



Life cycle assessment of stone consolidants for conservation of cultural heritage

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ABSTRACT

The field of the conservation and repair of built cultural heritage shows a growing attention towards the environmental sustainability of materials and treatments used for conservation projects. As a standardized methodology that is widely adopted for the comparative evaluation of construction and building materials, life cycle assessment (LCA) can be usefully applied to conservation materials, if specific field-related issues on the definition of functional units and reference flows are properly addressed.

In the present study, LCA is used to quantify the environmental footprint of four alternative consolidants for restoration of weathered carbonate substrates. An innovative treatment based on an aqueous solution of diammonium hydrogen phosphate (DAP) is compared against three commercial alternatives (lime nanoparticles, ethyl silicate, and acrylic resin). The issue of the definition of the reference flow (i.e., the amount of each consolidant required for the restoration of a given surface) is addressed through experimental tests on three model substrates (marble, limestone, and lime mortar), following two alternative criteria: i) application until apparent refusal, as recommended by product manufacturers, and ii) application to obtain a certain degree of consolidation, in terms of increase in compressive strength.

The novel DAP consolidant is shown to have lower impacts than the alternatives on several environmental impact categories, mainly thanks to the absence of organic solvents in its formulation. The evaporation of volatiles after application (volatile organic compounds for the commercial consolidants, ammonia for the DAP consolidant) is highlighted as an environmental hotspot for all the consolidants.

1. Introduction

The degradation of cultural heritage materials is one of the main threats to the preservation of historical buildings, monuments and artifacts for the future generations [1–3]. Carbonate substrates, such as marble, limestone, and lime-based mortars, which have been widely used in architecture and sculpture by civilizations across the globe [4,5], constitute a particularly vulnerable class of materials, as they might be severely affected by various weathering mechanisms when exposed outdoors [6]. Dissolution in rain due to calcite solubility in water [7], physical weathering due to temperature variations [8] and mechanical stresses inside the pores due to salt crystallization and freezing-thawing cycles [9] are among the main deterioration processes, leading to surface recession, cracking, powdering and material loss. Human-induced factors, viz. climate change [10,11] and atmospheric pollution [12–14], are expected to worsen carbonate stone deterioration.

To arrest and prevent these deterioration processes, conservation

treatments can be applied, including protectives and consolidants. *Protectives* are aimed at forming a surface layer with lower solubility than the carbonate substrate, thus preventing its dissolution. *Consolidants* are aimed at penetrating in depth into the substrate and bonding the grains, thus increasing cohesion and mechanical properties. At present, most commercial products exhibit limitations in terms of efficacy, compatibility with the substrate and/or durability when applied onto carbonate stones. Research is ongoing to develop improved protectives [15,16] and consolidants [17,18].

In recent years, a growing attention has been addressed towards the role of heritage management in the broader issue of sustainable development [19,20]. In the conservation of built heritage, this highlights the need to rethink the materials and the methods used in the conservation of built heritage, to include social, economic, and environmental sustainability considerations [21]. Therefore, in addition to the technical criteria linked to efficacy, compatibility and durability [22], also sustainability metrics should be considered among the decision-support

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criteria for the selection of conservation materials [23]. With reference to environmental sustainability, the use of life cycle assessment (LCA) is an increasingly common approach in building engineering to holistically analyze the environmental performance of construction methods [24], design choices [25], components [26] and materials [27,28]. More specifically, Settembre Blundo et al. [29] identified LCA as the most consolidated and recognized tool for a quantitative evaluation of the environmental impacts of conservation projects. However, to date only a few studies have applied LCA for the analysis of the environmental burdens of the traditional phases of cultural heritage conservation, namely cleaning, consolidation and protection. As for the *cleaning*, Franzoni et al. [30] carried out a comparative LCA of several alternatives for the on-site cleaning of historical façades. Regarding *consolidation*, Turk et al. [31] performed a cradle-to-gate LCA of three novel consolidants (calcium acetoacetate, calcium ethoxide, and calcium isopropoxide), while Mauko Pranjić et al. [32] investigated the environmental burdens associated to products for consolidation of carbonate substrates (calcium acetoacetate) and silicate substrates (a TEOS-based consolidant). For the final *protection*, Ferrari et al. [33] evaluated the environmental footprint of a nano-TiO₂ coating for the treatment of limestone surfaces, while Mauko Pranjić et al. [32] assessed the environmental burdens of a photocatalytic suspension for the self-cleaning protection of wall surfaces.

A critical aspect identified by all the aforementioned studies is the quantification of the reference flows of materials associated with the conservation work, considering the variety of possible practices and the site-specific nature of built heritage conservation projects. Indeed, focusing for instance on consolidating treatments, their use can encompass an extremely wide range of application techniques, on substrates with broadly different characteristics and according to treatment criteria that may vary depending on the objectives of each conservation project and on the expert judgment of each restorer [32]. As a result, the reference flow of consolidating material required to satisfy the functional unit, as well as any auxiliary input, might differ significantly for each specific restoration project.

In this context, the present study is aimed at providing a twofold contribution to the literature:

- 1) For the first time, a life cycle assessment (LCA) was performed for an innovative consolidant (namely, diammonium hydrogen phosphate [18]), which is receiving increasing attention given the very encouraging results it has provided both in laboratory studies [34] and in field applications to real case studies [35]. The LCA of the innovative consolidant was performed in comparison with the most common alternatives available on the market, namely dispersions of Ca(OH)₂ nanoparticles (the so-called “nanolimes” [36]), ethyl silicate [17] and solutions of acrylic resin [37]. The environmental hotspots in the life cycle of each material were quantified and the relative importance of direct impacts in the use phase versus impacts in the supply chain was assessed.
- 2) The main issue evidenced in literature, i.e., the quantification of the reference flows of materials required for the conservation projects, was explicitly addressed by supporting the LCA with an experimental campaign for the definition of the functional unit. Different criteria were considered to define the amounts of consolidant to be compared, namely: (i) application until apparent refusal, as recommended by manufacturers in the technical data sheet of commercial products, and (ii) application to produce a certain level of consolidation, in terms of increase in compressive strength. The effect on the comparative assessment of the alternative consolidants was thoroughly analyzed, with the aim of contributing to the discussion on the standardization of LCA practices in the cultural heritage field.

