

Data Quality Framework for Recyclability Assessment

Methodological Recommendations through Case Studies

on WEEE-embedded Batteries

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Abstract

In a circular economy, data form the foundation for good and reasonable decisions that consider the environment, people, and the economy. In the interest of promoting a circular economy, the design of new products and goods must take these three factors into full account. Recyclability is an important parameter that takes the lifecycle of a product into consideration in order to determine the ability of a product to produce secondary materials. In the case of waste batteries, the collection, recycling, and material characterization are key factors that influence recyclability at the end of life (EoL). Depending on the selected or applicable EoL scenario, different information and data are required to characterize flows, products, components, and materials, all of which determine the overall recyclability of a product. The generation and quality assurance of these data pose practical and methodological challenges.

This Ph.D. thesis addresses these methodological challenges and aims to develop a data quality framework for recyclability assessment (DQF-RA). To achieve this goal, data generation, data management, and data analysis methods were developed and tested in a bottom-up approach based on three case studies of WEEE-embedded batteries. The empirical data collected was harmonized using generated code lists and analyzed to validate and improve data quality. Data protocols were designed to make future data collections congruent and comparable. The case studies considered were:

- Identification and quantification of batteries in WEEE (Article I)
- Recycling efficiency of thermal treatment processes and recyclability of low-value batteries from WEEE (Article II)
- Applicability of simplified methods for chemical characterization of mineral battery residues (Article III)

The DQF-RA represents a methodological framework meeting the requirements of high-quality data: data generation (DGM), data management (DMM), data analysis (DAM), and dissemination of data (DDM). The application of the DQF-RA will ensure a common database with high-quality data to improve the assessment of technical recyclability. However, further case studies and the constant addition of suitable methods to the DQF-RA are required to improve its applicability for future recyclability assessments.

Zusammenfassung

In einer Circular Economy, bilden Daten das Fundament für gute und verhältnismäßige Entscheidungen unter Berücksichtigung von Umwelt, Mensch und Ökonomie. Das Design neuer Produkte und Güter muss, im Sinne einer zirkulären Wirtschaft, diese drei Faktoren im umfänglichen Maße berücksichtigen. Die Recyclingfähigkeit ist ein wichtiger Parameter, welcher unter Berücksichtigung des Lebenszyklus eines Produktes, deren Fähigkeit zur Herstellung von Sekundärmaterialien bestimmt. Bezogen auf Altbatterien stellen insbesondere die Sammlung, Verwertung und Analytik von Sekundärmaterialien wichtige Punkte dar, welche die Recyclingfähigkeit am Lebensende (End-of-Life, EoL) beeinflussen. Je nach gewählten bzw. zutreffenden EoL-Szenario bedarf es anderer Informationen und Daten zur Charakterisierung von Flüssen, Produkten, Komponenten, und Materialien, welche als Bestandteil die gesamte Recyclingfähigkeit eines Produktes bestimmen. Die Generation und Sicherstellung der Qualität dieser Daten bergen praktische sowie methodische Herausforderungen.

Die vorliegende Doktorarbeit widmet sich diesen methodischen Herausforderungen und hat als Ziel einen Datenqualitätsrahmen für die Bewertung der Recyclingfähigkeit (DQF-RA) zu entwickeln. Um dieses Ziel zu erreichen wurden, in einem Bottom-up-Ansatz anhand von drei Fallstudien zu Batterien aus Elektroaltgeräten, Methoden zu Datengenerierung, Datenmanagement und Datenanalyse entwickelt und getestet. Die erhobenen empirischen Daten wurden mit Hilfe entwickelter Codelisten harmonisiert erhoben und anschließend analysiert, um die Datenqualität zu validieren und zu verbessern. Datenprotokolle wurden entwickelt, um zukünftige Datenerhebungen kongruent und vergleichbar zu gestalten. Die betrachteten Fallstudien waren:

- Identifikation und Quantifizierung von Batterien in Elektroaltgeräte (Article I),
- Recyclingeffizienz thermischer Behandlungsverfahren und Recyclingfähigkeit wertstoffarmer Batterien aus Elektroaltgeräten (Article II),
- Anwendbarkeit vereinfachter Methoden zur chemischen Charakterisierung von mineralische Batteriereststoffen (Article III).

Der DQR-RA stellt einen methodischen Rahmen dar, der die Anforderungen an qualitativ hochwertige Daten erfüllt: Datengenerierung (DGM), Datenmanagement (DMM), Datenanalyse (DAM) und Datenbereitstellung (DDM). Die Anwendung des DQR-RA wird

eine gemeinsame Datenbank mit qualitativ hochwertigen Daten sicherstellen, um die Bewertung der technischen Verwertbarkeit zu verbessern. Um die Anwendbarkeit des DQR-RA für zukünftige Bewertungen der Recyclingfähigkeit zu verbessern, sind jedoch weitere Fallstudien und die Ergänzung des DQR-RA um geeignete Methoden erforderlich.

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Appended Publications and Author's Contribution

This doctoral thesis comprises a synopsis of the work presented in three published scientific articles, referred to with a number written with the Roman numerals I-III. To include parts of these articles, the related publisher must grant permission. The following articles were used with accordingly permissions.

Article no.	Title	Contribution by P.M. Mähltitz:
Article I	<p>Mähltitz, P.M., Korf, N., Sperlich, K., Münch, O., Rösslein, M., Rotter, V.S. (2020). Characterizing the Urban Mine—Simulation-Based Optimization of Sampling Approaches for Built-in Batteries in WEEE. <i>Recycling</i> 2020, 5, 19, https://doi.org/10.3390/recycling5030019.</p> <p>It was reprinted, partly adapted, updated, and complemented with the permission of MDPI. The following text refers to this article with (Mähltitz et al., 2020).</p>	<p>P. M. Mähltitz contributed significantly to the concept, methodology, software, validation, formal analysis, investigation, data curation, original draft preparation, review and editing, and visualization.</p>
Article II	<p>Mähltitz, P. M., Korf, N., Chryssos, G., & Rotter, V. S. (2022). Contributions of extended batch tests for assessing technical recyclability: A case study of low-value battery flows. <i>Journal of Industrial Ecology</i>, 26(3), 1061–1077. https://doi.org/10.1111/jiec.13250</p> <p>It was reprinted, partly adapted, updated, and complemented with permission of the Journal of Industrial Ecology. The following text refers to this article with (Mähltitz, Korf, Chryssos, & Rotter, 2022).</p>	<p>P. M. Mähltitz contributed significantly to the concept, methodology, software, validation, formal analysis, investigation, data curation, original draft preparation, review and editing, and visualization.</p>
Article III	<p>Mähltitz, P.M., Løvik, A.N., Figi, R., Schreiner, C., Kuntz, C., Korf, N., Rösslein, M., Wäger, P., Rotter, V.S. (2019). Characterizing the Urban Mine—Challenges of Simplified Chemical Analysis of Anthropogenic Mineral Residues. <i>Resources</i> 2019, 8, 132, https://doi:10.3390/resources8030132.</p> <p>It was reprinted, partly adapted, updated, and complemented with the permission of MDPI. The following text refers to this article with (Mähltitz, Løvik, et al., 2019).</p>	<p>P. M. Mähltitz contributed significantly to the concept, methodology, software, validation, formal analysis, investigation, data curation, original draft preparation, review and editing, and visualization.</p>

In addition, the following publications were prepared during this Ph.D. study. The content of each publication listed below is related to this Ph.D. thesis by providing additional information about methodology and uses cases.

Korf, N., **Mährlitz, P.M.**, Rotter, V.S. (2022). Round robin tests of secondary raw materials: a systematic review of performance parameters. *Reviews in Analytical Chemistry*, vol. 41, no. 1, 2022, pp. 98-111. <https://doi.org/10.1515/revac-2022-0033>.

Wagner, M. A., Huisman, J., Løvik, A.N., Habib, H., **Mährlitz, P.M.**, van der Voet, E. (2021). Methodology to prospect electronics compositions and flows, illustrated by material trends in printed circuit boards. *Journal of Cleaner Production*, 307, 127164. <https://doi.org/10.1016/j.jclepro.2021.127164>

Sperlich, K., **Mährlitz, P. M.**, Wagner, M., & Rotter, V. S. (2020). Where have all the Panels gone? Verbesserung der Datenverfügbarkeit für die Kreislaufwirtschaft am Beispiel von PV-Modulen. In O. Holm, E. Thomé-Kozmiensky, D. Goldmann, & B. Friedrich (Eds.), *Recycling und Sekundärrohstoffe* (13th ed., Vol. 13, pp. 394–410). Neuruppin: Thomé-Kozmiensky Verlag GmbH. ISBN 978-3-944310-51-0.

Korf, N., Løvik, A.N., Figi, R., Schreiner, C., Kuntz, C., **Mährlitz, P.M.**, Rösslein, M., Wäger, P., Rotter, V.S. (2019). Multi-element chemical analysis of printed circuit boards – challenges and pitfalls. *Waste Management* 92: 124–136.

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Løvik, A.N., Figi, R., Schreiner, C., Rösslein, M., Widmer, R., Bunge, R., Pohl, T., Korf, N., Kuntz, C., **Mährlitz, P.M.**, Rotter, V.S., Wäger, P. (2019). Variability and Bias in Measurements of Metals Mass Fractions in Automobile Shredder Residue. *Recycling* 4(3): 34. [10.3390/recycling4030034](https://doi.org/10.3390/recycling4030034).

Mährlitz, P.M., Sperlich, K., Rotter, V.S. (2019). Sekundärrohstoffinventare - Instrument für eine nachhaltige Kreislaufwirtschaft. In 16. Münsteraner Abfallwirtschaftstage, edited by M. Kranert et al. Münsteraner Schriften zur Abfallwirtschaft, Band 18. First edition February

2019. Münster: IWARU Institut für Wasser Ressourcen Umwelt an der Fachhochschule Münster. ISBN 978-3-9811142-7-0.

Huisman, J., Leroy, P., Tertre, F., Ljunggren Söderman, M., Chancerel, P., Cassard, D., Løvik, A. N., Wäger, P., Kushnir, D., Rotter, V.S., **Mährlitz, P.M.**, Herreras, L., Emmerich, J., Hallberg, A., Habib, H., Wagner, M., Downes, S. (2017). Final report - ProSUM project: Prospecting Secondary raw materials in the Urban mine and Mining wastes. Brussels, Belgium. <https://doi.org/10.13140/RG.2.2.10451.89125>

Huisman, J., Habib, H., Guzman Brechu, M., Downes, S., Herreras, L., Løvik, A., Wäger, P., Cassard, D., **Mährlitz, P.M.**, Rotter, V.S., Ljunggren Söderman, M., Chancerel, P. (2016). ProSUM: Prospecting Secondary raw materials in the Urban mine and Mining wastes. Systematic harmonisation and classification of data sources for mapping EU secondary raw materials in electronics, batteries, vehicles and mining waste. In EGG, Electronics Goes Green 2016+: International congress: Proceedings: Sept 7-9, 2016, Berlin, Germany: Inventing shades of green. Berlin, Germany: Fraunhofer-Institut für Zuverlässigkeit und Mikrointegration: Berlin, Germany, 2016; ISBN 978-3-00-053763-9.

Chancerel, P., **Mährlitz, P.M.**, Chanson, C., Binnemans, P., Huisman, J., Guzman Brechu, M., Rotter, V.S., Nissen, N.F., Lang, K.D. (2016). Stocks and flows of critical materials in batteries: Data collection and data uses. EGG, Electronics Goes Green 2016+: International Congress: proceedings: Sept 7-9, 2016, Berlin, Germany: Inventing shades of green; Fraunhofer-Institut für Zuverlässigkeit und Mikrointegration: Berlin, Germany, 2016; ISBN 978-3-00-053763-9.

Glossary

The following glossary is intended to provide an overview and explanation of terms that are important for further understanding of the work.

Term	Explanation	Example related to this work
Code list	Standardized list of harmonized and pre-defined terms, which lists all possible expressions of a property.	Chemical Analysis Methods; Unit of Measurement, UNU keys
Data Quality Dimension (DQD)	Data quality can best be expressed and evaluated by structuring the requirements according to Data Quality Dimensions (DQD).	Intrinsic DQD, contextual DQD, representational DQD, and accessibility to the data.
Framework	Theoretical construct for structuring methods using categories. A framework includes the necessary aspects that are required for the fulfillment of the goal, i.e. require attention.	Data Quality Framework
Methods	A systematic procedure, technique, or mode of inquiry employed by or proper to a particular discipline or art (Merriam-Webster Inc., 2022).	Methods for data generation (DGM), management (DMM), analysis (DAM) and distribution (DDM) supplemented by case-specific methods.
Protocol	Description of methodologies comparable to standard operation procedures (SOP).	Description of sampling, treatment, chemical analysis.
Data template	Pre-structured templates for collecting raw data and metadata facilitating the harmonized collection and consolidation of information. The template structures follow the “long format” principle for data tables which collects property information in one column and each data point in a separate row.	Excel files with pre-structured tables: Sampling template, process performance template, chemical analysis template

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1. Introduction

1.1. Approaching Circular Economy Goals

A circular economy (CE) is based, among other things, on the efficient use of products and materials and subsequent recycling at their end of life (EoL) and aims to minimize the generation of non-recyclable waste while maximizing the proportion of secondary raw materials (SRM) for recirculation into manufacturing and production (European Union, 2020). In the European Union (EU), efforts, strategies, and measures to achieve these CE goals are formulated in strategic plans such as the Green Deal (European Commission, 2019a), the CE Action Plan (European Union, 2020), and on a product level in directives, e.g., Eco-design (Directive 2009/125/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for the setting of ecodesign requirements for energy-related products, 2009), Waste Electrical and Electronic Equipment (WEEE) (European Parliament and Council, 2012), or Batteries (European Commission, 2020c; European Parliament and Council, 2006). This transition to a CE is accelerated through data and methods that must be collected, elaborated, and evaluated by initiatives and stakeholders along the value chain. In this regard, the European Commission (EC) initiated the European Innovative Partnership (EIP) on Raw Materials (European Commission DG GROWTH, 2019), aiming to support all actors through guidance in the implementation of a sustainable, resource-conserving, and circular society. The EIP Strategic Implementation Plan (SIP) formulated objectives, targets, and goals for the EU to be implemented. One of the main objectives of the SIP is “improving resource efficiency (including recycling),” which is defined in two more specific targets (European Commission, 2019b), relying on valid data and coherent methods.

- Framework conditions for **enhanced efficiency** in material use and waste prevention, re-use and **recycling**, and raw material-efficient **product design**
- European raw materials **knowledge base** with information, flows, and dynamic modeling system for primary and secondary raw materials

These targets must be addressed in the design phase, allowing the efficiency and feasibility of recycling ex-ante. Furthermore, “framework conditions” require defined guidelines concerning methods and structural specifications. “Enhanced efficiency” covers design to recycling and includes extending the service lifetime of products or reducing the

primary raw material (PRM) input for production and providing SRM for recirculation. A standardized “knowledge base” is required with defined framework conditions and data quality requirements for storing and processing data and information needed for these targets. The Raw Material Information System (RMIS) was established at the EU level to improve data availability on PRM and SRM (European Commission, 2022b). However, generating, collecting, and harmonizing data and information on SRM along the value chain is challenging, as shown in recent EU H2020 Projects (Huisman et al., 2017; Wagner et al., 2019). A European strategy for data exists (European Commission, 2020a) but faces significant challenges due to the complexity of systems and products. In addition to the collection and standardization of existing or collected data, data gaps (Di Persio et al., 2020; Huisman et al., 2017; Wagner et al., 2019) and aspects of data quality (Bergdahl et al., 2007, p. 11) are significant barriers to the establishment of a coherent knowledge database.

Nevertheless, these data are the basis for evaluating whether measures can be initiated and evaluated to achieve the CE goals. So far, CE indicators exist only for areas where a database exists and is organized by the framework for existing data collection. The ten indicators of the CE Monitoring Framework include overall recycling rates and waste flow-specific recycling rates. However, these only refer to selected products (WEEE, bio waste, and packaging) and focus on the end of life of a product or material with the recycling rate as a measurand. The European Commission (EC) confirms that the list of indicators is not yet complete and is continuing “to elaborate the indicators which need further developments, in particular regarding the methodology and/or data collections” (Eurostat, 2021).

Given an appropriate data and knowledge base, a promising indicator that can be used in the design phase to assess and decide on product alternatives and foster CE goals is product recyclability, which is why the “European Commission's Circular Economy Action Plan of 2015 [...] calls for more systematic analysis of recyclability” (European Commission, 2018b).

1.2. Recyclability and Its Assessment

Recyclability is the “ability of a product to be recycled at end-of-life” (DIN EN 45555, 2019). It serves as an indicator for choosing between product alternatives for designers or customers when buying a product. Thus, achieving the CE goal of material circularity is more straightforward the more recyclable the product or material is designed (Directive 2009/125/EC of the European Parliament and of the Council of 21 October 2009 establishing a

framework for the setting of ecodesign requirements for energy-related products, 2009) and the more adapted the recycling infrastructures and technologies are. However, against the background of increasingly complex products, stricter environmental requirements, and the demand for higher recycling efficiencies with rational energy consumption, quantifying recyclability with adequate validity and data quality is challenging.

Recyclability assessment (RA) is a not-yet standardized method, however, which is why various recyclability assessment methods (RAM) currently exist (Leal, Pompidou, Charbuillet, & Perry, 2018), some of which are widely used within one specific product sector, such as energy-related products (ErP). However, these methods are not generally applicable to other sectors since they imply certain sector specifics regarding product properties (such as composition, lifecycles, and value), use phase, legal framework, or supply risk of materials. The most established approaches focus on the vehicle sector (Technical Committee ISO/TC, 2017; Technical Committee ISO/TC 127, 2008; Technical Committee ISO/TC 22, 2002; Technical Committee ISO/TC 23, 2008), (waste) electrical and electronic equipment (WEEE) (Ardente & Mathieux, 2014; DIN EN 45555, 2019; Huisman, 2003; International Electrotechnical Commission [IEC], 2012; Zeng & Li, 2016), materials (Villalba, Segarra, Chimenos, & Espiell, 2004; Villalba, Segarra, Fernandez, Chimenos, & Espiell, 2002), or address more general subjects (Brunsmann, 2018a, 2018b; VDI 2243, 2002; Villalba, Segarra, Fernández, Chimenos, & Espiell, 2002; Xing, Abhary, & Luong, 2003; Yunhui, Guangfu, Zhifeng, & Shuwang, 2005).

In summary, it can be stated that recyclability depends heavily on three main aspects when comparing the assessment methods: 1) the (recycling-oriented) characteristics of a product, 2) the parameters and scope considered, and 3) the reference network comprising production, use, and end-of-life (EoL) phase (cf. Figure 1).

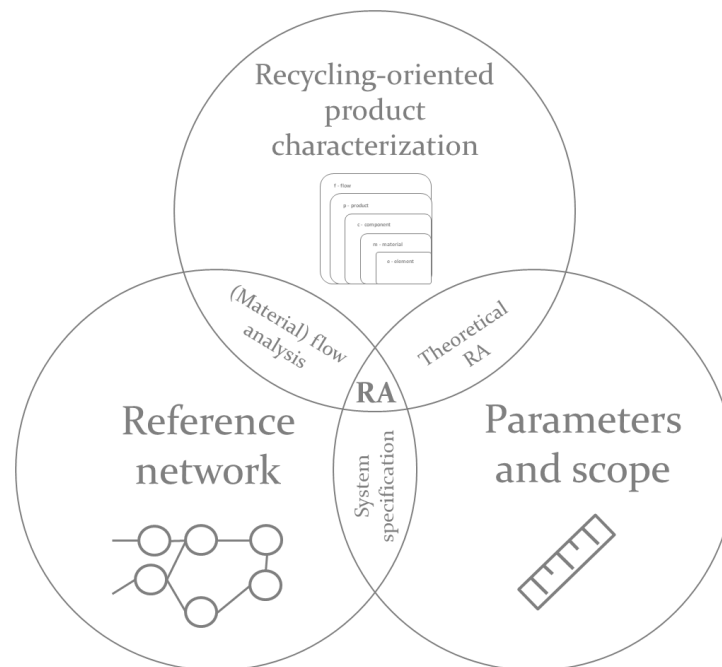


Figure 1. Conceptual setup of the three main aspects considered in recyclability assessment (RA).

Firstly, the characteristics to be evaluated for recyclability differ considerably between these methods. Thus, recycling-oriented characterization of products (Chancerel & Rotter, 2009b) is required. These characteristics can comprise, among others things: composition in terms of elements, material, and components, liberation behavior, as well as material and metal specification (Chancerel, Marwede, Mathieux, & Peiro, 2016; Chancerel & Rotter, 2009b). Secondly, parameters are used to describe the beforementioned product characteristics: mass (kg) (DIN EN 45555, 2019; IEC, 2012), material value (€, \$) (Villalba et al., 2004; Villalba, Segarra, Fernández, et al., 2002), entropy (/bit) (Zeng & Li, 2016), and exergy (MJ/kg) (Maris & Froelich, 2013). The quantifiability and comprehensibility of data for a product and its lifecycle are crucial for the applicability and establishment of the assessment method. Consequently, mass and material are often used as a first approximation for evaluating recyclability. Both product characteristics and parameters determine the theoretical recyclability (DIN EN 45555, 2019) that expresses the potential of an object to be recycled.

Theoretical recyclability considers only the potential but ignores or generalizes the influence of the reference network, in which the EoL phase considerably impacts the quality and quantity of recycled materials. Furthermore, influencing factors along the value chain, e.g., consumer behavior (hoarding, disposal) and an EoL scenario comprising available collection systems and recycling infrastructure, negatively affect the theoretical recyclability. Thus, the product value chain and all influencing factors are defined in a reference network

(third circle in **Figure 1**) to consider efficiency and material losses and determine the technical (i.e., real) recyclability (DIN EN 45555, 2019). The more complex the product and respective waste flow, the more challenging the data generation on end-of-life characteristics describing the reference network. Thus, RA requires extensive data, especially if the products themselves and their lifecycle are complex and short product innovation cycles cause fast changes. Consequently, improving RA results requires including methods to provide EoL characteristics with adequate data quality within a defined framework.

In this study, recyclability assessment refers to the mass-based approach described in DIN EN 45555 (2019), one of the most advanced approaches for calculating recyclability for energy-related products. In particular, the consideration of and requirements for possible EoL scenarios show that this RA method is more developed than other methods. However, methodological recommendations for the generation of data and their evaluation in terms of data quality are still lacking to ensure that the results are representative of the respective product. At present, transferability or further use of the results is still limited. That means guidance on the calculation of recyclability is given, but a framework to generate and validate high-quality data is not yet adequately established and poses an overall weakness in recyclability assessments and, subsequently in product design.

1.3. Conceptual Design of Reference Network

A reference network describes the system boundaries and specifies processes and flows for an object. **Figure 2** illustrates the conceptual design of a reference network for WEEE-embedded batteries as it can be used to describe a recycling scenario for RA.

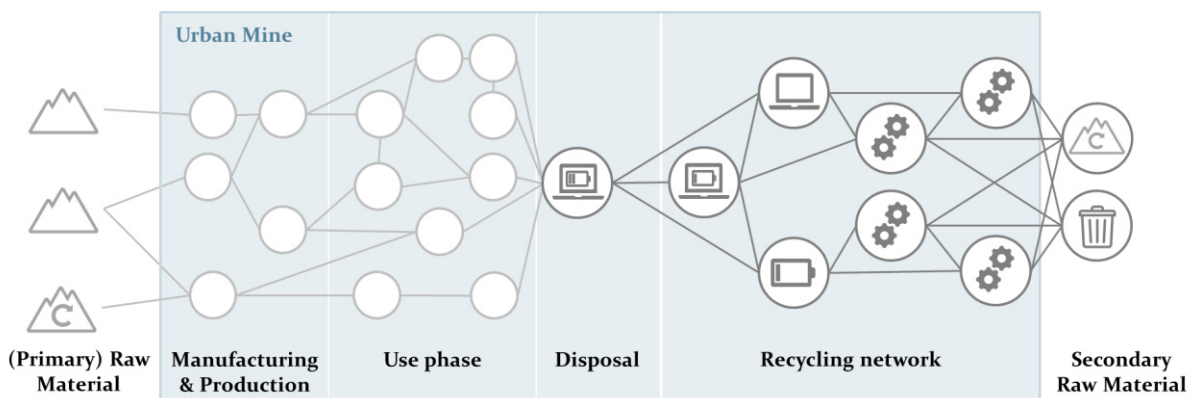


Figure 2. Conceptual design describing the reference network for WEEE batteries, highlighting scenarios in the recycling network.

Primary raw materials (PRM) from extraction and secondary raw materials (SRM) from recycling are used to manufacture and produce battery cells, modules, and systems. At this point, the future battery use decisively defines the subsequent production steps, use, and EoL phase. According to the Battery Directive, a distinction is made between three battery groups: automotive batteries, industrial batteries, and portable batteries (European Parliament and Council, 2006). This distinction results in different legal requirements for monitoring, collection, and recycling for these three groups. For example, vehicle batteries (almost exclusively lead-acid batteries) are subject to a deposit, whereas business-to-business (B2B) contracts or leasing models regulate the provision and collection of many industrial batteries.

Meanwhile, the use of batteries in appliances for private or commercial purposes is associated with more complex sales, use, and recycling networks. Furthermore, the equipment type influences the chemical battery system (Mährlitz et al., 2020) and the corresponding lifetime (Kalmykova, Berg, Patrício, & Lisovskaja, 2017). In summary, these factors determine whether re-use, remanufacturing, or cascade usage is probable in the use phase and consequently the number, condition, and product lifetime of batteries when entering the EoL phase.

In the case of portable batteries, 45% (German Environmental Agency, 2021) were collected in Germany and transported to sorting and recycling plants. A prerequisite for this was the separate collection and identifiability of battery systems in the sorting. However, given that these batteries are collected embedded in WEEE or via complementary flows, the resources are not available for high-quality recycling (European Commission, 2018a). These batteries are consequently diluted, landfilled, or immobilized and no longer recyclable. Furthermore, especially for lithium batteries, the fire and explosion risk (Herrerias-Martínez, Anta, & Bountis, 2021; Nigl, Bäck, Stuhlpfarrer, & Pomberger, 2021) is the reason to improve the separate and safe collection as stated in UN 3480, UN 3481, UN3090, International Air Transport Association (IATA), and European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR).

The recycling network further includes manual and automatic identification and sorting into the main chemical systems for batteries separately collected. These main chemical systems are subsequently recycled with different technologies comprising mechanical, cryogenic, thermal, pyrometallurgical, and hydrometallurgical processes (Georgi-Maschler, Friedrich, Weyhe, Heegn, & Rutz, 2012; Li et al., 2018; Lv et al., 2018; Ordoñez, Gago, & Girard, 2016;

Zhou, Yang, Du, Gong, & Luo, 2020). However, problems occur if batteries are stored at home for a long time (hibernation) or collected via complementary flows, such as WEEE (Bakas et al., 2014; Bigum, Petersen, Christensen, & Scheutz, 2013; Friege et al., 2016; Hobohm, Wasserberg, Kuchta, & Kuebart, 2016; Mähltitz et al., 2020; Savi, Kasser, & Ott, 2013), residual waste (Bigum et al., 2013; Terazono, Oguchi, Iino, & Mogi, 2015), or packaging waste (Nigl et al., 2020). The consequence is the reduction of recycling efficiency and loss of SRM, resulting in lower product recyclability.

To summarize, the recycling network impacts the overall recyclability result by largely defining the recycling efficiency processes and thus the mass share of secondary material recirculated into the economy. However, characterization approaches of the RN pose operational and methodological challenges for recycling complex products and providing appropriate information for RA, which needs to be improved. Thus, generating reliable data on characteristics of EoL scenarios is crucial for reliable recyclability assessment results.

1.4. Data Quality Requirements

A universal definition of quality does not exist. In general, quality is defined by the requirements that are to be met on an object, a method, a product, or similar. Related to the quality of data, Wang and Strong (1996) define, for example, “high-quality data should be intrinsically good, contextually appropriate for the task, clearly represented, and accessible to the data consumer” (Wang & Strong, 1996).

Data quality can best be expressed and evaluated by structuring the requirements according to Data Quality **Dimensions** (DQD). As various definitions of the term quality exist, selecting appropriate quality dimensions varies depending on the research question and the research field. Wang and Strong (1996) state that “the general definition of quality is operationalized by specifying a set of [...] dimensions that characterize the quality of the product.” That means quality is best described by the data quality dimensions (DQD) chosen for an application. The DQD from **Table 1** is taken from the synopsis of different references (Batini & Scannapieco, 2016; Godoy León & Dewulf, 2020; ISO/IEC 25024, 2015; Loshin, 2011; Strong, Lee, & Wang, 1997; Wang & Strong, 1996), so that these dimensions correspond to the requirements of the DQF. These DQD can be divided into intrinsic DQD, contextual DQD, representational DQD, and accessibility to the data (cf. **Table 1**).

Intrinsic DQD represents the quality of the data, which is valid on its own, i.e., without context. Intrinsic data quality includes the DQD accuracy, lineage, and semantic and structural consistency. The intrinsic data quality thus provides information about the quality of, for example, a data set. In contrast to intrinsic DQD, contextual DQD addresses how high the quality of a data set is in context, i.e., in comparison to other data sets, their temporal sequence, possible redundant duplications, and the scope for the task at hand. Contextual DQD includes timeliness, completeness, identifiability, reasonableness, and uniqueness. Furthermore, the quality of the data concerning user requirements is considered in the “representational DQD” by defining the DQD Interoperability and Consistency. The fourth and last DQD is the Accessibility DQD, which includes both the possibility of accessing data and its availability.

Table 1. Data quality dimensions (DQD) selected for comparison with DQF-RA purposes.

Data Quality Dimension	Definition
Intrinsic Data Quality	
Accuracy	The closeness of agreement between a test result and the accepted reference value (DIN ISO 3534-1, 2009).
Value accuracy	The closeness of agreement between the average value obtained from a large series of test results and an accepted reference value. Also known as accuracy of the mean or trueness (DIN ISO 3534-1, 2009).
Precision	The closeness of agreement between independent test results obtained under stipulated conditions (DIN ISO 3534-1, 2009).
Lineage	Lineage measures whether factual documentation exists about where data came from, how it was transformed, and where it went (DQMatters.com, 2017).
Structural consistency	Consistency in the representation of similar attribute values, both within the same data set and across the data models associated with related tables (Loshin, 2011).
Semantic consistency	Consistency of definitions among attributes within a data model, as well as similarly named attributes in different enterprise data sets (Loshin, 2011).
Contextual Data Quality	
Timeliness	The age of the data is appropriate for the task at hand (Batini & Scannapieco, 2016).
Completeness	The extent to which data are of sufficient breadth, depth and scope for the task at hand (Batini & Scannapieco, 2016).
Identifiability	Identifiability refers to the unique naming and representation of core conceptual objects as well as the ability to link data instances containing entity data together based on identifying attribute values (Loshin, 2011).
Reasonableness	General statements associated with expectations of consistency or reasonability of values, either in the context of existing data or over a time series (Loshin, 2011).
Uniqueness	No entity exists more than once within the system (Loshin, 2011).
Representational Data Quality	
Interpretability	Ability of the user to interpret correctly values from their format (Batini & Scannapieco, 2016)
Consistency	Cohesion, and coherence refer to the capability of the information to comply without contradictions to all properties of the reality of interest, as specified in terms of integrity constraints, data edits, business rules, and other formalisms (Batini & Scannapieco, 2016).
Accessibility Data Quality	
Accessibility	The ease and conditions with which [...] information can be obtained (United Nations, 2019).
Availability	The extent to which data (or some portion of it) is present, obtainable, and ready for use (Batini & Scannapieco, 2016), i.e., data can be available but the access can be denied.

1.5. Case Study of WEEE-embedded Batteries

CE efforts focus on resource-relevant products that contain economically valuable, critical (European Commission, 2017), or environmentally relevant substances since their recycling significantly influences both high resource-saving potentials and the reduction of environmental burden. Recent examples of such products are electrical and electronic equipment (EEE) and batteries (Huisman et al., 2017), both which reflect the trends to digitalization and mobility as key drivers of our modern society (German Advisory Council on the Environment, 2018). Over the last decades, both product groups have been characterized by enormous functionality and performance changes. In addition, the design of battery systems follows product requirements and is therefore subject to constant changes regarding capacity, dimension, and subsequent chemical composition.

1.5.1. Resource Relevance of Batteries

The chemical composition of the different battery systems (cf. **Table 4**) is dominated by a few elements with a high mass fraction (cf. **Figure 3**). These elements are Fe (ZnC, NiMH, NiCd, LiPrim, LiRecharge), Mn (ZnC, LiPrim, LiRecharge), Ni (NiMH, NiCd), Zn (ZnC), and Pb (PbA). While some batteries contain constant and defined mass fractions of a few elements, lithium-based batteries include various chemical battery subsystems with high elemental heterogeneity. Especially for EEE, the diversity of cell chemistries is high between appliances (Mählitz et al., 2020).

In addition, there is especially strong pressure to innovate lithium batteries due to e-mobility and the electronics industry, which is leading to the development of new chemical battery subsystems with heterogeneous and polymetallic compositions (Huisman et al., 2017; Tsiropoulos, Tarvydas, & Lebedeva, 2018). As a result, there are a variety of chemical subsystems within battery systems, especially within lithium-based batteries, containing valuable elements, such as Co, Li, and phosphorous. **Figure 3** shows that the lithium-based batteries depict a product flow with a highly varying composition due to pressures on price and increasing performance requirements. Nowadays, lithium-based battery technology and its composition vary depending on its usage in a specific product and sector (Huisman et al., 2018).

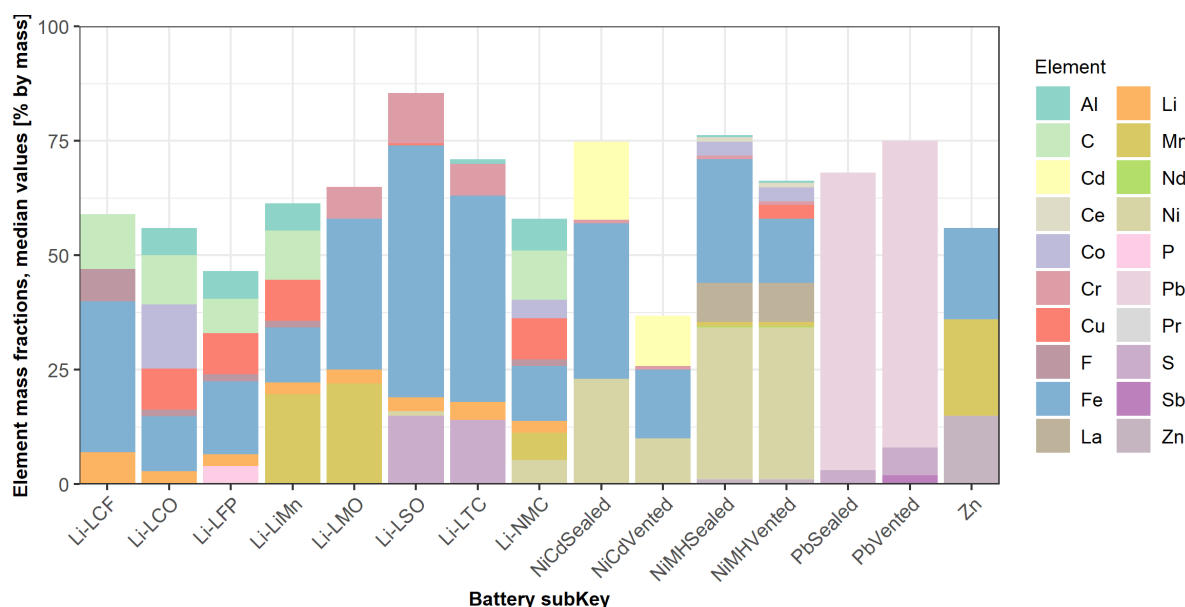


Figure 3. Mass fraction of elements (median mass percent) for different battery systems (Huisman et al., 2017).

1.5.2. Recycling of Batteries

In 2015, batteries embedded in EEE made up 15% of the single charge (primary) and 80% of the rechargeable (secondary) batteries placed on the market (EPBA, Sagis EPR, & Perchards, 2014). Considering this share of portable batteries in EEE and the stagnating low collection rate, ranging from 25 to 45% in the European Member States (EPBA et al., 2014), EEE represents a significant product flow that needs to be considered if collection rates are to be increased and RA must take into account the associated mass loss. A study on the collection rate of portable batteries differentiated by chemical system shows significant differences (German Environmental Protection Agency, 2013). For lead batteries, collection rates of over 100% are reported (cf. **Figure 4**), caused by the underlying calculation method (European Parliament and Council, 2006) and the fluctuating collection masses that change over the years. In contrast, zinc-based primary batteries (AlMn, ZnC, Zn-air) have collection rates of around 40-50% despite increasing sale figures (EPBA et al., 2014). The collection rates for secondary batteries, on the other hand, are lower. In addition to the low collected mass, the mass of batteries placed on the market (POM) is particularly decisive for the collection rate. In the case of NiCd, the ban on the heavy metal Cd leads to very low POM, whereas even small quantities collected generate a high collection rate. Whereas for lithium batteries, increased sales figures combined with the longer retention time of secondary batteries in the urban mine and the

influence of complementary flows on the collected quantities lead to low collection rates (cf. **Figure 4a**).

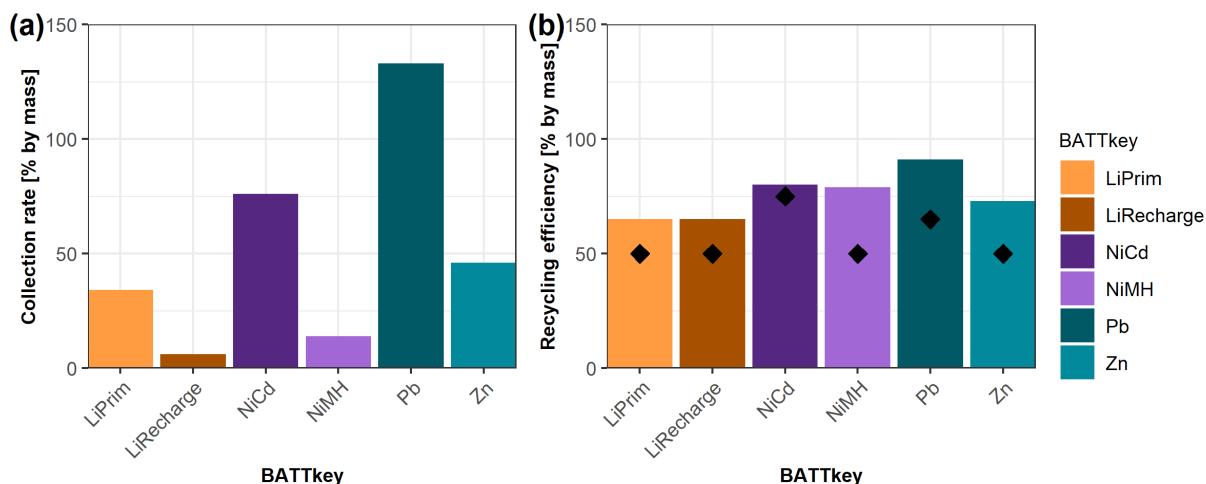


Figure 4. Specific collection rates and recycling efficiencies for portable batteries in Germany 2011, adapted from German Environmental Protection Agency (2013). The black squares indicate the minimum statutory objectives for recycling efficiencies (European Parliament and Council, 2006).

Regarding complementary waste flows, both the disposal of batteries in residual waste and the collection of batteries embedded in WEEE result in the loss of battery raw materials. As a result, WEEE-embedded batteries are shredded, and the ingredients are irretrievably distributed and lost for recycling (entropy problem). Studies of small WEEE showed that batteries remain in 13% of devices after collection (Mähltitz et al., 2020).

