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Review

Integrating phytoremediation with biomass valorisation and critical element recovery: A UK contaminated land perspective

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A B S T R A C T

In the UK, the widespread presence of elemental contaminants such as arsenic and nickel in contaminated sites and more widely release of platinum group metals into the biosphere are growing concerns. Phytoremediation has the potential to treat land contaminated with these elements at low cost. An integrated approach combining land remediation with post-process biomass to energy conversion and high value element recovery is proposed to enhance the financial viability of phytoremediation.

An analytical review of plant species suitable for the phytoremediation of nickel, Arsenic and platinum group metals is reported. Additionally, a preliminary model is developed to assess the viability of the proposed approach. A feasibility appraisal using Monte Carlo simulation to analyse project risk suggests high biomass yield plant species can significantly increase the confidence of achieving financial return from the project. The order of financial return from recovering elements was found to be: Ni > Pt > As.

Contents

1. Introduction

Soils contaminated with metal and metalloid elements pose a major environmental and human health risk. Amongst the identified elemental contaminants, Arsenic (As) and nickel (Ni) are two of the most common ones. Due to their ubiquitous occurrence on contaminated sites, concentration levels and high risk factors, both elements are listed as priority inorganic contaminants under the UK Part 2A regime [1]. Platinum group metals (PGMs) on the other hand, have only limited distribution in the environment and inert chemical and biochemical properties; therefore have not been

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recognised as priority soil contaminants. However, the increasing use of PGMs in the past few decades in vehicle exhaust catalysts, as well as in several other industrial and medical applications has led to a heightened soil concentration of PGMs, especially in urban high-traffic areas [2] as well as high value losses in mining areas. Consequently, these increases have given rise to public health concerns [2].

In the UK, metals and metalloids are the most widespread soil contaminants present in over 80% of all identified sites in England and Wales [3]. Management and remediation of these sites is clearly of public interest. From an environmental perspective it is desirable to rehabilitate contaminated sites to the highest possible standard, regardless of the potential costs. In practice, such approaches impose a heavy financial burden on government expenditure, as demonstrated by the Dutch government since their adoption of this approach in the early 1980s. According to Honders et al. [4], it was estimated that if all the identified sites in Holland were treated to the standard required by legislation, the total remediation costs would be in the order of 50 billion euros. By 1997, it was evident that the 'Dutch system' was not financially sustainable and the government changed their system to a more cost-effective 'function-orientated' approach adopting a risk-based management system, similar to the UK [5].

UK contaminated land is regulated by a framework of legislation and policies underpinned by the contaminated land regime (as stipulated in Part 2A of the Environmental Protection Act 1990, or simply Part 2A) and land-use planning regime Within this regime the Town and Country planning Act 1990 is the most important). The underlying concept of the UK system emphasises on a risk-based approach [6] and reliance on the land-use planning system (87% in England and 79% in Wales) to fund remediation work when the site is developed and redeveloped [3]. This approach, in contrast to the 'Dutch system' has proved to be more cost-effective for government intervention. However this approach is limited to urban areas where there is a rapidly expanding land requirement for residential and commercial development, and no lack of financial drive for developers to undertake remediation work. In rural and lower value areas where commercial land development is less competitive, there remain a large number of contaminated sites with remediation work pending due to financial barriers. According to the latest survey carried out by UK Environmental Agency, by the end of 2007, of the 746 contaminated sites which had been identified under Part 2A, only 144 were reported as completely remediated [3].

Remediation of elemental soil pollutants presents distinct scientific and technical challenges, as unlike organic pollutants these cannot be degraded further into non-harmful products. Therefore the only way to remediate toxic elemental pollutants is to remove or sequester them from the soil. Current technologies available for remediation of elemental pollutant including in-situ or ex-situ chemical treatment, biological treatment, soil washing, soil flushing, vitrification, incineration and landfilling [7].

Remedial treatments for contaminated sites in the UK are currently dominated by excavation and off-site disposal of material. This practice is used almost exclusively for remedial work of this type and regarded as the likely solution for all future work in the view of Environmental Agency [3]. Preference for this 'dig and dump' approach is due to its straightforward operation and short project time frame. However, volatile emissions, odour nuisance and noise during the excavation stage as well as possible secondary contamination during transport and landfill are evident risks. In addition to the environmental concern, increasing landfill taxation result in this method not being variable/feasible in the long term [8].

Phytoremediation technology uses plants to extract and translocate contaminants to above-ground tissues for later harvest, i.e. phytoextraction; converting the element to a less toxic chemical species, i.e. transformation; or at the very least sequestering the element in roots to prevent leaching from the site i.e. phytostabilisation. As a competing technology, phytoremediation offers a low cost, albeit slower alternative to physical and chemical treatment methods [9] and is viable in mitigating contamination levels for a wide range of organic and inorganic contaminants. However, as a biological method, phytoremediation is limited by a number of factors such as the long treatment time and site/contaminant specificity etc. In addition, a key inhibiting factor for commercial implementation of phytoremediation is the disposal of large quantities of contaminated plant biomass material that accumulate throughout the process [10,11]. When contaminant concentrations in the biomass exceed specific levels, the biomass material is regarded as potentially hazardous, therefore must be stored or disposed of appropriately [12]. Here, a radical approach to address this disposal problem by incorporating a thermochemical conversion of biomass to renewable energy followed by a metal(loid) recovery stage to the process is proposed. The feasibility of using phytoremediation technology to remediate selected elements from contaminated sites which are not on the local authorities' priority list is reviewed, then follows discussion of the feasibility of such an integrated approach to maximise economic benefit from phytoremediation alongside biomass energy production and high value metal recovery.

2. Phytoremediation and plant selection

Phytoremediation as a discipline in environment sciences was established in late 1970s following the discovery of a series of hyperaccumulators [13]. Since then the field has developed attracting not only scientific interest but attention from private and industrial site owners, regulators and the environmental engineering community [9]. To date, intensive research in this area has resulted in a significant improvement in knowledge of hyperaccumulators and their elements of affinity. It is now generally agreed that in order to distinguish 'hyperaccumulator' from normal or accumulator, a set of threshold values of elemental concentrations in plant biomass (dry weight) are used to define hyperaccumulation: Mn and Zn hyperaccumulators contain >10,000 μg/g [14], hyperaccumulators of As, Co, Cu, Ni, Se, and Pb have >1000 μg/g [14,15], and hyperaccumulators of Cd have >100 μg/g [14].

The mechanism and rationale of phytoremediation has been discussed in a number of reviews [16–20]. Depending on contaminants, the site conditions, level of clean-up required and the plant species, it involves the use of plants to extract, sequester, and/or detoxify pollutants [21]. The concept of using plants to uptake environmental contaminants from soil is not new, however it is only in the twentieth century, after a series of discovery of hyperaccumulator and vast advance of analytical techniques, has the concept of phytoremediation been rapidly developed [14].

In recent years, research on phytoremediation has shown the overall environmental and economic benefits from land remediation. Current research trends are focusing on maximising the use of by-products from phytoremediation process. Researchers are also exploring the use phytoremediation biomass as a renewable energy source [22,23]. In addition, the concept of moving from 'phytoremediation' to 'phytomining' to reclaim potentially valuable elements for further economic benefits is underway.