2. Context of application of the study

In the conservation and restoration of built cultural heritage, the

choice of materials for consolidating and protective treatments entails complex decision-making, involving a multitude of criteria [23,38]. As outlined by Masi et al. [39], a consolidant material should at least guarantee effectiveness (i.e., provide a significant strengthening action to the substrate), compatibility (i.e., not cause undesired changes in the substrate), and durability (i.e., maintain the strengthening action over time). For each of these criteria, multiple parameters can be adopted as relevant metrics: for example, effectiveness might be evaluated in terms of increase in modulus of elasticity or flexural, compressive or tensile strength [38], while compatibility indicators can include effect on color change, pore size distribution, water absorption and others [22]. In addition, the specificity of each consolidation project (which for instance is determined by the state of conservation of the monument, the type of deterioration patterns, the weather and the climate of the area, the presence and the nature of past intervention works [40,41]) strongly influences the design and, notably, the final result of the intervention.

As introduced in section 1, a growing attention towards sustainability also in the management of built heritage leads to the need to “measure” the environmental impact of materials and procedures adopted in conservation works. When introducing the dimension of environmental impact, the same considerations as above apply. An accurate quantification of the related environmental burdens would generally require a specific LCA study for each project. However, no consolidated protocol (such as, e.g., product category rules) exists to date to support practitioners in the conduction of LCA analyses that take into account the specific issues of the consolidation of built cultural heritage.

In this regard, the present study introduces possible approaches for the definition of an LCA on consolidating treatments depending on available information on the mode of application and/or the estimated consolidating ability. Moreover, this study systematically explores a set of 4×3 combinations of consolidants and carbonate substrates with the aim of determining the range of possible environmental performances achievable by consolidating treatments, assessing the typical trends of performance of the different types of consolidants and identifying the main environmental hotspots of each type.

The resulting dataset is aimed at offering a useful general reference on a wide range of representative situations and does not conflict with the execution of dedicated, tailored LCA studies of higher detail in the context of specific consolidation projects.

3. Materials and methods

3.1. Experimental definition of functional unit and reference flows

The environmental impacts associated with the life cycle of the alternative consolidants were studied by using the LCA methodology, following ISO 14040 [42]. In order to present a concise yet representative set of relevant situations for consolidant application, the LCA study was set up as sketched in Fig. 1.

The comparison between the four consolidants was performed by considering as a functional unit the treatment of 1 m² of three different substrates (namely, marble, limestone and slaked lime mortar), according to the following specifications. Specimens of each type of substrate were prepared and characterized (section 3.2.1), then treated by brushing with the four consolidants (section 3.2.2). The amount of consolidant needed to treat 1 m² (the so-called specific consumption, in L/m²) was then experimentally assessed for each type of substrate (section 3.3), considering two different scenarios: (1) the “*recommendation-based scenario*”, corresponding to application until “apparent refusal” (i.e., the condition when the substrate no longer absorbs the consolidant [43]), as recommended by the manufacturers in the technical data sheets of commercial consolidants; (2) the “*performance-based scenario*”, corresponding to a certain level of consolidation of the substrate, by application of different amounts of the different consolidants, depending on the chemical reactions involved.

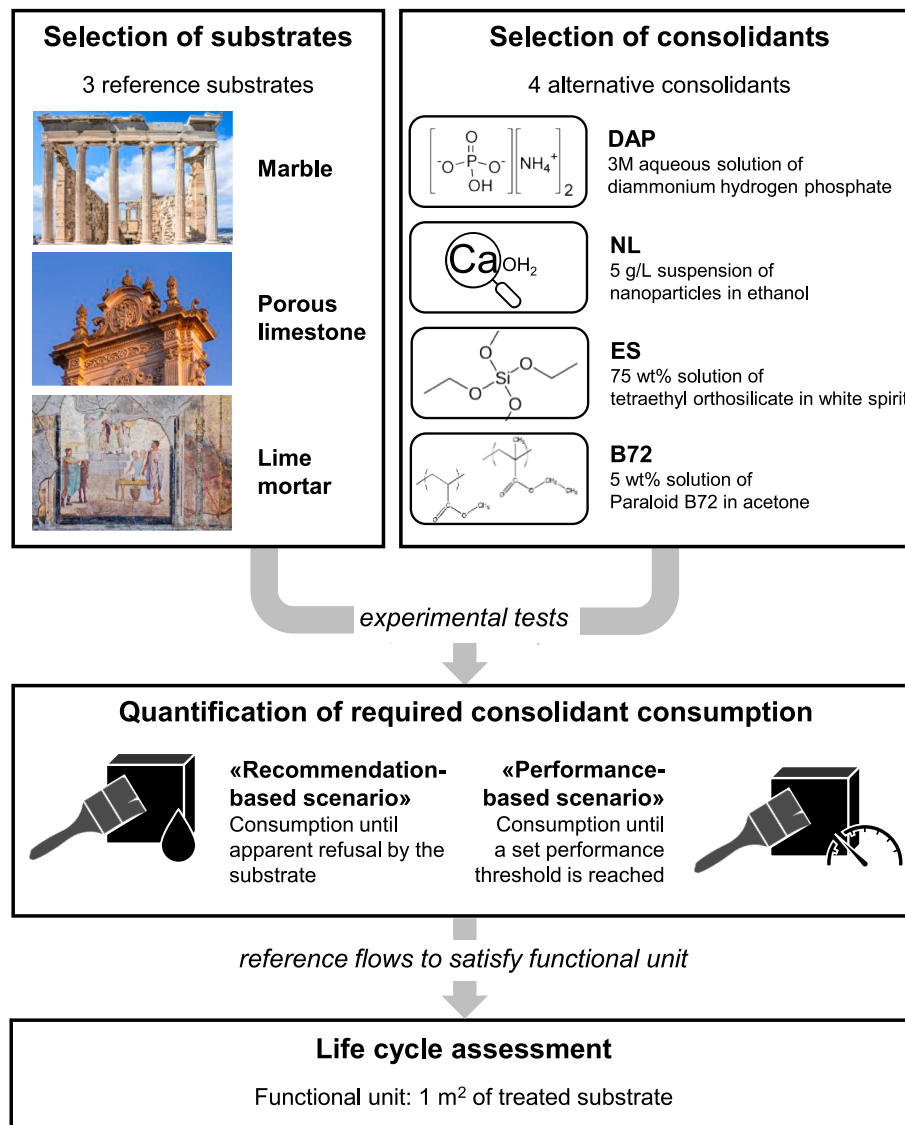


Fig. 1. Set up of the study: approach for the definition of the reference flows.