Furthermore, recycling efficiencies (RE) differ recognizably between battery systems based on their chemical constituents and respective processing technologies, such as hydrometallurgy, pyrometallurgy, thermal treatment, and mechanical treatment (Assefi, Maroufi, Yamauchi, & Sahajwalla, 2020; Berndt, 2014; Ellis & Mirza; EPBA & Recharge, 2015; Ferreira, Prados, Majuste, & Mansur, 2009; Fricke & Knudsen, 2003; Goldmann, 2009; Rentz, Engels, & Schultmann, 2001). However, despite this difference, NiMH, Zn-based, and lithium-based batteries have the same legislative RE targets as they are covered under “other batteries” (European Parliament and Council, 2006). Adaptations of RE targets and the consideration of recyclability are planned in the proposed revision of the Battery Directive (European Commission, 2020c). **Figure 4b** shows the recycling efficiencies relative to the minimum statutory objectives set in European Parliament and Council for Germany. Here, lithium batteries are recycled with an average efficiency of 65% by mass due to challenges in recycling and low recyclability.

1.6. Aim and Objectives

In regard to the problems described above, approaching the CE goals requires further data quality improvement along the recycling chain of WEEE-embedded batteries to assess recyclability and make recommendations for the design phase. However, data, data formats, and methods enabling the evaluation of data quality for recyclability assessment are neither available nor developed systematically for wide application. In addition, the diversity of RA methods and difficult data situations impede the performance of comparable and valid RA for use by designers and producers. Furthermore, due to technological innovations and miniaturization making products more complex and diverse, data and information about the products becoming waste is needed as the basis for adapting complex treatment steps at short notice (e.g., to comply with material-related recycling quotas). This complexity implies that information and data formats along the value chain must be made available through defined and harmonized methods for recyclability assessment. Such methods must include recycling-oriented product characterization (Chancerel & Rotter, 2009a; Dańczak et al., 2018; Ebin, Petranikova, & Ekberg, 2018; Ueberschaar, Jalalpoor, Korf, & Rotter, 2017; Ueberschaar & Rotter, 2015), the description of the recycling scenarios and technologies (reference network), as well as assurance of data quality.

So far, data and methods necessary for the characterization of WEEE-embedded batteries are mostly missing, not harmonized, or spread over different institutions (Huisman et al., 2017). Recently, these problems have been addressed in EU projects to increase data availability and harmonization (Huisman et al., 2017; Wagner et al., 2019), and thus make the data quality assessable. For example, the new proposal on the Battery Directive states “that there should be better harmonization of existing rules and an EU framework covering the entire battery lifecycle” (European Commission, 2020c). Achieving these goals requires continuous development, testing, and adaptation of methods, which is the motivation behind this Ph.D. thesis.

Based on case studies on the recycling of WEEE-embedded batteries, this Ph.D. thesis aims to develop a Data Quality Framework for Recyclability Assessment (DQF-RA) to improve future data quality. In more detail, the aim is to recommend methods for to improve data quality at critical points in the recycling network of WEEE-embedded batteries that significantly influence the recyclability and pose methodological challenges for its characterization.

Research questions

In this context, the following three more detailed research questions (RQ) were formulated:

- 1) How should a DQF-RA be structured, and what methodological categories should it include to cover the multiple aspects influencing data quality in recyclability assessment?
- 2) What are the requirements on data quality and how does the DQF-RA address them?
- 3) Which methods for data generation, management, analysis, and dissemination are suitable for ensuring data quality at selected process steps in recycling WEEE-embedded batteries, and to what extent can these methods be transferred to other use cases?

Objective and approach

The derived objective is to describe, test, and recommend methods assuring high data quality for **sampling, processing, and chemical analysis** of WEEE-embedded batteries.

The research approach followed these five steps:

- 1) Screening the **recycling network** of batteries for points critical for recyclability.
- 2) Selecting **case studies** addressing different methodological challenges to provide high-quality data for recyclability assessment (RA).
- 3) Developing **case study-specific methods** for generating, managing, and analyzing data.
- 4) Clustering the methods developed into **higher-level categories** and developing a **framework** to ensure data quality for recyclability assessment (DQF-RA).
- 5) Comparing the DQF-RA with prevalent data quality dimensions to assess its **applicability and completeness**.

2. Conceptional Design and Methods

The result of a recyclability assessment can only be as good as the data on which it is based. Ensuring data quality requires a multidisciplinary approach that includes at least four aspects: data generation, data management, data analysis, and data dissemination (cf. **Figure 6**). These aspects require methods for an individually adapted application to the RA problem. Within this Ph.D. study, a Data Quality Framework for Recyclability Assessment (DQF-RA) was developed by collecting and structuring methods in combination with the provision of (standard) operation procedures and case studies.

These methods are intended to generate high-quality data that is assessable, comparable, and exchangeable between stakeholders. These data include mass flows, compositions of flows, products, components, and materials (cf. Chapter 2.3.2 Calculation Sequence), and other urban mine characteristics (cf. Mährlitz et al., 2020; Mährlitz, Løvik, et al., 2019) such as transfer coefficients. The collection of necessary “descriptive data,” so-called metadata, is another cornerstone of data quality and indispensable for data interpretability. The bottom-up approach to building the DQF-RA is shown in **Figure 5**.

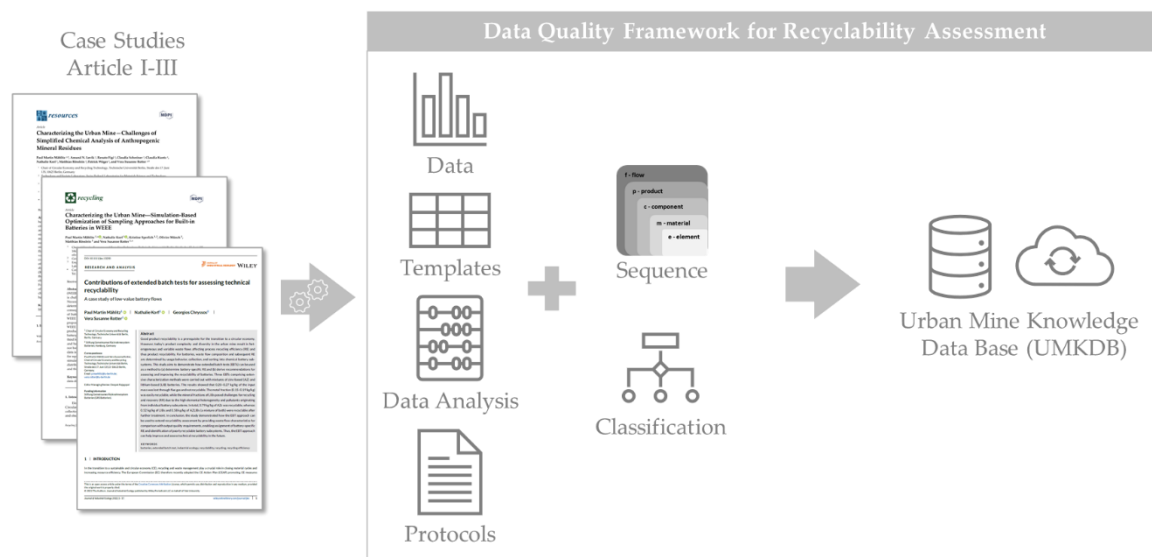


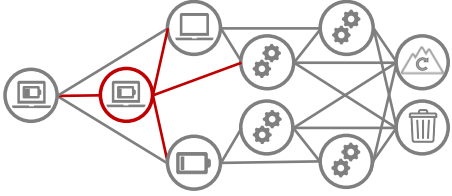
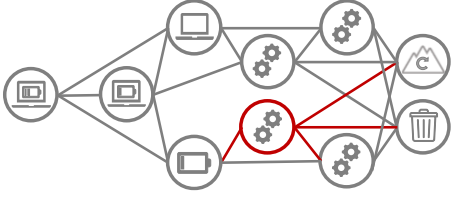
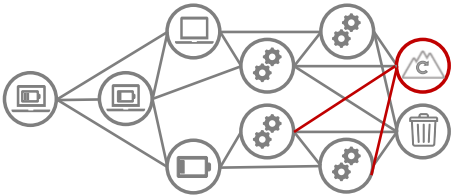






Figure 5. A bottom-up approach to building the DQF-RA.

Three articles were written addressing methodological challenges to provide more reliable results on EoL characteristics to be used in the recyclability assessment of WEEE batteries (cf. **Table 2**). Each article approaches a methodological characterization challenge at a different stage in the recycling network: collection of batteries embedded in WEEE (Article I),

treatment of batteries in mixed battery waste flows (Article II), and quantification of element contents of secondary raw materials as a prerequisite for material recovery (Article III).

Further, each study develops, describes, and tests methods for data analysis and provides data, templates, and protocols. The classification and calculation sequence supplement each case study. The results are intended to be made available in a comprehensive database, such as the Urban Mine Knowledge Database (UMKDB).

Table 2. Objectives and research questions of articles I-III.

Objectives and research questions (RQ)	Link to recycling network (cf. Figure 2)
<p>Article I: Sampling procedures for WEEE batteries</p> <p>Objective: Sampling and quantifying the mass share of batteries embedded in and collected with WEEE.</p> <p>RQ: How to assess representative sampling of built-in batteries in WEEE in the case of unknown or inconclusive sample distributions and fewer data points?</p>	
<p>Article II: Process performance assessment for waste battery flows</p> <p>Objective: Characterize and assess the product and waste flow recyclability of batteries</p> <p>RQ: How to assess the individual product recyclability for one battery system present in and treated jointly with a mixed battery flow. Further, how to identify poorly recyclable products in mixed battery flows lowering the recyclable content?</p>	
<p>Article III: Chemical analysis for complex battery materials</p> <p>Objective: Chemical analysis to characterize the element content of battery materials challenged by element variety, matrix complexity, and material heterogeneity</p> <p>RQ: How to assess the applicability of simplified multi-element chemical analysis methods?</p>	
<p>Legend:  WEEE-embedded batteries  WEEE, (separately) collected  Batteries separately collected or removed from WEEE  Process (e.g., mechanical, thermal, hydro-/pyrometallurgical)  Secondary raw material  Non-recyclable fraction.</p>	

Furthermore, in numerous co-publications (cf. Appended publications and author's contribution) within the framework of this Ph.D. study, further case studies were processed, methods were developed, and principles and concepts for the construction and requirements of an Urban Mine Knowledge Database (UMKDB) were introduced. This research was mainly

done in the EU projects ProSUM (Huisman et al., 2017) and ORAMA (Wagner et al., 2019) and considers many stakeholders' perspectives along the value chain and database developers.

2.1. Data Quality Framework for Recyclability Assessment (DQF-RA)

The DQF-RA is intended to frame data generation, management, analysis, and dissemination activities to guide and assure high-quality data for e.g., RA. The application of the RA serves as an example since the DQF offers guidance and direction for other applications such as lifecycle assessment (LCA), the Solid Waste Analysis (SWA) tool (European Commission, 2004), or compliance tasks. The four DQF-RA **categories** (arrow-shaped boxes in **Figure 6**) and related **methods** are shown in **Figure 6** and are further described in the following sections.

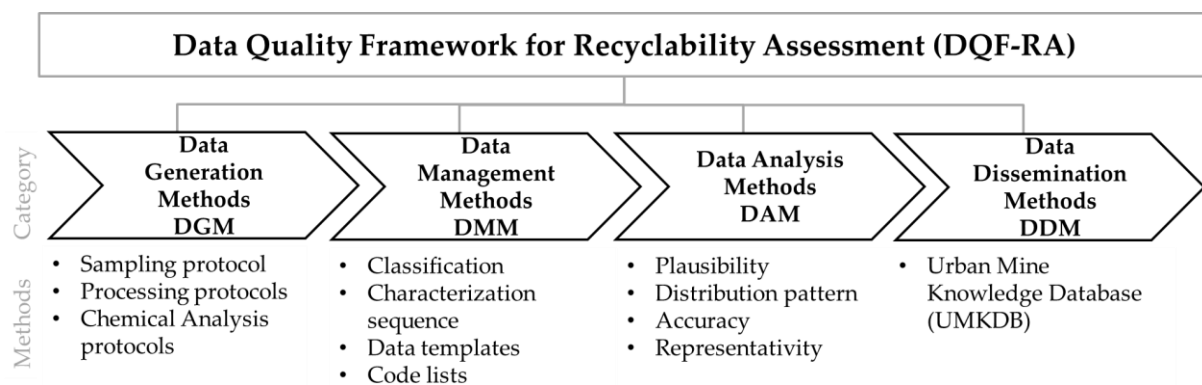


Figure 6. Modules of a data quality management framework for recyclability assessment with related methods.

2.2. Data Generation Methods (DGM)

➤ Application of **Protocols**

Data generation methods correspond to operational procedures for characterizing different aspects along the lifecycle of a material, a component, a product, or a flow. The measurement quantities can be very different, e.g., number, mass fraction, and percentage (corresponding transfer coefficients). The DGMs must be adapted, harmonized, and defined for these different aspects, measurement quantities, and reference quantities (m, c, p, f). Thus, case studies are advantageous to test procedures and document methods. Three scientific articles within this Ph.D. study describe the methodology (protocols) comparable to standard operation procedures (SOP), i.e., sampling, treatment procedures, or chemical analysis manuals. Common DGMs for the waste application context is the LAGA PN98 sampling

guideline for heaps and moving material flows (Länderarbeitsgemeinschaft Abfall [LAGA], 2001), the CENELEC CLC/TS 50625 for collection, logistics, and treatment requirements for WEEE (CENELEC, 2015), or the Solid Waste Analysis (SWA) tool for the sampling of municipal waste (European Commission, 2004). Depending on the question or objective of the investigations, new case-specific DGMs must be developed to extend the existing methods by further steps.

2.3. Data Management Methods (DMM)

- Application of **Classifications**
- Development of **Code Lists**
- Data Collection in **Templates**
- Use of **Calculation Sequence**

Data management methods (DMM) comprise all operations that generate technically correct, consistent data sets out of raw data (data cleaning) and produce harmonized and comparable data sets for processing as a result. The DMMs used in this Ph.D. study include the classification and harmonization of terminology, the use of a unified calculation sequence to relate information on elements, materials, components, products, and flows, and data templates and code lists for data collection. While classifications and the calculation sequences are directly applicable to other use cases, code lists may be adapted and expanded to the respective research scope and information depth.

2.3.1. Classification and Harmonization of Terminology

Since the use of batteries, their mass share, and battery subsystems are product specific (Mähltitz et al., 2020), a clear definition and distinction of diverse types of EEE and batteries are necessary. The classification of products varies according to application-specific requirements and specifications. Different classification systems exist within one product group and impede a comparison or validation of data. The combination and investigation of one or more products between studies necessitate the introduction of a defined reference, and unique identifiers, so-called “keys,” are used to harmonize the data. These keys cover most possible variations of (W)EEE or batteries, taking into consideration groups that share comparable characteristics and material compositions.

Data on EU- and Member State-level are not available in sufficient granularity to prospect accurate figures (Huisman et al., 2017). However, with the use of more sophisticated classification systems, scattered as well as incoherent data can be harmonized, and future data generation can be efficiently adapted.

(W)EEE Classification

As shown in **Table 3**, the WEEE Directive (European Parliament and Council, 2012) classified (W)EEE into ten categories until 2018 and then in six categories since 2018. In contrast, the United Nations University (UNU) introduced a more comprehensive approach to classifying EEE. The constant development of product-specific identifiers for (W)EEE, the so-called “UNU Keys” (Baldé et al.), aims to enable, among other things, the linkage of production data, composition data, and life span characteristics for lifetime distribution modeling (Baldé, Forti, Gray, Kuehr, & Stegmann, 2017; Baldé, Wang, Kuehr, & Huisman, 2014). The systems consist of three levels with a four-digit identifier on the most aggregated. The first two digits reflect the ten categories of Annex I of the WEEE Directive 2012/19/EU European Parliament and Council (2012), with the category “00” additionally introduced for “Central heating (household installed)” and “Photovoltaic panels.” As an example of the three levels for UNU keys, laptops are specified as 0303 IT laptop PCs (laptops, notebooks, netbooks, and tablets) – 030301 Laptops – 03030103 Laptop computers general (drive not specified).

Table 3. Classification of (W)EEE according to UNU classification (Baldé et al.) and WEEE Directive, Annex III (European Parliament and Council, 2012).

WEEE Directive, Annex II	UNU key	Description	WEEE Directive, Annex III	Description
-	0001	Central heating (CH, household installed)	01	Temperature exchange equipment
-	0002	Photovoltaic panels (PV)	02	Screens and monitors
01	010x	Large household appliance (LHA)	03	Lamps
02	020x	Small household appliances (SHA)	04	Large equipment
03	030x	IT and telecom equipment (ITCE)	05	Small equipment
04	040x	Consumer equipment (CE)	06	Small IT and telecommunication equipment
05	050x	Lighting equipment (LE)		
06	060x	Electrical and electronic tools (EET)		
07	070x	Toys, leisure, and sports equipment (TLS)		
08	080x	Medical devices (MD)		
09	090x	Monitoring and control instruments (MCI)		
10	100x	Dispensers (D)		

Battery Classification

Battery systems are legally defined in the Battery Directive (European Parliament and Council, 2006), differentiating batteries according to their use (portable, industrial, automotive) and chemistry (lead-acid, nickel-cadmium, other). The group “other batteries” comprises the alkaline (zinc-based), nickel-metal hydride (NiMH), lithium (primary), and lithium-ion (secondary) batteries. The “battery keys” listed in **Table 4** were used for the classification (Huisman et al., 2017; Huisman et al., 2020; Wagner et al., 2019), enabling a better allocation of the chemical composition to the battery system.

Table 4. Classification of battery systems by “keys” according to (Di Persio et al., 2020; Huisman et al., 2017; Huisman et al., 2020).

Battery key	Description	Battery sub key	Description
LiPrim	Lithium-based batteries, primary	LCF	Lithium Carbon Fluoride (Li(CF) _x)
		LSO	Lithium Sulfur Dioxide (LiSo ₂)
		LTC	Lithium Thionyl Chloride (LiSOCl ₂)
		LFS	Lithium Iron Disulfide (LiFeS ₂)
		LMO	Lithium Manganese Oxide (LiMn ₂ O ₄)
LiRecharge	Lithium-based batteries, rechargeable	LCO	Lithium Cobalt Oxide (LiCoO ₂)
		LFP	Lithium Iron Phosphate (LiFePO ₄)
		LMO	Lithium Manganese Oxide (LiMn ₂ O ₄)
		NCA	Lithium Nickel Cobalt Aluminum Oxide (LiNiMnCoO ₂)
		NMC	Lithium Nickel Manganese Cobalt Oxide
Zn	Zinc-based batteries	LTO	Lithium Titanate (Li ₄ Ti ₅ O ₁₂)
		AlMn	Alkali-Manganese
NiCd	Nickel-cadmium based batteries	ZnC	Zinc-Carbon
		NiCdSealed	Nickel-Cadmium, sealed
NiMH	Nickel-metal hydride batteries	NiCdVented	Nickel-Cadmium, vented
		NiMHSealed	Nickel-Metal hydride, sealed
Pb	Lead-acid batteries	NiMHVented	Nickel-Metal hydride, vented
		PbSealed	Lead-Acid, sealed
Other	Other batteries	PbVented	Lead-Acid, vented
		AgO	Silver-Oxide
		Etc.	Etc.

2.3.2. Calculation Sequence

The work of this Ph.D. study is based on the conceptional developments of the EU ProSUM Project (Huisman et al., 2017), in which a unified data model for the description of the urban mine was developed. The underlying calculation sequence (Wagner et al., 2021)

characterizes flows (f) on four different levels: products (p), components (c), materials (m), and elements (e). According to this calculation sequence, these levels can be interlinked using a hyphen between two levels. Following this logic, flows (f) can consist of products (p-f), components (c-f), material (m-f), or elements (e-f). Furthermore, products can be described by means of the components (c-p), materials (m-p), or elements (e-p). Similarly, components can be described using the mass fractions of materials (m-c) or elements (e-c), whereas materials compose of elements (e). While flows can be described on four levels, products in stock (like in the urban mine) can be described using c, m, or e (Wagner et al., 2021).

Recyclability is influenced on all these levels, which requires considering methodological challenges at each of these levels in recyclability assessment. Thus, to make the implication of each study comprehensible, this concept is followed throughout the project (cf. **Figure 9**).

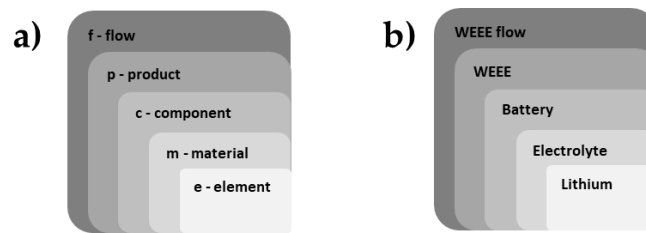


Figure 7. Calculation sequence of the Unified Data Model from the Urban Mine Platform to characterize the reference network and recycling scenario using (waste) flows (f), products (p), components (c), materials (m), and elements (e) (Huisman et al., 2017; Wagner et al., 2021).

Thus, an example of batteries in WEEE flows is shown in **Figure 7b**. WEEE flows are therefore f, WEEE are the products, and batteries are the components. The electrolyte would be an example of material and Li of an element contained in it.

2.3.3. Data Templates and Code Lists

During this Ph.D. study, data templates for collecting raw data and metadata were developed, facilitating the harmonized collection and consolidation of information. The template structures follow the “long format” principle for data tables (Harrison & Pius, 2021) and are thus consistent and can be adapted to the respective research questions. In addition, exhaustive lists of data entries were gained through literature research and the bottom-up design of each study, feeding into a collection of pre-defined and harmonized terms provided in code lists (Eurostat, 2022). This harmonized collection of raw data and metadata enables extensive data analysis with statistical and simulation tools, such as R (R Core Team, 2018) in

Article I, enabling data quality assessment and data-driven simulations to increase data precision.

The data templates and code lists used in this Ph.D. study are available online in the respective published articles and in the Annex for further use and adaptation.

2.4. Data Analysis Methods (DAM)

- Check for **Plausibility**
- Analysis of **Distribution Pattern**
- Validation of **Accuracy**
- Test on **Representativity**

Data analysis methods (DAM) comprise a multitude of different methods, which are selected based on the research objective. The grouping of the methods also depends on the field of application, the objective, and the scientific disciplines. In the following, the methods used in this Ph.D. study are briefly explained, and the added value is described. The sequence of the DAM categories shown in **Figure 8** follows the logic of checking the data for plausibility first. The evaluation of the accuracy, respectively, and the method for its evaluation requires an examination of the data distribution beforehand. Finally, the representativeness of the data, which is usually based on a sample from the population, must be checked.

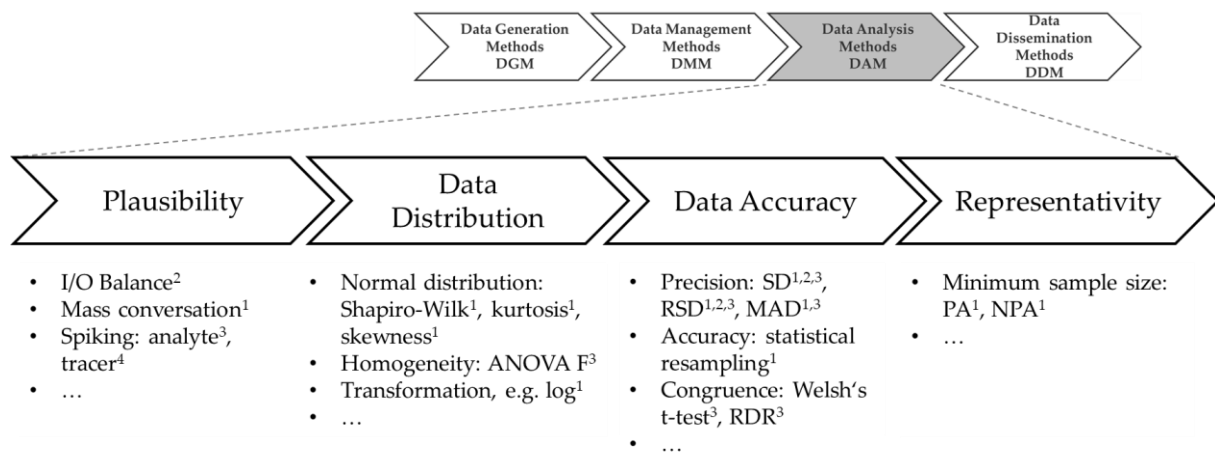


Figure 8. The sequence of data analysis methods to assess and improve data quality supplemented with a non-exhaustive list of case-specific methods. The superscripts refer to the methods used in case studies Article I (1), Article II (2), and Article III (3).

The DAM categories are described in the following sections, and examples for methods are given. Compared to Articles I-III, more methods are given to clarify the classification of

the methods to the four categories and highlight application fields that require an individual examination.

2.4.1. Data Plausibility

The plausibility of the collected data can be determined by the mass conservation between input and output masses via an input/output balance (I/O balance). For this purpose, recovery rates are determined which calculate the proportion of the input measurand (element, etc.). Also, the addition of selected substances in the input can increase the measurement limit or identify mass losses. For this purpose, elements present in the sample are added in a defined concentration, so-called spiking (Article II). Losses and sinks in the preparation can also be identified by adding elements not present (tracers) in the feed material. For example, in Løvik et al. (2019), Y and Yb were added to ASR prior to processing and analyzed for recovery in the output flows.

2.4.2. Data Distribution Pattern

The distribution of data points in a data set determines the applicability of other data processing methods and statistical tests, as well as the validity of descriptive statistics. When applying statistical tests, the first distinction is made according to the type of data (continuous data, discrete data, and proportions). The data distribution is used for continuous data, such as weight, length, or number. Next, a distinction is made between (log-)normally distributed data and skewed data (Colorado State University, 2019). Also, the expression parametric and non-parametric is used. Finally, testing is done for normal distribution, where a negative result (H_0 is false) indicates that the data is not normally distributed. Test methods for normal distribution are, for example, the Shapiro-Wilk (SW) test or Kolmogorov-Smirnov test (Bartlett, Kotrlik, & Higgins, 2001). In contrast to normality tests, kurtosis and skewness do not give a false or positive answer to a statistical hypothesis but a numerical value. Combined with a statistical test, the data distribution can be evaluated accordingly.

Furthermore, the data distribution determines the applicability of descriptive statistics. In the case of normally distributed data, the arithmetic mean and the standard deviation can be used to describe the location and shape. These parameters are biased for skewed distributions, so median and MAD (median absolute deviation) should be used instead.

For multiple measurements (more than two groups of data points for a sample), analysis of variances (ANOVA) can provide information about the distribution of data points of a measurand within samples. This information can be used to evaluate the homogeneity of a measurand (e.g., an element in a material) if the data are normally distributed. In case that no normal distribution is applicable, adaptations of the ANOVA test to the respective distribution function, e.g., F-distribution (ANOVA F), can be used (Wilcox, 2001).

2.4.3. Data Accuracy

Data accuracy can be differentiated into trueness and precision (DIN ISO 5725-1, 1997; Loshin, 2011). Trueness is known as value accuracy and expresses the closeness of a data or dataset to the true value or a reference value assumed to represent the reality properly. In contrast, precision expresses the “closeness of agreement [...] between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions” and is often expressed as standard deviation, relative standard deviation, or variance (ICH, 2005).

By increasing the sample size through more sampling or statistical resampling, value accuracy and precision can be improved. The latter comprises methods that randomly resample from the original data set (e.g., bootstrapping) or randomly create data on the basis of a given or stated data distribution function. Furthermore, sample preparation (practically) or classification (theoretically) can lead to higher homogeneity of the data and thus increase both trueness and precision.

2.4.4. Data Representativity

According to DIN 45555, representativity must be distinguished into product-related, technological, temporal, and geographical representativity (DIN EN 45555, 2019). Each representativity dimension requires respective data representativeness, which can be assessed with respect to the individual sample or the population. Data representativeness expresses whether a data set or statistic is within a specified reference or confidence interval (congruence) or meets a target value (e.g., reference value, p-value, minimum sample size).

Congruence test: The congruence test is used to compare samples with each other or with the population. Different test methods can be used depending on the type of data (discrete, continuous, proportion) and the distribution function. Standard test procedures include the z-

test, t-test, ANOVA, Wilcoxon Rank Sum test, Wilcoxon Signed Rank test, and non-parametric ANOVA for continuous data, χ^2 , Fisher's Exact test for discrete data or binominal tests, and others for proportions (Colorado State University, 2019). In addition, the position between two data sets can be described. For example, the relative deviation (to reference) (RD(R)) can be specified or the position of a mean or median within or outside a confidence interval.

The minimum sample size (MSS) can be approximated by parametric or non-parametric approaches (Mähltitz et al., 2020) and expresses whether the result is based on a sufficiently large database. The reference is a priori knowledge from previous studies or simulated distribution functions, e.g., by statistical resampling, such as bootstrapping (Mähltitz et al., 2020) or Monte Carlo simulations.

2.5. Data Dissemination Methods

➤ Distribution in **UMKDB**

Data dissemination methods (DDM) refer to making available or providing the data and descriptive metadata as well as the method for generating it. In addition to availability (e.g., access rights, open access, CC BY 4.0 certification), aspects of technical implementation (e.g., interoperability with IT systems, API) and linkage and extension to existing database systems (e.g., UMKDP, RMIS (European Commission, 2022b)) are also important aspects that should be considered. In the context of this Ph.D. study, the DDM is guided by the realized UMKDP, which is available at www.urbanmineplatform.eu and the database model for which was explained in (Heijboer et al., 2017; Mähltitz, Sperlich, & Rotter, 2019). Furthermore, the EU RMIS has already been implemented (European Commission, 2022b), and the extension by battery data (POM, Stock, EoL) has already taken place (Huisman et al., 2020).

3. Demonstration of DQF-RA for WEEE Batteries

In this chapter, selected methods of DQF-RA are described in three case studies to characterize products, flows, and materials. Each case study addresses a relevant intersection in the EoL scenario of WEEE-embedded batteries, which impacts the recyclability result. The following chapters briefly describe the individual study problem statement and design, followed by factsheets comprising the aim of the study, DGM, DMM, DAM, and conclusion.

The methods developed within the case studies and summarized in the factsheets were used to fill the DQF-RA. The three case studies are intended to provide orientation and demonstrate the principle of a uniform framework for very different problems in data generation, processing, and logging. The importance of a DQF-RA increases with the number of further case studies.

3.1. Product Characteristics: Sampling of Built-in Batteries in WEEE

If batteries remain in WEEE and are collected in it at the end of product life, data are needed regarding which WEEE certain battery systems are found in (cf. IEC 62902:2019, 2019) and what mass (proportions) they account for. This data will enable improvement of the identification and subsequent separation of the batteries and the estimation (on product level) of the material loss for the recycling of batteries. This data can then be used as the basis on which to adapt processes in such a way that the share of recycled batteries and thus the product recyclability are increased.

Article I aims to determine the proportion and mass of battery systems in WEEE and develop a method to assess representative sampling by approximating the minimum sample number.

Data Generation Methods (DGM)

In Article I, a sampling protocol was developed that counts and registers each product and its characteristics. This “product count” protocol and the respective sampling procedure for WEEE batteries were tested through a comprehensive empirical data collection of approximately 6,500 WEEE appliances and over 800 batteries. The sampling units and categories sorted are illustrated in Figure 9.

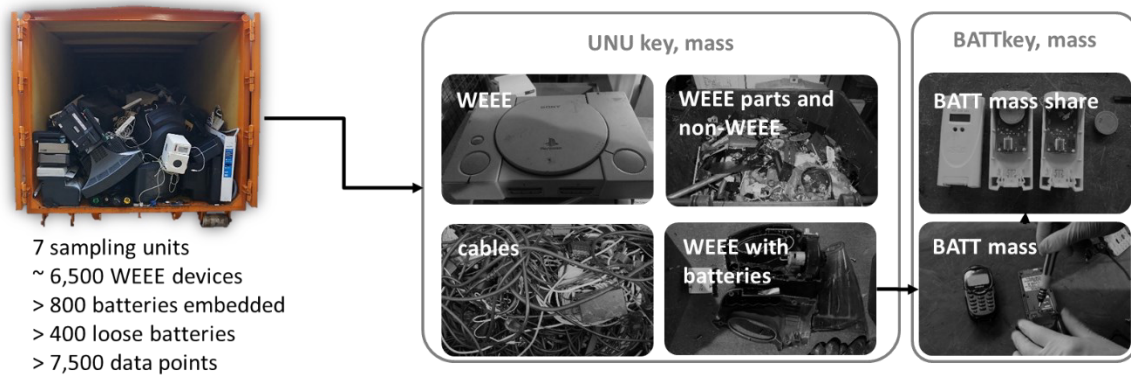


Figure 9. Sampling procedure to determine mass and mass share of WEEE batteries.

Data Management Methods (DMM)

All WEEE products were counted, weighed, and classified according to the UNU classification for EEE (cf. Table 3). Subsequently, the device was checked for battery compartments and batteries, which were then classified according to the BATTkey classification (Table 4). The mass share of each battery in WEEE (c-p) was calculated. All data were collected in a developed sampling template which is depicted in 6.3.1 Sampling template.

Figure 9 shows the sampling procedure implemented in Article I. Since the mass share of batteries in WEEE varies enormously between different WEEE products, a classification using more detailed nomenclature (UNU keys and sub-keys) proved to yield more valid results for most products.

Data Analysis Methods (DAM)

Data validation comprised a three-step approach to assess and improve the data quality. Firstly, the results are statistically analyzed and examined for commonly assumed distribution patterns (normal and lognormal distribution). Secondly, data-driven simulation (bootstrapping) using the original sample data is performed to obtain more accurate WEEE battery characteristics. Finally, both a parametric approach (PA) and a nonparametric approach (NPA) are employed to approximate the MSS to quantify the mass share of built-in batteries in WEEE.

The assumption of normally distributed data sets is not valid for most WEEE products in terms of data distribution. In some cases, the lognormal distribution assumption is better suited for the characterization of masses (and mass shares). Normal distribution cannot be assumed for battery mass (BM) and battery mass share (BMS) based on sampling results in most cases. Bootstrapping was shown to be likely to generate more accurate results on battery

characteristics in the case of unknown or inconclusive sample distributions and fewer data points.

Regarding data representativity, bootstrapping in combination with recycling-oriented product characterization can be used to perform the NPA, which provides a more robust approach to approximate the MSS. For example, to determine the mass share of lithium-based batteries in small household appliances, the minimum sample sizes (MSS) can be derived from the graphs in **Figure 10c**. To determine the MSS of LiPrim, approx. twenty devices must be investigated for batteries, whereas the MSS for LiRecharge in mobile phones requires approx. 50 devices.

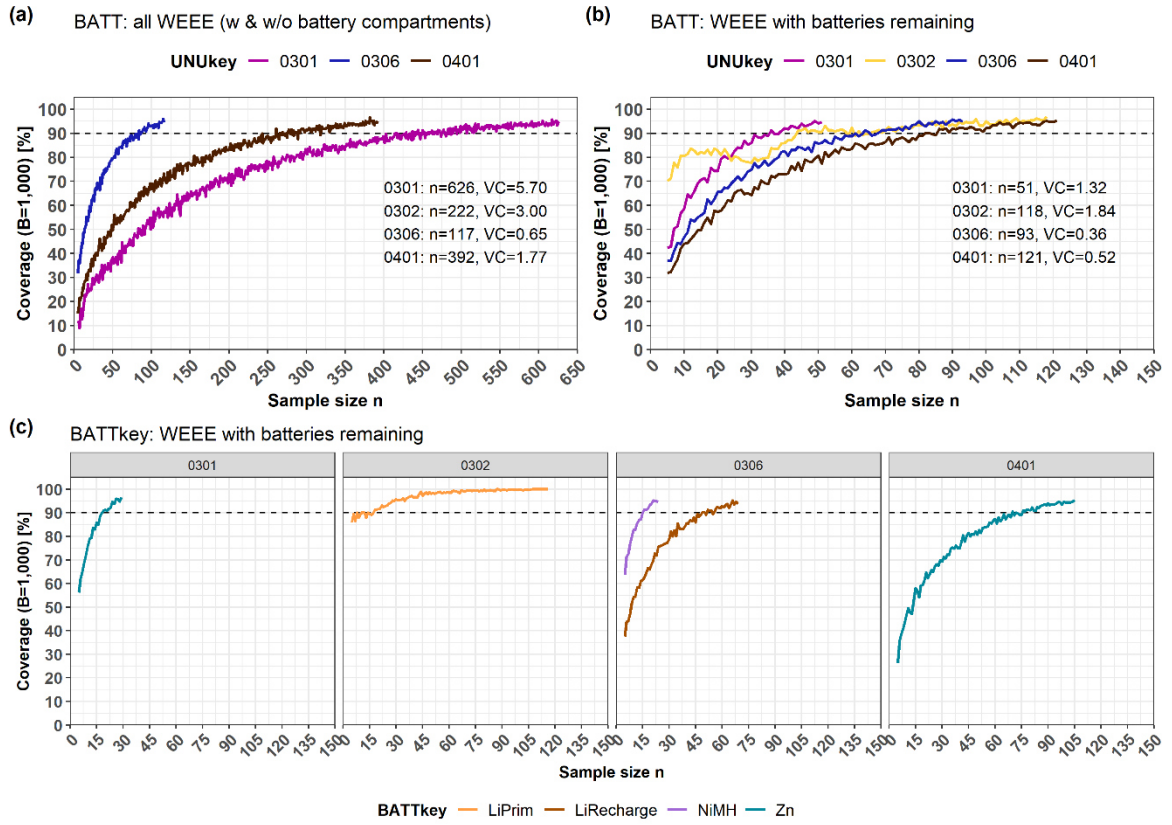
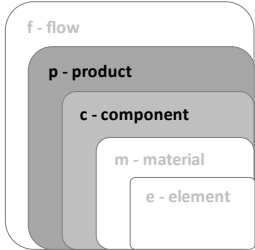


Figure 10. NPA: Simulation of MSS using bootstrap simulation. The proportion of sub-samples that lie within the simulated 95% CI* (coverage) is plotted against the number of samples used to draw the sub-samples. A coverage of 90% is considered acceptable to achieve representable results with the given sample size (dashed line). The graphs show the three possible combinations using small information technology (IT) (0301), desktop personal computers (PCs) (0302), mobile phones (0306), and small consumer electronics (0401) as examples: (a) all WEEE with and without battery compartment, (b) only WEEE with battery compartment without battery specification (BATT), (c) WEEE with batteries and BATTkey specification (Mählitz et al., 2020).

Table 5. Factsheet for Article I

Article I Characterizing the Urban Mine – Simulation-Based Optimization of Sampling Approaches for Built-in Batteries in WEEE	
Goal	Provision of detailed data sets on built-in batteries in WEEE and proposing a non-parametric approach (NPA) to determine the minimum sample size (MSS)
Objective	Sampling and quantifying the mass share of batteries embedded in and collected with WEEE
Research question	How to assess representative sampling of built-in batteries in WEEE in the case of unknown or inconclusive sample distributions and fewer data points?
Data	Transfer coefficient of batteries embedded in WEEE, product-specific mass share, minimum sample size per product and battery
Method	1.) Product count procedure: method for representative sampling of built-in batteries in WEEE 2.) Method to define MSS for representative results based on robust statistics and bootstrapping
Data Generation Methods (DGM) Sampling protocol for product count	
Data Management Methods (DMM)	
Classification	BATTkey, UNUkey
Charact. seq.	c-p: battery in WEEE
	
Data template	6.3.1 Sampling template
Code lists	EU10, UNU key, UNU subKey, BATTkey
Data Analysis Methods (DAM)	
Plausibility	Mass balance of single fractions (samples, product) and total unit mass
Distribution	Shapiro-Wilk test on normality, log-transformation
Accuracy	Bootstrapping
Representativity	Parametric approach (PA) and a nonparametric approach (NPA) to approximate the minimum sample size (MSS)
Data Dissemination Methods (DDM) Not yet established	

3.2. Flow Characteristics: Processing of Mixed Battery Flows

In case batteries are treated or recycled as a battery mixture, the process and the constituents of the different chemical battery systems determine the composition and quality of the output flows. Consequently, the recycling efficiency of the process and the recyclability of each battery system in the waste flow are significantly determined by the recycling options. The dependence of the recyclability on the batteries present in the waste stream is a crucial influencing factor in RA. Data on the battery systems present in the waste stream, their recycling efficiency, and the identification of interfering products are important to initiate appropriate measures (material stream management). In Article II, extended batch tests (EBT) were tested as a method to 1) characterize mixed battery waste flows aiming to infer the product (p-f) and elemental (e-f) composition of the input flows and 2) identify poorly recyclable battery systems.

