Urinary platinum excretion following occupational dermal and respiratory exposure to soluble platinum

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Introduction

- South Africa accounts for approx. 70% of global platinum (Pt) production. [1]
- In 2015, Pt supplies rose by 19% (the highest level in four years). It's estimated that the demand for Pt in the automotive industry will rise by 6% in 2016. [2,3]
- During the refining of Platinum Group Metals (PGMs), many complex intermediary compounds are formed.[4]
- PGM-salts such as ammonium hexachloroplatinate $(NH_4)_2PtCl_6$ are capable of inducing and eliciting type I hypersensitivity reactions in exposed workers. [5]
- Sensitisation = Permanent removal from any exposure and often removal from employment within the Pt-industry. [6,7]

[1] Chamber of Mines of South-Africa. (2014); [2] Johnson Matthey. (2015); [3] Johnson Matthey. (2016); [4] World Health Organisation. (2000); [5] Cristaudo *et al*. Allergy (2005) [6] Cristaudo *et al*. Anal Lett (2005) [7] Bullock, International Precious Metals Institute (2010).

Introduction

- The majority of studies focus solely on respiratory exposure to soluble Pt and there is no indication of the actual levels of skin exposure. [8,9,10,11,12]
- It has been reported that intact human skin can be permeable to soluble Pt. [13]
- It is unclear whether mainly respiratory exposure or a combination of respiratory and dermal exposure are involved in sensitisation. [14]
- Biological monitoring results can be used to demonstrate exposure via any route of exposure. [15]

[8] Calverley *et al.* Occup. Environ. Med (1995); [9] Linnett and Hughes. Occup. Environ. Med (1999); [10] Merget *et al.* Allergy Clin Immun (2000); [11] Kielhorn *et al.* Int J Hyg Environ Health (2002); [12] Violante *et al.* (2005) . J Environ Monitor; [13] Franken *et al.* Toxicol in Vitro (2014) [14] Maynard *et al.* (1997) [15] Angerer *et al.* J Hyg Environ Health (2007)

Introduction

- Objectives:
  - To evaluate the dermal and respiratory exposure of precious metal refinery workers to soluble Pt
  - To measure the quantity of absorbed Pt excreted via the urine
  - To correlate dermal and respiratory exposure of precious metal refinery workers to soluble Pt with urinary Pt concentrations

Methodology

- Dermal exposure: Ghostwipes™ were used as sampling media with 24 cm^2 acetate paper templates

Table 1: Layout of dermal sampling strategy

Anatomical Area	Number samples per day
Palm of hand	3
Wrist	3
Forehead	1
Neck	1
Total per worker per day	**8**

- Respiratory exposure: MDHS 46/2 was used utilising Institute of Occupational Medicine (IOM) samplers

Methodology

- Biological monitoring was conducted concurrently with that of the dermal and respiratory sampling.
- Urinary excretion reaches the maximum approx. 10 hours after exposure via inhalation[16]
  - Collecting samples on the following morning represented changes in urinary Pt excretion as a result of the previous shift's exposure
- Samples was collected pre-shift the morning of the first day (baseline) and on the morning of the 2nd and 3rd days.
- Results were corrected for creatinine

[16] Schierl *et al.* Occup. Environ. Med (1998)

Methodology – Summary

- All workers were sampled on two consecutive days

Table 2: Summary of samples collected

Day	Dermal	Respiratory	Biological
Day 1	8 Samples	8 hour sample	1 Morning urine sample (Baseline)
Day 2	8 Samples	8 hour sample	1 Morning urine sample
Day 3	-	-	1 Morning urine sample

- 13 Production workers
  - Bagging salts, process operators, crushing, melting and packing.
- 6 Non-production workers within the refinery
  - Administration, security and laundry

Results – Dermal Exposure

Table 3: Summary of average dermal exposure (µg/cm^2)

Group	n	Minimum	Maximum	Average	Median
Production	26	0.0007	2.496	0.340*	0.053
Non-Production	12	< 0.00021	0.003	0.001*	0.0007