Considering both scenarios is extremely important and significant, for two reasons: (i) depending on the characteristics of the substrate and the consolidant, apparent refusal may require an extremely high number of brush strokes, which is not always feasible in the practice of monument conservation, for technical and economic reasons; (ii) even if apparent refusal is reached, different consolidants may actually induce significantly different levels of consolidation of the substrate, depending on the type of interaction between the hardened consolidants and the substrate (e.g., chemical vs. physical-mechanical bonding [17]). In other words, a certain consolidant applied on a certain substrate until apparent refusal (with high specific consumption) may actually lead to much lower increases in mechanical properties than a different consolidant applied with lower specific consumption, if the second consolidant is able to bond more effectively to the substrate. Because the final goal of any consolidation work is to increase the mechanical properties of the substrate, thus extending its durability to deterioration processes, to compare the different products based on their performance is the most significant approach. Indeed, this is in closer agreement with the concept of functional unit, although such an approach is much more difficult to adopt, as the amounts of product leading to certain levels of consolidation are not data available *a priori*.

Moreover, it is worth pointing out that another relevant aspect in the

definition of the functional unit is the time dimension. In the quantification of the required reference flows of consolidants, the considered time frame could play a very significant role, because different treatments might exhibit different durability and, therefore, require an earlier re-application. However, obtaining adequate quantitative information from the available literature is difficult, because the durability of a treatment in the field is highly dependent on several site-specific factors, which hinders the comparability between results of different conservation projects, and because correlating the results of durability tests performed in the laboratory with durability experienced in the field is extremely challenging [85]. Hence, no assumptions are advanced in the present work about different durability of the analyzed consolidants for the purpose of the LCA study.

According to the aforementioned assumptions, the adopted experimental procedure allowed the quantification of the reference flows of consolidants to satisfy the functional unit under the different scenarios considered, as required by the Goal & Scope definition of the LCA. For each consolidant, a product system, including production, transportation and use, was assumed (section 3.4.1) and modelled in terms of life cycle inventory (section 3.4.2). The impacts arising along the life cycle of the alternative consolidants were evaluated according to the life cycle assessment method outlined in section 3.5.

3.2. Materials

3.2.1. Substrates

Three types of materials were considered as representative of carbonate substrates traditionally used in historic buildings and sculptures:

- **Marble.** Marble has been used since antiquity for its high aesthetic value and ease of carving. As a consequence of its microstructure (composed of tightly packed calcite grains, almost without intergranular voids), marble is highly sensitive to thermal weathering [8]. This leads to cracking, sugaring and bowing of thin slabs, so that consolidation of weathered marble is frequently needed [44,45]. For the experimental tests, cylindrical specimens (50 mm diameter, 20 mm thickness) were core-drilled from a single slab of Bianco Carrara from Carrara (Italy). To induce a deterioration condition similar to that of naturally weathered marble in need of consolidation, the specimens were subjected to an accelerated ageing procedure, able to rapidly induce the formation of microcracks inside the material [46]. According to a previously developed method, the samples were artificially aged by heating in an oven at 250 °C for 3 h [46]. After artificial weathering, the marble specimens had open porosity of ~3 %, as assessed by mercury intrusion porosimetry (MIP).
- **Limestone.** Porous limestones have been widely used in historic architecture. In this study, Lecce stone was selected for the tests, in the light of its widespread diffusion in the Baroque architecture in Southern Italy and its high susceptibility to deterioration [47], especially due to salt weathering that causes powdering, flaking and alveolization. Cylindrical specimens (50 mm diameter, 20 mm thickness) were core-drilled from a single slab from Lecce (Italy). Also in this case, to induce damage and to reproduce the condition of limestone needing consolidation, the specimens were artificially weathered by heating in oven at 250 °C for 3 h. The samples exhibited a final open porosity of ~26 %, as assessed by MIP.
- **Mortar.** Slaked lime has been used for centuries to prepare bedding mortars for masonries, plaster and renders, possibly with addition of pigments to prepare frescoes and wall paintings. In this study, mortar samples (30 × 30 × 20 mm³) were prepared by mixing hydrated lime (Colacem, Italy) and calcareous aggregate (maximum size 4 mm), adopting a binder-to-aggregate ratio of 1:2 v/v and a water-to-binder ratio of 1:1 v/v. After casting, the mortar samples were left to cure in a climatic chamber at T = 21 ± 2 °C and RH = 90 ± 2 % for 4 months, then in laboratory conditions for further 6 months. At the end of curing, the mortar specimens had open porosity ~21 %, as assessed by MIP, and compressive strength of ~3 MPa. The relatively good mechanical properties, in spite of the fact that historic mortars in need of consolidation often show lower strength, were the result of the mortar mix design, aimed at obtaining a material suitable for handling for the laboratory tests.

The choice of these three types of substrates was aimed at proposing three case studies of consolidant application onto carbonate materials that are different in terms of chemical-mineralogical composition, open porosity, and pore size distribution. Clearly, such selection of substrates does not cover the entire variety of heritage materials and their state of deterioration, but still it is highly significant, since (i) carbonate substrates were widely used historic architecture and sculpture, (ii) they suffer from severe deterioration processes and (iii) their consolidation is often considered more challenging than that of other types of substrates (e.g., silicate stones, for which silicate consolidants usually work quite well).

For each test described in the following, triplicate specimens were used and the average values were considered. Practical constraints dictated the use of different shapes for the specimens (cylinders for the stones, prisms for the mortar). However, this limitation has negligible influence in the discussion of the results, as the scientific problem addressed in the study is the comparative analysis of the environmental

impacts of different consolidants for each substrate, not of the impacts across different substrates.

3.2.2. Consolidants

Four consolidants were considered, which are all recommended for application onto carbonate substrates, according to the respective technical data sheets. For ready-to-use consolidants (i.e., nanolimes and ethyl silicate), the products were used as received, without further dilution; for consolidants that are supplied in powder/pellets and need to be dissolved (i.e., diammonium hydrogen phosphate and acrylic resin), solutions were prepared adopting the concentrations described in the following. As reported in detail in section 3.3, each consolidant was applied by brushing onto one face of the specimens (one circular face for the stones, one 30 × 30 mm² face for the mortar), then post-treatment operations were carried out, when needed (Table 1).