Data Generation Methods (DGM)

EBT was carried out for three low-value battery mixtures comprising 1) zinc-based batteries (AZ), 2) lithium-based batteries (LIB), and 3) a mixture of both (AZLIB). As shown in **Figure 11**, the batch test procedure was extended by three steps. Firstly, comprehensive characterization was performed for the input (product identification by manual sorting, element composition through literature research), the process (screening samples), and the output (physical and chemical analysis). Secondly, the mass conservation of selected elements was checked by input-output balancing for target elements with a high mass fraction (Al, Fe, K, Mn, Zn), hazardous potential (Cd, Pb, Cr), and higher value (Co, Cu, Ni). Thirdly, a recyclability assessment of the individual products in the input flow was performed by combining the process recycling efficiency (RE) and output specifications of recycling and recovery options to deduce recommendations on increasing RE by identifying poorly recyclable battery systems.

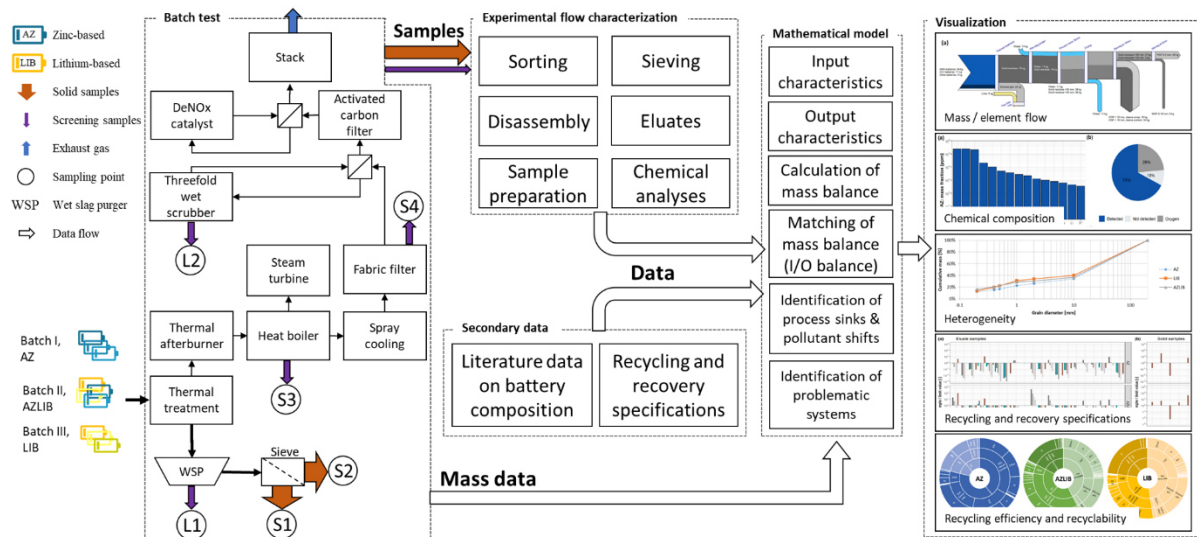


Figure 11. Basic flow scheme of the thermal treatment process and description of extensions of the batch test design (Mähltitz et al., 2022).

Data Management Methods (DMM)

The manual sorting of the battery systems was carried out according to the BATTkey classification. Code lists were created for Fraction, UoM, Parameter, and valueType. All data were recorded in data templates according to the calculation sequence.

Data Analysis Methods (DAM)

Data validation was performed by checking the plausibility and compliance of mass conservation by input-output (I/O) mass balancing. For this, screening samples from different process locations were taken to evaluate process sinks and close mass balances. Further, sieving of solid output was performed to increase material homogeneity and decrease results variances. I/O mass balancing for target elements was performed to prove mass conservation by combining the results of the input sorting analysis (products) with elemental battery contents from the literature and comparing them to the output characteristics. The last step comprises the calculation of recycling efficiencies based on the calculation of recyclable contents by comparing the output characteristics with recycling and recovery (RR) specifications as well as landfill criteria. Data accuracy was increased by subdividing the sample heap according to LAGA PN98 (LAGA, 2001) and carrying two parallel samples.

Table 6. Factsheet for Article II

Article II	
Contributions of Extended Batch Tests for Assessing Technical Recyclability: A Case Study of Low-Value Battery Flows	
Goal	Demonstration of how extended batch tests (EBTs) can be used as a method to a) determine battery-specific recycling efficiency (RE) and b) derive recommendations for assessing and improving the recyclability of batteries
Objective	Characterize and assess product and waste flow recyclability of batteries
Research question	How to assess the individual product recyclability for one battery system present in and treated jointly with a mixed battery flow. Further, how to identify poorly recyclable products in mixed battery flows lowering the recyclable content?
Data	Transfer coefficient of recyclable content (recycling efficiency) and poorly recyclable battery subsystems
Method	Method extension for batch tests (EBT) for recyclability assessment of individual batteries in mixed waste flows
Data Generation Methods (DGM)	
Extended batch test (EBT) procedure (Mährlitz et al., 2022)	
Data Management Methods (DMM)	
Classification	BATTkey
Charact. seq.	e-m: element mass fraction of output materials e-p: element mass fraction of input products (batteries) p-f: battery subsystems in battery waste flow
Data template	6.3.2 Process performance template
Code lists	Fraction, UoM, Parameter, valueType
Data Analysis Methods (DAM)	
Plausibility	Input-output balance
Distribution	N/A
Accuracy	Sampling according to LAGA PN 98 with parallel samples
Representativity	N/A
Data Dissemination Methods (DDM)	
Not yet established	

3.3. Material Characteristics: Chemical Analysis of Heterogeneous Battery Materials

The variety of chemical battery systems and their different chemical compositions (especially of lithium batteries, as shown in **Figure 3**) lead to heterogeneous material mixtures if the separation of the batteries is insufficient (cf. Article II). Depending on the treatment and recycling processes, chemical and thermal transformation processes take place, which can strongly change the properties and composition of the material to be recycled. To determine the recyclable fraction of a product within the RA, it is therefore necessary to determine the material compositions of the process outputs that are both valid and affordable.

In Article III, the material characterization method comprised the chemical analysis (e-m) and was tested for complex waste materials from processing to 1) assess the applicability of simplified multi-element chemical analysis methods and 2) determine element- and method-specific uncertainties as well as methodological recommendations. The study was conducted on two mineral waste samples, one of which was obtained from thermal pre-treatment of lithium-ion batteries described in Article II. This material, namely battery ash sample, is the mineral fine fraction from various low-value lithium battery subsystems and is composed of the burned-out active material of different lithium subsystems, leading to challenges for chemical characterization methods.

Data Generation Method

Data generation included the performance of chemical analyses with a sophisticated validated method and the application of simplified “in-house” methods (cf. **Figure 12**). Element-specific and extensive ‘validated methods’ comprised wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry as well as wet-chemical analysis using inductively coupled plasma (ICP) in combination with optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS). Routine in-house wet-chemical methods and energy dispersive X-ray fluorescence (ED-XRF) spectrometry were tested for their applicability. Simplified wet-chemical methods based on the validated methods using the same element masses (ICP-MS) and spectral lines (ICP-OES) but applying simplification with usual resource constraints, such as material-unspecific measurement settings, the avoidance of hydrofluoric acid, the limitation of reaction gas for ICP-MS.

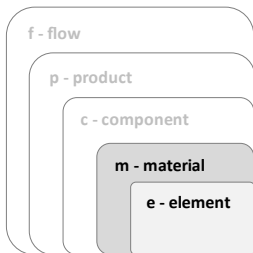
Data Management Methods

According to the calculation sequence (cf. **Figure 7**), elements in the material (e-m) were determined, and the analysis data and metadata were recorded in the form of long tables. The developed data templates can be found in the Annex. In addition to the chemical elements (“elements”), the following code lists were developed and used to describe and interpret the analysis data: elementGroup, approach, digestionType, digestionAcid, measurementMethod, measurementDeviceDetector, measurementDevice, measurement-Detector, valueType, valueTypeGroup, UoM, and uncertaintyType.

While the ‘validated method’ used labor-intensive and sophisticated testing of measurement parameters (analysis-driven approach) for data validation, the simplified in-house method applied a three-step data-driven validation approach comprising internal quality assurance and the comparison of results to the validated method as a reference. Firstly, material homogeneity was checked using the ED-XRF pre-scanning results and ANOVA F test (Wilcox, 2009). Secondly, method precision and accuracy were tested. Method precision, i.e., the repeatability of the analytical procedures, was assessed based on the coefficient of variation (relative standard deviation, RSD) (ICH, 2005, p. 8). Method accuracy was validated by means of spiking tests and the calculation of element recovery rates (RR) at three points of the analytical procedure: with liquid standards (RRL), in blind samples (RRB), in the respective

sample matrices (RRS) added before digestion. Thirdly, method applicability of simplified analysis methods was evaluated based on the relative difference of mass fraction, as well as using Welch's *t*-test for significant differences.

Table 7. Factsheet for Article III

Article III Characterizing the Urban Mine – Challenges of Simplified Chemical Analysis of Anthropogenic Mineral Residues	
Goal	Assessment of the applicability of simplified multi-element chemical analysis methods for complex mineral waste matrices that show highly different mass contents of many elements
Objective	Chemical analysis to characterize the element content of battery materials challenged by element variety, matrix complexity, and material heterogeneity
Research question	How to assess the applicability of simplified multi-element chemical analysis methods?
Data	Element composition and element- as well as method-specific uncertainties Uncertainty factor element recovery
Method	Method to assess applicability of chemical analysis methods to characterize material for recycling
Data Generation Methods (DGM) Simplified in-house chemical analysis method	
Data Management Methods (DMM) Classification BATTkey Charact. seq. e-m: element mass fraction of mineral battery fraction  Data template 6.3.3 Chemical analysis Code lists elementGroup, approach, digestionType, digestionAcid, measurementMethod, measurementDeviceDetector, measurementDevice, measurementDetector, valueType, valueTypeGroup, UoM, uncertaintyType	
Data Analysis Methods (DAM) Plausibility RRL, RRB Distribution ANOVA F test for homogeneity Accuracy RSD to a reference value, significance test: Welsh's t-test Representativity N/A	
Data Dissemination Methods (DDM) Not yet established	

3.4. Recommendations from Case Studies

Both quantitative and methodological insights can be gained for WEEE batteries from the three case studies presented. In the following section, the main conclusions of the studies for the improvement of the recyclability as well as improvement of its evaluation are presented. The recommendations are intended to help the actors along the value chain of the products to derive options for action.

3.4.1. Improving the Recyclability of WEEE-embedded Batteries

This section summarizes the key findings of Articles I-III under the aspect of improving recyclability. General recommendations and options for action are formulated for the prevention of the loss of embedded batteries in WEEE recycling processes, the thermal treatment of low-material battery mixtures, and the simplified chemical analysis of complex mineral battery samples.

Sampling

The percentage of batteries missing, i.e., not installed, removed prior to collection, or dropped out during collection or transport, differs between the WEEE categories and the UNUkeys. On average, 34% of the more than 1,200 devices with battery compartments were found without batteries. In other words, 66% of WEEE with a battery compartment were discarded with the battery still embedded. For most UNUkeys with a battery compartment, the removal rate of batteries prior to collection/treatment was below 50%. In the case of 0204, 0205, 0306, 0601, 0701, and 0901, batteries were found in over 75% of the devices contaminating subsequent material flows if prior identification and separation of the batteries are not carried out. Regarding rechargeable batteries, LiRecharge and NiMH were dominantly present in WEEE. LiRecharge is characterized by high power and energy density, high voltage, long storage life, and low self-discharge rate (Gulbinska, 2014; Li et al., 2018), which is why they can be found among most UNUkeys (Figure 4). However, only laptops (0303) and mobile phones (0306) show a predominant use of LiRecharge batteries, having mass shares of $13 \pm 5\%$ and $24 \pm 7\%$ by mass, respectively. The random occurrence of these batteries in some device types makes their systematic identification challenging. In summary, product-specific occurrences of battery types with precise (VC $\pm 20\%$) BM or BMS were rarely found.

It is recommended to reduce the loss of batteries in WEEE through targeted separation of individual WEEE and subsequent removal of the batteries. In addition, the product-related information about contained batteries assists designers in adapting markings and construction methods for simplified removal, if necessary, and distributors and collectors in improving educational work and sensitization for the topic of resource loss through WEEE-embedded batteries in the population.

Processing

The results of the EBT showed that separation criteria in sorting (low material content) and process selection have a decisive influence on waste flow recyclability. Due to the heterogeneous fine materials, the thermal treatment of low-value lithium batteries poses great challenges to downstream RR concepts, resulting in RE below 50% by mass without further processing. On the other hand, more homogeneous AZ batteries can also be treated in thermal treatment with RE significantly above 50% by mass (cf. **Figure 13**). Joint treatment of both systems is legally possible but economically and ecologically not reasonable.

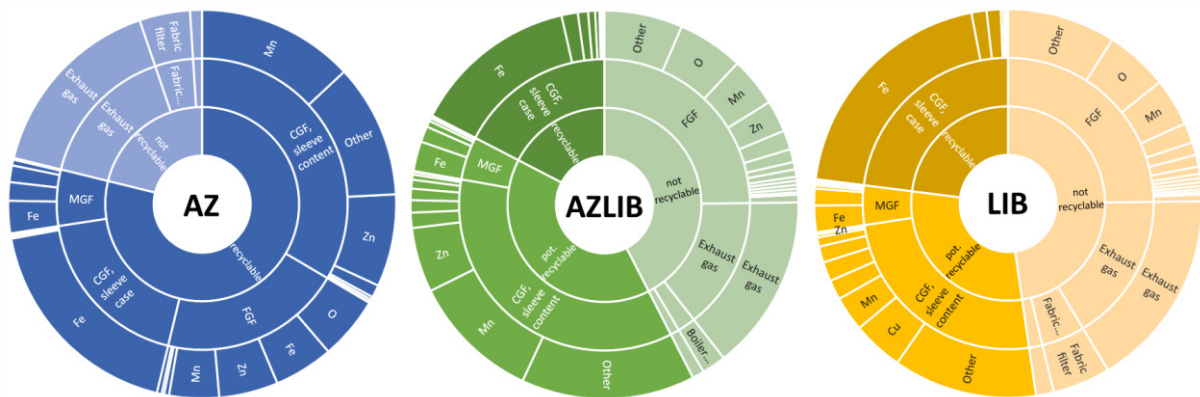


Figure 13. Proportions of recyclable, non-recyclable, and potentially recyclable components after further treatment (Mährlitz et al., 2022).

It is recommended to improve the recycling efficiency for thermal treatment of low-value batteries by separating interfering chemical battery systems (fluorine and chlorine-containing) and providing information about poorly recyclable chemical battery systems and the relevant constituents to designers and manufacturers. Furthermore, high recycling efficiencies and thus higher recyclability can only be achieved by a homogeneous and contaminant-free fine fraction, which can be achieved by identifying and bundling similar chemical battery subsystems.

Chemical Analysis

Article III shows that a simplified application of microwave-assisted digestion with aqua regia and subsequent measurement with ICP-OES or ICP-MS did not prove to be applicable for half of the analyses. There is no clear dependence of acid selection or mass concentration on the accuracy of the in-house method. Nevertheless, a tendency is discernible that elements with high mass fractions can be more accurately determined. The analyses with ICP-OES and ICP-MS frequently showed deviations of 10–25% and 25–75%, respectively. Despite internal quality assurance, significant deviations from the validated value were observed, demonstrated as high precision (RSD) and good accuracy (RRL, RRB, RRS).

ED-XRF analysis can only be used to a limited extent without matrix-specific calibration. However, semi-quantitative analysis with deviations that were below 100% proved to be feasible for most elements (except Co) having (a) an atomic number between Z 12 and Z 50, and (b) mass fractions above 1,000 ppm. Strong deviations up to 90 times the validated value were observed, particularly for elements with low mass fractions.

It is recommended not to generally apply simplified chemical analysis methods for anthropogenic mineral matrices without additional quality assurance measures. The mineral character and many elements in different mass concentrations make simplified methods prone to errors due to matrix interferences.

3.4.2. Improving the Assessment of Recyclability of WEEE-embedded Batteries

This section summarizes the key findings of Articles I-III under the aspect of improving methods to provide relevant data to assess recyclability.

Sampling

The sampling of batteries and batteries embedded in WEEE should be done product by product in the future with a detailed description of the devices and battery systems (BATTkey, UNUkey). The individual data collected in this way can then be approximated more precisely by bootstrapping and, in the next step, checked for representativity by the NPA-MSS method developed. This methodological recommendation can, for example, be incorporated into existing sampling guidelines, such as LAGA PN98 (LAGA, 2001) or the SWA tool. The data collected in this way are of better quality and can better estimate losses via WEEE and consequently better represent technical recyclability within the RA.

It is recommended to apply product count procedure supplemented by MSS-NPA for validation.

Processing

The EBT method provides valuable insight for the RA via the RE calculation required under Commission Regulation EU No 493/2012 (Commission Regulation (EU) No 493/2012, 2012). By applying and extending the batch test supplement by I/O balance for target elements, process balances can be closed, pollutant shifts can be identified, and recycling impeding constituents can be defined. The findings on impurities and disruptive chemical battery systems should be “communicated” upstream in the value chain to adapt waste and material flow management (e.g., collection systems) and influence design decisions (design for recycling). The extension of Commission Regulation EU No 493/2012 or a specification adapted for batteries comparable to or CENELEC CLC/TS 50625 (CENELEC, 2015) for WEEE would be conceivable approaches to take up the presented methodology.

It is recommended to apply EBT supplemented by I/O balancing for target elements.

Chemical Analysis

The methodological challenges in the analysis of mineral residues from battery recycling are the absence of reference methods and reference material due to material complexity and heterogeneity. The instructions outlined in DIN EN ISO/IEC 17025 (2017) are the minimum standard for quality assurance. If simplified chemical analysis methods under resource constraints are necessary, it is recommended to involve external laboratories in addition to the internal quality assurance measures since it was shown in Article III that despite plausible recoveries (RRL; RRB; RRS), the deviation from reference methods could be high. If this is not possible, a homogeneity test (ANOVA F test based on XRF screening data) and spiking of the blind (RRB), liquid standards (RRL), and sample (RRS) is the recommended procedure to reduce biased results.

Internal quality assurance steps for the simplified method did not ensure the identification of these interferences. For complex mineral matrices, it is recommended to apply additional quality assurance measures such as laborious method development, the provision of appropriate reference materials, or sample- and element-specific method validation within interlaboratory tests.

It is recommended to validate chemical analysis methods by means of reference material, reference method, and/or interlaboratory tests supplemented by homogeneity checks, spiking, and statistical congruence tests.

4. Synthesis

This chapter represents the synthesis of this Ph.D. study and is structured according to the three research questions formulated in chapter 1.6.

The structure and required methodological categories of a DQF-RA to be developed, which covers the multiple aspects of data quality in RA (Research Question 1), are comprehensively presented and explained in chapter 2.1.

The suitability of the developed DQF-RA for ensuring high-quality data (Research Question 2) is examined using data quality dimensions (cf. chapter 4.1).

Research Question 3 is addressed in chapter 4.2 - 4.4. Firstly, the data and methods from the three core papers are summarized and mapped to the categories of the DQF-RA. These results form the beginning of a DQF to be successively filled. Secondly, the DAMs described in Articles I-III are examined for their transferability to show further fields of application of DAMs and demonstrate their broad applicability. Finally, the key findings from the development of the DQF-RA are explained concerning possible implications for actors along the value chain.

4.1. Contribution of DQF-RA to DQ Dimensions

Chapter 3 presented the four categories of the DQF for RA: DGM, DMM, DAM, and DDM. The recommended methods for its implementation depend on the individual objectives but are also often transferable so that a bottom-up approach through different case studies results in a collection of methods that can be expanded continuously to supplement the DQF-RA.

The three case studies presented (Article I-III) provide a variety of methods for DGM, DAM, and DMM (cf. 4.2 Contribution of Case Study Results to DQF-RA). The extent to which these methods can lead to assurance and improvement of data quality can best be illustrated by contrasting the methods with the data quality dimensions (DQD) introduced in chapter 1.4, **Table 1**.

The DQF-RA aims to cover the mentioned DQDs in the best possible way through methodical procedures and thus to make the quality of the data assessable and make its quality improvement even more comprehensible. The fulfillment of these requirements goes beyond the dataset itself and concerns data generation and data management, analysis, and dissemination. Therefore, it can be concluded that a DQF is necessary to address data quality

comprehensively. **Table 8** shows the comparison of the DQD (cf. **Table 1**) with the categories of the DQF-RA developed in this Ph.D. study. The “X” marking indicates which methods of the DQF-RA (left column) address the respective DQD and contribute to an improvement or assurance.

It should be noted that the categories and methods of the DQF-RA cover all DQDs, with some categories primarily addressing one DQD (e.g., intrinsic DQ through DAM) or multiple DQDs (e.g., DMM). DAM is often performed to ensure intrinsic data quality, but DMM is necessary across all DQD, mainly for consistency and contextual DQD. In summary, the developed DQF-RA fulfills all important aspects specified by the DQD. Consequently, it can be recommended as a methodological framework for ensuring high data quality for data handling. Following this basic structure consisting of DGM, DMM, DAM, and DDM can also be extended via high-quality data for the RA.

4.2. Contribution of Case Study Results to DQF-RA

The results of this Ph.D. thesis are twofold: The data are meant to be used for the future recyclability assessment of WEEE batteries as they are harmonized and thus can be consolidated with and compared to other data. Further, the DGM, DMM, and DAM will help to generate more reliable and consistent data in future studies to fill gaps impeding good recyclability assessment. **Table 9** on page 45 summarizes the contributions of Articles I–III to the DQF-RA under the aspects of data and methods.

Table 8. Contribution of DQF-RA methods to the fulfillment of data quality dimension (DQD). The X means that the method meets the requirements of the respective DQD.

DQF-RA		Intrinsic DQD					Contextual DQD					Repr. DQD		Access. DQD	
Category	Methods	Accuracy		Lineage	Structural Consistency	Semantic Consistency	Timeliness	Completeness	Identifiability	Reasonableness	Uniqueness	Interpretability	Consistency	Accessibility	Availability
		Value accuracy	Precision												
Data Generation Methods (DGM)															
	Application of Protocols			X	X			X				X	X	X	X
Data Management Methods (DMM)															
	Application of Classifications				X	X		X	X	X	X	X	X	X	X
	Development of Code Lists				X	X		X	X	X	X	X	X	X	X
	Data Collection in Templates			X	X	X		X	X	X	X	X	X		
	Use of Calculation Sequence				X	X		X	X	X	X	X	X		X
Data Analysis Methods (DAM)															
	Check for Plausibility	X								X					
	Analysis of Distribution Pattern	X	X												
	Validation of Accuracy	X	X												
	Test on Representativity	X								X			X		
Data Dissemination Methods (DDM)															
	Distribution in UMKDB			X			X	X				X	X	X	X

Table 9. Contribution of article results to the DQF-RA.

	Article I	Article II	Article III
Data	Transfer coefficient of batteries embedded in WEEE, product-specific mass share, minimum sample size per product and battery	Transfer coefficient of recyclable content (recycling efficiency) and poorly recyclable battery subsystems	Element composition and element- as well as method-specific uncertainties. Uncertainty factor element recovery.
Data Generation Methods (DGM)			
Application of Protocols	Sampling protocol for product count	Extended batch test (EBT) procedure	Simplified inhouse chemical analysis method
Data Management Methods (DMM)			
Application of Classifications	BATTkey, UNUkey	BATTkey	BATTkey
Development of Code Lists	EU10, UNU key, UNU subKey, BATTkey, UoM	Fraction, UoM, Parameter, valueType	elementGroup, approach, digestionType, digestionAcid, measurementMethod, measurementDeviceDetector, measurementDevice, measurement-Detector, valueType, valueTypeGroup, UoM, uncertaintyType
Data Collection in Templates	6.3.1 Sampling template	6.3.2 Process performance template	6.3.3 Chemical analysis
Use of Characterization seq.	c-p	e-m, e-p, p-f	e-m
Data Analysis Methods (DAM)			
Check for Plausibility	Mass balance of single fractions (samples, product) and total unit mass	Input-output (I/O) Balance	RRL, RRB
Analysis of Distribution Pattern	Shapiro-Wilk test on normality, log-transformation	N/A	ANOVA F test for homogeneity
Validation of Accuracy	Bootstrapping	Sampling according to LAGA PN 98 with parallel samples	RSD to a reference value, significance test: Welsh's t-test
Test on Representativity	Parametric approach (PA) and a nonparametric approach (NPA) to approximate the minimum sample size (MSS)	N/A	N/A

4.3. Transferability of Methods to Other Use Cases

When considering the transferability of methods to other case studies, the focus will be on DAM. For DDM, the UMKDP is assumed as the basis, which can be extended as desired. With respect to DMM, the calculation sequence is defined, whereas templates, code lists, and classification can be arbitrarily extended with respect to the objective. Although the DGMs can be related to other case studies, the DAMs offer the most significant potential to increase data quality without additional physical effort.

I have illustrated through the applied DAM that for a good assessment of data quality, the existence of harmonized raw data is indispensable. Only then do advanced statistical methods (Articles I & III) and holistic approaches to RA (Article II) become possible, which lead to a better evaluability and comparability of the results. In summary, three types of DAM for quality assurance and improvement were identified, which take place at different steps in the data processing:

- 1) Ex-ante: validation of precision and accuracy of a measurement method before the actual measurement, e.g., by spiking/recovery rates (Article III)
- 2) Integrated: plausibility check of the measurement method by verifying, e.g., the mass conservation of selected target elements (Article II)
- 3) Ex-post: data-based statistical evaluation, e.g., of the necessary number of samples for representative sampling (Article I)

Providing characteristics for the recycling network of WEEE-embedded batteries is challenging in many places and at different levels (cf. **Figure 7**). Identifying the “critical points” for recycling was illustrated by a schematic representation of the reference network (cf. **Figure 2**). In this Ph.D. study, the collection of portable batteries incorporated in WEEE (Article I), the processing of mixed battery waste (Article II), and the determination of recyclable battery materials by chemical analysis (Article III) were considered. Due to the operations applied at each step, the considered level in the calculation sequence changes along the lifecycle. Consequently, to make the methods more transparent, the concept from Figure 7 was applied, as shown in **Table 10**, and distinguishes between e, m, c, p, and f as reference values. Thus, the location in the recycling network can be determined, but the scope of the methods can also be considered. For example, spiking refers to adding defined amounts of elements (e) to the sample material (m) to determine the element recovery (e-m). Whereas EBT

can be used to derive the elemental composition (e) of the battery flow (f) (equivalent to e-f). Following this logic, the methods used here can also be applied to other levels and for different EoL characteristics and locations in the reference network. **Figure 10** lists the methods applied in Articles I–III to increase data quality and shows the scope and the possible transferability of methods to further application scenarios.

Table 10. Transferability of data analysis methods to other possible application scenarios to describe and better characterize the urban mine and points in the recycling network.

Article	Data analysis method	Purpose and principle	Scope		General applicability and transferability
I	Bootstrapping	Increase accuracy by statistical resampling	c-p	S	To all levels having a minimum number of 15 data points in the data set
I	NPA for MSS	Non-parametric approach (NPA) using bootstrap confidence intervals to approximate minimum sample size (MSS)	c-p	S	To all levels having a minimum number of 15 data points in the data set
II	Extended batch tests	Infer elemental input composition, process transfer coefficients	e-f, p-f	P	m, c, p in other flows
II	I/O balancing	Element mass balancing to check plausibility, i.e., mass conservation	e-f	P	To processing and mass balancing (e-m, e-f) (Løvik et al., 2019; Mährlitz et al., 2022)
III	Homogeneity test (ANOVA F)	Element-specific testing of measurement variances	e-m	C	c-p, e-f, e-f
III	Significance test (Welsh t-test)	Compare two data sets for significant differences	e-m	C	To all levels having two harmonized datasets with 5 to 5,000 data points
III	Element recovery rates (spiking)	Add a defined amount of element to the original sample and determine recovery rate to evaluate measurement precision	e-m	C	To processing and mass balancing (e-m, e-f) (Løvik et al., 2019; Mährlitz et al., 2022)

In addition to the article in which the respective DAM was used, the purpose, principle, scope, calculation sequence, and field of application in the respective study (S sampling, P processing, C chemical analysis) are given in **Table 10**. Finally, the column “general applicability and transferability” indicates the general conditions for the transferability of the DAM to other case studies. For example, the NPA for MSS can be used for all datasets that include at least 15 data points and can be used for S, P, C, and other application fields to estimate the minimum sample number. Similarly, the homogeneity test can be applied, for example, to check the homogeneous distribution of battery weights in WEEE (c-p), etc. The

presentation of the transferability is consequently a critical aspect to strengthen the use of DAM and improve the (intrinsic) data quality in the best possible way. Furthermore, the possible fields of application in which the DQF-RA can bring about an improvement are thus increasing.

4.4. Implications of key findings

The involvement of relevant stakeholders is a prerequisite for the applicability and success of the DQF-RA. Relevant stakeholders are researchers, practitioners (plant operators, recyclers), QA/QC and standardization bodies, authorities, data storage institutions (incl. statistical bodies), data analysts (statisticians, data scientists, etc.), producers (incl. designers, OEMs), and the general public (i.e., product users). These stakeholders provide as well as require both methods and data.

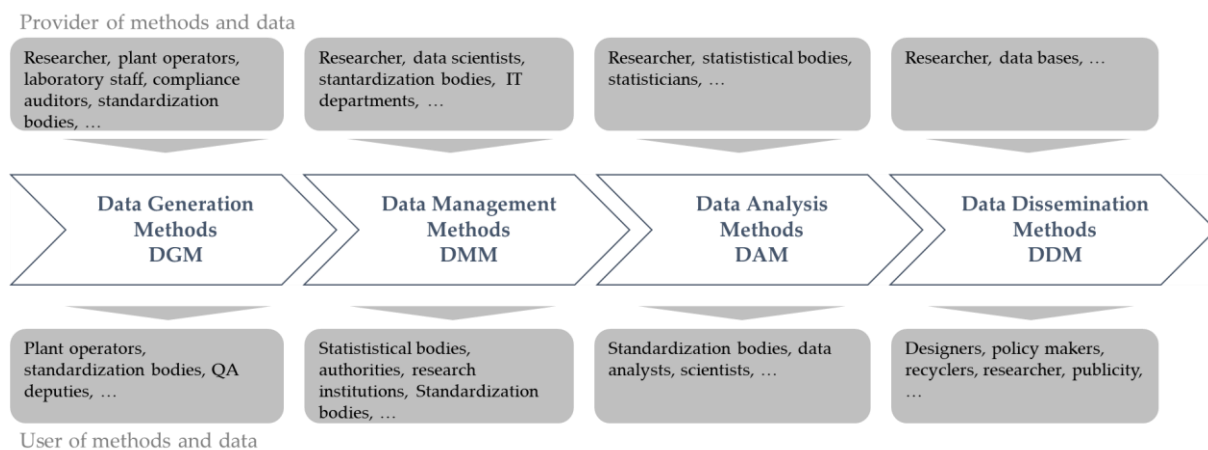


Figure 14. Exemplary stakeholders and their function as “provider” and “user” in the DQF-RA.

The possible implications the results of this Ph.D. study (may) have on the above stakeholders are presented in the following. This list is not exhaustive and focuses on the key findings and their implications.

In general, making data quality assessable requires the cooperation of all actors along the value chain of a product. Thus, all actors of different disciplines should be aware of their role regarding the recyclability of products and provide the necessary data and methods.

Data Generation Methods

Harmonized data sets on EoL characteristics with suitable descriptors (metadata) are required to be collected and exchanged across the value chain to improve their applicability by closing data gaps and avoiding redundant work. Research, practitioners, and other

stakeholders should be aware of the repeatability of methods when generating data and either provide them as part of the DQF-RA, draw from the growing pool of methods, or develop new methods based on the DQF-RA recommendation.

Data Management Methods

Harmonization and subsequent standardization of terminology of products, components, and materials and methods for sampling, processing, and chemical analysis become substantial measures to decrease time and labor-intensive work by combining coherent data from different sources and stakeholders along the product value chain. Research, standardization bodies such as DIN or ISO, and data storage institutions such as RMIS, should implement the calculation sequence to precisely reference data and store information transparently. Further, classifications, code lists, and templates should be published to ensure a comprehensive and consistent use to maximize transferability, consistency, and accessibility (cf. **Table 8**).

Data Analysis Methods

The analysis of the raw data offers the potential to make statements about the accuracy, precision, representativeness, and data distribution and improve the data quality, e.g., via simulations. Further, harmonization of data collection, nomenclature, and raw data (protocols) enable advanced data analysis, data-driven simulations, and quality assurance. Research and practice should provide raw data that enables ex-post data quality improvement using advanced data analysis, data-driven simulations, and quality assurance measures as recommended methods in the DQF-RA.

Data Dissemination Methods

Setting up an urban mine knowledge database with harmonized information (data, metadata, methods) increases the data availability and is an essential and overarching basis for all approaches to assess the recyclability of WEEE batteries. Therefore, data storage institutions, researchers, and practitioners should check the linkage of existing databases concerning the information needs for RA and, if necessary, make corresponding tables available to provide data for RA. Possible starting points are the EU RMIS (European Commission, 2022b), the EU data portal (Publications Office of the European Union, 2022), the

www.urbanmineplatform.eu (Huisman et al., 2018), or tools for process accounting, such as the WF-RepTool (WEEE Forum, 2021).

5. Conclusions

Product recyclability is an important indicator for assessing the conformity of a product with the goals of the circular economy and presents a valuable criterion for product design decisions. Although the use of recyclability assessment (RA) is currently not standardized, all approaches have the common requirement of high data quality for parameters used in the calculation.

However, the demand for high-quality data is complicated by the great diversity of elements, materials, and components in products to be assessed. This diversity results in high distributional and constitutional heterogeneity of waste products and flows at EoL and poses considerable methodological challenges for their characterization and thus the assessment of product recyclability. The generation of high-quality data forms the basis for RA but requires uniform guidelines for generating, managing, analyzing, and disseminating data. The Data Quality Framework for Recyclability Assessment (DQF-RA) developed in this Ph.D. thesis represents a methodological framework based on multidisciplinary research and a bottom-up approach supplemented by three detailed case studies.

The results are four main categories in the DQF-RA which must be taken into account in order to meet the requirements of high-quality data: data generation (DGM), data management (DMM), data analysis (DAM), and dissemination of data (DDM).

With the help of three case studies at three selected intersections in the recycling network of WEEE batteries, methods were developed, described, tested, and evaluated. These case studies address 1) sampling of batteries from WEEE (c-p), 2) treatment processes to determine recycling efficiency and recyclability (e-m, p-f, e-f), and 3) the applicability of simplified chemical analysis for battery residues. All case studies cover different methodological challenges. Thus, applying the methodological recommendations will ensure a common database with high-quality data to improve the assessment of technical recyclability.

In conclusion, the following recommendations can be drawn that should be considered in future studies:

- DQF-RA: The presented data quality framework for recyclability assessment (DQF-RA) serves to enhance the data quality in terms of accuracy (DAM), consistency (DMM), completeness (DGM, DMM), and data accessibility (DGM, DMM, DDM) along the value chain relevant to implementation in the recyclability assessment of WEEE batteries.
- DGM: Congruent and harmonized data sets with suitable descriptors (metadata) are to be collected by means of standardized data collection protocols.
- DMM: Harmonization and subsequent standardization of terminology and methods become substantial measures to decrease time and labor-intensive work for all stakeholders by combining coherent data from different sources and stakeholders along the product value chain. The calculation sequence (cf. **Figure 7**) combined with standardized classification, code lists, and templates boosts transparency of future research.
- DAM: The analysis of the raw data offers the potential to make statements about the accuracy, precision, representativeness, and data distribution and improve the data quality, e.g., via simulations. Further, providing raw data enables ex-post data quality improvement using advanced data analysis, data-driven simulations, and quality assurance measures. Harmonization of data collection, nomenclature, and the provision of raw data (protocols) with the methods presented in this Ph.D. thesis enable advanced data analysis, data-driven simulations, and quality assurance.
- DDM: Data dissemination will be improved if harmonized data are linked and made available to existing databases, platforms, and tools since data provision is the key to assessing products' recyclability and data quality. Derived from the harmonization efforts, a data collection protocol must be accessible to properly collect primary data and respective metadata that allow subsequent data validation methods. Extending data platforms (e.g., UMKDP, RMIS) to an urban mine knowledge database with harmonized information (data, metadata, methods) increases the data availability and is an essential and overarching basis for all approaches to assess the recyclability of WEEE batteries.

- The methods are showcased in specific case studies of WEEE batteries but are transferable to other areas of application (cf. **Table 10**).

Outlook

These conclusions are formulated in the DQF-RA as methodological recommendations and options for action for users and providers of data and methods. The need for further research consists of the constant addition of suitable methods to the DQF-RA for additional “points” in the lifecycle for WEEE-embedded batteries and other products. Furthermore, cooperation along the value chain and between the relevant stakeholders from industry, science, politics, and society is crucial to increasing the data quality and thus the informative value of RA assessments, and therefore also to making informed decisions in the design phase to move a little closer to CE. This is because potential enablers of a CE and the RA, such as digitalization, blockchain, etc., need a framework with accurate data requirements providing high-quality data, to which the DQF-RA will contribute in the future. The DQF-RA can thus form the basis for the provision of high-quality data serving to satisfy e.g., the objectives of the Sustainable Products Initiative (European Commission, 2022c) and the requirements of the new Eco-Design Directive (European Commission, 2022a).

A current area of application of the DQF-RA would be the design of the specifications of a “battery passport”, which must be implemented by 2026 according to the new Battery Regulation (European Commission, 2020b).

6. Annex

6.1. Abbreviations

Abbreviation	Definition
AlMn	Alkali-Manganese batteries
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
ANOVA	ANalysis Of VAriances
AZ	Alkali-Manganese and Zinc-Carbon battery mix (Mährlitz et al., 2022)
AZLIB	Alkali-Manganese and Zinc-Carbon and Lithium Ion Battery mix (Mährlitz et al., 2022)
BM	Battery Mass
BMS	Battery Mass Share
CE	Circular Economy
CENELEC	European Committee for Electrotechnical Standardization
DAM	Data Analysis Method
DDM	Data Dissemination Method
DGM	Data Generation Method
DMM	Data Management Method
DQD	Data Quality Dimension
DQF	Data Quality Framework
EBT	Extended Batch Test
ED-XRF	Energy-Dispersive X-Ray Fluorescence
EIP	European Innovative Partnership
EoL	End-of-Life
ErP	Energy-related Products
IATA	International Air Transport Association
ICP-MS	Inductively Coupled Plasma (ICP) in combination with Mass Spectrometry
ICP-OES	Inductively Coupled Plasma (ICP) in combination with Optical Emissions Spectrometry
LCF	Lithium Carbon Monofluoride
LCO	Lithium-Cobalt oxide LIB cathode
LFP	Lithium-Iron-Phosphate oxide LIB cathode
LIB	Lithium Ion Batteries (EBT mix (Mährlitz et al., 2022))
LiMn	Lithium-Manganese
LiPrim	Lithium Primary batteries
LiRecharge	Lithium Rechargeable batteries
LMO	Lithium–Manganese oxide
LSO	Lithium–Sulphur dioxide
LTC	Lithium Thionyl Chloride

Abbreviation	Definition
MAD	Median Absolute Deviation
MSS	Minimum Sample Size (Mährlitz et al., 2020)
NiCd	Nickel-Cadmium batteries
NiMH	Nickel-Metal Hydride batteries
NMC	Lithium-Nickel-Manganese-Cobalt oxide LIB cathode
NPA	Nonparametric approach (Mährlitz et al., 2020)
OEM	Original Equipment Manufacturer
PA	Parametric Approach (Mährlitz et al., 2020)
POM	Put-On-the-Market
PRM	Primary Raw Materials
ProSUM	Prospecting Secondary Raw Materials in the Urban Mine and Mining Waste (Huisman et al., 2017)
QA	Quality Assurance
QC	Quality Control
Rcyc	Recyclability
Rcov	Recoverability
RD(R)	Relative Difference (to Reference)
RE	Recycling Efficiency
RA	Recyclability Assessment
RAM	Recyclability Assessment Methods
RMIS	Raw Material Information System (European Commission, 2022b; Huisman et al., 2020)
RN	Reference Network
RR	Recycling and Recovery; Recycling Rate
RRL	RR in Liquid standards (RRL)
RRB	RR in Blind samples (RRB)
RRS	RR in the respective Sample matrices
RSD	Relative Standard Deviation
SIP	Strategic Implementation Plan
SOP	Standard Operation Procedure
SRM	Secondary Raw Materials
UMKDB	Urban Mine Knowledge Data Base
UNU	United Nations University
WD-XRF	Wavelength-Dispersive X-ray fluorescence
WEEE	Waste Electrical and Electronic Equipment
ZnC	Zinc-Carbon

6.2. Calculation sequence

Table 11. Calculation sequence codes to describe a system (Huisman et al., 2017) .

