Wolverhampton case study of the characterisation of groundwater interaction with contaminated soils

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Abstract: When reclaiming industrial sites the quantity and types of materials present, the prevailing and future hydrogeological conditions and the possible uses of the site need to be considered especially in relation to the potential for the mobilisation of contaminants.

Redevelopment of former industrial areas, particularly the formation of open spaces can change infiltration patterns and result in soil leaching. Cessation of mining and reduced groundwater abstraction often allows the water table to rise and saturate contaminated land. In former coalfields, sulphide oxidation can produce acidic groundwater and enhance the potential for mobilising contaminants.

As part of a broader study into the impact of contaminated land on groundwater during the redevelopment of Wolverhampton, UK, a wide range of waste material and fills that are present in the City of Wolverhampton were sampled and subjected to XRF analysis and ICP-AES analysis following dissolution in aqua regia, and to batch leaching with a range of likely groundwater compositions including acid rain, acid mine drainage waters, groundwater, and humic rich water.

It was found that a significant number of the samples were contaminated with high levels of various PHEs. Parallel determinations of PHEs by XRF analysis and ICP-AES analysis, following dissolution in aqua regia, give similar values for most PHEs in most of the soils tested, confirming that ICP-AES determination provides an acceptable indication of the total concentrations of PHEs present in these materials.

Leaching of the soils using standard batch leaching methods indicated that only a very small proportion of the total PHE present was liable to be leached using a range of likely groundwater compositions. Sequential extraction tests indicated that this is because much of the PHE present is in forms that are not liable to be mobilised under normal groundwater conditions. It was also confirmed that the amount of the various PHEs leached from the soils was dependant on the composition of the leaching fluid. Although broadly speaking more acidic conditions lead to greater mobilisation of PHEs, the mineralogy and character of the materials, including the presence of carbonates, clay minerals, organic matter and iron oxides and hydroxides are liable to contribute to these differences, but further investigation of this aspect is required.

The results also suggest that drying samples prior to batch leaching can lead to a reduction in the amount of PHE apparently present in samples. Clearly this has implications for the assessment of such contaminated materials and it is recommended that samples are stored at low temperature (0-4 ^{0}C).

Résumé: Il faut considerer la quantite et les types de materiaux actuels, les conditions hydrogeologiques actuelles et futures et l'utilisation possible de l'emplacement particulierement par rapport au potentiel pour la mobilisation des contaminants en reprenant les emplacements industriels.

La reconstruction d'anciens secteurs industriels et en particulier la formation des espaces ouverts peuvent changer le modele et le resultat d'infiltration dans la lixiviation de sol. Cessation du mien et de l'abstraction reduite d'eux souterraines permet souvent a la table de l'eau de monter et de saturer la terre souillee. Dans d'anciens bassins houillers, l'oxydation de sulfurepeut produire les eaux souterraines acides et augmenter le potenntial pour les contaminants de mobilisation.

En tant qu'element d'une plus large etude sur l'impact de la terre souillee sur des eaux souterraines pendant le reconstruction de Wolverhampton, le RU, un evantail de dechets et des suffisances qui sont presents a Wolverhampton ont ete preleves et sournis a l'analyse XRF, l'analyse ICP – AES apres la dissolution dans le aqua regia et au groupe lixiviant avec une gamme de compositions probables d'eaux souterraines comprenant les pluies acides, les eaux acides de mines, les eaux souterraines et l'eau rich humic.

On a trouve qu'une chiffre significatif de samples ont ete souilles avec les niveaux eleves de divers PHE. Les determinations paralleles de PHE par l'analyse XRF et, L'analyse ICP-AES apres la dissolution dans l'aqua regia, donnent les valeurs semblables pour la plupart de PHE dans la plupart des sols examines. Ceci confirme que la determination d'ICP-AES frounit une indication accetpable de toutes les concentrations de PHE actuelles en ces materiaux.

La lixiviation des sols employent des methodes standard a indique que seulement une proportion tres petite de tout le present de PHE etait exposee et lixiviee en utilisant une gamme de compositions probables d'eaux souterraines les essais sequentiels d'extraction ont indique que c'est parcequ'une grand partie du present de PHE est sous les formes qui ne sont pas exposee a etre mobilisees dans des etats normaux d'eaux souttiraines. On l'a egalement confirme que la qualite de divers PHEs lixiviee des sols dependait de la composition du fluide de lixiviation. Bien que des condition s plus acides menent a une plus grande mobilisation de PHEs, la mineralogie et caractere materiaux comrennant la presence des carbonates, les minerals aargile, la matiere organique es les oxydes et les hydroxydes de fer sont exposes a contribuer a ces differences, mais davanage de recherche sur cet aspect est exigee. Les resultats suggerent egalement que les echantillons de sechage avant de lixivier puissent mener a une reduction de la quantite de PHE apparent actuel dans les echantillons. Clairement ceci a des implications pour l'evaluation de tels. Les materiaux souilles et on lui recommende que des echantillons soient stockes a la basse temperature.

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Keywords: Contaminated land, groundwater contamination.

INTRODUCTION

The city of Wolverhampton occupies around 70 km^2 within a region commonly referred to as the Black Country, which is located in the midlands of England, on the western edge of the South Staffordshire Coalfield (Figure 1). During and subsequent to the industrial revolution in the late 18th and 19th centuries, major heavy industries such as coal mining, pig-iron smelting and brass foundries became established in the area. Associated industries included coke and coal-gas making, manufacture of iron and steel products, tin plating, galvanising and chemicals manufacture. The rise and decline in this diverse range of industries is documented by Gale (1966) who reports that in 1790 the then largely rural area contained a total of 11 blast furnaces and that by 1863 the total had risen to 200. Due to a rapid decline in this industry during the 20th century, by 1959 there were only 2 furnaces remaining in a single works. During the period of industrialisation the population grew and the urban area expanded. There was a parallel increase in the transport infrastructure of the area, starting with the construction of the canal network during the 18th century. Many of these canals remain to the present day, but their cargo carrying capacity was hugely superseded by railways in the 19th century. The area is now also served by a network of motorways and trunk roads. The nature of the industries and their decline has given rise to a legacy of brownfield land, some of which is contaminated, and a need for urban redevelopment. This is required in order for the city to be attractive for inward investment and remain viable.