- **Diammonium hydrogen phosphate** (labelled “DAP”). The principle of this consolidating treatment is to bond the grains in the substrate by means of new calcium phosphates, resulting as the reaction product between calcium ions from the substrate and phosphate ions provided by soaking the substrate with a DAP solution [18]. Several different formulations of the treatment have been proposed in recent years, differing in terms of DAP concentration, possible addition of a calcium source and/or of organic solvents directly into the DAP solution [34]. Based on previous studies highlighting its effectiveness even on highly deteriorated substrates [45,48,49], in the present study a 3 M DAP aqueous solution (corresponding to an active principle concentration of 396 g/L) was used (DAP was kindly supplied by CTS, Italy). At the end of the brushing application, a plastic film was used to wrap the samples in order to prevent evaporation. After 24 h, samples were unwrapped, rinsed with water and left to dry in laboratory conditions. A post-treatment step was then carried out, consisting in the application of a poultice made of cellulose pulp and limewater, aimed at providing additional calcium ions for the

Table 1

Consolidants considered in the study and their typical application process (the duration of the curing phase for NL and ES is that recommended in the technical data sheets).

	DAP	NL	ES	B72
Composition	Aqueous solution of (NH ₄) ₂ HPO ₄ (3 M)	Dispersion of Ca(OH) ₂ nanoparticles in ethanol (5 g/L)	Solution of [Si (OEt) ₄] _n in white spirit (75 wt%)	Solution of Paraloid B72® (ethyl-methacrylate copolymer) in acetone (5 wt %)
Density	1.40 kg/L	0.79 kg/L	0.98 kg/L	0.78 kg/L
Application	Direct brushing on substrate + application of plastic film for 24 h	Brushing over a sheet of Japanese paper	Direct brushing on substrate	Direct brushing on substrate
Rinsing of excess product	Water	–	White spirit	Acetone
Post-treatment	Application of a sheet of Japanese paper and then a poultice of cellulose pulp and limewater + application of plastic film for 24 h	Application of a poultice of cellulose pulp and water	–	–
Curing	Drying for 3 d	Drying for 3 d + Curing for 4 weeks	Curing for 4 weeks	Drying for 3 d

reaction and then removing unreacted DAP during drying in contact with the substrate [48,49]. To prevent sticking, a sheet of Japanese paper (provided by AN.T.A.RES srl, Italy) was inserted between the specimen and the poultice. The poultice was wrapped in a plastic film to avoid evaporation. The film was removed after 24 h and the poultice was left to dry over the Japanese paper (approximately for 3 days).

- **Nanolimes** (labelled “NL”). The principle of this consolidating treatment is that new bridges are created among the grains in the substrate by treating it with a dispersion of $\text{Ca}(\text{OH})_2$ nanoparticles, which react with the CO_2 in the atmosphere to form new calcium carbonate that bonds the grains in the substrate [36]. In the present study, the commercial product Nanorestore® (kindly supplied by CTS, Italy) was used. The product is a suspension of $\text{Ca}(\text{OH})_2$ nanoparticles in ethanol with a 5 g/L concentration of the active principle. Following the recommendation in the product’s technical data sheet, the dispersion was not applied directly onto the substrate but a sheet of Japanese paper was applied before brushing the consolidant. At the end of the application, a poultice of cellulose pulp and deionized water was applied onto the Japanese paper to favor the nanoparticle carbonation, as recommended by the producer.
- **Ethyl silicate** (labelled “ES”). The principle of this consolidating treatment is that a solution of ethyl silicate is applied onto the substrate and then, by reaction with atmospheric humidity, hydrolysis-condensation reactions take place and amorphous silica is finally formed [17,50]. In the case of silicate stones, this amorphous silica can chemically bond to the substrate, thus significantly improving mechanical properties, while in the case of carbonate substrates only physical-mechanical bonding is expected [17]. Nonetheless, ethyl silicate is frequently used in the conservation practice also in the case of carbonate substrates, such as weathered marble, because the formation of amorphous silica in the intergranular fissures reduces grain loss, although scarce mechanical improvement is achieved [51]. In the present study, the commercial product Estel 1000® (kindly supplied by CTS, Italy), made of 75 wt% ethyl silicate (including 1 % dibutyltin dilaurate, DBTDL, as catalyst) and 25 wt% white spirit, was used. In the case of application until apparent refusal, excess product was removed by using the pure solvent. After the consolidant application, the specimens were left to cure in laboratory conditions for 4 weeks, as recommended in the technical data sheet.
- **Acrylic resin** (labelled “B72”). The principle of this consolidating treatment is to bond the grains in the substrate by means of a polymeric compound: the polymer is first dissolved in a suitable solvent, the so-obtained solution is then applied onto the substrate and finally, as the solvent evaporates, the polymer solidifies, thus bonding the grains in the substrate. In the present study, the commercial product Paraloid B72® (kindly supplied by CTS, Italy) was used. Paraloid B72 is an ethyl-methacrylate copolymer, which has been widely used as a consolidant, a protective and an adhesive [37]. Among the various concentrations of the active principle recommended in the technical data sheet (ranging between 2 and 10 %), a concentration of 5 % was selected, as often done in the conservation practice. The polymer was hence dissolved in acetone with a 5 w/v concentration, then the solution was brushed onto the specimens. In the case of application until apparent refusal, excess product was removed by using the pure solvent. At the end of the consolidant application, the specimens were left to dry until complete evaporation of the solvent.

3.3. Quantification of the consolidant consumption and effectiveness

As mentioned in section 2.1, two different scenarios were considered, corresponding to different consumption of the consolidants:

- **“Recommendation-based scenario”**. In this case, the comparison among the consolidants was aimed at answering the question: “Which consolidant has the highest environmental impact, if they are all applied as recommended by the supplier?” To maximize the consolidating efficacy, the manufacturers of commercial products usually recommend application until the substrate no longer absorbs the product. Therefore, the four consolidants were applied onto the substrates by brushing until “apparent refusal”, defined as the condition when the treated surface remains wet for more than 1 min after application of a brush stroke [43]. This condition should ideally correspond to full saturation of the substrate, although it is known that the pore size distribution influences the kinetics of the product adsorption [17,49], so refusal may actually occur before saturation is reached.
- **“Performance-based scenario”**: In this case, the comparison among the consolidants was aimed at answering the question: “To reach the same level of mechanical improvement of the substrate, which consolidant has the highest environmental impact?” Because the consolidating ability of each consolidant on each substrate is not known from technical literature, the consolidants were applied to the substrates in increasing amount and the resulting mechanical improvement was quantified. In particular, marble was treated with the four consolidants by 3-5-7 brush strokes, while limestone and mortar were treated by 10-20-30 strokes with DAP, NL and ES, and by 10-15-20 strokes with B72. The level of mechanical improvement was assessed in terms of compressive strength, as discussed below.