Code	Description
e-m	Mass or mass fraction of an element in a material
e-c	Mass or mass fraction of an element in a component
e-p	Mass or mass fraction of an element in a product
e-f	Mass fraction of an element in a flow or stock
m-c	Mass, mass fraction or volume of a material in a component
m-p	Mass, mass fraction or volume of a material in a product
m-f	Mass fraction of a material in a flow or stock
c-c	Mass, mass fraction, number, length, volume, area or other extensive property of a component in another component
c-p	Mass, mass fraction, number, length, volume, area or other extensive property of a component in a product
c-f	Mass fraction of a component in a flow or stock
p-p	Mass, mass fraction, number, length, volume, area or other extensive property of a product in another product
p-f	Mass fraction of a product i a flow or stock
f-f	Mass fraction of a flow or stock in a flow or stock
c	Mass, length, area, volume or other extensive property of a component
p	Mass, length, area, volume or other extensive property of a product

6.3. Data Templates and Code Lists

6.3.1. Sampling template

Table 12. Data collection protocol for the sampling of batteries from WEEE as used in Article I.

Information	Description
samplingID	Identifier for each sampling campaign
EU10	WEEE categories 1-10 according to WEEE Directive 2012/19/EC Annex III
key	UNU key (cf. SI Article I)
subKey	UNU subKey (cf. SI Article I)
Mass	Mass of each WEEE product in g
batteryDriven	WEEE is driven by battery: Yes/No
battRemoved	Battery was removed or is missing
BATTkey	Battery key classification (cf. Table 4)
BATTmass	Battery mass in g
BATTmassShare	Battery mass share in % by mass
BATTpresence	Battery presence: built-in battery (builtInBATT), no battery (noBATT)

6.3.2. Process performance template

Table 13. Data collection protocol for the chemical analysis and subsequent assessment of method applicability as used in Article II.

Information	Description
batch	Name of batch
fraction	Fraction of the in- or output with the following attributes: FGF, MGF, CGF, Boiler ash, Fabric filter ash, Exhaust gas
subfraction	Subfractions by preparation, treatment, separation of fractions, e.g. CGF, sleeve content or sleeve case
Parameter	Parameters, e.g., elements, etc.
valueType	Type of value, e.g., mass fraction, mass balance fraction
UoM	Unit of measurement, e.g., mg/mg, mg/kg
n	number of data points
value.fraction	Value related to the respective fraction
sd	standard deviation
f2b_ratio	Fraction to batch ratio
value.input	Value related to total input
recyclable	Assignment of whether a component is recyclable with the following attributes: recyclable, not recyclable, potentially recyclable

6.3.3. Chemical analysis template

Table 14. Data collection protocol for the chemical analysis and subsequent assessment of method applicability as used in Article III.

Information	Description
sampleName	Original sample name from the analyses
sampleType	Defined name of sample type, such as MIN or BATT
repetition	Repetition of one analysis indicated by 1, 2, 3, ...
subSample	Sub-samples taken from the original sample and analyzed separately, indicated by A, B, C, ...
grainSize	Grain size given in mm
laboratoryName	Laboratory name, here: TUB, EMPA
description	Description that gives more precise information of the sample, such as "reference value"
comment	Comments that describe special observation during analysis or highlight remarkable extreme values, such as outliers
date	Date in the format DD.MM.YYYY
element	Element name according to periodic system of elements
elementGroup	Grouping of elements. No fixed system right now. Here: http://wedocs.unep.org/handle/20.500.11822/8702
atomicNumber	Element atomic number according to periodic system of elements
approach	Approach specifies validated method by Empa "val" and in-house method "ih"
valApproachAvailFor	Specifying for which element validated methods are available
digestionType	Digestion type combines information on digestion system, such as microwave digestion "MW" and digestion acid
digestionAcid	Digestion acid, such as Aqua regia, HNO ₃ , etc.
measurementMethod	Combination of digestion acid and measurement device and detector
measurementDeviceDetector	Combination of measurement device and detector
measurementDevice	Measurement device, such as: XRF, ICP
measurementDetector	Measurement detector, such as: MS or OES (for ICP), or ED or WD (for XRF)
measurementLine	Measurement line in nm for ICP-OES, also used for mass for ICP-MS
ICPReactionGas	ICP reaction gas: helium, oxygen
sampleMassINmg	Sample mass in milligram
sampleMassINg	sample mass in gram
volumeAcidINmL	Acid volume used for digestion in mL
totalVolumeINmL	Total volume of digestion mixture in mL
LODINmgPERL	Limit of detection in mg/L

Information	Description
LODINmgPERkgORppm	Limit of detection in mg/kg or ppm
LOQINmgPERl	Limit of quantification in mg/L
LOQINmgPERkgORppm	Limit of quantification in mg/kg or ppm
elementConcentrationINmgPERl	Element concentration in mg/L
spiking	Spiking was added prior to digestion: with spike (wSpike) or without spike (woSpike)
spikeAddedINmgPERl	Concentration of spike added to the (blind) sample in mg/L
spike_valueReal	Real measured value of spiked (blind) value
spike_valueTheoret	Theoretical value, calculated by adding the measured value of (blind) sample without spike plus spike concentration added
valueType	Value type for filtering and selection: blind, single value, mean, factor, recovery rate, ...
valueGroupType	Grouping value types to: blind, value, recovery_blind, recovery_sample
value	Measurement value (mass fraction, recovery rate)
UoM	Unit of measurement: mg, g, kg, %, mL, L
uncertainty	Uncertainty in the same UoM as value
uncertaintyType	Indication of the uncertainty type, such as standard deviation (SD) or two-times SD (2SD)
ID	Identifier to identify the row precisely

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7. Article I

Characterizing the Urban Mine - Simulation-Based Optimization of Sampling Approaches for Built-in Batteries in WEEE

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Article

Characterizing the Urban Mine—Simulation-Based Optimization of Sampling Approaches for Built-in Batteries in WEEE

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Abstract: Comprehensive knowledge of built-in batteries in waste electrical and electronic equipment (WEEE) is required for sound and save WEEE management. However, representative sampling is challenging due to the constantly changing composition of WEEE flows and battery systems. Necessary knowledge, such as methodologically uniform procedures and recommendations for the determination of minimum sample sizes (MSS) for representative results, is missing. The direct consequences are increased sampling efforts, lack of quality-assured data, gaps in the monitoring of battery losses in complementary flows, and impeded quality control of depollution during WEEE treatment. In this study, we provide detailed data sets on built-in batteries in WEEE and propose a non-parametric approach (NPA) to determine MSS. For the pilot dataset, more than 23 Mg WEEE (6500 devices) were sampled, examined for built-in batteries, and classified according to product-specific keys (UNUkeys and BATTkeys). The results show that 21% of the devices had battery compartments, distributed over almost all UNUkeys considered and that only about every third battery was removed prior to treatment. Moreover, the characterization of battery masses (BM) and battery mass shares (BMS) using descriptive statistical analysis showed that neither product- nor battery-specific characteristics are given and that the assumption of (log-)normally distributed data is not generally applicable. Consequently, parametric approaches (PA) to determine the MSS for representative sampling are prone to be biased. The presented NPA for MSS using data-driven simulation (bootstrapping) shows its applicability despite small sample sizes and inconclusive data distribution. If consistently applied, the method presented can be used to optimize future sampling and thus reduce sampling costs and efforts while increasing data quality.

Keywords: built-in batteries; WEEE; urban mine; sampling; UNUkeys; minimum sample size; data-driven simulation; bootstrapping; recycling-oriented characterization

1. Introduction

Electrical and electronic equipment (EEE) is one of the key product value chains of the New Circular Economy Action Plan [1]. Besides their design and durability, there is a focus upon sound collection and treatment. One of the challenges of a sound collection and treatment of waste electrical and electronic equipment (WEEE) are batteries still remaining in the WEEE when being discarded.

These built-in batteries in WEEE are of increasing interest in recycling as they exist in a large variety with rapidly changing contents of economically, environmentally, and health-related relevant substances. Furthermore, safety aspects due to the high energy content of Li-batteries are gaining importance. To avoid the release of hazardous substances such as Pb and Cd (health, environment) or their entry into fractions for recycling (contamination decreases the quality of secondary raw materials) and to reduce the risk of fire from damaged Li-batteries, sound collection and treatment of WEEE containing batteries is crucial. Both digitalization and the intensified mobile use of EEE sharply boost the number of portable batteries placed on the market (POM) in recent years [2]. In 2015, 15% of the single charge (primary) and 80% of the rechargeable (secondary) batteries were embedded in EEE when placed on the market [3].

At their end-of-life, these batteries must be directed to the dedicated collection, treatment, and recycling paths in order to produce secondary raw materials (SRM). However, the collection rate of portable batteries throughout European Union (EU) member states is low and stagnating between 25 and 45% [3] caused by, among others, hibernation in the 'urban mine' [2] and disposal via complementary waste streams such as residual waste [4–13]. Furthermore, batteries still contained in WEEE might not be separated prior to or during WEEE treatment [13–20] and will accordingly not be sent to an adequate battery treatment. In particular, built-in batteries can only be separated with great effort. Since the collection of built-in batteries within WEEE is permitted in some EU member states like Germany [21], the separation of batteries during processing is mandatory [22] to prevent resource loss, contamination of subsequent material streams, and to fulfill legal reporting and collection obligations [22,23]. Moreover, the specification for depollution [24] prepared by the European Committee for Electrotechnical Standardization (CENELEC) sets a target value of 1.8 kg batteries per Mg of small WEEE appliances to be separated.

Nonetheless, batteries often remain in WEEE products when discarded [14] due to the challenging identification of battery-powered devices in mixed WEEE flows and their impeded removability [14] as a result of varying size, shape, and assembly type. Consequently, the removal rate of batteries from WEEE is estimated to be 7% on average, ranging from 1 to 20% for the 19 EU countries investigated [3]. Thus, the knowledge of quantity and composition of WEEE batteries is fundamental to improve waste management concepts for the identification and separate collection of batteries, as well as to set up reasonable treatment requirements. One strategy to determine these characteristics of WEEE batteries involves methods for recycling-oriented characterization of waste flows, products, components, and materials [25–29].

The basis for the development of waste management concepts is a comprehensive urban mine knowledge database with harmonized and comparable data with a defined statistical validity (i.e., robustness [30]), which allows inferring information regarding the entire data population. To accomplish the generation of such data, representative sampling [31–33] is necessary. Regarding the latter, no legally binding methodologies exist for the sampling of solid waste, although the Waste Framework Directive (2008/98/EC, Article 28) does require the development of waste management plans. Several non-binding guidelines have been developed on the European and regional level. However, these guidelines focused on domestic residual waste and were not adapted for WEEE and built-in batteries.

In addition to the extraction of the sample, sampling comprises the determination of an adequate sampling unit and sample size to achieve representative results with reasonable (economic) effort [31,33]. In general, two approaches for the determination of minimum sample sizes (MSS) are practiced in waste sampling [34]: (1) a fixed percentage of the population or lot (empirical, non-statistics-based sampling) [35–38] or (2) statistical sampling [31,34,39,40]. However, determining the MSS through statistical procedures [33,40–49] is dependent on a priori knowledge and thus, due to lack of data, not readily transferable for built-in batteries in WEEE. For sampling of domestic residual waste, the recommended sampling unit is often defined as one collection container, e.g., 1.1 m³ containers [33]. However, WEEE and built-in batteries are more challenging due to their high

(product) heterogeneity, locally different collection groups, inconsistent nomenclature, unharmonized classifications, as well as various influencing factors on the composition, such as short innovation cycles and varying product lifetime.

Therefore, the application of statistical approaches to determine MSS requires the provision of a priori knowledge in the form of harmonized raw data sets using uniform and consistent as well as spatially unified classifications for batteries and WEEE. Moreover, the statistical analysis of data sets regarding distribution patterns is a pre-requisite to apply parametric approaches assuming a normal distribution. Furthermore, recommendations are required for dealing with unknown or inconclusive distribution patterns caused by, e.g., data sets that are too small or inappropriate nomenclature.

This article aims to improve representative sampling of built-in batteries in WEEE. For this, we provide both detailed and harmonized pilot data sets on mass and mass shares of built-in batteries in WEEE and investigate an alternative approach to determine the MSS. The results will help to improve both (a) the recycling-oriented product characterization enabling to identify and separate battery-containing WEEE prior to subsequent treatment as well as (b) the availability of harmonized data sets for statistical analysis and simulations to derive recommendations on circular economy measures. For instance, the results can complement previous studies on modeling and assessing the share of batteries in WEEE and related resource losses in WEEE treatment [19]. Specifically, this study addresses the following recycling-oriented and methodological objectives on the sampling of built-in batteries in WEEE:

1. Identification of WEEE with and without battery compartment and determination of the proportion of remaining batteries.
2. Statistical description and analysis of distribution patterns for WEEE mass, battery mass (BM), and battery mass share (BMS) of built-in batteries in WEEE.
3. Recommendation for determining MSS in the case of small data sets and unknown or inconclusive distribution patterns for BMS of built-in batteries in WEEE.

2. Materials and Methods

This study is based on comprehensive empirical data collection and harmonized classification of built-in batteries in WEEE constituting a pilot data set for further analysis. Firstly, the results are statistically analyzed and examined for commonly assumed distribution patterns (normal and lognormal distribution). Secondly, data-driven simulation (bootstrapping) using the original sample data is performed to obtain more accurate results on WEEE battery characteristics. Finally, both a parametric approach (PA) and a nonparametric approach (NPA) are employed to approximate the MSS for quantification of the mass share of built-in batteries in WEEE. The detailed data sets, as well as the recommendations on MSS, will provide the a priori knowledge necessary for future sampling campaigns.

For all data analyses, the computational framework R [50] was employed using the packages “base”, “stats” [50], and “e1071” [51]. The respective R commands are listed in the Supplementary Materials Table S2.

2.1. Sampling and Classification

Between 2015 and 2017, seven sampling campaigns were carried out at primary treatment plants for WEEE in Germany, France, and Belgium. The WEEE originated from private households, and the samples were taken prior to any treatment, i.e., as collected. In total, 23 Mg WEEE were sampled, comprising 6457 WEEE devices and 814 built-in batteries. The ‘product count’ procedure developed in the H2020 project ProSUM [2] with the corresponding sampling template [52] was used for data collection. Each device was individually weighed, classified according to the UNUkeys, and subsequently examined for battery compartments (with/without). Built-in batteries were removed,

weighed and classified according to the BATTkeys (see Table 1). Table S1 in the Supplementary Materials shows the total mass and number of WEEE and BATT sampled in each sampling campaign.

Table 1. Classification of waste electrical and electronic equipment (WEEE) categories (UNUkey main structure, the detailed classification can be found in Supplementary Materials Tables S16 and S17) and battery systems (BATT keys).

UNUkey	Description	BATTkey	Description
0001	Central Heating (CH, household installed)	LiPrim	Lithium-based batteries, primary
0002	Photovoltaic panels (PV)	LiRecharge	Lithium-based batteries, rechargeable
010x	Large household appliances (LHA)	Zn	Zinc-based batteries
020x	Small household appliances (SHA)	NiCd	Nickel-cadmium based batteries
030x	IT and telecom equipment (ITCE)	NiMH	Nickel-metal hydride batteries
040x	Consumer equipment (CE)	Pb	Lead-acid batteries
050x	Lighting equipment (LE)	Other	Other batteries (e.g., silver-oxide)
060x	Electrical and electronic tools (EET)	Unspecified	Not specified or identifiable
070x	Toys, leisure, and sports equipment (TLS)		
080x	Medical devices (MD)	BATT	No distinction of the battery system.
090x	Monitoring and control instruments (MCI)		
100x	Dispensers (D)		

A more comprehensive system was used for classification, compared to the official classification defined in Directive 2012/19/EU [22] for WEEE and Directive 2006/66/EC [23] for batteries, respectively. For WEEE, the so-called ‘UNU-keys’ and more detailed ‘UNUsubKeys’ (hereinafter referred to as UNUkeys and subKeys) were employed [53]; for batteries, the so-called BATTkeys [2] were used. The employed ‘keys’ are hierarchical and harmonized, allowing further data stratification, evaluation of distribution patterns and data quality, comparisons among studies, and the application to other scenarios and models.

The ‘UNUkey’ classification system was developed by the United Nations University (UNU) to enable the linkage of production and composition data as well as life span characteristics for lifetime distribution modeling [54,55]. The systems consist of three levels with a four-digit identifier on the most aggregated level. The first two digits reflect the ten categories of Annex I of the WEEE Directive 2012/19/EU [22] (see Table 1). Moreover, the UNUkeys and subKeys can be allocated to the new six categories (Annex III, WEEE Directive 2012/19/EU), which have been in force since 2018 (see Supplementary Materials Tables S16 and S17).

For batteries, the ‘BATTkeys’ shown in Table 1 were used. This classification system was defined in the H2020 Project ProSUM [2] and considers the allocation of battery type-specific materials, fire hazard (Li) [56], and environmental aspects (Cd, Pb). The term “BATT” was used if no distinction between the battery keys was possible.

The hierarchical structure of the UNUkeys and subKeys for WEEE, as well as BATT and BATTkey for batteries, allows the analysis and calculation for different ‘key’ combinations (UNUkey-BATT, subKey-BATTkey, etc.). We focus on combinations of UNUkey-BATT and UNUkey-BATTkey for an explanation of the methods and presentation of the results. The corresponding results for other combinations can be taken from the Supplementary Materials, provided that sufficient data points are available.

2.2. Statistical Analysis

Data description for all ‘key’-combinations comprised the calculation of mean (\bar{x}), standard deviation (SD), and coefficient of variation (VC). Mass and mass share are described in the results section with $\bar{x} \pm \text{SD}$. While these parameters assume a normal distribution, more robust descriptors were calculated to comply with the requirements set by the European Solid Waste Analysis (SWA) tool [40]: 95% confidence interval (95% CI), median (\tilde{x}), and additionally median absolute deviation ($\text{MAD} = \text{median}(x_i - \tilde{x})$) [57]. Of the different methods for determining the 95% CI, we chose to calculate the value range between 2.5 and 97.5% quantiles [58].

Moreover, distribution patterns were analyzed to assess the commonly applied assumption of normal distribution in sampling and data management. The Shapiro–Wilk (SW) test on normality was employed, which has the highest test power compared to other tests [58,59] but is sensitive to the sample size. If the calculated probability value p is below 0.05, the null hypothesis that the data set is normally distributed is rejected. The weakness of the SW test with small sample sizes is considered by calculating the shape parameters of the distribution: skewness and kurtosis [60]. Normally distributed data is symmetrical, i.e., they have a kurtosis and skewness of 0. Negative values for kurtosis and skewness mean thin-tailed and left-skewed distributions, whereas positive values stand for fat-tailed and right-skewed [51].

2.3. Data-Driven Simulation: Bootstrapping

Bootstrapping is a statistical method that provides an estimate of the data distribution by resampling one or more small samples with replacement [30,61–63]. The bootstrap method was used to simulate sampling distributions and to estimate the properties of the statistic (e.g., \bar{x} , \widetilde{x} , SD, VC, MAD) more accurately [62–67]. Following the central limit theorem, the bootstrap method gives a reasonable approximation of the real probability curve when the number of bootstrap samples (B) is high enough [30]. In contrast to other parametric simulations, which assume specific population distributions (e.g., normal distribution), the non-parametric bootstrapping method requires no assumption regarding the statistical distribution [65] and uses the original data and resamples from this data set with many repetitions (number of repetitions = B). For each of the B bootstrap samples (resample), a simple random sample $x = (x_1, x_2, \dots, x_n)$ of size n_{orig} with replacement is drawn from the original dataset. For each bootstrap sample, the resample statistics are calculated [64], indicated by an asterisk (*). The distribution of a resample statistic is called bootstrap distribution $S^* = S(x_1, x_2, \dots, x_n)$, which approximates the characteristics (center, spread, shape) of the population distribution [64]. For example, the approximated population mean (μ^*) is the arithmetic mean of the bootstrap means and can be calculated according to Equation (1).

$$\mu^* = \frac{1}{B} \sum_{i=1}^B (\bar{x}_i^*) \quad (1)$$

In Equation (1), μ^* is the bootstrap population mean; B is the number of bootstrap samples; and \bar{x}_i^* is the mean of each bootstrap sample i . Accordingly, the standard deviation (SD) of the bootstrap distribution approximates the standard error of the mean (SEM) [63], shown as SD^* .

In this study, the number of samples taken with replacement was set to the original number of samples (data points) n_{orig} , the number of repetitions is set to $B = 5000$. Adequate bootstrap simulation results depend on the minimum number of data points in the original dataset [58]. Guided by [58], we chose 15 as the minimum number of data points for bootstrap simulations ($n_{\text{orig}} \geq 15$), which reduces the number of combinations for simulation of batteries and WEEE. Nevertheless, the robustness of this method is always based on the number of original data and repetitions B . While B is a matter of computational capacity, the challenge is to collect a sufficient amount of harmonized raw data for the simulation to increase robustness.

2.4. Determining the Minimum Sample Size (MSS)

The determination of MSS for any sampling campaign is necessary to gain representative results while limiting the expenditures for sampling. The methods to determine MSS vary in literature [34,35,37,39,40,42,43,68–72]. Most statistical approaches require the description of the variation of the targeted characteristics and the assumption of the data distribution to approximate the MSS. Therefore, statistical parameters such as the VC are calculated based on data from pilot studies. In this study, the sampling data is used to test two approaches to approximate the MSS: a parametric approach (PA) with the assumption of an underlying distribution pattern and a non-parametric approach (NPA), which bases on all single data points and their probability in the pilot data set.

2.4.1. Parametric Approach (PA): Assumption of Data Distributions

Parametric approaches base on the assumption of distinct data distributions to approximate the MSS given a calculated uncertainty. The calculation in Equation (2) is referred to in various references [31,72,73], assuming t -distributed data. The t -distribution is used alternatively for normal distribution in situations where the sample size is small, and the population standard deviation is unknown [74]. For a given probability level assuming an error probability of $\alpha = 0.05$, a two-sided t -distribution, and an infinite number of degrees of freedom, $t_{\alpha/2}$ is 1.96 [31]. The coefficient of variation (VC) is used to express the data uncertainty gained by, e.g., a pilot study. We accept a relative error of $\pm 10\%$ ($e_{rel} = 0.1$) to describe the whole population sufficiently accurate [33].

$$n_{min} = \left(\frac{t_{\alpha/2} \cdot VC}{e_{rel}} \right)^2 \quad (2)$$

Keeping $t_{\alpha/2}$ and e_{rel} constant in Equation (2), the number of samples depends solely on the VC of the samples. The PA is performed for both the original data (VC) and the bootstrap distribution (VC*) to illustrate the influence of bootstrapping on the variation of the data.

2.4.2. Non-Parametric Approach (NPA): Data-Driven Simulation with Bootstrapping

The NPA represents an alternative for determining the MSS without requiring a specific statistical distribution or large sample sizes in the original dataset [65]. This method is carried out in three steps (see Figure 1): (a) estimation of population characteristics and bootstrap confidence interval (CI*), (b) simulation of sampling with a smaller sample size to test whether the results lie within the 95% CI*, (c) determination of the MSS if the results are sufficiently covered within 95% CI*.

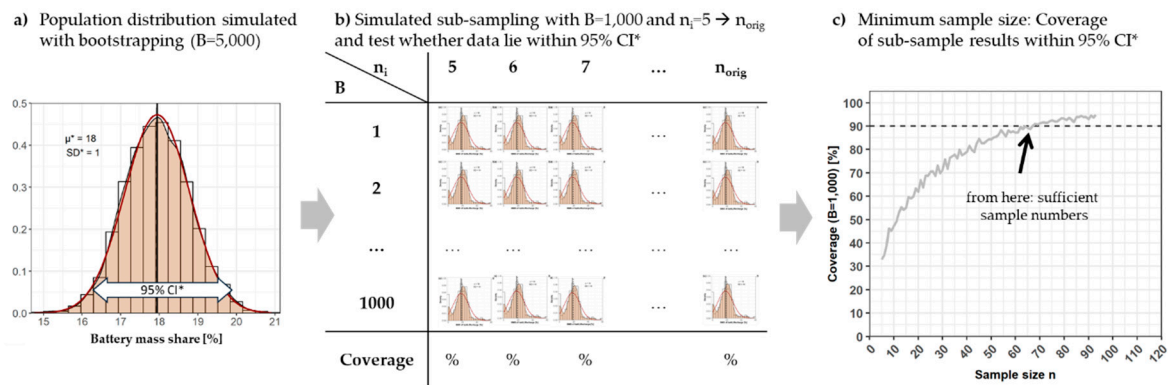


Figure 1. Non-parametric approach (NPA) to approximate the minimum sample sizes (MSS) with data-driven simulations. (a) Simulated bootstrap population, (b) sub-sampling from datasets with increasing sample size and 1000 repetitions, (c) coverage of sub-sample results in percent lying within the population 95% confidence interval (CI*).

Firstly, we generate the bootstrap distribution for BMS by resampling from the original dataset with $B = 5000$ repetitions and calculating the arithmetic mean of each bootstrap sample. The sample size was set to the original number of data points ($n_i = n_{orig}$). The generated probability distribution approximates the population characteristic and is used to calculate the bootstrap confidence interval (95% CI*) (Figure 1a). Only combinations of WEEE and batteries (UNUkey-BATT, UNUkey-BATTkey) with at least 15 data points in the original dataset were used for simulation to ensure reasonable results [58] (see Supplementary Materials).

Secondly, bootstrapping was used again to resample from the original dataset randomly but with smaller sample numbers starting from $n_i = 5$ and increasing n_i to the original number of samples

n_{orig} . For each subsample of n_i , 1000 subsamples ($B = 1000$) were drawn [60], and the arithmetic mean (bootstrap mean x_i^*) was calculated (see Figure 1b).

Thirdly, we checked whether each bootstrap mean x_i^* lies within the 95% CI* of the simulated population distribution [58]. The proportion of the 1000 bootstrap means x_i^* within the 95% CI* was defined as 'coverage'. As for the PA, we assume a relative error of 10%, i.e., a coverage of $\geq 90\%$, as sufficient to represent the population at a given n_i . Thus, the MSS is approximated at $n_i = MSS$, if the coverage increases above 90% (see arrow in Figure 1c). In other words, a sample number n with 90% coverage means that in 90% of samples with this sample size, the resulting value is likely to be within the 95% CI* of the population and consequently representative.

3. Results and Discussion

The results section first shows in which WEEE (expressed as UNUkeys) batteries were found. In addition, the percentage of devices with battery compartments and the percentage of devices with remaining batteries is presented. WEEE characteristics are briefly addressed. The battery masses (BM) and battery mass shares (BMS) of the built-in batteries in WEEE are investigated in detail. The investigations comprise the description of UNUkey-specific battery types, BM, and BMS, as well as statistical testing of commonly assumed data distribution patterns. Moreover, bootstrap simulation is introduced to show the effects on data accuracy in case of unknown or inconclusive distribution patterns. Finally, recommendations to determine the MSS are given by comparing a parametric approach and a non-parametric approach using bootstrapping.

Here, only example UNUkeys and BATTkeys with a focus on BMS are shown and discussed. All detailed results on WEEE mass, BM, and BMS are available in the Supplementary Materials.

3.1. Share of Waste Electrical and Electronic Equipment (WEEE) with and without Battery Compartment

In total, 5967 WEEE products were investigated for battery compartments, of which 4693 (79%) are not for use with batteries. This corresponds to a total mass of WEEE of 20.9 Mg, of which 18.6 Mg (89% by mass) are products without a battery compartment (see Supplementary Materials Table S3). Both results correspond to recently published data, as Friege et al. [14] determined a 79% share of devices without a battery compartment, and Hobohm et al. [17] reported results between 85% and 92% by mass in sampling campaigns in Germany in 2014 and 2015. Figure 2a shows the proportion of WEEE devices according to UNUkeys (0106—Household Heating and Ventilation; 0108—Fridges; 0114—Microwaves; 0201—Other Small Household; 0202—Food; 0203—Hot Water; 0204—Vacuum Cleaners; 0205—Personal Care; 0301—Small IT; 0302—Desktop PCs; 0303—Laptops; 0304—Printers; 0305—Telecom; 0306—Mobile Phones; 0307—Professional IT; 0308—Cathode Ray Tube Monitors; 0309—Flat Display Panel Monitors; 0401—Small Consumer Electronics; 0402—Portable Audio and Video; 0403—Music Instruments, Radio, Hi-Fi; 0404—Video; 0405—Speakers; 0406—Cameras; 0407—Cathode Ray Tube TVs; 0408—Flat Display Panel TVs; 0501—Lamps; 0506—Household Luminaires; 0507—Professional Luminaires; 0601—Household Tools; 0602—Professional Tools; 0701—Toys; 0702—Game Consoles; 0801—Household Medical; 0901—Household Monitoring and Control; 0902—Professional Monitoring and Control) distinguishing products with or without a battery compartment. Battery compartments are predominately present in small household appliances (SHA, 0201–0205), information technology (IT) and telecom equipment (ITCE, 0301–0303, 0305–0308), consumer equipment (CE, 0401, 0402, 0406), toys, leisure, and sports equipment (TLS, 0701), medical devices (MD, 0801), and monitoring and control instruments (MCI, 0901). Whereas most devices within one WEEE category are equipped with as well as without a battery compartment, the devices in UNUkey 0303, 0306, and 0406 all have a battery compartment. Also, more than 75% of the devices in UNUkey 0302 have a battery compartment.

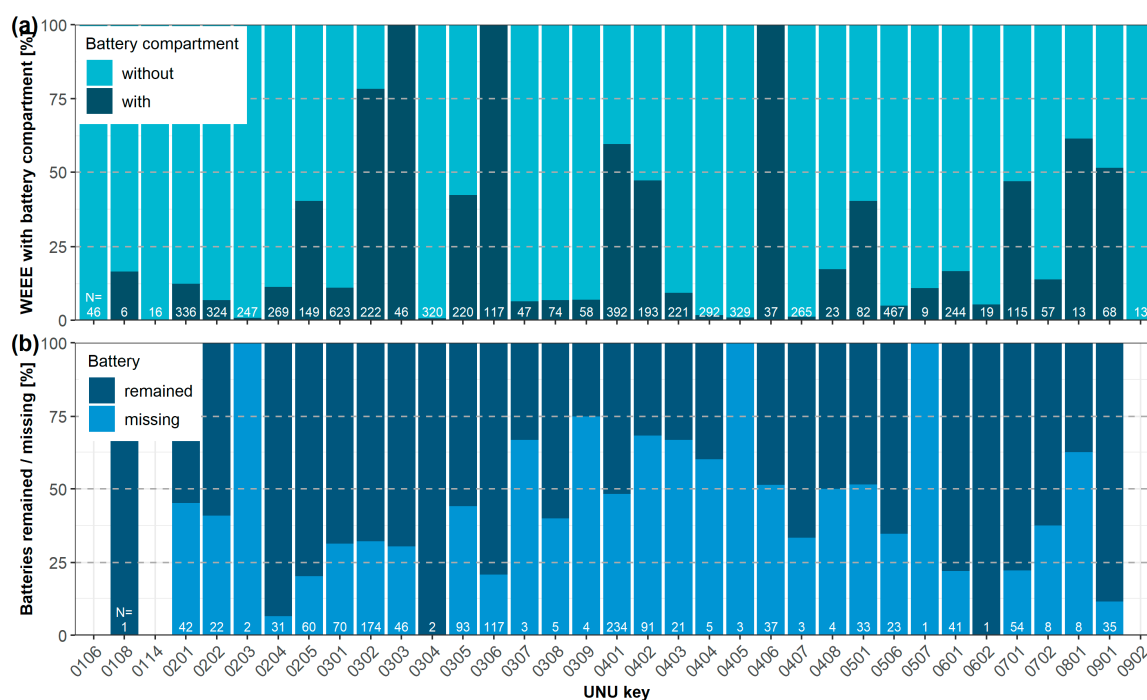


Figure 2. The proportion of WEEE devices (UNUkeys) with and without battery compartment (a) and the proportion of WEEE with a battery compartment in which batteries remained or were missing (b). The total number of appliances (N) is shown in white at the bottom. Figure data available in Supplementary Materials Table S3.

The percentage of batteries missing, i.e., not installed, removed prior to collection, or dropped out during collection or transport, differs between the WEEE categories and the UNUkeys. On average, 34% of the more than 1200 devices with battery compartments were found without batteries. In other words, 66% of WEEE with a battery compartment were discarded with the battery still embedded. For most UNUkeys with a battery compartment, the removal rate of batteries prior to collection/treatment was below 50% (Figure 2b). In the case of 0204, 0205, 0306, 0601, 0701, and 0901, batteries were found in over 75% of the devices. Thus, mainly these equipment types contribute to the contamination of subsequent material flows, if prior identification and separation of the batteries are not carried out.

The further breakdown of the UNUkeys into subKeys allows a more precise determination of devices with a high potential of remaining batteries. Within one UNUkey, there are subKeys without battery compartments as well as devices with exclusively remaining batteries. In this case, the more detailed product classification can improve the separation efficiency and increase data accuracy and precision. Detailed data on battery compartments and remaining/missing batteries at UNUkey and subKey level can be found in the Supplementary Materials Figure S1 (proportion) and Figure S2 (mass share).

As seen in Figure 2, three different variables to which the results can refer become apparent and must always be distinguished in further data evaluation and interpretation. Accordingly, the following distinction is made between WEEE: (1) with and without battery compartment, corresponding to all devices (Figure 2a), (2) with battery compartment and the battery is missing or remained in the device (Figure 2b), and (3) with battery compartment, and the battery has remained in the device. Therefore, battery-specific statements on raw material losses by WEEE batteries always require the determination of the proportion of (1) and (2).

3.2. WEEE Characteristics

The WEEE characteristics are not the focus of this work but can be relevant for the interpretation of the battery mass shares. The descriptive statistics for all product weights of WEEE broken down by UNUkey and subKey can be found in the Supplementary Materials Tables S4 and S5.

3.3. Battery Characteristics

3.3.1. Mass and Mass Share of Built-in Batteries

Figure 3 shows the mass and mass share of all batteries differentiated according to their chemical system (BATTkey). Figure 3a illustrates that the total mass of batteries in WEEE ranges from a few grams for lithium primary (LiPrim) to more than five kilograms for Pb batteries. In total, 322 rechargeable batteries (LiRecharge, NiCd, NiMH, Pb) and 452 primary batteries (LiPrim, Zn) are identified. Sixteen batteries could not be specified due to missing labels or destroyed sleeve surfaces. These batteries show a wide mass range and thus could be assigned to all of the battery types.

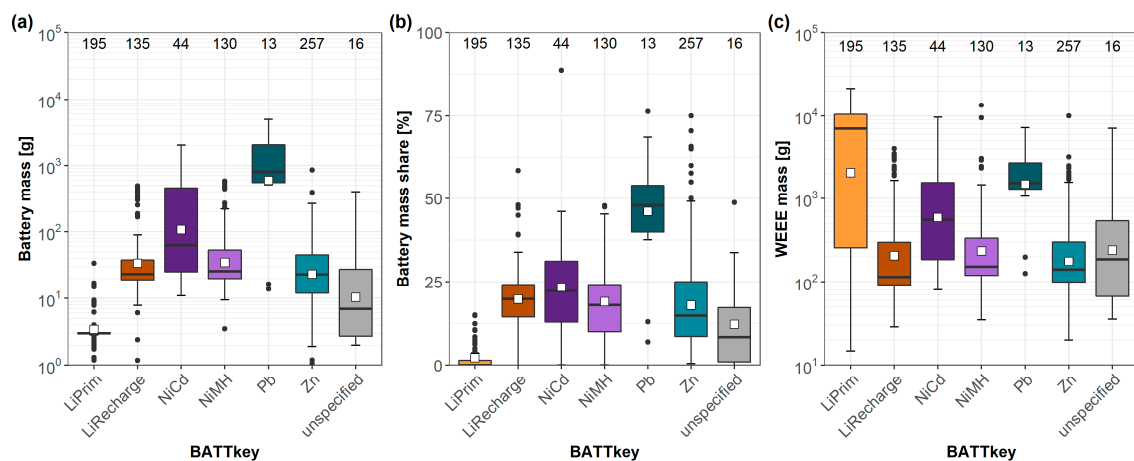


Figure 3. Battery mass (a), battery mass share (b), and WEEE mass (c) differentiated according to their chemical systems (BATTkey). The mass is illustrated with a logarithmic scale. The lower and upper hinges of the boxplots correspond to the first and third quartiles (the 25th and 75th percentiles). The median is drawn as a bold horizontal line; the mean is shown as a square. Upper/lower whisker is the largest/smallest observation less/greater than or equal to upper/lower hinge $\pm 1.5 \times$ interquartile range (IQR). The black dots represent values that lie outside of this range.

LiPrim batteries have the most distinct mass with 3 g as the median value corresponding to the mass of CR2032 button cells [13] as used on IT mainboards. In contrast, the other primary battery type based on Zn shows a large mass range varying between 2 g and 150 g with an average value of 38 g and a median of 23 g. Similar to LiPrim, Zn batteries are used in many of the WEEE devices investigated covering 16 UNUkeys and 29 subKeys (see Table A1). However, in contrast to LiPrim, they were found in a much higher variety of designs (AAA to D, block format), which causes a higher mass range (VC 170%, MAD 17).

Comparing the secondary battery systems, NiMH and LiRecharge batteries show a similar mass range and usually weigh between 10 g and 430 g (95% CI). Even though LiRecharge is gradually replacing the NiMH system [2], both were found in similar numbers of UNUkeys (16 LiRecharge, 15 NiMH) and subKeys (27 LiRecharge, 24 NiMH) which demonstrates that this technology trend of recent years is now detectable in the waste stream.

The number of NiCd and Pb batteries found in WEEE was the lowest. These batteries were installed in fewer types of devices. Besides the required restrictions of the Battery Directive to use hazardous materials [23], the reasons for this are a high weight with lower energy density compared

to LiRecharge and NiMH [75]. NiCd batteries weigh between 14 and 1500 g (95% CI), whereas Pb batteries are the heaviest batteries weighing between 15 g and 4300 g (95% CI). These values are consistent with the results of Bigum et al. [13] and Terazono et al. [20].

The battery mass share per BATTkey is shown in Figure 3b. The mass share of LiPrim is the lowest at about 2%. Except for Pb, the battery mass fraction for LiRecharge, NiCd, NiMH, and Zn is about 20% by mass among all WEEE considered (mean 18–23%, median 15–22%). In contrast, Pb batteries have higher mass shares of about 45% (see Table A1). Depending on battery mass (Figure 3a) and WEEE mass (Figure 3c), these values vary highly, showing a coefficient of variation of 40% to 70%. For primary batteries in particular, WEEE masses vary widely between a few grams to several kilograms (Figure 3c). The varying composition of WEEE flows thus causes a wide spread of BMS and the BM, complicating the identification and quantification of built-in batteries.

