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Exploratory analysis of elements in incineration bottom ash with numerous values below the detection limit using selected substitution methods

Monika Chuchro[1], Mateusz Zaręba[2], Radosław Jędrusiak[3]

[1] *AGH University of Krakow, Faculty of Geology, Geophysics and Environmental Protection, Krakow, Poland, e-mail: chuchro@agh.edu.pl (corresponding author), ORCID ID: 0000-0002-0381-4697*
[2] *AGH University of Krakow, Faculty of Geology, Geophysics and Environmental Protection, Krakow, Poland, e-mail: zareba@agh.edu.pl, ORCID ID: 0000-0002-9663-6593*
[3] *Krakowski Holding Komunalny S.A. w Krakowie, Krakow, Poland, e-mail: rjedrusiak@khk.krakow.pl, ORCID ID: 0000-0003-0008-4075*

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Abstract: This study investigates the influence of substitution methods for left-censored values on exploratory data analysis (EDA) of the incineration bottom ash (IBA). IBA, a by-product of municipal solid waste incineration, contains a wide range of economically valuable elements, many of which are frequently reported below detection limits due to analytical constraints. The study aims to evaluate the impact of different substitution methods on descriptive statistics, correlation analysis, and regression modeling outcomes.
Four widely used substitution approaches were compared: (i) replacement with half of the detection limit, (ii) random values from a uniform distribution, (iii) robust regression on order statistics (ROS), and (iv) tobit regression (applied in both small and large variants). Five trace elements with different proportions of censored values (13–67%) were analyzed using a dataset of 52 weekly samples collected throughout 2021 at the Krakow Thermal Waste Treatment Plant. The impact of each method was assessed using descriptive statistics, Pearson correlation matrices, and multiple linear regression models. Additional analyses incorporated 11 auxiliary elements to enhance correlation and regression model robustness.
The results show that substitution methods significantly affect data distributions, particularly for elements with high censoring rates. ROS and tobit regression produced more stable statistical outputs and narrower histograms compared to simpler methods. Furthermore, regression model performance improved with substitution compared to raw data, with tobit methods demonstrating the highest accuracy for elements with strong inter-element correlations. The findings provide methodological guidance for reliable data handling in IBA analysis and recovery assessments.

Keywords: incineration bottom ash, robust regression on order statistics, tobit regression, left-censored, exploratory data analysis

INTRODUCTION

Incineration bottom ash (IBA) generated in municipal solid waste incinerators is a free-flowing bulk solid with a density of approximately 1.2 Mg/m^3. This waste is made up of several key components which include a mineral fraction with particles larger than 2 mm, such as glass, porcelain, tiles, pottery, cement, and sintered grit. It also contains slag, which is solidified partially molten material, and native metals larger than 2 mm, including both ferrous and non-ferrous metals. Additionally, there is unburnt organic matter larger than 2 mm, such as books, leather, and wood. Finally, there is fine-grained grit, smaller than 2 mm, which consists of a mixture of all the previously mentioned materials, along with metal oxides, filler materials from paper and plastics, and wood ash (Bunge 2019). Furthermore, IBA is a substantial repository of valuable elements, including rare earth metals, precious metals, and other strategic elements of significant economic and industrial importance (Morf et al. 2013, Funari et al. 2015). The analysis of element flow reveals that the proportion of elements present in municipal solid waste IBA residues is considerable. This highlights the potential of Municipal Solid Waste Incineration (MSWI) residues as an important secondary source of valuable raw materials. Given the increasing demand for critical elements and the challenges associated with mining them – due to environmental, economic, and geopolitical factors, recovering these elements from waste offers a promising strategy for reducing dependence on primary resources. It also helps minimize the environmental impact of conventional mining while contributing to circular economy practices by reintroducing valuable materials back into production cycles (Jędrusiak et al. 2023). The extraction of valuable elements from bottom ash is achievable through the utilization of diverse techniques, including magnetic separation, electrostatic separation, and hydrometallurgical processes (Nørgaard et al. 2019, Šyc et al. 2020, Back & Sakanakura 2022). Within the framework of a circular economy, the recovery of elements from bottom ash can generate substantial economic and environmental advantages, including reduced primary raw material consumption, decreased greenhouse gas emissions, and minimized waste disposal (Brunner & Rechberger 2016).

In addition to its complex composition, IBA can be treated as a matrix containing compositional data, which describes the proportions or components of a mixture (Aitchison 2003). Therefore, it is essential to understand the properties and behavior of compositional data in the context of IBA. Moreover, the presence of values below the limit of detection (left-censored) in datasets is a significant issue that can impact data analysis and interpretation (Filzmoser et al. 2009, Buccianti & Grunsky 2014).

The presence of left-censored values in datasets is a consequence of the inherent limitations of analytical methods, including instrument sensitivity, reagent quality, and external factor influences (Helsel 1990). These values, which fall below the limits of detection (LOD), can significantly impact data analysis and interpretation. The omission or incorrect substitution of left-censored values can lead to biased statistical conclusions and erroneous predictions (Singh & Nocerino 2002). In the context of element recovery from IBA, the neglect of left-censored values can result in the underestimation of estimated recovery rates, potentially leading to inaccurate assessments of economic viability (Filzmoser et al. 2009). Conversely, the failure to account for left-censored values can also lead to overestimation of recovery quantities, resulting in misguided investment decisions (Filzmoser et al. 2009, Tekindal et al. 2017). To mitigate these risks, it is crucial to employ suitable statistical methods and analytical techniques that accommodate left-censored values, thereby ensuring accurate estimates of element recovery quantities from IBA (Tekindal et al. 2017).