For both scenarios, the consumption (in L/m^2) of each product on each substrate was determined by weighing the containers with the consolidant before and after application by brushing apparent refusal (first scenario) or for the intended number of brush strokes (second scenario). It is important to note that several factors may affect the determination of the product consumption: (i) the open porosity and the pore size distribution of the substrate, which determine the amount of product absorbed into the pores and also the kinetics of the process; (ii) the application procedure, because the amount of material applied by the operator by each brush stroke and the timing of the single brush strokes affect the amount of solvent evaporated during application; (iii) the environmental conditions, which influence the evaporation process. Even though the absolute consumptions determined in this study (where small specimens were treated under a hood by academic researchers) may differ from the consumptions occurring in the field (where large surfaces are treated outdoors by professional restorers), the preparation of specimens in consistent conditions (i.e., same operator, same procedure, same environment) is deemed to provide reliable data for the relative comparison among the alternative consolidants.

Mechanical improvement was considered as representative of the consolidating ability according to the following reasoning. The main goal of any consolidant is to increase the substrate durability, which is threatened by deterioration processes (such as freeze-thaw and salt crystallization cycles) that cause stress inside the material. Because damage occurs when this stress exceeds the substrate’s tensile strength, this latter property is the ideal one to measure for assessing the efficacy of a consolidant. Nonetheless, given the practical difficulties of measuring the tensile strength of stone and mortar specimens, in the present study compressive strength was adopted as a significant mechanical parameter, considering that the two properties are correlated and that, consequently, compressive strength is often used to assess the consolidating ability [17,22]. Compressive strength was determined by double punch test [52], which allows for a more reliable characterization than a standard compressive test, where the small specimen is directly placed in contact with the loading machine, and it is particularly suited for testing specimens with irregular shapes [53–55]. The test consists in loading the specimens perpendicular to their 20 mm thickness, by means of 2 steel platens with 20 mm diameter. The size of the platens was selected based on previous studies, indicating that more

reliable results are obtained when the platens diameter equals the thickness of the specimen [56]. Although the various consolidants have different curing times (Table 1), all the specimens were tested at the same time, namely after curing for 4 weeks (as needed by NL and ES specimens).

3.4. LCA study

3.4.1. System boundaries

The life cycle of the consolidants was analyzed considering a cradle-to-gate boundary. Therefore, as depicted for the general case in Fig. 2, the considered product systems comprise: i) the production stage, ii) the applicable transport phases, and iii) the use stage. The production stage consists of the supply chain of the consolidant (its manufacturing and the production of the material and energy inputs required to its manufacturing), of the packaging and of the main auxiliary materials required for its application. The transport phases include the delivery of all the materials required for the synthesis of the consolidant and the delivery of the consolidant to the application site. The use stage included the relevant procedure for the application of each consolidant, as summarized in Table 1, and the relevant exchanges with the environment occurring after the treatment (typically, emissions of volatile

components or reaction products). No end-of-life phase is defined for the consolidant, while disposal is considered for packaging. This choice, which is in line with the common practice in the LCAs of technical-chemical products in the building and construction industry for environmental product declaration purposes [57,58], reflects the specificity of the real system under modelling: after application, the consolidant bonds with the substrate and becomes part of the historical structure that should be preserved for as long as possible [32]. No re-application of the consolidant is considered within the time frame of the analysis. Accordingly, also for the acrylic resin B72, which is in principle removable from the substrate even after aging, although with several reported limitations [59,60], the possibility of removal prior to the application of other consolidants is neglected. An outline of how the foreground processes in the system boundaries were modelled is given in section 3.4.2.

3.4.2. Inventory modelling

The generic product system of Fig. 2 was specified for each consolidant as detailed in the following. In particular, the production chains of the consolidants were modelled by coupling relatively limited direct information from patents and technical sheets with process engineering techniques for perspective life cycle inventory compilation [61–63]. The

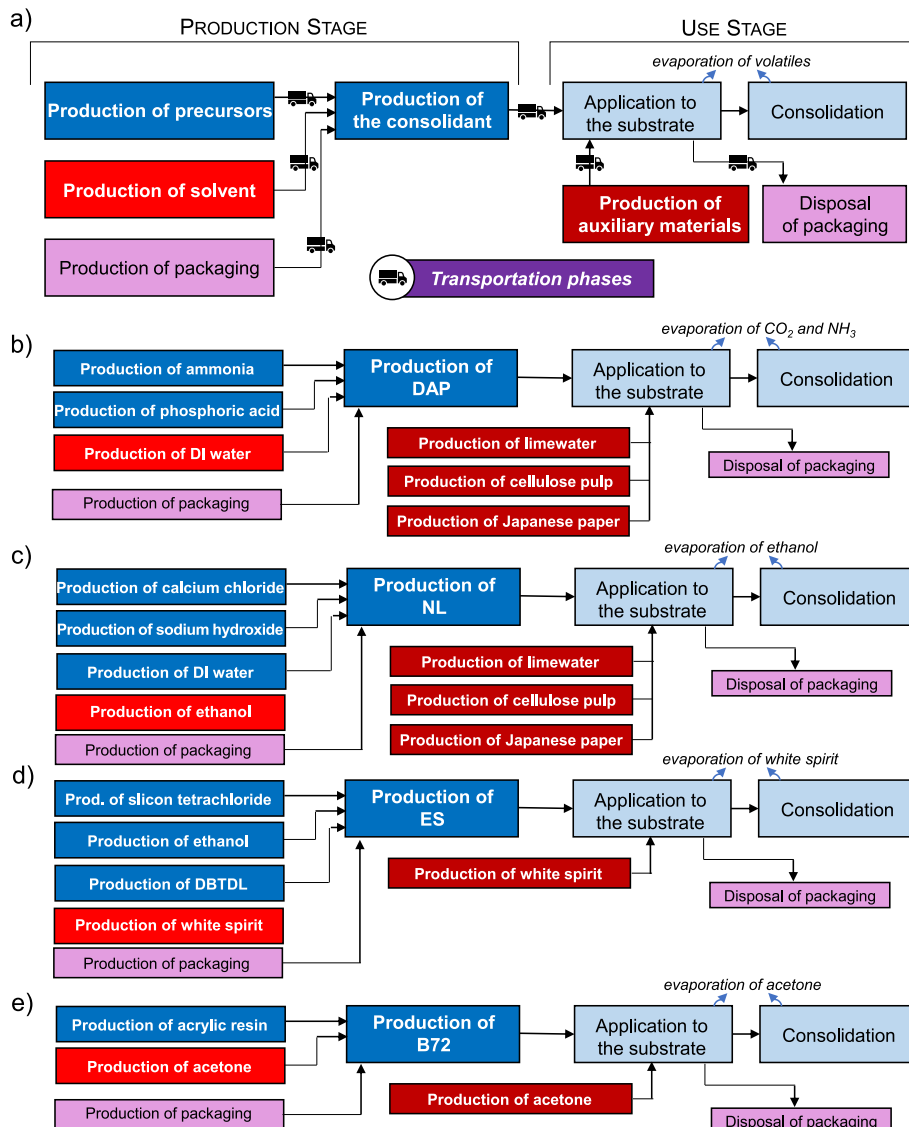


Fig. 2. a) Generic product system considered for the alternative consolidants, and translation into specific product systems for: b) DAP, c) NL, d) ES, e) B72.

detailed indication of background processes and the specific product system for each consolidant are reported in section S1 of the Supporting Information (SI).

