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Precious metals in urban waste

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Abstract

Samples of incinerator ash from sewage operations in the UK have been analysed and all contain concentrations of over 1 ppm gold (Au), ranging up to 7 ppm, showing a remarkable consistency of enrichment for all the 9 incinerators sampled. Samples analysed from 2005 to 2007 and in 2014 all have elevated values showing a consistency of high Au grades over time as well as between incinerators. One dried sewage sample also has elevated Au values averaging 721 ppb. Rounded grains of Au, 2–3 microns in diameter, have been located in the incinerator ash. Our results indicate that this ash produced from incinerated sewage contains Au, with associated platinum-group elements (PGE) and silver (Ag). This forms a polymetallic resource which may be economic to recover and recycle. Tests to extract these precious metals from the ash are ongoing.

Introduction

It is becoming increasingly clear that the quantities of precious metals building up in urban waste all over the world are sufficient to warrant investigation with a view to recovery and recycling. Studies have shown that industrial areas yield higher Au values in sewage sludge than rural areas in Germany (Lottermoser 1994). Gold concentrations in urban waste are extremely enriched over background values of less than 1 ppb away from natural geological Au occurrences. Legislation in many countries around the world now requires that vehicles use catalytic converters to convert poisonous gases into safe ones. More than 50% of all the annual production of platinum (Pt), palladium (Pd) and rhodium (Rh) are used in the manufacture of these catalytic converters (Cowley 2013) and during operation these precious metals are ejected onto roads. Here they concentrate in road dust at levels that are extremely enriched compared to normal background levels of less than 1 ppb. From roads these precious metals are dispersed into the environment (Rauch *et al*. 2005; Jackson *et al*. 2007; Prichard *et al*. 2009).

Precious metals are reconcentrated in several types of urban waste, especially in incinerated sewage ash. There have been a number of studies and news articles over the years indicating anomalously high values of Au, Ag and other metals in incinerated sewage ash and sludge, from various sewage plants around the world. These include Gulbrandsen *et al*. (1978), who demonstrated average values of 30 ppm Au and 660 ppm Ag in incinerated ash from plants in Palo Alto, California; and Reeves *et al*. (1999) in which average values of 0.77 ppm Au and 18.8 ppm Ag were measured in sewage sludge from Melbourne, Australia. The highest Au values have been reported from the Suwa facility, in Nagano Prefecture in Japan, which includes values of up to 1 890 ppm Au, or more than a kilogramme per tonne of ash (Yoshikawa 2009). This seems to be the only sewage plant worldwide which produces Au from sewage for economic gain. These grades are very high, in comparison to some of the world's largest gold mines, which averaged grades of just 1.1 ppm Au in 2012 (Dashkov 2013). Platinum, Pd and Rh have been recorded in sewage ash from UK incinerators with maximum values as high as 602 ppb Pt and 710 ppb Pd (Jackson *et al*. 2010). The mineralogy of these precious metals is not well known but recent studies have shown the presence of a cluster of Pt particles in sewage ash (Prichard and Fisher 2012) and 100–500 nm diameter Pt, Pd and Au particles in sewage sludge (Westerhoff *et al*. 2015). The aim of this study was to investigate the concentrations and mineralogy of Au in UK incinerated sewage ash with a view to possible recovery of these metals.

Methods

Samples of incinerator ash from 9 UK sewage incinerators were collected from 2005 to 2007 and then again in 2014. Samples were also collected from a sewage drying plant in Coventry. Data for Au collected as part of a Senior Brian Mercer Royal Society project to locate precious metals in urban

