Wet deposition is the primary sink for sub-micrometer particles in the atmosphere.

6.1.3 Condensation and evaporation

Aerosols that are smaller than a certain diameter might evaporate if the saturation in the ambient atmosphere is sub-critical. This is expressed by the equation

$$D_{kelvin} = \frac{4\gamma v}{kT \ln(s)} \quad \text{Equation 6.4}$$

where γ is the surface tension, v is the molecular volume, k is the Boltzmann constant, T is the temperature and s is the saturation level. Reversely, when the air is super-saturated, gases tend to condensate and form aerosols.

6.1.4 Condensation on particles

Large particles might act as seeds for condensation and formation of droplets in the atmosphere, since the critical saturation degree is small. The droplets may grow through condensation to a size of about 30 μm . Small particles constitutes small interstitial droplets in the cloud. Hence, cloud formation acts as a particle sink in the atmosphere.

$$\frac{P}{P_0} = e^{\frac{4\sigma M}{\rho RDT}} \quad \text{Equation 6.5}$$

6.2 Transport of aerosols to Greenland

The motivation for the research presented here is the finding of elevated PGE concentrations in recent ice from Central Greenland, which is attributed to both automobile catalysts and Russian smelters (Rauch et al., 2005).

There have been attempts to source attribute various contaminants and trace elements found in Greenland snow and ice core samples. Kang et al. used historical non-sea salt Magnesium (nssMg^{2+}) as a dust aerosol proxy indicator. A major source of dust aerosol is the spring dust storms that occurs mainly between mid February and late May over the central Asian arid and semi-arid regions. The nssMg^{2+} concentrations were determined in an ice core that was drilled from site 20D on Greenland ($65^{\circ}01'N$, $44^{\circ}52'W$) and were correlated with regional sea level pressure data (SLP) from AD 1899-1996 for key regions to explain spring transport pathways of dust aerosols, finding that certain meteorological conditions over Siberia may strengthen transport of aerosols to southern Greenland (Kang, Mayewski et al. 2003).

Lead concentrations and lead isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$) in fresh and semi-aged Greenland snow (Dye 3, $65^{\circ}11'N$, $43^{\circ}50'W$) were used by Rosman et al. to assess seasonal variation and source appoint the aerosol lead. The isotope ratio analysis showed that lead aerosols during spring and early summer season originated predominantly from Eurasia (~ 1.14), while autumn and winter lead aerosol originate mainly from North America (~ 1.20) (Rosman, Chisholm et al. 1998).

Due to its remote location, only particles that is less than approximately $6 \mu\text{m}$ can reach Greenland, thus it is only the fraction smaller than $6 \mu\text{m}$ that is of interest when trying to source appoint anthropogenic PGE found in Greenland ice and snow (Steffensen 1997).

7 Modeling of atmospheric transport

Modelling of atmospheric dispersion is the use of numerical models to calculate the spatial movement of air masses to or from a specific geographical location. Models are used to determine the source of air pollutants at a site or predict the dispersion of pollutants emitted from a source. Generally the models are divided into two categories; Eulerian and Lagrangian models. Eulerian models use a fixed grid to solve the advection-diffusion equation while the Lagrangian models typically solve the advection and diffusion independently. Eulerian models are generally better suited for complex emission scenarios and normally require the emissions to be defined on a scale comparable to the computational grid. The reverse is true for Lagrangian models; they are used for simple emission situations, like single source point emissions, that can be defined at any resolution (Draxler and Hess 1998).

There are many models available in both categories, often written with a specific purpose in mind, and therefore they usually have some strong and some weak points because of priorities and compromises that had to be made during model construction. In an intercomparison of four atmospheric dispersion models (AERMOD, HPDM, PCCOSYMA and HYSPLIT)² it was demonstrated that different models produce varying results in the simulation of a single point pollution source and real metrological data. The output from two of the models is exemplified in Figure 3.

² AERMOD (American Meteorology Society-Environmental Protection Agency Regulatory Model), HPDM (Hybrid Plume Dispersion Model), PCCOSYMA (PC Code System from Maria) and HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory)

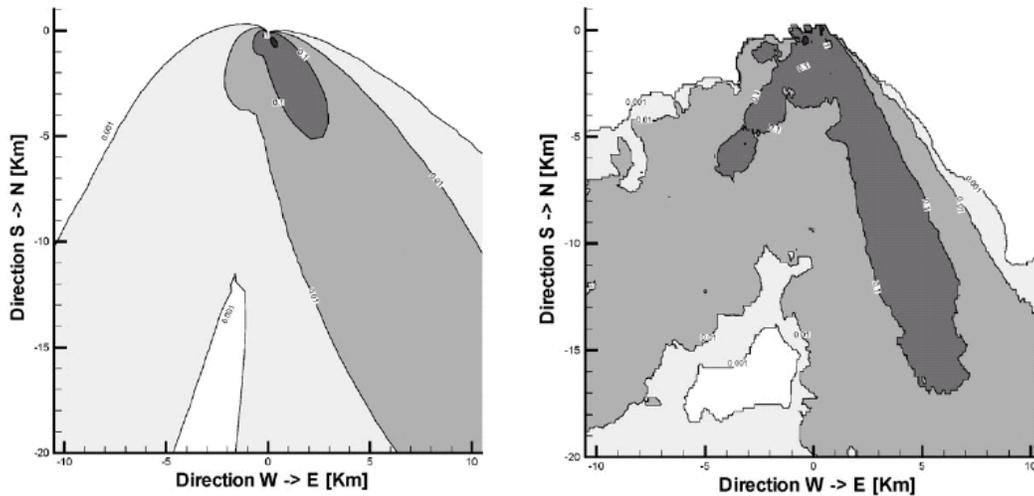


Figure 3. Concentration contours in $\mu\text{g m}^{-3}$ at 1 meter level produced by the AERMOD (left panel) and HYSPLIT (right panel) dispersion models (Caputo, Gimenez et al. 2003).