3.3.2. Product-Specific Battery Characteristics

For improved battery recycling and thus resource management, product-specific characteristics such as the occurrence of only certain batteries or specific mass/mass share are advantageous. A direct assignment of battery to product facilitates the selective separation of pollutants or recyclables prior to further treatment with mixed WEEE. With an increasing proportion of Li batteries, the safe and non-destructive removal of the batteries is also gaining importance in terms of safety aspects. Additionally, product-specific BM and BMS improve the estimation of associated raw material losses of batteries through complementary flows.

Figure 4 illustrates the assignment of UNUkeys and BATTkeys embedded as present in all 790 WEEE with built-in batteries. Some battery types are only present in a few WEEE (NiCd, Pb), while other battery types are found in almost all types of devices (Zn, LiPrim, LiRecharge). Furthermore, an accumulation of battery types can be observed in some equipment groups, such as Zn in 0401 or LiPrim in 0302. Moreover, it is noteworthy that many of the device groups contain all or nearly all battery types. In this context, Pb and NiCd pose a risk of contamination with heavy metals for subsequent processing steps.

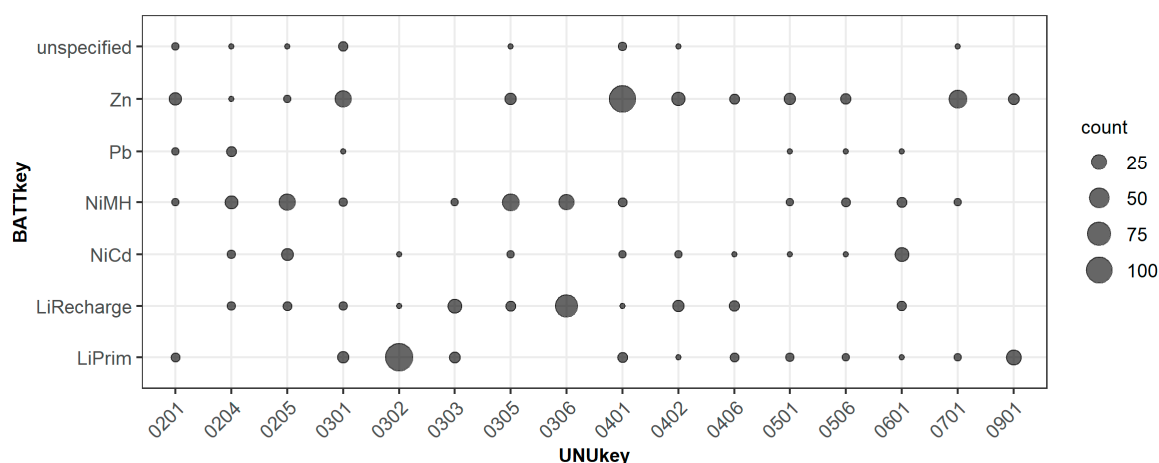


Figure 4. Occurrence and count of battery types (BATTkeys) in UNUkeys. Total number of devices considered: 790. Figure data are given in the Supplementary Materials Table S7.

Considering the subKey level (shown in Supplementary Materials Figure S3), it can be observed that both NiCd and Pb batteries occur together or with NiMH or LiRecharge systems within a subKey. This indicates that the substitution of batteries containing lead and cadmium by other batteries is still ongoing and visible in the waste stream and thus requires special attention when sampling and treating WEEE. An exception from this grouping is 050103 (other lamps for insects or tanning) for NiCd and

060104 (power supplies and adapters) for Pb batteries, which were both found with exclusively one battery system embedded.

Figure 5a,b shows the mass and mass share of built-in batteries in WEEE per UNUkey, respectively. The distribution of all battery data (BATT) is illustrated as a boxplot, whereas all 790 single batteries are displayed as dot-plots colorized by the respective BATTkey. The subdivision into UNUkeys shows that the values for BM and BMS within a WEEE category (first two digits of the UNUkey) are considerably different. The box plots in both figures show that the mean and median values differ from each other, which indicates skewed, i.e., not normally distributed data. In addition, the values for some UNUkeys differ, in some cases, very widely (0301, 0303), while other UNUkeys show only minor variations (0306, 0901). A further subdivision into subKeys leads to a reduction of the variance and more precise results for BM and BMS for the respective key (see Supplementary Materials Figure S4, Table S9, Table S11, Table S13, and Table S15).

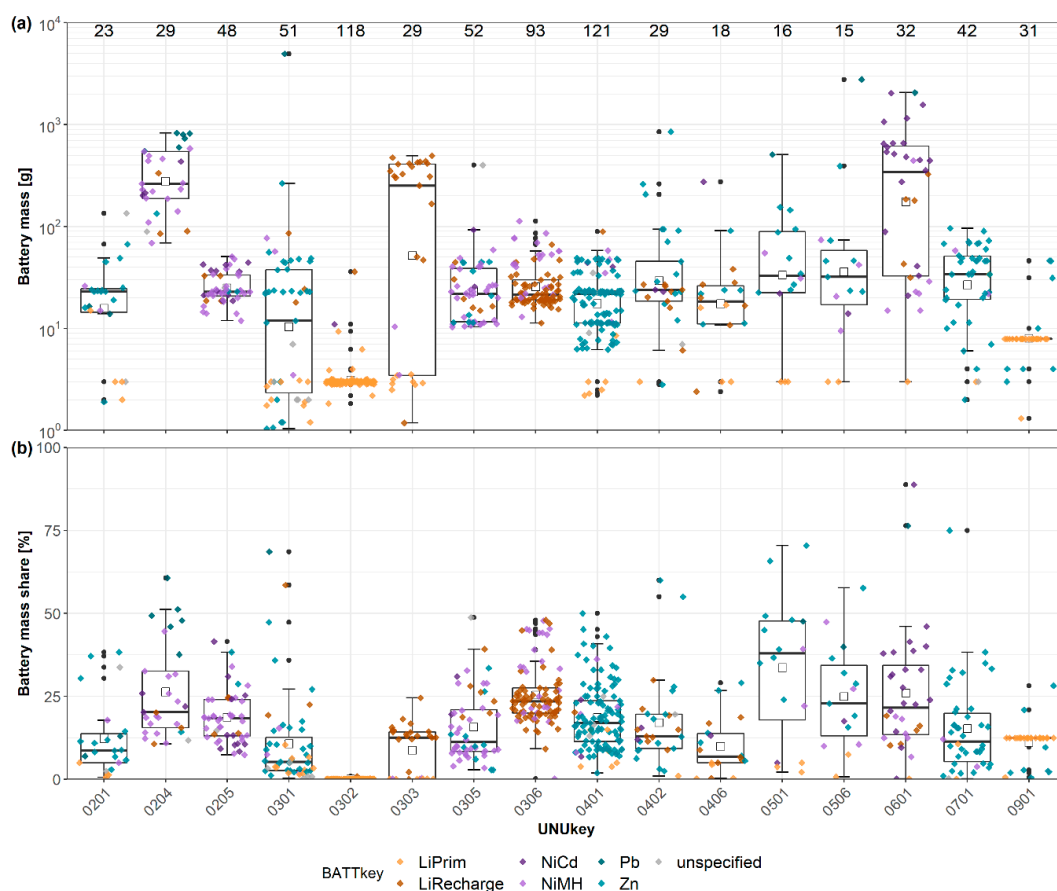


Figure 5. Mass (a) and mass share (b) of batteries remaining in WEEE classified as UNUkeys and distinguished by their chemical system (BATTkey). The number of observations (n) is displayed on top of the graph (a). The lower and upper hinges of the boxplots correspond to the first and third quartiles (the 25th and 75th percentiles). The median is drawn as a bold horizontal line; the mean is shown as a square. Upper/lower whisker is the largest/smallest observation less/greater than or equal to upper/lower hinge $\pm 1.5 \times \text{IQR}$. The data of this figure can be found in the Supplementary Materials Table S7, Table S8, Table S10, Table S12, and Table S14.

Both the BM and the BMS show considerable differences between the UNUkeys regarding the order of magnitude as well as variation (Figure 5). Some UNUkeys have batteries below 10 g (0302, 0901), whereas other devices have battery weights well above 100 g (0204, 0303, 0601). Devices with batteries that typically weigh 10 to 100 g are 0201, 0205, 0305, 0306, 0401, 0402, 0406, 0501, 0506, and 0701.

Primary batteries can be found in the majority of UNUkeys. In addition to IT and telecommunication equipment (UNUkey 03xx), LiPrim batteries can be found in almost all UNUkeys shown in Figure 5. This battery type is predominately used for button cells, like CR2032, which weighs on average 3 g. In contrast to cylindrical or prismatic cells, button cells are often used as a constant power supply to store system settings on the mainboard of ITCE devices, not for supplying the device with energy itself. Increasing WEEE mass is consequently not leading to higher battery mass resulting in small BMS in heavier WEEE (see Figure 3b,c), which means batteries are difficult to identify, locate, and remove.

The largest group of primary batteries are Zn-based systems (Zn), which also include zinc-carbon and alkaline manganese systems. Zinc batteries were found in both cylindrical and prismatic (9V block) design, which were mainly embedded in small consumer electronics, such as remote controls (040104), portable audio (0402), small IT (0301), and small toys (070101) [76]. The dominant design is R6 (formerly AA), which weighs about 23 g (corresponding to the median mass for Zn in this study). Within a device type (subKey), primary and secondary lithium systems, NiMH, and NiCd occur in addition to Zn systems (see Supplementary Materials Figure S3).

Regarding rechargeable batteries, LiRecharge and NiMH were dominantly present in WEEE. LiRecharge is characterized by high power and energy density, high voltage, long storage life, and low self-discharge rate [77,78], which is why they can be found among most UNUkeys (Figure 4). However, only laptops (0303) and mobile phones (0306) show a predominant use of LiRecharge batteries having mass shares of $13 \pm 5\%$ and $24 \pm 7\%$ by mass, respectively. The random occurrence of these batteries in some device types makes their systematic identification challenging.

NiMH was mainly found in SHA (handheld vacuum cleaners (0204), toothbrushes (0205)), telephones (0305), and mobile phones (0306). The mass variation is between 7 ± 5 g (0303) and 296 ± 165 g (0204), with a 95% CI between 10 and 490 g. Considering the high variation ($VC = 170\%$), the indication of median and MAD is advisable. NiMH most frequently weighed about 26 ± 21 g (median+/-MAD), which corresponds to a mass share of about $18 \pm 11\%$ (see Table A1).

Pb and NiCd batteries were rarely present within WEEE, predominately as a result of the ban of cadmium and lead in portable batteries since 2006 [23]. Pb batteries are by far the heaviest batteries used in WEEE and were mostly found in portable vacuum cleaners (0204). With 15 to 4300 g (95% CI), Pb batteries make up 50% of the weight of the device. NiCd batteries have lower energy density compared to NiMH, causing a decrease of NiCd in WEEE. In total, 44 NiCd were found in the devices, which were mainly used in personal care and tools. Besides, NiCd batteries often weigh more than twice as much (300 ± 440 g) and thus constitute a larger share of the equipment mass ($23 \pm 15\%$).

In summary, individual hotspots, i.e., a significant accumulation of certain BATTkeys, can be identified for some UNUkeys and especially subKeys. Devices with only one type of battery were rarely found except for LiPrim in desktop PC 0302. Thus, no product-specific allocation can be made for the majority of the devices. Moreover, the technological development of batteries in recent years is apparent in the occurrence of NiCd and NiMH in tools (0601) as well as NiMH and LiRecharge in mobile phones (0306). Moreover, most combinations of UNUkey/subKey and BATTkey show high data variability for BM and BMS, which is why no distinct product-specific characteristics can be ascertained, leading to increased MSS. Thus, considering the different numbers of samples per UNUkey, only indicative statements can be made, and more precise statements can only be made by considering the data distribution pattern, which is derived from a sufficient number of samples.

3.3.3. Distribution Pattern and Bootstrap Simulation

When research results are described with mean value (position parameter) and standard deviation (shape parameter), a normal distribution is assumed. However, these parameters are not robust for describing data sets, i.e., they are sensitive to extreme values, outliers, and skewed distributions. The latter is likely if mean values are low, variances large, values have a lower limit (usually zero for concentrations), or datasets are “closed” like for mass shares or compositional data (from 0 to 100%) [79,80]. In this case, testing for distribution patterns (e.g., lognormal distribution) to improve the

data description is recommended [58,79,80]. All data on WEEE mass, battery mass, and battery mass share were tested for normal and lognormal distribution. Moreover, skewness and kurtosis for these parameters were calculated. This section focuses on battery mass share to demonstrate a) the influence of the shape of the distribution and what difference a few data points can make, and b) bootstrapping as a method to simulate the impact of resampling on data precision and accuracy.

In general, the assumption of a normal distribution is not applicable for BM and BMS data of the different battery types (see Supplementary Materials Tables S7, S10, S11, S14, and S15). In most cases, mean values and medians deviate strongly, and the variation (SD, VC) is large, indicating a skewed and heterogeneous data distribution. Moreover, the analysis of skewness and kurtosis (both 0 for normal distribution), as well as the SW test ($p > 0.05$ for normal distribution), confirm that neither normal distribution nor lognormal distribution is present. Thus, without further examination of distribution patterns or collection of additional data, no distinct distribution patterns are given, and the data description using mean and SD may be biased.

Figure 6 shows the data distribution of battery mass shares as a histogram and probability density function (PDF) for the original data (a), the log-transformed data (b), and the bootstrap simulation (c) using the example of mobile phones (0306). The results for the other UNUkeys and subKeys are given in the Supplementary Materials Tables S7, S10, S11, S14, and S15. In Figure 5, the range in which the mass share lies with a probability of 95% is marked as a semi-transparent grey box (95% CI). The black curve shows the smoothed density estimate of the raw data, whereas the red curve shows the PDF of the normal distribution for the sample mean and SD. If both curves coincide, there is a normal distribution of the data, which can be confirmed by the SW test and the results of kurtosis and skewness.

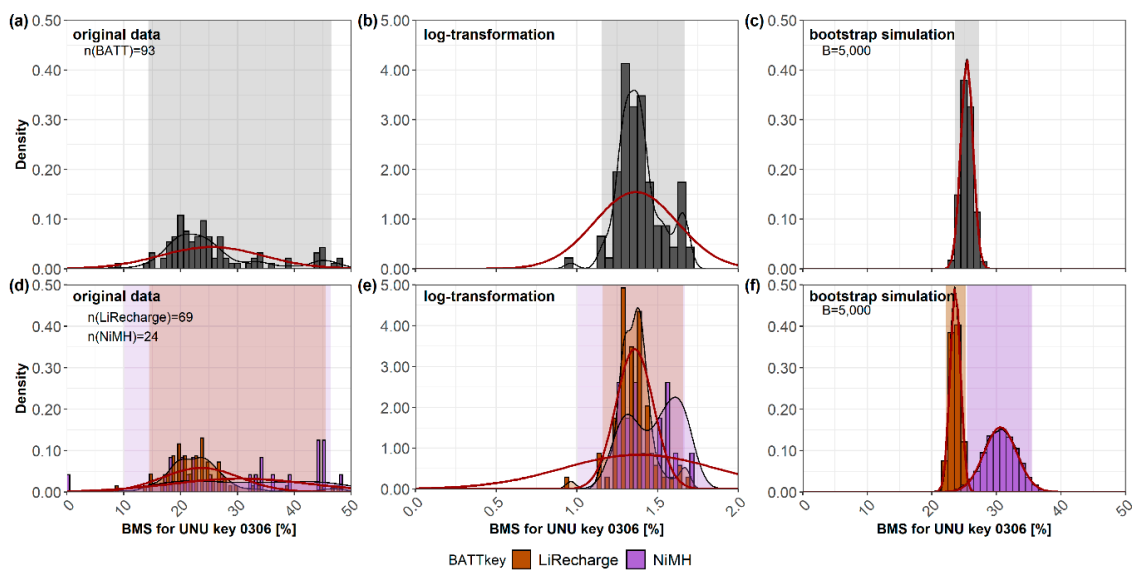


Figure 6. Histogram and density distribution for the battery mass share (BMS) of LiRecharge and NiMH for mobile phones (UNUkey 0306). Original data (a,d), log-transformed data (b,e), and bootstrap sample means with $B = 5000$ (c,f). The (log-)normal distribution curve for the sample mean and SD is shown in dark red. The 95% CI* is drawn as a semi-transparent area in the corresponding BATTkey color.

Figure 6a–c show the results for mobile phones (0306) without differentiation of battery systems (dark grey bars), whereas Figure 6d–f distinguishes between LiRecharge and NiMH. The example datasets comprise 93 batteries in mobile phones, of which 69 are LiRecharge batteries and 24 are NiMH batteries. In Figure 6a, most BMS are between 15 and 30% by mass, with some values up to 50% by mass (Figure 6a). Considering BATTkeys, the result is a more distinct BMS for LiRecharge, which concentrates around 20% by mass, whereas NiMH accounts for a BMS of 30% by mass (Figure 6f).

The description of these datasets using mean and SD, however, is not always applicable since normal distribution must be validated. In the example shown, neither BATT nor LiRecharge are normally distributed, but the SW confirms normal distribution for NiMH. By inspecting Figure 6b,e, we can assume that log-transformation for closed data sets like BMS does not improve the data description, which is confirmed by the results for SW, kurtosis, and skewness. Normal or (log-)normal distribution could rarely be confirmed when examining the original and log-transformed BMS data sets on UNUkey-BATT, UNUkey-BATTkey, subKey-BATT, and subKey-BATTkey level. Nevertheless, given the number of samples, two observations could be made. The proportion of data sets with lognormal distribution is higher than for normal distribution. This confirms that closed data sets can be better described by log transformation [79,80]. Furthermore, the specification of subKey and BATTkey increases the proportion of normal and lognormal distributions. Therefore, the applied classification improves the description of BMS and provides more accurate results with less variation of the data.

The bootstrap simulation in Figure 6c shows the BMS result of $B = 5000$ mean values drawn randomly from the original data set (Figure 6a). The simulated results are product- and battery-specific estimates for the mean mass fraction and depend on the underlying data. The mean (μ^*) and the VC^* of the simulated mean values were calculated for the simulated 5000 bootstrap samples. While the bootstrap simulation has only a minor influence on the mean value (compare \bar{x} and μ^*), it becomes apparent that the variation (SD^* , VC^*) and 95% CI^* decrease strongly, providing more precise data on BMS [64]. Moreover, the bootstrap distribution is symmetric, i.e., not skewed, which allows using SD^* and VC^* to describe the data uncertainty. However, this does not imply that bootstrap distributions are normally distributed. For instance, BATT (Figure 6c) and LiRecharge (Figure 6f) are normally distributed in 0306, but NiMH (Figure 6f) is not.

The investigation of other UNUkeys showed that only a few of the bootstrap distributions have an SW p-value of more than 0.05 and are therefore considered normally distributed. The distribution shape, on the other hand, showed that the data is marginally skewed (skewness near 0), but very often has a thin-tailed shape (negative kurtosis). Consequently, the description of the bootstrap results with Gaussian statistics is biased. Therefore, we always recommend a critical review of statistical assumptions for the original data and the additional use of more robust descriptors, such as median and MAD or confidence intervals.

3.4. Minimum Sample Size to Determine Battery Mass Shares in WEEE

Investigations on distribution patterns of the BMS for different batteries and WEEE have shown that, in most cases, no normal distribution can be assumed for the data. The inherent variation of the original data makes it challenging to define MSS with statistical approaches applicable for future investigations. Hence, the influence of inaccurately assumed distribution patterns on the calculation of MSS must be considered to derive recommendations. Therefore, two approaches were compared: a PA and an NPA. For the PA, a normal distribution is assumed using the coefficient of variation of the original data set (VC) and the bootstrap distribution (VC^*) in Equation (2). The NPA is based on bootstrapping with an increasing number of samples drawn from the original data set while testing iteratively whether each bootstrap mean lies within the bootstrap 95% CI^* , which was simulated with the initial number of sample in the data set (compare Figure 6e,f).

The approaches are demonstrated on the example of UNUkeys 0301 (small IT), 0302 (Desktop PCs), 0306 (mobile phones), and 0401 (small consumer electronics), all of which have at least 15 data points to generate reasonable simulation results.

Table 2 compares the NPA and the two PA showing the results of the original (VC) and bootstrap variation coefficient (VC^*) for PA. For each UNUkey, the results of the battery mass shares are shown without consideration (BATT) and with consideration of the BATTkey. BATT shows stronger deviations resulting in higher MSS. The VC is high for many UNUkeys because the underlying data are not normally distributed (see the section on product-specific battery characteristics). Consequently, the highest MSS are calculated for the PA(VC), which is the methodology of the SWA tool [40].

Table 2 shows that except for 0306 BATT, 0306 LiRecharge, and 0401 BATT and Zn, the sample size was too small.

Table 2. Comparison of the approaches to determine the MSS with the PA using the original PA(VC) and bootstrap coefficient of variation PA(VC*) as well as the NPA.

UNUkey	n	BATTkey	PA(VC)		PA(VC*)		NPA	
			VC	MSS	VC*	MSS	95% CI*	MSS
0301	51	BATT	1.32	670	0.18	12	[7.2; 15]	40
	29	Zn	1.03	420	0.19	14	[6.9; 14]	20
0302	118	BATT	1.84	1300	0.17	11	[0.03; 0.06]	70
	116	LiPrim	0.63	150	0.10	4	[0.03; 0.04]	20
0306	93	BATT	0.36	50	0.04	1	[24; 27]	70
	24	NiMH ND	0.40	60	0.08	2	[26; 35]	20
	69	LiRecharge	0.29	30	0.06	1	[22; 25]	60
0401	121	BATT	0.52	100	0.05	1	[17; 20]	90
	105	Zn	0.51	100	0.06	2	[17; 21]	80

n: number of samples, VC: coefficient of variation, PA(VC): a parametric approach using the VC of the original data, PA(VC*): a parametric approach using the VC of the bootstrap samples, NPA: non-parametric approach, MSS: minimum sample size, ND (superscript): normal distribution of original data. Results are rounded to two significant digits.

The result of the bootstrap simulation is a more precise data distribution characterized by smaller VC. If this VC* is used in the PA, the MSS is consequently reduced compared to PA(VC). Besides, bootstrap simulation with high repetitions (B) can produce very narrow distributions, resulting in very small MSS. However, the advantages of bootstrapping for improving accuracy and precision often lead to implausible results when using PA. In these cases, too small VC are calculated, resulting in sample sizes of one to two devices (see Table 2, column PA(VC*)).

The explanations above have shown that a general assumption of normally distributed data in the calculation of the MSS is both biased and leads to very high MSS. Regardless of the classification used, distribution functions can only be validly determined if the sample size is sufficient. Since extensive sampling in waste management is economically critical and organizationally complex, we have tried to determine MSS using an alternative approach. This NPA is independent of large data sets or certain distribution assumptions.

By simulating an iterative sampling with an increasing number of samples (n), we approached the confidence interval of the population. The results of selected UNUkeys and BATTkeys are shown in Figure 7. With a sufficient number of samples n the graph should asymptotically approach 100%, which would correspond to complete coverage of all sub-samples within the 95% CI*. A coverage of 90% means that the MSS is reached for 900 of 1000 sub-samples within the 95% CI*.

Figure 7a–c illustrates the extent to which a specification of the sampling aim and battery type influences the MSS. Figure 7a shows the NPA results for all devices of one UNUkey, regardless of whether the device had a battery compartment or a battery. The intersection of the graphs with 90% coverage, representing the MSS, is noted in Table 2 as NPA. Depending on the proportion of devices with a battery compartment (see Figure 2), the total number of devices is correspondingly larger than in Figure 7b. As a result, a high proportion of devices without a battery compartment (BMS is zero) leads to a higher MSS, as it influences the location and shape of the simulated distribution function and, thus, the 95% CI*. For example, the difference between the MSS of 0306 in Figure 7a,b is small, whereas 0306 (90% without batteries) and 0401 (70% without batteries) show significant differences. Consequently, the MSS decreases if devices with a battery compartment are separated beforehand (Figure 7b).

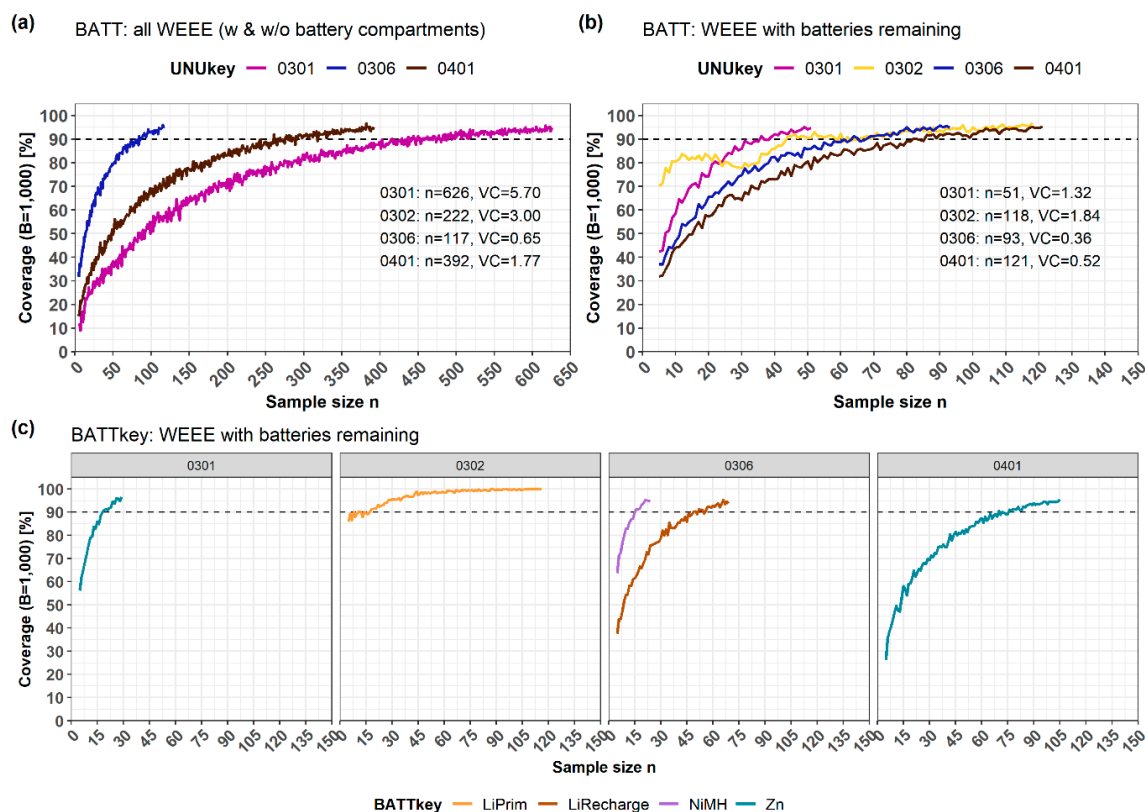


Figure 7. NPA: Simulation of MSS using bootstrap simulation. The proportion of sub-samples that lie within the simulated 95% CI* (coverage) is plotted against the number of samples used to draw the sub-samples. A coverage of 90% is considered acceptable to achieve representable results with the given sample size (dashed line). The graphs show the three possible combinations using small information technology (IT) (0301), desktop personal computers (PCs) (0302), mobile phones (0306) and small consumer electronics (0401) as examples: (a) all WEEE with and without battery compartment, (b) only WEEE with battery compartment without battery specification (BATT), (c) WEEE with batteries and BATTkey specification.

As shown in the section on bootstrapping, specifying the battery type increases the accuracy and precision of the result. For example, simulating the data at BATTkey level for 0306 (see Figure 6) shows that more distinct distributions are generated (Figure 6f). As a result, the sub-sample means of the NPA approach are more often within the defined range of the 95% CI*, which increases the coverage even at low sample numbers and reduces the MSS compared to Figure 7a,b. Furthermore, this example demonstrates the purpose of considering additional stratification variables (here BATTkey) for sampling. In this case, the age of WEEE implies the installation of older NiMH or newer LiRecharge batteries. With the ongoing technology change towards LiRecharge, the density distribution in Figure 6c will shift to the left and approach the density distribution of LiRecharge (Figure 6f). Without consideration of relevant stratification variables, a new determination of the MSS is, therefore, inevitable to avoid biased results. One possibility to identify these stratification variables is a comprehensive recycling-oriented characterization.

The comparison of all three approaches PA(VC), PA(VC*), and NPA illustrates the challenges in the determination of MSS using statistical approaches. A fundamental problem for the PA is the use of VC under the assumption of normal distribution. The heterogeneous composition of devices and device groups in the waste stream and the changing use of battery systems due to technological change or substance bans cause constant changes resulting in high variabilities. The consequence of these rapid changes can be very high or low WEEE and battery masses in the sample, which lead to extreme values for BMS, increased data variation within a UNUkey, and consequently biased results of PA.

The example of lithium primary batteries in desktop PCs (0302) shows that both PA(VC*) and NPA calculate a very small MSS. Bootstrapping increases the precision of the results, but can result in too small VC* for the application of PA, as it will result in implausible MSS. Consequently, MSS for PA is smaller for VC* if the acceptable error is kept constant. However, the use of VC is prone to be biased, since not only the original data, but also the bootstrap data (VC*) is not always normally distributed. Even with large amounts of data, a normal distribution cannot automatically be assumed. PA(VC*) is not a preferred method because the variance of the bootstrap simulation is very small for many repetitions ($B = 5000$), and the coefficient of variation leads to much too low MSS. This problem is overcome in most cases with the NPA using 95% CI*.

However, the NPA method also has its limitations. For instance, the example 0302 additionally shows that a very small and specific BMS results in a very narrow 95% CI* (see Table 2). The consequence is that the values from the bootstrap simulation are not within the 95% CI*, especially if there are zero values (Figure 7a) in the original data set. As a result, 0302 is not shown in Figure 7a, as all bootstrap results are outside the confidence range. This problem can only be overcome by adequate specification, in this case, by determining LiPrim batteries.

The PA was shown to be highly biased for estimating MSS due to indistinct data distribution patterns or the wrong assumption of normally distributed data. Bootstrap simulation can help to generate both more precise and accurate sampling results, which helps to approximate MSS and thus reduces the economic costs of sampling. If only a few WEEE devices are sampled (at least 15), and the data distribution pattern is indistinct or unknown, the NPA presented here shows advantages in comparison to PA. In contrast to PA, extreme values or outliers have less influence on the confidence interval when using NPA. Since the occurrence probabilities of the original values are decisive in bootstrap simulation, the most frequent values will have a more considerable influence on the result. For example, single extreme values caused by, e.g., new technology trends, like the change to LiRecharge batteries in tools, would not have a significant influence on the variation of the data when NPA is applied. Nevertheless, the number of data in the pilot data set also determines the validity of the statements for the NPA, which increases with an increasing number of sample values.

3.5. Sampling Recommendation

The shortcomings of current sampling methods are: (1) the lack of harmonization of the WEEE and BATT nomenclature at the product level and (2) the aggregated statistical description of the results, mostly based on normal distribution. Thus, data-driven optimization of sampling results, e.g., through merging of data from different sources and data-driven simulations, such as bootstrapping and the NPA, is not achievable. These quasi cost-neutral improvements of sampling results are not yet used.

Therefore, we recommend the following procedural adjustments for future investigations, which are not only applicable to the case of built-in batteries in WEEE, but also to other objects of sampling investigations. Firstly, standardized codes for WEEE (UNUkeys) and batteries (BATTkeys) should be used, enabling the exchange and comparison of the collected data, e.g., by supplementing existing guidelines such as the SWA-tool [40]. Secondly, the data should be recorded according to a standardized sampling protocols [52]. Thirdly, instead of describing the results of large individual samples under the assumption of normal distribution, several smaller samples should be taken, the results of which should be described with more robust descriptors (median, MAD, 95% CI). Such harmonized data will provide the necessary a priori knowledge for future investigations, which should be made publicly available together with other data about the urban mine [81–83] in an urban mine knowledge database [84]. Fourthly, the raw data obtained by sampling can be combined with data from public sources, such as statistics, monitoring reports, scientific publications. These combined datasets can be used to calculate and adjust the MSS of future investigations using the NPA.

4. Conclusions

Methodically coherent procedures for the determination of battery characteristics in WEEE products as well as a shared database providing a priori knowledge about product characteristics are missing or are insufficient, which makes it challenging to derive recommendations on sampling procedures and MSS.

The applied harmonized nomenclature using UNUkeys for WEEE and batteries proved to extend the possibilities for data stratification and evaluation. The results show that specific battery types (BATTkeys) were frequently identified in certain UNUkeys and subKeys. This concentration of BATTkeys in UNUkeys can simplify battery identification since batteries remain in two-thirds of WEEE with a battery compartment when discarded. Furthermore, it could be observed that secondary batteries are usually installed in fewer groups of devices, whereas primary batteries were found in many different devices with strongly varying mass shares. Product-specific values for mass and mass share could not be ascertained, which impedes a more precise assessment and leads to increased sample sizes of built-in batteries in WEEE.

Concerning the statistical description of sampling results, we showed that the assumption of normally or lognormally distributed data proved to be rarely valid to characterize these samples. Using mean and SD or VC for the statistical description of the data leads to biased results. In addition, more robust descriptors like median and MAD or data-driven simulation (bootstrapping) are recommended to improve the quality and representativeness of sampling results.

With regard to the approximation of the MSS, we conclude that the PA is strongly affected by the assumed distribution pattern as well as the number of samples. Bootstrapping was shown to be favorable to generate more accurate results on battery characteristics in the case of unknown or inconclusive sample distributions and fewer data points. Moreover, bootstrapping in combination with recycling-oriented product characterization, can be used to perform the NPA, which provides a more robust approach to approximate the MSS. However, for both approaches, the future availability of harmonized data is required and defines the validity of the results.

Consequently, recyclers, researchers, and policymakers should focus on a common harmonized method to generate and collate consistent data, which is crucial for an urban mine knowledge database. The product count procedure enables to (1) identify (safety) relevant products in WEEE, (2) set depollution targets as defined by CENELEC [24], (3) lower the labor costs for sampling due to simulation-based optimization of results and MSS, (4) display trends to plan recycling strategies, and (5) derive more valid results on waste characteristics to improve resource efficiency in WEEE and waste battery management.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2313-4321/5/3/19/s1>, Figure S1: Proportion of WEEE devices (UNU subKey) with and without battery compartment, Figure S2: Mass share of WEEE devices (UNU subKey) with and without battery compartment, Figure S3: Occurrence and count of battery types (BATTkeys) in subKeys, Figure S4: Mass (a) and mass share (b) of batteries remained in WEEE classified as subKeys and distinguished by their chemical system (BATTkey), Table S1: Number and mass of WEEE and BATT sampled, Table S2: R packages, Table S3: Number of electronic devices (UNUkey level) with or without battery compartment and share of batteries remained in a product, Table S4: Descriptive statistics for mass of all WEEE investigated differentiated in UNUkeys, Table S5: Descriptive statistics for mass of all WEEE investigated differentiated in UNU subKeys, Table S6: Descriptive statistics for mass of batteries in WEEE differentiated in UNUkeys, Table S7: Descriptive statistics for mass of batteries in WEEE differentiated in UNUkeys and BATTkeys, Table S8: Descriptive statistics for battery mass share of WEEE differentiated in UNUkeys, Table S9: Descriptive statistics for battery mass share of WEEE differentiated in subKeys, Table S10: Descriptive statistics for battery mass share of batteries in WEEE differentiated in UNUkeys and BATTkeys, Table S11: Descriptive statistics for battery mass share of batteries in WEEE differentiated in subKeys and BATTkeys, Table S12: Descriptive statistics for battery mass share of batteries in WEEE differentiated in UNUkeys, Table S13: Descriptive statistics for battery mass share of batteries in WEEE differentiated in subKeys, Table S14: Descriptive statistics for battery mass share of batteries in WEEE differentiated in UNUkeys and BATTkeys. Table S15: Descriptive statistics for battery mass share of batteries in WEEE differentiated in subKeys and BATTkeys, Table S16: UNUkey classification and allocation to WEEE categories EU-10. The pilot dataset and R code are also available at DepositOnce: <http://dx.doi.org/10.14279/depositonce-9338> (accessed on 13 July 2020).

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Appendix A

Table A1. Battery mass and mass share differentiated by BATTkey.

BATTkey	n	LiPrim	LiRecharge	NiCd	NiMH	Pb	Zn	Unspecified
		195	135	44	130	13	257	16
Mass (BM)	\bar{m} [g]	3.9	74	310	69	1300	38	47
	SD [g]	3.2	120	440	110	1400	66	100
	VC [-]	0.8	1.6	1.4	1.7	1.1	1.7	2.2
	\tilde{m} [g]	3.0	23	67	26	800	23	7.0
	MAD [g]	0.074	8.1	71	21	430	17	7.4
	95% CI [g; g]	[1.9; 8.8]	[8.9; 430]	[14; 1500]	[10; 490]	[15; 4300]	[2.3; 150]	[2; 300]
	SW/SWlog [-]	0/0	0/0	0/0	0/0	0/0	0/0	0/0
	S/Slog [-]	5.4/1.9	2.2/0.99	2.1/0.28	3.0/0.93	1.3/−1.1	8.4/−0.27	2.7/0.7
	K/Klog	42/4.7	3.5/1.2	4.5/−1.5	8.4/0.76	0.59/0.046	92/1.6	6.3/−0.87
Mass share (BMS)	\bar{x} [%]	2.3	20	23	19	46	18	12
	SD [%]	4.3	9.0	16	12	19	15	14
	VC [-]	1.90	0.46	0.66	0.61	0.42	0.76	1.1
	\tilde{x} [%]	0.045	20	22	18	48	15	8.4
	MAD [%]	0.031	7.2	14	11	12	11	12
	95% CI [%; %]	[0.02; 12]	[1.9; 43]	[0.5; 46]	[0.65; 45]	[8.8; 74]	[2.0; 53]	[0.096; 43]
	SW/SWlog	0/0	0/0	0/0	0/0	0.28/0	0/0	0/0.12
	S/Slog	1.8/0.92	0.83/−4.0	1.6/−2.8	0.72/−2.4	−0.58/−1.5	1.4/−0.69	1.1/−0.76
	K/Klog	1.5/−0.87	2.9/21	4.9/8.7	−0.083/8.2	−0.4/1.1	2.2/0.27	0.43/−0.57
Occurrence in	UNUkeys	19	16	11	15	7	16	9
	subKeys	23	27	15	24	8	29	10

n: number of observations, \bar{m}/\bar{x} : mean, SD: standard deviation, VC: coefficient of variation, \tilde{m}/\tilde{x} : median, MAD: median absolute deviation, 95% CI: confidence interval [2.5th quantile, 97.5th quantile], SW: p-value of Shapiro-Wilk test (normally distributed if $p > 0.05$, highlighted in bold), S: skewness, K: kurtosis; log(subscripted): respective values after log-transformation. Results are rounded to two significant digits.

Table A2. Statistics on battery mass and mass share, differentiated by UNUkey.