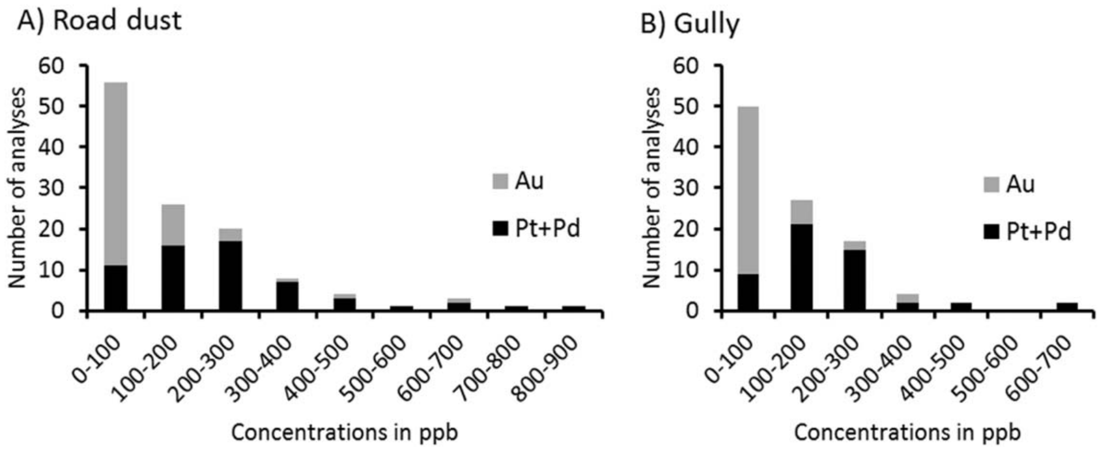

Fig. 1. Comparison of Au and Pt + Pd concentrations in samples of (a) road dust and (b) gullies from the city of Sheffield, UK.

waste, as part of the Cardiff University contribution to this project, have been used here to examine specifically Au data in urban waste samples from sewage works and sewage incinerators that were previously unpublished. All the samples were either analysed by fire assay followed by ICP-MS analysis at Genalysis and Ultratrace laboratories, Perth Western Australia or at SGS laboratories, Cornwall, UK. The samples collected in 2014 were analysed at Mintek laboratories in Johannesburg, South Africa.

Samples of incinerator ash with the highest concentration of precious metals were examined at Cardiff University using a FEI XL30 ESEM FEG scanning electron microscope. A back-scattered detector was used to search at magnifications of ×250 to ×5000. Qualitative analyses on unpolished grains were made using an Oxford Instruments INCA energy dispersive X-ray system. This system has been quantitatively calibrated using a full set of Au and associated elements standards supplied by Micro-Analysis Consultants Ltd. of St. Ives, Cambridge, UK. XRD analysis was used at Mintek laboratories to analyse the mineralogy of the incinerator ash.

Results

Sources of precious metals

Previous results have shown that anomalous Au values in dust occur on city pavements and outside schools. So some Au is likely to be sourced from abrasion of jewellery worn by people (Prichard *et al*. 2009). In contrast Pt, Pd and Rh are predominantly sourced from catalytic converters fitted to car exhaust systems (e.g. Jackson *et al*. 2007).

Comparison of Au and Pt + Pd data (Fig. 1) taken from Prichard *et al*. (2009) shows that there is a different distribution of Au versus Pt + Pd in road dust and in gullies in the city of Sheffield. Most Au values are low in the 1–100 ppb concentration class with a few higher values whereas Pt + Pd show a much more normal distribution with peaks in 100–300 ppb concentration classes also with a few higher values. In the light of this comparison and now a better understanding of the mineralogy of these precious metals the distribution of these metals in their source sediments of road dust and gullies can be explained. Platinum, Pd and Au are all precious metals that have a very high density. Gold is present ubiquitously at low concentrations with a few larger grains and is concentrated at the bottom of drains or gullies. Thus Au grains are behaving as individual fine very heavy particles giving many samples a low Au concentration and the heavy particles concentrate at the bottom of gullies or drains. Mineralogical studies show that the Pt and Pd are present as multiple nanoparticles attached to catalytic converter fragments (Prichard and Fisher 2012) and Pt and Pd are not located at the bottom of drains (Prichard *et al*. 2009). The presence of many Pt and Pd nanoparticles on a single catalytic converter fragment results in a lower number of road dust samples with a higher concentration of Pt + Pd as Pt + Pd coated fragments are not as common as individual fine grains of Au. The presence of Pt and Pd at the top of drains and gullies occurs because the overall weight of the Pt and Pd fixed to the light catalytic converter fragments is as a whole particle not particularly heavy.

Thus the sources of these precious metals are different but their movement through the urban environment results in them all collecting and reconcentrating in sewage and then being concentrated further during drying and incineration. The routes taken by the precious metals from road and pavement dust are shown on Fig. 2.