Consequently, various methods have been developed to address this problem, including replacing values with half of the detection limit (Helsel 1990), Aitchison's method (Aitchison 2003), Cohen's method (Cohen 2016), random substitution (Singh & Nocerino 2002), Kaplan–Meier estimation (Kaplan & Meier 1992), maximum likelihood estimation (Helsel 1990), robust regression on order statistics (Helsel 2005), tobit regression (Tobin 1958, Mikšová et al. 2020), and Weibull regression (Rodrigues et al. 2022). Moreover, log-normal regression, gamma regression, and bootstrapping can also be used for replacing values below the detection limit (Helsel 1990, 2005). However, each method has its strengths and limitations, and the choice of method depends on the specific characteristics of the dataset and the research question being addressed. As Helsel noted, replacing values below the detection limit with random values can lead to incorrect conclusions and imprecise estimates (Helsel 1990, 2005). For instance, the half of detection limit method is commonly utilized in environmental sciences, such as assessing chemical contaminants in soil or water (Singh & Nocerino 2002), with censoring rates ranging from 1% to 50%. Robust regression on order statistics is recommended for small datasets with left-censored values between 15% and 50% (EPA 2006). Conversely, the maximum likelihood estimation (MLE) approach is recommended when dealing with datasets containing left-censored values with multiple levels of LOD, as it provides a robust framework for estimating parameter values in the presence of complex censorship patterns (Helsel 1990).

The study examines and compares several widely used methods for the substitution of values below the detection limit, using actual environmental data sets that contain different proportions of censored values, which is a frequent issue in this field. The primary objective of the research was to determine how different substitution methods influence the outcomes of exploratory data analysis, including descriptive statistics, distributional characteristics, correlation structures, and the performance of multiple regression models. By systematically evaluating these methods across datasets characterized by different censorship levels, the study provides a comprehensive assessment of the robustness, consistency, and potential biases introduced through substitution. Moreover, the analysis aimed to quantify how treating below-detection values as missing data may distort statistical inference, thereby affecting interpretation in applications such as element recovery assessment, environmental monitoring, and material flow analysis. Through this comparative framework, the study offers practical guidance for selecting appropriate substitution strategies in environmental research involving censored values.

MATERIALS AND METHODS

Incineration bottom ash (IBA)

The research concept for analyzing metal content in bottom ashes from municipal waste incineration was developed at the Krakow Thermal Waste Treatment Plant in 2020–2021 (Fig. 1A). The plant, commissioned in 2016, has two independent incineration lines with a total processing capacity of 245,000 Mg/year.

The feedstock consists of two municipal waste streams: mechanically and biologically treated waste (60%) and non-recyclable waste (40%). The incineration technology employs a grate furnace with a natural circulation steam boiler, generating bottom ash that undergoes a two-week ageing period to reduce leachability and change the moisture content from 30% to 12–20%.

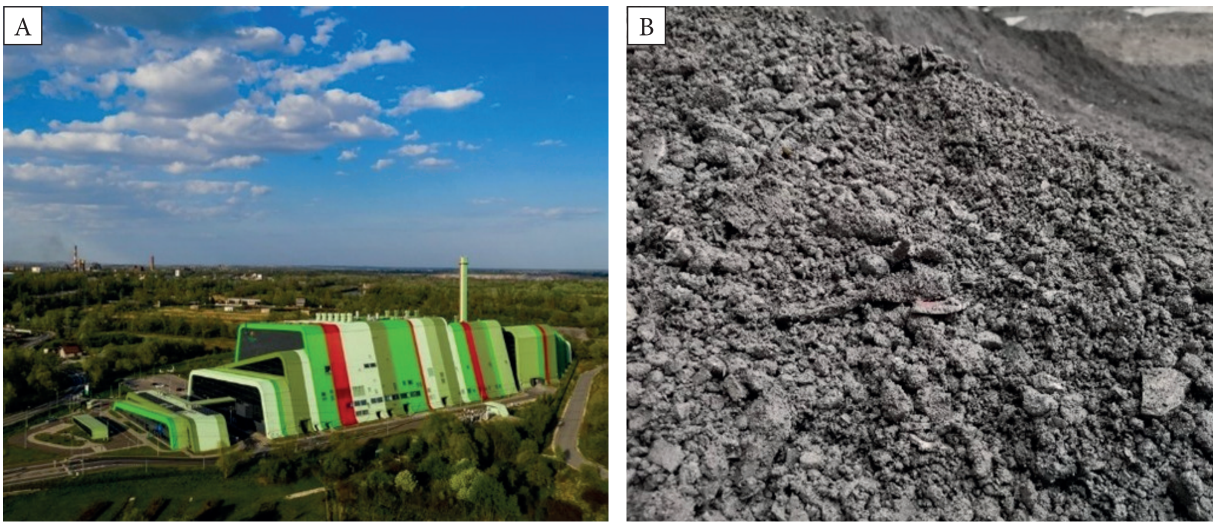

Fig. 1. *Krakow Thermal Waste Treatment Plant (A) and incineration bottom ash (B)*

Sampling and laboratory analyses

Sampling and analysis were conducted on bottom ash subjected to preliminary ageing and partial metal recovery. Samples were collected weekly from January to December 2021, as per PN-EN 14899 standard (PKN 2006, Skutan et al. 2018), and it was known in advance that 52 samples would be taken over the course of the year. Eight primary samples (3.5–4.0 Mg each) were combined into a composite sample, reduced in size through a series of divisions, and finally yielded approximately 10 kg laboratory samples (Fig. 1B). These samples were crushed (<2 mm) and milled (<75 μm) before analysis via inductively coupled plasma mass spectrometry. Metal content was determined using a Perkin Elmer ELAN 9000 mass spectrometer, with quality control ensured through certified reference materials and blank sample analysis. Quality control procedures utilized the reference standards STD BVGEO01 and OREAS 262. The analysis of the bottom ash chemical composition was conducted at the Bureau Veritas Commodities Canada Ltd. laboratory.

Data

To evaluate the performance of different methods for replacing missing values, a dataset of 5 elements with varying numbers of observations below the detection limit was selected. The elements were measured in IBAat regular intervals throughout 2021, resulting in 52 observations per element, expressed in parts per billion (ppb). Furthermore, to assess the effect of replacement methods on exploratory data analysis and modeling, a subset of 11 elements (Ag, Ba, Ca, Cr, Fe, Li, Mg, Mn, Ni, S, and Sb) without missing or censored values was used. These elements exhibited linear correlations with the analyzed elements, and linear regression models could be successfully fitted for most of them.