Although the models produce different results it is concluded that they are still comparable. Table 8 show the maximum ground level concentrations in the south-west direction in the simulation as calculated by the models. The results are indicating that all models perform adequately under the conditions of the simulation, though it is concluded that the PCCOSYMA and HYSPLIT models produce a more realistic description of the concentrations at larger scales (Caputo, Gimenez et al. 2003).

Table 8. Maximum ground level concentrations in the south-west direction (Caputo, Gimenez et al. 2003).

Code	Conc. ($\mu\text{g m}^{-3}$)	Distance from the source (m)	Angle from the north ($^{\circ}$)
AERMOD	1.47	240	210
HPDM	1.22	270	211
PCCOSYMA	1.49	300	213
HYSPLIT	1.50	600	225

7.1 HYSPLIT

The HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) dispersion model was developed by the Bureau of Meteorology of Australia and ARL-NOAA of the USA to assist in determining an effective response in case of catastrophic pollution episodes.

The HYSPLIT calculation model is a hybrid between Lagrangian and Eulerian approaches. Advection and diffusion is calculated in a Lagrangian framework, while the concentrations are calculated on a fixed grid. One advantage of the Lagrangian model, compared to Eulerian

or Gaussian, is the ability to incorporate more detailed meteorological data, if such is available.

There are several different modes on how the dispersion is calculated in HYSPLIT. These are combinations of particle, Gaussian puff and Top Hat puff approaches to describe air concentrations of the pollutant. In the particle approach the source is simulated as releasing many particles, the trajectory, air concentration and dispersion is calculated on an individual particles basis. Thus the air concentration at any given moment is calculated by summing the mass of particles in the given grid cell.

In the puff approach the emission is treated as a ‘parcel’ containing the pollutant mass, expanding as the pollution disperse. The puff is then allowed to split into smaller components once they exceed certain dimensions, usually the dimensions of the meteorological grid. The difference between Gaussian and Top Hat puffs is mainly the way they are split; Gaussian puffs split into five parcels where the central parcel contain 60% of the pollutant mass and the other four contain 10% each. Top Hat puffs are split into four equal parcels containing 25% pollutant mass each (Draxler and Hess 1998).

7.1.1 Deposition

The HYSPLIT software models three types of removal; dry deposition and wet deposition and radioactive decay, which was not used in this work. The dry deposition in HYSPLIT is computed only when the bottom of the puff or particle centre position is within the surface layer using an assumption that the deposition velocity (V_d) is uniform across the pollutant layer (ΔZ_p). From this a removal constant (β_{dry}) is calculated in Equation 7.1 (compare to Equation 6.3).

$$\beta_{dry} = V_d \Delta Z_p^{-1} \quad \text{Equation 7.1}$$

The deposition velocity may be specified directly through user input, or calculated as a gravitational settling velocity based on particle size, particle density and air density.

The removal through wet deposition is divided into two components – in cloud scavenging and below cloud scavenging (or rainout and washout as described in section 6.1.2). Calculations are complicated by the limited data available in most meteorological data archives, therefore a simplifying scavenging ratio (S_r) assumed and a removal constant is calculated according to

$$\beta_{inc} = F^t F_b S_r P \Delta Z_p^{-1} \quad \text{Equation 7.2}$$

Where F^t is the fraction of the pollutant layer that is below the cloud top and F_b is the fraction above the cloud bottom, P is the precipitation rate and ΔZ_p is the depth of the pollutant layer.

The removal by washout, or below cloud scavenging, is treated similarly.

$$\beta_{bel} = S_c (1.0 - F_b)$$

Equation 7.3

In Equation 7.3 S_c is the scavenging ratio (Draxler and Hess 1998).

7.1.2 Validation

The validation of atmospheric dispersion and deposition models present some unique difficulties since it is often hard to exclude interfering sources of pollution when measuring pollutant concentration and deposition. However, the nuclear incident at Chernobyl in 1986 provided an opportunity to evaluate the model deposition algorithms. The model was run with archived meteorological data and the output was compared to a deposition map generated from actual measurements of Cs-137 across Europe (see Figure 4).