Gold along with other precious metals travel through natural drainage, through lakes and streams, rivers and estuaries and out to sea (Prichard *et al*. 2008) or through drains and gullies in the artificial drainage system into sewage works. Some precious metals are collected by gully flushers and road sweepers and this waste probably goes to land fill (Prichard *et al*. 2009). The routes taken by the precious metals are all inter connected, so for example Au may pass from

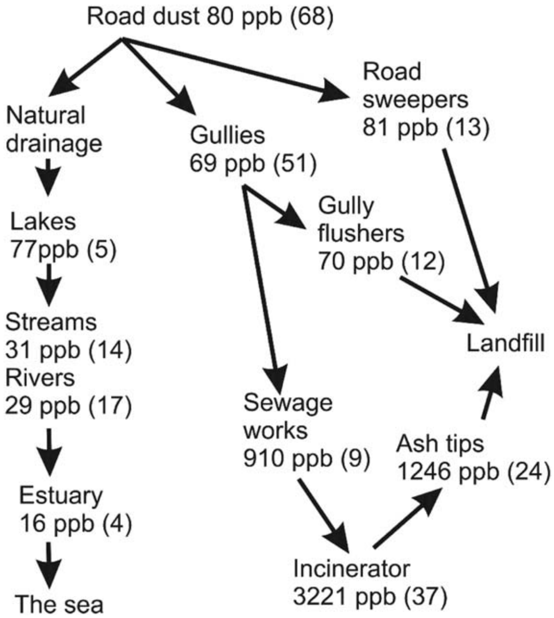

Fig. 2. Routes taken by gold through the urban environment showing average gold concentrations (ppb) in each type of urban sediment. Number of samples collected is shown in brackets. Data on road dust, gully, road sweeper, gully flushers and lakes are from Sheffield city. Stream samples were collected downstream of a busy roundabout in Sheffield. Rivers were sampled from Sheffield to the Humber estuary. Estuary samples were collected from the Humber estuary. Three sewage works were sampled for raw sewage including Minworth/Roundhill in Birmingham which has some of the highest values of Au in incinerator ash. Nine incinerators were sampled (Fig. 3). Traverses across stored ash tips of different ages were collected at the Browns site at the Blackburn Meadows sewage works in Sheffield.

artificial drains into rivers. At sewage works some raw sewage is dried and/or incinerated and then may be stored in ash tips and sent to landfill. The concentrations in the different types of urban waste show that precious metals are dispersed in natural drainage whereas in sewage works they are concentrated. Further concentration occurs by drying and incineration and then dispersal occurs in landfill (Fig. 2).

Precious metal concentrations in incinerated ash

Raw sewage already has high concentrations of Au averaging 910 ppb (including samples from the very enriched Roundhill/Minworth sewage in Birmingham) (Fig. 2) but the concentrations are increased on incineration. Samples of incinerated ash collected from 2005 to 2007 were taken from 9 incinerators (Fig. 3) and analysed for Au.

All incinerator ash samples, without exception, give Au values of over 1 ppm (Table 1). The highest values of 3–7 ppm Au are present in the ash from the two incinerators in Birmingham (Coleshill and Minworth/Roundhill), with values of 1–4 ppm from the two London incinerators (Becton and

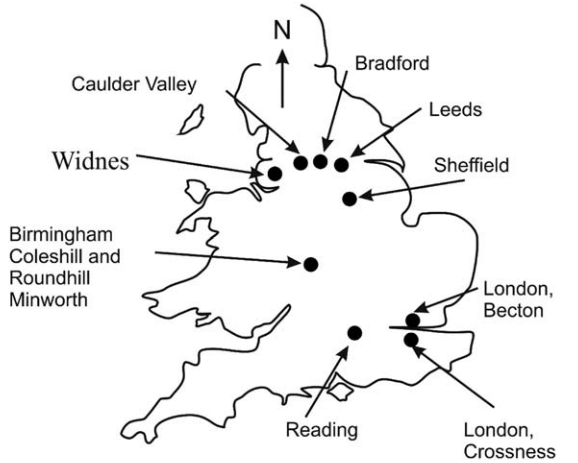

Fig. 3. Location of incinerators from which samples were collected in 2005–2007.

Crossness) and values of 1–3 ppm Au in ash from the Blackburn Meadows incinerator in Sheffield. To test for consistency of grade 11 samples were collected at approximately 2 monthly intervals during 2005–2007 at the Blackburn Meadows incinerator in Sheffield (Table 2). The average in this incinerated ash is 2715 ppb Au with maximum and minimum values of 3495 and 1761 ppb respectively. Incineration of waste is less popular now and since 2007 the Birmingham incinerators have closed and also the Sheffield incinerator was closed as a result of flooding in 2007; the incinerator is currently being rebuilt. Drying sewage rather than incinerating it is becoming increasingly popular and so a sample of dried sewage from a plant in Coventry was analysed for Au and platinum-group elements (PGE) (Table 3) and average Au values were 721 ppb. Sometimes ash is stored at the incinerator before it is sent to landfill and mixed with other waste where concentrations of precious metals are dispersed. A survey of such a site at Browns at Blackburn Meadows in Sheffield was undertaken in 2005 (Table 4) where ash was stored before it was mixed and sent to landfill. Again values