Methods

Four popular methods for replacing values below the detection limit were selected and their impact on data analysis was evaluated. The methods under consideration included: replacement with half of the detection limit (h), replacement with a random value from a uniform distribution between 0 and the detection limit (g), robust regression on order statistics (r), and tobit regression in two variants: a small variant (t), which included only data from the 5 elements with values below the detection limit, and a large variant (tl), which additionally included a set of 11 elements.

ROS is a semiparametric method designed to estimate the concentration of censored values in datasets. This approach assumes an underlying parametric distribution for the uncensored values and utilizes ordered detected values and distributional quantiles to estimate the concentration of censored observations. ROS is particularly useful when dealing with multiple censored values, as it provides a robust and efficient way to estimate the true concentrations of the analytes (Helsel 1990, 2005). The substitution process involves finding a distributional model that fits the joint sample of detects and left-censored values, constructing a partial ranking of the data and determining the cumulative probability associated with each distinct LOD. In the last step, the fitted distributional model is used to impute values for non-detects through linear regression between detected values and z-scores from the censored probability plot (Helsel 2005).

Tobit regression is a type of regression analysis that models the relationship between a dependent variable and one or more independent variables when there are censored observations. The method assumes that the censored values follow a normal distribution and uses MLE to estimate the model parameters. Tobit regression is particularly useful when dealing with datasets containing a large number of censored observations, as it provides a way to account for the censoring mechanism and obtain unbiased estimates of the relationships between variables (Tobin 1958, Mikšová et al. 2020).

To test whether the application of substitution methods affects the results of EDA, the following analyses were performed for both the raw data (where values below the detection limit were replaced with missing values) and the transformed data using various substitution methods: descriptive statistics, histograms, linear Pearson correlation matrices, and multiple regression models.

All of the listed analyses were performed in R (version 4.3.2), using standard statistical and data-processing tools available in this environment. The computational workflow included procedures for data cleaning, substitution of values below the detection limit, exploratory data analysis, and statistical modelling.

RESULTS

The analysis involved 5 elements detected in IBA after municipal waste incineration, which differed in the number of values below the detection limit (left-censored) in a dataset of 52 measurements.

For germanium, 27 left-censored values (52% of the dataset) had a LOD of 100 ppb (Fig. 2A). The mean values obtained using various substitution methods were similar (137.4–140.6 ppb), whereas the raw data mean was significantly higher (236 ppb). The median and lower quartile values varied among substitution methods, with the random method and ROS yielding lower values (Table 1, Fig. 2A, B). Additionally, the lower quartile value and median for the raw data were 100 ppb, which was at least twice as high as the lower quartile value for selected substitution methods. For minimum values, a greater spread of predicted left-censored values was observed for ROS and the random method (Fig. 2B). The tobit method, based on both small and large datasets, yielded similar minimum values to the half-method. Notably, the standard deviation and skewness of the data differed significantly between the substitution methods and the raw data (Table 1).

Hafnium had 16 observations below the detection limit (31% of all observations) with a LOD of 20 ppb (Fig. 2C). The mean values obtained using various substitution methods were similar but differed substantially from the raw data mean (approx. 26 ppb). Minimum values for the random method and ROS were lower than those for other substitution methods (1 ppb and 2.7 ppb, respectively), whereas the minimum value for other substitution methods exceeded 8.8 ppb. As evident from the histogram (Fig. 2D), the left-skewed distribution for the random method and ROS was more elongated than that for other substitution methods. The lower quartile values for substitution also exhibited variability but were significantly lower than those for the raw data, ranging from 9.0 ppb (tobit method) to 16.8 ppb (random method), whereas the raw data had a lower quartile value of 30 ppb. The median, standard deviation, and skewness values were similar or identical for all substitution methods and differed significantly from those calculated for the raw data (Table 1).

Indium exhibited the lowest number of values below the detection limit (13% of all values – 7 observations) with a LOD of 20 ppb (Fig. 2E). The mean value for all methods was very similar (differences not exceeding 0.5 ppb), whereas the raw data mean was higher (116 ppb). Minimum values for the random method and ROS were lower than those obtained by other substitution methods (Table 1). The first quartile and median values are identical for all substitution methods and also lower than those calculated for the raw data. The left-skewed distribution of the data for the random method is significantly elongated due to the minimum value, similarly to the distributions for the ROS and half-methods (Fig. 2F). The third quartile value is identical for all datasets, including the raw data. The standard deviation and skewness values for all substitution methods are similar to each other. The largest difference in skewness between substitution methods was observed between the half-method and ROS, with a difference of 0.24. The difference in skewness between the raw data and imputed data is 0.24 (for ROS), see Table 1.

Palladium had 14 observations below the detection limit (27% of the entire dataset) with a LOD of 10 ppm (Fig. 2G). The mean values for each method were very similar (41.27–41.61 ppb), whereas the raw data mean was higher (54.7 ppb). The median value was identical for all substitution methods (18 ppb), which was 10 ppb lower than that calculated for the raw data. Similarly, for the upper quartile, all substitution methods yielded a single value of 39.75 ppm, which is lower than the value calculated for the raw data (46 ppb). The lowest minimum values were obtained for the random method (2 ppb) and ROS (1.4 ppb), as evident from the elongated left-skewed histogram (Fig. 2H). For the remaining three substitution methods, the minimum value was 5 ppb. The standard deviation values for all substitution methods are 102 ppb, whereas for the raw data, it is 117 ppb. Skewness, except for the half-method, is 5.9 (Table 1).