The greatest advantage of phytoremediation is low cost. According to a European scale study [7], the average cost for on-site phytoremediation and off-site landfilling are 122 and 231 Euro per m^3, respectively. In the American market, similar cost advantages from phytoremediation exist. It is generally agreed that the estimated cost for phytoremediation of soil is in the range of 25–100 US dollars per ton [9], in contrast to approximately 150–350 US dollars per ton for conventional excavation-landfill approaches [24]. In addition to the cost, phytoremediation offers better performance compared to the conventional approach, e.g. permanently removal of the contaminants, less disturbance to the site. It has to be noted that phytoremediation will more readily remove the bioavailable fraction of the contamination, and is therefore more compatible with risk-based contaminated land management systems [9]. The common perception towards disadvantages of phytoremediation is the substantially longer time scales required for remediation to be completed. This disadvantage has excluded phytoremediation as a mainstream technology solution for urban contaminated sites. It should also be noted that the specificity of hyperaccumulators result in selective remediation which is less effective for sites with multiple contaminants [25].

Selecting the right plants for phytoremediation from the wide range of candidates is the most important stage of such project. In general rule achieving a high bioaccumulation factor (BF, defined as the ratio of element concentration in plant biomass to that in soil) and high translocation factor (TF: defined as the ratio of element concentration in above ground shoots to that in roots) is key. However, when land remediation is not the sole goal of the project and downstream processes for element and energy recovery are desired, other factors such as high biomass yield and tolerance to the contaminants also become relevant. The rationale to support this decision making is discussed in the following section.

2.1. Arsenic phytoremediation

Arsenic is a metalloid which is considered non-essential and toxic at high concentration to plants and animals. In the UK, particularly in the Southwest, large areas of soil are considered contaminated with As, either geogenically or from anthropogenic activities such as mining and smelting [26]. In other part of the world, Arsenic-contaminated soil is one of the major sources of arsenic in drinking water [27], and also results in high arsenic level in cereals, vegetables and fruits grown on the contaminated soil. All chemical species of arsenic are bioactive [28] and therefore can be readily absorbed by animals and plants. This biochemical property of arsenic gives rise to intensive research into hyperaccumulators which can be applied for the phytoremediation of arsenic. A number of studies report that the ability to tolerant and accumulate arsenic in many plant and phytoplankton species. This can be largely attributed to the production of intracellular thiols such as glutathione (GSH) and phytochelatins (PCs) which are chelators with a strong affinity to arsenic [29–31].

Among the numerous arsenic hyperaccumulating plants reported to date, the majority belong to the fern *Pteris* family (Table 1). The first arsenic hyperaccumulator *Pteris vittata* was reported in 2001 by Ma et al. [15]. The plant is a mesophytic fern that capable of accumulating arsenic in the above ground frond within the range of 2500–22,630 mg kg^{-1} on a dry weight (DW) basis, ~100-fold higher than soil concentrations [15,28]. This discovery has led to intensive screening of the fern *Pteris* family for other potential arsenic hyperaccumulators [28,32]and as a result, a number of species in the family such as *Pteris cretica* and *Pteris umbrosa*, have been recognised as arsenic hyperaccumulators.

The high BF, TF and reasonable biomass yield of *P. vittata* has prompted notable attention from commercial phytoremediation projects. Field studies have been conducted on a number of occasions. Gray et al. [26] demonstrated in field studies carried out in southwest England that *P. vittata* and *P. cretica* are both suitable for climate conditions in that region. After exposure of soil total arsenic concentrations of 471 mg kg^{-1}, both species exhibited a high efficiency of bioaccumulation and root to shoot translocation, with most of the arsenic accumulated in the frond (4371 and 2344 mg kg^{-1} for *P. vittata* and *P. cretica*, respectively.) However the relatively low above ground biomass yield from *P. vittata* which averaged at 0.76 t ha^{-1} of (on dry weigh basis) has been concluded to be the main drawback for achieving high arsenic extraction in the field study.

Kertulis-Tartar et al. [33] carried out a 2-year field study using *P. vittata* for phytoremediation of the soil contaminated with chromated copper arsenate on a 30.3 m^2 plot. Soil arsenic concentrations at the beginning of the study were measured between 190 and 278 mg kg^{-1} from samples taken at depths within the range of 1–60 cm. During the 2-yr period, a total of 26.3 g of arsenic was removed from the plot. Reported biomass yield was approximately 1.3 t ha^{-1}. This improved yield was possibly due to the subtropical climate in Florida where the test was carried out. Similarly, elevated biomass yield have also been reported by Chen et al. [34] in a field study carried out in a subtropical climate region, in which an average above ground biomass yield of just below 2 t ha^{-1} was achieved.

Biomass yield of the pollutant accumulators is the determining factor for the success and duration of the phytoremediation process [35]. For *P. vittata*, although it has a significantly higher biomass

Table 1
Plant species with potential for arsenic phytoremediation.

Species	Plant type	Reported accumulation rates (mg kg^{-1} DW[a])	Reference
Agrostis canina L.	Perennial herb[b]	460	[40]
Agrostis stolonifera L.	Perennial herb	1350	[40]
Agrostis tenuis Sibth.	Perennial herb	3470	[40]
Calluna vulgaris	Perennial shrub	4131	[40]
Helianthus annuus	Annual herb	1550	[39]
Holcus lanatus	Perennial herb	560	[32,40]
Jasione montana L.	Annual/biennial herb	6640	[40]
Pityrogramma calomelanos	Fern	5000–8350	[67]
Pteris biaurita L.	Fern	2000	[68]
Pteris cretica	Fern	3500–4000 in frond; 2200–2600 in root	[28,32]
Pteris longifolia	Fern	4308	[28,32]
Pteris quadriaurita	Fern	2900	[68]
Pteris ryukyuensis	Fern	3700	[68]
Pteris umbrosa	Fern	3735–5000	[28,32]
Pteris vittata	Fern	2500–22,630	[15,28]
Reynoutria sachalinensis	Perennial shrub	1900	[69]

Note.
[a] DW = Dry Weight.
[b] Herb = Herbaceous plant.

yield compared to most of the hyperaccumulators, it is still far less than those of high yield economic crops such as sunflower and cultivars in the willow family.

Shelmerdine et al. [36] examined the suitability of *P. vittata* for phytoremediation of 21 sites historically contaminated with arsenic at various levels around England. The study found that the fraction of As removed generally declined as soil As concentration increased. An uptake model was developed using experimental data to predict the time frame required for site cleanup to the target level. It is concluded by the authors that *P. vittata* is only suitable for soils with minor levels of arsenic contamination and that major limitation to successful phytoremediation is low biomass yield of *P. vittata*.

Increasingly, research evidence suggests that although species in the *Pteris* family exhibit a high capacity of bioaccumulation of arsenic, the low biomass *P. vittata* production hinders its application on heavily contaminated sites [37,38]. High yield common plants and economic crops, on the other hand, have been demonstrated in a number of studies to have more promising field application [38–40].