Development of brownfield land

In the UK, recent governments have responded to the decline in traditional industries and demographic changes by favouring a policy of increased pressure for the development of brownfield land. Such a policy also reduces the need for transportation and aims to reduce the pressure for development in rural areas. Recent data indicates that about 10% of land in some cities is classed as derelict, which means that it requires some form of treatment or clearance of structures before it can be beneficially reused and declassified as sterile land. The Government's Urban White Paper (Anon, 2000) set a target that 60% of all new housing in England should be constructed on brownfield or previously developed sites. While this target is concerned with housing, the major reason for redeveloping brownfield land is for industrial, commercial and leisure purposes. Not all unused and derelict land is contaminated, much of it is occupied by buildings that are no longer used or where there was a former, non-contaminating use. Contaminated land is defined as such in Part IIa of the Environmental Protection Act (DETR, 2000) as land that contains substances that may cause significant harm to receptors. In this definition, receptors include human beings, controlled waters, ecological systems and property. Nathanail and Bardos (2004) point out that whether significant harm is caused depends on the probability or frequency of occurrence of a harmful process, and that this requires that the nature and degree of harm, the susceptibility of receptors and the timescale within which the harm might occur also need to be considered. Under this definition, the fact that a piece of land contains potentially harmful substances does not mean that it will be classified as 'contaminated' if there is no pathway linking the harmful substance to a recipient. This does not mean that it might not be desirable to remediate such a piece of land, but it would not be included within this definition of contaminated land.

Not only is it the case that not all brownfield land is contaminated, but conversely some contaminated land is not vacant, derelict or otherwise defined as brownfield land. Existing and former industrial sites and reclaimed areas may need to be assessed in order to determine whether they constitute a threat to receptors.

Figure 1. Location of Wolverhampton

Potential for groundwater contamination in Wolverhampton

The possible leaching of contaminants from wastes and fills was the driver for a broad study of contaminant sources and groundwater, which is both a receptor and a pathway for the transport of contaminants, in Wolverhampton. This paper presents some of the results from this study. The main waste materials from the former industries comprise colliery spoil, metal rich slags, spent ores, ferrous and non-ferrous metal processing and engineering, chemical and gas works wastes, foundry moulding sand, canal dredgings and ash. In addition there is domestic refuse, building wastes and sewage sludge. Considering its origins, there is good reason to believe that much of this waste would contain high concentrations of potentially harmful elements (PHEs), particularly heavy metals. These materials were variously disposed of, usually close to their origins, without adherence to waste disposal protocols or compaction control. The possible impacts of any harmful substances they might contain were not formally considered. Some were used as materials for the construction of infrastructure embankments, or as fill to level land. In addition, largely uncontrolled discharges to the atmosphere and surface water courses by industry and road traffic have also contributed to contaminants deposited in the area. Some former industrial areas and areas of waste disposal in the city have been reclaimed as parks or playing fields. As most of this waste was utilised or deposited before the Waste Management Legislation of the mid 1980s was introduced, little, if any, attention was given to the potential for environmental damage posed by these materials.

Much data about the geological, hydrogeological and geochemical conditions and land use in Wolverhampton is presented in a GIS based experimental urban environmental survey called WolGIS (Bridge et al. 1997), carried out by the British Geological Survey (BGS). Figure 2, which shows the areas of made ground and extent of mining in Wolverhampton is taken from this report. A detailed account of the geology of the area of Wolverhampton is given by Whitehead et al. (1928) and is summarised by Czerewko et al. (2002). The south-eastern quarter and the north-eastern corner of the city are underlain by Middle Coal Measures rocks of Carboniferous age. This sequence contains exploited deposits of coal, ironstone and fireclay. A small area in the south of the city is underlain by limestones and mudrocks of Silurian age. These and the Middle Coal Measures rocks are in faulted contact with Upper Carboniferous Barren Measures and Permian rocks that underlie the central area and the remainder of the north-eastern quarter of the city. Triassic deposits, consisting mainly of sandstones, occupy the western half of the city and adjacent rural areas. Although glacial deposits are present in the eastern parts of the city, much of the outcrop of the Triassic sandstones is free of superficial deposits. As Figure 2 shows, much of the south-eastern quarter of the city is covered by made ground (mainly composed of colliery, foundry and metal works waste together with building waste and ash)

Although some coal was mined by surface methods and, on a limited scale during the second half of the 20th century, by open cast methods, the majority of the coal was extracted by underground methods. In order to accomplish this, and also to satisfy the demand for water, extensive groundwater pumping took place, leading to the lowering of groundwater levels by several tens of metres. The cessation of mining in this area at the end of the 20th century and the decline in the industrial demand for water has resulted in recovery in the levels of groundwater, probably to pre-industrial levels, by the early part of the 21st century. A hydrograph showing this recovery is presented by Czerewko et al. (2002).

The presence of industrial and domestic wastes in locations lacking facilities for controlling the migration of contaminants they might contain, gives rise to fears that surface and ground waters may become polluted due to saturation of, and infiltration into, these materials. The possibility of this happening is increased by the fact that wastes were often deposited in low-lying areas and valleys, close to their sources. Although the parts of the city that are underlain by Coal Measures rocks have a low groundwater resource potential, the western parts of the city and surrounding rural areas to the north, west and south of this, are underlain by Triassic sandstone, which is a regionally important aquifer. The saturation and leaching of the waste materials poses the risk of contamination of these groundwaters. The lack of significant superficial deposits covering the sandstone outcrops renders this formation particularly vulnerable to pollution due to infiltration from surface sources (Figure 3, Bridge et al 1997). Although it is unlikely that exploitable quantities of groundwater are present in the Carboniferous sequence, there is potential for contamination of surface water from this underground source. In addition, as the Permo-Triassic rocks are faulted against the Carboniferous sequence, extraction of water from the aquifer could result in it becoming contaminated by the migration of polluted mine water. Due to extensive mining within the Coal Measures sequence, the hydrological regime is liable to be much modified by the presence of open workings and fractured ground. Furthermore, mining subsidence effects increases the likelihood that fills or wastes would become saturated by rising groundwater.

Studies based on the chemical analysis of shallow soil samples for the urban and neighbouring rural area of Wolverhampton carried out by the BGS (Bridge et al., 1997) show extensive and serious contamination, particularly in the urban area. Figures 4 and 5 respectively illustrate the distribution of copper and lead, of which concentration levels and therefore contaminative effect is much greater in the urban area. Within this area the pattern of contamination is heavily controlled by the location of industry and main infrastructure routes along the valleys. Figure 3 shows the areas where lead in soils exceeds 500ppm, which is the trigger value set by ICRCL (1996). This trigger value has now been superseded by a risk based method of assessment based on Soil Guidance Values (Nathanail and Bardos, 2004). It should be appreciated that Figure 3 is based on the trigger value for gardens and the highest values of lead and the other PHEs occur in areas shown in Figure 2 to include many non-residential land uses. Nevertheless, it is important that the potential impact on ground and surface waters of this contamination is considered. It is also important to take into account the implications of any changes in land uses, particularly if this involves changes to groundwater chemistry or the introduction of sensitive targets to the area.