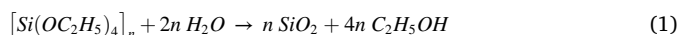
- **DAP treatment.** DAP is produced by reacting ammonia with phosphoric acid in a wet process. Here, it was assumed that the process occurs in a batch reactor, loaded with aqueous solutions of the two reactants (25 % by weight ammonia in water and 40 % by weight phosphoric acid in water). A previous study preliminarily outlined the key inputs for the batch production of DAP [64]: the batch requires stirring and cooling, considering that the reaction is exothermic and a temperature lower than 50 °C is needed to avoid the decomposition of the DAP produced. The upscaling framework proposed by Piccinno et al. [62] was adopted to estimate cooling and stirring energies. The use of recirculated cooling water was considered to model the cooling duty, while mixing of the batch content was assumed to take place by use of an axial flow impeller. The associated electrical consumption was quantified considering moderate stirring (rotational speed = 50 rpm [62]). Fugitive emissions of ammonia equal to 0.2 % of its consumption in the process were conservatively assumed [65].
- **NL treatment.** Lime nanoparticles can be prepared at industrial level by heterogeneous or homogeneous synthesis [36]. Here, the homogeneous synthesis by aqueous precipitation route, as described in Ambrosi et al. [66], was taken into account, considering that it is adopted in the production of commercial nanolime products for stone consolidation (including the specific commercial product used in this study [36]) and it is less energy-intensive and costly to scale up than other methods. Data about the laboratory process were used as basis for the application of the upscaling framework proposed by Piccinno et al. [62] to estimate the inventory of the production at commercial scale. The process was assumed to occur in a batch reactor from solutions of CaCl₂ and NaOH (0.4 M and 0.8 M in DI water, respectively). Mixing and heating duties for the batch process were calculated assuming an operating temperature of 90 °C and stirring at a speed of 100 rpm [62]. Ca(OH)₂ nanoparticles are recovered as precipitate and rinsed from water using ethanol. Then, anhydrous ethanol is used to disperse the nanoparticles up to the final concentration of the product (5 g/L). The total consumption of ethanol was estimated to be 1 kg per L of final product. A 5 % loss of Ca(OH)₂ associated with solubility in water was calculated.
- **ES treatment.** Ethyl silicate is typically synthesized by alcoholysis of silicon tetrachloride with ethanol [67]. Its production was assumed to take place as a continuous process, with a reaction stage at ambient conditions followed by distillation as separation/purification stage. The mass and energy balance of the process was traced following Sanchez-Ramirez et al. [68]. The emissions of the main gaseous by-product, hydrogen chloride, were assumed to be minimized by the use of sodium bicarbonate as sorbent [69]. The impacts related to the DBTDL catalyst were approximated considering the production of the precursors of the organotin synthesis, i.e., tin chloride and butylmagnesium chloride [70]. The inventories for the two precursors were modelled according to de la Iglesia et al. [71] and Andre et al. [72], respectively.
- **B72 treatment.** The acrylic resin Paraloid B72® is a copolymer of methyl methacrylate and ethyl acrylate, produced through emulsion polymerization [73] and marketed in the form of beads. In typical practice, restorers directly dissolve resin beads using acetone at the site of application (5 wt% concentration being a common choice for the resulting solution). In the absence of specific inventory data for the commercial product B72®, a general dataset for the production of polyalkyl methacrylate beads as provided by the European Council of Paint (CEPE) was considered. Acetone was assumed to be produced via the cumene route.

The foreground inventory for the production of the consolidants is

summarized in Table 2. Datasets from life cycle inventory databases, viz. Nodes of the European Platform on LCA [74], were used to model the inventories of the input substances. Where needed, further approximations and assumptions were introduced, as detailed in section S1 of the SI.

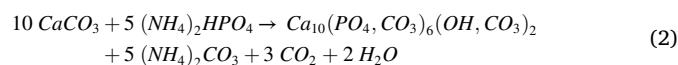
Application to the substrate was considered by brushing, consistently to what was done in the experimental part of the study. As introduced in Table 1, treatment may require auxiliary materials as support for the application process or for rinsing excess product, in case of application until apparent refusal. The amount of auxiliary materials was quantified by experimental practice (see again section 3.2) and literature references [30]. After application, it was assumed that volatile compounds in the consolidants evaporate to air. For the NL, ES and B72 systems, the entire mass of ethanol, white spirit and acetone, respectively, is therefore released into the atmosphere. For white spirit, which is a mixture of aliphatic and aromatic C₇–C₁₂ hydrocarbons, a reference composition was assumed [75].

The ES treatment releases further ethanol to air by the sol-gel process (catalyzed by the presence of DBTDL) that leads to formation of amorphous silica as the new binding phase according to the reaction [76]:



This emission was estimated based on reaction stoichiometry.

For the DAP treatment, the interaction of DAP with the substrate results in the formation of calcium phosphates (ideally hydroxyapatite, possibly carbonated):

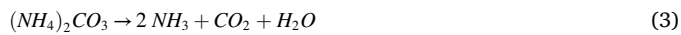


Carbon dioxide is released into atmosphere, while ammonium carbonate, (NH₄)₂CO₃, can further decompose:

Table 2

Foreground inventory of consolidant production. Production of the inputs is discussed in section S1 of the SI.