Among the plant species proposed in these studies, shrub willow (*Salix* spp.) and sunflower (*Helianthus annuus*) are the most promising for phytoremediation field applications due to their relatively high accumulation ability and substantial biomass yield. According to January et al. [39] *H. annuus* is capable of uptake of arsenic up to 1550 mg kg^{-1} in the plant shoot under hydroponic conditions. The study also suggests *H. annuus* is capable of hyperaccumulating simultaneously a range of other metal contaminants such as nickel, cadmium and chromium. A number of recent studies have addressed the potential of *Salix* spp. for a range of phytoremediation applications [38,41]. Purdy and Smart [38] examined arsenic accumulation affinity in four willow clones grown hydroponically. In the highest accumulating clone, arsenic was accumulated at 329, 201 and 5800 mg kg^{-1} in the leaf, stem and root, respectively. In a similar hydroponic study, Puckett et al. [41] found accumulation of an As-tolerant willow (*Salix viminalis* × *Salix miyabeana*) reached 66.8, 34.2, and 3170 mg kg^{-1} and an As-sensitive willow (*Salix eriocephala*) reached 20.3, 16.8, and 2380 mg kg^{-1} (DW) for leaf, stem, and root, respectively.

Although it seems the arsenic accumulation abilities of these plants are 2–3 times less than in *P. vittata*, the significantly higher biomass yield (at least 10–20 fold) drastically reduces the remediation time. It is also recognised that biomass produced during the phytoremediation process can be reconsidered as a locally produced, renewable feedstock for bioenergy and bioproducts [42].

2.2. Nickel hyperaccumulators

In the UK, nickel was chosen as one of the eight contaminants examined by a study conducted by the British Geological Survey (BGS) in order to give further guidance on the recently published revised Part 2A Contaminated Land Statutory Guidance [43]. It is also recognised by the Environmental Agency as one of the fifty six priority contaminants in the UK [44].

Distribution and concentration of nickel in the UK soil is influenced mostly by the underlying geology, i.e. parent material of soil; whereas nickel pollution in soil caused by human activity is not as significant as seen with some other contaminants [45]. In a recent study conducted by BGS [43,45], significantly high concentrations of nickel were identified in areas at the southern tip of Cornwall (Lizard serpentinites), ironstone rock rich areas in Oxfordshire and areas in the Peak District where mineralisation and Ni-rich parent material are responsible for high Ni concentration in soil (Fig. 1).

Since the discovery of the world's first 'nickel accumulator, so far no less than 320 plant species have been reported, which makes nickel hyperaccumulators possibly the largest family amongst

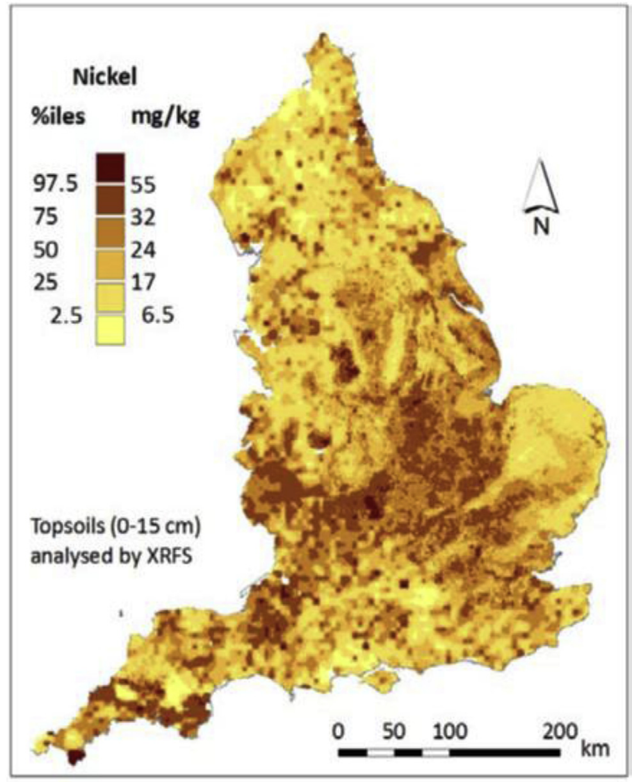


Fig. 1. Ni concentration in topsoil in England as a percentile classified interpolated image.
Source: Defra Technical Guidance Sheet No. TGS05 [45].

other hyperaccumulators [14]. The plant family most strongly represented are *Euphorbiaceae*, *Brassicacceae, Asteraceae*, *Flacourtiaceae*, *Buxaceae* and *Rubiaceae* [14]. Table 2 selectively lists a number of plant species with potential for application in phytoremediation projects. Detailed summaries of species can be found in earlier works by Baker and Brooks [46], Reeves et al. [47,48] and Reeves and Baker [14]. The reason for the large number of nickel hyperaccumulators is partially due to the extensive analytical work carried out on ultramafic floras, but more fundamental explanation can be attributed to million years of evolution of plants colonised in the Ni-enriched ultramafic, which is by far the most widespread on a global scale [14].

The extensive distribution of nickel in soil and the large selection of nickel hyperaccumulators has encouraged intensive research for phytoremediation of land contaminated by nickel. Additionally, the high biomass yield and high bioaccumulation factors exhibited in some of the nickel hyperaccumulators makes it possible to use these plants to extract nickel from low grade nickel ores which cover large areas of the Earth crust [49].

Amongst hundreds of nickel hyperaccumulators, there are a number of species that have so far been applied in field studies and have demonstrated their potential for commercial phytoremediation and phytomining. *Alyssum bertolonii* was reported by Robinson et al. [50] in a field trial as capable of accumulating Ni at 0.8% (8 g kg^{-1}) dry matter of its biomass. Reasonably good biomass yield was achieved with moderate fertilization (N, P and K) at 9.0 t ha^{-1}, which gave a metal yield of 72 kg ha^{-1} assuming all nickel in the biomass is recovered. The authors concluded that the net return from this Ni hyperaccumulator per hectare could be comparable to that of wheat based on a conservative calculation. However if energy yield from biomass via thermochemical conversion, e.g. gasification is considered, even higher returns can be

Table 2
Plant species with potential for nickel phytoremediation.