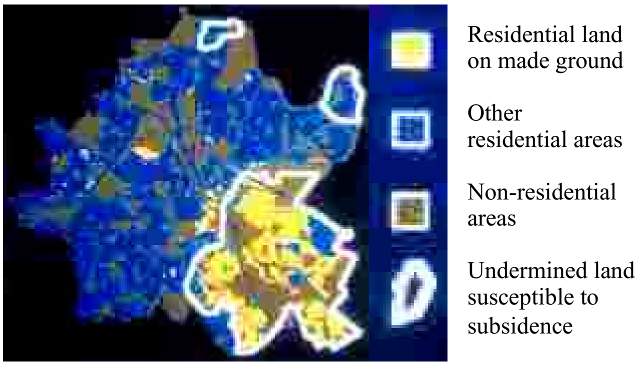


Figure 2. Residential areas of Wolverhampton in relation to made ground and mining.

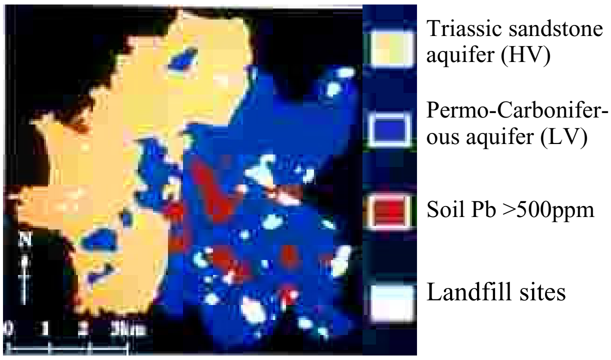


Figure 3. Aquifer vulnerability (HV – high, LV – low) and areas of high lead in soils

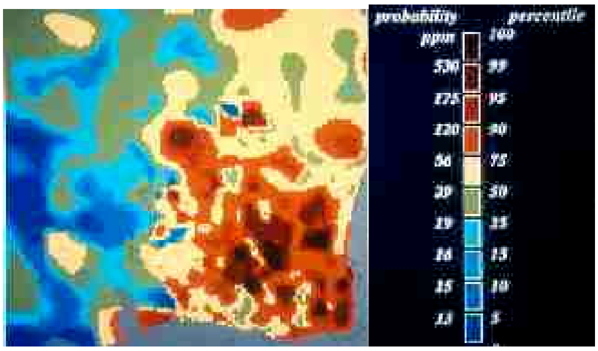


Figure 4. Concentration of copper in urban and rural soils in Wolverhampton. Urban area shown in Figs 2 and 3 outlined. For explanation of key see Fig 5.

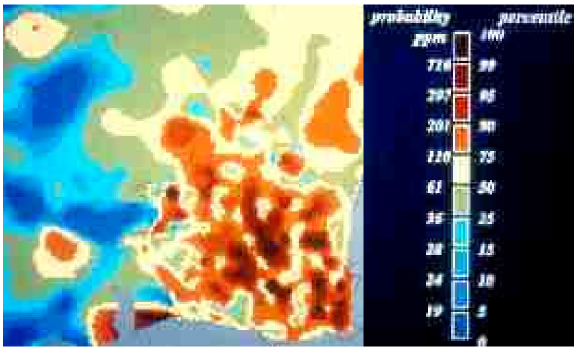


Figure 5. Concentration of lead in urban and rural soils. Values shown in ppm and probability of value more than amount shown.

The possibilities for contamination of ground and surface waters outlined in this paper apply to many other industrial cities in the UK and other countries. Nearly all the industrial cities of the north of England, the central valley of Scotland and South Wales, such as Manchester, Leeds, Sheffield and Glasgow, owe their presence to the availability of coal that resulted in heavy industry, including mining, metal working, chemical and gas works. The urban areas themselves generate wastes, including domestic refuse, building and sewerage and water treatment wastes. Like Wolverhampton it is unlikely that wastes and contaminated land were disposed of or remediated with due regard to any adverse impacts on the quality of the local ground and surface. Furthermore, rising groundwater levels are a common feature of urban areas in the UK.

Aims and objectives

The impact of contaminants in the range of fills and wastes present in Wolverhampton, and which are liable to be leached by surface infiltration of rising groundwaters, is strongly controlled by their solid and aqueous chemical speciation. This was assessed by carrying out detailed chemical characterisation on a suite of samples selected from a range of sites typical of the area. The sample site selection was assisted by the findings of the WolGIS report (Bridge et al., 1997) and advice was also provided by Wolverhampton City Council. The sample characterisation and assessment findings are supported by data from leaching experiments designed to simulate the reaction of contaminated land to a range of water types. These data along with speciation studies and detailed sample characterisation are being incorporated into a risk based model that will assist with the assessment of the vulnerability of areas to the effects of leaching. The overall aim is to help regulators formulate scientifically based strategies to mitigate against industrial pollution from the former industrial areas. Two aspects of the project are described here:

- Assessment of the composition of fill and waste materials and
- Effect of water composition on the leaching of heavy metals from the fills and waste materials.

SOIL SAMPLING AND TESTING

To satisfy the objectives of the project, samples of commonly occurring fills and wastes were collected from 30 sites in various parts of the city. These were subjected to total elemental analysis and selected samples were then subjected to detailed mineralogical studies and leached using different procedures in natural and simulated waters of various compositions, including groundwater, acid rain, acid mine drainage water and organic rich waters. The samples varied in soil type, origin and potential contaminants as shown in Table 1. The procedure used for taking the samples and for processing them in the laboratory is described by Czerewko et al. (2001). They were collected from below any topsoil present over a depth range of 0.12 m to 1.70 m below ground level using the procedure described by

Hooker et al. (1998). Care was taken to keep the samples cool and to prevent cross-contamination between sites. The individual sub-samples were thoroughly mixed and then a representative sample was taken and dried at 40°C for up to 5 days before being stored in hermetically sealed HDPE containers (following air evacuation) and finally stored at between 0 and 4°C until required for testing. Before testing each sample was carefully sieved to remove the >2 mm size fraction. Sampled material was also stored at natural moisture content for comparative leach testing.