Table 1 Average Au, Pd and Pt concentrations (ppb) in incinerated ash from nine incinerators in the UK (Fig. 3)

Au	Pd	Pt	Incinerator location
2700	224	181	Average (14) Blackburn Meadows Sheffield
5393	504	430	Average (6) Coleshill, Birmingham
4362	435	333	Average (5) Round Hill, Birmingham
1093	266	35	Average (2) Calder Valley, near Bradford
1640	80	49	Esholt, Bradford
1897	101	62	Knostrop, Leeds
1490	290	66	Widnes, united utilities plant
3088	350	513	Beckton, North of Thames, London
1585	126	142	Crossness, South of Thames, London

Pt and Pd values taken from Jackson et al. 2009

Table 2 Consistency of concentrations (ppb) of precious metals in sewage ash samples collected from the Sheffield incinerator at Blackburn Meadows on the river Don

Au	Pd	Pt	Rh
2880	573	226	
2812	171	222	45
3495	209	222	28
2812	171	222	
2447	424	212	23
3065	211	167	
3056	211	167	24
2423	179	157	
2423	179	157	
1761	150	140	
2690	155	138	22

Pt, Pd and Rh values taken from Jackson *et al*. 2009

Table 3 Dried sewage samples from Coventry, precious metal concentrations shown in ppb

Au	Ir	Os	Pd	Pt	Rh	Ru
862	2	nd	68	36	3	11
580	2	nd	118	50	3	7

PGE values taken from Jackson *et al*. 2009

are consistently enriched in Au averaging 1300 ppb. Samples were taken at different points in the heaps of ash and the Au values tend to be higher at the top of the heaps suggesting that rain water is leaching the Au from the lower parts of the heaps.

Table 4 Distribution of Au concentrations (p.p.b.) in stored ash at Browns, Blackburn Meadows and Sheffield

Au	
1661	Top of hole 1998
1162	
778	
1291	Bottom of hole
1320	Top of the heap 2001
1376	
1418	
1393	
1253	
1278	Bottom of heap
1521	Top of the heap 2003
1112	
1199	
1557	
1289	
1188	Bottom of heap

Three traverses were taken through heaps of different ages. The sampling was done in 2005 and the age of the heap or hole through stored ash is given by the date in the table.

In addition to Au, Ag is also present at ppm levels in the samples. Taking an average of 2.6 ppm Au and 80 ppm Ag, the 'Au equivalent' figure of the value of both the Au and the Ag, as commonly used in the mining industry, can be calculated at current prices, using the formula:

$$\text{Au Equivalent Value} = \text{Au ppm} + (\text{Ag price}/\text{Au price}) \times \text{Ag ppm}$$

So that: $\text{Au Equivalent Value} = 2.3 + ((14/1072) \times 80)^{*} = 3.34$ ppm Au equivalent.

*Spot Au/Ag prices as of 24/12/2015

In 2014, further sampling was conducted at Becton and Crossness and analysed producing Au values similar to those recorded in 2006–2007, indicating that the Au grades are fairly static over time. This is an important consideration for financial modelling of extraction.

There are also considerable concentrations of the precious metals Pt and Pd with average concentrations of 240 ppb Pt and 307 ppb Pd in the 9 incinerator ashes (Table 1) with prices as of December 2015 of $864/oz Pt and $555/oz Pd. If these can be extracted then this is an additional financial consideration.

Mineralogy of the ash

The minerals in this incinerator ash consist of whitlockite $Ca_9(MgFe)(PO_4)_6PO_3OH$ 45.14%, albite ($NaAlSi_3O_8$) 21.84%, quartz (SiO_2) 15.25%, magnesioferrite ($Mg(Fe^{3+})_2O_4$) 6.23%, talc ($Mg_3Si_4O_{10}(OH)_2$) 3.42%, haematite (Fe_2O_3) 2.71%, anatase (TiO_2) 2.46, ilmenite ($FeTiO_3$) 1.82% and rutile (TiO_2) 1.13%. Several grains of Au were identified with sizes of 2–3 microns as shown in Fig. 4.

