#### Chemosphere 358 (2024) 142135

Contents lists available at ScienceDirect

### Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# A novel algorithm for optimizing hydrocyclone operations in the decontamination of potentially toxic elements in soils

X. Corres<sup>a</sup>, N. Gómez<sup>b</sup>, C. Boente<sup>c,\*</sup>, J.R. Gallego<sup>a</sup>, C. Sierra<sup>b,d</sup>

<sup>a</sup> INDUROT and Environmental Biogeochemistry & Raw Materials Group, Campus de Mieres, Universidad de Oviedo, Mieres, Asturias, Spain

<sup>b</sup> Department of Mining, Topography and Structure Technology, Universidad de León, Campus de Vegazana, 24006, León, Spain

<sup>c</sup> Laboratorio de Estratigrafía Biomolecular, ETSI Minas y Energía, Universidad Politécnica de Madrid, 28003 Madrid, Spain

<sup>d</sup> European University on Responsible Consumption and Production, Campus de Vegazana, 24006, León, Spain

#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

- A novel method for optimizing yield parameters in soil washing is presented.
  The algorithm holds potential for
- determining optimal operating conditions.
- Grade, recovery and concentrate yield were the parameters to optimize.
- The key to the method is maximizing grade and recovery while minimizing yield.



#### ARTICLE INFO

Handling Editor: Lena Q. Ma

Keywords: Metallurgical accounting Process efficiency Process design Control of experiments

#### ABSTRACT

We present the Three-Parameter Penalized Attributive Analysis for Upgrading (3PPAA-U) method as a tool for selecting the Best Upgrading Condition (BUC) in process engineering. Conventional approaches tend to consider only maximizing recovery ( $\varepsilon$ ) and minimizing yield ( $\gamma$ c); in contrast, the proposed 3PPAA-U introduces and seeks to maximize a third parameter, the grade ( $\lambda$ ). This multi-parameter approach has not yet been explored in existing literature. In addition to controlling multiple parameters, the method is also superior to others as it includes inverse standard deviation weighting to avoid the distortion of results due to data dispersion. This reduces the possibility of drawing conclusions based on extreme values. Furthermore, the method can be used with a target-to-distance correction to optimize separation for multi-component feeds. To illustrate our method, we present a practical application of 3PPAA-U. Soil contaminated with potentially toxic elements (PTEs) was subject to hydrocycloning under 12 different experimental conditions. Results of these 12 experiments were compared using 3PPAA-U and conventional methods to identify the best upgrading conditions (BUC). Analysis reveals that the 3PPAA-U approach offers a simple and effective criterion for selecting BUC. Furthermore, 3PPAA-U has uses beyond soil remediation. It offers a versatile tool for optimizing operations across various

\* Corresponding author.

E-mail address: c.boente@upm.es (C. Boente).

https://doi.org/10.1016/j.chemosphere.2024.142135

Received 3 January 2024; Received in revised form 13 April 2024; Accepted 22 April 2024 Available online 24 April 2024

0045-6535/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/).





Chemosphere



#### 1. Introduction

#### 1.1. Soil washing: key concepts

Soil pollution includes numerous potentially toxic elements (PTEs) such as lead, cadmium, arsenic, and mercury, as well as polycyclic aromatic hydrocarbons (PAHs) (c.f., Sun et al., 2019; Wu et al., 2015). PTEs not only affect soil fertility but also pose a risk to human health. For example, ingesting or inhaling contaminated soil particles can lead to serious health issues including cancer, respiratory problems, and neurological disorders (Rieuwerts et al., 2014). Furthermore, PTEs are known to leach into watercourses and this can cause even more widespread environmental degradation and risks to public health (Khalid et al., 2017).

Therefore, it is crucial to address the issue of contaminated soil through effective remediation strategies, for instance, phytoremediation (Ashraf et al., 2019; Chen et al., 2016), microbial remediation (Chen et al., 2023), electrokinetic remediation (Wang et al., 2021), and soil washing (Guo et al., 2022; Khum-in et al., 2023; Lee and Kim, 2010; Pinto et al., 2014)These strategies can help to reduce the levels of PTEs and other pollutants, restoring the soil and preventing further damage to the environment and human health.

Soil washing is a highly efficient and rapid technique (Khum-in et al., 2023) for the removal of PTEs and organic compounds from soil (Guo et al., 2022). Additionally, this technique represents one of the few methods able to provide a permanent solution for soil contamination, particularly in cases where levels of pollutants are significant (Lee and Kim, 2010; Pinto et al., 2014).

There are two types of soil washing, namely physical and chemical. The latter involves mixing the soil with an extraction solution to chemically dissolve or mobilize the contaminants. Physical soil washing, on the other hand, separates and extracts pollutants by exploiting the differences in physical properties, for example, size, density, magnetic properties, and hydrophobicity, that exist between soil particles and pollutant-bearing particles (Dermont et al., 2008). The strategies involved in physical soil washing are based on well-established methods employed in the mining industry for the extraction of elements from mineral ores (Ye et al., 2022; Sierra et al., 2013). However, these techniques can be expensive and time-consuming, thus there is a need for reducing costs and improving the efficiency of these remediation methods.