Family	Species	Plant type	Reported accumulation rates (mg kg^{-1} DW)	Reference
Asteraceae	*Berkheya coddii*	Perennial herb	11,600	[51]
	Berkheya zeyheri	Perennial herb	17,000	[47,48]
	Pentacalia (10 species)	Herb	16,600	[47,48]
	Helianthus annuus	Annual herb	510–1070	[39,70]
	Senecio coronatus	Herb	24,000	[71]
Brassicaceae	*Alyssum* (48 taxa, all in section Odontarrhena)	Annual or perennial herbs	1280–29,400	[46,72,73]
	Bornmuellera (6 taxa)		11,400–31,200	[48,74,75]
	Thlaspi (23 taxa)	Annual or perennial herbs	2000–31,000	[48]
Buxaceae	*Buxus* (17 taxa)	Shrub	1320–25,420	[47]
Euphorbiaceae	*Leucocroton* (27 species)	Herbs	2260–24,600	[76]
	Phyllanthus (16 taxa)	Herbs	1090–38,100	[77]
	Phyllanthus chamaecristoides (2 subsp: chamaecristoides and baracoensis)	Herbs	3400–31,740	[47]
	Cleidion viellardii	Herbs	9900	[48]
	Baloghia sp.	Herbs	5380	[48]
Flacourtiaceae	*Homalium* (7 species)	Shrub (within willow family)	1160–14,500	[78]
	Xylosma (11 species)	Shrub (within willow family)	1000–3750	[78]
Rubiaceae	*Psychotria douarrei*	Shrub	14,900–27,700	[79]

achieved. In a later study carried out by the same research group [51], a high biomass yield Ni hyperaccumulator *Berkheya coddii* was reported. In the field test, the plant was capable of accumulating 1.8–7.8 g kg^{-1} Ni in the above ground biomass (on dry weight basis) whilst achieving 22 t ha^{-1} of dry biomass. Additionally, the ease of propagation and culture, as well as its tolerance to cool climatic condition render this species a suitable agent for phytoremediation particularly in the UK. The economic aspects of using *B. coddii* are discussed by the authors in this study. It is concluded that at the highest Ni concentration in the biomass archived in this study (7.8 g kg^{-1}), 1 ha of *B. coddii* crop can remove 168 kg of Ni assuming the biomass yield of 22 t ha^{-1}. When combined with energy from biomass combustion, assuming at 25% of the total biomass calorific value, an estimated return of US$ 1548 per ha is predicted by the authors at the time the study.

2.3. PGM phytoremediation

In the UK, PGMs such as Pt and Pd are not listed as soil contaminants in the Part 2A regime. However due to the wide usage of catalytic convertor, high level of these metals in roadside soil and road dust have become a growing concern. Studies have identified in soils, dusts and plants exposed to high-traffic density, concentrations of PGMs far exceeding natural background levels [52]. Long term monitoring of these environmental samples shows an upward trend of PGM concentration and a strong correlation with traffic conditions [53].

Automobile derived PGMs releases are mainly in the oxidation status of zero or as oxide [54]; therefore are commonly assumed to be inert and immobile in the environment. However solubility studies of exhaust fume and road dusts suggest PGMs of such origin are at least partly soluble and therefore mobile in the environment [55]. To date, little is known about the biological mechanism of how these noble metals interact with plants.

A few early works which studied bioaccumulation rates and effects of platinum by plants were carried out under hydroponic conditions.

Pallas and Jones [56] have exposed 9 horticultural important crops to 0.057, 0.57 and 5.7 mg l^{-1} Pt in a Hoagland nutrient solution. All species accumulated a significantly high amount of Pt in their roots. For cauliflower and tomato in particular, the Pt concentration exceeds 1000 mg kg^{-1} on dry weight basis when exposed to 5.7 mg l^{-1} Pt. During a six-week exposure to the Pt, an accumulation factor of 6952 in the roots was achieved.

Ballach and Wittig [57] carried out a hydroponic experiment using poplar (*Populus maximowiczii*) to examine the accumulation of Pt and its toxic effect on biomass growth. The growth nutrient solution was spiked with 34.8 μg l^{-1} $PtCl_4$. The study agreed with previous literature that the Pt was predominately accumulated in the root and the translocation factor to other parts of the tissue was very limited. However the authors noted that the accumulation of Pt simultaneously caused a gradual depletion of the plants' water supply.

Due to the stable chemical and biochemical properties of PGMs, bioaccumulation of these elements from soil by plants is heavily dependent on their chemical forms. Despite this, hydroponic experiments where plants were exposed to high concentrations of dissolved Pt-salts can provide insight of metal distribution after uptake. In order to assess the feasibility of phytoremediation/phytomining of PGMs as a commercially viable option, experimental data collected from realistic field conditions is of high importance. To date, only a limited number of studies have been conducted to sufficiently simulate natural conditions. Helmers and Mergel [58] analysed PGM concentration in grass samples collected within close radius of highways and monitored the concentration trend over a 3-year period. It was found that average concentrations of Pt increased from 3.6 to 10.6 μg kg^{-1} and Rh from 0.65 to 1.54 μg kg^{-1}. The study also reported one particular sample which exposed to street dust for a much longer period, that contained 96 μg kg^{-1} (Pt) and 15 μg kg^{-1} (Rh) nearly 10 times higher than average concentration levels.

In a greenhouse experiment, Schäfer et al. [59] investigated concentrations of Pt, Rh and Pd in plants grown on contaminated highways soils. The PGM concentrations analysed in plants (dry material) reached up to 8.6, 1, and 1.9 μg kg^{-1} for Pt, Rh and Pd, respectively. The order of uptake rates for the three elements in all plants test were found to be: Pd > Pt ≥ Rh.

Most of the existing literature concerning plant uptake of PGM discusses the question only in the context of effects of their release to the biosphere. To the authors' best knowledge, one PGM uptake study was carried out in context of phytoremediation/phytoextraction under field conditions. Nemutandani et al. [60] examined the bioaccumulation capability of an indigenous species *B. coddii* grown on contaminated land where platinum and palladium concentrations were 0.04 ± 0.03 and 0.18 ± 0.07 mg kg^{-1} (on dry weight basis), respectively. Platinum was found accumulated in the leaves and roots at 0.22 ± 0.15 and 0.14 ± 0.04 mg kg^{-1} dry weight, respectively. The concentrations of palladium in the leaves and roots were 0.71 ± 0.52 and 0.18 ± 0.07 mg kg^{-1} dry weight, respectively. Due to the lack of PGM contaminated sites and difficulty of analysis, phytoremediation of these valuable elements are certainly not intensively studied compared to other elements such as arsenic and nickel. The study using *B. coddii* as accumulator for uptake of PGM demonstrats the potential of phytoremediation/phytoextraction technology for remediation and more importantly recovery of these scarce metals.

3. Improvement of financial feasibility of phytoremediation project by plant biomass utilisation and element recovery

Currently in the UK, the high land values in urban areas are the driving force for developers to remediate contaminated sites under the planning system. Whereas in many areas away from profitable land development, funding for remediation is limited. Consequently, a large number of contaminated sites are left untreated. According to the latest report published by Environment Agency [3], by 2007 only 18.4% of the determined contaminated sites in England and Wales have been remediated. Additionally, the majority of these contaminated sites were dealt with through the

