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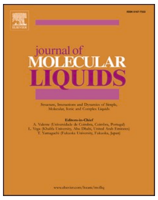

Selective cobalt recovery from battery black mass enabled by eutectic effect in choline chloride-based deep eutectic solvents

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ABSTRACT

The selective recovery of critical metals from end-of-life lithium-ion batteries is essential for closing material loops and reducing reliance on primary resources. Deep eutectic solvents (DESs) have emerged as promising alternatives to conventional hydrometallurgical systems, yet the extent to which their eutectic structure governs metal dissolution and selectivity remains unclear. Herein, we present a systematic solvometallurgical study addressing this knowledge gap through a direct comparison between choline chloride-based DESs and composition-matched aqueous analogues in the leaching of battery black mass. A microwave-assisted water treatment removed over 80% of lithium, phosphorus, and aluminium, yielding a residue enriched in cobalt, nickel, and manganese. Subsequent leaching experiments using choline chloride-based DESs (choline chloride:ethylene glycol, choline chloride:glycerol, and choline chloride:Urea) revealed that these systems show markedly different behaviour than their aqueous counterparts, suggesting that enhanced extraction may be associated with eutectic effects, as the individual components and their aqueous analogues fail to reproduce the observed performance. Among the investigated systems, choline chloride:ethylene glycol achieved the highest cobalt extraction and an exceptional cobalt selectivity of 97.1% over nickel and manganese, corresponding to a synergy factor of 19 relative to aqueous analogues. Choline chloride:glycerol also exhibited strong cooperative effects, with high cobalt selectivity (87.2%) and enhanced manganese dissolution, whereas choline chloride:Urea showed limited cobalt extraction and poor selectivity. Aging and alkaline treatment tests further demonstrated that DES composition critically controls metal-solvent interactions and solution stability. ChCl:EG and ChCl:GLY form highly stable metal-DES complexes, with less than 2% spontaneous cobalt precipitation after five days; under alkaline conditions, no precipitation is observed for ChCl:GLY even at pH 14. In contrast, ChCl:Urea undergoes extensive and non-selective metal precipitation, leading to co-recovery of cobalt, nickel, and manganese. Overall, this work provides evidence that DESs may influence metal dissolution beyond simple solvent effects. To complement the extraction and mechanistic results, the sustainability of the three DES systems was evaluated using the LEACH framework, which assesses solvometallurgical processes across economic, technical, and safety dimensions. This analysis revealed clear differences in overall sustainability between the DESs, highlighting the critical role of solvent composition, stability, and recyclability in determining process viability.

1. Introduction

In the global push for decarbonization and energy security, lithium-ion batteries (LIBs) have become indispensable. Battery capacity surged to over 2.400 GWh in 2023, a fourfold increase since 2020, with electric vehicles alone consuming more than 750 GWh annually, accounting for over 90% of this demand. Projections estimate that LIB demand will grow nearly sevenfold by 2030, reaching around 4.7 TWh. This soaring demand underscores the need for critical materials such as lithium, cobalt, nickel, and manganese [1]. Despite this massive consumption, Europe remains poorly positioned within the upstream battery materials supply chain. The continent relies heavily on imports for critical raw materials, especially cobalt and nickel, and has limited domestic capabilities to process both raw materials and fabricate cathode and anode

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electrodes. The European Commission's 2025 report highlights these bottlenecks, stressing the importance of secure sourcing, processing, and recycling to meet its climate-neutral targets [2]. This vulnerability has spurred interest in “urban mining” as alternative pathway for recovering valuable materials from spent batteries. Mechanical pre-treatment generates black mass (BM), a heterogeneous mixture of cathode and anode powders, binders, and electrolytes [3]. BM is rich in strategic metals like Li, Co, Ni, and Mn, with concentrations frequently surpassing those in primary ores [4]. Characterization of BM from $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_{1\text{-}x\text{-}y}O_2$ (NCM) cathodes typically reveals abundant transition metals, residual graphite, alluminum, and copper current collectors, and fluorinated organic compounds [5,6]. Among the available technologies for the extraction and recovery of critical metals from BMs [7,8], solvometallurgy, especially employing deep eutectic solvents (DESs), has emerged as a promising route for metal recovery from BM. Unlike conventional hydrometallurgy, DES-based solvometallurgy operates under milder conditions, offering greater tunability, lower toxicity, and reduced water consumption [9]. DESs such as choline chloride-based mixtures have demonstrated strong coordination with transition metal ions and selective leaching performance, though lithium recovery remains a challenge [10]. Beyond battery-recycling applications, the rapid development of new binary and ternary DES formulations has further expanded the chemical space available for solvometallurgical process design. Recent examples include choline chloride (ChCl) acid binary and ternary DESs, cetyltrimethylammonium chloride acid DESs, and TTAB/LCA/Fe^{3+}-based formulations, which have been reported mainly for biomass fractionation and lignocellulose pretreatment rather than black-mass leaching [11–14]. Although these systems have not yet been systematically investigated for LIB black mass processing, they illustrate how acidity, Lewis-acid additives, surfactant-like ammonium salts, and hydrogen-bond network modulation can be used to tailor DES properties. Despite growing interest, the mechanistic underpinnings of DES-mediated extraction from BM remain poorly understood. Key questions persist about whether the eutectic mixture is essential for effective extraction or whether individual components alone could achieve similar results. Recent achievements from some of us highlighted the unique behaviour of even dilute solutions of DES in acting as an active co-solvent rather than a mere ionic solute dissolved in water: the case of DES-assisted selective extraction of lanthanides and actinides with an associated catalytic effect in the partitioning process is a clear example of the complexity of the solvation behaviour of choline and the gap still existing in the deep understanding of the action mechanism [15]. Interestingly, tests on the isolated components of the DES gave poor results, confirming that the local structuration of the DES components plays an important, though not fully understood, role in the mechanism of action. This is further confirmed from the fact that the DES activity as co-solvent seems to continue even in the so-called “DES in water” regime, confirming the unique solvation properties of the binary systems making up the DES. Despite the rapid growth of DES-based solvometallurgical approaches, the fundamental mechanisms governing metal dissolution remain poorly clarified. Early studies demonstrated that choline-chloride-based eutectics dissolve several transition-metal oxides through the formation of chloride-rich complexes such as $[MCl_4]^{2-}$, which stabilize divalent metal ions in low-water-activity environments and promote the breakdown of layered oxide lattices. Abbott et al. showed that the dissolution of CoO and NiO in ChCl-based DESs is driven by chloride coordination and enhanced by the structured hydrogen-bond network of the eutectic phase [16]. More recently, mechanistic investigations have highlighted that DES components do not act independently: rather, cooperative solvation, the combined effect of hydrogen-bond donors and acceptors, operating within a micro-structured liquid, creates solvation domains that modulate metal speciation and redox behaviour. Tran et al. demonstrated that ethylene-glycol-based DESs promote the formation of $[CoCl_4]^{2-}$ species even at moderate temperatures, whereas the individual components fail to generate comparable complexation environments [17]. In parallel, spectroscopic and electrochemical data have revealed that certain DESs also induce redox-driven dissolution pathways, in which Co(III) species are reduced to soluble Co(II). This is particularly evident in Urea-based DESs, where Urea acts as a mild reducing ligand capable of coordinating through both oxygen and nitrogen. Yu et al. reported that ChCl:Urea systems yield characteristic Co(II)-Urea complexes detectable by UV–Vis and FT-IR spectroscopy, confirming that ligand-assisted reduction and coordination both contribute to the dissolution process [18,19]. Altogether, literature suggests a consistent interpretation: DES-mediated leaching is governed by a combination of chloride coordination, hydrogen-bond-network cooperativity, redox transformations, and temperature-dependent solvation dynamics. Recent studies on binary and ternary DESs for lithium-ion battery recycling have shown that the addition of acidic, coordinating, or redox-active components can markedly enhance metal dissolution. For example, ternary ChCl-based systems containing ethylene glycol and p-toluenesulfonic acid have achieved high extraction of Co, Ni, Mn, and Li from NCM cathodes, highlighting how DES composition can modulate acidity, redox behaviour, and metal coordination [20]. However, most of these studies primarily optimize leaching efficiency [21,22], while the specific contribution of the eutectic environment itself is rarely isolated through comparison with composition-matched non-eutectic analogues. This work addresses that gap by directly comparing ChCl-based DESs with corresponding aqueous analogues under identical conditions, thereby focusing on eutectic effect rather than on the screening of additional DES formulations. However, a direct comparison between DESs and composition-matched aqueous analogues remains largely unexplored. Beyond elucidating dissolution mechanisms and extraction selectivity, it is increasingly important that emerging solvometallurgical routes be evaluated within a broader sustainability framework. To address this, we incorporated the LEACH (Low-impact Extraction and Assessment of CHemical solvometallurgy) tool [23], a modular, penalty-based methodology specifically developed for early-stage solvometallurgical processes, to quantify the sustainability of each DES both at the formulation level and during black-mass leaching. Integrating LEACH into this study enables a unified comparison of extraction efficiency, operational stability, safety considerations, and material circularity, thereby strengthening the relevance of our findings for future process development.