UNUkey	n	Battery Mass					
		\bar{m} [g]	SD [g]	VC [-]	\tilde{m} [g]	MAD [g]	95% CI
0201	23	26	28	1.1	23	12	[2; 98]
0202	13	39	35	0.89	46	64	[2.9; 100]
0204	29	360	240	0.67	260	260	[80; 820]
0205	48	26	9.6	0.36	23	6.2	[14; 47]
0301	51	120	690	5.7	12	16	[1.1; 220]
0302	118	3.4	3.2	0.94	3	0	[2.8; 6.5]
0303	29	210	190	0.92	250	300	[2.1; 480]
0305	52	33	54	1.7	22	15	[11; 84]
0306	93	29	18	0.61	21	5.1	[15; 77]
0401	121	22	14	0.66	22	16	[3; 48]
0402	29	73	160	2.2	24	12	[2.9; 440]
0403	7	71	73	1	37	21	[10; 200]
0406	18	36	63	1.8	18	11	[2.7; 200]
0501	16	79	120	1.6	33	39	[3; 380]
0506	15	240	710	3	32	27	[3; 1900]
0601	32	470	560	1.2	340	460	[12; 2000]
0701	42	38	25	0.66	34	24	[3; 90]
0702	5	33	6.2	0.19	35	4.1	[24; 38]
0901	31	10	11	1	7.9	0	[2.6; 46]
all	750	76	270	3.6	21	23	[2.1; 546]

Battery mass share							
UNUkey	n	\bar{x} [%]	SD [%]	VC [-]	\tilde{x} [%]	MAD [%]	95% CI
0201	23	12	12	0.94	8.7	6.5	[1; 38]
0202	13	4.5	6.1	1.4	2.3	3.1	[0.15; 18]
0204	29	26	14	0.54	20	9.4	[11; 54]
0205	48	19	7.8	0.41	18	8.4	[7.9; 38]
0301	51	11	14	1.3	5.2	5	[0.88; 56]
0302	118	0.045	0.082	1.8	0.031	0.009	[0.019; 0.098]
0303	29	8.7	7.6	0.87	13	6.3	[0.061; 20]
0305	52	16	10	0.66	11	7.2	[3; 38]
0306	93	25	9.1	0.36	23	5.4	[14; 47]
0401	121	19	9.7	0.52	17	9.6	[5; 41]
0402	29	17	13	0.78	13	7.7	[2.1; 57]
0403	7	19	24	1.3	3.5	3.1	[1.5; 60]
0406	18	9.9	8.5	0.85	6.9	7.8	[0.27; 28]
0501	16	34	22	0.64	38	19	[2.7; 69]
0506	15	25	16	0.64	23	18	[3.1; 54]
0601	32	26	19	0.74	22	16	[0.14; 79]
0701	42	15	14	0.92	11	9.9	[0.23; 38]
0702	5	19	9.4	0.49	25	1.8	[8.3; 26]
0901	31	11	5.6	0.51	12	0	[0.6; 23]
all	750	16	14	0.89	13	14	[0.02; 48]

n: number of observations, \bar{x} : mean, SD: standard deviation, VC: coefficient of variation, \tilde{x} : median, MAD: median absolute deviation, 95% CI: confidence interval [2.5th quantile, 97.5th quantile]. Results are rounded to two significant digits.

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8. Article II

Contributions of Extended Batch Tests for Assessing Technical Recyclability: A Case Study of Low-Value

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Contributions of extended batch tests for assessing technical recyclability

A case study of low-value battery flows

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Abstract

Good product recyclability is a prerequisite for the transition to a circular economy. However, today's product complexity and diversity in the urban mine result in heterogeneous and variable waste flows affecting process recycling efficiency (RE) and thus product recyclability. For batteries, waste flow composition and subsequent RE are determined by usage behavior, collection, and sorting into chemical battery subsystems. This study aims to demonstrate how extended batch tests (EBTs) can be used as a method to (a) determine battery-specific RE and (b) derive recommendations for assessing and improving the recyclability of batteries. Three EBTs comprising extensive characterization methods were carried out with mixtures of zinc-based (AZ) and lithium-based (LIB) batteries. The results showed that 0.20–0.27 kg/kg of the input mass was lost through flue gas and not recyclable. The metal fraction (0.15–0.19 kg/kg) was easily recyclable, while the mineral fractions of LIBs posed challenges for recycling and recovery (RR) due to the high elemental heterogeneity and pollutants originating from individual battery subsystems. In total, 0.79 kg/kg of AZs was recyclable, whereas 0.52 kg/kg of LIBs and 0.58 kg/kg of AZLIBs (a mixture of both) were recyclable after further treatment. In conclusion, the study demonstrated how the EBT approach can be used to extend recyclability assessment by providing waste flow characteristics for comparison with output quality requirements, enabling assignment of battery-specific RE and identification of poorly recyclable battery subsystems. Thus, the EBT approach can help improve and assess technical recyclability in the future.

KEYWORDS

batteries, extended batch test, industrial ecology, recyclability, recycling, recycling efficiency

1 | INTRODUCTION

In the transition to a sustainable and circular economy (CE), recycling and waste management play a crucial role in closing material cycles and increasing resource efficiency. The European Commission (EC) therefore recently adopted the CE Action Plan (CEAP) promoting CE measures

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for various key product value chains (European Commission, 2020b). Batteries are one example of these key products. Lithium-ion batteries, in particular, have been designated as a key enabler of a low-carbon economy and are notable for their versatile range of uses, rising sales figures (Eurostat, 2019; Kwade & Diekmann, 2018b), and potential fire risk (Kwade & Diekmann, 2018a). One CEAP measure to promote sustainable product designs is the proposal of a new regulatory framework including more systematic durability, recyclability, and recycled content in EU Ecolabel criteria (European Commission, 2020a; European Union, 2020). The design and lifecycle of batteries are therefore becoming the focus of sustainable product policies (European Commission, 2019b) leading to the proposal of an amended battery directive (European Commission, 2020a).

Over the past several years, the design and composition of batteries, especially lithium-ion batteries, have evolved rapidly as a result of product innovations in vehicles as well as in electrical and electronic equipment (EEE) technologies. The increasing demands for battery capacity, efficiency, and cost savings have led to continuous development of new chemical battery subsystems with ever-changing chemical compositions, such as the development from NMC111 to NMC811 (Battery University, 2021; Huisman et al., 2017; Karabelli et al., 2020). This development has resulted in (a) reduction or substitution of cost-intensive battery material such as cobalt and nickel (Huisman et al., 2020) and (b) polymetallic subsystems enhancing battery performance while reducing costs. The resulting product diversity, in combination with varying lifetimes for EEE-specific battery systems (Mählitz et al., 2020) and the hoarding of batteries by end users (Pistoia, 2005), has led to a mixture of battery subsystems in the urban mine with high variability and heterogeneity (Huisman et al., 2017).

At the end of life (EoL), these battery mixtures require suitable treatment technologies (Mohr, Weil, et al., 2020) to meet recycling efficiency (RE) targets and enable good recyclability (European Commission, 2019a) despite the high material heterogeneity of batteries with critical (Amato et al., 2016) and safety-relevant elements (Huisman et al., 2020). In addition to available treatment capacities, economic and ecological trade-offs, and regulatory requirements (Commission Regulation [EU] No. 493/2012, 2012), the choice of treatment technologies is determined by the composition of battery waste flows, which can be influenced by sorting processes. Given the increasing share of low-value lithium batteries in the main waste flow, the separation of cobalt- and nickel-rich battery subsystems is one possible measure to increase the recovery rate of Co and Ni from the main waste flow in established recycling processes. The result is a waste flow containing various low-value subsystems subjected to alternative and cost-effective recycling processes, such as thermal treatment (Lombardo et al., 2020; Schwich et al., 2021).

In contrast to RE, which is limited to one process and input, recyclability is an indicator for assessing the “ability of a product to be recycled at end of life” (DIN EN 45555, 2019). It comprises a variety of scenarios consisting of setup of processes with individual efficiencies. The recyclability assessment (RA) results are prone to errors, since potential recyclability is based solely on product-related characteristics, such as composition, construction, size as well as (type of) connections between materials and does not include such EoL scenarios and their influence on recycling efficiencies. However, the composition of waste flows in which the product is treated plays a key role in determining process efficiency and, consequently, the recyclability of the waste flow and each product it contains. This influence on recyclability becomes more significant as the constitutional and distributional heterogeneity (Gy, 1995) of the products in the flow increases.

Going beyond potential recyclability requires considering the feasibility of recovery and the respective qualities of anthropogenic resources (UNECE, 2018) to model possible EoL scenarios for RA. Each scenario contains a combination of sorting and treatment scenarios with individual efficiencies that depend on both waste flow composition and treatment technology. The result is an indicator that can be referred to as technical recyclability, which permits a more realistic assessment of product design.

However, including such EoL scenarios in RA is rarely considered and is made challenging by a lack of data. This challenge of collecting harmonized data on waste flows characteristics and process efficiencies to create EoL scenarios can be approached top down (e.g., by modeling; Donati et al., 2020; Wagner et al., 2021) or bottom up (by collecting data on a process level with batch tests). In waste management, batch tests are an established method for internal quality management and assessing process performances (NVMP Association, 2014; Ueberschaar et al., 2017) for waste EEE (WEEE) (Chancerel et al., 2011, 2016; Savi et al., 2013; WEEE Forum, 2013) and EoL vehicles (ELV) (Widmer et al., 2015). Ueberschaar et al. (2017) demonstrated how extending the scope of conventional batch tests can further increase informative value for assessment of element-specific RE by describing the fate of elements, identifying recycling drivers or barriers, assessing output qualities, recommending process optimizations for increased recoveries, and so on.

This study aims to demonstrate the use and design of extended batch tests (EBTs) for characterizing mixed battery waste flows and deriving recommendations to assess and improve product and waste flow recyclability. To achieve these goals, a case study comprising three batch tests with mixtures of low-value (zinc- and lithium-based) battery systems were carried out in a full-scale thermal treatment plant. Comprehensive characterization of input, process, and output in combination with the specification of quality requirements for recycling and recovery serves to determine battery-specific RE and identify battery subsystems that negatively affect RE. The methodology presented using the recycling problem for low-material battery mixtures is applicable to other battery systems and the results can be used to derive recommendations for improved RA as well as for separation and treatment processes of batteries.

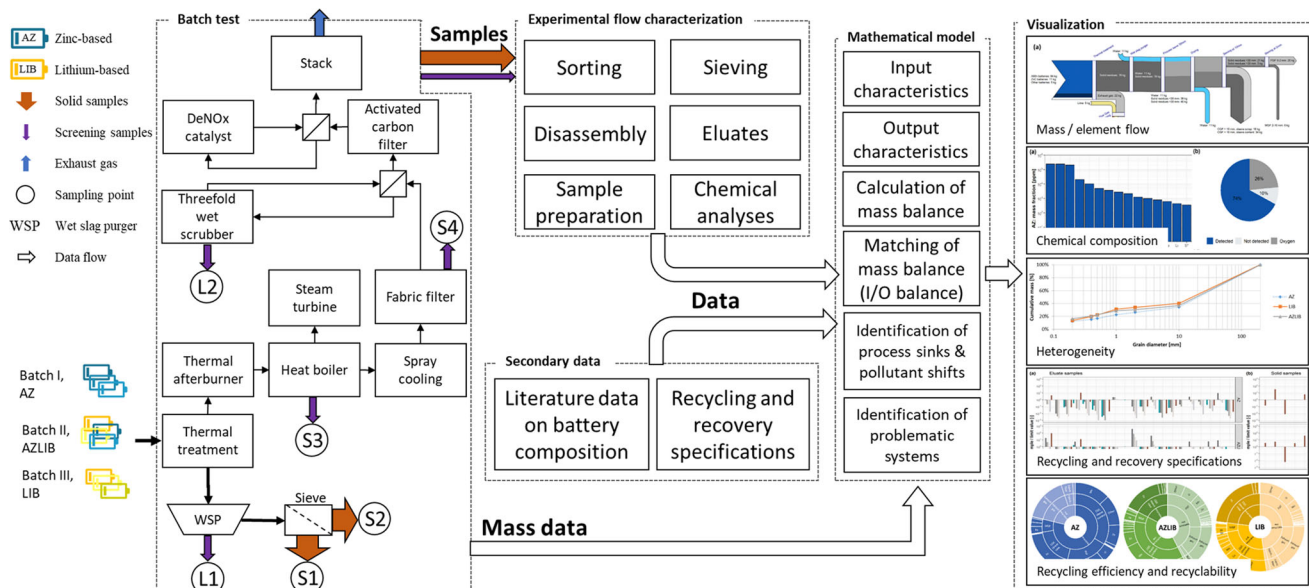


FIGURE 1 Basic flow scheme of the thermal treatment process and description of extensions of the batch test design, based on Ueberschaar et al. (2017)

2 | METHODS

2.1 | General approach

In this study, EBTs were performed based on Ueberschaar et al. (2017) to determine battery-specific RE and assess the recyclability of batteries in mixed waste flows by extending the scope of conventional batch tests by four levels. Firstly, in addition to mass balancing, the EBTs included comprehensive characterization of input and output materials supplemented by screening samples throughout the process to identify process sinks, the fate of targeted elements, and pollutant shifts (see Figure 1). Secondly, the plausibility of the results was checked in terms of mass conservation using mass balancing in an input–output (I/O) balance of selected target elements. Thirdly, the overall batch test RE was calculated by determining the fraction accounting for recycling (Commission Regulation (EU) No. 493/2012, 2012) by comparing output characteristics with quality specifications for possible recycling and recovery options. Fourthly, parameters and elements that would prevent a particular recycling option were identified and studied in terms of their occurrence in specific battery subsystems present in the waste flow. Thus, battery subsystems containing problematic constituents can be prospectively sorted out to prevent reduction of RE and waste flow recyclability and consequently increase the product recyclability of other battery subsystems treated jointly within this waste flow.

2.2 | Experimental design of the extended batch tests

The EBTs were carried out at a full-scale thermal treatment plant for the disposal of ammunition, explosives, and hazardous waste. Input was treated in a ceramic-lined rotary kiln for 30–45 min. at 750–850°C. Flue gas cleaning complies with the emissions limits of the 17th Federal Emission Control Act (Federal Ministry of Justice, 2013) and comprises spray cooling, fabric filter, threefold wet scrubber, activated carbon filter, and SNCR-DeNOx catalyst. The burned-out solid material is discharged via a wet slag purger (WSP) and subsequently sieved on-site with a screen size of 30 mm to separate coarse components (Figure 1, S1) from the fine fraction (Figure 1, S2).

The battery mixtures for the EBTs originated from an industrial sorting plant that separates, among other things, three different battery systems with low intrinsic value. These low-value battery systems are (1) zinc-based batteries (i.e., alkali-manganese “AlMn” and zinc-carbon “ZnC” batteries), (2) primary lithium-based batteries (“LiPrim”), and (3) secondary lithium-based batteries (“LiRecharge”). The three battery systems were provided in 60 L barrels and mixed upon feeding into the treatment plant to simulate different sorting and treatment scenarios (EBT1–3). Under the current battery directive (Directive 2006/66/EC on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC, 2006/26.09.2006), all three battery systems belong to the same “other batteries” group, which means that the same RE targets of 50% by mass apply, and the choice of treatment technology is primarily an economic and ecological trade-off. The first and third EBT simulated the EoL scenario with zinc-based and lithium-based batteries treated separately, whereas the second EBT was used to evaluate the possible benefits

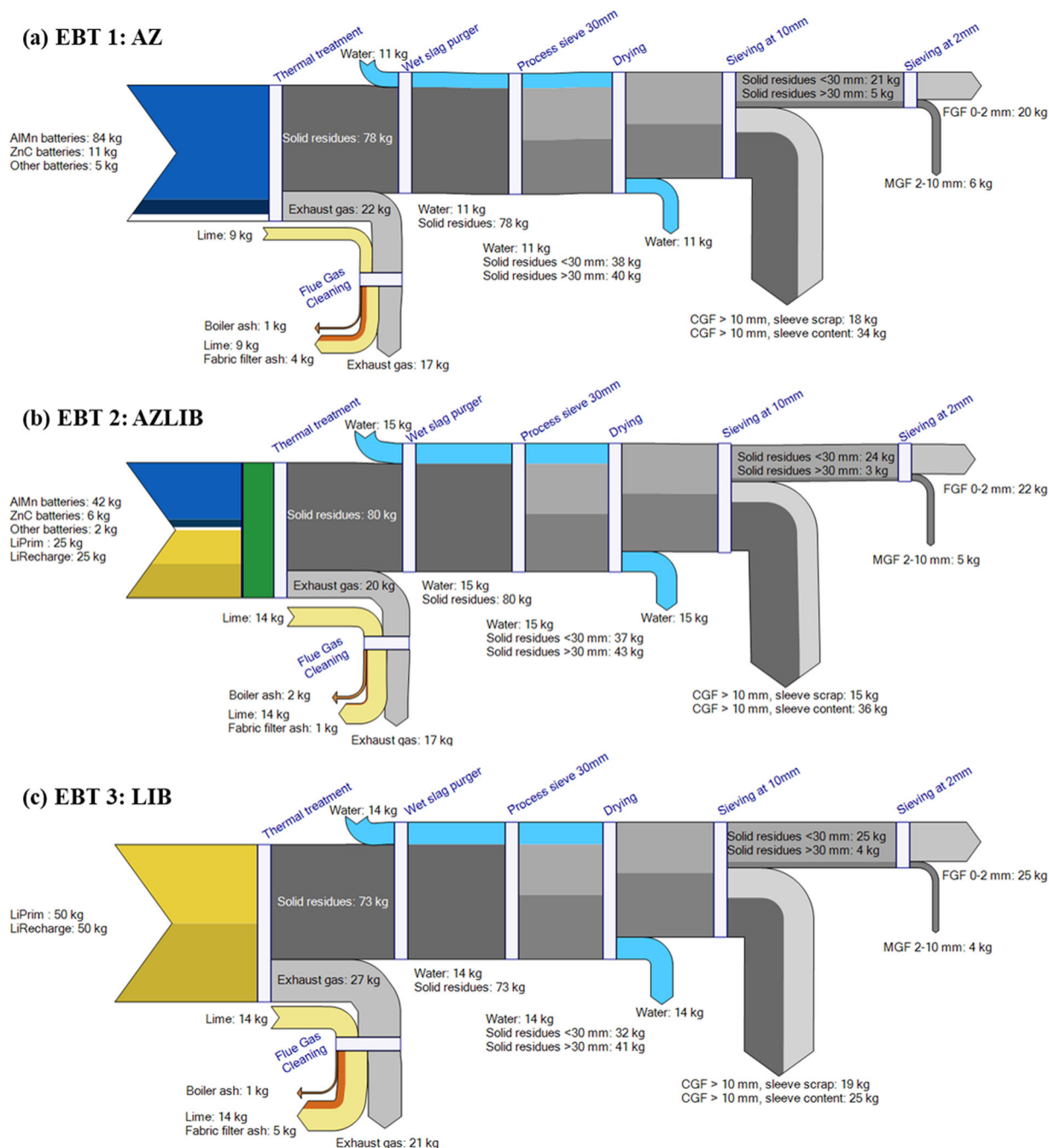


FIGURE 2 Process mass balances for the batches (a) AZ, (b) AZLIB, and (c) LIB. The mass values are normalized to 100 kg input of treating AZs and LIBs jointly in terms of RE and recyclability. In detail, the three EBT inputs were composed of the following battery systems in percentages by mass:

EBT 1: AZ 100%, in total 9.9 Mg

EBT 2: AZLIB 50% AZ and 50% LIB, in total 10.5 Mg

EBT 3: LIB 50% LiPrim and 50% LiRecharge batteries, in total 10.8 Mg

2.3 | Characterization of input material

Since a direct chemical analysis of untreated batteries is challenging in terms of sample preparation and chemical analysis, we chose the method of indirect waste analysis based on product count in combination with a literature review of element mass fraction in batteries. For AZs and LiPrims,

individual samples of 3–4 L batteries were taken upon feeding into the treatment plant over the complete processing time in regular intervals. The total sample mass corresponded to approx. 0.5% of the input quantity supplied. Cylindric, prismatic, coin cells, and pouch cells were sorted by means of labels and imprinted nominal voltages in the subsystems such as AlMn, ZnC, LiMnO₂/Li(CF)_n (3 V), LiSOCl₂ (3.6 V), LiSO₂ (3 V), and others. LiRecharge batteries are built into casings, impeding the direct identification of subsystems. Separation of low-value LiRecharge batteries in the industrial sorting plant is based on product-specific use, such as in tools or e-bikes. Thus, three-quarters of these barrels were visually categorized, and the respective product-specific use of subsystems in such devices was researched in the literature (Huisman et al., 2020; Stiftung Gemeinsames Rücknahmesystem Batterien, 2007; Tsiropoulos et al., 2018). The elemental composition of the battery subsystems was determined from the literature (European Portable Battery Association [EPBA], 2007; Stiftung Gemeinsames Rücknahmesystem Batterien, 2007; Würfel & Teipel, 2013) and is provided in Supporting Information S2.

2.4 | Characterization of output material

2.4.1 | Sampling

As shown in Figure 1, eight samples were taken in total, comprising two samples of the solid output material (S1 and S2 in duplicates), two solid screening samples (S3 and S4), and two liquid screening samples (L1 and L2). The sampling of the flue gas path (boiler ash—S3, fabric filter ash—S4, wet scrubber water “WSW”—L2), and wet slag purger “WSP” (L1) helped to close mass balances and assess pollutant shifts in the process (see Figure 1). The solid output material (S1 and S2) was collected in containers behind the process sieve and sampled according to LAGA PN98 (Länderarbeitsgemeinschaft Abfall [LAGA], 2001). For this purpose, containers were divided into two sectors, from each of which eight individual samples of 5 L were taken and combined to form two laboratory samples (S1a, S1b and S2a, S2b) representing approximately 1% of the total solid output mass. Both laboratory samples were analyzed in parallel for internal quality assurance and consideration of possible uncertainties from sampling. The screening samples were taken toward the end of each test and comprised approximately 1 kg of the solid and approximately 1 L of the liquid samples. The detailed sampling procedure is described in Supporting Information S1.

2.4.2 | Physical characterization

After drying (DIN EN 14346, 2007), the solid output samples were sieved in a Haver EML 450 DIGITAL PLUS using sieve trays with the nominal diameter of 0.2, 0.4, 0.5, 1.0, 2.0, and 10.0 mm. The subsequent visual inspection resulted in three different grain size fractions with uniform characteristics, which were merged to examine possible recycling routes and adapt further analyses: fine-grain fraction < 2 mm (FGF), medium-grain fraction 0–10 mm (MGF), and coarse-grain fraction > 10 mm (CGF).

2.4.3 | Chemical characterization

Selection of preparation and analysis methods was based on the distinction between metal and mineral fractions. The metal fraction consisting of battery sleeves (i.e., metallic cell casings) and magnetically separated metal occurs in the CGF and MGF, whereas the mineral fraction is present in all three grain size fractions. The metal fraction was analyzed directly by energy-dispersive X-ray fluorescence (ED-XRF), and a larger amount of the battery sleeve sample was analyzed indirectly by melting. After comminution to analytical size, the mineral fraction was analyzed using XRF and wet chemical analysis (for FGF). The elements and parameters studied include Al, As, Ba, C, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, K, Li, Mo, Mg, Mn, Na, Ni, Pb, S, Sb, Ti, Zn, cyanides, and organic compounds. The detailed method by grain size fraction is described in Supporting Information S1.

2.5 | Process and element mass balances

Mass balances were performed for input and output masses as well as for target elements. The input mass was determined at the sorting plant, whereas the output mass is the sum of solid residues, flue gas cleaning residues, and exhaust gas emissions. The solid residues were collected in containers. Boiler ash and filter dust were collected in BigBags and weighed on a truck scale. The mass of added lime was subtracted from the total filter dust mass by counting spray shocks with a defined lime mass. Metal oxides in the FGF were approximated to close mass balances, assuming the main constituents to be present as stable metal oxides (see Supporting Information S1).

Element mass balance was performed for target elements with a high mass fraction (Al, Fe, K, Mn, Zn), hazardous potential (Cd, Pb, Cr), and higher value (Co, Cu, Ni). As shown in Equation (1), the total output mass fraction of the *k*th element ($\bar{c}_{\text{output}}^k$) is the sum of the element mass share

per fraction j ($m_j\%$) multiplied by the respective average mass fraction of element k (c_j^k):

$$\bar{c}_{\text{output}}^k = \sum_{j=1}^n m_j\% \cdot \bar{c}_j^k \quad (1)$$

To check the plausibility and compliance of input and output, the results of input sorting of battery subsystems were combined with elemental battery contents from the literature (Almeida et al., 2019; Al-Thyabat et al., 2013; EPBA, 2007; Huisman et al., 2020; Mudgal et al., 2011; Tsiropoulos et al., 2018; Würfel & Teipel, 2013).

2.6 | Calculation of recycling efficiency and recyclability

Process mass balancing and output characterization are used for calculation of overall process RE, which is legally required for battery recycling processes (Commission Regulation [EU] No. 493/2012, 2012) and described in European Commission (2012). According to Equation (2), RE is the sum of the output flows m_{output} accounting for recycling (recyclable content) divided by the input mass m_{input} :

$$R_E = \frac{\sum m_{\text{output}}}{m_{\text{input}}} \cdot 100\% \quad (2)$$

In contrast to RE, which describes a treatment step for a specific waste flow and process, recyclability is an indicator that considers the proportion of a product type in different waste flows with different EoL scenarios and efficiencies. However, calculation of recyclability is not legally established for batteries. Following DIN EN 45555 for (W)EEE, recyclability for a specific waste flow and process can be expressed as the quotient of the sum of recycled components of a product divided by the total mass of a product.

2.7 | Options for recycling, recovery, and disposal

The focus of recycling and recovery (RR) options was on the solid residues: FGFs, MGFs, and CGFs. No further recycling options were evaluated for flue gas cleaning residues. Identified RR options included (1) metal recycling for pig iron, steel, and copper, (2) recycling as construction materials, and (3) backfilling. In the case that RR is not possible, landfill criteria have been evaluated. RR requirements and limit values were researched in regulations, literature, and through inquiries with metal recyclers that provided product- and process-specific requirements for the respective industry. A general description of the requirements is given in Table 1. Detailed information as well as limit and reference values are provided in Supporting Information S1 and Supporting Information S2.

If a recycling option specifies limit or allocation values, the measurement result is normalized to the limit value by dividing the measurement result by the limit value. If the quotient is greater than 1, the limit value is exceeded. If it is less than 1, the limit value is not reached. For recycling routes in which there are no limit values but instead guidance values for secondary raw materials, the qualities are compared with these requirements.

3 | RESULTS

3.1 | Input characteristics

The manual sorting of the low-value battery systems AZ, LiPrim, and LiRecharge used to mix the EBT input resulted in the following mass fractions of battery subsystems:

1. AZ: 84% AlMn, 11% ZnCd, 0.1% LiPrim, 0.2% NiCd, 0.7% NiMH, and 4% other batteries
2. LiPrim: 51% lithium-manganese-oxide (LiMn_2O_4) and lithium graphite fluoride ($\text{Li}(\text{CF})_n$), 39% lithium thionyl chloride (LiSOCl_2), 6.4% lithium sulfur dioxide (LiSO_2), 2.1% LiPrim unknown, 0.8% lithium iron disulfide (LiFeS_2), 0.6% other
3. LiRecharge: 32% power tools (lithium-nickel-manganese-cobalt oxide LiNiMnCoO_2 : NMC, lithium-manganese oxide— LiMn_2O_4 : LMO), 32% e-bikes (NMC, LMO, lithium-cobalt oxide LiCoO_2 : LCO, lithium-iron phosphate LiFePO_4 : LFP), 20% round cells (NMC, lithium-nickel-cobalt-aluminum oxide LiNiCoAlO_2 : NCA, lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or Li_2TiO_3 : LTO), 11% flat cells (Li-Polymer), 5% other

TABLE 1 Material property requirements for selected recycling and recovery options

Recycling and recovery routes		Desired properties	Disturbing properties
Metal recycling	Pig iron "DK process" (DK Recycling und Roheisen GmbH, 2009)	Optimum: Fe contents $\geq 40\%$ by mass, lower Fe contents possible	Solid: Cu, S, Cr, As, Sb, Pb, Co, Mo, Ni, etc., high contents of slag formers (SiO_2 , CaO, MgO, Al_2O_3) Eluate: –
	Steel (Martens & Goldmann, 2016; Willeke, 1998)	Unalloyed steel: Low content of alloying metals Alloyed steel: Valuable alloying metals	Solid: Cu, S, Sb, As, Sn, Pb, etc. Eluate: –
	Copper (Lossin, 2012; O. Cekel, personal communication, December 22, 2014)	High Cu contents, a favorable ratio of valuable metals and accompanying elements	Solid: High impurity content Eluate: –
Construction materials	Recycling according to LAGA M20 (Joint Working Group of the Federal States on Waste, 2003) and LAGA M19 (Joint Working Group of the Federal States on Waste, 1994)	Low-pollutant, inert material	Solid: TOC, EOX Eluate: Heavy metals (Pb, Cd, Cr, Cu, Ni, Hg, Zn), anions (chloride, sulfate, cyanide), pH value, el. conductivity DOC
Cement industry	Cement industry: Clinker production (Scur, 2013; Verein Deutscher Zementwerke e.V., 2002)	SiO_2 , Al_2O_3 , Fe_2O_3 (CaO) Good bulk material properties (low dust, nonsticky, lumpy), as high homogeneity as possible	Solid: Heavy metals and high levels of minor components (MgO, K_2O , SO_3 , Cl, etc.) Eluate: –
	Cement industry: Grinding (InformationsZentrum Beton GmbH, 2014; Verein Deutscher Zementwerke e.V., n.d., 2002)	Binding effect, improvement of the grain structure in the milling grain range	Solid: Heavy metals Other: Negative impact on the hardening of the cement, the strength and durability of the concrete, the corrosion protection of the reinforcement
Backfilling	Backfilling of waste underground according to Stowage Ordinance (Federal Ministry for the Environment, Nature Conservation & Nuclear Safety, 2002)	Low-pollutant, inert material with low contents of valuable metals	High valuable metal contents Solid: Heavy metals (As, Pb, Cd, Cr, Cu, Ni, Hg, Zn), cyanide (total), organic pollutants, TOC, loss on ignition Eluate: Heavy metals (As, Pb, Cd, Cr, Cu, Ni, Hg, Zn), cyanide (total, easily releasable), organic pollutants
Landfilling	Landfilling according to Landfill Ordinance (Bundesministeriums der Justiz und für Verbraucherschutz sowie des Bundesamts für Justiz, 2009)	Compliance with allocation criteria of the respective landfill class	Solid: Organic pollutants, loss on ignition, TOC, extractable lipophilic substances Eluate: Heavy metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn), anions (Cl^- , F^- , CN^- , SO_4^{2-}), total dissolved solids, DOC, phenol index
	Landfill substitute material according to Landfill Ordinance (Bundesministeriums der Justiz und für Verbraucherschutz sowie des Bundesamts für Justiz, 2009)	Mineral waste Compliance with allocation criteria of the respective landfill class	Solid: Organic pollutants, loss on ignition, TOC, extractable lipophilic substances Eluate: Heavy metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn), anions (Cl^- , F^- , CN^- , SO_4^{2-}), total dissolved solids, DOC, phenol index

The composition of these fractions was combined with the literature data in the earlier-mentioned mixing ratio for calculation of elemental input composition (see Supporting Information S2).

3.2 | Process mass balance

The mass balance results were normalized to 100 kg input masses and are shown in Figure 2a–c. For all batches, 0.20–0.27 kg/kg of the input was discharged via the flue gas cleaning system comprising of exhaust gas (0.17–0.21 kg/kg), boiler ash (0.01–0.02 kg/kg), and filter dust (0.01–0.04 kg/kg). The metal-rich and mineral solid residues left the process via the WSP and account for 0.73–0.80 kg/kg.

After drying and sieve classification of the samples, more homogeneous grain size fractions were obtained. Extrapolated to the normalized input, these grain size fractions account for 0.20–0.25 kg/kg FGF (<2 mm), 0.05–0.06 kg/kg MGF (2–10 mm), and 0.48–0.53 kg/kg CGF (>10 mm) in relation to the normalized plant input (see Supporting Information S2). Comparing the three batches shows similar mass distributions of the output fractions across both the flue gas path and the solid treatment residues. Slight differences are observed for the treatment of LIB.

3.3 | Characteristics and recyclability assessment of EBT output

3.3.1 | Coarse-grain fraction (CGF)

After treatment, the CGF contained both completely opened and cracked battery sleeves. The latter still contained their components and fine mineral material, while volatile constituents were released to the gas phase. Subsequent manual sorting and opening of the cracked sleeves resulted in a proportion of 0.15–0.19 kg/kg of pure battery sleeve cases (hereinafter referred to as sleeve scrap) without adhesions and 0.25–0.36 kg/kg of sleeve content. As shown in Figure 3a, the sleeve scrap analysis showed that the AZ is comprised of low-alloyed steel with 0.98 kg/kg Fe, whereas the LIB sleeve scrap contains more alloying elements, such as Ni (0.04 kg/kg), Cr (0.04 kg/kg), and C (0.01 kg/kg).

The sleeve contents of all battery systems contained about 0.50 kg/kg ferromagnetic constituents (Fe, Ni). The ED-XRF screening showed Mn (0.25 kg/kg) and Zn (0.08 kg/kg) as the AZ fraction's main constituents (see Figure 3b). Other constituents were present in low mass fractions. The LIB sleeve content is characterized by higher material diversity with several elements in mass fractions between 0.02 and 0.04 kg/kg (Al, Cu, Fe, Zn, Si, Ni).

Direct metal recycling of the CGF fraction is only possible considering the impact of pollutants from the more heterogeneous sleeve contents and may require conditioning in line with subsequent use. The investigations showed that the steel qualities in AZs and LIBs are different: low-alloy steels are used in AZ batteries, while higher-alloy steels were identified in LIBs. Joint metal recycling of the sleeve scrap is possible, accepting a downcycling of the LIB steel fraction. Provided that S, Se, Sb, and Cu are within the acceptance range, the LIB sleeve content can be used to produce alloy steel. Due to its high metal content, the LIB sleeve content remaining in the CGF is different from the FGF released by thermal treatment and thus could be of interest for copper recycling with integrated nickel and cobalt recovery. For the AZ coarse fraction, separation of the sleeve scrap from the remaining contents is not necessary. Based on the composition, this fraction could be used to produce a pig iron–manganese alloy (e.g., in the DK process with zinc recovery; DK Recycling und Roheisen GmbH, 2009), provided that it contains no accompanying interfering elements.

3.3.2 | Medium-grain fraction (MGF)

Figure 3c shows the composition of the MGF that differs strongly from the FGF. For all three batches, the magnetic separation resulted in approximately 0.50 kg/kg ferromagnetic metals. The non-ferromagnetic fraction of AZs consists mainly of Mn and Zn (oxidized MnO_2 and ZnO). Except for slightly higher Cu contents (approximately 0.01 kg/kg), the ED-XRF screening showed no significant impurity contents for the AZ MGF. This Cu content is within the acceptance range, making direct recycling of 0.75 kg/kg of the AZ MGF possible in the DK process or steel processing.

In contrast, the non-ferromagnetic components of the LIB MGF are present in lower mass fractions (0.12 kg/kg Mn, 0.08 kg/kg Al, 0.05 kg/kg Fe, 0.04 kg/kg Cu), which are too low and heterogeneous for recycling in one of the metal routes considered.

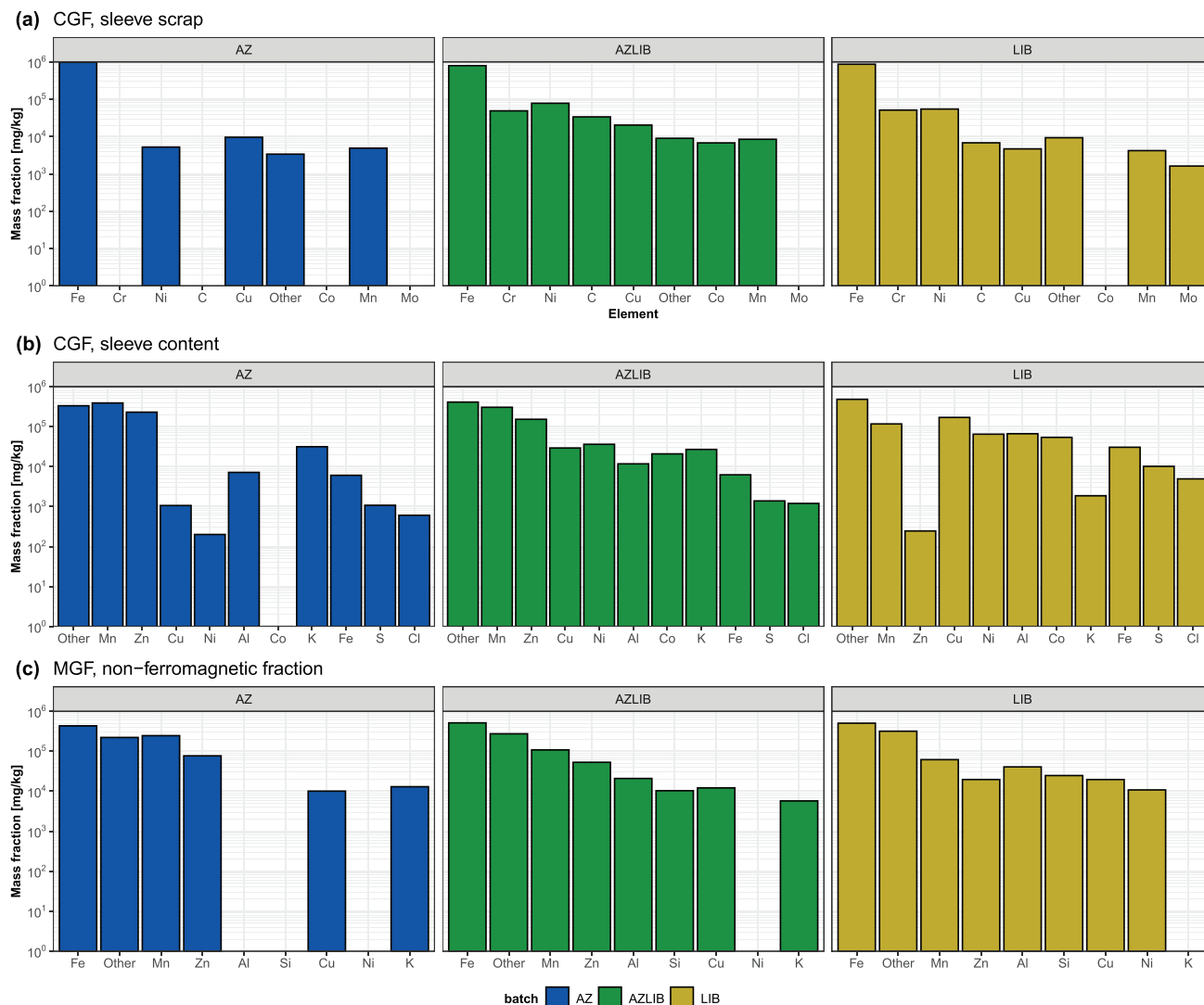


FIGURE 3 Elemental mass fractions in the coarse-grain fraction (CGF): (a) sleeve scrap, (b) sleeve content as well as the (c) non-ferromagnetic medium-grain fraction (MGF). The underlying data for this figure can be found in Supporting Information S2

3.3.3 | Fine-grain fraction (FGF)

The chemical compositions of the burned-out FGF (LOI < 0.01 kg/kg) of AZs and LIBs differ significantly from each other. AZs show higher contents of Fe, Zn, and Mn (>0.10 kg/kg). In contrast, the LIB fine material shows a much higher material diversity. With wet chemical analysis, 0.42 kg/kg (LIBs) to 0.74 kg/kg (AZs) of the FGF material composition could be identified (see Figure 4b,d,f). Assuming that the FGF main components are present as stable metal oxides, calculated oxygen contents of 0.21–0.26 kg/kg are obtained (see Figure 4). The FGF main constituents in the AZ fraction are Fe (0.24 kg/kg), Zn (0.24 kg/kg), and Mn (0.20 kg/kg) with a mass fraction above 0.20 kg/kg TS. The main constituents of LIBs are Mn (0.16 kg/kg), Fe (0.06 kg/kg), Al (0.04 kg/kg), and Cu (0.02 kg/kg), whereas AZLIBs contained mainly Mn (0.17 kg/kg), Zn (0.11 kg/kg), Fe (0.06 kg/kg), Al (0.04 kg/kg), and Cu (0.02 kg/kg). Organic pollutants such as PCBs, PAHs, or CHCs were not detected.

Comparing the FGF characteristics with requirements for metal recycling, construction material recycling, backfilling, and landfilling did not reveal any clear recycling options for all batches. Figure 5 shows the FGF characteristics normalized to the specifications of LAGA M20/M19, landfill classes (LC 0-III), and the Stowage Ordinance for backfilling. The recyclability for metal recycling was estimated via the main components (see Table 1) and validated by individual queries to the respective industry.

For AZs, the high content of Fe, Zn, and Mn (Figure 4a) allows for integrated recycling in pig iron production (DK process), steel recycling, or use as a construction material. However, the limits for halogens and heavy metals in the eluate must be met as a prerequisite. The content of Zn, Ni, and Cu exceeds the specifications (Figure 5b) for backfilling. In the eluate, exceedances of As and Cl are limiting. The DOC content is generally too high for possible landfill. However, given possible alternatives, backfilling or landfilling for AZs is not necessary.