Table 1
Descriptive statistics of raw data and data after substitution of LOD values

Descriptive statistics	**German (Ge), ppb, LOD = 100 ppb, number of left-censored values = 27–52%**					
	raw	**half (h)**	**random (g)**	**ROS (r)**	**tobit_small (t)**	**tobit_large (tl)**
mean	236.00	139.40	140.62	138.86	137.44	137.65
1st Q	100.00	50.00	35.50	30.72	44.44	44.85
median	100.00	50.00	96.50	100.00	62.91	63.21
3rd Q	100.00	100.00	100.00	100.00	100.00	100.00
min	NA	50.00	3.00	7.35	41.27	41.71
max	2,900.00	2,900.00	2,900.00	2,900.00	2,900.00	2,900.00
standard deviation	557.43	393.74	394.04	394.79	394.23	394.18
skewness	4.63	7.02	6.99	6.97	7.01	7.01
Descriptive statistics	**Hafn (Hf), ppb, LOD = 20 ppb, number of left-censored values = 16–31%**					
	raw	**half (h)**	**random (g)**	**ROS (r)**	**tobit_small (t)**	**tobit_large (tl)**
mean	93.33	67.69	68.23	67.47	67.41	67.44
1st Q	30.00	10.00	16.75	13.05	9.04	9.25
median	40.00	30.00	30.00	30.00	30.00	30.00
3rd Q	95.00	70.00	70.00	70.00	70.00	70.00
min	NA	10.00	1.00	2.68	8.88	8.81
max	420.00	420.00	420.00	420.00	420.00	420.00
standard deviation	105.23	95.44	95.16	95.61	95.61	95.59
skewness	1.71	2.26	2.26	2.25	2.25	2.25
Descriptive statistics	**Indium (In), ppb, LOD = 20 ppb, number of left-censored values = 7–13%**					
	raw	**half (h)**	**random (g)**	**ROS (r)**	**tobit_small (t)**	**tobit_large (tl)**
mean	116.20	101.90	102.20	101.72	102.03	102.03
1st Q	30.00	20.00	20.00	20.00	20.00	20.00
median	50.00	40.00	40.00	40.00	40.00	40.00
3rd Q	100.00	100.00	100.00	100.00	100.00	100.00
min	NA	10.00	2.00	3.46	10.39	10.38
max	2,030.00	2,030.00	2,030.00	2,030.00	2,030.00	2030.00
standard deviation	299.12	280.20	280.16	280.31	280.20	280.20
skewness	6.02	6.50	6.27	6.26	6.27	6.27
Descriptive statistics	**Pallad (Pd), ppb, LOD = 10 ppb, number of left-censored values = 14–27%**					
	raw	**half (h)**	**random (g)**	**ROS (r)**	**tobit_small (t)**	**tobit_large (tl)**
mean	54.71	41.30	41.61	41.27	41.36	41.36
1st Q	15.25	5.00	10.00	7.95	5.90	5.90
median	28.50	18.00	18.00	18.00	18.00	18.00
3rd Q	46.00	39.75	39.75	39.75	39.75	39.75
min	NA	5.00	2.00	1.40	5.01	5.01
max	731.00	731.00	731.00	731.00	731.00	731.00
standard deviation	117.33	102.40	102.28	102.42	102.38	102.38
skewness	5.27	6.10	5.94	5.92	5.93	5.93
Descriptive statistics	**Ren (Re), ppb, LOD = 1 ppb, number of left-censored values = 35–67%**					
	raw	**half (h)**	**random (g)**	**ROS (r)**	**tobit_small (t)**	**tobit_large (tl)**
mean	2.53	1.16	1.15	1.03	1.10	1.12
1st Q	1.00	0.50	0.35	0.12	0.37	0.43
median	1.00	0.50	0.75	0.32	0.43	0.44
3rd Q	2.00	1.00	1.00	1.00	1.00	1.00
min	NA	0.50	0.06	0.01	0.35	0.39
max	18.00	18.00	18.00	18.00	18.00	18.00
standard deviation	4.06	2.47	2.49	2.52	2.49	2.48
skewness	3.52	6.30	5.99	5.85	6.03	6.06

NA – not available.