Table 1. Details of samples selected for study

Sample , date and nat MC%	Sample locality, depth and area	Site description and former use	Geological conditions	Sample description
B1 19/02/99 17.1%	Greenfield Lane, Moseley. N. Wolves 0.12→0.75m bgl 5 holes: 3m×3m.	Residential area.	Triassic (Sherwood SST) Overlain by Boulder Clay & Sand and Gravel (Sa+Gr)	Silty fine SAND. With gravel of sandstone brick, clinker, ash and rootlets.
B8 30/03/99 20.2%	Oxley Moor, nr. Canal & Sewage wks. N.W. Wolves 0.20→0.80m bgl 5 holes: 3m×15m.	Park underlain by canal dredgings and possibly sewage sludge.	Triassic (Mercia SST) Overlain by Boulder Clay & Sa+Gr	Silty fine to medium SAND. With gravel of coal, ash, rock, tarmac, metal, concrete, brick, polystyrene and rootlets. Strong putrescent odour.
B12 19/05/99 17.9%	Pheonix Park.S. Wolves 0.30→0.85m bgl 5 holes: 5m×5m.	Former landfill site for domestic and industrial waste.	Carboniferous (Middle Coal Measures) overlain by Boulder Clay	Fine to coarse ash. With much gravel of brick, glass, stone, leather coal, bone, ceramic and polythene.
B14 20/05/9 18.4%	Monmore Green (Victoria iron works). E. Wolves 0.25→1.05m bgl 5 holes: 4m×4m.	Industrial area, site of derelict iron works, with much building waste.	Permo-Carboniferous (Enville Beds) Overlain by Boulder Clay & Sa+Gr	0.25-0.85m: Silty fine SAND. With gravel of ceramic, ash, brick, stone, coal, coke, metal and glass. 0.85-1.05m: Recovered as hard, blue grey, weathered mudstone.
B16 20/05/99 21.5%	Dudley Street, Coseley. S.E.Wolves 0.20→0.48m bgl 6 holes: 25m×25m.	Industrial area consists of derelict land and building refuse.	Carboniferous (Middle Coal Measures)	Silty fine SAND. Gravel of slag, metalliferous slag, ash, coal, brick, clinker and hard blue grey, weathered mudstone and rootlets.
B20 02/06/99 17.1%	Kenmar Way, of Rookery St., Heath Town E. Wolves 0.20→0.52m bgl 5 holes: 10m×10m.	Area of former metal works.	Carboniferous (Middle Coal Measures) Overlain by Boulder Clay & Sa+Gr	Fine to coarse SAND. With gravel of quartzite, brick, sandstone, slag, metalliferous slag, metal and soft cream concretions.
B23 02/06/99 13.2%	Blakenhall Gdns. /Infant Sch., Blakenhall.S. Wolves 0.30→0.75m bgl 5 holes: 3m×3m.	Residential area on the edge of area of light eng-ineering works.	Permo-Carboniferous (Enville Beds) Overlain by Boulder Clay & Sa+Gr	Silty fine to medium SAND. With gravel of sandstone, quartz, brick, cellophane, ceramic and rootlets.

Sample characterisation

Representative portions of the <2 mm fraction were analysed as follows:

- Total elemental contents by aqua regia digestion (3:1 HCl : HNO_3) and ICP-AES analysis
- Total major and minor elemental contents by XRF analysis of fused discs and pressed powder samples.
- Batch leaching experiments using leachates of various compositions with leachants analysed by ICP-AES.

The total elemental determinations were carried out on materials that had been milled to produce fine powders. As aqua regia does not break down silicate minerals, it is possible that this method might under-estimate the total amount of elements that are chemically bonded in silicate minerals. HF dissolution achieves complete dissolution of e samples, including silicates, however HF is a highly dangerous substance that requires special handling, such that its use was deemed to be too hazardous. The compositions of the leachants used in the batch leaching experiments are shown in Table 2. One of the tests was carried out on samples that had not been dried, and therefore it was at its natural moisture content. Simulated rainwater was used for this test and undried samples are therefore designated SRWn. For all other leaching tests oven dried samples were used, so in the case of the batch leaching tests the designation SRWo, AMWo etc is used.

In addition to the tests listed above, the mineralogy of each sample was quantified by means of whole rock XRD and the distribution of leachable elements was determined by sequential extraction following a 4-stage procedure modified from Tessier et al. (1979), but the results of these tests are not reported here. Further tests that were carried out, but not reported here, were total carbon and nitrogen concentrations using high temperature combustion and a variety of different leaching tests. The leaching included column leaching experiments and sequential batch leaching tests in which several phases of leaching were carried out, with fresh leachant solutions for each phase. Some additional batch tests in which the liquid to solid ratio was changed from the standard 10:1 were also performed. In the case of the leaching tests, the leachants were analysed using ICP-AES.

Table 2. Characteristics of leaching solutions used in batch leaching experiments

Type of water	Source	pH	Redox (Eh)	Symbol
Simulated rainwater	Deionised water equilibrated by overnight exposure to atmosphere	5.9	240	SRW
Deionised water	Laboratory deionised water	4.83	197	DIW
Acid mine water	Sampled at coal seam discharge	5.6	223	AMW
Equilibriated mine water		7.3	263	EMW
Sheffield groundwater	Sampled from 62m deep borehole in Coal Measures	6.8	42	SGW
Natural humic water	Sampled from moorland peat spring	3.9	391	NHW
Acid humic water	Sampled from acid mine discharge passing through peaty soil	5.0	373	AHD
Simulated acid rain	Simulated rainwater acidified with HNO_3	1.9	541	SAR1
		3.3	472	SAR2
		4.2	423	SAR3

RESULTS AND DISCUSSION

Two sets of results are presented and discussed: comparison of the total elemental determinations by XRF and the aqua regia dissolution with ICP-AES analysis of the resulting leachate and the results of batch leaching experiments in which different leachant compositions were employed. Comment is also made on implications of the type of contaminants detected in the samples.

Comparing XRF with ICP-AES analyses

The results of the XRF and ICP-AES determinations for certain PHEs in the samples chosen for detailed study are presented in Table 3. Descriptions of the samples are presented in Table 1. As shown in Figure 6, the most significant PHEs are copper and zinc. Cadmium is high in the sample of fill consisting mainly of colliery spoil and there are also significant amounts of chromium, nickel, arsenic and lead in several of the samples. Comparing these values with the Soil Guidance Values for gardens indicates that several of these results would be of concern if sensitive land uses were planned. It is noticeable that apart from Samples B1 and B12, there is generally good agreement between the two methods of determination, suggesting that in most cases the PHEs are not associated with the acid resistant minerals, such as silicates. On the other hand it does not mean that they are liable to be leached into groundwater under normal groundwater conditions. However, it is reassuring that for 5 out of the 7 samples dissolution using aqua regia and analysis by ICP-AES, which is cheaper and more convenient method to carry out than XRF, provides a reliable indication of the present and amount of these PHEs. The work also confirms that there is no obvious advantage in using HF dissolution compared with aqua regia.