Flow	Amount	Unit	Type
Production of DAP			
DAP	1	L	Reference flow
Ammonia	1.02×10^{-1}	kg	Input
Phosphoric Acid	2.94×10^{-1}	kg	Input
DI water	2.12×10^0	kg	Input
Energy (stirring)	2.83×10^{-5}	MJ	Input
Ammonia	2.04×10^{-4}	kg	Output (air)
Production of NL			
NL	1	L	Reference flow
Calcium chloride	7.92×10^{-3}	kg	Input
Sodium hydroxide	5.71×10^{-3}	kg	Input
DI water	5.35×10^{-1}	kg	Input
Ethanol	1.33×10^0	kg	Input
Energy (heating)	9.82×10^{-2}	MJ	Input
Energy (stirring)	1.08×10^{-4}	MJ	Input
Ethanol	3.00×10^{-1}	kg	Output (water)
Calcium ion	1.56×10^{-4}	kg	Output (water)
Sodium ion	3.28×10^{-3}	kg	Output (water)
Chlorine ion	5.06×10^{-3}	kg	Output (water)
Production of ES			
ES	1	L	Reference flow
Silicon tetrachloride	6.16×10^{-1}	kg	Input
Ethanol	7.41×10^{-1}	kg	Input
Dibutyltin dilaurate	1.00×10^{-2}	kg	Input
White spirit	2.50×10^{-1}	kg	Input
Energy (heating)	7.54×10^{-1}	MJ	Input
Energy (stirring)	6.01×10^{-4}	MJ	Input
Ethanol	7.18×10^{-2}	kg	Output (water)
Hydrogen chloride	5.76×10^{-2}	kg	Output (air)
Production of B72			
B72	1	L	Reference flow
Acrylic resin (Paraloid B72®)	4.13×10^{-2}	kg	Input
Acetone	7.84×10^{-1}	kg	Input



The decomposition pathway of eq. (3) might not occur quantitatively, as the excess product applied to the substrate is typically rinsed with water at the end of the application process. However, in line with the assumption of complete volatilization of organic solvents for the other consolidating treatments, in the following complete decomposition of $(NH_4)_2CO_3$ and emission in air of the resulting ammonia (NH_3) and carbon dioxide (CO_2) according to stoichiometry were assumed.

The foreground inventory for the application of the consolidants is summarized in Table 3.

3.5. Impact assessment method

The environmental burdens related to the consolidating treatments were assessed assuming a midpoint problem-oriented approach. Six environmental impact categories were considered: namely, resource depletion – fossil fuels (RD, measured in MJ); global warming (GW, kg CO_2 eq.); photochemical ozone formation (POF, kg ethylene eq.); human toxicity (HT, kg 1,4-DCB eq.); acidification (ACD, kg SO_2 eq.); and eutrophication (EUT, kg PO_4 eq.). The CML-IA database (version August 2016 [77]) was used as source for the related characterization factors. The six impact categories were selected considering those with the lowest associated uncertainty in terms of characterization of impacts [78] and those that the findings of previous LCAs in the field of conservation treatments of built heritage identified as most significant [30, 32]. The selection of the impact categories and of the characterization method favors the comparison with the results of the few existing LCA studies on stone consolidants [31,32].

4. Results

4.1. Determination of the consolidant consumption in the two scenarios

Table 4 and Table 5 respectively report the amounts of product consumed to treat each type of substrate until apparent refusal (“recommendation-based scenario”) and for the intended number of brush strokes (“performance-based scenario”). The consumption for the highest number of brush strokes coincides with the condition of

Table 3
Foreground inventory for consolidant application (FU: 1 m² of substrate).

Exchanges	Unit	DAP	NL	ES	B72
Inputs					
Reference product	kg	\dot{m}_{DAP}^a	\dot{m}_{NL}^a	\dot{m}_{ES}^a	\dot{m}_{B72}^a
Water	kg	5			
Acetone	kg				3
White spirit	kg			2	
Limewater	kg	7	7		
Cellulose pulp	kg	0.6	0.6		
Japanese paper	kg	0.009	0.009		
Outputs to air					
Carbon dioxide	kg	0.212 · \dot{m}_{DAP}^b			
Ammonia	kg	0.102 · \dot{m}_{DAP}^b			
Ethanol	kg		0.995 · \dot{m}_{NL}^c	0.663 · \dot{m}_{ES}^d	
White spirit	kg			0.250 · \dot{m}_{ES}^c	
Acetone	kg				0.950 · \dot{m}_{B72}^c

^a depending on the substrate and the application criteria (see section 3.1).

^b assuming complete decomposition of ammonium carbonate according to Eq. 2.

^c assuming complete evaporation of the solvent in the reference product.

^d assuming reaction with substrate according to Eq. 2.

Table 4

Product consumption in the “recommendation-based scenario”, involving application until apparent refusal.

	Product consumption (L/m ²)			
	DAP	NL	ES	PB72
Marble	0.93 ± 0.06	1.21 ± 0.08	0.86 ± 0.06	1.15 ± 0.08
Limestone	3.89 ± 0.22	4.79 ± 0.29	2.80 ± 0.16	3.79 ± 0.23
Mortar	6.01 ± 0.45	9.93 ± 0.79	6.56 ± 0.51	6.93 ± 0.55

Table 5

Product consumption in the “performance-based scenario”, involving application by different numbers of brush strokes to reach different levels of mechanical consolidation.

	Brush strokes	Product consumption (L/m ²)			
		DAP	NL	ES	PB72
Marble	3	0.40 ± 0.03	0.52 ± 0.04	0.37 ± 0.03	0.49 ± 0.03
	5	0.66 ± 0.05	0.86 ± 0.06	0.62 ± 0.05	0.82 ± 0.06
	7	0.93 ± 0.06	1.21 ± 0.08	0.86 ± 0.06	1.15 ± 0.08
Limestone	10	1.30 ± 0.07	1.60 ± 0.10	0.93 ± 0.05	1.90 ± 0.11
	20	2.59 ± 0.14	3.19 ± 0.19	1.87 ± 0.11	2.85 ± 0.17
	30	3.89 ± 0.22	4.79 ± 0.29	2.80 ± 0.16	3.79 ± 0.23
Mortar	10	2.00 ± 0.15	3.31 ± 0.26	2.19 ± 0.17	3.46 ± 0.28
	20 (15 for B72)	4.01 ± 0.30	6.62 ± 0.53	4.37 ± 0.34	5.19 ± 0.41
	30 (20 for B72)	6.01 ± 0.45	9.93 ± 0.79	6.56 ± 0.51	6.93 ± 0.55

apparent refusal.

The measured values depend, on the one hand, on the open porosity (3 % for marble, 26 % for limestone, 21 % for mortar) and on the pore size distribution (the bigger the pore size, the quicker the adsorption [17]) of each substrate and, on the other hand, on the properties of each consolidant (especially the viscosity and the volatility of the solvent).