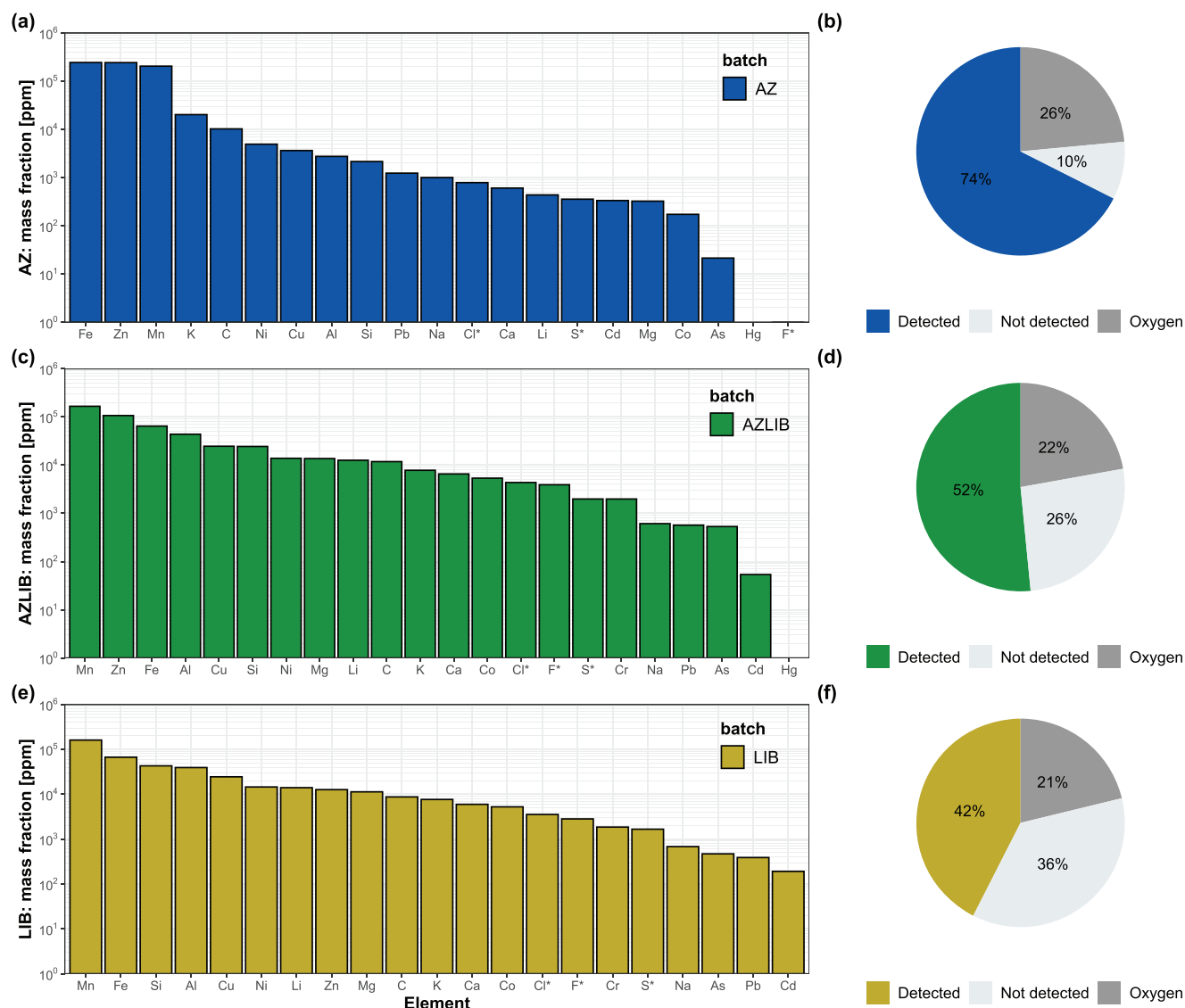


FIGURE 4 Element mass fraction of the FGF for AZ (a), AZLIB (c), and LIB (e) with the respective mass share of identified elements and oxygen (b, d, f). The underlying data for this figure can be found in Supporting Information S2

The heterogeneous composition of lithium batteries, which contain both valuable and harmful substances in low mass fractions (Figure 4c), impedes RR options. The contents of valuable substances (such as Cu, Ni, Zn, Fe) are too low for metallurgical processes (pig iron, steel, copper; see Supporting Information S1), whereas the allocation values for backfilling are exceeded (Figure 5b). High contents of As, Cd, F, Cl, and Mo in the eluate and As, Cd, and Cr in the solids interfere with all RR options (Figure 5a). High contents of disturbing halogens can be traced back to individual battery systems (e.g., F from $\text{Li}(\text{CF})_n$ and Cl from LiSOCl_2). However, the As, Cd, and Cl contents are limiting for usage as construction materials. Under certain circumstances, recycling as construction material may be possible after further processing and immobilization or segregation of halogens and heavy metals. Use in the cement industry requires case-by-case examination and further long-term elution tests. The problem of recovering this polymetallic and heterogeneous material is illustrated particularly well by the fact that all landfill class limits are exceeded.

Joint treatment of LIBs and AZs leads to unintended reduction of valuable substances (see Figures 3 and 4) and does not yield compliance with limit values or RR specification. Finding appropriate RR options for AZLIBs is thus approximately as difficult as for LIBs. The complete results can be found in Supporting Information S2.

3.4 | Input-output balance

The input-output (I/O) balancing of target elements enables us to draw a conclusion about process sinks and check the plausibility of mass conservation. Elements with more than one mass percent of the total process output (Al, Co, Cr, Cu, Fe, K, Mn, Ni, Zn, Cd, and Pb) were considered. For AZs,

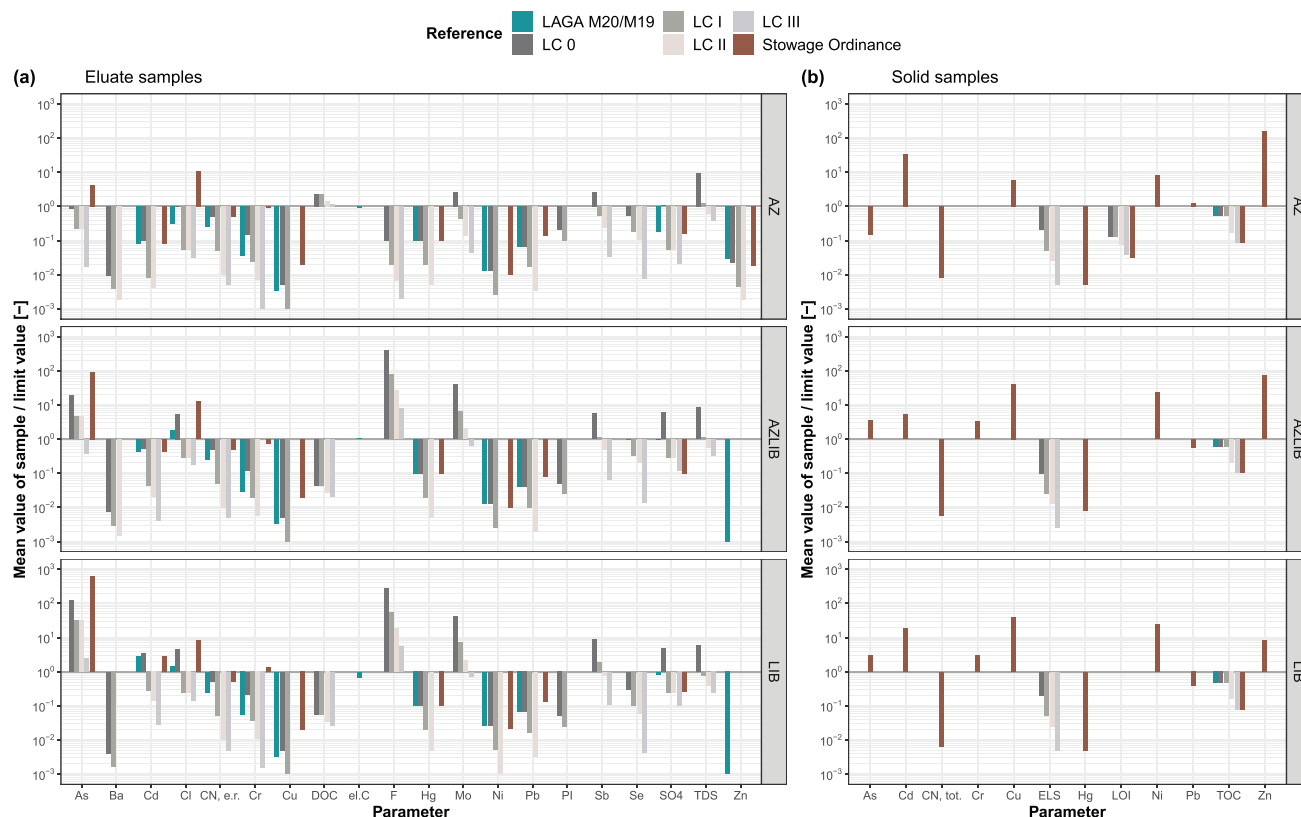


FIGURE 5 Deviation from the limit value (sample mean/limit) for eluates (a) and solids (b), referencing LAGA M20/M19, landfill classes (LC 0-III), and Stowage Ordinance for backfilling. Easily releasable cyanide (CN, e.r.), dissolved organic carbon (DOC), extractable lipophilic substances (ELS), loss on ignition (LOI), phenol index (PI), total dissolved substances (TDS). The underlying data for this figure can be found in Supporting Information S2

the results in Table 2 show the approximate match (output divided by input O/I) between the element mass in the output and the calculated input composition. For LIBs, slight differences between input and output are observed. Lower Al and Co contents were measured, whereas the Cu, Fe, and Mn contents matched well. Increased Cr and Ni contents in LIBs and AZLIBs can be traced back to the alloyed steel sleeves. The low Al content can be explained, among other things, by the challenges of ED-XRF analysis for light elements in complex matrices (Mählitz et al., 2019). The low Co content in LIBs and AZLIBs is plausible due to the prior separation of cobalt-rich lithium subsystems. In summary, the I/O balancing proves EBT plausibility and shows an approximate match between input and output characteristics. Thus, the EBT approach can serve as a characterization method for complex battery flows to infer their approximate elemental composition.

As part of the revision of the Battery Directive, new measures and requirements will be imposed on lithium-ion batteries, among others, which include, for example, element-specific recycling efficiencies and the verification of heavy metal contents (Cd, Pb) (European Commission, 2020a). The EBT approach can provide this information as demonstrated in Table 2, which shows the element-specific recycling efficiencies of the target elements. The minimum RE (RE_{\min}) considers the target element in the recyclable fraction of the output, whereas the maximum RE (RE_{\max}) also considers the potentially recyclable fraction. A very low RE is observed for elements in LIB and AZLIB, which are predominantly present in the FGF (e.g., Li).

4 | DISCUSSION

This section discusses the EBT approach's contribution to assessing and improving recyclability and its use in characterizing mixed battery waste flows from the urban mine.

TABLE 2 Mass fraction of selected target elements in input and output (data in mg/kg)

Batch	Element	AZ				AZLIB				LIB				
		Input	Output	O/I	RE ^a	Input	Output	O/I	RE _{min}	RE _{max}	Input	Output	O/I	RE _{min}
Al	3,400	3,000	0.88	1.00	17,400	16,000	0.92	0.00	0.32	27,100	28,000	1.03	0.00	0.65
	100	70	0.70	1.00	80	10	0.13	0.00	0.00	70	50	0.71	0.00	0.00
Co	35	35	1.00	1.00	8,000	9,900	1.24	0.12	0.86	17,300	14,700	0.85	0.00	0.91
Cr	1	0	-	-	4,400	9,000	2.05	0.95	0.95	11,300	12,200	1.08	0.97	0.97
Cu	1,800	3,500	1.94	1.00	21,600	20,500	0.95	0.17	0.70	53,200	50,300	0.95	0.02	0.88
Fe	242,000	262,000	1.08	1.00	179,700	181,000	1.01	0.76	0.91	221,000	246,000	1.11	0.81	0.93
K	14,500	15,000	1.03	1.00	9,900	11,700	1.18	0.00	0.84	2,500	2,400	0.96	0.00	0.19
Li	0	90	-	-	1,500	3100	2.07	0.00	0.00	3,000	3,500	1.17	0.00	0.00
Mn	193,000	189,000	0.98	1.00	162,000	155,500	0.96	0.01	0.73	82,700	72,600	0.88	0.01	0.45
Ni	1,000	2,100	2.10	1.00	23,800	29,800	1.25	0.46	0.88	33,100	32,700	0.99	0.38	0.89
Pb	1,000	250	0.25	1.00	300	140	0.47	0.00	0.00	600	100	0.17	0.00	0.00
Zn	134,000	131,000	0.98	1.00	85,300	82,900	0.97	0.00	0.68	5,000	4,100	0.82	0.00	0.23

Comparison of output and input (O/I) and element-specific recycling efficiencies (RE). RE_{min} refers to recyclable content whereas RE_{max} includes the potentially recyclable content.
^aFor AZ, RE_{min} equals RE_{max}.

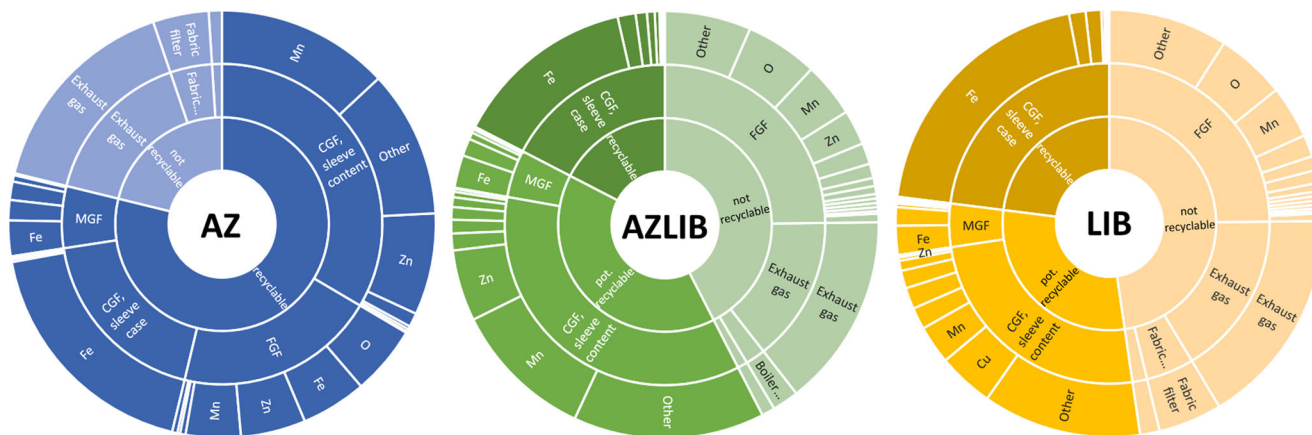


FIGURE 6 Proportions of recyclable, nonrecyclable, and potentially recyclable components after further treatment

4.1 | Recycling efficiency of thermal treatment

Thermal treatment allows cost-efficient and safe treatment of low-value batteries with a high explosion risk. The high temperatures crack all sleeves, releasing the electrolyte, rendering the active material inert, and producing an inactive burned-out material comprising metal and mineral fractions. However, in terms of high RE, 0.17–0.22 kg/kg of volatile constituents are lost in the first step via flue gas and are thus non-recyclable (see Figure 6).

While most of the metal-rich CGF and medium-grain fraction (MGF) can be recycled in subsequent metal-recycling processes, the fine-mineral fraction (FGF) of LIBs and AZLIBs consists of heterogeneous material mixtures bearing low contents of valuables and pollutants. The scenario of treating AZs and LIBs jointly did not result in process or output quality improvements with constant or higher RE. Compared to the pure AZ fraction with an overall RE of 79%, AZLIBs result in lower sleeve scrap qualities and higher material diversity of the mineral fraction that lowers RE. For all batches, the proportion of metal scrap is the decisive material fraction relevant for determining total recyclable content and meeting mass-based RE targets. The EBT results showed that the potentially recyclable components could be made available for recycling by subsequent crushing of the closed battery sleeves and adjusting the screen diameter from 10 to 2 mm to separate the heterogeneous fines (FGF). Thus, RE of more than 50% by mass is achievable for lithium-based systems provided that the metal content of battery sleeves does not decrease, which is regarded as critical in view of the low-metal battery pouch cells.

The results indicate that separation and subsequent thermal treatment of low-value batteries can achieve the specified RE targets. Consequently, the legally required RE for the low-value battery mixtures addressed in this study can be achieved with thermal treatment. Given that the mass share of low-value batteries is expected to grow continuously (Huisman et al., 2017), separate treatment of subsystems must be the goal if subsystems are identifiable in sorting. The scenario of separating AZs and LIBs and subsequent recycling (EBT1 and EBT3) enables better recycling and recovery (RR) options due to more homogeneous material characteristics and increases the RE.

4.2 | EBT for recyclability assessment of batteries

The product-centric RA described in DIN EN 45555 (2019) is only applicable if a product is treated and recycled separately. As a result of available collection and treatment infrastructures as well as product identifiability and separability into chemical battery subsystems, however, the recyclability of the product is more dependent on the recyclability of the waste flows in which the products are collected.

Consequently, both easily and poorly recyclable products influence the RE and thus the recyclability of other products in the waste flow. Waste flow characteristics and the selection of recycling processes are thus decisive factors influencing individual product recyclability. These factors must be considered for an improved description of EoL scenarios aiming to include the technical aspects in RA (DIN EN 45555, 2019). However, these data are not yet available on a sufficiently detailed level. EBT can help to fill necessary data gaps in RA here. Batch tests that are legally required to determine RE (Directive 2006/66/EC on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC, 2006/26.09.2006; Commission Regulation (EU) No 493/2012, 2012) can be extended by including the product focus on the input and evaluation of potential RR to allow characterization of mixed battery waste flows regarding technical recyclability and allocation of RE to battery subsystems. Further, EBTs can identify battery (sub)systems containing elements such as Cl and F that prevent recycling options by exceeding limit values. Furthermore, the detailed results of the EBT and the comparison with RR options can be used to define end-of-waste criteria (European

Commission, 2018) to create legal certainty and a level playing field as well as remove unnecessary administrative burdens (European Commission, 2021). However, this depth of information requires an equally higher (analytical) effort, as this study shows.

Nevertheless, representative RA results for one battery subsystem require data on the characteristics of all waste flows in which the product is present. Data from different studies on other treatment processes must be collected in a harmonized way to determine the product recyclability independent of a process, providing comparable results that are representative for the corresponding product (Commission Regulation (EU) No 493/2012, 2012). Making results from the EBT approach available, for example, in an urban mine knowledge database (Huisman et al., 2017; Korf et al., 2019; Mähltitz et al., 2020) as a possible extension of the Raw Material Information System (RMIS) (EU Science Hub, 2021), is seen as a long-term goal of improving RA. This knowledge allows the calculation of recyclability in different scenarios and the assessment and definition of targets effectively focusing on the most (environmentally) relevant materials.

For LIBs and AZLIBs, this study showed that separating low-value batteries from the mixed lithium battery waste flow can lower the recyclability of the waste flow. This separation results in lower RE of the considered waste flows, favoring higher RE of the better recyclable and more valuable subsystems of the main flow. Vice versa, without separation of low-value systems from the main flow, RE is decreased in favor of meeting fixed mass-based RE targets. Therefore, we recommended linking efficiency targets to the incoming battery waste flow's recyclability rather than static mass-based targets since maximum material recovery was not always favorable under environmental aspects (Mohr, Peters, et al., 2020). Thus, the safe treatment of currently minor flows of separated low-value battery mixtures becomes feasible and legally compliant. Nevertheless, the results from the EBT approach must be included in future RA to derive both eco-design guidance that includes technical recyclability (DIN EN 45555, 2019) and guidance for recycling processes to cope with challenging waste flows not yet properly recyclable.

4.3 | High-quality recycling

High-quality recycling is mentioned in the amended waste framework directive (WFD) (European Commission, 2018), which is an essential component of CE measures and should be prioritized when deciding between recycling options. However, the RE calculation is based on the definition of recycling from the WFD and does not distinguish between high quality and downcycling. At present, there are no standardized methods for evaluating recycling quality. For example, environmental performance (Reuter et al., 2015), environmental relief (Geyer et al., 2016), and the cumulative energy input of recycling processes (Schäfer, 2021) are used to calculate recycling quality. A next step in weighing recycling processes would be development of a systematic and harmonized evaluation method for high-quality recycling based on a solid database of modeling and empirical surveys such as the EBT approach.

In terms of generating pure and defined output qualities, thermal treatment of low-value batteries does not represent high-quality recycling for all scenarios examined here. In particular, the generated mixed mineral fraction of the LIB or AZLIB fraction must be critically considered. After separating the remaining metal components, high-quality recycling of the mineral fraction is hindered by insufficient contents of valuable materials and the presence of disturbing impurities. Thus, the EBT approach can be used to assess high-quality recycling by providing comprehensive output characterization for comparison with detailed recycling specifications. Thermal treatment of the investigated battery mixtures primarily serves the purpose of safe and legally compliant treatment to achieve mass-based RE targets. In the future, backfilling and downcycling of metal alloys will have to be excluded as recycling options in the sense of a CE.

5 | CONCLUSION

This study demonstrates how the EBT approach was designed and can be applied to (1) determine RE, (2) approximately infer elemental input composition, and (3) identify problematic battery subsystems that prevent recycling options.

The EBT approach encompassing three scenarios for the thermal treatment of low-value battery systems showed that 0.20–0.27 kg/kg of battery components are lost via flue gas and about 0.15–0.19 kg/kg can be recycled as steel scrap. However, while the mineral fraction of the zinc-based AZ fraction can be recycled (overall RE of 79%), the heterogeneous elemental composition of lithium-based batteries negatively affects the recyclability of the mineral fraction with an overall RE of 0.52–0.58 kg/kg. In particular, individual battery subsystems contribute to the entry of interfering substances such as halogens. Nevertheless, LIBs and AZLIBs can achieve static mass-based RE targets with further processing.

In conclusion, the results from the EBT approach in simulating different collection and sorting scenarios for batteries can serve as the basis for assessing and improving the recyclability of both the treated waste flow and battery subsystems. Harmonized data from sorting and treatment trials are essential for achieving and evaluating CE measures. Furthermore, with appropriate methodological extension of such batch tests, the EoL data generated could serve multiple purposes, such as determining technical recyclability, and should be made available for product design and evaluation of realistically achievable RE.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supporting information of this article.

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SUPPORTING INFORMATION

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9. Article III

Characterizing the Urban Mine—Challenges of Simplified Chemical Analysis of Anthropogenic Mineral Residues

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Article

Characterizing the Urban Mine—Challenges of Simplified Chemical Analysis of Anthropogenic Mineral Residues

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Abstract: Anthropogenic mineral residues are characterized by their material complexity and heterogeneity, which pose challenges to the chemical analysis of multiple elements. However, creating an urban mine knowledge database requires data using affordable and simple chemical analysis methods, providing accurate and valid results. In this study, we assess the applicability of simplified multi-element chemical analysis methods for two anthropogenic mineral waste matrices: (1) lithium-ion battery ash that was obtained from thermal pre-treatment and (2) rare earth elements (REE)-bearing iron-apatite ore from a Swedish tailing dam. For both samples, simplified methods comprising ‘in-house’ wet-chemical analysis and energy-dispersive X-ray fluorescence (ED-XRF) spectrometry were compared to the results of the developed matrix-specific validated methods. Simplified wet-chemical analyses showed significant differences when compared to the validated method, despite proven internal quality assurance, such as verification of sample homogeneity, precision, and accuracy. Matrix-specific problems, such as incomplete digestion and overlapping spectra due to similar spectral lines (ICP-OES) or element masses (ICP-MS), can result in quadruple overestimations or underestimation by half when compared to the reference value. ED-XRF analysis proved to be applicable as semi-quantitative analysis for elements with mass fractions higher than 1000 ppm and an atomic number between Z 12 and Z 50. For elements with low mass fractions, ED-XRF analysis performed poorly and showed deviations of up to 90 times the validated value. Concerning all the results, we conclude that the characterization of anthropogenic mineral residues is prone to matrix-specific interferences, which have to be addressed with additional quality assurance measures.

Keywords: multi-element chemical analysis; mineral residues; simplified chemical analyses; lithium battery ash; mining waste; urban mine; recycling; resource recovery

1. Introduction

Anthropogenic mineral residues are low-grade inorganic resources that arise as by-products or wastes from the extraction of primary raw materials or recycling processes (synthetic minerals) with

high annual mass flows [1]. Recently, these residues came into focus, as they play a significant role in the European Union (EU) Raw Materials Initiative ‘RMIS’ [2] to recover secondary raw materials from the urban mine and ensure raw material supply. In addition to increasing resource efficiency, the strategies of the EU RMIS for securing the supply of raw materials include the characterization of mineral residues from the urban mine and the creation of an improved knowledge database for mineral deposits [2]. Extraction from anthropogenic ores is to be considered, particularly if elements (a) occur in high mass fractions, (b) are of environmental concern, or (c) economically interesting to be recovered, e.g., due to the classification as a critical element defined by the EU [3].

For an improved urban mine knowledge database, as well as for the evaluation of recoverability and compliance with environmental limits, valid information on the composition or presence of individual elements is essential. Prerequisites for this information are suitable and quality-assured analytical methods with proven applicability (specific to element and sample), high accuracy, and repeatability of the measurement for the respective sample matrix.

However, chemical analysis of the anthropogenic mineral samples is often challenging, due to element variety, matrix complexity, and material heterogeneity. These characteristics lead to the fact that analytical quality assurance using, e.g., standardized operation procedures or matrix-specific certified reference materials are intricate and elaborate. The chemical analysis of anthropogenic mineral residues lacks applicable reference methods, so that the methods that are used for similar sample matrices often vary. An indicative literature review showed that the methods that are applied for multi-element chemical analysis of anthropogenic ores are based on various references, comprising general national and international standards for waste, soil, and water [4–7] or individual methods that were developed and validated for a specific application. The procedures include sample preparation by means of fusions [8] or acid digestion with various acid blends comprising sulfuric acids [9–14], nitric acids [15], aqua regia [16,17], hydrochloric, hydrofluoric, nitric, and perchloric acids [18], or other blends [11,19,20]. Measurement methods comprise non-destructive X-Ray Fluorescence (XRF) [19,21,22], Inductive Coupled Plasma (ICP) with Optical Emissions Spectrometer (ICP-OES) [9–11,14–16,19,20,23–27], and Mass Spectrometry (ICP-MS) [19,28] or Atomic Absorption Spectrometry (AAS) [9–15,17,26,29].

Validated methods aim to generate reliable results under consideration of the material complexity, and thus the high variability of the influencing effects caused by, e.g., complexing, precipitation, volatilization, interferences, and measurement inaccuracies [8]. Consequently, the analytical effort increases, since multiple method variations must be tested, such as measurement devices, mode settings, reagents, and the additional measurement of potentially disturbing elements. This complexity leads to the consideration of method simplifications, which reduces the expenditure of the analytics or allows for examining a higher number of primary samples in order to evaluate the sampling uncertainty better. However, procedural modifications and simplifications carry the risk that systematic errors lead to significant deviations from the true analytical value, as demonstrated for multi-element chemical analysis of other organic-rich waste matrices, such as Paper/Cardboard and Composites [30] or printed circuit boards [31].

In this article, we assess the applicability of simplified multi-element chemical analysis methods for complex mineral waste matrices that show highly different mass contents of many elements. This study is part of an extensive effort to investigate multi-element chemical analysis of different anthropogenic ore matrices, addressing printed circuit boards [31], automobile shredder residues (submitted to recycling), and mineral residues (this article). The overall objective of this research effort is to examine the sample- and element-specific effects of multi-element chemical analysis on the resulting compositional data.

This study was conducted on two mineral waste samples that were obtained from the thermal pre-treatment of lithium-ion batteries and an iron-apatite tailing dam. Firstly, the matrix-specific validated methods were developed to determine the elemental composition of the samples. Secondly, the results were compared to more simplified methods comprising non-destructive energy-dispersive X-ray fluorescence (ED-XRF) spectrometry and routine ‘in-house’ wet-chemical methods. Method

validation was performed by spiking experiments of liquid standards, blank samples, as well as in the sample matrix. The applicability of the simplified methods was checked by the relative difference from the validated values and a significance test (Welch's *t*-test).

2. Materials and Methods

2.1. Sample Origin and Physical Sample Preparation

Two anthropogenic mineral samples were used to assess the applicability of simplified multi-element chemical analysis methods. The samples have a similar matrix, i.e., they are inorganic, completely oxidized, and have a high element diversity. The origin, sampling, and physical sample preparation are explained in the following.

2.1.1. Battery Ash Sample (BATT)

The battery ash sample (BATT) originates from the thermal pre-treatment of approximately 10 t of cobalt-poor lithium batteries and accumulators. The lithium batteries that were investigated comprise a large number of different chemical subsystems consisting of the following components: metal sleeve, positive electrode (e.g., LiFePO_4 , LiCoO_2 , LiNiO_2 , LiMn_2O_4 , Li/SOCl_2 [32]), negative electrode (metal oxide that also intercalates Li-ions, such as Li_xCoO_2 , Li_xNiO_2 , or $\text{Li}_x\text{Mn}_2\text{O}_4$), electrolyte (organic solvents with salts, such as LiPF_6 or LiAsF_6), and separator foils (Al, Cu) [33].

The batteries were continuously placed over 24 h in a brick-lined rotary kiln and thermally treated at approximately 850 °C, after the removal of all residual incinerated material. The battery cases immediately exploded due to the chemically bound residual energy, so that the contained components were almost completely liberated. As a result, the volatile components, such as the electrolyte, were transferred to the gas phase and separated by built-in filter systems. The remaining mineral masses oxidized almost entirely at a residence time of approx. 30 min. Before being sieved at a mesh size of 30 mm, the process output went through an installed water quench, which was used to cool down the sample material and impede further incineration reactions. The main constituents of the coarse material were metal sleeves and construction aids, such as screws or metal grids. The mineral fine fraction that accounted for approximately 40% of the total process input was sampled according to 'Guideline for the procedure for physical, chemical and biological investigations in connection with the recycling/disposal of waste to the guideline for sampling (LAGA PN98)' [34]. Subsamples were taken, mixed, and reduced to a lab sample of 40 L final volume.

The lab sample was dried at 105 °C, according to DIN EN 14346 'Characterization of waste—Calculation of dry matter by the determination of dry residue or water content' [35]. Subsequently, a sieve analysis machine (Haver EML digital plus) was used to sieve the dry material to a particle size < 1 mm. This material was further ground to a final particle size < 0.2 mm while using a planetary mill (Retsch PM400) in combination with tungsten carbide grinding bowls (see Figure 1a) and it constitutes the sample that was investigated in this study. The powdery sample mainly consists of the inorganic electrode material and it still contains metallic and other valuable constituents.

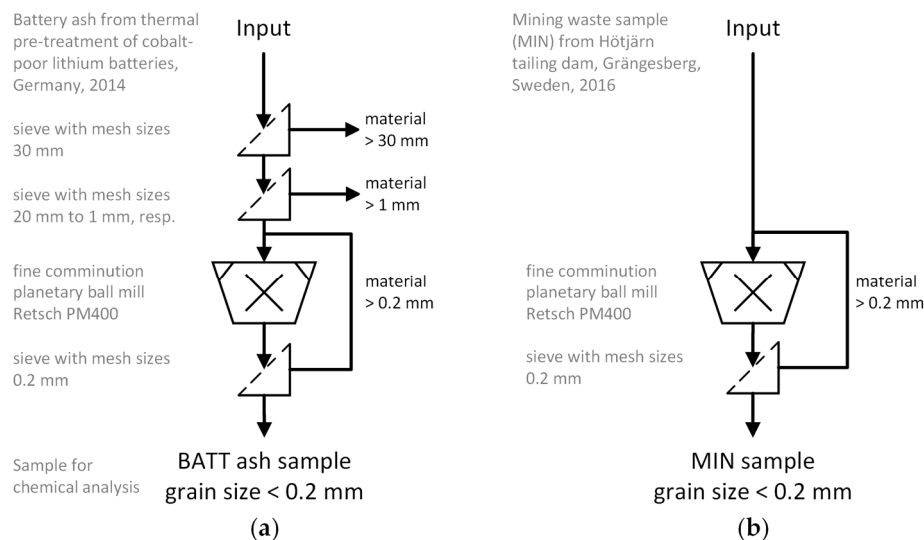


Figure 1. Scheme of mechanical processing for the battery ash sample (a) and mining waste sample (b).

2.1.2. Mining Waste Sample (MIN)

The mining waste sample (MIN) originates from the Hötjärn tailing dam of the concentrator that was located at the Grängesberg deposit in Sweden. Tailings from the Grängesberg deposit are estimated at 5.6 million tons (Mt), of which most were deposited in the Hötjärn tailing dam. The dominant mineral in Grängesberg was apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) with magnetite (Fe_3O_4) [36], containing on average Fe 42.0%, Mn 0.14%, P_2O_5 1.97% [37]. The primary purpose of the ore processing was to enhance the iron metal grade, rather than remove apatite or other constituents from the concentrate [38]. Hence, the apatite minerals are often rich in rare earth elements (REE) [39] or they may contain, depending on their location and extraction technology, other elements that are classified as critical [40], such as Mg, Ga, Si, W, Co, Nb, and V (mass fractions around 1%).

The MIN sample was taken from the upper layer on top of the Hötjärn tailing dam. Approximately 10 kg of the dark gray and powdery sample material was mixed and then reduced to a 2 kg laboratory sample. A planetary ball mill (Retsch PM400) with tungsten carbide grinding bowls was used to grind the material to a particle size of <0.2 mm. Subsequently, a rotary sample divider (Retsch PTZ) was used to create 64 aliquots for the chemical analysis. Figure 1b shows the mechanical processing of the mining waste sample.

2.2. Chemical Analysis

2.2.1. General Approach

For each of the two samples, chemical analyses were performed comprising of a sophisticated validated method, a simplified wet-chemical in-house method, and non-destructive energy-dispersive X-ray fluorescence (ED-XRF) analysis.

Firstly, validated methods were developed by Empa, Advanced Analytical Technologies (L1) by undertaking an element-specific and extensive investigation according to DIN EN ISO/IEC 17025 'General requirements for the competence of testing and calibration laboratories' [41]. Wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry and wet-chemical analysis using Inductively Coupled Plasma (ICP), in combination with Optical Emissions Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS) for element detection were employed. The wet-chemical analysis was validated while using sophisticated testing of, among other things, varying acid mixtures, measurement settings, as well as gas reaction and collision modes for ICP-MS. Method validation was realized with (1) analysis of potentially interfering elements, such as oxygen, carbon, and halogens, (2) element

spikes added before digestion, (3) dilution experiments, and (4) the use of certified standard reference material for MIN (CCRMP REE-1 from National Resources Canada [42]).

Secondly, routine in-house wet-chemical methods were carried out at Technische Universität Berlin, Chair of Circular Economy and Recycling Technology (L2), while applying general quality assurance measures, also based on DIN EN ISO/IEC 17025. The term ‘in-house methods’ refers to procedures that are assessed in-house according to national and international guidelines and standards, such as DIN EN 13657 ‘Characterization of waste-Digestion for subsequent determination of aqua regia soluble portion of elements’ [4]. The in-house methods are based on the validated methods, but apply simplification, which represents common procedures for routine analysis with usual resource constraints. Simplifications comprise standard measurement settings for general sample matrices, the avoidance of hydrofluoric acid (HF) for digestion, and the limitation of helium as the reaction gas for ICP-MS. Nevertheless, for a better comparison, the element detection was done while using the same element masses (ICP-MS) and spectral lines (ICP-OES), if applicable. Element recovery rates in liquid standards, blanks, and samples served for method validation.

Thirdly, ED-XRF spectrometry was employed by L2 to analyze both of the samples.

Finally, the results of in-house and ED-XRF measurements were compared to the reference values that were determined with the validated methods to assess the applicability of simplified methods and to identify particularly difficult cases.

2.2.2. Element Selection

Factors, such as sample origin, the criticality of elements [40], ED-XRF pre-scan results, and potential chemical interferences that affect the analysis result were considered for the selection of elements. The elements were grouped in ferrous metals (Cr, Fe, Mn, Nb, Ni, V), non-ferrous metals (Al, Co, Cu, Mg, Pb, Sn, Ti, Zn), precious metals (Au, Pd), specialty metals (As, Ba, Cd, Ga, Li, Sb, Sr, W, Zr), rare earth elements (Ce, Dy, Gd, La, Nd, Pr, Sm, Y, Yb), and other elements (Ca, Cl, K, P, Rb, Si). Among these elements, Co, Ga, Mg, Nb, P, Pd, Sb, W, and all REE were classified as critical raw materials for the European Union in 2017 [40]. As, Cd, Cr, and Pb, are particularly relevant for compliance with environmental limit values. In addition to Cl, F was determined with the validated method, since halogens can lead to interferences that are caused by precipitation as a result of salt formation with metals [8]. The determination of C and O was used to characterize the sample matrix and to select the digestion acids. A total of 19 elements for BATT and 32 elements for MIN were selected, analyzed, and used for comparison with the simplified methods (see Table 1).

Table 1. Element group and elements measured in the Battery Ash Sample (BATT) and Mining Waste Sample (MIN) sample.

Element Group	Battery Ash Sample (BATT)	Mining Waste Sample (MIN)
Ferrous metals	Fe, Mn, Ni, V	Cr, Fe, Mn, Nb ^c , Ni, V
Non-ferrous metals	Al, Co ^c , Cu, Pb, Ti, Zn	Al, Co ^c , Mg ^c , Sn, Zn
Precious metals	Au, Pd ^c	-
Specialty metals	As, Cd, Sb ^c	As, Ba, Ga ^c , Li, Sr, W, Zr
REE	Ce ^c , La ^c	Ce ^c , Dy ^c , Gd ^c , La ^c , Nd ^c , Pr ^c , Sm ^c , Y ^c , Yb ^c
Other	Cl, P, F [*] , C [*] , O [*]	Ca, K, P ^c , Rb, Si, C [*] , O [*]

*: not included in comparison but analyzed for interpretation of results and possible interferences, ^c: Classified as critical raw materials [40].

2.2.3. Wet-Chemical Analysis

Table 2 summarizes the wet-chemical analysis of the validated and in-house method for BATT and MIN. The validated wet-chemical analysis of BATT comprised two different reagent mixtures: Acid (1) HNO₃-HCl (aqua regia, AR) and Acid (2) HNO₃-H₂O₂. For wet-chemical analysis of MIN, two reagent mixtures were performed: Acid (1) HNO₃-HCl (aqua regia) and Acid (2) HCl-HNO₃-HF. Additionally,

Acid (3) $\text{H}_2\text{SO}_4\text{-HNO}_3$ was used as the reference digestion for As in both samples to take into account its high volatility as a hydride builder in wet-chemical digestion processes that occur even with closed digestion systems like microwave-assisted digestion (MWD) or high-pressure asher (HPA-S, Anton Paar) [43]. MWD was carried out while using a microwave MLS START, followed by element detection with ICP-OES Varian Vista Pro Radial and ICP-MS Agilent 8800 QQQ. Measurements with ICP-MS were done with an Octopole Reaction System (ORS), varying the reaction gases helium and oxygen.

For in-house wet-chemical analysis of BATT and MIN samples, six replicates were weighed in on 0.2 g ($n = 6$) and then dissolved with microwave-assisted digestion. For BATT, two reagent mixtures were performed for the selected elements based on L1 comprising Acid (1) $\text{HNO}_3\text{-HCl}$ (aqua regia) and Acid (2) $\text{HNO}_3\text{-H}_2\text{O}_2$. The MIN sample was dissolved in one reagent mixture that consisted of 10 mL aqua regia. MWD for BATT and MIN were performed with CEM MarsXpress and CEM Mars 5, respectively. After cooling to approx. 30 °C, all of the solutions were filtered through a Munktel 131 filter (rinsed with 0.5 M HNO_3) in a 50 mL flask and filled up with 0.5 M HNO_3 . The elemental mass fractions were determined with ICP-OES Thermo Scientific iCap 6000 Series and ICP-MS Thermo Scientific iCap Q using kinetic energy discrimination mode (KED) with the reaction gas mode helium as shown in Table 2.