Table 3. Comparison of selected PHE concentrations determined by XRF and ICP-AES

Method	XRF							ICP-AES					
Sample	Cr	Ni	Cu	Zn	As	Cd	Pb	Cr	Ni	Cu	Zn	Cd	Pb
B1	169.1	240.5	946.4	829.4	< 3.4	4.9	226.6	11.45	7.803	10.05	43.64	0.122	18.28
B8	63.9	26.9	99.5	226.1	<1.8	1.6	101	31.78	22.93	94.21	220.7	0.481	107.3
B11	150.3	42	99.6	322.9	11.5	1.7	200	46.3	29.08	82.24	307.6	1.213	204
B12	38.1	16.4	34.1	88.6	< 1.0	0.8	29.9	70.79	173.4	559.7	678.7	1.388	246
B14	104.1	52.7	182.5	534.2	7.4	2	692.5	37.27	43.07	129.8	510.2	1.446	2663
B16	185.8	106.9	260.7	3067	42.3	25.9	878.9	124.9	100.5	231.4	4691	9.601	1246
B17	135.6	45	35.7	84.4	6.2	0.4	30.8	32.02	34.64	29.54	74.31	0.074	12.42
B20	187.1	92.3	328.6	928.3	26.4	4.9	225.7	166.4	57.1	275.6	828.1	1.19	248.1
B23	105.9	97.4	310.4	576.1	15.6	2.8	183.2	35.58	92.04	279.8	575.1	2.036	179.1

In the case of sample B1, it would appear that there is a very large amount of zinc and copper present in a form that is resistant to dissolution by aqua regia. Similarly high amounts of copper and zinc have been found in other samples, but in these it was taken into solution by the aqua regia. On the other hand, the behaviour of Sample B12, in which the amounts of copper and zinc found by XRF are much lower than those found by acid dissolution and ICP-OAS analysis, is more difficult to explain, although it may be caused by spectral interference caused by carbonaceous or synthetic materials in the sample. In both cases, consideration of the mineralogy and the possible presence of exotic constituents could clarify the position, but this is not possible here.

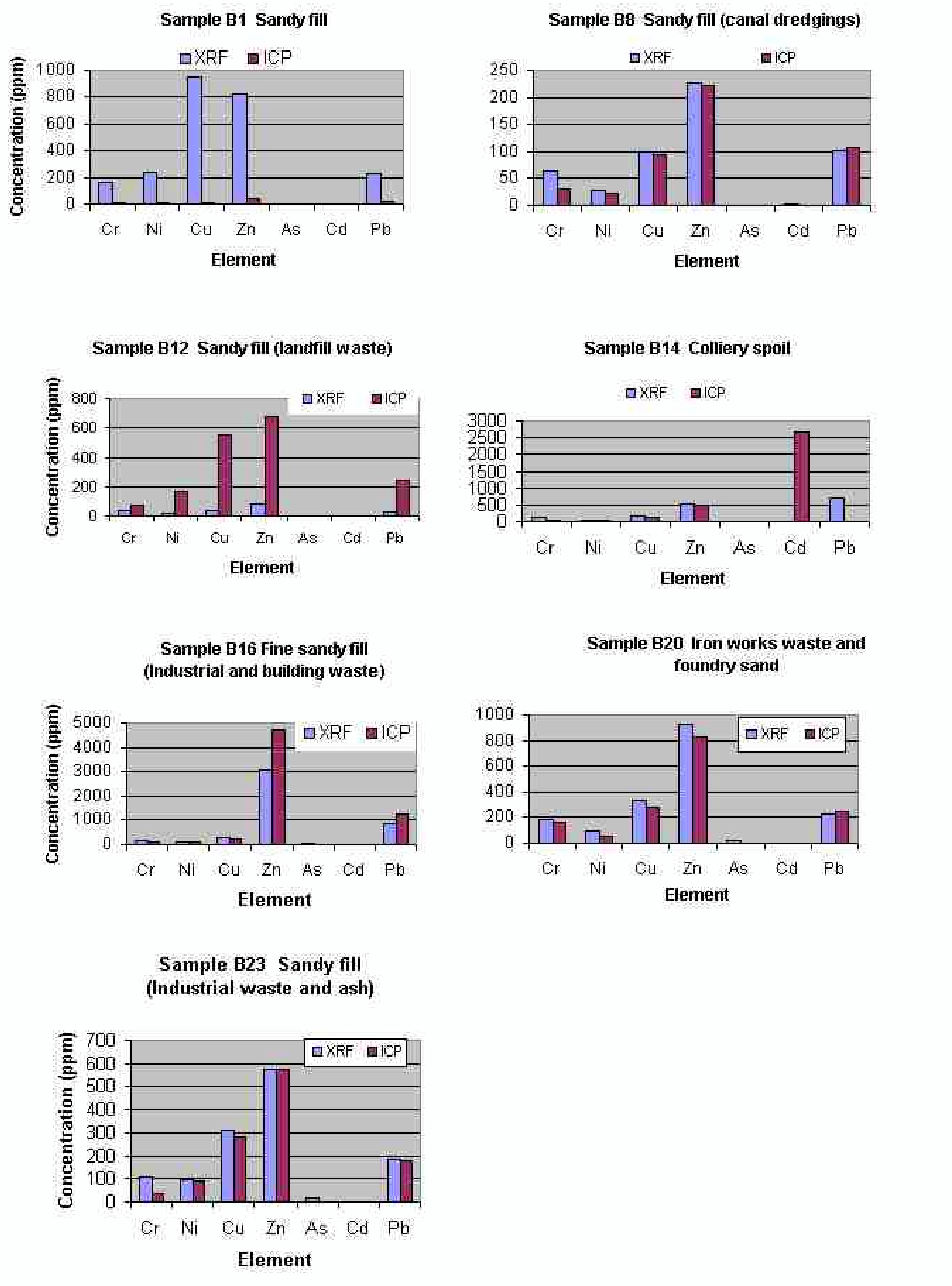


Figure 6. Compositions of samples determined by XRF and ICP-AES

Effects of different leaching solutions

Standard leaching tests were carried out using deionised water. Such conditions would not normally be found in nature; therefore it is of interest to investigate the effects of using the waters of other compositions, as shown in Table

2. As shown, the leachates vary in acidity (pH) and redox (Eh) which control the stability of chemical species in solution. In fact the pH and Eh are approximately linearly related, as Figure 7 demonstrates. The results of these tests for the range of PHEs are shown graphically in Figure 8, where the elements are presented in the order Cr, Ni, Cu, Zn, As, Cd and Pb. Overall the amounts of PHEs liberated by the waters are tiny compared with the total amounts present. This effect was investigated by carrying out sequential extraction tests in which samples are subjected to a 3-stage dissolution, the preliminary results of which are presented by Czerewko et al. (2002). This shows that for all the PHEs except cadmium, only a small proportion of the PHE present in the material is an exchangeable or available form. In some cases a high percentage is present in the inert residual form. Further PHEs are present in reducible and oxidisable forms. As the oxidisable conditions are equivalent to the carbonate phase such chemically aggressive conditions are considered unlikely in normal groundwater.