* $p = 0.0020$; Detection limit = 0.00021 µg/cm^2

- Highest exposure was measured on the wrist

Results – Anatomical Positions

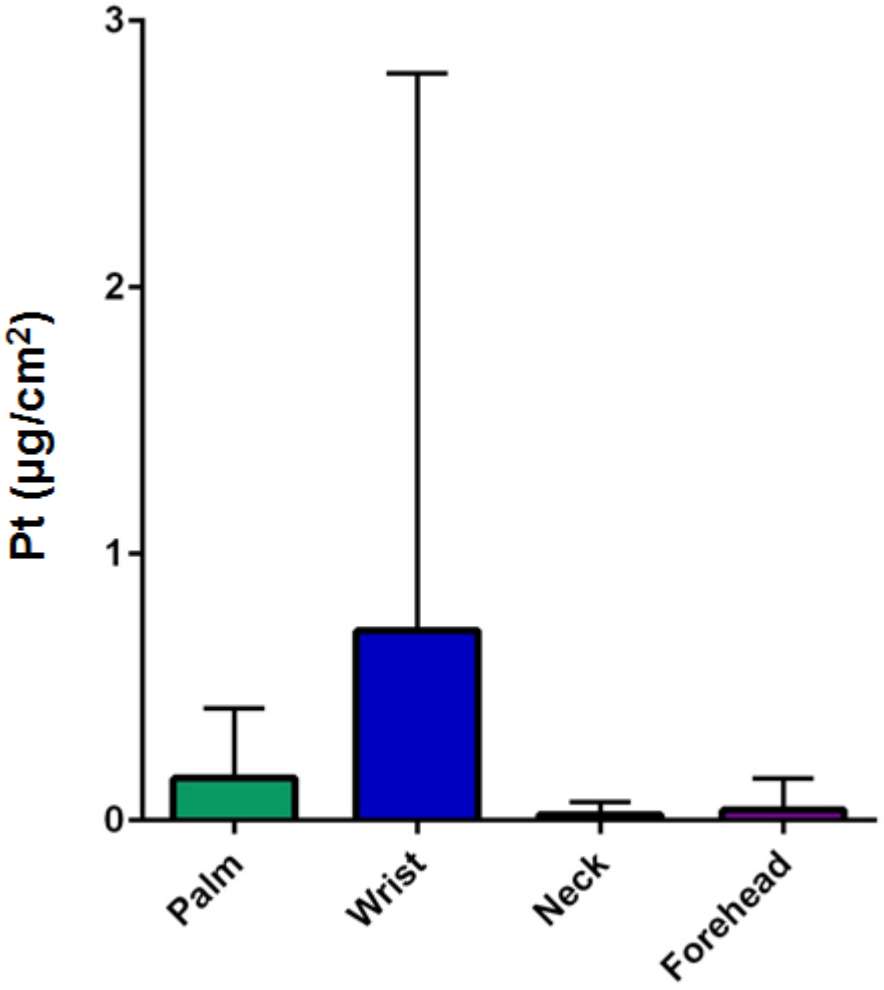


Figure 1: Average soluble Pt measurements collected on different anatomical positions

Results – Respiratory Exposure

Table 4: Summary of respiratory exposure TWA (µg/m^3)

Group	n	Minimum	Maximum	Average	Median	> OEL of 2
Production	26	< 0.005	113.441	12.448*	0.424	10
Non-Production	12	< 0.005	0.161	0.034*	0.001	0