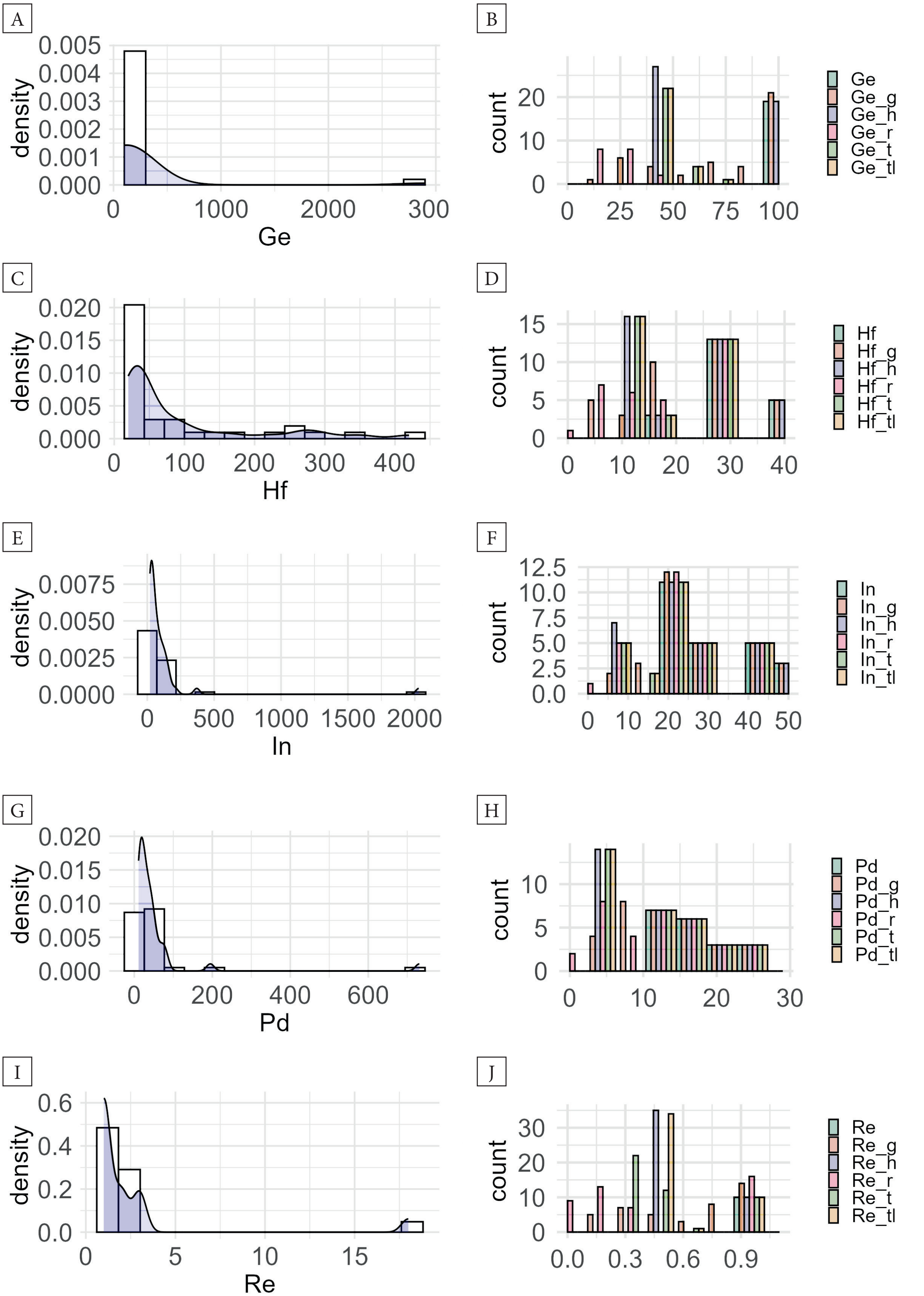

Fig. 2. *Data distribution: raw data – left; values lower then median – right*

Rhenium exhibited the highest number of values below the detection limit among the analyzed elements, with 35 observations below the LOD of 1 ppb (67% of the entire dataset). The mean values for the selected substitution methods were significantly lower than those in the raw data. Median values were substantially lower than the mean values, ranging from 0.32 ppb for the ROS method to 0.75 ppb for the random method. A significant spread of values was observed for the minimum values (Table 1, Fig. 2I). The lowest minimum values were obtained for the ROS and random methods, at 0.01 ppb and 0.06 ppb, respectively. In contrast, the tobit and half-methods yielded significantly higher minimum values (Table 1, Fig. 2J). Similar results were obtained for the substitution methods when calculating the upper quartile. The standard deviation for the imputed data ranges from 2.47 ppb (half) to 2.52 ppb (ROS). Consistent with previous statistics, skewness exhibits higher variability than in the case of other analyzed elements, but is also higher than that calculated for the raw data. Skewness varies from 5.9 for the ROS method to 6.3 for the half-method, whereas for the raw data, it is 3.52.

The distribution of elements in the raw data is a distribution close to log-normal with occurring outliers and extreme right-handed observations. For all of the analyzed elements, changes in the distribution can be seen depending on the method used. In the case of random substitution and ROS methods, lower minimum values resulted in a greater extension of the histogram to the left with a smaller number for each histogram interval. This effect is most visible for Rhenium and Germanium. At the same time, the tobit and half-substitution methods, compared to the previously mentioned methods, allow for obtaining a narrower distribution. In the case of Rhenium, the high frequency of observations below the detection limit and the half-substitution method disrupts the data distribution. A similar effect visible for Rhenium is also observed for the tobit method. For the remaining elements, the half-substitution and tobit methods allow for obtaining a narrower distribution (Fig. 2).

Correlation matrices were constructed for the 5 analyzed elements and an additional 11 elements that did not contain values below the detection limit or missing data (Table 2). The variability of statistically significant Pearson linear correlations (Pearson's *r*) was analyzed for $p \leq 0.05$ and 52 pairs of observations. For this sample size, correlations with absolute values greater than 0.275 can be considered statistically significant. The interpretation of correlation strength was based on established classification ranges provided in the referenced publication (Schober et al. 2018). Additionally, patterns of variability were analyzed for non-statistically significant correlations but higher than 0.2. The correlation matrices are presented in Table 2.

Germanium does not exhibit any statistically significant correlations or correlations with values higher than 0.2.

Hafnium is significantly correlated with manganese and chromium. The correlation value for manganese with raw data is moderate (0.46). For substitution methods, the correlation with chromium is moderate (0.46), except for the random method, where it remains moderate (0.45). The correlation with chromium for the raw data and all substitution methods is weak (0.30).

Indium exhibits one statistically significant correlation with manganese and one non-statistically significant but higher than 0.2 correlation with chromium. The correlation with manganese for both raw data and substitution methods is weak (0.32). Similarly, the correlation with chromium for raw data and substitution methods is weak (0.24).

Palladium does not exhibit any statistically significant correlations with the selected elements. Only a slight correlation with iron is observed, which is just below the statistical significance level. For raw data, this correlation is weak (0.25), and for substitution methods, it is also weak (0.26).

Rhenium shows statistically significant correlations with silver and magnesium. The correlation with silver for raw data is moderate (0.46), and for the half-method, ROS, and tobit substitution methods, it is also moderate (0.45). A slightly weaker correlation with silver is observed for the random method, at 0.43 (moderate). The correlation with magnesium for raw data is weak (0.33), and for substitution methods, it remains weak (0.31).