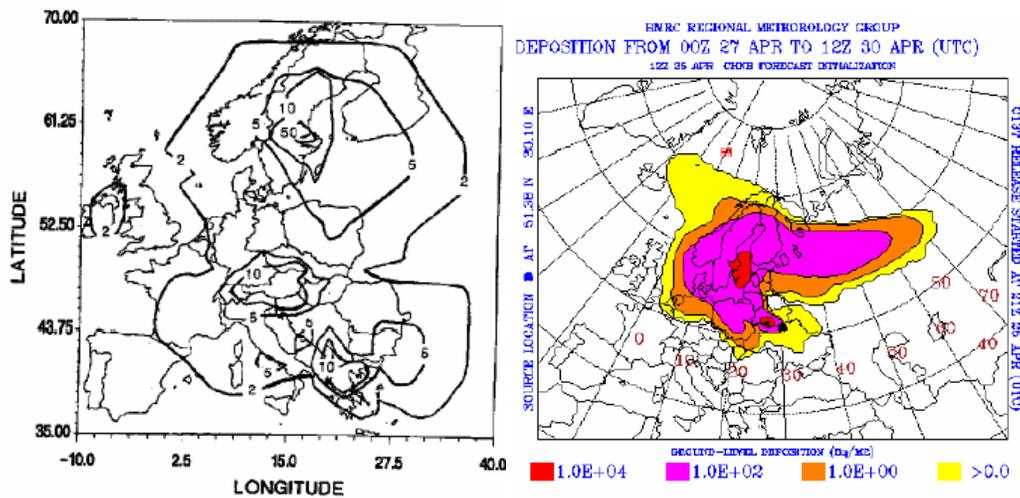


Figure 4. Comparison between reproduced Cs-137 deposition map and a top-hat/particle HYSPLIT model simulation for the first 24 hours of the Chernobyl accident in 1986 (Draxler and Hess 1998).

A second validation was performed on the volcanic eruption of Rabaul in 1994, simulating the atmospheric dispersion of the volcanic ashes and comparing the results to observations by satellite imagery.

In general the results compared favourably to observations although it was concluded that there is room for improvements of the vertical distribution modelling of pollutants. The results showed model sensitivity to vertical mixing coefficients and interaction between vertical distribution and rainfall for air concentration and deposition respectively (Draxler and Hess 1998).

8 Results and discussion

8.1 Omissions and limitations

A number of important limitations of the results in this report should be mentioned as an important limitation when interpreting the results.

- a) Production volumes for different smelter facilities was not known so two hypothetical cases were assumed; all production in the Norilsk area or all production in the Monchegorsk area.
- b) The emission factors had to be estimated from proxy data, as there are no known reports on actual emission factors for PGE in the literature. Emission factors and therefore emission rates for PGE in this report build on the assumption that they fall within the extremes of the emission factors for metals reported in the literature. This report makes no statement on the probability that this assumption is valid, and this should be considered when interpreting the data.
- c) Since there are no published data on particle size fractions emitted from Russian smelters, nor the distribution of PGE in the emitted particles. Therefore more assumptions had to be made regarding the particle size and PGE distribution to be used in the simulation. Future work should include characterization of particular emissions to minimize this source of uncertainty.
- d) The actual mining occur mainly in Taymir, however it is unknown where the smelting and processing of the PGEs occur. Therefore two scenarios are described.
- e) In the case of the model validation simulations there were no available archived meteorological data for the period when snow samples were collected, data from the subsequent year was used.

8.2 Model sensitivity to parameter variation

A number of input parameters were selected to assess the model sensitivity to variations in the assignment of parameter value. A base set of parameter input values were selected (see appendix for input parameter values) and the parameters were systematically varied in a total of 17 simulation runs. Monchegorsk (67°55'N 32°51'E) were selected as the emission point source and the simulation were run for 360 hours using meteorological data for January 2004.

Table 9. Model input parameters and variation levels used to examine model sensitivity.

Parameter	Value 1	Value 2	Value 3	Value 4	Value 5
Particle size (μm)	0.5	2.5	5	7	10
Model type	TH-part	GS-part	TH-puff		

Particles per cycle	100	500	1000
Max number particles	5000	10000	45000
Emission point altitude (m)	100	200	500

8.2.1 Particle size

Particle size has a profound significance for atmospheric dispersion and deposition. Smaller particles will tend to have lower settling velocity and thus disperse further before depositing through gravitational settling. Primary removal mechanisms of fine particles are no longer gravitational settling, but rather wet deposition. It was expected for this to show in the model output as the particle size parameter was varied between 0.5-10 μm . Indeed, the deposition output around the Summit area, Greenland, decreased by approximately nine orders of magnitude as the particle size parameter was increased from 0.5 to 10 μm (see Figure 5).

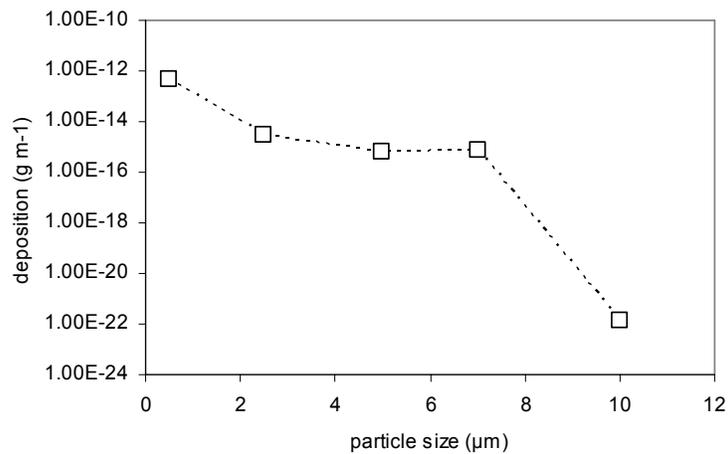


Figure 5. Accumulated 14-day deposition at selected grid cells for different input values on the particle size parameter.