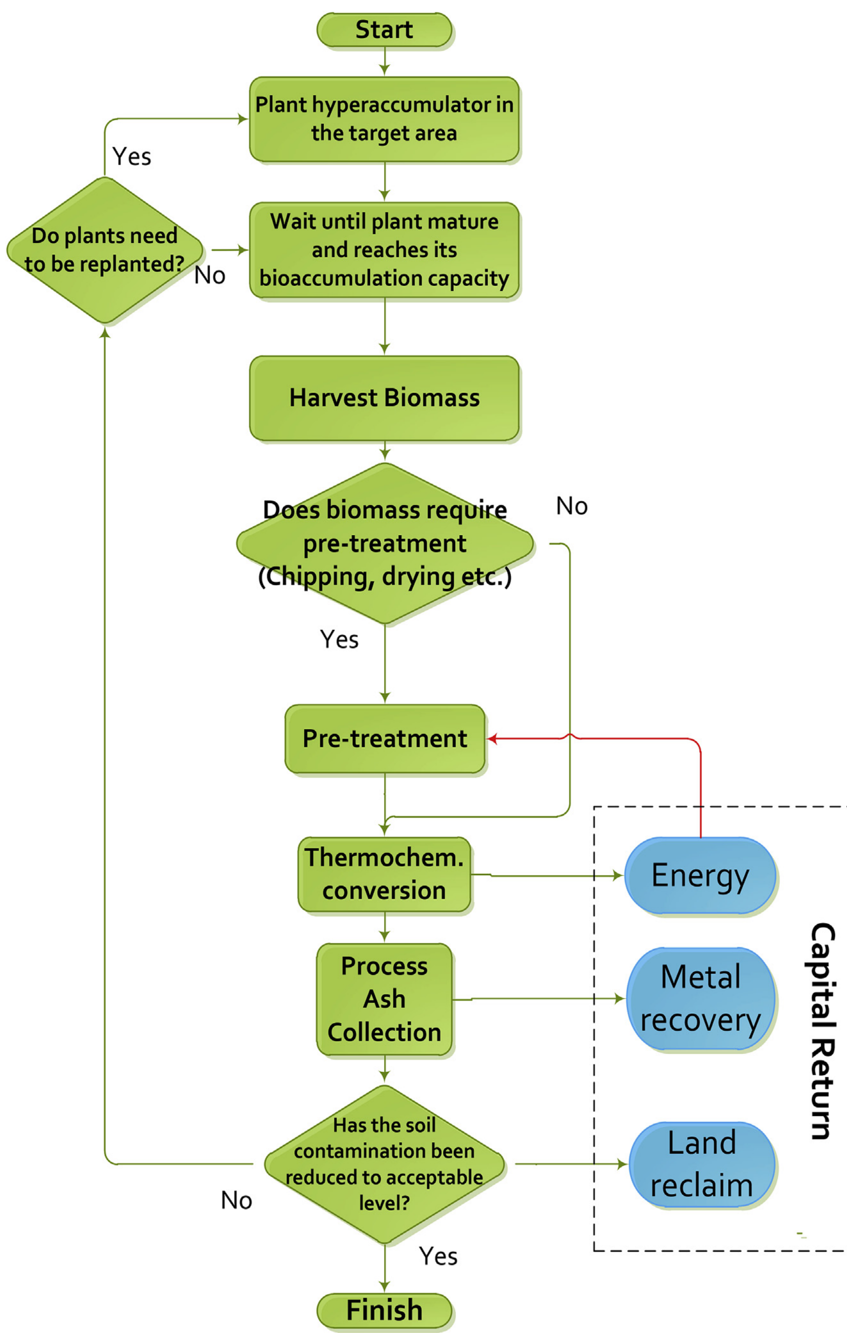


Fig. 2. Logic flowchart of the proposed integrated phytoremediation project.

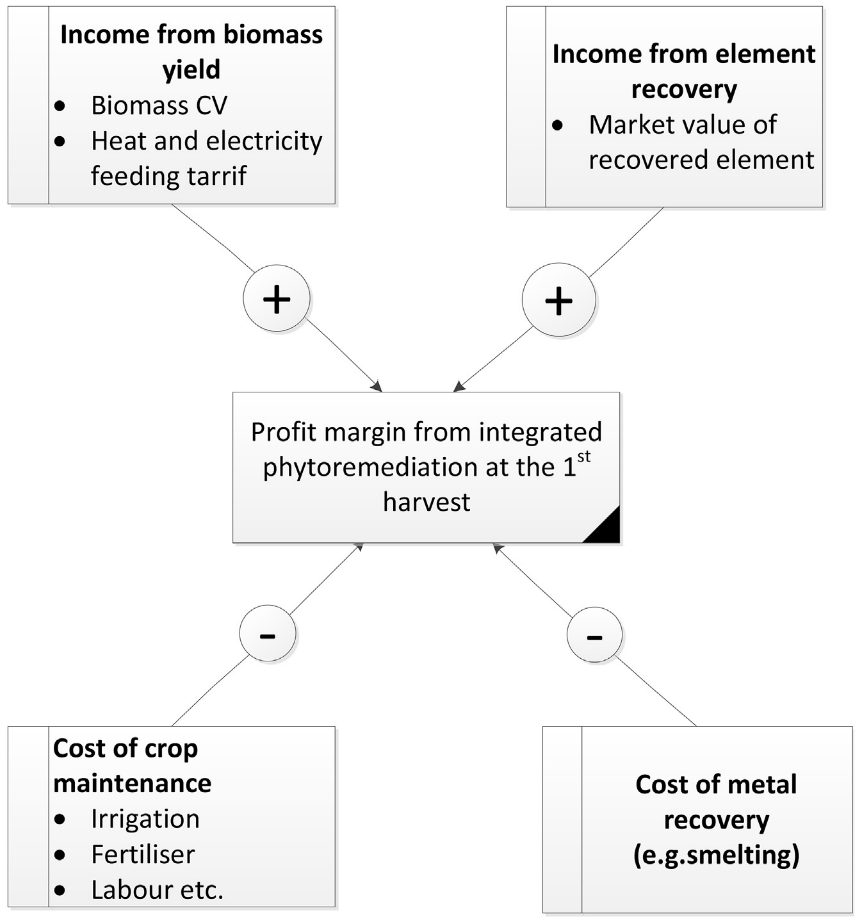


Fig. 3. Determinants for the economic model of integrated phytoremediation.

planning system and it was estimated only 10% was dealt with under Part 2A. Following the gradually reduced government funding for contaminated land and the announcement of the closing of the Contaminated Land Capital Programme (CLCP) at the end of 2013, it is likely these sites will be remain untreated in the future and continue to pose risk to ecosystem and public.

There is, therefore, an urgent requirement for financially viable technologies which offer financial incentive to remediate contaminated sites of low land value. As metal(loid)s are the predominant soil pollutants, phytoremediation offers an opportunity for site with such pollutants which lack funding to carry out remediation work.

From a resource security perspective, most of the metal(loid) soil contaminants are also valuable nature resources, which have been dispersed throughout the environment via industrial and commercial activities in much lower concentrations than their natural deposits. It has already been recognised that the recovery of these elements is critical for the sustainability of industrial development, as natural reserves are depleting a. Arsenic is predicted to be run out between 5 and 50 year if the consumption continues at present rates [61]. Nickel and PGMs are also identified as critical materials to the UK economy at risk of depletion in the Resource Security Action Plan (RSAP) [62]. However, despite increasing demand, none of this supply is supported by recycling [63]; due to the high cost of recovery from low concentrations when compared to conventional mining. Thus, low cost technologies that offer higher economic incentive raise commercial interest.