#### 1.2. Determining best upgrading conditions (BUC)

Assessing the performance of an upgrading process requires the definition of several parameters. Firstly, if the material subject to the upgrading process has a feed mass flow rate, F, then the products of the upgrading process are the concentrate and the tailings with, respectively, mass flow rates, C, and F. In some cases, there may be intermediate outputs, known as middlings, which will have a mass flow rate, M. These flow rates are related thus:

$$F = C + M + T \tag{1a}$$

Dividing Eq. (1a) by F, we get the yield ( $\gamma$ ) for each fraction, that is, the mass percentage of the feed (F) reporting to each fraction:  $\gamma_c$ , the concentrate yield;  $\gamma_m$ , the midlings yield; and  $\gamma_t$ , the tailings yield;  $\gamma_F = 1$ , the feed yield (Eq. (1b)):

$$\gamma_F = \gamma_c + \gamma_m + \gamma_t \tag{1b}$$

The grade of a fraction is defined as the concentration of a given

element or compound in that fraction, and it is denoted as  $\alpha$  for the feed and  $\lambda$  for the concentrate.

Finally, the percentage of useful (or desired) content that reports to a specific fraction relative to the feed is known as the recovery,  $\varepsilon$ , and this is used to assess the quality of the upgrading process. Of most relevance here is the concentrate fraction and, for the concentrate mass stream, the recovery for this fraction is expressed as (Eq. (2)):

$$\varepsilon = \frac{\lambda}{\alpha} \gamma_c \tag{2}$$

In physical soil washing scenarios, the pollutants to be removed are held in the concentrate fraction while the tailings comprise the partially decontaminated soil. Thus, to optimize soil decontamination, the goal is to minimize  $\gamma_c$  and maximize  $\lambda$ .

Traditionally, to find optimal operating conditions, pairs of the parameters  $\gamma_c$ ,  $\lambda$  and  $\varepsilon$  can be plotted on separation curves (e.g., Drzymała, 2006). However, such methods are naturally limited to a consideration of only two components at a time and this can be misleading. For example, an apparently optimal experiment with a high value of  $\varepsilon$  and low  $\gamma_c$  might simply contain very little material that would report to the concentrate, thus it is necessary to consider  $\lambda$  too. Similarly, an experiment might provide a high value of  $\varepsilon$  might also give a high  $\lambda$ , however we cannot tell if this is truly an optimal set up without looking at  $\gamma_c$  since a high  $\lambda$  might simply be a consequence of a low  $\gamma_c$ .

Furthermore, most traditional methods are only able to consider single component separations and many soil washing operations involve soils with multiple contaminants. By including  $\lambda$ , in its calculations, 3PPAA-U enables optimization for multicomponent separations and allows the identification of operating conditions that will preferentially address the most dangerous pollutants.

#### 1.3. Aim and specific objectives

Following from the previous discussion, the aim of this research, is to develop an effective method to select the optimal conditions for soil upgrading operations. In this way we will:

- a) introduce the 3PPAA-U method
- b) apply the method to a real-life soil washing operation using a hydrocyclone to decontaminate soil from an ex-industrial site in Asturias, Spain.

We will then compare the results of traditional separation-curve optimization to 3PPAA-U with and without target-to-distance correctionand discuss the implications of this new method.

#### 2. Materials and methods: a real-life soil washing operation

#### 2.1. Soil sampling and chemical analysis

The soil sample used in this study was collected from a 35,000 m<sup>2</sup> brownfield location in Asturias (Northern Spain). Fig. 1 depicts the location of the brownfield and the sampling area. More information about the site and its environment can be found in Boente et al. (2020). Superficial soil samples were collected from various points across the study site to obtain a bulk sample of 50 kg. Rocks, gravel, and other large debris were removed in situ by passing the soil through a 2 cm mesh. The sample was then dried at ambient temperature before being passed through a 4 mm mesh. Finally, the soil sample was sieved using standardized Restch separating screens, and two major fractions were recovered (0  $\mu$ m - 125  $\mu$ m and 125  $\mu$ m - 4000  $\mu$ m).



Fig. 1. Brownfield location and sampling location in Asturias, Spain (Latitude: 43.2964; Longitude: 5.68254).

Of the two major fractions recovered, the finer (grain size  $<\!125\,\mu\text{m})$  had the highest PTE content. Thus, this fraction was divided into 12 subsamples for separation. Representative 1g subsamples from each subsample were subjected to chemical analysis: first they were leached using an "Aqua regia" solution (HCl + HNO\_3) and the digested samples were analysed by ICP-MS instrument (model HP 7700 from Agilent Technologies)for major and trace element content.

#### 2.2. Separation experiments

Separation tests were completed in a lab-scale plant (C700 Mozley) capable of running hydrocyclones from 10 mm to 50 mm in diameter. The hydrocyclone uses gravity to separate aqueous suspensions of particles (slurries) into fractions based on particle density (Karim et al., 2021). It comprises a conical chamber with two outlets, one at the top and one at the bottom, and is fed tangentially with high pressure slurry. When the slurry enters the hydrocyclone chamber, it experiences a centrifugal force which pushes denser fractions outwards and downwards towards the lower outlet (underflow) while lower-density fractions exit via the upper outlet (overflow). The hydrocyclone used in this experiment offers four operating configurations: conic with apex diameters of 9.5 mm, 6.4 mm, and 3 mm; or flat bottom (FB). Samples were tested in each of the available configurations at pressures of 100 kPa, 200 kPa, and 300 kPa, thus there were twelve experimental runs in total. The solid concentration of the feed slurry was maintained at a constant 20% by weight.