In this context, we present a work tackling with the effective role of DES in metal extraction, providing a contribution to address this gap mentioned above by conducting a systematic comparative study. We investigate metal recovery from BM using DESs versus composition-matched aqueous analogues, with a specific focus on: (I) demonstrating the necessity of the DES phase for achieving high selectivity and enhanced extraction, (II) elucidating the coordination and metal–DES interactions that drive extraction efficiency, (III) evaluating stability and recovery mechanisms in aging and post-treatment scenarios.

This study fills a critical knowledge gap by clarifying whether the solvent's eutectic structure is key to enhanced dissolution and selectivity for strategic metals-advancing solvometallurgical methods toward scalable, sustainable battery recycling.

2. Experimental part

2.1. Chemicals

Black mass samples were provided by Spirit SRL (Vicenza, Italy). This black mass is composed of a mixture of LCO and NCM cathodes, along with graphite in about 30 wt%. The BM was subjected to a thermal process at moderate temperatures (under 700 °C) to eliminate most of the volatile fraction.

Choline chloride (ChCl, 98%), ethylene glycol (EG, 99%), glycerol (GLY, 99%), and Urea (99%) were purchased from Merck Europe.

2.2. DESs preparation

According to a previously reported protocol [24], hydrogen bond donors and acceptors were mixed and stirred for 2 h at 50 °C. Then, the system was cooled down and stirred for 16 h at room temperature. The molar ratio between hydrogen donor and acceptors were the following: ChCl:EG (1:2), ChCl:GLY (1:1.5), ChCl:Urea (1:2).

Water-based leaching solutions were prepared starting by replacing the same weight of each element in the corresponding DES formulation by water.

2.3. Microwave processing and water leaching

The residual black mass (RES1_BM) is the material obtained from black mass (BM) after microwave treatment followed by water leaching.

Microwave treatments of the BM were performed using a PYRO Advanced Microwave Muffle Furnace (Milestone S.r.l., Bergamo, Italy), equipped with a refractory chamber and a susceptor to ensure uniform heating. The system operates in an air atmosphere and features self-adjusting power control. For each experiment, 5 g of black mass (BM) samples were placed in a quartz crucible inside the microwave chamber and treated at 600 W for 5 min, following the the patented protocol published by Cornelio et al. [25].

The microwave-treated BM was then subjected to water leaching with 10 wt_{eq} of Milli-Q water (e.g., 2 g of microwave-treated BM mixed with 20 g of water) at 80 °C for 2 h. The resulting suspension was filtered under vacuum to separate the leachate from the solid residue (RES1_BM).

2.4. DES leaching experiments

Black mass/RES1_BM (typically 0.5 g) was placed into a vial containing 40 wt_{eq} of DES or its aqueous analogues (20 g) and a magnetic stirrer. The mixture was stirred for 5 h at 95 °C and then filtered while still hot to provide a leaching solution and a further residual BM (RES2_BM).

2.5. XRD analysis

Powder XRD analyses of BM samples (RES1_BM and RES2_BM) were also performed using an X'Pert Pro diffractometer (PANalytical, Malvern, UK) equipped with a Cu anode (Cu Kα, 1.5406 Å) and an X'Celerator detector. The instrument was operated at 40 kV and 40 mA, and diffraction patterns were collected over a 2θ range of 10–90°. Qualitative phase identification was performed using Profex 5.2.0 by comparing the collected patterns with crystallographic index files (CIFs) from the Crystallographic Open Database (COD).