Phytoremediation technology satisfies both requirements for low cost land clean-up and element recovery by concentrating low levels of metal(loid)s in soil within biomass tissues. Additionally, large quantities of biomass produced during phytoremediation are a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics, which contains substantial amount of calorific value. When treated thermochemically, e.g. through gasification or pyrolysis, rapid valorisation can be achieved to provide fuel gas that can be used for heat and electricity generation [64]. The metal(loid) content in process ash retrieved at the thermochemical process is further concentrated compared to its concentration in the original biomass, due to the efficient bulk reduction during the thermochemical process. Therefore recovery of these elements can be much more cost-effective, whist avoiding the disposal cost for large quantities of potentially toxic biomass.

Here we propose an integrated phytoremediation concept coupling remediation with renewable energy production from biomass and subsequent metal(loid)s recovery. Each of the integrated stages and their interactions are illustrated in the flowchart below (Fig. 2).

From an environmental perspective, integrated phytoremediation addresses both land contamination and renewable energy demand simultaneously. However, as the remediation industry is largely market-driven, it is essential to assess whether this approach is financially viable. Furthermore, optimisation of the profitability of this approach is key. Following this, a preliminary model is defined to analyse the profitability of a single biomass harvest on 1 ha of contaminated land. Guidance from prior research is used within the model to assess the profitability of an integrated land remediation project for various scenarios, i.e. target element and plant type. It should be noted that the results from the model

Table 3
Deterministic parameters of the model.

Symbol	Parameter	Value
V_{th}	Heat feed in tariff (£/kWh)	0.01[a]
E_p	Cost of growing plants per hectare (£/ha)	245[b]
E_s	Cost of metal smelting £/kg	0.4[b]
V_m	Market value of As (£/kg)	0.88
	Market value of Ni (£/kg)	8.69
	Market value of Pt (£/kg)	27,086.6

[a] Source of data: Department of Energy & Climate Change, UK. http://chp.decc.gov.uk/cms/renewable-heat-incentive/.
[b] Source of data: Gray et al. [26].

are not intended to provide an accurate estimation of financial return; rather to provide an insight into how decision on plant selection and the prioritised target element can affect the profitability and overall financial risk of such a project.

3.1. Economic model of a phytoremediation project

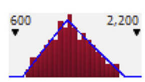
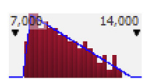
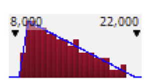
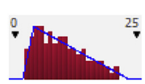
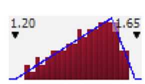
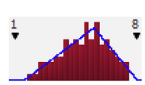
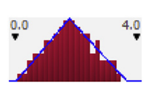
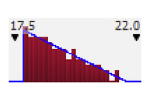
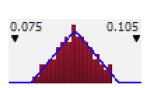
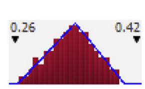
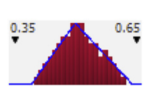
A number of previous studies have attempted to address the financial aspects of a phytoremediation project. Lewandowski et al. [65] evaluated the economic value of combination of biomass production from cadmium contaminated land and the potential financial return from crop production from the land after remediation has been achieved. The work demonstrated the economic benefit of the phytoremediation by subsidising the cost of selling biomass alongside the potential long-term income from the cleaned area. However, this model offers only limited immediate income to the stakeholder, as remediation can take decades for the soil to reach a suitable condition for growing commercial crops.

Robinson et al. [50] calculated the required biomass for a hyperaccumulator having a metal content of 1% (on dry weight basis) to achieve a financial return of 500 US dollars solely from the recovered metal. The study concluded that under the assumption that average annual biomass yield of 30 t/ha, only cobalt, nickel, tin, cadmium, manganese and noble metals (Au, Ag and Pt etc.) would be financially viable.

Clearly there are economic limits in terms of biomass production and metal content when using phytoremediation for metal(-loid) element recovery. When one takes into consideration energy production and land reclamation, the overall environmental benefits increase thus affecting the overall economic balance of such projects.

To simplify the model, intangible and indirect economic benefits, such as cost reductions from using phytoremediation in place of more costly ex-situ clean-up technology and avoidance of

Table 4
Stochastic parameters of the model and their probability distributions.

Symbol	Parameters	Graph[a]	Min	Mean	Max	5%	95%
Y	*P. vitatta* yield (kg/ha)		798	1353	1945	932	1789
	H. annuus yield (kg/ha)		7814	9777	12994	8047	12200
	B. coddii yield (kg/ha)		9170	13473	20491	9775	18701
	P. vitatta As uptake (g/kg)		3.01	9.89	20.89	3.81	17.95
C	*H. annuus* As uptake (g/kg)		1.25	1.47	1.61	1.30	1.59
	B. coddii Ni uptake (g/kg)		2.00	5.03	7.44	2.78	6.94
	B. coddii Pt uptake (g/kg)		0.21×10^{-4}	1.82×10^{-4}	3.57×10^{-4}	0.62×10^{-4}	3.09×10^{-4}
C_v	Range of HHV of woody Biomass (MJ/kg)		18.00	19.17	21.30	18.08	20.70
V_e	Elec. Feed in Tariff (£/kWh)[b]		0.0803	0.0810	0.0986	0.0830	0.0965
η_e	Electrical efficiency (%)		27.1	33.7	39.4	29.0	38.0
η_{th}	Heat efficiency (%)		40.6	51.0	61.7	43.2	59.0

[a] The graphs show the distribution of probability of the input data, vertical length of the bar indicates the probability of occurrence.
[b] Assuming advanced thermochemical biomass to energy technology is used, and therefore receiving 2 Renewable Obligation Certificates (ROCs)/MWh. Value of ROCs varies between £40–50. Source of data: Department of Energy & Climate Change, UK. http://chp.decc.gov.uk/cms/renewables-obligation-2/.

disposal of biomass are not considered.

A schematic overview of the main factors that influence the profit of an integrated phytoremediation project is shown in Fig. 3.