For each experimental run, once a steady state was attained, samples from both the hydrocyclone underflow and overflow were collected in borosilicate flasks. Samples (from the overflow and underflow) were subjected to low temperature drying (45 °C) in an oven to minimize the potential loss of Hg and As due to volatilization. The dry weights of these samples were then measured before representative sub-samples were taken for ICP-MS analysis (model HP 7700 from Agilent Technologies).

#### 2.3. Attributive analysis

## 2.3.1. Selection of the concentrate, tailings, and middlings fractions in multicomponent separations

A major consideration in designing an algorithm to find the BUC is the fact that soil washing operations generally deal with multicomponent contamination. Thus, the first issue to address is which fraction should be considered the concentrate (to be removed for further processing) and which the tailings (to be isolated and returned to original site) as this may vary for each PTE. For our purposes, the concentrate fraction (CF) is taken as that for which  $\varepsilon > \gamma_c$  (c.f., Fuerstenau and Han, 2003) for more than half of the PTEs under consideration. Those experiments in which  $\gamma_c > 50\%$  were not included in our analysis, as soil washing is not interested in scenarios where the concentrated fraction is larger than the tailings fraction.

#### 2.3.2. Basic attributive analysis

Basic Attributive Analysis (BAA) was developed as a means of optimizing soil washing by Sierra et al. (2010) and applied first in the context of remediating soils contaminated with Pyrite ash (Sierra et al., 2010; Boente et al., 2017).

In the case where a set of *m* soil-washing experiments have been carried out under a range of experimental conditions, BAA aims to identify which conditions maximize the recovery of a number, *n*, of target elements while minimizing the yield. The performance of a given experiment, *i*, for target element, *j*, is then expressed as a quality factor  $Q_i^i$  calculated as (Eq. (3)):

$$Q_{j}^{i} = \frac{Min\{\gamma\}}{\gamma^{i}} + \frac{\varepsilon_{j}^{i}}{Max\{\varepsilon_{j}\}}$$
(3)

#### Table 1

Operating conditions for the twelve experimental runs.

Run	Apex	Pressure
	mm	kPa
1	9.5	100
2		200
3		300
4	6.4	100
<u>5</u>		200
6		300
7	3	100
8	_	200
9		300
10	FB	100
11		200
12		300

Where:

- *i* = 1, ..., *m* and identifies a specific experiment with a particular set of separation parameters.

- j = 1, ..., n and refers to results for a specific target element or contaminant and in this study, m = 10 (see Table 1 for all target elements considered).

-  $Q_j^i$  = Efficiency factor of experiment *i* for element *j*.

-  $\gamma^{i}$  = Yield of experiment *i*.

-  $\varepsilon_i^i$  = Recovery of element *j* for experiment *i*.

As discussed in 2.3.1, there are generally numerous PTEs to consider and, due to their differing toxicity levels, each will have a safe threshold concentration (the *target grade*) after soil washing. This consideration can be included in the quality factor for each experiment as a weighting coefficient. For each PTE, this coefficient is the ratio of the PTE's grade after soil washing and its target grade; it is known as the target-todistance correction and for an element *j* separated in experiment *i* it is defined as (*Eq.* 4):

$$A_j^i = \frac{\alpha_j^i}{\alpha_j^{target}} \tag{4}$$

Where:

- *i* and *j* are defined as before.

-  $\alpha_i^i$  = Feed grade of element *j* in experiment *i*.

-  $\alpha_i^{target}$  = Target grade for element *j* 

The sum of these coefficients for all j = 1, ..., n elements must add up to 1.

To obtain the correct weighting for each element's contribution to overall contamination levels, the following transformation is implemented (Eq. (5)):

$$A_j^{i'} = \frac{A_j^i}{\sum\limits_{i}^m A_j^i}$$
(5)

This allows us to define a global quality index for a given experiment, i, for all elements under consideration (Eq. (6)):

$$Q_{T}^{i} = \sum_{j=1}^{n} Q_{j}^{i} A_{j}^{i'}$$
(6)

The experiment with optimal separation conditions is that for which this value is maximal (Eq. (7)):

$$Q_{optimal} = Max \left\{ \sum_{j=1}^{n} Q_j^i A_j^{i'} \right\}$$
(7)

#### 2.3.3. Three-Parameter Penalized Attributive Analysis (3PPAA)

Here we present the Three-Parameter Penalized Attributive Analysis (3PPAA) as a tool to find the BUC. This method builds on the BAA model

and is an extension of a previous, two parameter (yield and recovery) version, Penalized Attributive Analysis (PAA) which was described in Corres et al. (2024).

The three parameters in question are:  $\Gamma^i$ ,  $E_j^i$ , and  $\Lambda_j^i$ , respectively, the normalised weighted values of the yield in experiment *i*, and the normalised weighted values of recovery, and grade concentration in experiment *i* for element *j*. The weighting of parameters in this way reduces the influence of noisier experiments in the final analysis of experimental quality.