8.2.2 Dispersion model type

Three of the different modes for dispersion modelling were tested and compared. These were horizontal Top-Hat puff and vertical particle (TH-part), Gaussian puff and particle (GS-part) and Top-Hat puff both vertical and horizontal (TH-puff). The variance in the deposition output between the models was the most significant of the studied parameters. The largest difference was observed between GS-part and TH-puff where the former yielded 2.78 times higher deposition results for Greenland (see Figure 6).

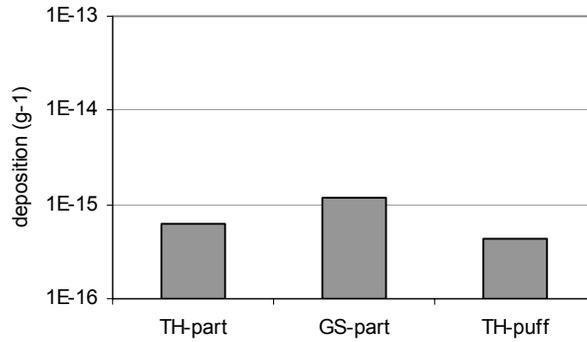


Figure 6. Accumulated 14-day deposition at selected grid cells using different dispersion models.

8.2.3 Particles per cycle

The number of particles per emission cycle that is used by the software in the simulation affects only dispersion modelling that is using a particle approach (top hat-particle, Gaussian-particle and 3D-particle). In this setup the maximum number of particles was set to 45,000, and the emission cycle was set to 24h. This equates to 15 emissions cycles for the entire simulation. Input parameters were set similar to those described in Table 13. The simulation using 1000 particles per cycle yielded a factor 1.19 higher deposition on Greenland.

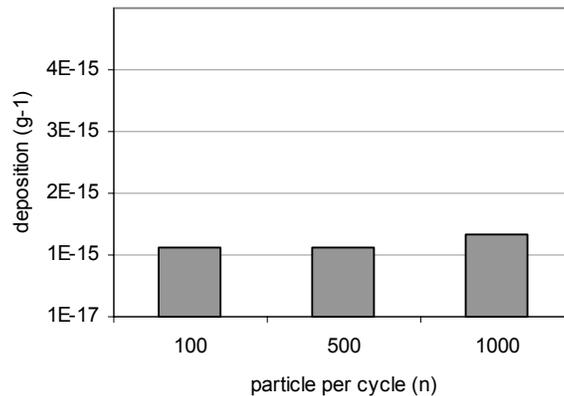


Figure 7. The effect of different max number of particles per emission cycle on deposition results.

8.2.4 Maximum number of particles

The software enables the setting of the maximum number of particles simultaneously allowed in a simulation run. Higher number of total particles should according to the HYSPLIT documentation result in less noisy spatial distribution of concentration and deposition. The

impact on remote deposition is small, as can be seen in Figure 8, representing approximately a factor of 1.06. Input parameters were set similar to those described in Table 13.

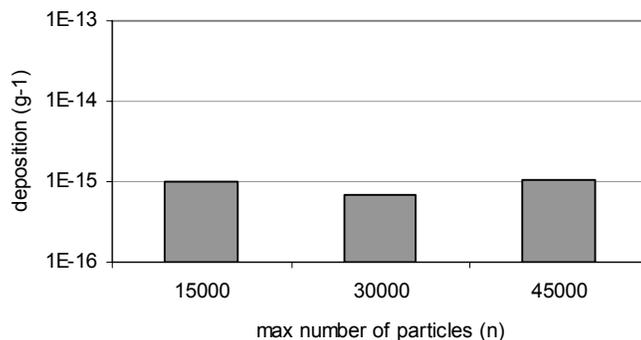


Figure 8. The effect of different max total number of particles in a simulation on deposition results.

8.2.5 Emission point altitude

There is relatively little impact of the emission point altitude, a slight enhancement of deposition on the Summit can be observed (see Figure 9). The largest relative difference observed was a factor 1.38. Input parameters were set similar to those described in Table 13.

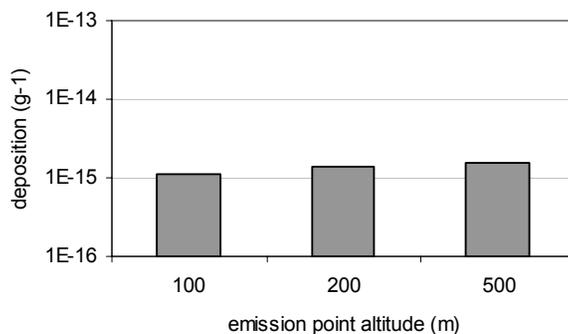


Figure 9. The effect of the emission point altitude (in meters) on deposition results.

8.3 Estimation of emission rates

Since empirical data for PGE emission factors were unobtainable at the time of the completion of this report it was necessary to estimate reasonable approximations for the emission factors, and from this calculate estimates for emission rates. The selected approach was to use copper and lead emission factors for primary production of copper and lead respectively, as reported by Pacyna and Pacyna (2001). This gives a range of 2000-3000 g emitted metal per ton of produced metal (using the data for Asia, Africa and South America).

The applicability on PGE production of the emission factors reported for copper and lead production is uncertain, thus the range was widened to 500-5000 g t⁻¹, to cover one order of magnitude. Further, production data reported by Kendall (2004) was used to calculate emission rates, resulting in 1.05-10.50 g h⁻¹ Pt, and 4.36-43.63 g h⁻¹ Pd (Table 10).