2.6. ICP analysis

Elemental quantification of the BM samples was carried out using a single-quadrupole inductively coupled plasma mass spectrometer (ICP-MS, NEXION 2000, Perkin Elmer) operated in helium mode with kinetic energy discrimination. Prior to analysis, the samples were digested through microwave-assisted treatment (ETHOS EASY, Milestone Srl) using 9 mL of ultrapure aqua regia at 230 °C for 15 min, and the resulting solutions were subsequently diluted in ultrapure 1% nitric acid. Instrument calibration was performed with multielement standard solutions (I.V. Labs, Inc.) covering the full concentration range required for accurate quantification.

2.7. Scanning electron microscopy (SEM) analysis

Morphological analysis of the solid residues was carried out using a scanning electron microscope (SNE-ALPHA, SEC Co., South Korea). Samples were mounted on aluminium stubs using conductive carbon tape and sputter-coated with a thin gold layer to minimize charging effects. SEM images were acquired in high-vacuum mode using a secondary electron (SE) detector at an accelerating voltage of 20 kV, at different magnifications (including 1500×) to evaluate particle morphology.

Elemental composition was investigated by energy-dispersive X-ray spectroscopy (EDS) on selected areas of the samples. As the measurements were performed on localized regions of the surface, the obtained elemental compositions should be considered semi-quantitative.

3. Results and discussion

3.1. Pre-treatment of the BM

As previously reported, the microwave-assisted water leaching effectively removed more than 80% of lithium [25], along with soluble P and Al species. This pre-treatment simplified the chemical matrix of the solid residue (RES1_BM), enriched in Co, Ni and Mn (Fig. 1) [26].

No relevant phase changes were observed prior and after microwave-assisted leaching in water, as confirmed by XRD analysis (see Fig. S1 in the Supporting Information). Then, residual RES1_BM was subjected to a solvometallurgy procedure with three different known DESs: ChCl:EG (A) [27], ChCl:GLY (B) [28], ChCl:Urea (C). [29].

3.2. DES vs aqueous analogues leaching of BM

The three leaching systems herein studied have already been reported as efficient systems for the extraction of metals from BM [28–30]. Typically, the leaching temperature reported was elevated (up to 180 °C).

In this context, the main aim of the present research was to assess whether metal extraction is impacted by eutectic interactions rather than by the individual solvent components and to exploit this knowledge to develop highly sustainable processes. Thus, DES-based leaching systems were systematically compared with composition-matched aqueous controls in which one DES component was replaced by H_2O. All the experiments were conducted at 95 °C. The choice of H_2O was determined considering that (i) it cannot dissolve any element present in RES1_BM as the material already was leached with H_2O and (ii) ChCl, EG, GLY, and urea are soluble in H_2O, guaranteeing a homogeneous liquid phase in the operating conditions. The amount in mg of extracted Co, Li, Mn, and Ni for each leaching system is reported in Table 1.

The data suggest that deep eutectic solvents markedly outperform their aqueous counterparts for the extraction of transition metals, particularly cobalt. A potential limitation of Table 1 is that the aqueous control systems contain a large excess of H_2O, which may in principle alter the physicochemical environment (e.g., water activity, viscosity, and solvation structure) relevant to DES-mediated metal solubilization. To address this concern, we considered independent leaching data obtained on the same BM using pure glycerol as a solvent, i.e., in the complete absence of water. As reported by Mannu et al., [30] pure glycerol displays negligible extraction of transition metals and only modest Li solubilization under conditions comparable to those used in our aqueous controls. This suggests that manganese-containing oxides, typically resistant to aqueous leaching, become destabilized in DES environments. Rather, it indicates that neither glycerol nor water alone, nor their mixtures, can reproduce the dissolution and selectivity patterns observed in ChCl:GLY, thereby supporting the hypothesis that the enhanced extraction observed in DESs is associated with eutectic cooperativity rather than with the intrinsic leaching ability of the individual components. These results provide direct experimental evidence that the metal-solubilization ability of ChCl, EG, GLY, and Urea is fundamentally altered when these components are organized into a eutectic system. Thus, it seems that the extraction performance of the investigated DESs is not an additive consequence of the individual HBA and HBD properties but emerges from the specific supramolecular

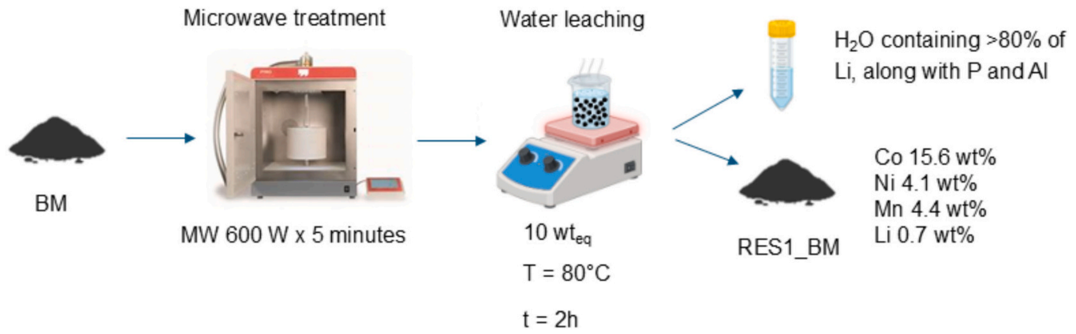

Fig. 1. General scheme of the overall recycling process. The distribution of the main elements in RES1_BM is taken from Mannu et al. [26].

Table 1
Extraction performances for the seven considered systems.

Leaching system	Co (mg)*; Δ	Li (mg)*; Δ	Mn (mg)*; Δ	Ni (mg)*; Δ
DES ChCl:EG	6.61; 0.7%	1.49; 0.4%	0.12; 0.8%	0.08; 6.4%
DES ChCl:GLY	4.43; 1.3%	1.71; 1.0%	0.36; 1.5%	0.29; 1.6%
DES ChCl:Urea	0.75; 1.0%	2.77; 1.5%	0.26; 6.5%	0.62; 12.7%
H_2O:GLY	0.03; 1.6%	3.32; 1.9%	0.02; 8.8%	0.03; n.c.
H_2O:Urea	0.35; 2.4%	6.29; 2.5%	0.03; 4.6%	1.27; 1.7%
H_2O:ChCl	0.33: 3.5%	3.20; 0.3%	0.02; n.c.	0.04; n.c.
H_2O:EG	0.01; n.c.	1.35; 2.3%	<0.0056; n.c.	<0.0042; n.c.