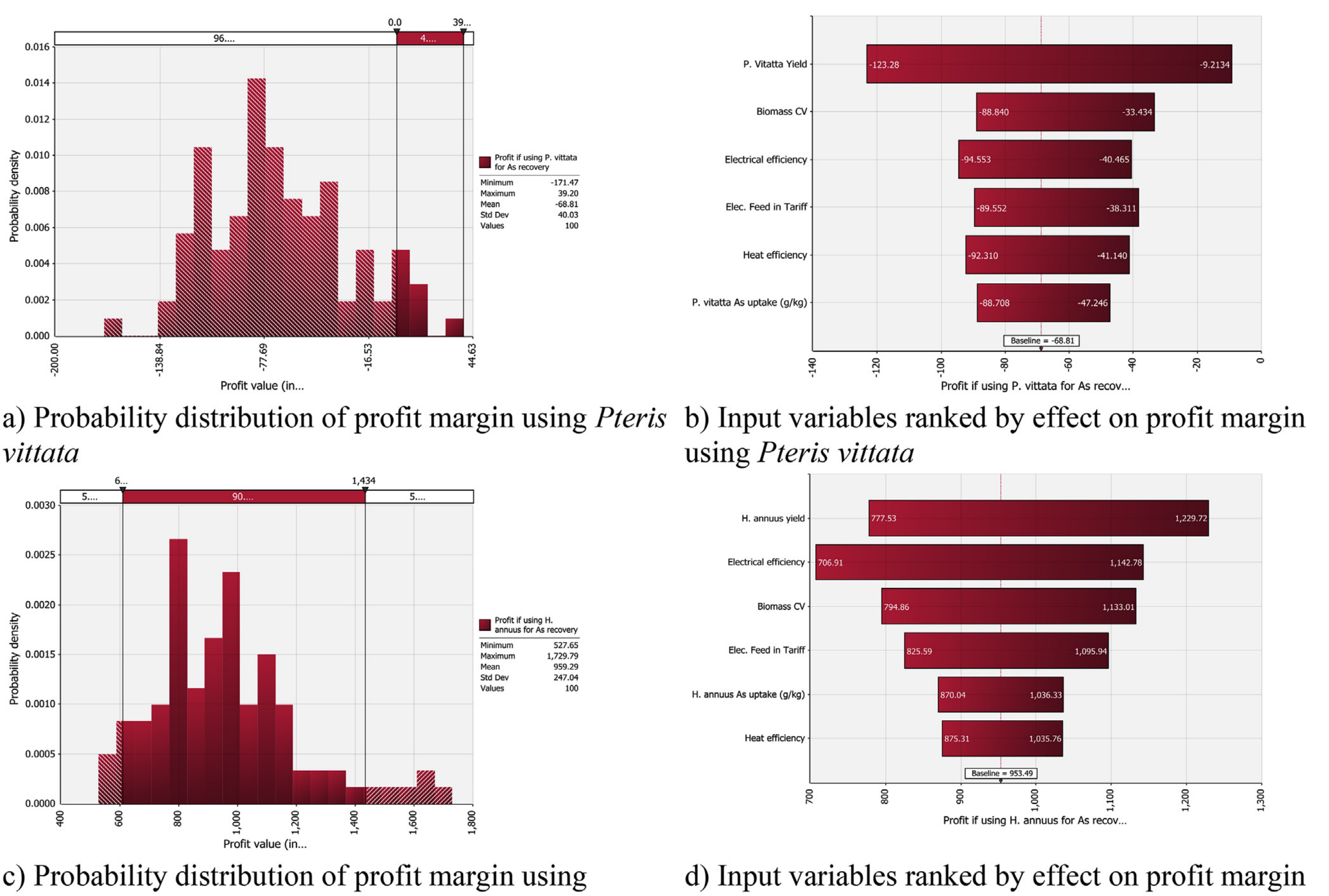
Two direct income streams are taken into account in the model: 1.) harvested biomass of which biomass calorific value (CV), electricity and thermal efficiency of the combined heat and power (CHP) unit, heat and electricity tariff are the determinants (Assuming advanced gasification technology is used to produce fuel gas for a small scale (50–1000 KW) gas engine CHP unit). Currently, as a incentive to the rapid and sustained deployment of renewable energy, a feed-in tariffs (FITs) or similar schemes have been implemented in 63 jurisdictions worldwide by the regulators. This schemes offer guaranteed prices for fixed periods of time for electricity/heat produced from renewable energy sources [66]. As a result, this significantly reduces the uncertainties to the project income by eliminating price fluctuation in energy market. 2.) Elemental recovery from biomass, of which market value of the element is the determinant. Concomitant process costs, i.e. cost of planting and maintaining the crop and cost of metal recovering are deducted from the income. Therefore the net profit model on the 1st harvest (per each hectare land) of an integrated phytoremediation project is calculated as following:

$$P = Y \times C \times V_m \times R_m + 0.2778\ kWh\ MJ^{-1} \times Y \times C_v \times (V_e \times \eta_e + V_{th} \times \eta_{th}) - 0.1 \times Y \times E_s - E_p \tag{1}$$

Where:

Y = Biomass yield (kg dry weight ha^{-1}): Can range from 2000 to 20,000 depending on plants
C = Metal concentration in the biomass (g kg^{-1} on dry weight basis)
C_v = Biomass calorific value (CV) (MJ kg^{-1}) (16.7–18.6 MJ kg^{-1})
V_m = Market value of metal (£ Kg^{-1})
V_e = Electricity feeding Tariff (£/kWh)
V_{th} = Heat feeding Tariff (£/kWh)
R_m = Metal recovery (%): Assuming 100% here
η_e = Electrical efficiency of a CHP unit
η_{th} = Heat efficiency of a CHP unit (Generally η_{th}/η_e = 1.2–1.8)
E_s = Cost of metal recovery per kg of dry biomass (£ kg^{-1}): Estimated at £0.4 kg^{-1} from biomass ash (10% of DM biomass) by smelting according to Gray et al. [26].
E_p = Cost of growing plants per hectare (£ ha^{-1})

Equation (1) attempts to capture the major determinants that affect gross margin of an integrated phytoremediation project. Within the variables in Equation (1), V_{th}, V_m, E_s and E_p are more deterministic and tend to be project specific. Once the project location, scale of operation, local government incentive policies are determined, these variables will not contribute significantly to the financial risk of the project. To present a UK scenario, values of these variables used in this study are UK specific (typical values that used for calculation in this study are listed in Table 3). However, before applying the method described here in any real life project, it is critically important to collect these deterministic data per project in order to obtain realistic results.



a) Probability distribution of profit margin using *Pteris vittata*

b) Input variables ranked by effect on profit margin using *Pteris vittata*

c) Probability distribution of profit margin using *Helianthus annuus*

d) Input variables ranked by effect on profit margin using *Helianthus annuus*

Fig. 4. Output of financial risk analysis of 2 hypothetical scenarios – using *Pteris vittata* and *Helianthus annuus* in integrated phytoremediation projects on an arsenic contaminated site.

Other variables such as biomass yield (Y), metal concentration in biomass (C), biomass calorific value (C_v), and electrical and heat efficiency (η_e and η_{th}) of the CHP unit have a wide range of reported values as can be seen in the previous review. This causes uncertainty, and thus a ‘risk’ to the financial return of the project. Indeed, the range and distribution of input data for these stochastic variables determine the level of profit that can be made alongside the probabilities of achieving, or failing to achieve a profit. To understand how these stochastic variables influence the outcome of the economic model, a quantitative analysis based on Monte Carlo simulation method was carried out using risk analysis software @RISK (Palisade Corp. Ithaca, NY, USA). Four scenarios of different target element and their corresponding accumulating plant (As/*P. Vitatta*, As/*H. annuus*, Ni/*B. coddii* and Pt/*B. coddii*) were studied to compare the profitability of an integrated phytoremediation approach under each scenario. From the comprehensive literature review of (hyper) accumulators for the elements of interest in the previous section, sets of data for the stochastic variables have been complied and their ranges and triangular probability distributions used for the simulation are shown in Table 4. Based on these input distributions, all valid combinations of the values were calculated to simulate all possible outcomes of the model.