Table 10. Production, estimated emission factor ranges and calculated emission rate ranges for platinum and palladium production in Russia.

Element	Yearly production (ton y ⁻¹)	Emission factor low estimate (g ton-1)	Emission factor high estimate (g ton-1)	Emission rate low estimate (g h-1)	Emission rate high estimate (g h-1)
Pt (2003)	18.4	500	5000	1.05	10.50
Pd (2003)	76.5	500	5000	4.36	43.63
Pt (2005)	23.4	500	5000	1.33	13.35
Pd (2005)	97.4	500	5000	5.56	55.56

8.4 Particle size distribution

The mass - size distribution of particulate emissions are crucial for the atmospheric dispersion, since primarily only particles smaller than approximately 6 µm are transported to Greenland (Steffensen 1997). There are no measurements that indicate the particle size distribution of emitted particles from the studied smelters, thus some underlying assumptions had to be made. It was assumed that particles small enough to be transported to Greenland represents 25% of the emitted mass, since smaller particles generally contribute less to the total mass. These particles were represented by a 0.5 or 5 µm particle size in the simulations. It was further assumed that the remaining 75% were emitted as larger particles, represented in the simulations as 15 µm particles.

Yet another assumption was made regarding the distribution of PGE among the emitted particles. For simplicity it was assumed that the relative distribution of PGE were homogeneous among all size fractions.

The applicability of these assumptions is partially confirmed in the short range validation simulations described below.

8.5 Model validation

The model was put to verification and validation experiment against deposition rates derived PGE concentrations from snowpack samples reported by Gregurek et al (1999). Gregurek et al analysed PGE concentrations in snow collected at various point near the Monchegorsk plant during the winter 1995/96. HYSPLIT was configured according to Table 13 found in the appendix and simulations were run for a total of 77 days between January 1st March 31st 1997. This period was selected since there was no available archived meteorological data for dates

prior to 1997. It was assumed that the simulated period is sufficiently long to cancel out most short term variations in meteorological conditions.

The deposition rates were then calculated from the accumulated deposition in a location approximately 8 km SSE of the plant (67°51'N 32°56'E, sample point M-5 in Gregurek et al, 1999). The results from the simulation are presented in Table 11. There is a good agreement between deposition rates derived from the Gregurek et al (1999) data and the high emission rate scenario for Pt and Pd (11 and 8% overestimation respectively).

Table 11. Comparison of deposition rates derived from HYSPLIT and data reported by Gregurek et al. (1999)

	Pt (g km ⁻² year ⁻¹)		Pd (g km ⁻² year ⁻¹)	
	Low emission scenario	High emission scenario	Low emission scenario	High emission scenario
HYSPLIT derived deposition rate	11	114	47	473
Gregurek et al. (1999)	101		437	

The close match of the deposition rates derived from two independent sources indicates that the underlying assumptions are reasonable and these results support the findings of the long-range transport simulations used to calculate PGE input to the Summit from smelters in the Kola Peninsula and Taymir.

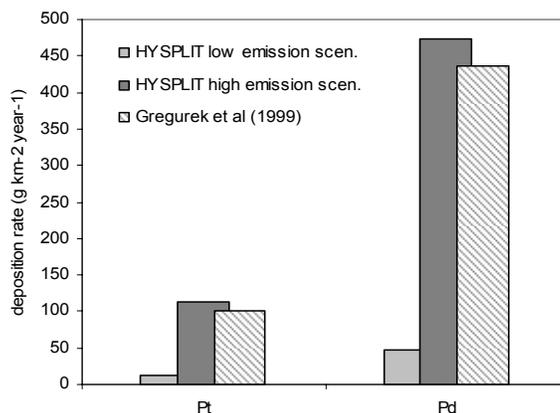


Figure 10. HYSPLIT derived deposition rates at 67°51'N 32°56'E, at sample point M-5 in Gregurek et al, 1999, between January and March 1997. The bars represent the high and low emission rate scenarios for Pt and Pd respectively, compared to deposition rates derived from Gregurek et al., (1999) data.

8.6 Deposition results for Summit, Greenland

The HYSPLIT model was run for a total of 100 days (representing 27% of a full year) to estimate the contribution from Russian smelters to deposition of PGE on the Summit. The base parameter input is specified in Table 13 in the appendix. The meteorological data used was split into files covering one half of a month. To select which periods to use in the deposition simulation 10 numbers were randomly generated and associated with a meteorological data file. The randomly selected data were then used to run ten 14-day simulations. In the output deposition data the first four days of each simulation run were omitted from the calculations to minimize the impact of transport dead time.

The output from the HYSPLIT simulations indicate that deposition rates of Pt over the Summit originating in Monchegorsk and Taymir are $\sim 10^6$ - 10^7 times less than the estimated Pt deposition rate associated to automotive catalytic converters reported in the literature, see Figure 11 (Rauch, Hemond et al. 2005). Even when considering uncertainties and variance from input parameters and underlying assumptions regarding the characteristics and amounts of the emitted PGE, it is unlikely that emissions from Russian smelters significantly contributes to deposition rates of Pt and Pd over Greenland.