[*] The amount of extracted metal is expressed in mg as all the experiments were conducted on the same scale and in the same conditions (see Section 2.2) and thus the mg extracted in each experiment are comparable; Δ indicates the standard deviation (%); n.c. stands for not calculated.

environment generated by DES formation. Among the investigated systems, ChCl:EG exhibits a dominant cobalt extraction performance, exceeding aqueous analogues by up to two orders of magnitude. In contrast, aqueous systems containing either choline chloride or ethylene glycol extract only trace amounts of cobalt, pointing to a cooperative solvation effect characteristic of the eutectic phase, possibly related to the polyol environment. A similar, though less pronounced, enhancement is observed for manganese and nickel. Manganese remains essentially insoluble in all aqueous systems, whereas measurable dissolution occurs exclusively in DESs, with ChCl:GLY showing the highest Mn extraction. This behaviour suggests that manganese-containing oxide phases, which are highly resistant to aqueous leaching, become destabilized under the low water activity and structured hydrogen-bond network of DESs. Nickel extraction also increases in DESs compared to aqueous systems, although its response is more sensitive to the nature of the hydrogen-bond donor. Lithium displays a fundamentally different behaviour. The highest Li concentrations are consistently observed in aqueous systems, particularly those containing Urea or choline chloride, while DESs extract significantly lower amounts. This is coherent with the idea that residual lithium following the initial water-leaching pretreatment remains governed by aqueous solubility rather than by complexation mechanisms involving the mixture's components. Importantly, the suppressed lithium dissolution in DESs underscores their intrinsic selectivity toward transition metals, an advantageous feature for downstream separation once lithium has been largely removed upstream. In previous work, ChCl:EG exhibits a strong temperature dependence that enables process-level selectivity: Cu is almost quantitatively removed at 90 °C, while Co extraction reaches 90% at 180 °C within 18–24 h and Ni extraction remains low (10%) [27]. In contrast, our ChCl:EG system achieves a Co selectivity of 97.1% at substantially milder conditions, indicating that the structured hydrogen-bond network and cooperative chloride coordination within the DES can induce strong selectivity even without resorting to the temperatures used by Schiavi et al. [19]. To quantitatively evaluate the cooperative effects between DES components, synergy factors were calculated by comparing metal extraction data reported in Table 1 for the DESs and for the corresponding aqueous systems (Table 2). These factors provide direct insight into the extent to which the eutectic environment enhances metal dissolution beyond the additive contribution of its constituents.

Looking at the data reported in Table 2, it is worth highlighting that ChCl:EG exhibits the strongest synergistic behaviour, particularly for Co, with a synergy factor of more than 19. This pronounced enhancement is consistent with a favourable solvation–complexation environment. In contrast, ChCl:Urea displays a substantially lower and negligible synergisticeffect for Co, suggesting a more limited ability of the Urea-based eutectic to disrupt cobalt-containing solid phases. For manganese, the highest synergy is observed in ChCl:GLY, pointing to a DES-specific solvation geometry that favours Mn(II) dissolution. Consistently, the solvent showing the highest Mn synergy factor (ChCl:GLY) also yields the highest dissolved Mn amount among the DES systems (0.36 mg, Table 1), whereas the lowest Mn synergy (ChCl:EG) corresponds to the lowest Mn extraction (0.12 mg).These results suggest that DES composition can be deliberately tuned to preferentially activate distinct metal dissolution pathways. The synergy factor used in this work should be regarded as a semi-empirical, comparative descriptor rather than a rigorous thermodynamic or kinetic parameter. Its purpose is to quantify deviations from additive behaviour between DES components and their corresponding aqueous analogues under identical experimental conditions, thereby highlighting cooperative effects within the eutectic phase. However, this parameter does not explicitly account for factors such as the initial metal distribution in RES1_BM, leaching kinetics, possible secondary equilibria in solution, or full propagation of analytical uncertainty. Consequently, the absolute values of the synergy factor (e.g., 19.4, 12.3, 1.1) should be interpreted cautiously, while the relative trends across different DES systems are considered more robust and informative.

Analysing the data reported in Table 2 it is also evident an opposite behaviour of the three DES systems toward Li extraction. In that case, the DES is less effective (0.3 synergy factor for all three systems) than the two analogue aqueous solutions. In terms of practical applicability of a DES system, this is not a relevant issue, as the herein studied process is conducted on a BM already Li depleted from the previous microwave and water leaching tandem process. Nevertheless, this evident difference between the DES and the corresponding aqueous solution of the HBD or HBA suggests an effect (negative in this case) on the extraction of the Li directly related to the intermolecular interactions (here mainly hydrogen bonds) within the constituents of the solvent.

Table 2
Comparison between the synergy effects among the different systems.

Metal	Synergy Factor for ChCl:EG	Synergy Factor for ChCl:GLY	Synergy Factor for ChCl:Urea
Co	19.4	12.3	1.1
Mn	6	9	5.2
Ni	2	4.14	0.5
Li	0.3	0.3	0.3

The implications of these synergistic effects are also reflected in the cobalt selectivity values reported in Table 3.This alignment between synergy and selectivity suggests that the cooperative chloride-HBD hydrogen-bond network does not simply increase dissolution but preferentially stabilizes Co^{2+} in the eutectic environment relative to competing Ni and Mn species. ChCl:EG achieves exceptionally high cobalt selectivity (97.1%) over nickel and manganese, consolidating its role as the most effective solvent system for targeted cobalt recovery. ChCl:GLY also exhibits high selectivity, whereas ChCl:Urea shows a marked decline, consistent with its weaker cobalt synergy. In aqueous systems, cobalt selectivity remains below 40%, confirming that selective cobalt extraction is a unique feature of the eutectic environment. Overall, the combined analysis of extraction efficiencies, synergy factors, and selectivity ratios suggests that DESs not only enhance metal dissolution but also influence the relative distribution of metals between phases under the investigated conditions. Thus, among the investigated systems, ChCl:EG emerges as the most promising solvent within the scope of this study, based on its high cobalt selectivity, extraction efficiency, and short-term leachate stability.

The reported selectivity values are calculated based on the relative concentration of dissolved metals in the leachate and therefore reflect solution-phase selectivity under the applied experimental conditions. A complete solid–liquid mass balance, including residual metal content in the solid phase and potential unaccounted fractions, was not performed in this study. Consequently, the selectivity values should be interpreted as comparative indicators rather than absolute process selectivity metrics.