Table 2
Pearson linear correlation matrices

Pearson's *r*	Raw data															
	Ge	**Hf**	**In**	**Pd**	**Re**	**Ag**	**Ni**	**Mn**	**Cr**	**Ba**	**S**	**Ca**	**Fe**	**Mg**	**Li**	**Sb**
Ge	–	−0.09	0.00	−0.01	−0.03	−0.01	−0.05	−0.05	−0.06	0.00	0.11	0.12	0.03	0.01	0.08	0.11
Hf	−0.09	–	−0.07	−0.11	0.02	0.11	0.17	0.46	0.30	0.02	−0.10	−0.13	0.01	0.02	−0.17	−0.12
In	0.00	−0.07	–	−0.03	−0.04	−0.09	−0.08	0.32	0.24	0.00	−0.02	0.06	−0.03	0.01	−0.06	−0.05
Pd	−0.01	−0.11	−0.03	–	−0.05	−0.03	−0.07	−0.10	−0.01	−0.17	0.19	0.11	0.25	0.02	−0.01	−0.06
Re	−0.03	0.02	−0.04	−0.05	–	0.46	−0.06	0.17	−0.06	−0.05	−0.05	0.04	−0.04	0.33	−0.05	0.01
Pearson's *r*	**Half (h)**															
	Ge_h	**Hf_h**	**In_h**	**Pd_h**	**Re_h**	**Ag**	**Ni**	**Mn**	**Cr**	**Ba**	**S**	**Ca**	**Fe**	**Mg**	**Li**	**Sb**
Ge_h	–	−0.09	0.01	0.01	0.00	−0.01	−0.05	−0.04	−0.06	0.00	0.12	0.12	0.05	0.00	0.08	0.10
Hf_h	−0.09	–	−0.07	−0.11	0.02	0.12	0.16	0.46	0.30	0.04	−0.11	−0.13	0.01	0.03	−0.17	−0.12
In_h	0.01	−0.07	–	−0.03	−0.05	−0.09	−0.08	0.32	0.24	0.00	−0.02	0.06	−0.03	0.01	−0.06	−0.05
Pd_h	0.01	−0.11	−0.03	–	−0.02	−0.03	−0.07	−0.09	−0.01	−0.16	0.19	0.12	0.26	0.02	−0.01	−0.06
Re_h	0.00	0.02	−0.05	−0.02	–	0.46	−0.06	0.15	−0.05	−0.06	−0.05	0.03	−0.03	0.31	−0.06	0.00
Pearson's *r*	**Random (g)**															
	Ge_g	**Hf_g**	**In_g**	**Pd_g**	**Re_g**	**Ag**	**Ni**	**Mn**	**Cr**	**Ba**	**S**	**Ca**	**Fe**	**Mg**	**Li**	**Sb**
Ge_g	–	−0.07	0.01	0.01	0.00	−0.01	−0.06	−0.04	−0.06	0.00	0.11	0.12	0.05	0.10	0.07	0.12
Hf_g	−0.07	–	−0.07	−0.11	0.04	0.12	0.16	0.45	0.30	0.03	−0.10	−0.13	0.01	0.03	−0.17	−0.11
In_g	0.01	−0.07	–	−0.03	−0.06	−0.08	−0.08	0.32	0.24	0.00	−0.02	0.06	−0.03	0.01	−0.06	−0.05
Pd_g	0.01	−0.11	−0.03	–	−0.02	−0.03	−0.07	−0.09	−0.01	−0.17	0.19	0.12	0.26	0.02	−0.01	−0.06
Re_g	0.00	0.04	0.06	−0.02	–	0.43	−0.05	0.13	−0.06	−0.06	−0.08	0.00	−0.04	0.31	−0.05	0.20
Pearson's *r*	**ROS (r)**															
	Ge_r	**Hf_r**	**In_r**	**Pd_r**	**Re_r**	**Ag**	**Ni**	**Mn**	**Cr**	**Ba**	**S**	**Ca**	**Fe**	**Mg**	**Li**	**Sb**
Ge_r	–	−0.11	0.01	0.01	0.02	−0.02	−0.04	−0.04	−0.06	0.10	0.12	0.12	0.05	0.00	0.10	0.12
Hf_r	−0.11	–	−0.07	−0.11	0.03	0.11	0.16	0.46	0.30	0.04	−0.11	−0.13	0.01	0.03	−0.18	−0.11
In_r	0.01	−0.07	–	−0.03	−0.06	−0.08	−0.08	0.32	0.24	0.00	−0.02	0.06	−0.03	0.01	−0.06	−0.05
Pd_r	0.01	−0.11	−0.03	–	0.00	−0.03	−0.07	−0.09	−0.01	−0.16	0.19	0.11	0.26	0.02	−0.02	−0.06
Re_r	0.02	0.03	−0.06	0.00	–	0.45	−0.05	0.14	−0.03	−0.07	−0.03	0.04	−0.03	0.31	−0.07	0.00
Pearson's *r*	**tobit_small (t)**															
	Ge_t	**Hf_t**	**In_t**	**Pd_t**	**Re_t**	**Ag**	**Ni**	**Mn**	**Cr**	**Ba**	**S**	**Ca**	**Fe**	**Mg**	**Li**	**Sb**
Ge_t	–	−0.09	0.01	0.01	0.10	−0.01	−0.05	−0.04	−0.06	0.00	0.12	0.13	0.06	0.00	0.08	0.10
Hf_t	−0.09	–	−0.07	−0.12	0.02	0.12	0.16	0.46	0.30	0.04	−0.11	−0.13	0.01	0.03	−0.18	−0.12
In_t	0.01	−0.07	–	−0.03	−0.05	−0.09	−0.08	0.32	0.24	0.00	−0.02	0.06	−0.03	0.01	−0.06	−0.05
Pd_t	0.01	−0.12	−0.03	–	−0.01	−0.03	−0.07	−0.09	−0.01	−0.16	0.19	0.12	0.26	0.02	−0.01	−0.06
Re_t	0.10	0.02	−0.05	−0.01	–	0.45	−0.06	0.15	−0.05	−0.06	−0.05	0.04	−0.03	0.31	−0.05	0.00
Pearson's *r*	**tobit_large (tl)**															
	Ge_tl	**Hf_tl**	**In_tl**	**Pd_tl**	**Re_tl**	**Ag**	**Ni**	**Mn**	**Cr**	**Ba**	**S**	**Ca**	**Fe**	**Mg**	**Li**	**Sb**
Ge_tl	–	−0.09	0.01	0.01	0.10	−0.01	−0.05	−0.04	−0.06	0.00	0.12	0.12	0.05	0.00	0.08	0.10
Hf_tl	−0.09	–	−0.07	−0.12	0.02	0.12	0.16	0.46	0.30	0.04	−0.11	−0.13	0.01	0.03	−0.18	−0.12
In_tl	0.01	−0.07	–	−0.03	−0.05	−0.09	−0.08	0.32	0.24	0.00	−0.02	0.06	−0.03	0.01	−0.06	−0.05
Pd_tl	0.01	−0.12	−0.03	–	−0.01	−0.03	−0.07	−0.09	−0.01	−0.16	0.19	0.12	0.26	0.02	−0.01	−0.06
Re_tl	0.10	0.02	−0.05	−0.01	–	0.46	−0.06	0.15	−0.05	−0.06	−0.05	0.03	−0.03	0.31	−0.06	0.00

Pearson's *r* value	−1.00	−0.80	−0.60	−0.40	−0.20	0.00	0.20	0.40	0.60	0.80	1.00

For the analyzed elements, six multiple regression models were constructed for raw data and data subjected to substitution. The set of potential independent variables included elements of the same type as the dependent variable and a pool of 11 variables used for correlation matrices. Stepwise backward regression was employed. Initially, each model contained all independent variables. In subsequent iterations, one variable with the highest p-value was removed from the model until a statistically significant model was obtained. Due to the small sample size (52 observations) and large number of independent variables, it was decided not to split the data into training and testing sets. Subsets were also not created due to the possibility of disrupting the assessment of the impact of values below the detection limit on the regression model by creating unbalanced subsets of data. The models were evaluated using the coefficient of determination (R^2), mean absolute percentage error (MAPE), mean absolute error (MAE), and Akaike information criterion (AIC). The collective results are presented in Table 3.