Recovery of the gold

Test work was carried out to trial optimal methods to extract the Au and Ag from the ash. Bottle roll leach test-work, using cyanide leaching methods used to extract Au and Ag in the mining industry, showed low recoveries of 15–20% in the ash samples. This may be due to silica ash particles being fused to the Au and Ag, thus preventing extraction. Various additional techniques are currently being trialled to adjust this process to improve recovery values. This paper is focused on the origin and concentrations of precious metals in sewage ash waste not on their extraction and recovery. It is very likely that with further research conventional methods used to extract precious metals from geological ores will be applicable to recovery of these precious metals. Less conventional methods more suitable for this type of waste may also be able to extract the precious metals. This ongoing research will be the subject of a future paper.

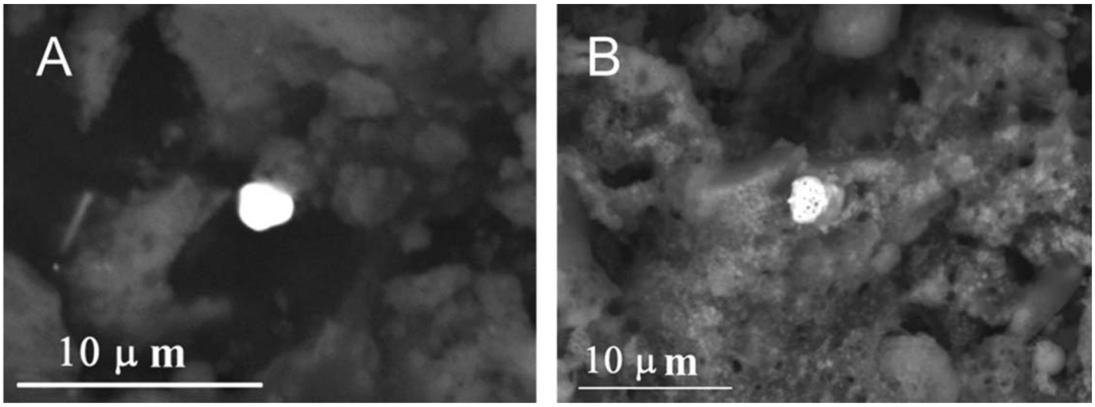

Fig. 4. (a) A gold grain in Birmingham incinerator ash and (b) A Pd-Sn-Au grain in Sheffield incinerator ash.

Discussion

The precious metal values in incinerated ash vary from city to city. The contribution from abrasion of jewellery worn by people is common to all cities, as is the contribution from emissions from catalytic converters, provided that catalytic converters are a requirement for vehicles by law, as is the case for most cities in the developed world. The variations between cities of precious metals in sewage ash will be a function of a number of factors. The natural and artificial drainage networks in each city can be quite different depending on their age and design and will channel the precious metals either towards or away from the sewage works. There may be additional sources of precious metals. For example the high gold values in the Birmingham sewage ash may result from a contribution from industry, especially from the manufacture of jewellery in the jewellery quarter. We obtained an extremely high value for gold in a gully sample taken from the jewellery quarter in Birmingham. Other metal concentrations vary from city to city too. For example the highest value of Ru was recorded in sewage ash from Sheffield and the values of Ru varied with time suggesting a variable industrial source (Jackson *et al*. 2010).

In comparison with mining, tonnages produced from sewage ash are quite low: 161,000 tonnes of sewage sludge was incinerated in the UK in 2012 (UK Government data request by Wedin 2012), whereas the larger operating gold mines usually produce millions of tonnes of ore per annum. However this precious metal resource in the incinerator ash still equates to 17,315 troy ounces of Au equivalent produced per annum that is currently going into landfill. At current prices, and assuming the average values quoted above, this is an *in situ* value of US$18.56 million of potential value per annum, just for the value of the Au and Ag within the ash, UK-wide. This is not including other metals that could be recovered, such as PGE or the base metals such as Ni and Cu. In addition, high levels of phosphorous could be extracted and used as fertiliser, which would add further value. The incinerator ash already has a very fine particle size and so recovery of this urban Au does not have to incur the large mining and crushing costs associated with the mining of geological Au ores. From an environmental perspective, the removal and recycling of precious metals from sewage waste worldwide would reduce the global need for mining and has the potential to clean up the environment, reducing the polluting effects of these metals.

Conclusions

(1) Incinerated sewage ash contains potentially economic concentrations of precious metals that are worth recovering provided suitable extraction methods can be put in place.
(2) The UK has tonnages of this incinerated ash that is Au-bearing in common with other incinerated ash in other parts of the world.

Acknowledgements

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