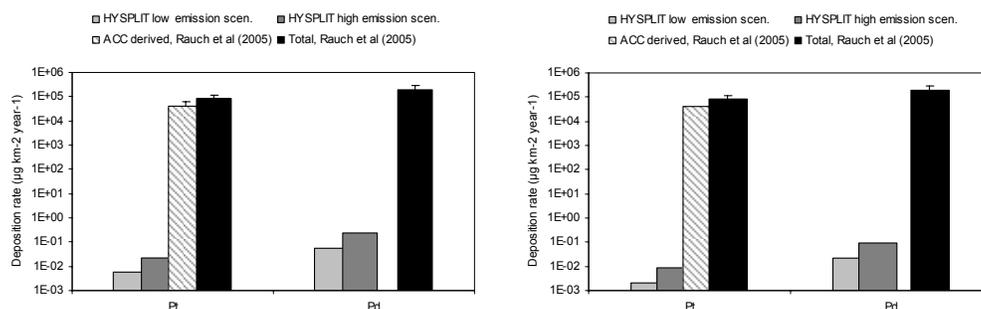


Figure 11. Comparison of deposition rates over the Summit, derived from HYSPLIT simulations of emissions originating in Monchegorsk (left panel) and Taymir (right panel) and estimates published by Rauch et al. (2005). The error bar represents the range of the estimate.

Deposition in the simulations occurs mainly during January and April as can be seen in Figure 12. This is most likely due to weather patterns facilitating transport of particles to the target location during these months.

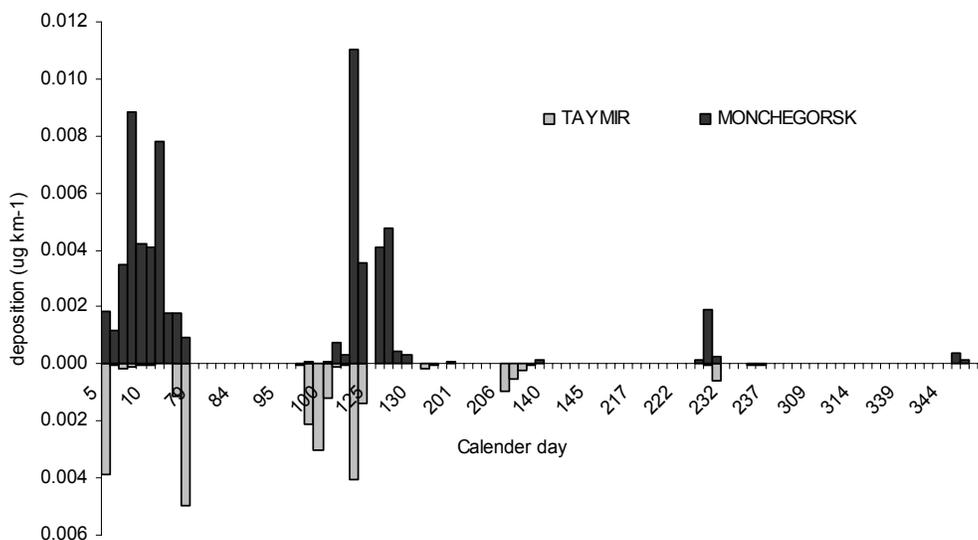


Figure 12. Deposition at the Summit for PGE originating from Monchegorsk and Taymir sites. Output from HYSPLIT simulation for randomly selected periods covering 100 days during 2005.

For comparison a complementary set of simulations for a total of 200 days were performed using a particle size of $0.5 \mu\text{m}$ and production data for 2005. The smaller particle size facilitates long range transport and this is reflected in the results. Using these input parameters the derived deposition on Summit were 3.3 and $13.7 \mu\text{g km}^{-2} \text{y}^{-1}$ for Pt and Pd respectively (high emission scenario). This represent $\sim 10^3$ - 10^4 times lower deposition rates than the literature estimates (see Figure 13).

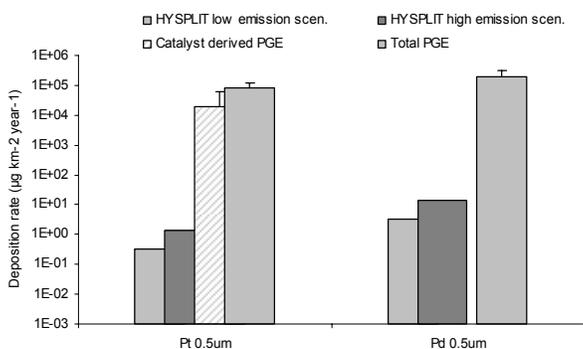


Figure 13. Deposition rates over the Summit, derived from HYSPLIT simulations of emissions originating in Monchegorsk, using $0.5 \mu\text{m}$ particle size, year 2005 production data and 200 simulated days, compared to estimates published by Rauch et al. (2005).

The temporal deposition pattern for this scenario looks slightly different than the $5 \mu\text{m}$ scenario (compare Figure 12 and Figure 14). A very large peak deposition occurred in February, with other peaks in January, April and December.