* p = 0.0023; Detection limit = 0.005 µg/m^3

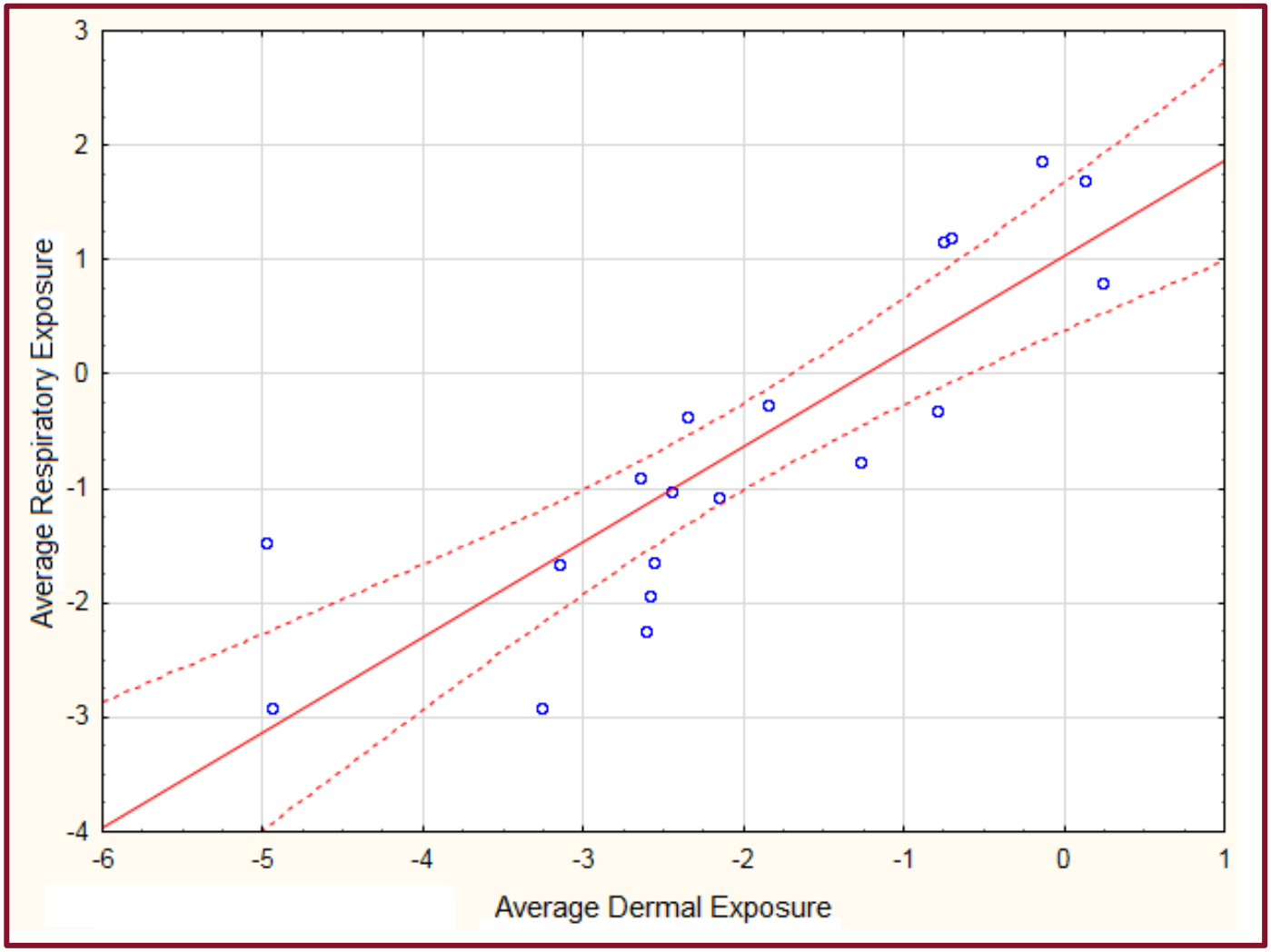
Results – Biological Monitoring

Table 5: Summary of average urinary Pt concentrations (µg/g creatinine)

Group	n	Minimum	Maximum	Average	Median
Production	39	< 0.1	3.0	0.916*	0.5
Non-Production	18	< 0.1	0.2	0.068*	0.044