A common feature of the results is the dominance of zinc (the 4th bar from the left) in nearly all the samples. Copper is another PHE that occurs in many of the leachates. In the case of Sample B20, the amount of zinc recorded for simulated acid rain (SAR2) is probably anomalously high (a value of 609.03 ppm) and in order to allow the display of the results for the other PHEs present in the leachant, the amount of zinc is not shown.

The results allow a comparison to be made between the results obtained for samples that were preserved at their natural moisture content until they were tested, and samples that were dried and stored before being tested. The leachant used in these particular tests was simulated rain water (SRW), see Table 2. By comparison of the results for SRWn and SRWo in Figure 8, it would appear that for most samples drying has caused a reduction by about 50% in the amount of PHE leached, when other variables such as temperature, liquid to solid ratio, time and degree of agitation are equal. Presumably this is because drying caused the precipitation of certain PHE containing compounds which were not redissolved during leaching. The exceptions to this behaviour are Samples B20 and B23, iron works waste plus foundry sand and industrial sandy fill with ash respectively, which do not show sensitivity to having been dried. It is hoped that further investigations into the chemical and mineralogical hosts for the PHEs will provide an explanation for this behaviour.

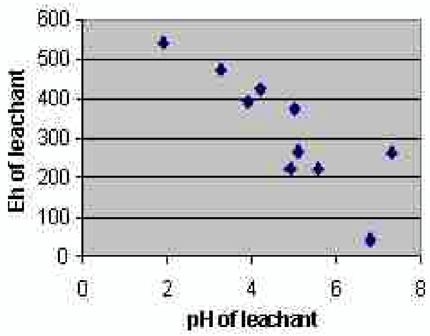


Figure 7. Relationship between Eh and pH of leachant solutions

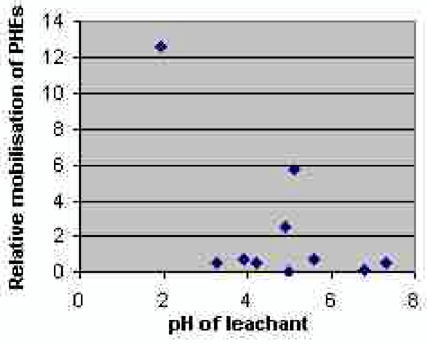


Figure 9. Relationship between relative mobilisation of PHEs and pH of leachants

As Figure 8 (the data for which is shown in Table 4) demonstrates, the amount of PHE taken into solution varies with PHE type and also depends on the composition of the leachant. The type of leachant acts selectively on different PHEs with, in the cases of Samples B8 and B12 which are sandy wastes arising respectively from canal dredgings and landfill wastes, sorption of zinc in the acid humic water (AHW). Generally speaking the acid mine waters, the humic water and lower acidity simulated acid rain leach smaller amounts of PHEs than the simulated rainwater, deionised water and high acidity acid rain. To investigate whether there was a correlation between the amount leached and pH and/or Eh the relative PHE mobility for each leachant was plotted against the original pH of the leachant in Figure 9. The relative mobility for leachant L is given by the following equation:

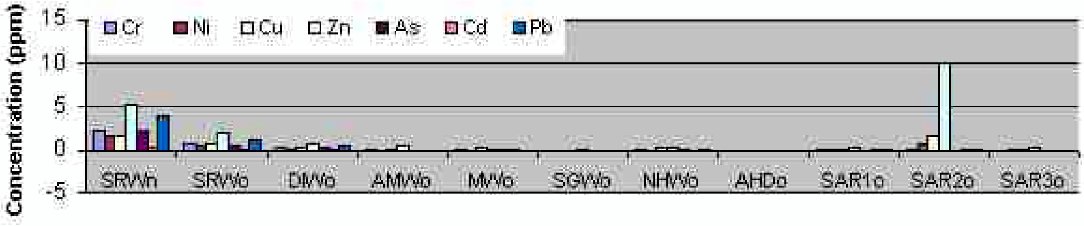
$$\text{Relative mobility} = \sum \left\{ \frac{\sum_{e} c_{e,s,L}}{\sum_{l} \left[\sum_{e} c_{e,s,L} \right]} \right\}$$

where e denotes element, s the sample type, and l the leachant type. It can be seen that the correlation between relative mobility and pH is poor as there is much scatter in the data, giving relatively low dissolution of PHEs in some samples in spite of low pH conditions. At this stage, all that can be said for the samples tested is that there is not a simple relationship between leachant chemistry and the amount of PHE taken into solution. More work is required on the detailed mechanisms of dissolution given the mineralogy and chemistry of the samples concerned.

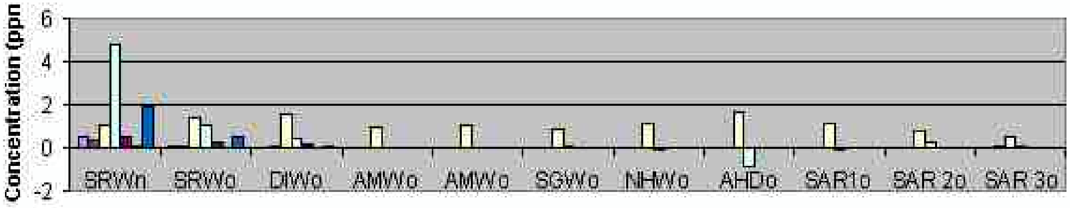
Table 4. Concentrations of PHE mobilised in batch leaching tests with different leachant compositions.