Our aim is to minimize yield while maximizing the recovery of a range of PTEs and their grade concentrations. Recalling the relationship between  $\gamma_c$ ,  $\mathcal{E}$  and  $\lambda$  (Eq. (2)), then, as in PPA, the appropriate parameters for yield and recovery are defined as (Eqs. (8)–(11)):

$$\Gamma^{i} = \frac{Min\{\gamma_{c}\}}{\gamma^{i}} \left( \frac{\sum_{i=1}^{m} |\gamma_{c}^{i} - \overline{\gamma_{c}}|}{m} \right)^{-1}$$
(8)

$$\Gamma^{i'} = \frac{\Gamma^{i}}{\sum\limits_{i} \Gamma^{i}}$$
(9)

$$\mathbf{E}_{j}^{i} = \frac{\varepsilon_{j}^{i}}{Max\{\varepsilon_{j}\}} \left( \frac{\sum_{i=1}^{m} \left| \varepsilon_{j}^{i} - \overline{\varepsilon}_{j} \right|}{n} \right)^{-1}$$
(10)

$$\mathbf{E}_{j}^{i'} = \frac{\mathbf{E}_{j}^{i}}{\sum_{i}^{m} \mathbf{E}_{j}^{i}} \tag{11}$$

The newly introduced grade parameter is similarly defined thus (Eqs. (12) and (13)):

$$\Lambda_{j}^{i} = \frac{\lambda_{j}^{i}}{Max\{\lambda_{j}\}} \left( \frac{\sum_{i=1}^{m} \left| \lambda_{j}^{i} - \overline{\lambda}_{j} \right|}{n} \right)^{-1}$$
(12)

$$\Lambda_j^{i'} = \frac{\Lambda_j^i}{\sum\limits_{i} \Lambda_j^i} \tag{13}$$

The sum of these three parameters gives us  $C_j^i$  the quality index of experiment *i* for element *j* (Eq. (14)):

$$C_{i}^{i} = \Gamma^{i'} + E_{i}^{i'} + \Lambda_{i}^{i'}$$
(14)

Where:

- i = experiment.
- m = number of experiments.
- j = specific PTE or another contaminant.
- n = number of elements.
- $\gamma_c^i$  = yield of experiment "i"
- $\overline{\gamma_c}$  = mean yield
- $\varepsilon_i^i$  = recovery of element "j" at experiment "i"
- $\overline{\varepsilon}_j$  = mean recovery for element "j"
- $\lambda_i^i$  = concentrate grade of element "j" at experiment "i"
- $\overline{\lambda}_i$  = Mean concentrate grade of element "j"
- $C_i^i$  = quality index of element "j" at experiment "i".

As in BAA, to account for the fact that different PTE's have different safe soil concentrations a target-to-distance correction can be used  $B_j^i$  (Eq. (15)):

$$B_{j}^{i} = \frac{\alpha_{j}^{i}}{\alpha_{j}^{ig}} \left( \frac{\sum\limits_{i=1}^{m} \left| \alpha_{j}^{i} - \overline{\alpha}_{j} \right|}{n} \right)^{-1}$$
(15)

Where:

-  $B_i^i$  = Weighting factor for element *j* in experiment *i* 

-  $\alpha_j^{tg}$  = Target decontamination grade, i.e., the acceptable threshold grade after decontamination

-  $\alpha_i^i$  = Grade of element *j* in experiment *i* 

-  $\overline{\alpha}_j$  = Grade of element *j* in experiment *i*Here, the ratio of the post separation grade,  $\alpha_j^i$ , to the target grade,  $\alpha_j^{tg}$  for the PTE of interest is weighted to minimize the final standard deviation of the result.

Normalizing this relative to its weight in the sum of m similar parameters  $B_i^i$  we obtain (Eq. (16)):

$$B_j^{i'} = \frac{B_j^i}{\sum\limits_{j}^m B_j^i}$$
(16)

Although optional, this correction factor is immensely useful given the diverse nature of soils and their varying levels and types of contamination. As will be demonstrated in the case study, its use can make a significant difference to the choice of an optimal separation method. It enables the prioritisation of certain PTEs based on their initial concentration in the soil and their corresponding safe concentration as specified by regulatory standards (Boente et al., 2017).

Finally, we define the decontamination quality index  $(Q_T^i)$  for all PTEs for a given experiment as (Eq. (17)):

$$Q_{T}^{i} = \sum_{j=1}^{n} C_{j}^{i} B_{j}^{i'}$$
(17)

The maximum value of  $Q_T^i$  corresponds to the BUC (Eq. (18)):

$$Q_{optimal} = Max \left\{ \sum_{j=1}^{n} C_{j}^{i} B_{j}^{i'} \right\}$$
(18)

A worked example with this methodology is provided in SM1.

#### 3. Results and discussion

#### 3.1. Separation results

Soil from the study site was tested to find the feed concentration grades ( $\alpha$ ) of a nine PTEs (Cr, Ni, As, Cu, Zn, Pb, Sb, Cd, Mo) and the values obtained were compared against Dutch standards (e.g., Buchman and Office of Response, n.d.) (Table 2). These standards provide an intervention value (IV) and target value (TV) for a range of PTEs and

Table 2

Bulk sample mean  $\alpha$  for the nine PTEs compared to their Dutch standard (e.g., Buchman and Office of Response, n.d.) intervention values (IV) and target values (TV). Elements are ordered by contamination level (CL) from the highest to the lowest.

PTE	Grade (α)	Intervention value (IV)	Target value (TV)	Contamination Level (CL)		
	ppm	ppm	ppm	TV/α		
Cr	55.7	0.35	220	159.03		
Ni	37.3	0.26	100	143.38		
As	60.7	0.9	55	67.45		
Cu	111.1	3.4	96	32.67		
Zn	377.1	16	350	23.57		
Pb	319.9	55	530	5.82		
Sb	9.5	3	15	3.16		
Cd	1.3	0.8	12	1.67		
Мо	4.1	3	190	1.37		

Chemosphere 358 (2024) 142135

were chosen as being among the most well-known and respected of available standards.