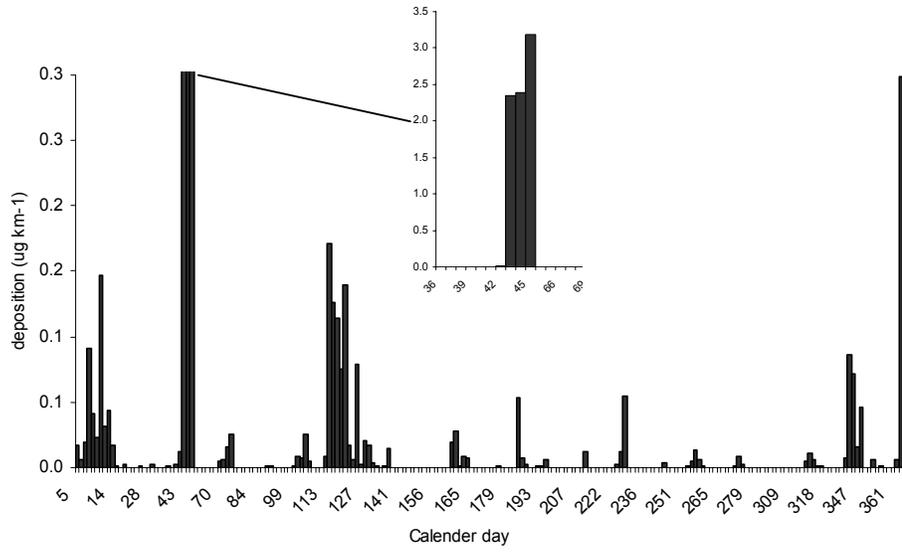


Figure 14. Deposition at the Summit for PGE originating from Monchegorsk, $0.5 \mu\text{m}$ particles. Output from HYSPLIT simulation covering 200 days during 2005..

9 Conclusions

The findings in this report indicates that the input of Pt and Pd from Russian smelters to the Summit is insignificant in comparison to the input from automotive catalytic converter derived PGE. This conclusion is backed up by the deposition data output from HYSPLIT simulations and differences in elemental ratios between PGE found on Greenland and those emitted by smelters on the Kola Peninsula. The deposition rate for Pt found in this report is roughly one million times lower than the estimates published for automotive related Pt deposition rates over Greenland.

The atmospheric dispersion model (HYSPLIT) that was used managed to accurately simulate deposition of Pt and Pd at relatively short distance (approx. 8 km) from the smelter when compared to previously reported data. Even if this validation approach does not reveal explicit information on long range transport simulation performance of the software it indicates the validity of the underlying assumptions.

The results in this report indicate also that the Russian PGE production contributes approximately 90 and 380 kg to the annual global flux of Pt and Pd respectively. This should be compared to the estimated 500-1400 kg Pt from catalytic converters and 149 and 84 kg annual flux from cosmic dust of Pt and Pd respectively (Barbante, Veysseyre et al. 2001). Thus, this work indicates that the emissions from Russian smelters are of a significant order of magnitude on the scale of global flux of Pt and Pd, but also concludes that the emissions are mainly deposited regionally. The prevailing weather patterns over the northern polar region appear to facilitate transport of particulate matter to the site of interest from smelters at the investigated locations only during limited periods of the year.

To summarize the findings of this investigation, the Russian PGE producing facilities contribute up to 0.008% (Platinum) and 0.034% (Palladium) of the total deposition of PGE on Greenland, if all production is assumed to occur in Monchegorsk and 0.5 μm particles. For the Taymir scenario this share is less (0.3 ppm and 0.4 respectively, 5 μm particles).

Considering the results put forward here it is unlikely that emissions from the investigated smelter facilities were a significant source of Pt and Pd deposited on Greenland. This conclusion is further reinforced by the observation that PGE elemental ratios found in Greenland and Kola Peninsula does not match, indicating other major sources.

10 Recommendations for future work

It is important that the characteristics and amounts of smelter emissions are better investigated to increase the fidelity of the simulation input parameters, thus also the output. Data regarding particle size distribution and elemental distribution within size fractions needs to be collected together with specific emission rates. This, coupled with additional measurements of PGE concentrations in well defined snow pack samples at locations of various distance from the smelters would provide increased information on model performance.

11 References

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12 Appendix

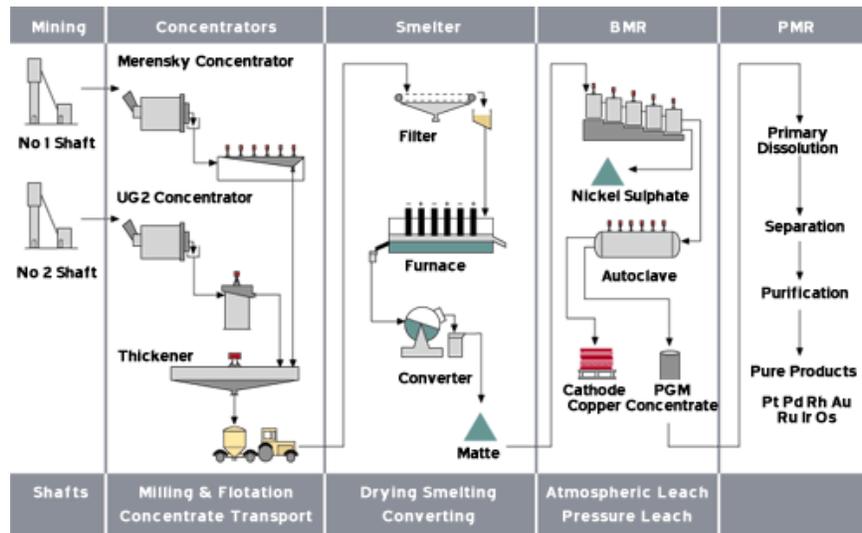


Figure 15. Example of a PGE production process. From Northam Platinum Unlimited, South Africa (Northam 2003).