Fig. 2 provides a compact three-variable view linking eutectic effect, extraction yield, and separation performance for the three DES systems. The x-axis reports the Co synergy factor (Table 2), the y-axis reports the amount of Co extracted (Table 1), while bubble size is proportional to cobalt selectivity (Table 3). A consistent trend is observed: DESs with a stronger eutectic effect also show higher Co extraction and higher selectivity. In particular, ChCl:EG (highest synergy) achieves the largest Co dissolution and the highest selectivity, whereas ChCl:Urea (lowest synergy) yields markedly lower Co extraction together with reduced selectivity. Overall, the plot highlights that eutectic cooperativity and cobalt selectivity evolve in the same direction, suggesting that cooperative DES interactions promote not only dissolution but also preferential cobalt extraction over competing metals. Therefore, the proposed mechanism is intended as a working hypothesis consistent with the present data and previous literature, rather than as a direct spectroscopic demonstration of metal speciation in the investigated leachates.

The trend in Fig. 2 reflects fundamental differences in metal-DES interactions. The strong selectivity of ChCl:EG likely arises from a cooperative effect between chloride coordination and EG-mediated hydrogen bonding, lowering the energy barrier for Co dissolution relative to Ni and Mn. In contrast, ChCl:Urea appears unable to enhance Co solvation to the same extent, resulting in significantly lower selectivity. These observations support the idea that DES structure governs not only extraction efficiency but also the hierarchy of metal–solvent affinities. The extraction trends observed for the three DESs align closely with mechanistic models reported in recent solvometallurgical literature. In ChCl:EG, cobalt dissolution is consistent with the formation of tetrahedral chloride complexes such as $[CoCl_4]^{2-}$, whose UV–Vis signatures have been consistently detected in EG-based DES systems. Abbott and co-workers [16] reported that such complexes arise only when chloride anions are embedded within a hydrogen-bond-structured eutectic environment, explaining why aqueous mixtures of choline chloride and ethylene glycol fail to reproduce the same metal-solvation behaviour. This interpretation is consistent with the high synergy factor measured here and with the remarkable solution stability, as $[CoCl_4]^{2-}$ complexes are known to resist hydrolysis and precipitation even under alkaline conditions. In ChCl:GLY, the increased ability of glycerol to engage in multi-dentate hydrogen-bonding interactions appears to modulate both solvation and redox equilibria. Polyol-based DESs featuring triols have been shown to preferentially stabilize Mn(II) complexes while maintaining Co(II) solubility across broad pH ranges. Tran et al. proposed that the higher H-bond density and stronger solvation shells around metal ions in GLY-rich systems can shift dissolution pathways toward ligand-assisted destabilization of Mn-bearing phases, consistent with the enhanced Mn extraction and the complete suppression of precipitation observed for ChCl:GLY [17]. Conversely, the behaviour of ChCl:Urea reflects a fundamentally different mechanism. Urea is known to reduce Co(III) species to Co(II), forming transient Co-Urea complexes that lack long-term stability. Yu et al.[18]reportedthat such complexes undergo progressive re-aggregation and precipitation, especially in the presence of competing transition metals. This explains both the lower initial extraction of cobalt and the extensive, non-selective precipitation of Co, Ni, and Mn from aged ChCl:Urea leachates. In addition, the broad redox activity of Urea-containing mixtures can disrupt the hierarchy of metal-solvent affinities established during leaching, further reducing selectivity [18]. Altogether, these mechanistic considerations support the central conclusion of this study: DES cooperativity, defined as the combined effect of eutectic structuring, hydrogen-bond-network organization, chloride availability, and ligand-specific coordination, appears to play a key role in promoting selective cobalt dissolution and is not reproduced by the non-eutectic aqueous systems investigated in this study.

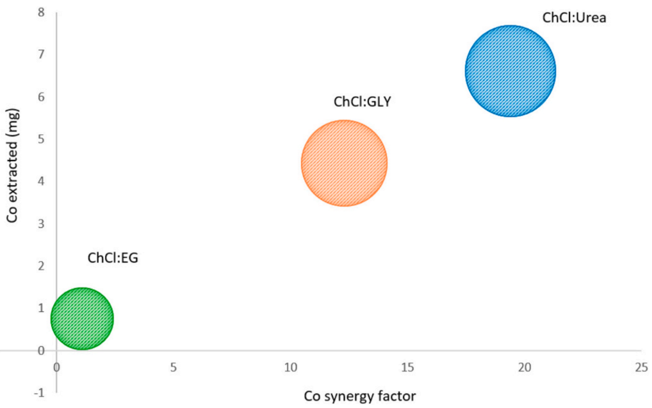

Fig. 2. Three-variable bubble plot linking eutectic cooperativity and separation performance for the DES systems. The x-axis reports the Co synergy factor (Table 2), the y-axis the extracted Co amount (Table 1). The bubble's dimensions are proportional to the Co selectivity. Higher Co synergy corresponds to higher Co extraction and increased cobalt selectivity.

Table 3
Selectivity for Co over Ni and Mn.

Solvent	Co selectivity
DES ChCl:EG	97.1%
DES ChCl:GLY	87.2%
DES ChCl:Urea	46.0%
Aqueous systems	generally <40%

In the eutectic phase, choline chloride supplies chloride ions capable of coordinating dissolved transition-metal cations, while the hydrogen-bond donor (HBD) establishes a structured solvation environment characterized by low water activity. This combination creates a unique chemical medium in which both coordination and solvation effects act cooperatively. The origin of cobalt selectivity can be interpreted by considering both intrinsic coordination chemistry and solvent structuring. Co^{2+} exhibits a higher propensity to form stable chloride complexes [31] compared to Ni^{2+} and Mn^{2+}, [32] particularly under low-water-activity conditions. [33] Within the DES, the hydrogen-bond network suppresses competitive hydration and selectively stabilizes these Co—Cl species, thereby favouring cobalt dissolution over competing metals. This cooperative effect appears more pronounced in ChCl:EG, where ethylene glycol provides an optimal hydrogen-bonding environment that enhances Co—Cl stabilization, leading to the highest cobalt extraction and selectivity. In ChCl:GLY, a similar cooperative mechanism operates, although the stronger and more extensive hydrogen-bond network of glycerol also promotes manganese stabilization, resulting in slightly lower cobalt selectivity. Conversely, in ChCl:Urea, the solvation environment is less effective in stabilizing Co—Cl species, as the coordination chemistry is altered by the presence of Urea, which can act as a competing ligand and modify the hydrogen-bond network [29]. This results in weaker cobalt solubilization and promotes non-selective precipitation during aging, reflecting a reduced ability of the eutectic medium to maintain stable metal-chloride complexes compared to EG-based systems. In contrast, the corresponding aqueous analogues lack this eutectic structuring: the high-water activity promotes strong hydration of all metal ions, suppresses selective chloride coordination, and ultimately leads to poor cobalt extraction and low selectivity. Overall, selective cobalt recovery arises from the combined action of chloride coordination, reduced water activity, and the structured hydrogen-bond network of the DES, which together selectively stabilize cobalt species relative to nickel and manganese. It should be noted that replacing a DES component with water alters multiple physicochemical properties simultaneously (including viscosity, ion activity, acid–base equilibria, and hydrogen-bonding structure). Therefore, this comparison is not intended to isolate a single variable but rather to assess whether DES-specific behaviour can be reproduced in non-eutectic systems.