As can be seen on Table 2, out of the 9 PTEs studied, 7 (As, Cr, Cu, Ni, Pb, Sb, Zn) exceeded their respective IVs, while As, Cu and Zn also exceeded their TVs. To compare the severity of contamination associated with the PTEs under investigation, the ratio of the soil concentration of a given PTE to its TV was calculated to give a contamination level (CL). The PTEs were ranked in order of CL with the highest value, 159.3 recorded for Cr and the lowest, 1.37, recorded for Mo. Beyond the quality factor calculated for different experimental set ups (see 3.2) this provides a further criterion for selecting the optimum conditions. Specifically, optimal separation conditions should not only produce a high overall quality factor but also target the most serious pollutants.

Separation of soil samples was conducted under the 12 different experimental conditions identified on Table 1, and, in each case, the experimental concentrate yield,  $(\gamma_c^i)$  was calculated as were the recoveries  $(\varepsilon_i^i)$  of all PTEs off interest. The results are shown in Fig. 2.

In the following analysis, we shall discuss only the separation results for those experiments complied with the constraint  $\overline{\epsilon^i} < \gamma_c^i$  (thus experiments 5, 6, 7, and 10 have been omitted). The full set of raw separation results is presented in SM2 (Tables 1 and 2).

Fig. 2 ranks experiments, from left to right, in descending order of mean recovery value for the nine PTEs studied ( $\overline{\epsilon^i}$ ). Experiments 8 and 9 have by far the lowest mean recovery values ( $\overline{\epsilon^8} = 36.2\%$  and  $\overline{\epsilon^9} = 30.4\%$ ) while mean recovery values for the remaining experiments are similar, varying within a range from 54.6% (Experiment 4) to 59.8% (Experiment 3).

Referring to Fig. 3, the values for  $\gamma_c^i$  found in each experiment show a similar trend to that seen for  $\overline{\epsilon^i}$  (Fig. 2). Specifically, experiments 8 and 9 have the lowest values of  $\gamma_c^i$  ( $\gamma_c^8 = 16.1$  and  $\gamma_c^9 = 14.8$ ), while for the remaining experiments these values are not only significantly higher but also very similar:  $\gamma_c^i$  ranges from 34.1% (Experiment 2) to 43.5% (Experiment 3).

Based on these results it is unclear which experimental conditions would be optimal. Experiment 3 maximizes overall recovery but has the highest yield, while the experiments with the lowest yield (8 and 9) also have the lowest overall recoveries. Based on Cr recovery, six experiments record their highest recovery for this PTE, however, for all except Experiment 3, the recovery of Ni (the next most important contaminant in the sample, see Table 2) is their lowest recovery value.

To further assess the efficiency of our separation experiments, we can plot the mean PTE recovery value for each experiment ( $\overline{e^i}$ ) against the experimental concentrate fraction yield ( $\gamma_c^i$ ) and compare our results to the theoretical perfect, typical and non-separation curves (PSC, TSC and NSC: see for e.g., Richardson and Morrison, 2003). Experiments for which separation has been most successful should approach the PSC while less successful separation experiments will be closer to the NSC.

Referring to Fig. 4, the points representing Experiments 8 and 9 lie closest to the TSC. This suggests that these two experiments might provide the best upgrading conditions.

#### 3.2. Three-parameter attributive analysis for optimizing soil upgrading

While comparing experimental results to theoretical separation curves is adequate in many scenarios, that this method uses mean recovery values across all contaminants is a severe limitation since some PTEs are significantly more harmful than others. By its incorporation of a target-to-distance correction,  $B_j^i$ , 3PPAA-U offers a superior approach in this respect because it is able to consider recovery values for individual elements and therefore enables optimization of soil upgrading for specific PTEs.

In the following we compare 3PPAA-U with and without target-todistance correction in order to highlight its importance. Without this correction, the 3PPAA-U quality index ( $Q_{optimal}$ ) offers information on



Fig. 2. Recovery values for each experiment and PTE in the concentrated fraction ( $\varepsilon_j^i$ ). Results are in descending order of mean recovery,  $\overline{\epsilon^i}$ , (left to right). Only experiments in which  $\overline{\epsilon^i} < \gamma_c^i$  are shown.



**Fig. 3.** Yield for the concentrated  $(\gamma_c^i)$  and tailings  $(\gamma_t^i)$  fractions. Results are ordered by descending value of  $\gamma_c^i$ . Only experiments in which  $\overline{\epsilon^i} < \gamma_c^i$  are shown.

which experimental parameters lead to the overall most efficient soil upgrading process, that is, it ranks experiments according to their average performance with respect to all PTEs considered without addressing the relative toxicity of different elements. With target-todistance correction, 3PPAA-U can help adapt and optimize a soil washing process to the precise contamination properties of a given soil.

Table 3 shows the quality indices for all of the experiments calculated using 3PPAA-U without target-to-distance correction. The best performing experiments still appear to be Experiments 8 and 9 with quality indices 0.6 and 0.7 units greater than the third best performer (Experiment 2) (Table 3).