* p = 0.0009; Detection limit = 0.1 µg/g creatinine

Results – Correlations

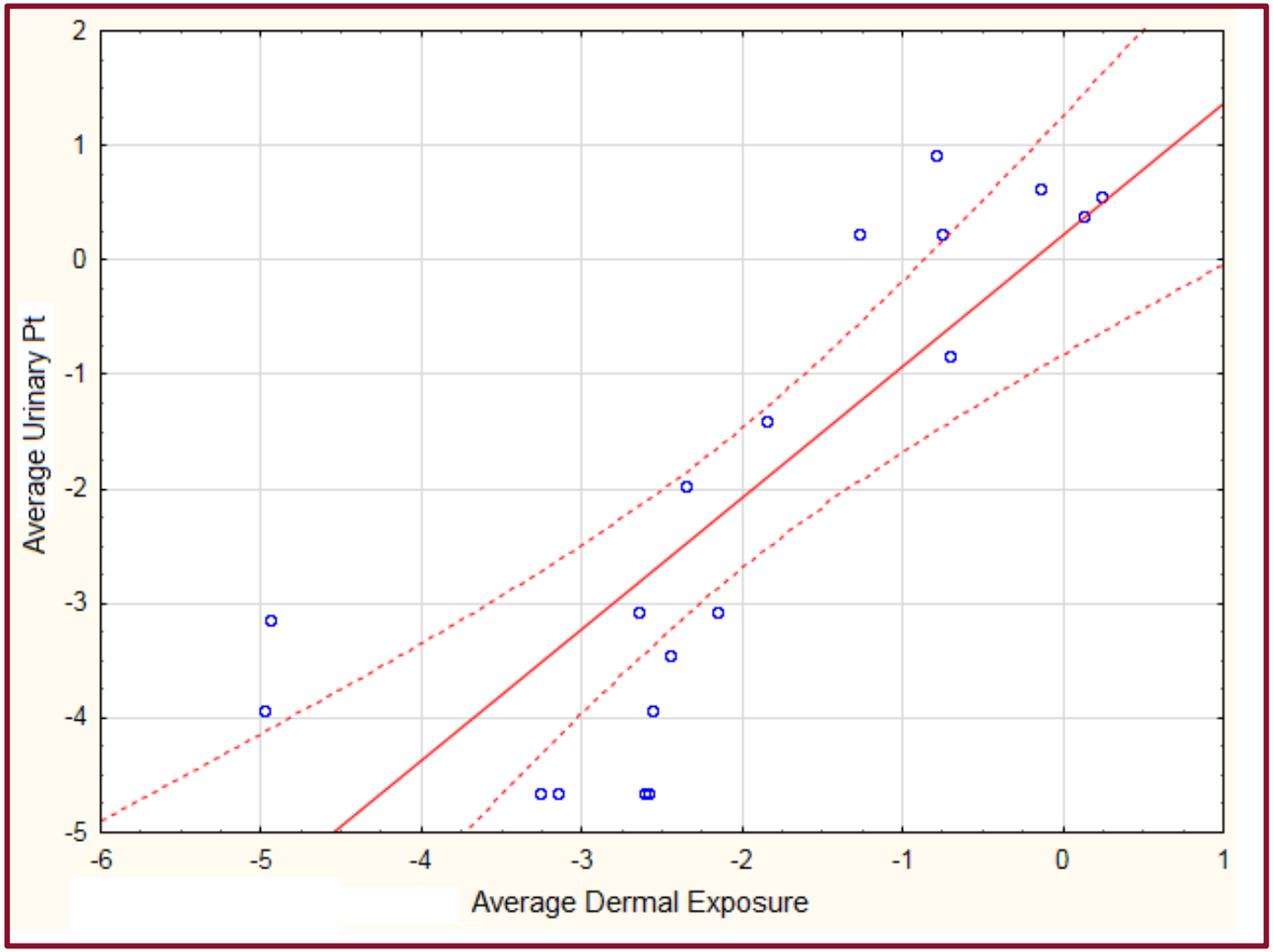


r = 0.853

p < 0.001

Figure 2: Correlation between average dermal exposure and average respiratory exposure