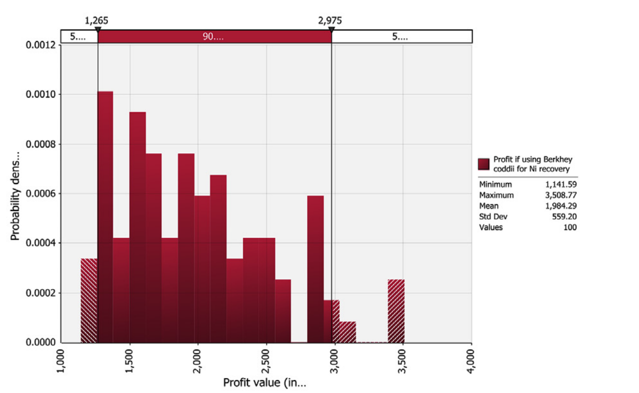
3.2. Risk management of the integrated phytoremediation project

Whilst phytoremediation is a mature technology, an integrated approach increases the uncertainty of the overall financial viability of the project. Therefore economic challenges and risks that reside within the integrated remediation have to be appraised alongside the economic motivations needed to establish wider application of this technology.

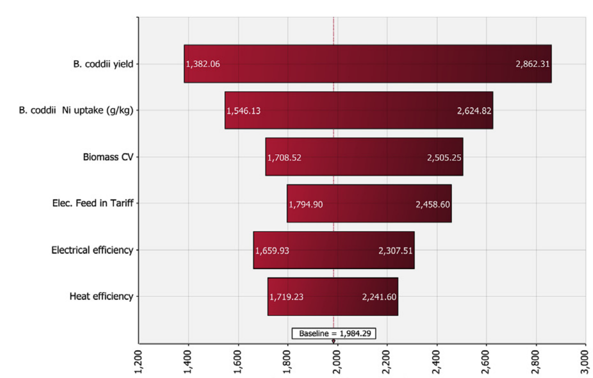
In the scenario using the low biomass yield hyperaccumulator *p. vittata* in an integrated land remediation project to recover arsenic and produce energy, the probability distribution of the profit (P) clearly suggests a high risk of low economic return. In all possible data combinations simulated, 96% of the outcomes failed to achieve a positive margin and only 4% of outcomes achieve a limited financial gain of £0–44.63 per ha (Fig. 4a). Among all stochastic variables, biomass yield is the most significant variable affecting the margin (Fig. 4b). This is understandable as a large proportion of income obtained in this scenario is achieved from energy generated from biomass.

In a different scenario, *P. vittata* is replaced with a high biomass yield plant *H. annuus*. Although it has a lower accumulation capacity for arsenic, its high biomass energy value gives a significantly improved financial return. There is a high certainty (90% of simulated combinations) of achieving a margin of between £610–1434 per ha with the highest calculated margin of £1730 per ha (Fig. 4c). In both scenarios, the bioaccumulation capacity is less important due to the low market value of As (Fig. 4d). Therefore it can be concluded that recovery of low value arsenic is not financially viable unless high value products can be subsequently developed. This finding is consistent with previous work carried out by Gray et al. [26].

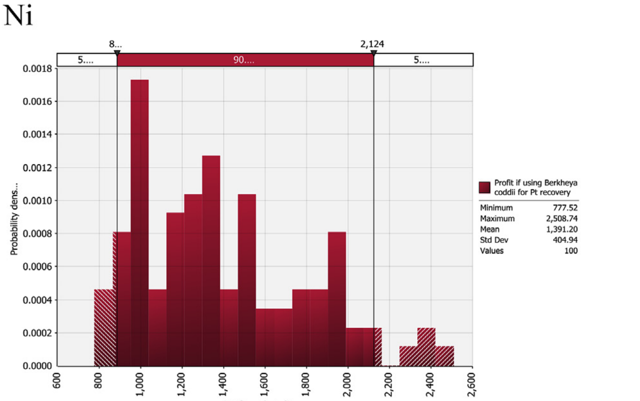
Based on simulation results from these 2 scenarios, it can be expected that the financial gain can be further improved if high biomass producing plants with high accumulating capacity are used in projects to recover metals such as nickel.



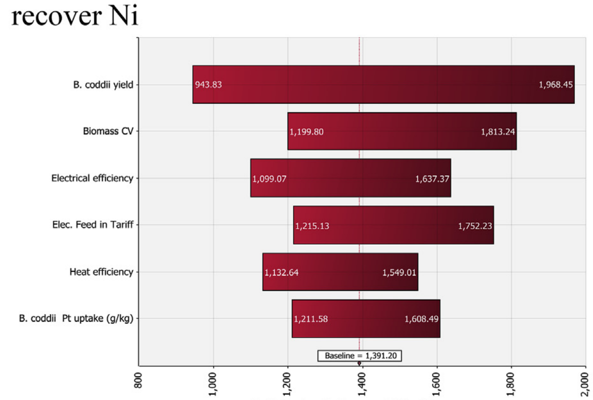
a) Probability distribution of profit margin to recover Ni



b) Input variables ranked by effect on profit margin to recover Ni



c) Probability distribution of profit margin to recover Pt



d) Input variables ranked by effect on profit margin to recover Pt

Fig. 5. Outputs of financial risk analysis of 2 hypothetic scenarios in an integrated phytoremediation project using *Berkhey coddii* in to recover Ni and Pt, respectively.

Scenario 3 and 4 simulate the outcomes of integrated phytoremediation projects using the high biomass yield plant *Berkhey coddii* on Ni and Pt contaminated sites, respectively. From the probability distribution of profit, it is clear that both scenarios indicate a substantial financial return (Fig. 5a and c). In 90% of the simulated possibilities, the profit achieved is within £1265–2975 per ha for Ni site and £887–2124 for Pt site.

In all 4 scenarios simulated, biomass yield is the most significant variable to affect profit (Fig. 4b, d, Fig. 5b & d), reflecting the substantial proportion of renewable energy value that contribute to the overall profit of integrated phytoremediation projects. Whilst from economic perspective, it appears that the value of elements recovered from the process is limited; in view of the scarcity of these elements, it could be argued that there is scope to consider the strategic importance of recovering these elements.

It is noteworthy that simulation results in this study are not intended to provide accurate projections of financial outcomes, as deterministic values vary unpredictably depending on the individual projects conditions and the resources of contractors carrying out the work. Additionally, in the probabilistic risk assessment method applied in this study, the dependencies between variables were not considered and the simulation is based on random sampling of data from the distribution of each variable. In reality, this potentially can lead to biased result. For example, the concentration of contaminants in the soil might affect the biomass yield, in high contaminated area there is a higher likelihood to have lower biomass yield. To treat these two stochastic variables as independent will obviously result an underestimation of risk. Therefore the simulation result must be interpreted with caution.

Nevertheless, the financial model and the simulation results offer basis for decision making to optimise financial outcomes at the project planning stage of remediation initiatives.

4. Conclusion

A review of potential plants for phytoremediation of arsenic, nickel and PGMs has been carried out. It is evident that phytoremediation is suitable for the clean-up of elemental contaminants for land banks of low development value.

Post-process energy and element recovery from biomass significantly increases the financial viability of phytoremediation projects and reduces the environment impacts of disposal for contaminated biomass.

The selection of plant and target element determines the project outcome and financial risks. A quantitative risk analysis tool suggests high biomass yield plants and high value elements contribute significantly more to profit.

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