Halogens are of analytical importance due to their high electronegativity and reactivity, which can lead to interferences, for example, which are caused by precipitation due to the salt formation with metals. The total halogen content (F, Cl) in BATT was analyzed with a PARR[®] Oxygen digestion bomb (IKA) with 30 bar of pressure and ion-chromatography (IC) detection following DIN EN 14582 [44] (see Supplementary Materials Table S1). Oxygen and carbon contents were determined with the melting combustion method. Both of the samples were combusted at 3000 °C for O and 2000 °C for C and detected by infrared while using LECO CS844 and LECO TC-500, respectively.

2.2.4. Wavelength Dispersive X-ray Fluorescence Spectrometry (WD-XRF)

In addition to the validated wet-chemical method, the MIN sample was analyzed with WD-XRF. After testing other sample preparations, such as the direct measurement on the powder sample and the production of a wax pellet, the fusion method with the following specifications was selected. A fusion of 8 g Lithium tetraborate and Lithium metaborate was added to 1 g mining waste and then melted at 1200 °C in a muffle furnace Fluxana Vitriox. The melted material was subsequently transferred into a platinum dish. After cooling down, the main elements were directly measured in the standardless measurement mode (10 min) with WD-XRF Primus IV (Rigaku, Japan), following the Empa-SOP No. 6000 (see Table 3). WD-XRF measurement was performed for Al, Ca, Fe, K, Mg, Mn, Na, P, Rb, Si, V, Y, and Zn with replicates of five. Elements with an atomic number $< Z$ 12 cannot be detected with the applied method, since the elements do not provide sufficiently meaningful energy spectra to enable quantification. For quality assurance, the certified reference sample CCRMP REE-1 [42] was included in the measurement series. The detection limit for the elements in the fusion tablet corresponds to approximately 0.01% due to dilution with the fluxing agent.

Table 2. Wet-chemical analysis procedure.

Validated Method								In-House Method			
Microwave-assisted digestion (MWD)											
Samples		BATT			MIN			BATT		MIN	
Device name	MLS START			MLS START			CEM Mars 5		CEM MarsExpress		
Acid (1): mixture	7 mL aqua regia (AR)			7 mL aqua regia (AR)			7 mL aqua regia (AR)		10 mL aqua regia (AR)		
Acid (1): elements	As, Au, Ce, La, P, Sb, Ti			As, Ce, Dy, Gd, La, Li, Nd, Pr, Sm, Yb			As, Au, Ce, La, P, Sb		As, Ba, Ce, Co, Cr, Dy, Ga, Gd, La, Li, Nb, Nd, Ni, Pr, Sm, Sn, Sr, V, Y, Yb, Zn, Zr		
Acid (2): mixture	6 mL HNO ₃ + 1 mL H ₂ O ₂			7 mL aqua regia (AR) + 1.5 mL HF			6 mL HNO ₃ + 1 mL H ₂ O ₂		-		
Acid (2): elements	Al, Cd, Co, Cu, Fe, Li, Mn, Ni, Pb, Pd, V, Zn			Ba, Co, Cr, Ga, Nb, Ni, Sn, Sr, W, Zr			Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Pd, Zn		-		
Acid (3): mixture	7 mL H ₂ SO ₄ + 1 mL HNO ₃			7 mL H ₂ SO ₄ + 1 mL HNO ₃			-		-		
Acid (3): elements	As			As			-		-		
Quality of acids	MERCK HCl 30% (s.p.); MERCK HNO ₃ 65% (s.p.); MERCK H ₂ O ₂ 30% (s.p.); MERCK H ₂ SO ₄ 48% (p.a)			MERCK HCl 30% (s.p.); MERCK HNO ₃ 65% (s.p.); MERCK HF 40% (s.p.); MERCK H ₂ SO ₄ 48% (p.a)			Roth HNO ₃ 69% (s.p.); Roth H ₂ O ₂ 35% (pure)				
Digestion program	Step	Power (W)	Time (min)	Temp. (°C)	Power (W)	Time (min)	Temp. (°C)	Power (W)	Time (min)	Temp. (°C)	Hold. (min)
	1	700	6	150	700	11	200	1600	5	150	6
	2	800	5	200	800	16	240	1600	5	200	5
	3	800	18	215	0	30	0	1600	5	215	18
	4	0	25	0	-	-	-	1600	5	0	25
No. of digestions	<i>n</i> = 5			<i>n</i> = 3			<i>n</i> = 6		<i>n</i> = 6		
Sample mass digested	0.2 g			0.1 g (0.5 g for Acid (3))			0.2 g		0.2 g		

Table 2. Cont.

Validated Method			In-House Method	
Final volume	50 mL (PP tube); filled with 2 mol/L HCl s.p (Acid (1)); H ₂ O deionized (Acid (2) and Acid (3))	50 mL (PP tube), filled with 2 mol/L HCl s.p. (Acid (1) and Acid (2)); H ₂ O deionized (Acid (3))	50 mL (PP tube); filled with 0.5 M HNO ₃	
Validation	Element spikes for samples added before digestion.	Element spikes for samples added before digestion. Dilution experiments (1:10, 1:100). Certified reference material CCRMP REE-1.	Element spikes for samples and blinds added before digestion as well as for liquid standards without digestion.	
Analytical determination				
ICP-OES name	Varian Vista Pro Radial	Varian Vista Pro Radial	Thermo Scientific iCap 6000 Series	
ICP-OES elements	Al, As, Co, Cu, Fe, Li, Mn, Ni, P, Pb, Sb, Ti, Zn	Ce, La	Al, As, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, Sb, Zn	As, Ba, Ce, Co, Cr, Dy, Ga, Gd, La, Li, Nb, Nd, Ni, Pr, Sm, Sn, Sr, V, Y, Yb, Zn, Zr
ICP-MS name	Agilent 8800 QQQ	Agilent 8800 QQQ	Thermo Scientific iCap Q	-
ICP-MS elements	Au (O ₂), Cd (He), Ce (O ₂), La (O ₂), Pd (He), V (O ₂)	As (He), Ba (O ₂), Co (O ₂), Cr (He), Dy (O ₂), Ga (O ₂), Gd (O ₂), Li (He), Nb (O ₂), Nd (He), Ni (He), Pr (O ₂), Sm (He), Sn (He), Sr (O ₂), W (He), Yb (He), Zr (He)	As, Au, Cd, Ce, La, P, Pb, Pd, Sb, Zn	-
ICP-MS gas mode	He (collision), O ₂ (reaction gas)	He (collision), O ₂ (reaction gas)	He (collision)	-

Table 3. Wavelength-dispersive X-ray fluorescence (WD-XRF) analysis procedure for MIN sample.

Specification	Validated Method
Pre-Treatment	
Samples	MIN
Fusion	8 g $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO_2
Sample mass	1 g
Muffle furnace	Fluxana Vitriox
Temperature	1200 °C
Number of replicates	$n = 5$
Validation	Certified reference sample CCRMP REE 1
WD-XRF Measurement	
WD-XRF device name	Primus IV (Rigaku, Japan)
Calibration	Standardless calibration
X-ray source	Rhodium source 4 kW
Measurement time	10 min
WD-XRF elements	Al, Ca, Fe, K, Mg, Mn, Na, P, Rb, Si, V, Y, Zn
LOD	Approximately 0.01%

2.2.5. Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF)

Chemical analysis using ED-XRF is gaining importance for fast and non-destructive testing. This technology is used for the analysis of scrap metals or soil samples and, more recently, for the analysis of additives in plastics [45–49]. ED-XRF analysis was conducted by L2 with a handheld 50 keV ED-XRF ‘NITON XL3t-Air’ (Analyticon). Without further sample preparation, the powdery material was transferred to the sample cups (SC-4331 by FluXana) while using a polypropylene foil. The subsamples (seven for BATT, eight for MIN) were measured in ‘MINING’ mode with a total measuring time of 120 s, 30 s per filter: main, low, high, and light. The limits of detection (LODs) vary element-wise from a few ppm to a few hundred ppm for light elements, such as Mg [50]. Elements with an atomic number less than Z 12 cannot be detected. Limit of quantification (LOQ) is approximately 0.05%. This instrument is calibrated for the following elements in a mineral SiO_2 matrix (MINING mode): Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, Hf, Ta, W, Re, Pt, Au, Pb, La, Ce, Pr, Nd, Th, and U. The number of individual measurements per subsample was 36 for BATT and 24 for MIN. If the double standard deviation of one measurement is more than 0.5 times the measured value, the ED-XRF returns ‘<LOD’ and the number of measurements per sample decreases.

2.3. Data Analysis

Firstly, material homogeneity was checked while using the ED-XRF pre-scanning results and ANOVA F test. Secondly, method accuracy was assessed based on element recovery rates using spiking tests with and without the sample matrix. Thirdly, consistency between the results that were obtained with simplified and validated methods was tested regarding significance while using a t -test and relative difference.

2.3.1. Test of Sample Homogeneity

Material homogeneity for the tested materials is a prerequisite to allow for the comparison of the different chemical analysis methods and to exclude deviations due to the heterogeneous distribution of elements. Sample homogeneity was tested element-wise with ANOVA F test [51] while using the ED-XRF results, by comparing the variance between the n subsamples to the variance of repeated measurements within each subsample. The number of detectable elements in both samples decreased due to the element concentration being below LOD and the measuring range of the ED-XRF. Consequently, the number of used elements decreased from 13 to 19 for BATT and from 22 to 32 for MIN. The parameters for the ANOVA F test are:

- Null hypothesis H_0 : all subsample mean values are equal
- Level of significance $\alpha = 0.01$
- BATT: $n = 5$, $v_1 = 6$ and $v_2 = 28$ (degrees of freedom for the F distribution)
- MIN: $n = 3$, $v_1 = 7$ and $v_2 = 16$

The null hypothesis H_0 is rejected if $F(\alpha = 0.01) \geq f$, i.e., the mean values are not equal, and the sample cannot be assumed to be homogeneous. The values for f are 3.53 and 4.03 for BATT and MIN, respectively.

2.3.2. Method Validation: Accuracy and Precision

Method precision, i.e., the repeatability of the analytical procedures, was assessed based on the coefficient of variation (relative standard deviation, RSD) [52]. The method accuracy was validated by means of spiking tests and the calculation of element recovery rates (RR) at three points of the analytical procedure: with liquid standards (RRL), in blind samples (RRB), in the respective sample matrices (RRS) BATT and MIN added before digestion (see Table 4). This procedure, which is known as ‘standard addition’ or ‘spiking’, is used to test the accuracy of an analytical procedure and expresses the congruence between the results of the spiked and the theoretical concentration. The spiking of blinds examines the accuracy of analytical procedures, excluding interferences of other elements and matrix effects. Nevertheless, the spiking of the samples assesses the accuracy under present interdependencies that are caused by the sample matrix. RRS was determined for all the elements measured wet-chemically with the validated as well as the in-house method. Additionally, RRL and RRB were conducted for the in-house method to evaluate the method suitability, excluding the potential matrix effects.

Table 4. Overview of the objectives and procedures for element recovery rates in liquid standards (RRL), blind samples (RRB), and sample matrices (RRS).

Spiked Sample		Objective	Analysis Procedure
Liquid standards	RRL	Test of measurement accuracy without the influence of acid digestion or sample matrix.	Multi-element standards (Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sr, Ti, V, Zn) in different concentrations were dissolved in HNO_3 and measured with ICP-OES (Supplementary Materials Table S2).
Blind samples	RRB	Test of measurement accuracy with influence caused by digestion acid due to, e.g., volatilization, complex formation, precipitation, etc. but without the influence of the sample matrix.	Element standards for all elements and acids mixtures added before digestion and measured with ICP-OES/MS.
Sample matrices (BATT, MIN)	RRS	Test of measurement accuracy with both influences, acid digestion and sample-specific, such as chemical reactions, overlapping of measuring lines (ICP-OES) or element masses (ICP-MS).	Element standards for all elements and acids mixtures added before digestion and measured with ICP-OES/MS.

Therefore, elements were added (spiked) at defined concentrations as determined with the ED-XRF analysis. Both spiked and non-spiked samples were digested and analyzed with the same method and settings. The Equations (1) and (2) to calculate the recovery rates are given in the following:

$$RR(B, S)_i = \frac{\left[\frac{1}{n} \sum_{i=1}^n \left(\frac{c_{B,i}}{\frac{m_{S,B}}{V_S}} \right) \right]}{\left[\frac{1}{n} \sum_{i=1}^n \left(\frac{c_{A,i} + c_{SP,i}}{\frac{m_{S,A}}{V_S}} \right) \right]} \times 100\% \quad (1)$$

where $c_{A,i}$ is the concentration of the unspiked sample of element i in mg/L, $c_{B,i}$ is the concentration of the spiked sample of element i in mg/L, c_{SP} is the spike concentration in mg/L, $m_{S,A}$ is the sample mass for digestion of unspiked sample in g, $m_{S,B}$ is the sample mass for digestion of spiked sample in g, $RR(B, S)_i$ is the recovery rate of the blind (B) or in the sample (S) of element i in %, and V_S is the volume of the digestion solution (L).

$$RRL_i = \frac{c_i}{c_{LS,i}} \times 100\% \quad (2)$$

In Equation (2), c_i is the measured concentration of liquid standard of element i in mg/L, $c_{LS,i}$ is the concentration of element i in the liquid standard in mg/L, and RRL_i is the recovery rate of liquid standards of element i in percent.

Based on [52,53], we consider a recovery rate of $100 \pm 20\%$ to be acceptable and thus regard the analysis method as accurate for the element in the respective sample.

2.3.3. Relative and Significant Differences Between Chemical Analysis Methods

The applicability of simplified analysis methods was evaluated based on the relative difference of mass fraction, as well as a significance test while using a Welch's t -test. For the relative difference, we accept a deviation of $100 \pm 20\%$ (see Section 2.3.2) and consider the analysis method as accurate for the element in the respective sample. The calculation is carried out with the following equation:

$$relative\ difference\ (\%) = \frac{\bar{x}_{validated} - \bar{x}_{simplified}}{\bar{x}_{validated}} \times 100\% \quad (3)$$

in this equation, $\bar{x}_{simplified}$ is the average mass fraction of an element in ppm measured with the simplified method, whereas $\bar{x}_{validated}$ is the average mass fraction of an element in ppm measured with the validated method.

In contrast to relative differences, the t -test considers the deviation of single values around the mean value. A two-sided Welch's t -test of independent (unpaired) samples was performed [51], with the following specifications:

- Null hypothesis H_0 : mean values of both samples are equal
- Level of significance $\alpha = 0.01$
- heterogeneity of variances

3. Results and Discussion

This chapter presents the results of the chemical analysis and discusses the applicability of the simplified methods. Firstly, the results of the homogeneity assessment are addressed, followed by a description of the chemical composition of the two samples that were measured with the validated methods. Subsequently, the applicability of the investigated simplified methods is discussed while using the significance test, the relative difference to the validated analysis results, and the element recovery rates.

3.1. Sample Homogeneity

The homogeneity was tested with ED-XRF results and ANOVA F test for 13 elements for BATT and 22 elements for MIN (see Supplementary Materials Table S3). In the case of BATT, the ANOVA

F test shows homogeneous distributions between the subsamples for all elements: Al, As, Cd, Cl, Cu, Fe, Mn, Ni, P, Pb, Sb, Ti, Zn, Zr. The MIN sample can be assumed homogeneous for the following 15 elements: Ba, Ca, Ce, Cl, Co, Ga, La, Nb, Nd, P, Pr, Sn, W, Y, Zn, and Zr. No homogeneous distribution between the subsamples could be achieved in the sample, despite the same sample preparation, i.e., comminution by planetary ball mill, sieving, and sample division by rotary sample divider. Al, K, Si, and Sr exhibit clear heterogeneity (values for F between 6 and 17), whereas Fe, Mg, and Rb only show minor heterogeneity with F close to the critical value ($f = 4.03$). One possible explanation could be that sample preparation to a particle size < 0.2 mm is insufficient for producing a homogeneous sample for these elements. With regard to Al, Si, and Mg, it is crucial to mention that ED-XRF analysis for light elements is prone to errors (see Section 3.4). Therefore, the results of these elements must be considered with caution in the subsequent evaluation, since significant differences in the measurement results cannot be exclusively attributed to the analytical method.

3.2. Elemental Composition Determined with the Validated Method

Figure 2 displays the elemental mass fraction of both samples, determined with the validated method. All of the results show high precision and accuracy within the given range of $100\% \pm 20\%$, expressed as relative standard deviation (RSD) and the recovery rate in sample matrices (RRS), respectively. The results of the validated method are used as reference for the comparison of the simplified methods because of the in-depth analysis and the quality assurance measures applied. The determined mass fractions of the elements in both samples range from double-digit mass percentages to a few milligrams per kilogram (ppm).

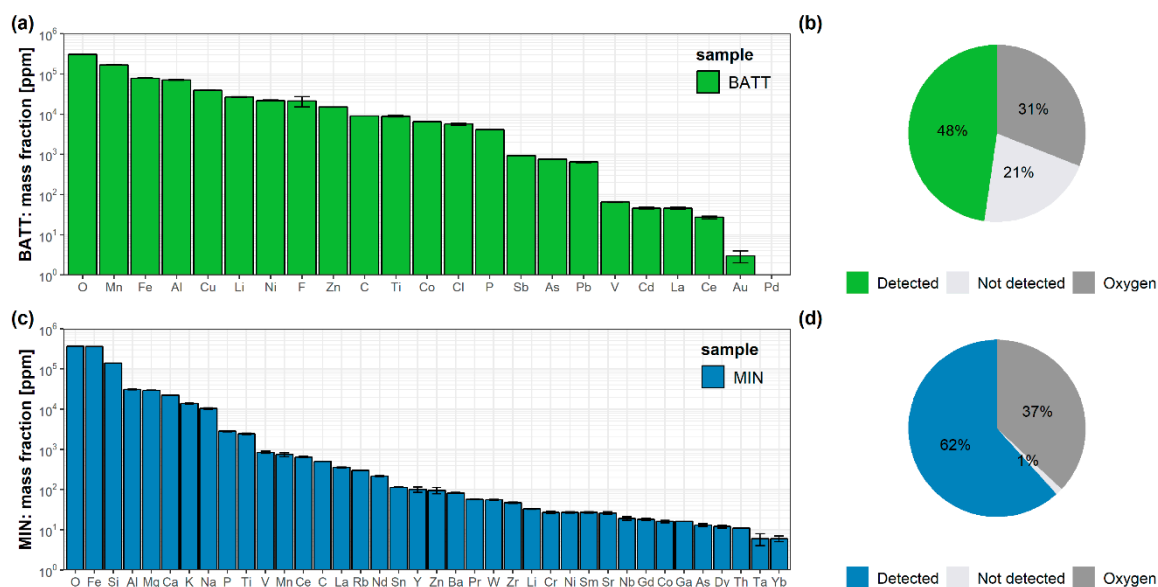


Figure 2. Element mass fraction determined with the validated method for BATT (a) and MIN (c). Error bars represent standard deviation. The mass share of detected and not detected elements as well as oxygen is depicted in (b,d). Figure data are presented in the Supplementary Materials Table S4.

The BATT sample is an oxidized mineral matrix with an oxygen mass fraction of 31% and several metals above one percent by mass, as shown in Figure 2a: Mn (17%), Fe (8%), Al (7%), Cu (4%), and Zn (1.5%). In addition to oxygen, the analyzed elements comprise 48% of the sample material (Figure 2b). The halogens fluorine and chlorine, which originate from battery cathode and electrolyte, show mass fractions of 2% and 0.6%, respectively. The metals Co and Ti, as well as P and carbon (0.9%), have mass fractions of less than one mass percent. Furthermore, the BATT sample contains the following elements in mass fractions below 0.1%: As, Sb, Pb. Precious metals (Au, Pd), REE (Ce, La), as well as Cd and V,

occur in mass fractions below 100 ppm ($<0.01\%$). We assume that heavy metals (Pb, Cd) originate from other battery systems in the sample, such as nickel-cadmium (NiCd) or lead-acid (PbA) batteries.

The MIN sample is an oxidized iron-silicon-matrix (O: 37%, Fe: 36%, Si: 14%) with portions of Mg (3%), Al (3%), Ca (2%), and K (1.4%). Together with oxygen, the proportion of detected elements is 99% (see Figure 2c,d). Phosphorus occurs in the apatite, tailing with a mass fraction of 0.3%. Other metals (Mn, V, Sn) and non-metals (Rb) can be found in mass fractions of 100 to 1000 ppm. Moreover, the REE Ce (650 ppm), La (350 ppm), Nd (220 ppm), and Y (100 ppm) are present in mass fractions above 100 ppm (0.01%). In contrast, the other analyzed REE (Dy, Gd, Pr, Sm, Yb) and all specialty metals (As, Ba, Ga, Li, Sr, W, Zr) show a mass fraction below 100 ppm.

All elements, except As in $\text{HNO}_3\text{-H}_2\text{O}_2$ (Acid (2)), showed good recovery rates. The low carbon content in the samples ($<20\%$) reduces the risk of absolute loss of arsenic in the form of arsenic hydride compounds in digestions with aqua regia or nitric acid processes [43]. However, when comparing the acid mixtures tested, the use of $\text{HNO}_3\text{-H}_2\text{O}_2$ resulted in an underestimation of approximately 40% and low recovery of 11%. In contrast, the use of aqua regia and $\text{H}_2\text{SO}_4\text{-HNO}_3$ provided good results and showed RRS close to 100% (see Supplementary Materials Figure S1).

3.3. Applicability of Wet-Chemical In-House Methods

The results of the validated method are used as the reference value for assessing the applicability of simplified methods. Overall, the simplified methods include analysis with AR and ICP-OES for both of the samples. In addition, a second digestion acid ($\text{HNO}_3\text{-H}_2\text{O}_2$) and the change of the detection device (OES, MS) were tested for the BATT sample. The method accuracy of the simplified analysis setup (digestion acid and detector) was checked by means of (a) element recovery in the blind sample (RRB), (b) spiking of the sample matrices (RRS), and (c) method precision expressed as RSD. The applicability of the simplified methods was verified while using the relative difference from the validated value and the Welch's *t*-test results. All of the detailed results can be found in Supplementary Materials Tables S5–S8.

Good measurement accuracy was proven for RRL (without the influence of digestion and sample matrix), RRB (with the influence of the digestion acid), as well as RRS (with matrix influence) for all method variations and most of the elements in both samples showing element recoveries of $100\% \pm 20\%$. Moreover, high precision can be observed for most elements having an average RSD of approx. 6%. Nonetheless, underestimations were detected for Zn that was analyzed with $\text{HNO}_3\text{-H}_2\text{O}_2$ and ICP-MS (RRB 77%, RRS 71%). In contrast, high overestimations in RRS are observed for ICP-MS measurements of Cd ($\text{HNO}_3\text{-H}_2\text{O}_2$, 245%), Ce (AR, 142%), and La (AR, 160%).

Figure 3 shows the mass fractions of the analyzed elements of both samples as a comparison of the in-house (y-axis) and validated method (x-axis), being differentiated by digestion acid and the detection method. If an element is precisely on the 1:1 slope, the deviation between both methods is close to or exactly 0. Furthermore, the upper figures show the elements without significant difference ('No') whereas the lower figures show elements with a significant difference to the validated methods ('Yes'), according to the *t*-test.

3.3.1. Acid Digestion

Both acid mixtures for the BATT sample led almost exclusively to underestimations, whereas the relative difference generally decreased with increasing element concentration. On the other hand, both under- (down to -65%) and overestimation (up to $+450\%$) is observed for the AR digestion of the MIN sample, in which only the elements below 1000 ppm were wet-chemically analyzed. Although AR is commonly applied for various ores in literature [8,54], the application of HF blends is necessary for breaking silicate structures. For the analysis of trace elements in carbon-containing and silicate-rich samples, the complete digestion with mixtures of $\text{HNO}_3\text{-HF}$ or AR-HF is recommended [54–56].

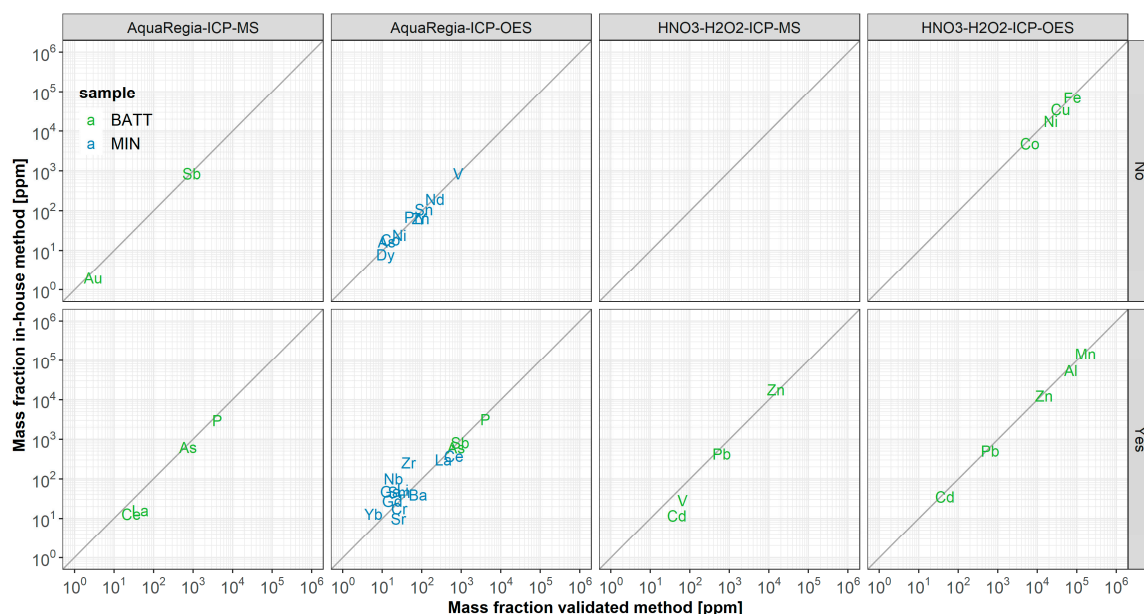


Figure 3. Comparison of the element mass fractions determined with in-house and validated methods, differentiated by sample, measurement method, and the result of the significance test. ‘No’ means no significant difference to the validated method, whereas ‘Yes’ indicates a significant difference.

Hence, underestimations in the silicon-rich MIN sample (13% Si) can mainly be attributed to incomplete digestion. Nevertheless, the use of AR to digest REE and other specialty elements (As, Au, P, Sb) proved to work well for both samples in the validated method. Moreover, HNO₃-H₂O₂ can be used for the ferrous and non-ferrous metals in BATT. Therefore, deviations to the simplified methods are mainly caused by the detection method and matrix interferences. In contrast, the validated method applied HF in MIN for Cr, Nb, Ni, Co, Sn, and most specialty metals. For the other target elements, non-destructive WD-XRF was employed to avoid any interferences of acid digestion.

3.3.2. Element Detection with ICP-OES

The concentration range of the element to be measured and the device-specific determination limit (LOQ) primarily limit the applicability of ICP-OES and ICP-MS. When changing detectors for the BATT sample, some ferrous and non-ferrous elements (Fe, Mn, Ni, Al, Co, Cu) cannot be measured with the ICP-MS (above detection range) and most of the elements below 100 ppm (Au, Ce, La, V, Pd) cannot be measured with the ICP-OES (below LOQ).

Regardless of the acid choice, ICP-OES shows underestimations of about 10–25% for almost all elements of the BATT sample for RRS as well as in comparison to the validated method. Given the similar sample preparation and acid selection for BATT, the deviation from the validated method can be attributed to matrix interferences in ICP-OES, such as inter-element effects due to ionization or chemical interferences (halogens), and spectral interferences [57]. Examples of possible spectral interferences occurring in the BATT sample are Fe (238.2 nm) and Co (238.8 nm), as well as Zn (206.2 nm) and Sb (206.8 nm).

Similarly, the use of ICP-OES (with AR) for MIN shows slightly lower element recoveries (RRS), except for Ga and Dy. However, in comparison to the validated method, both over- and underestimations with partly significant deviations are observed for several elements. This simplified method proved to be applicable for some elements (Ni, V, Co, Sn, and Nd), with relative differences below 20%. Higher relative differences, but no significant differences, were identified for Zn, As, Dy, Pr, and Y. However, single elements deviate remarkably from the reference value, despite good element recoveries, such as Nb (440%), Ga (200%), Zr (450%), and Yb (120%).

In other words, the simplified use of ICP-OES (with aqua regia) did not provide satisfying results for any of the two samples (MIN and BATT). In contrast to BATT, the results for MIN show two-sided tendencies with, e.g., quadruple overestimations as compared to the reference value.

3.3.3. Element Detection with ICP-MS

Figure 3 shows the ICP-MS measurement results of the BATT sample. In comparison to ICP-OES, element recovery rates in the sample (RRS) deviate more due to matrix interferences. Accordingly, Zn shows low RRS (70%), whereas Cd (250%), Ce (150%), and La (160%) show very high RRS (Supplementary Materials Table S8). A low RRS leads to an underestimation of the element (negative relative difference), as observed for As (−16%), Au (−33%), P (−16%), Pb (−33%), and Sb (−6%). However, this relationship cannot always be confirmed due to matrix interferences, so that underestimations can be observed for Ce (−52%), La (−65%), and Cd (−74%), despite high RRS and overestimations for Zn (+21%), despite low RRS.

While the ICP-OES results frequently showed underestimations of 10–25%, the ICP-MS deviations are for most elements between −25 and +75%. The simplified analysis using ICP-MS and AR showed good results exclusively for Sb and As with small deviation and no significant difference. Matrix interferences in ICP-MS measurement were identified for most of the elements in BATT. La, Ce, and V are disturbed on all available isotopes due to the main elements of the sample, which can cause large analytical errors on REEs with ICP-MS technique [56]. An interference-free measurement, i.e., avoidance of overlapping peaks in the analysis spectrum, was only possible with the ICP-MS while using oxygen reaction gas mode shifting the element mass to the respective oxide mass, e.g., ^{139}La to ^{155}LaO and ^{140}Ce to ^{156}Ce . However, this technique required appropriate laboratory equipment and it was explicitly excluded in the simplified method.

3.4. Applicability of ED-XRF Measurements

The ED-XRF is a less precise measuring method when compared to the wet-chemical analysis, showing a higher average RSD of 15%, but rarely exceeding 20%. Figure 4a shows the mass fractions of the analyzed elements of both samples when comparing the ED-XRF (y-axis) and validated method (x-axis). Elements that lie directly on the 1:1 slope depict no deviations from the reference value. Elements in black have no significant difference, whereas red elements have a significant difference to the validated methods according to the *t*-test.

For mass fractions below 1000 ppm (0.1%), the measurement is only accurate for a few elements, while most of the values deviate significantly and are generally over-estimated. For element concentrations above 1000 ppm, the ED-XRF method shows good precision (RSD < 20%) and lower deviations for the tested samples. In general, only a few elements deviate less than 20% from the reference value, i.e., Al, As, Cd, Cu, Fe, Mn, Ni, Pb in BATT and Ca, Ce, Fe, Nb, P, Rb, Si, Y in MIN. Even fewer elements show no significant difference, i.e., As, Fe, Mn in BATT and Ca, Ce, Nb, Y in MIN.

LODs for ED-XRF are dependent on influencing factors, such as testing time, matrix composition, level of statistical confidence [50], and element selection (overlapping peaks). For mining matrices, LODs that are below 100 ppm are stated for elements $Z > 12$ except Co, which in silicon matrices with Fe shows higher LODs [50] due to possible interferences. In the two samples, Co shows remarkable deviations, as it is strongly under-estimated in BATT (−92% at 6500 ppm) and strongly over-estimated in MIN (+9200% at 16 ppm).

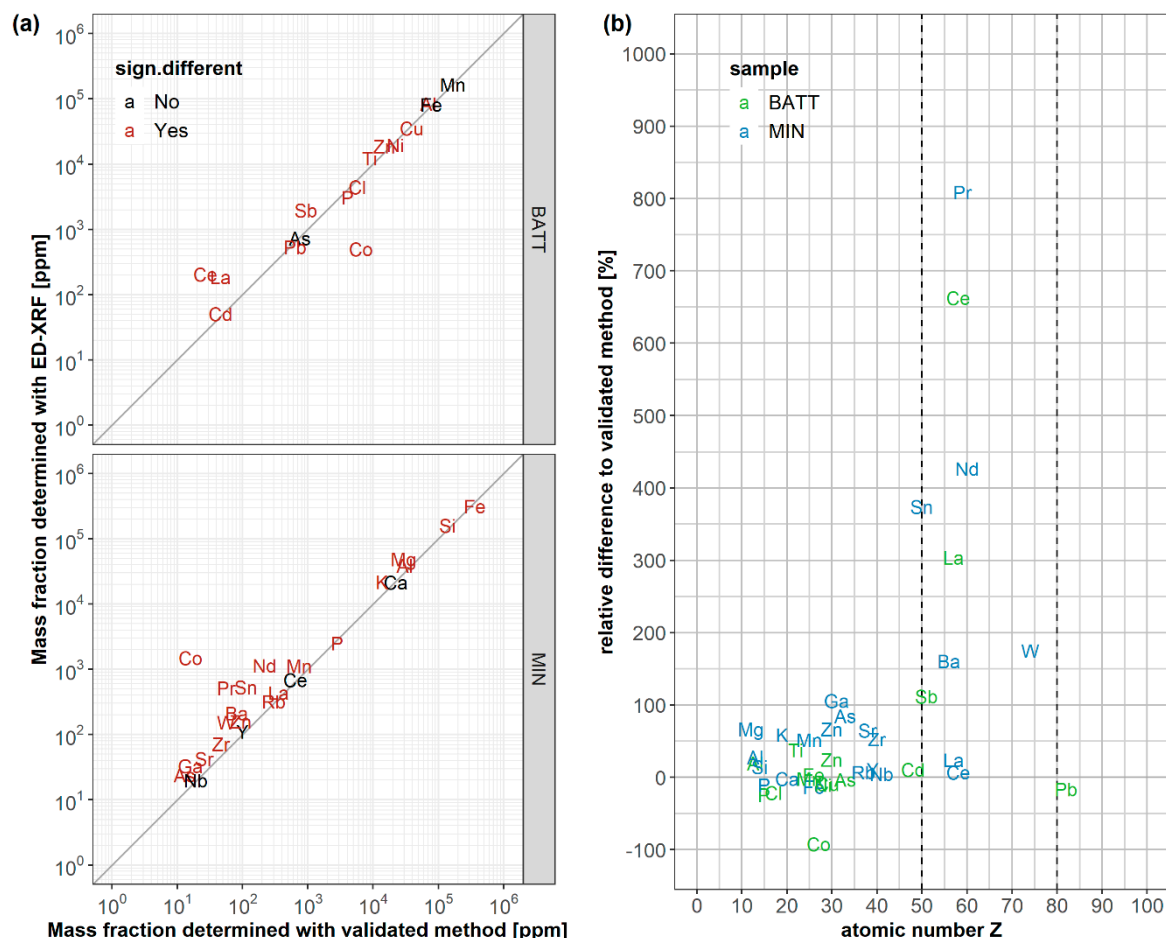


Figure 4. Comparison of the element mass fractions per sample determined with ED-XRF and validated methods, indicating no significant difference in black and significant differences in red letters (a). Relation of the relative difference to the reference values and the element's atomic number Z for BATT (green) and MIN (blue) (b). Note: Co in MIN is not depicted in the graph (b). Figure data can be found in Supplementary Materials Tables S6–S8.

Figure 4b shows the relative difference of the measured element mass fractions from the reference value in relation to the atomic number (Z). In principle, the detection of heavier elements, such as REE, is feasible with the applied high-energy (50 keV) ED-XRF due to the increased excitation energy [22]. However, it can be seen for almost all REE in BATT and MIN that ED-XRF performs poorly (see detailed data in Supplementary Materials Tables S7 and S8). The examples of Ce and La in BATT show to what extent matrix interferences can influence the result, depending on the individual sample composition. In other words, elements up to Z 50 are usually detected while using the characteristic emission spectra of $K\alpha$ and $K\beta$. In contrast, heavier elements are quantified by their L-lines due to the limited excitation energy, but consequently these spectra may overlap with the K-lines of light elements. This effect will be reinforced if the interfering element occurs at high mass fractions in the sample and it will lead to a decrease in precision and partly significant deviations [22,58]. While Ce and La deviate slightly in MIN, significant deviations of 300% and over 600% can be observed in BATT for La and Ce, respectively. For instance, the high mass fraction of Ti (8900 ppm, $K\alpha$ 4.51, $K\beta$ 4.93) originating from, e.g., TiO_2 lithium battery systems [59], can cause interferences with the detection of Ce ($L\alpha$ 4.84, $L\beta$ 5.26) and La ($L\alpha$ 4.65, $L\beta$ 5.04) [60]. The ED-XRF energy spectra of Co and La in BATT can be found in Supplementary Materials Figures S2 and S3.

4. Conclusions

The investigated battery ash BATT and mining waste MIN samples present complex minerals matrices exhibiting highly different mass contents of many elements. Generating valid and accurate data on the composition of these anthropogenic mineral residues for an urban mine knowledge database poses challenges to chemical analysis due to matrix interferences. This is in agreement with the results of our recent study on printed circuit boards [31], which indicated that multi-element chemical analysis of complex anthropogenic matrices with a high organic content is challenging and it can easily lead to inaccurate compositional data.

Reliable results were obtained developing validated methods applying laborious matrix- and element-specific investigations while using varying acid mixtures, detection methods, and different parameter settings, in combination with sophisticated quality assurance measures.

This study shows that a simplified application of microwave-assisted digestion with aqua regia or $\text{HNO}_3\text{-H}_2\text{O}_2$ and subsequent measurement with ICP-OES or ICP-MS did not prove to be applicable for half of the analyses. There is no clear dependence of acid selection or mass concentration on the accuracy of the in-house method. Nevertheless, for BATT, a tendency is discernible that elements with high mass fractions can be more accurately determined. The analyses with ICP-OES and ICP-MS frequently showed deviations of 10–25% and 25–75%, respectively. Significant deviations from the validated value were observed, despite internal quality assurance, demonstrated as high precision (RSD) and good accuracy (RRL, RRB, RRS).

ED-XRF analysis can only be used to a limited extent without matrix-specific calibration. However, semi-quantitative analysis with deviations that were below 100% proved to be feasible for most elements (except Co) having (a) an atomic number between Z 12 and Z 50, and (b) mass fractions above 1000 ppm. Strong deviations up to 90 times the validated value were observed, particularly for elements with low mass fractions.

In conclusion, the tested simplified chemical analysis methods are not generally applicable to the tested anthropogenic mineral matrices. The mineral character and the presence of many elements in different mass concentrations make simplified methods prone to errors due to matrix interferences. Internal quality assurance steps for the simplified method did not ensure the identification of these interferences. Consequently, additional measures are required for complex mineral matrices, such as laborious method development, the provision of appropriate reference materials, or sample- and element-specific method validation within interlaboratory tests.

Supplementary Materials: The following are available online: at <http://www.mdpi.com/2079-9276/8/3/132/s1>, Figure S1: Mass fraction and recovery of arsenic in BATT and MIN sample, Figure S2: The ED-XRF energy spectrum (4–14 keV) of the BATT measurement, Figure S3: The ED-XRF energy spectrum (3–7 keV) of the BATT measurement, Table S1: Parameters of the validated method for determination of total halogens F and Cl, Table S2: Recovery rates measured in liquid standard samples, Table S3: Homogeneity test results for BATT and MIN sample, Table S4: Element composition of BATT and MIN sample determined with the validated method, Table S5: Chemical analysis results of the wet-chemical in-house method, Table S6: Chemical analysis results of the XRF in-house method, Table S7: Overview of applicability of in-house methods for MIN sample, Table S8: Overview of applicability of in-house methods for BATT sample.

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