3.3. Morphological analysis of residual BM

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) was used to investigate the morphology and elemental distribution of the residual samples obtained after each one of the three DES leaching (RES2_BM_A, RES2_BM_B, and RES2_BM_C). The SEM images reveal for all the samples a heterogeneous assemblage of granular particles with predominantly sub-rounded to irregular morphologies (Fig. 3).

Sample A exhibits relatively larger and more compact particles with smoother surfaces and limited fragmentation. In contrast, Sample B shows a higher degree of particle breakage and a broader particle size distribution, suggesting mechanical fragmentation or increased processing. Sample C displays the highest morphological heterogeneity, characterized by the coexistence of large aggregates and fine particulate fractions, indicating a more advanced degree of structural disruption.

Elemental mapping performed via EDS highlights the spatial distribution of carbon (C), manganese (Mn), cobalt (Co), and nickel (Ni). Carbon appears widely distributed across the particulate surfaces in all samples, likely reflecting either a carbonaceous matrix or conductive carbon phases associated with the material. Transition metals (Mn, Co, and Ni) are detected as localized clusters within individual particles, indicating that these elements are associated with discrete mineral or oxide phases rather than being uniformly dispersed throughout the matrix. Additional SEM-EDS images at different magnifications are provided in the Supporting Information (Fig. S2) to further support the observed morphological features.

3.4. Metal distribution and precipitation during aging of DES leachates

Once analysed the extraction performances of the three DESs, the possibility to recover the leached metals was considered. At first, the clear solutions were rested for 5 days and for the three DESs, a precipitate was formed. Then, the pH of the filtered solutions was settled to 14 by adding a saturated solution of NaOH and after 2 days, additional precipitate was recovered (Table 3).

The data reported in Tables 3 and 4 suggest that ChCl:EG and ChCl:GLY form highly stable metal-DES complexes, particularly for cobalt. The precipitated solids were analysed in terms of metal content by ICP; however, no structural or phase characterization (e.g., XRD, FTIR, Raman, or SEM-EDS) was performed. Therefore, the nature of the precipitated species cannot be unambiguously assigned, and they may consist of hydroxides, basic salts, hydrated complexes, or mixed phases. Accordingly, the following discussion focuses on metal distribution and

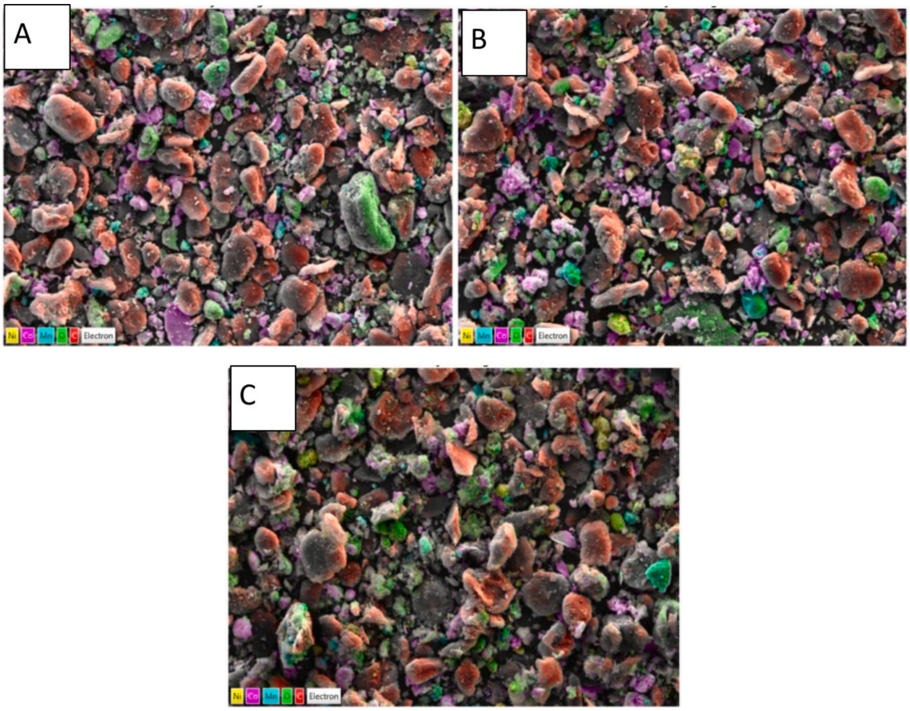

Fig. 3. SEM-EDS of residual BM after DES leaching: RES2_BM_A (A, after ChCl:EG leaching); RES2_BM_B (B, after ChCl:GLY leaching); RES2_BM_C (C, after ChCl:Urea leaching).

Table 4
Recovery of metals from DES leaching solutions.