However, as previous results show (see Figs. 1 and 2), these two experiments have not only the lowest values of  $\gamma_c^i$  (both are nearly half the value found for Experiment 2 which has the next lowest  $\gamma_c^i$ ) but also

the lowest values of  $\overline{\epsilon^i}$  ( $\overline{\epsilon^8} = 36.2\%$  and  $\overline{\epsilon^9} = 30.4\%$  corresponding to, respectively, nearly half and two thirds that the next lowest mean recovery,  $\overline{\epsilon^4} = 54.6\%$ ). That 3PPAA-U points to these experiments as potentially giving the BUC suggests that optimal conditions are favoured more by minimizing  $\gamma_c^i$  than maximizing  $\overline{\epsilon^i}$ . This becomes clear if we consider that both these values are higher for Experiment 8 than for Experiment 9 but the difference is greatest for  $\overline{\epsilon^i}$  (for  $\gamma_c^i$  is 1.33% higher and  $\overline{\epsilon^i}$  is 5.76% higher); thus, since Experiment 9 has the higher quality index, it would seem that more is gained by a marginal minimisation of  $\gamma_c^i$  compared to a far larger gain in  $\overline{\epsilon^i}$ .

Referring back to Fig. 4, it can be seen that compared to the points representing all other experiments, those representing Experiments 8 and 9 were closest to the TSC. Thus, 3PPAA-U without target-to-distance



**Fig. 4.** Mean recovery and concentrate yield for each experiment ( $\overline{\epsilon^i} < \gamma_c^i$ ) plotted for comparison to curves for perfect separation (PSC), non-separation (NSC), and typical separation (TSC).

Table 3	
3PPAA-U before the target-to-distance-to target correction for experiments	where $\overline{\varepsilon^i} < \gamma_i^i$

Experiment				$C_j^i$					$\sum_{j=1}^{n} \mathbb{C}_{j}^{i}$	
	As	Cd	Cr	Cu	Мо	Ni	Pb	Sb	Zn	
1	0.3974	0.3692	0.3772	0.3796	0.3958	0.3462	0.3939	0.4292	0.3648	3.4533
2	0.3961	0.3719	0.4022	0.3869	0.3674	0.3616	0.4032	0.4295	0.3813	3.5003
3	0.3384	0.3339	0.4002	0.3506	0.3724	0.3646	0.3454	0.3425	0.3458	3.1937
4	0.3262	0.4407	0.3084	0.3444	0.2744	0.3593	0.3172	0.2528	0.3770	3.0004
8	0.4768	0.4384	0.4989	0.4526	0.4447	0.4137	0.4737	0.4799	0.4460	4.1247
9	0.4795	0.4584	0.4798	0.4650	0.4479	0.4362	0.4861	0.4944	0.4571	4.2044
11	0.2914	0.2928	0.2791	0.3102	0.3690	0.3570	0.2864	0.2672	0.3110	2.7640
12	0.2942	0.2947	0.2542	0.3107	0.3283	0.3615	0.2941	0.3045	0.3170	2.7592

Table 4

3PPAA-U after the distance to target correction for experiments where  $\overline{\epsilon^i} < \gamma_c^i$ .

Experiment					$\mathbb{C}^{i}_{j} \boldsymbol{B}^{i^{'}}_{j^{'}}$					$\sum_{j=1}^{n} \mathbb{C}_{j}^{i} B_{j}^{i'}$
	As	Cd	Cr	Cu	Мо	Ni	Pb	Sb	Zn	
1	0.0612	0.0486	0.0598	0.0508	0.0467	0.0440	0.0668	0.0742	0.0496	0.5017
2	0.0654	0.0510	0.0630	0.0563	0.0514	0.0471	0.0658	0.0721	0.0570	0.5290
3	0.0514	0.0462	0.0735	0.0516	0.0547	0.0525	0.0511	0.0444	0.0513	0.4768
4	0.0446	0.0853	0.0425	0.0455	0.0334	0.0549	0.0411	0.0292	0.0602	0.4368
8	0.0496	0.0506	0.0608	0.0447	0.0419	0.0475	0.0545	0.0589	0.0448	0.4533
9	0.0656	0.0542	0.0500	0.0547	0.0475	0.0442	0.0659	0.0811	0.0541	0.5173
11	0.0220	0.0227	0.0199	0.0319	0.0529	0.0394	0.0186	0.0172	0.0276	0.2524
12	0.0223	0.0260	0.0167	0.0379	0.0426	0.0431	0.0217	0.0191	0.0314	0.2608

correction suggests similar BUCs to those derived from conventional separation curve methods.

Table 4 shows the quality indices of each experiment calculated with target-to-distance correction. In this way, the quality index now includes a consideration of the grade concentrations for individual PTEs of interest for each experimental set up studied. Referring to Table 4, while Experiment 9 still comes out as one of the best methods, Experiment 2, ranked third before target-to-distance correction, now appears to be optimal with Experiments 1 and 3 also performing well.

Fig. 5 shows a plot of quality indices for each of our experimental set ups to highlight the differences between which separation conditions would seem optimal without (curve A) and with (curve B) target-todistance correction.

As can be seen in the tables included in SM2, while recovery and yield vary relatively little between experiments (the standard deviation is between 10.02 and 12.73 for both these values), the grades found for different PTEs varies greatly in each experiment (the standard deviation in  $\lambda$  for some elements [for instance Cd] is as low as 0.67 while for others [such as Pb] it is as high as 181). In this way, it is no surprise that the calculation with target-to-distance correction produces very different results compared to previous methods.