Sample	PHE	Leachant (n – sample not dried, o – sample oven dried during preparation, minus – element sorbed)										
		SRWn	SRWo	DIWo	AMWo	EMWo	SGW	NHW	AHDo	SAR1o	SAR2o	SAR3o
B1	Cr	2.202	0.671	0.239	0.019	0.020	0.000	0.030		0.014	0.104	0.000
	Ni	1.349	0.474	0.199	0.000	0.000	0.000	0.000		0.016	0.027	0.090
	Cu	1.538	0.682	0.419	0.0166	0.250	0.000	0.271		0.124	0.790	0.109
	Zn	5.162	1.903	0.758	0.566	0.211	0.143	0.371		0.283	0.272	0.299
	As	2.144	0.633	0.349	0.000	0.035	0.000	0.064		0.000	0.000	0.000
	Cd	0.429	0.102	0.040	-0.005	0.008	0.000	-0.108		0.010	0.021	0.000
	Pb	3.978	1.325	0.538	0.000	0.000	0.000	0.057		0.021	0.000	0.000
B8	Cr	0.571	0.671	0.050	0.025	0.037	0.000	0.035	0.000	0.019	0.012	0.024
	Ni	1.349	0.474	0.0130	0.000	0.000	0.000	0.000	0.000	-0.005	0.027	0.080
	Cu	1.538	0.682	1.620	0.971	1.113	0.929	1.185	1.651	1.154	0.017	0.570
	Zn	5.132	1.903	0.480	0.014	0.035	0.102	-0.037	-0.083	-0.071	0.000	0.092
	As	2.144	0.633	0.180	0.000	0.000	0.000	0.1810	0.000	0.000	0.028	0.029
	Cd	0.429	0.102	0.010	-0.017	0.003	0.000	-0.113	0.000	0.004	2.636	0.000
	Pb	3.978	1.325	0.120	0.000	0.000	0.000	0.000	0.000	0.000	0.0523	0.000
B12	Cr	0.000	0.021	0.030	0.000	0.000	0.000	0.000	0.000		0.000	0.000
	Ni	0.046	0.079	0.060	-0.149	0.000	0.000	0.000	0.000		0.017	0.068
	Cu	0.170	0.606	0.699	0.0.822	0.724	0.700	0.899	0.682		0.885	0.633
	Zn	0.107	0.102	0.529	0.0235	0.039	0.158	-0.116	-0.770		1.571	0.072
	As	0.0160	0.094	0.160	0.000	0.000	0.000	0.000	0.000		0.000	0.000
	Cd	0.003	0.004	0.000	-0.021	0.004	0.000	-0.012	0.000		0.022	0.003
	Pb	0.111	0.123	0.015	0.000	0.000	0.000	0.000	0.000		0.000	0.000
B14	Cr	0.524	0.293	0.0180	0.000	0.0003	0.000	0.000	0.000		0.000	0.000
	Ni	0.331	0.241	0.150	0.000	0.000	0.000	0.000	0.000		0.000	0.053
	Cu	0.991	0.762	0.719	0.251	0.386	0.068	0.530	0.125		0.214	0.200
	Zn	5.874	2.606	7.139	0.881	0.468	0.529	0.490	0.117		6.370	0.427
	As	0.575	0.479	0.340	0.000	0.000	0.041	0.000	0.000		0.0180	0.000
	Cd	0.069	0.037	0.010	-0.018	0.006	0.018	-0.018	0.000		0.029	0.000
	Pb	6.727	2.943	1.818	0.134	0.279	0.077	0.603	0.000		0.338	0.161
B16	Cr	0.091	0.0168	0.0185	0.051	0.0158	0.026	0.064		0.120	0.067	0.0146
	Ni	0.581	0.040	0.040	-0.023	0.000	0.000	0.000		-0.020	0.028	0.042
	Cu	0.135	0.396	0.390	0.289	0.299	0.119	0.442		0.270	0.086	0.0173
	Zn	1.383	0.187	0.305	0.393	0.138	0.394	-0.022		-0.020	1.070	0.110
	As	0.036	0.036	0.095	0.000	0.000	0.000	0.000		0.000	0.000	0.000
	Cd	0.017	0.005	0.000	-0.006	0.003	0.000	-0.017		0.010	0.034	0.000
	Pb	0.410	0.058	0.000	0.000	0.000	0.000	0.000		0.010	0.000	0.000
B20	Cr	0.0126	0.266	0.0140	0.019	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Ni	0.146	0.273	0.220	0.000	0.000	0.000	0.000	0.000	0.000	2.636	0.048
	Cu	1.419	1.336	0.863	0.166	0.000	0.000	0.379	0.000	0.179	2.699	0.004
	Zn	5.682	7.945	5.221	0.566	3.758	7.241	5.092	11.76	4.776	609.29	2.600
	As	0.908	1.029	0.654	0.000	0.000	0.000	0.064	0.000	0.000	0.305	0.070
	Cd	0.027	0.072	0.025	-0.055	0.000	0.000	0.007	0.000	0.011	0.288	0.000
	Pb	0.981	1.996	0.988	0.000	0.000	0.000	0.156	0.000	0.000	0.000	0.188
B23	Cr	0.378	0.415	0.065	0.008	0.000	0.000	0.000		0.010	0.036	0.000
	Ni	0.579	0.791	0.195	0.000	0.000	0.000	0.000		0.000	0.523	0.091
	Cu	1.532	2.241	0.993	0.477	0.459	0.394	0.969		0.640	0.970	0.537
	Zn	4.974	5.003	0.963	0.442	-0.610	0.195	0.094		0.190	13.979	1.361
	As	0.486	0.638	0.224	0.000	0.000	0.000	0.035		0.030	0.270	0.066
	Cd	0.058	0.064	0.005	-0.016	0.000	0.000	0.003		0.030	0.081	0.000
	Pb	1.606	1.602	0.274	0.000	0.000	0.000	0.044		0.040	0.112	0.000

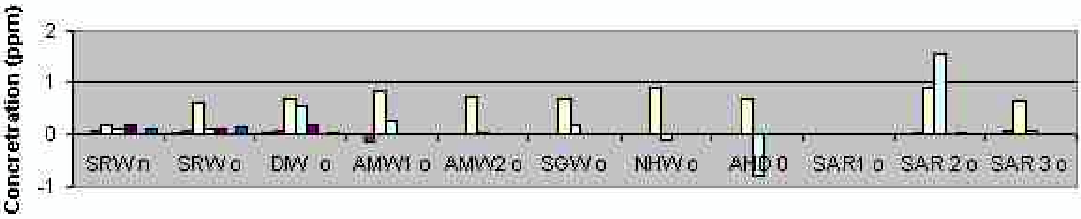
Sample B1 Sandy fill



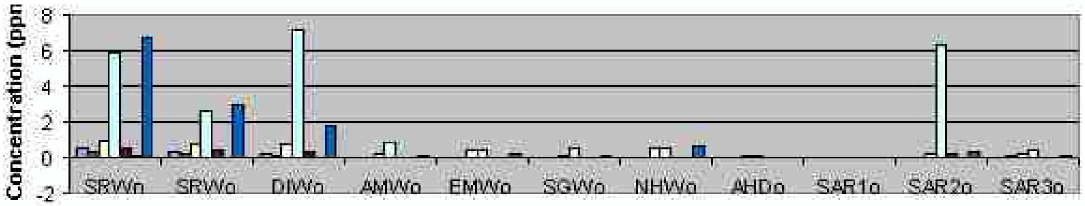
B8 Sandy fill (canal dredgings)