Results – Correlations

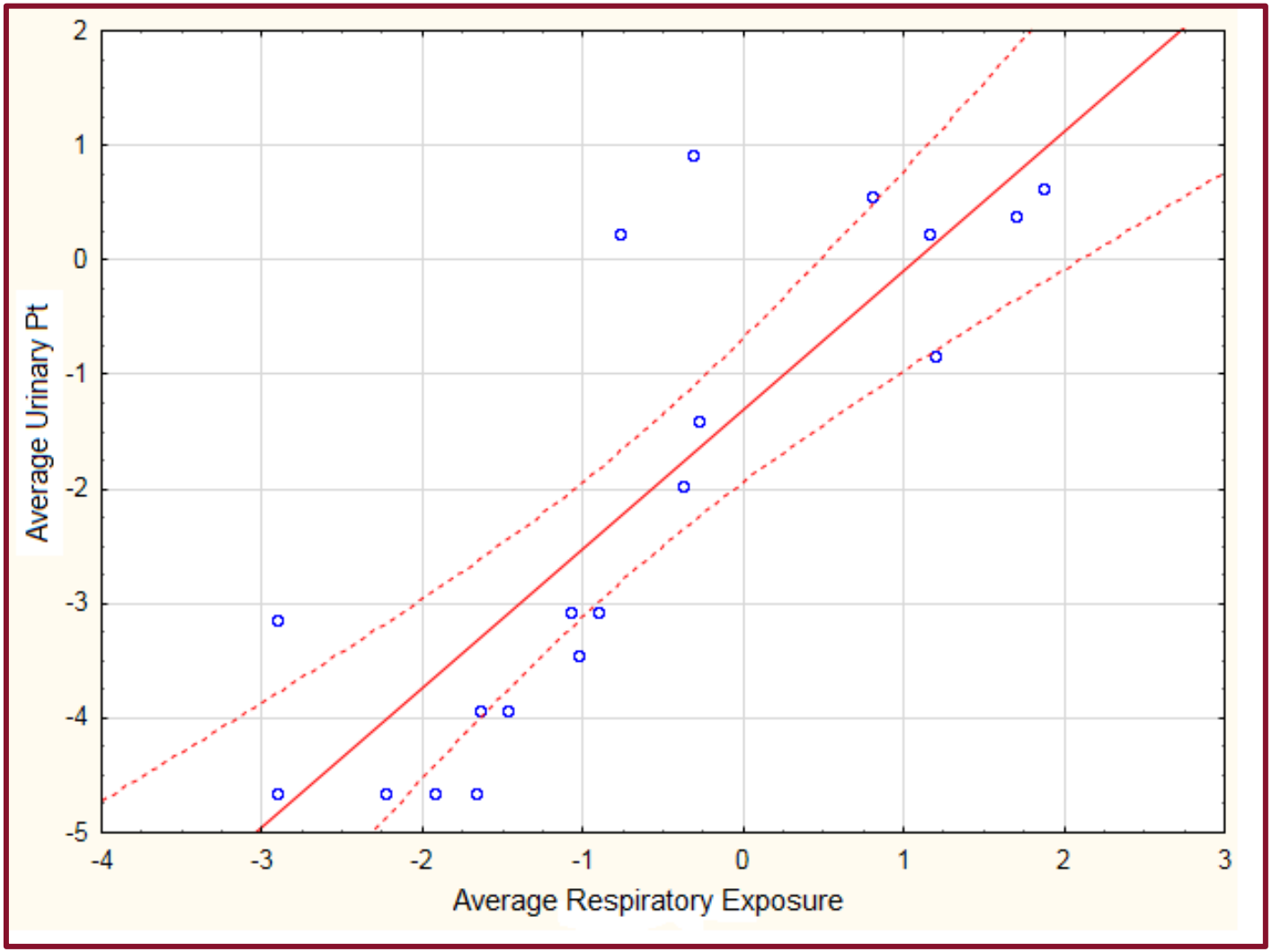


r = 0.814

p < 0.001

Figure 3: Correlation between average dermal exposure and average urinary Pt concentration

Results – Correlations



r = 0.840

p < 0.001

Figure 4: Correlation between average respiratory exposure and average urinary Pt concentration

Discussion

- Correlation analyses showed very strong positive monotonic relationships between:

(i) Average dermal exposure and average respiratory exposure to soluble Pt

(ii) Average dermal exposure to soluble Pt and average urinary Pt concentration

(iii) Average respiratory exposure to soluble Pt and average urinary Pt concentration

This suggests the following pattern:

Discussion

Route 1

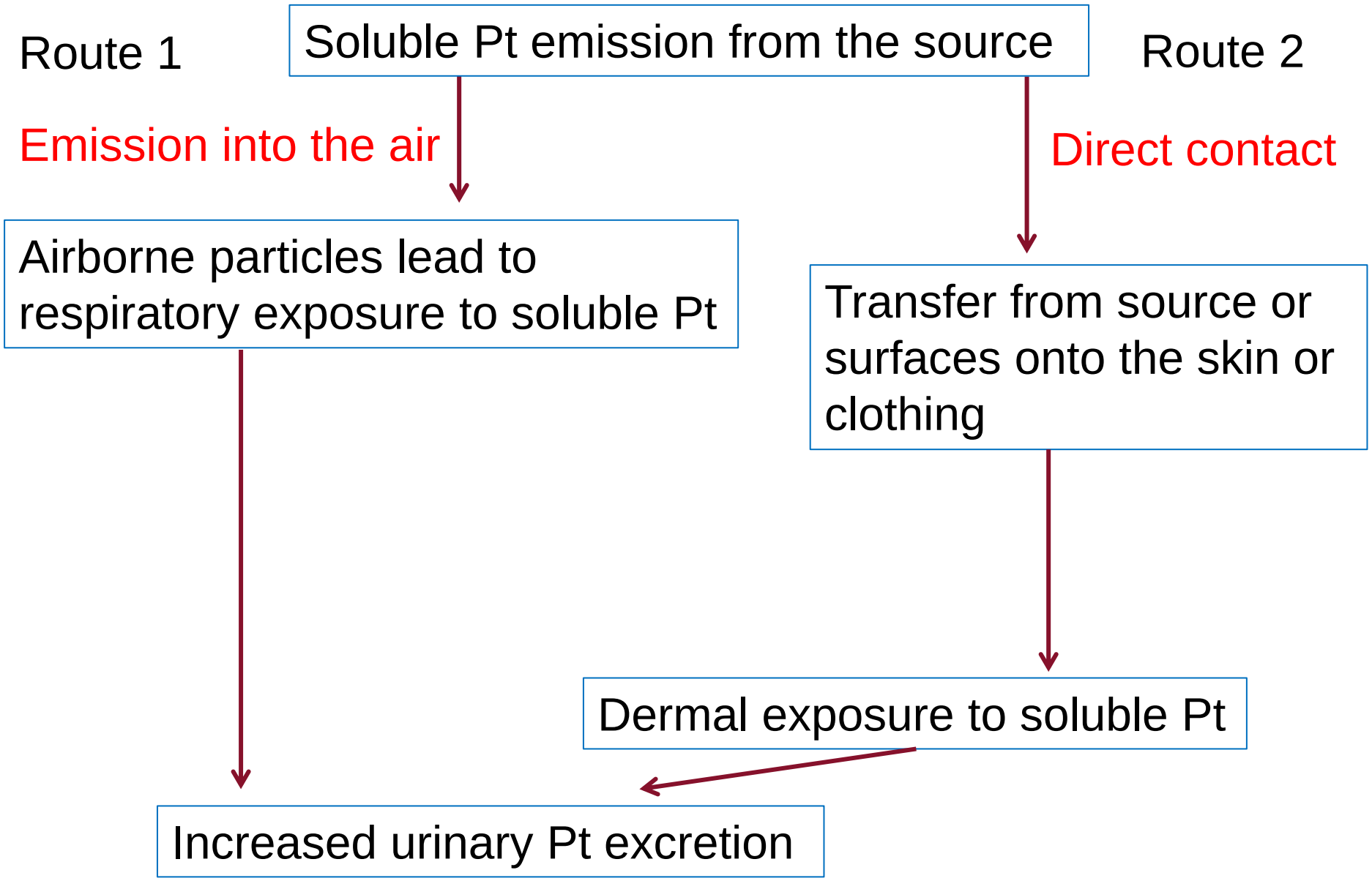
Soluble Pt emission from the source

Emission into the air

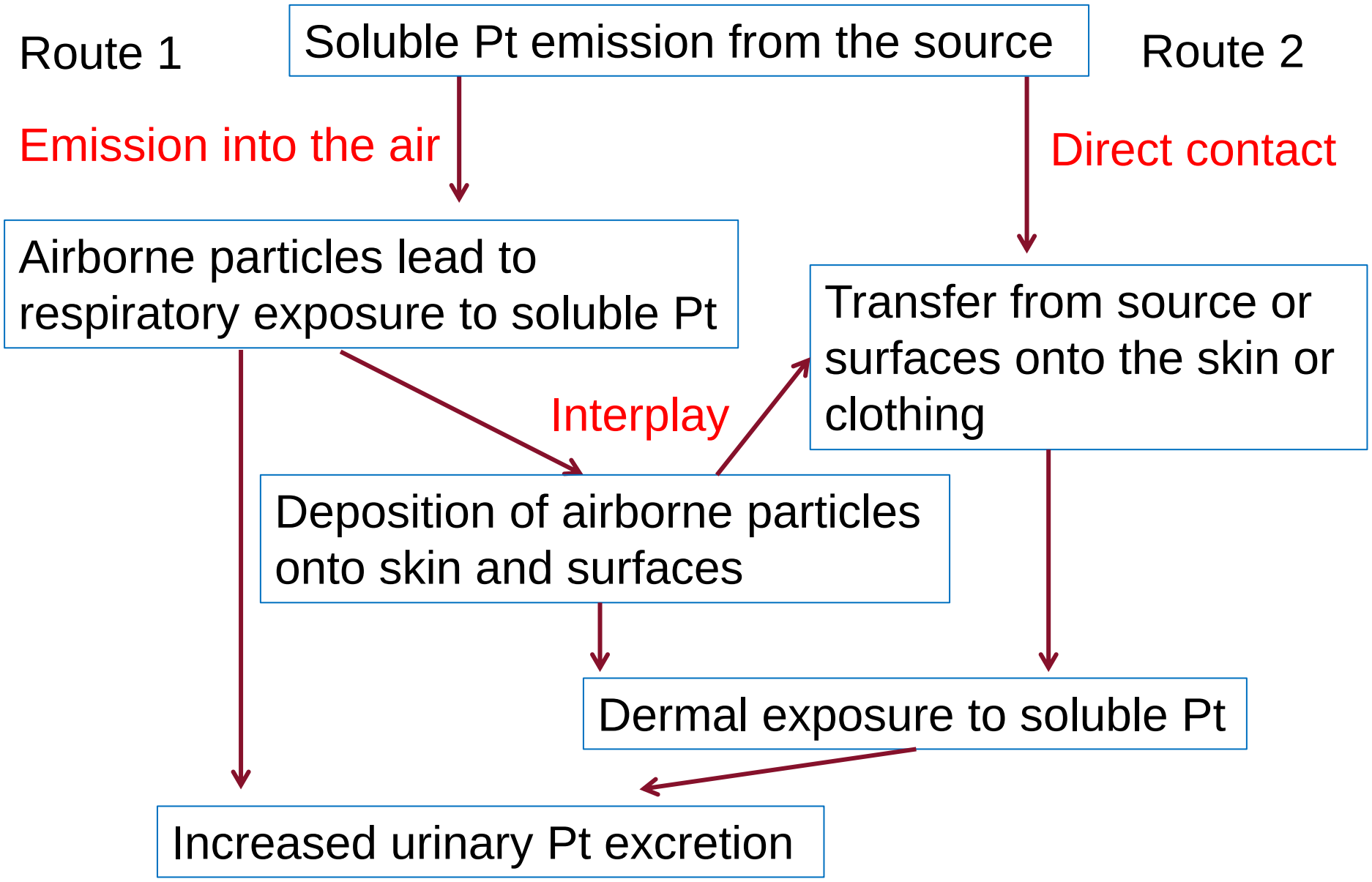
Airborne particles lead to respiratory exposure to soluble Pt

Increased urinary Pt excretion

Discussion


Route 1
Soluble Pt emission from the source
Route 2
Emission into the air
Direct contact
Airborne particles lead to respiratory exposure to soluble Pt
Transfer from source or surfaces onto the skin or clothing
Dermal exposure to soluble Pt
Increased urinary Pt excretion

Discussion


Route 1
Soluble Pt emission from the source
Route 2
Emission into the air
Direct contact
Airborne particles lead to respiratory exposure to soluble Pt
Transfer from source or surfaces onto the skin or clothing
Interplay
Deposition of airborne particles onto skin and surfaces
Dermal exposure to soluble Pt
Increased urinary Pt excretion

Conclusion

- Workers in the precious metal refinery were exposed to soluble Pt via the respiratory and dermal routes
- Both the respiratory and dermal routes contributed to the excretion of Pt via the urine
- The dermal route should be considered when investigating occupational exposure to soluble Pt
- In this study the wrist was the anatomical area most exposed to soluble Pt
- Production workers such as process operators are most at risk

The study was approved by the Health Research Ethics Committee (HREC) of the North-West University with the approval number NWU-000128-14-A1

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