

**AUTOCATALYST-DERIVED PLATINUM GROUP
ELEMENTS IN THE ROADSIDE ENVIRONMENT
– OCCURRENCE, MOBILITY AND FATE**

by

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I declare that this thesis is my own account of my research, unless otherwise stated. It contains as its main content work which has not previously been submitted for a degree at any tertiary institution.

Jason D. Whiteley

PUBLICATIONS

The following papers based on research presented in this thesis have been published or submitted for publication:

- Whiteley, J. D. and Murray, F. (2003). Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. *The Science of the Total Environment*, 317:121–135.
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ABSTRACT

The emission of the platinum group elements Pt, Pd and Rh (PGE) from automobile catalytic converters has led to rapid increases in Pt, Pd and Rh concentrations in roadside media. The vast majority of previous research examining autocatalyst-derived PGE in the urban environment has been performed in Europe or North America. Although catalytic converters became mandatory on all new cars sold in Australia from 1986, no prior studies have focussed on urban platinum group element (PGE) concentrations in Australian environments.

In general, the results of previous studies suggest a limited post depositional mobility of catalyst derived PGE. However, these findings are from research conducted in cool-temperate climate zones with regular rainfall and from environments where soils and sediments differ from the typically coarse grained, sandy soils with low levels of organic matter found in Perth. The relevance of European and North American findings to other regions with different climates and soils is therefore unclear and where the climate regime and properties of soils and sediments are not comparable to those previously studied, the potential exists for different geochemical behaviour of autocatalyst-derived PGE. Through investigations of spatial and temporal distribution and the identification of some of the main factors controlling transport and fixation, the principal aim of the research presented in this thesis was to elucidate aspects of the post depositional geochemical behaviour of

autocatalyst derived PGE in selected roadside environments in Perth, Western Australia..

The quality of some of the reported PGE data has been questioned by a number of workers. Possibly the most intractable difficulty in the determination of low concentrations of PGE in environmental samples by ICP-MS is the control of interferences from common matrix components. To ensure accurate and reliable data in this research, prior to the analysis of environmental samples, the optimal instrumental conditions for PGE determination and two commonly applied matrix separation methodologies (tellurium coprecipitation and ion-exchange) were investigated. The most effective matrix separation technique for the accurate determination of PGE in the environmental samples applicable to this study, such as road dusts and roadside soils, was found to be cation exchange.

The lack of knowledge regarding urban PGE concentrations in an Australian context was addressed through examinations of PGE levels in road dusts, roadside soils and infiltration basin and wetland sediments. Data show significant elevation of all three PGE above local background and average upper crust values. PGE ratios in surface road dusts and soils were consistent with known catalytic converter compositions and while Pt and Rh concentrations are comparable with European studies, Pd levels were generally higher in these Australian samples.

The effect of climate on PGE levels in roadside environments was investigated by repeat sampling of road dusts and roadside soils over a twelve month period. Both sample media exhibited seasonal variations. The presence of seasonal variability in PGE concentrations in roadside soils suggests that this environmental compartment does not represent a long term accumulative matrix for autocatalyst-derived PGE. Further examination of spatial distribution revealed that the PGE exhibit greater vertical

mobility in the soils of Perth than has previously been reported, with elevations above local background concentrations occurring at depths of 14–20cm. Neither small scale spatial variability nor vertical mobilisation were of sufficient magnitude to explain the observed temporal variability. Based on the pattern of seasonal PGE distribution and that of rainfall, temporal fluctuations are attributed to transport by stormwater. The mobilisation of PGE by stormwater is thought to occur principally via the water-mediated transport of PGE bearing particulates. However, PGE fractionation leading to a greater post-depositional mobility of Pd may occur during transport through the urban stormwater system.

In the urban environment of Perth, infiltration basin and wetland sediments represent a sink for autocatalyst-derived PGE. Based on the examination of PGE ratios, and the vertical distribution of PGE in infiltration basin sediments, Pt and Rh remain associated, whereas Pd may be differentially mobilised. For both soils and infiltration basin sediments, variation in pH was limited and does not show any correlation with vertical profiles of PGE, suggesting that pH does not act as a major control on PGE mobility. The role of organic matter is less clear, and although no straightforward relationships were apparent, where high levels of organic matter were present, profiles suggest an increased mobilisation of Pd. This differential mobilisation of Pd may therefore be caused by the formation of an organo-metallic species.

Temporal fluctuations in PGE levels in road dusts and roadside soils indicate that inputs of PGE to aquatic environments are likely to occur as seasonal pulses. The routing of road runoff into urban wetlands therefore represents a major pathway by which aquatic ecosystems may be exposed to autocatalyst-derived PGE. The impact of such inputs is

unclear, however, as other recent studies have shown that a portion of autocatalyst-derived PGE, and especially Pd is bioavailable, the potential for ecosystem degradation due to PGE contamination represents a major avenue for further research.

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