Our results show 3PPAA-U provides a good general method for the



**Fig. 5.** Results of 3PPAA-U without (A) and with (B) target-to-distance correction for experiments with  $\overline{\epsilon^i} < \gamma_c^i$ 

identification of promising experimental configurations for soil upgrading operations. However, it is only a guide, and to select the BUCs for a particular soil, it is recommended that the top 2 or 3 configurations identified by 3PPAA-U be examined more closely to fine tune values of  $\gamma_c$  and  $\varepsilon$ . This is particularly important where, as in the current set of experiments, the analysis shows two configurations (Experiments 2 and 9) to have very similar efficiencies.

The 3PPAA methodology extends beyond identifying BUCs for soil washing, offering potential to identify optimal operating conditions across a broad spectrum of materials processing and manufacturing scenarios. The methodology could be extended to include a range of variables— from temperature and pressure to particle size, alongside environmental and economic considerations, such as energy consumption or  $CO_2$  generation—to address a number of complex operational challenges simultaneously.

#### 4. Conclusions

Three Parameter Attribute Analysis for soil upgrading is a method that allows the identification of and prioritizing of operational outcomes; thus, it can enable the fine tuning of operations to the specific problems of a given site.

A particular strength of 3PPAA-U for soil upgrading lies in how it deals with multicomponent feeds to derive the BUC. Firstly, the method has a clear criterion for establishing which fraction constitutes the concentrate and which the tailings so avoiding the issue that in some experiments, pollutants might report to different fractions. In addition, its target-to-distance correction selects the optimal upgrading conditions based on preferential contribution of the most harmful pollutants. The method is also robust to extremes of variation in parameters due to the way in which these are weighted.

3PPAA-U assess separation experiments based on three parameters, the grade ( $\lambda$ ) and recovery ( $\varepsilon$ ) of pollutants to be targeted and the concentrate yield ( $\gamma_c$ ). The method ranks different experimental configurations dependent upon how well they maximize the grade and recovery while minimizing yield and appears to prioritize the minimisation of yield over maximizing recovery. Without target-to-distance correction, 3PPAA-U is at least as good at selecting optimal experimental conditions as methods based on other criteria, such as the proximity to the perfect separation curve. The additional correction enables 3PPAA-U to exceed these traditional methods and so potentially improve the outcome of soil washing processes.

It is important to recognize that the 3PPAA-U is not an absolute guide for identifying the BUC, but rather a heuristic methodology. Thus, although it provides a structured and objective approach for evaluating and comparing different options, it is based on a set of assumptions and simplifications, so it may not capture the full complexity of a given soil washing operation. In this way, researchers and practitioners are advised to take this methodology only as an indicator of which experimental configurations are most promising and worth looking into further. The full decision-making process for choosing the best approach for a particular site must also consider a full range of subjective and qualitative factors such as cost, feasibility and risk. Consequently, although 3PPAA-U can be a useful tool for decision-making, it should be used in conjunction with other methods and criteria and should be applied with caution and critical thinking. One of the most obvious improvements of this method would be to include a third parameter, the grade, as part of the calculation for the experimental quality index  $(C_j^i)$ . This additional constraint could potentially mitigate the impact of anomalous values and improve the overall accuracy of the method. Further research might include expanding the 3PPAA-U methodology to assess a fuller range of criteria important to the success of soil washing operations.

#### CRediT authorship contribution statement

**X.** Corres: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **N.** Gómez: Writing – review & editing, Validation, Methodology. **C.** Boente: Writing – review & editing, Methodology, Formal analysis. J.R. Gallego: Writing – review & editing, Supervision, Resources, Funding acquisition. **C.** Sierra: Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Formal analysis, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgements

Carlos Sierra thanks the EURECA-PRO phase I 2020–2023 co-funded by the Erasmus+ Program of the European Union (Ref.: 101004049). Open Access funding provided thanks to the Read and Publish. Nacional. Periodo 2021-2024 agreement between Universidad Politécnica de Madrid and Elsevier.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.142135.

#### X. Corres et al.

#### References

Ashraf, S., Ali, Q., Zahir, Z.A., Ashraf, S., Asghar, H.N., 2019. Phytoremediation: environmentally sustainable way for reclamation of heavy metal polluted soils. Ecotoxicol. Environ. Saf. 174, 714–727. https://doi.org/10.1016/J. ECOENV.2019.02.068.

Boente, C., Sierra, C., Rodríguez-Valdés, E., Menéndez-Aguado, J.M., Gallego, J.R., 2017. Soil washing optimization by means of attributive analysis: case study for the removal of potentially toxic elements from soil contaminated with pyrite ash. J. Clean. Prod. 142, 2693–2699. https://doi.org/10.1016/j.jclepro.2016.11.007.

Boente, C., Gerassis, S., Albuquerque, M.T.D., Taboada, J., Gallego, J.R., 2020. Local versus regional soil screening levels to identify potentially polluted areas. Math. Geosci. 52, 381–396. https://doi.org/10.1007/s11004-019-09792-x. Buchman, M., Office of Response, N., 2008. SQuiRT Cards.

Chen, Z., Ma, Y., Liao, X., 2016. Phytoremediation of heavy metal pollution from mining and smelting activities: a review. J. Clean. Prod. 127, 19–30.

Chen, L., Wang, F., Zhang, Z., Chao, H., He, H., Hu, W., Zeng, Y., Duan, C., Liu, J., Fang, L., 2023. Influences of arbuscular mycorrhizal fungi on crop growth and potentially toxic element accumulation in contaminated soils: a meta-analysis. Crit. Rev. Environ. Sci. Technol. 53, 1795–1816. https://doi.org/10.1080/ 10643389.2023.2183700.