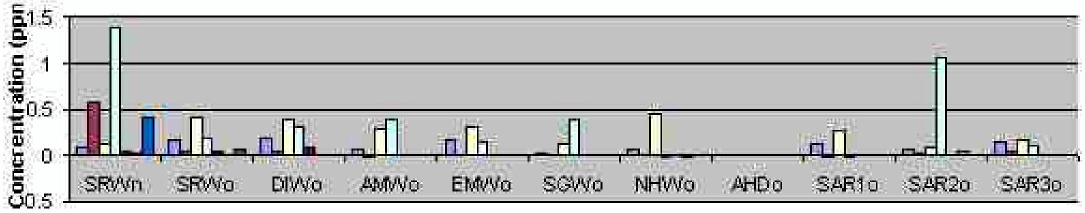
Sample B12 Sandy fill (landfill waste)



Sample B14 Sandy fill (Iron and foundry works waste)



Sample B16 Fine sandy fill (Indusrial and building waste)



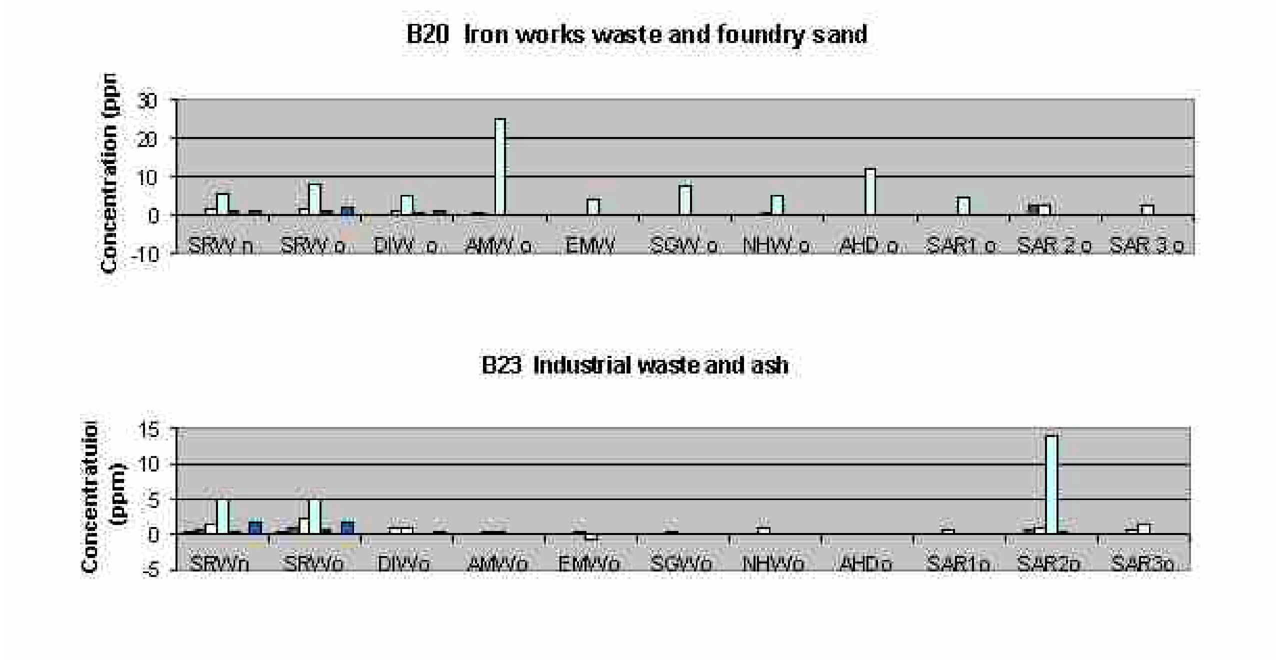


Figure 8. Effects of leachate compositions on the mobilisation of PHEs in batch leaching tests

Multi-stage batch and column tests

Although simple to carry out, the batch tests reported above suffer a number of disadvantages. Probably the most important of these is the swamping of the solution with relatively soluble anionic species, which then inhibits the release of PHEs. Column leaching tests in which a continuous supply of fresh leachate percolates through the sample at a predetermined rate and multiple stage tests in which the leached sample is repeatedly placed in fresh leachate were also carried out on these samples.

These tests and also batch tests in which the liquid to solid ratio has been changed from the standard 10:1 allowed the effects of time of leaching to be simulated. Simple batch tests give results that are representative of short-term (perhaps a few days to a few months) in situ leaching depending on groundwater and surface water infiltration rates, whereas column tests are more representative of conditions in which leaching continues for tens of years. The preliminary results of these tests are presented by Czerewko et al. (2001). Briefly, they confirm the restriction of leaching that occurs in the single stage batch test. They also show that the 3 stage batch, or cascade tests provide results that are similar to the column tests, however, they are much easier to carry out. Furthermore, it is less difficult to standardise the cascade test procedure compared with the column test, in which the results may be affected by the packing of the sample in the column and the possibility of preferential flow of leachant between the sample and the inside wall of the column.

CONCLUSIONS

- This study of waste material and fill collected from redeveloped and brownfield sites that are present in the City of Wolverhampton confirm that a significant amount of these are contaminated with high levels of various PHEs. Therefore with rising groundwater levels and changes in the pattern and composition of infiltration that may occur with redevelopment of brownfield sites, there is potential for mobilisation of PHEs and the risk of pollution of surface and groundwaters.
- Parallel determinations of PHEs by XRF analysis and ICP-AES analysis, following aqua regia extraction, give similar values for most PHEs in most of the soils tested. This confirms that ICP-AES determination, which is cheaper and more convenient to carry out, provides an acceptable indication of the total concentrations of PHEs present in these soils.
- Leaching of the soils using standard batch leaching methods indicates that only a very small proportion of the total PHEs present are liable to be leached using a range of likely groundwater compositions. Sequential extraction tests indicate that this is because most of the PHEs present are in forms that are not liable to be mobilised under normal groundwater conditions.
- The results suggest that drying samples prior to batch leaching can lead to a reduction in the amount of PHEs apparently present in samples. Clearly this has implications for the assessment of such contaminated materials and it is recommended that samples are stored at low temperature (0-4 ^{0}C) in air evacuated hermetically sealed containers and tested as soon as practically possible after sampling.
- No strong correlation was found between the pH of the leaching solution and the amount of, PHEs are released. Scatter in the data is attributed to such factors as variation in the buffering capacity and the availability of sorption sites in the soils tests

Further consideration of the composition and structure of the soils tested is required for a fuller understanding of PHE mobilisation, including the impact on water quality. Laboratory leaching tests are limited in that they only consider short- to medium-term scenarios, whereas in the longer term or under conditions of increased volumetric flushing by groundwater and under variable redox states, the removal of inert cements of coating minerals such as oxides and sesquioxides may eventually expose PHE to the leaching environment. Notwithstanding this possibility, in view of the widespread occurrence of these contaminated materials in the City, careful consideration should be made of the implications of development proposals entailing changes to groundwater levels and composition and of land uses, especially ones that are liable to increase risk to sensitive targets such as people.

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