Table 3
Regression models

Element	Substitution method	Model parameters	R^2	MAPE	MSE	AIC
Ge	raw	−492.95 + 40.27Sb	0.18	1.35	244,387	387.11
	half (h)	no statistically significant model				
	random (g)	no statistically significant model				
	ROS (r)	no statistically significant model				
	tobit_small (t)	no statistically significant model				
	tobit_large (tl)	no statistically significant model				
Hf	raw	−11.52 + 0.43Sb	0.16	1.22	9,055	436.16
	half (h)	111.9 − 0.11In + 0.06Mn + 0.11Cr − 0.002Ca	0.42	1.57	5,196	604.47
	random (g)	10.05 − 0.11In + 0.06Mn + 0.10Cr	0.36	3.42	5,694	607.23
	ROS (r)	112.6 − 0.11In + 0.06Mn + 0.11Cr−0.002Ca	0.42	1.96	5,199	604.50
	tobit_small (t)	111.6 − 0.11In + 0.06Mn + 0.11Cr − 0.002Ca	0.42	1.70	5,216	604.77
	tobit_large (tl)	111.6 − 0.11In + 0.06Mn + 0.11Cr − 0.002Ca	0.42	1.68	5,213	604.63
In	raw	87.77 − 0.53Ni + 0.47Cr	0.17	2.46	72,765	639.00
	half (h)	59.62 − 1.19Hf − 0.49Ni + 0.13Mn + 0.53Cr	0.32	3.89	52,696	725.00
	random (g)	244.45 − 1.15Hf − 0.93Ni + 0.14Mn + 0.78Cr − 0.11S + 24.05Li	0.41	4.72	45,016	720.74
	ROS (r)	244.19 − 1.15Hf−0.92Ni + 0.14Mn + 0.78Cr − 0.11S + 24.87Li	0.41	5.60	45,240	720.99
	tobit_small (t)	244.26 − 1.15Hf−0.93Ni + 0.14Mn + 0.78Cr−0.11S + 25.01Li	0.42	4.17	45,072	720.8
	tobit_large (tl)	244.26 − 1.15Hf−0.93Ni + 0.14Mn + 0.78Cr − 0.11S + 25.01Li	0.42	4.17	45,072	720.8
Pd	raw	no statistically significant model				
	half (h)	24.8 − 0.21Ba + 0.003Fe	0.14	2.66	8,847	628.14
	random (g)	25.98 − 0.21Ba + 0.003Fe	0.14	2.65	8,819	627.98
	ROS (r)	24.70 − 0.21Ba + 0.003Fe	0.14	3.41	8,856	628.19
	tobit_small (t)	24.89 − 0.21Ba + 0.003Fe	0.14	2.60	8,844	628.12
	tobit_large (tl)	24.89 − 0.21Ba + 0.004Fe	0.14	2.60	8,844	628.12
Re	raw	0.07 + 0.0004Ag	0.60	1.07	6.12	85.04
	half (h)	0.54 + 0.0001Ag	0.20	0.90	4.75	234.57
	random (g)	2.42 + 0.0001Ag − 0.0007Ca + 0.0004Mg	0.30	1.52	4.26	232.89
	ROS (r)	1.84 + 0.0002Ag − 0.0006Ca + 0.0004Mg	0.29	4.86	4.42	234.89
	tobit_small (t)	−0.5 + 0.0001Ag + 0.0002Mg	0.24	1.26	4.58	234.75
	tobit_large (tl)	2.02 + 0.0001Ag − 0.0006Ca + 0.0004Mg	0.30	1.24	4.21	232.44

Germanium is an element for which a model was successfully constructed only for raw data. The created model is of low quality and contains one independent variable: Sb.

The quality of the hafnium models, as determined by the coefficient of determination, is non-uniform. For raw data, the model is of very poor quality, with $R^2 = 0.16$, and contains only one independent variable: Sb. The MAPE for this model is lower than for models with substitution data and equals 1.22. Due to the small number of independent variables, the AIC value is also the lowest and equals 436. Models for substitution methods have a quality ranging from 0.36 (random) to 0.42 (other substitution methods). The highest MAPE values were calculated for the model with random substitution (3.42). Other models with substitutions have lower MAPE values, ranging from 1.68 to 1.96. The absolute error is lower than for the raw data model. Independent variables for models with imputed data contain from 3 to 4 variables, including In, Mn, and Cr. Models except for random substitution also include Ca. AIC values for models with imputed data are similar.

Models for indium can be divided into three groups. The first model for raw data has the lowest quality ($R^2 = 0.17$), the lowest MAPE value of 2.46, a higher absolute error, and two independent variables: Ni and Cr. The second model is for half-substitution method data and has a higher R^2 value of 0.32, a higher MAPE value, a lower absolute error, and a higher AIC value. The model for half-substitution method data contains more independent variables: Hf, Ni, Mn, and Cr. Other models have similar R^2 values, similar MSE values, and similar AIC values but differ in MAPE values, with the highest achieved by the model for ROS-imputed data. These models possess the same six independent variables with very similar regression coefficients.

For palladium, it was possible to construct multiple regression models only for data with substitution. These models have very similar R^2 values, absolute error values, and AIC values. In the case of MAPE, the model calculated for ROS data has worse results. Each model has the same independent variables with similar regression coefficients.