Corres, X., Sierra, C., Diez-Mestas, A.J., Gallego, J.R., Baragaño, D., 2024. A novel heuristic tool for selecting the best upgrading conditions for the removal of potentially toxic elements by soil washing. J. Hazard Mater. 466, 133529. https:// 10.1016/j.jhazmat.2024.133529.

 Dermont, G., Bergeron, M., Mercier, G., Richer-Laflèche, M., 2008. Soil washing for metal removal: a review of physical/chemical technologies and field applications. J. Hazard Mater. 152 (1), 1–31. https://doi.org/10.1016/J.JHAZMAT.2007.10.043.
 Drzymała, J., 2006. Atlas of upgrading curves used in separation and mineral science and

 technology. Physicochem. Probl. Miner. Process. 40 (1), 19–29.
 Guo, J., Yuan, C., Zhao, Z., He, Q., Zhou, H., Wen, M., 2022. Soil washing by biodegradable GLDA and PASP: effects on metals removal efficiency, distribution, leachability, bioaccessibility, environmental risk and soil properties. Process Saf. Environ. Protect. 158, 172–180. https://doi.org/10.1016/J.PSFP.2021.12.004.

Karim, A.V., Jiao, Y., Zhou, M., Nidheesh, P.V., 2021. Iron-based persulfate activation process for environmental decontamination in water and soil. Chemosphere 265, 129057. https://doi.org/10.1016/j.chemosphere.2020.129057.

Khalid, S., Shahid, M., Niazi, N.K., Murtaza, B., Bibi, I., Dumat, C., 2017. A comparison of technologies for remediation of heavy metal contaminated soils. J. Geochem. Explor. 182, 247–268. https://doi.org/10.1016/J.GEXPLO.2016.11.021.

Khum-in, V., Suk-in, J., In-ai, P., Piaowan, K., Praimeesub, Y., Rintachai, K., Supanpaiboon, W., Phenrat, T., 2023. Combining magnet-assisted soil washing and soil amendment with zero-valent iron to restore safe rice cultivation in real cadmium-contaminated paddy fields. Chemosphere 340, 139816. https://doi.org/10.1016/j.chemosphere.2023.139816.

Lee, K.Y., Kim, K.W., 2010. Heavy metal removal from shooting range soil by hybrid electrokinetics with bacteria and enhancing agents. Environ. Sci. Technol. 44 (24), 9482–9487. https://doi.org/10.1021/ES102615A/SUPPL\_FILE/ES102615A\_SI\_001. PDF.

Pinto, I.S.S., Neto, I.F.F., Soares, H.M.V.M., 2014. Biodegradable chelating agents for industrial, domestic, and agricultural applications—a review. Environ. Sci. Pollut. Control Ser. 21 (20), 11893–11906. https://doi.org/10.1007/S11356-014-2592-6/ METRICS.

Richardson, J.M., Morrison, R.D., 2003. Metallurgical balances and efficiency. In: Fuerstenau, M.C., Han, K.N. (Eds.), Principles of Mineral Processing. Society for Mining, Metallurgy, and Exploration, 2003.

Rieuwerts, J.S., Mighanetara, K., Braungardt, C.B., Rollinson, G.K., Pirrie, D., Azizi, F., 2014. Geochemistry and mineralogy of arsenic in mine wastes and stream sediments in a historic metal mining area in the UK. Sci. Total Environ. 472, 226–234. https:// doi.org/10.1016/j.scitotenv.2013.11.029.

Sierra, C., Gallego, J.R., Afif, E., Menéndez-Aguado, J.M., González-Coto, F., 2010. Analysis of soil washing effectiveness to remediate a brownfield polluted with pyrite ashes. J. Hazard Mater. 180, 602–608. https://10.1016/j.jhazmat.2010.04.075.

Sierra, C., Martínez, J., Menéndez-Aguado, J.M., Afif, E., Gallego, J.R., 2013. High intensity magnetic separation for the clean-up of a site polluted by lead metallurgy. J. Hazard Mater. 248–249 (1), 194–201. https://doi.org/10.1016/j. ihazmat.2013.01.011.

Sun, Y., Li, H., Guo, G., Semple, K.T., Jones, K.C., 2019. Soil contamination in China: current priorities, defining background levels and standards for heavy metals. J. Environ. Manag. 251, 109512 https://doi.org/10.1016/J. JENVMAN.2019.109512.

Wang, Y., Li, A., Cui, C., 2021. Remediation of heavy metal-contaminated soils by electrokinetic technology: mechanisms and applicability. Chemosphere 265, 129071. https://10.1016/j.chemosphere.2020.129071.

Wu, Q., Leung, J.Y.S., Geng, X., Chen, S., Huang, X., Li, H., Huang, Z., Zhu, L., Chen, J., Lu, Y., 2015. Heavy metal contamination of soil and water in the vicinity of an abandoned e-waste recycling site: implications for dissemination of heavy metals. Sci. Total Environ. 506–507, 217–225. https://doi.org/10.1016/J. SCITOTENV.2014.10.121.

Ye, B., Lan, J., Nong, Z., Qin, C., Ye, M., Liang, J., Li, J., Bi, J., Huang, W., 2022. Efficiently combined technology of precipitation, bipolar membrane electrodialysis, and adsorption for salt-containing soil washing wastewater treatment. Process Saf. Environ. Protect. 165, 205–216. https://doi.org/10.1016/j.psep.2022.07.015.