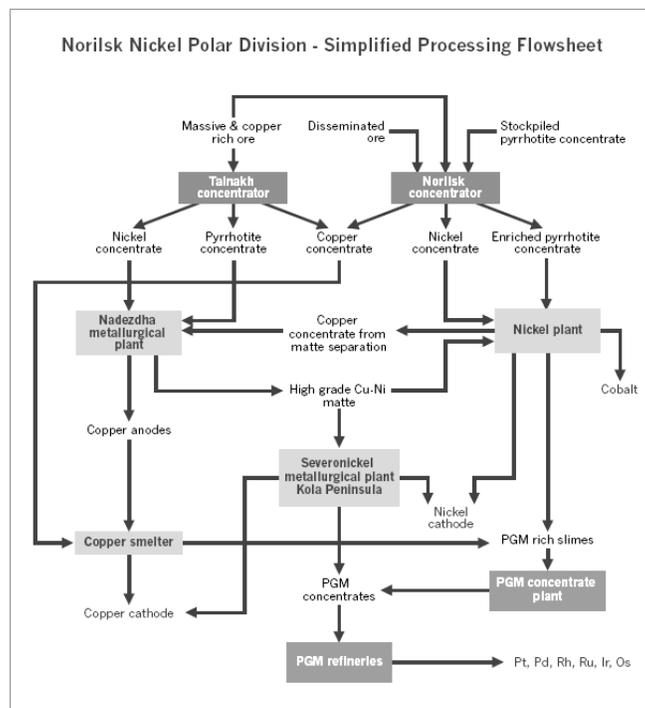


Figure 16. Schematic description of the Norilsk Nickel PGE process flow on the Taymir Peninsula (Kendall 2004).

Table 12. Locations of interest and their lat lon positions.

Location	Latitude, longitude and elevation
Greenland	<i>Summit</i> 72°34'N 37°37'W

		3238 m	
Kola Peninsula	Nikel	69°24'N	30°12'E
		126 m	
	Monchegorsk	67°58'N	32°53'E
		132 m	
Taymir peninsula	Norilsk	69°20'N	88°06'E
		62 m	

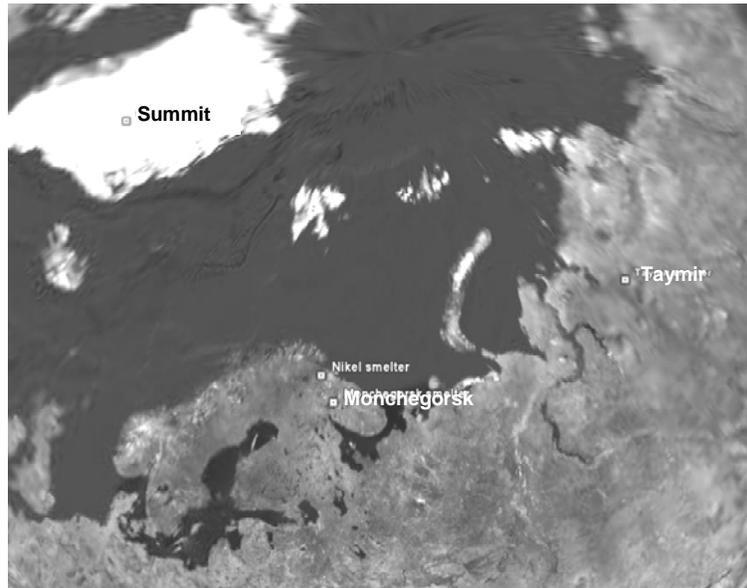


Figure 17. Overview map showing the locations of the sites studied in this report.

Table 13. Base settings used for HYSPLIT validation simulations.

<u>Base settings</u>	
<u>Concentration setup</u>	
Total runtime	336
Direction	Fwr
Top of model (m agl)	10000
Vertical	data
<u>Definition of pollutant group 1</u>	
Identification	PGE
Emission rate	(as estimated)
Hours of emission	336
Release start	00 00 00 00 00
<u>Definition of Concentration grid 1</u>	
center of Lat and Lon	0.0 0.0
Spacing (deg) Lat, Lon	0.05 0.05
Span (deg) Lat, Lon	1 1
Output grid directory	./
Output grid filename	cdump
Num of vertical levels	1
Height of leveles	0
Sampling start	00 00 00 00 00
Sampling stop	00 00 00 00 00
Interval	00 24 00
<u>Deposition definition for Pollutant 1</u>	
Particle or gas	Particle

Dry deposition	Yes
Wet deposition	Yes
Particle diameter	15.0
density	6.0
shape	1.0
Henrys	1.0E+05
In-cloud	3.2E+05
Below cloud	5.0E-05
Radioactive half-life decay	0.0E+00
Pollutant resuspension factor	1.0E-06
<u>Concentration namelist configuration setup</u>	
Timestep selection criteria	set ratio
Timestep	0
Stability ratio	0.75
Meteorological subgrid size	10
Vertical grid coordinate system	AGL
Model type	TH-part
Particles per cycle	500
Max number particles	45000
Repeat emission cycle	24
Max duration (hrs)	24
Turbulence	Standard
Dispersion	Linear
Concentration packing	On
Initialization file	PARINIT
Particle dump file	PARDUMP
Method	1
Dump intervals	0
In-line special conversion modules	None
Ensamble Configuration Values	1 1.0 1.0 0.01