In the case of rhenium, the model for raw data achieved the highest coefficient of determination value and the lowest AIC value. At the same time, this model has the highest absolute error value. The model for half-substitution method has only one independent variable: Ag. Despite this, model is significantly weaker, with a higher AIC value, but lower MAPE and absolute error values. Models for other substitution methods have variable quality, ranging from 0.24 for tobit method for a small dataset to 0.30 for random and tobit method for a large dataset. AIC values are very similar and higher than for the raw data model. Absolute error values are also similar and lower than for the raw data model. The largest variation in results is for MAPE. The MAPE value for the ROS data model equals 4.86, while for models with other substitution methods, it does not exceed 1.52. All models include Ag as an independent variable. Models for the random, ROS, and tobit substitution methods also include Ca and Mg, except for the tobit method with a small dataset, which does not include Ca.

DISCUSSION

This article presents an exploratory analysis of four substitution methods for left-censored data using real-world data from the measurement of elements in IBA. The analyzed data exhibit a variable number of left-censored values (ranging from 13% to 67%) with a small sample size of 52 observations.

Most of the existing literature focuses on analyzing substitution methods for non-parametric and half-substitution methods using synthetic or real-world data (Singh & Nocerino 2002, Verbovšek 2011, Tekindal et al. 2017, Tekindal 2021, Rodrigues et al. 2022). These studies have examined the impact of imputing left-censored values on mean values and other statistical metrics (Singh & Nocerino 2002, Filzmoser et al. 2009, Tekindal et al. 2017). We also decided to compare the tobit regression method for compositional data with other methods, despite its typical application to compositional data, when other methods do not have such a limitation (Aitchison 2003, Buccianti & Grunsky 2014, Mikšová et al. 2020). Currently, R supports two methods for estimating summary statistics from censored data sets: MLE and ROS. Previous studies have demonstrated that non-parametric methods yield better results when dealing with a higher number of substitutions (Singh & Nocerino 2002, Tekindal et al. 2017, Tekindal 2021). However, based on Helsel's findings regarding MLE, we focused on ROS (Helsel 2005). Another method, the Kaplan–Meier method, is commonly used in other disciplines and is also available in R; however, the KM method is only recommended when there are multiple censoring levels (i.e., multiple detection limits in the analyzed data set). Therefore, we did not apply the KM method and instead tested the ROS method. Additionally, ROS is recommended for smaller datasets (Helsel 2005).

Simple substitution by zero ignores the measurement distribution in favor of an a priori assumption about what non-detects might represent. Substitution by half LOD or by the LOD itself ignores the larger distributional pattern, especially since this distribution will rarely be uniform in the interval [0, LOD] (Helsen 2005, EPA 2006). When using the half of LOD method with a higher number of imputed values, we observed a problem with data distribution, resulting in a histogram with significant skewness, and higher kurtosis (Table 1, Fig. 2). However, when using this method with fewer substitutions, the effect was less pronounced. The similarity between the descriptive statistics obtained for Indium and other elements (such as Palladium and Hafnium) suggests that the half of LOD method can be used as a convenient and quick substitution method for left-censored data with a lower number of censored values. This conclusion is supported by the Environmental Protection Agency (EPA), which recommends this substitution method when the number of non-detects is less than 15%: "As a guideline, if 15% or fewer of the values are not detected, replace them with the method detection limit divided by two and proceed with the appropriate analysis using these modified values" (EPA 2006).

CONCLUSIONS

Analyzing changes in data distribution after the application of selected substitution methods revealed that random and ROS methods typically generate lower minimum values compared to other methods. The tobit regression method generates minimal observations around half of the LOD. Each substitution method is better than replacing values below the LOD with NA. When dealing with a lower number of censored values, the results for all substitution methods are quite similar (Table 1).

However, when using a higher number of substitutions, the discrepancy between results increases, particularly in descriptive statistics, data distribution, and regression models. Applying regression models to substituted methods datasets generates smaller mean absolute error (MAE) values compared to replacing left-censored with NA. In regression models, we observed changes in model quality, calculated as the coefficient of determination (R^2), and changes in independent variables used for modeling specific elements (Table 3).

The tobit regression method better fits the left-censored values to data when there are strong correlations between the imputed variable and other variables (Tables 1 and 3). This method yielded similar parameters for substituted values in both small and large datasets.

Methods for replacing values below the limit of detection, such as random substitution, ROS, and tobit regression, exert varying influences on data analysis outcomes. The random substitution method is suitable for elements with fewer left-censored values, whereas ROS and tobit methods are more applicable to elements with a larger number of such values (Tables 1 and 3). The correlation values are similar for all methods of replacing left-censored values and very close to the values for the raw data, indicating that replacing left-censored values does not disrupt the relationships between the variables with left-censored values and the remaining variables in the dataset (Table 2).

When applying to the calculation of potential returns on investment in extracting elements from IBA, it is essential to consider that not replacing values below the detection limit can impact return calculations. Given the changes in descriptive statistics (mean, median, lower quartile) and their significantly higher values for raw data where left-censored values were replaced with NA, the actual return on investment may be substantially lower than calculated. Additionally, using simpler methods to replace a large number of left-censored values can also lead to distorted results, but this error is significantly lower than ignoring left-censored values in the data.

Generally, the choice of method for replacing values below the limit of detection depends on the type of analysis and the characteristics of the dataset. It is essential to note that each substitution method has its strengths and limitations, and the selection of an appropriate method should be based on a thorough understanding of the data and the underlying mechanisms generating the missing values. Additionally, the use of multiple substitution methods can provide a more comprehensive understanding of the data and help to identify potential biases or errors in the analysis.

In summary, replacing values below the detection limit is a critical step in data analysis, particularly in environmental sciences and analytical chemistry. The choice of substitution method depends on the specific characteristics of the dataset and the research question being addressed. By using appropriate substitution methods and considering the limitations and strengths of each approach, researchers can ensure that their results are accurate and reliable.

Finally, future studies should focus on developing and evaluating new substitution methods for replacing values below the detection limit, as well as exploring the application of existing methods in different fields and contexts. This will help to improve our understanding of the data and provide more accurate and reliable results in various areas of research.

The results of this study can help researchers and practitioners select the most suitable method for their specific needs and improve the accuracy of exploratory data analysis (EDA) in the context of IBA.

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