Entry	Matrix	Co; Δ	Li; Δ	Mn; Δ	Ni; Δ
1	ChCl:EG	6.61; 2.1%	1.49; 3.2%	0.12; 2.2%	0.08; 0.004%
2	Precipitate from ChCl:EG after 5 days	0.107; 1.1%	0.001; 3.4%	0.004; 2.3%	0.006; 2.7%
3	Precipitate from ChCl:EG after 5 days + NaOH	0.322; 1.2%	0.001; 2.5%	0.005; 1.2%	0.003; 6.4%
4	ChCl:GLY	4.43	1.71	0.36	0.29
5	Precipitate from ChCl:GLY after 5 days	0.047; 0.7%	0.002; 1.0%	0.007; 0.7%	0.007; 0.9%
6	Precipitate from ChCl:GLY after 5 days + NaOH	n.o.	n.o.	n.o.	n.o.
7	ChCl:Urea	0.75; 0.7%	2.77; 3.0%	0.26; 0.5%	0.62; 0.8%
8	Precipitate from ChCl:Urea after 5 days	0.524; 0.7%	0.001; 0.3%	0.196; 0.5%	0.473; 0.8%
9	Precipitate from ChCl:Urea after 5 days + NaOH	0.069; 0.6%	0.001; n.c.	0.141; 0.6%	0.005; 2.7%

The amount of extracted metal is expressed in mg as all the experiments were conducted on the same scale and in the same conditions (see Section 2.2) and thus the mg extracted in each experiment are comparable; Δ indicates the standard deviation (%); n.o. stands for not observed.

recovery trends rather than on specific precipitation mechanisms.

After 5 days of aging, only marginal spontaneous precipitation is observed. For ChCl:EG, cobalt precipitation amounts to 1.6% of the initially dissolved Co (0.107 mg vs. 6.61 mg). For ChCl:GLY, cobalt precipitation is even lower (1.1%). These results indicate that Co^{2+} remains predominantly in solution, consistent with the high selectivity and synergy factors discussed previously. Mn and Ni show similarly low precipitation levels, confirming that these DESs maintain metals in solution over time. In contrast, the behaviour of ChCl:Urea leachate fundamentally alters the interpretation. Unlike the other DESs, ChCl:Urea initially extracts much lower amounts of cobalt but relatively high amounts of lithium and nickel, in agreement with its low cobalt selectivity (Table 3). After 5 days, ChCl:Urea exhibits substantial spontaneous precipitation of transition metals, showing a substantial transfer of cobalt to the solid phase. This behaviour sharply contrasts with ChCl:EG and ChCl:GLY and indicates that ChCl:Urea is unable to maintain metals in solution over time. Importantly, precipitation in ChCl:Urea is non-selective, with Co, Ni, and Mn co-precipitating in comparable quantities. This suggests that the Urea-based DES fails to preserve the hierarchy of metal–solvent affinities established during the leaching step, in line with its low cobalt selectivity and synergy factor.

3.5. Alkaline treatment and evolution of metal distribution in DES leachates

NaOH addition produces moderate and system-dependent effects. In ChCl:EG, alkaline treatment increases cobalt recovery from 0.107 mg to 0.322 mg, indicating partial destabilization of Co–DES complexes. In ChCl:Urea, NaOH addition reduces cobalt and nickel in the precipitate (Co: 0.069 mg; Ni: 0.005 mg), while manganese remains comparatively high (0.141 mg).This indicates a redistribution of metals between solid and liquid phases under alkaline conditions. Overall, NaOH treatment does not restore selectivity in ChCl:Urea and further highlights the intrinsic instability of this DES system. In ChCl:GLY, no precipitation is observed upon NaOH addition, confirming the exceptional stability of metal–glycerol–chloride coordination even under strongly alkaline conditions.

3.6. Sustainability assessment of DES leaching systems using the LEACH framework

To complement the extraction and selectivity analysis, the three DES systems investigated in this work (ChCl:EG, ChCl:GLY, ChCl:Urea) were evaluated through the LEACH (Low-impact Extraction and Assessment of CHemical solvometallurgy) framework [23], a modular sustainability tool specifically developed for assessing early-stage solvometallurgical processes. LEACH quantifies sustainability by assigning penalty points (PP) across economic, technical, and safety dimensions, with lower PP indicating a more sustainable configuration. The tool has been designed to capture aspects typically overlooked in early laboratory studies, such as operational safety, regulatory burden, solvent stability, recyclability, and mass-intensity constraints.

Notably, the LEACH “stability (aging)” penalty aligns with the experimental aging behaviour of the leachates: ChCl:Urea exhibits marked instability with substantial, non-selective Co-Ni-Mn precipitation upon standing, whereas ChCl:EG and ChCl:GLY remain largely stable with only marginal precipitation.

In this work, LEACH was applied to both the solvent formulation (Module 1) and the BM leaching step (Module 2). The overall sustainability score (Module 3) was calculated using the EcoScale logic (Module 3 = 100 – average (PP_M1, PP_M2)), as detailed in the Supporting Information. For clarity, Table 5 reports the overall penalty total (ΣPP) used in the calculation rather than the rescaled M3 score. The assessment uses experimental data collected in this study (temperature–time footprint, recyclability, intrinsic hazards, selectivity, and PMI), complemented with hazard classifications and biodegradability information available from material safety data. A complete description of the LEACH methodology, the scoring rules, and the analytical calculation of penalty points for each DES is provided in the Supporting Information, while in Table 5 a summary of the assessment for the three systems is reported.

The LEACH summary in Table 5 reveals how the three DESs differ when sustainability is evaluated at the level of solvent formulation (M1), leaching operation (M2), and full process (M3). In Module 1 (solvent formulation), ChCl:EG attains the highest score (87), marginally ahead of ChCl:Urea (78) and ChCl:GLY (77). This indicates comparatively lower penalties at the formulation stage for the EG-based mixture under the present assumptions (component hazards, renewability, stability/biodegradability, and cost), despite EG's known intrinsic toxicity, and highlights that M1 is especially sensitive to component-resolved choices rather than to operational behaviour. In Module 2 (BM leaching), ChCl:EG again leads (59.5), with ChCl:GLY close behind (56.5) and ChCl:Urea substantially lower (46.5). This ranking mirrors the experimental trends: EG shows very high Co selectivity and stable leachates upon aging, while GLY combines good stability (even after strong alkalinisation) with only slightly lower Co selectivity; conversely, the Urea system suffers non-

Table 5
LEACH assessment outcome for the three considered systems. The score for each module has been calculated as 100 – penalty points (PP). Higher scores indicate higher sustainability.

DES	Solvent formulation (M1)	BM Leaching (M2)	Overall LEACH score (M3)
ChCl:GLY (1:1.5)	77	56.5	55.5
ChCl:EG (1:2)	87	59.5	52.5
ChCl:Urea (1:2)	78	46.5	65.5

selective precipitation on aging and after NaOH, which elevates the penalties associated with stability, work-up complexity, and recyclability in M2. Consistently, the LEACH Module-2 "Selectivity" subparameter mirrors the experimental Co selectivity trend: ChCl:EG (97.1%) falls in the >90% band (0 PP), ChCl:GLY (87.2%) in the 70–90% band (2 PP), and ChCl:Urea (46.0%) in the <70% band (4 PP).

The overall Module 3 scores, however, emphasise a critical point about LEACH's independent whole-process appraisal: ChCl:Urea reaches the highest M3 score (65.5) under the present module-3 assumptions (including a conservative treatment of yield and a high Co-selectivity setting at the overall level), whereas ChCl:GLY and ChCl:EG score 55.5 and 52.5, respectively. This divergence between M2 and M3 underscores that LEACH M3 does not aggregate M1 + M2, but rather rescores the complete set of economic, technical, and safety categories at the overall process level. In practice, the Urea system benefits in M3 from a benign HBD profile and economic simplicity, which partly offsets its operational drawbacks observed in M2; by contrast, the EG system carries strong chemical performance yet accumulates higher overall penalties due to intrinsic hazard and limited solvent reusability, while the GLY system sits in between with a balanced hazard profile and robust recyclability but a slightly lower M1 score under the present assumptions. Taken together, Table 5 shows that module-specific and overall rankings need not coincide. For process design, the actionable levers differ by solvent: for ChCl:EG, improvements should target hazard mitigation and closed-loop solvent handling; for ChCl:GLY, gains will come from incremental selectivity enhancement at constant safety/recyclability; for ChCl:Urea, any route to practical implementation must first resolve aging-induced instability and non-selective precipitation observed during leaching, otherwise the favourable whole-process attributes captured in M3 will remain misaligned with operational reliability. It is important to note that the overall LEACH score (M3) does not necessarily correlate with the chemical suitability of a system for selective metal recovery. In particular, the higher M3 score observed for ChCl:Urea reflects favourable intrinsic properties at the formulation and regulatory level, rather than effective operational performance. In fact, despite its higher M3 value, ChCl:Urea exhibits poor selectivity and pronounced leachate instability, which limit its practical applicability for selective cobalt recovery. Therefore, LEACH results should be interpreted as complementary to, rather than substitutive of, extraction efficiency and selectivity metrics.

This modular reading, EG leading at the unit-operation level (M2), Urea advantaged in the whole-process assessment (M3), and GLY offering a well-balanced compromise, illustrates the diagnostic value of LEACH for guiding solvent redesign and scale-up choices in DES-based solvometallurgy.

4. Conclusions

This study demonstrates that choline chloride–based deep eutectic solvents can enable selective cobalt recovery from pre-treated battery black mass enriched in transition metals following microwave-assisted water leaching. Among the investigated systems, ChCl:EG emerged as the most effective DES, achieving the highest cobalt extraction (6.61 mg) and an exceptional cobalt selectivity of 97.1% over nickel and manganese. This behaviour, together with the comparison against composition-matched aqueous analogues, suggests that cobalt dissolution is influenced by the DES environment rather than by individual components. ChCl:GLY also displayed significant cooperative behaviour, with high cobalt selectivity (87.2%) and the highest manganese synergy factor (9), highlighting the possibility of tailoring DES composition to target specific metals. In practical terms, the hydrogen-bond donor controls which metal is preferentially stabilized in the eutectic environment: EG maximizes Co selectivity, whereas GLY promotes Mn dissolution, enabling composition-driven tuning of metal–solvent affinity hierarchies.

In contrast, ChCl:Urea exhibited limited cobalt extraction (0.35 mg) and low selectivity, accompanied by extensive and non-selective precipitation of Co, Ni, and Mn upon aging. These aging outcomes show that leachate stability is a process determinant: non-selective precipitation undermines downstream separation and operational reliability even when apparent "easy" metal recovery is observed. This represents the central novelty of the study: ChCl, ethylene glycol, glycerol, and Urea do not retain the same metal-solubilization behaviour when incorporated into DESs, and the observed leaching performances cannot be rationalized as the simple sum of the individual HBA and HBD effects. This behaviour indicates weak metal-DES stabilization and dynamic re-equilibration, rendering Urea-based DESs unsuitable for selective cobalt recovery despite their apparent ease of metal precipitation. Metal recovery experiments further revealed that ethylene glycol- and glycerol-based DESs form remarkably stable metal-solvent complexes, with less than 2% cobalt precipitation after 5 days and no precipitation observed for ChCl:GLY even after alkaline treatment at pH 14. While this stability represents a challenge for downstream cobalt recovery, it also provides a robust platform for designing controlled and selective stripping strategies beyond simple pH adjustment. Overall, this work shows that DESs do not enhance metal dissolution but also influence the relative distribution of metals between phases under the investigated leaching conditions. These findings underscore the importance of evaluating DESs across the entire process chain and suggest that ChCl:EG-based systems may represent a promising basis for sustainable, selective cobalt recycling from lithium-ion batteries. Finally, the application of the LEACH framework provided an independent sustainability perspective that complements the chemical performance trends observed experimentally. In particular, LEACH makes explicit that stability, workup complexity, and solvent recyclability can weigh as much as extraction yields in determining overall process viability.

While ChCl:EG excelled in cobalt extraction and selectivity, LEACH highlighted the superior overall sustainability of ChCl:GLY, driven by its benign hazard profile, high stability, and effective recyclability, whereas ChCl:Urea was penalized for its intrinsic instability and non-selective precipitation. By combining experimental insights with a structured sustainability assessment, this work demonstrates how LEACH can guide solvent optimisation and support the development of DES-based recycling strategies that are not only efficient but also robust and sustainable. Future work should quantify solvent reuse over repeated cycles (including impurity build-up and property drift) to translate eutectic-driven selectivity into a closed-loop, scalable recycling process.

CRediT authorship contribution statement

Alberto Mannu: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Maria Enrica Di Pietro:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Formal analysis, Conceptualization. **Eros Mossini:** Writing – original draft, Supervision, Formal analysis. **Elena Macerata:** Validation, Supervision, Resources. **Gabriele Magugliani:** Validation, Supervision, Investigation. **Vincenzo Anania:** Investigation, Formal analysis, Data curation. **Francesca Bianchi:** Writing – original draft, Methodology, Investigation, Formal analysis. **Elza Bontempi:** Writing – original draft, Supervision, Resources, Data curation. **Andrea Mele:** Writing – original draft, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

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Data availability

Data will be made available on request.

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