The strengthening effect caused by each consolidant on each substrate is reported in Table 6, which compares the compressive strength of untreated specimens with that of samples treated with a given amount of brush strokes. Negative strengthening effects (i.e., a slight decrease in compressive strength after treatment) are originated by the experimental error of the test (the error is in the same range as the average value of the difference in compressive strength before and after treatment) and they should be practically interpreted as no appreciable consolidating effect observed. In brief, the consolidating ability of each product can be described as follows:

- DAP was effective on all types of substrate, especially marble (where it outperformed all the other consolidants) and limestone (where only application of a high number of brush strokes of ES shows competing performances). The high strengthening ability of DAP was expected, as the newly formed calcium phosphates are able to form bridges among the calcite grains and significantly improve mechanical properties [34].
- NL showed limited efficacy on all substrates, without any evident advantage deriving from an increased number of applications. This can be explained considering that, as pointed out in the literature [79], nanolimes tend to be transported back to the surface during drying, so that accumulation of the consolidant near the surface is frequently found, without in-depth strengthening.

Table 6

Consolidating ability in the “performance-based scenario”. Samples treated with different amounts of the analyzed consolidants are compared in terms of compressive strength (MPa) with the untreated weathered sample (UT).

	Compressive strength (MPa)					
	UT		After treatment			
		Brush strokes	DAP	NL	ES	PB72
Marble	69.5 ± 1.0	3	72.7 ± 3.8	70.6 ± 1.5	71.2 ± 1.6	69.6 ± 1.3
		5	76.1 ± 3.1	70.8 ± 1.3	72.7 ± 1.6	69.8 ± 2.3
		7	85.7 ± 8.5	71.5 ± 0.7	84.4 ± 6.5	69.2 ± 1.7
Limestone	14.5 ± 2.1	10	17.6 ± 1.4	15.9 ± 0.9	15.1 ± 1.8	14.9 ± 0.6
		20	18.5 ± 2.1	13.3 ± 0.6	15.3 ± 0.8	15.3 ± 1.9
		30	19.3 ± 3.3	13.3 ± 1.1	20.4 ± 2.2	13.8 ± 1.3
Mortar	3.2 ± 0.4	10	3.4 ± 0.2	3.5 ± 0.1	7.3 ± 2.9	3.5 ± 0.3
		20 (15 for B72)	3.8 ± 0.7	3.3 ± 0.3	9.7 ± 0.3	3.1 ± 0.4
		30 (20 for B72)	3.6 ± 0.4	3.4 ± 0.5	10.9 ± 2.6	3.2 ± 0.3

- ES showed limited efficacy on marble (as expected, given the impossibility to form chemical bonds to the substrate [17]), while a remarkable consolidating ability was found in limestone and, especially, mortar. A possible reason for this could be the presence of some silicate fractions in the limestone and in the aggregates used to prepare the mortar, which could allow for chemical bonding between the hardened consolidant and the substrate [80]. FT-IR analyses of the two substrates confirmed the presence of silicate minerals in the limestone and in the aggregate used for mortar specimens.
- B72 showed very limited efficacy on all substrates. This is thought to be a consequence of its very limited penetration into the substrates (for B72 apparent refusal occurred at a lower number of brush strokes than for the other consolidants, as shown in Table 5), so that no in-depth strengthening was possible.

4.2. Global life cycle impacts for the “recommendation-based practice” scenario

Assuming the perspective of the “recommendation-based practice”, the life cycle impacts related to the use of the four alternative consolidants were quantified based on the consumption rates estimated in Table 4, considering the life cycle stages outlined in Fig. 2. The numerical results for the six indicators adopted in the assessment (see section 3.5) are reported in section S2 of the SI with reference to all the substrates, and, for ease of discussion, are shown in Fig. 3 as normalized to the highest value in each category.

For the application to all the analyzed substrates, the main pattern that can be observed is that the DAP treatment exhibits the lowest impacts in the RD, GW and POF indicators and the highest impacts in the HT, ACD and EUT categories. In particular, the reduction of impact of the DAP treatment compared to the closest alternative is in all cases higher than 70 %, 36 % and 99.3 % for the RD, GW and POF categories, respectively. Conversely, in the other three categories the burdens of the DAP treatment are significantly higher than those of the alternatives. These burdens are mainly related to the volatilization of ammonia owing to the reaction in eq. (3), as indicated by the shaded areas in Fig. 3 and discussed more in detail in section 3.3. It is worth mentioning that the assumption of quantitative decomposition of ammonium carbonate is conservative and the actual release of ammonia into atmosphere might be lower. However, an inversion of the ranking for DAP in the HT, ACD,

and EUT categories is unlikely, as it would occur only for ammonia emissions lower than 1 % of those considered.

Among the other treatments, NL presents the lowest impacts in all the categories, apart from the POF indicator where its impacts are invariably the highest. The ranking between ES and B72 is instead influenced by the substrate. B72 outperforms ES in case of application to lime mortar and has lower impacts in most categories for the limestone case. For marble, ES has lower impacts apart from the POF and HT categories.

No previous studies are available in the literature for a direct comparison of the present findings on the life cycle impacts of DAP, NL and B72. For ES, the present findings can be usefully compared with the LCA study of Mauko Pranjić et al. [32], who found slightly higher life cycle impacts than those quantified here (e.g., for the GW indicator: 3.8 kg CO₂ eq./L of consolidant, instead of the present 3.0 kg CO₂ eq./L of consolidant, see Table S5 in the SI). Differences are owing to slightly different formulations for the ES consolidant and different background modelling (e.g., among others, a different country energy mix for the energy demand of the production stages).

4.3. Contribution analysis

Fig. 4 presents a contribution analysis to better understand the role of the different life cycle stages in determining the overall impacts of the consolidating treatments shown in section 3.2.

The case of the limestone substrate is taken as reference for Fig. 4, but only minor differences in contribution can be observed across the substrates, as a consequence of slightly different ratios between amount of consolidant and amount of auxiliary materials and rinsing products in the application process across substrates.

For the DAP treatment (Fig. 4a), the production chain of diammonium phosphate (from the extraction of raw materials to the production of ammonia and phosphoric acid and their use in the synthesis of DAP) dominates the impacts in the RD, GW and POF categories, with contributions higher than 60 %. In the same categories, a relatively small share of burdens (~ 5 %) is related to the production of the auxiliary materials required for the application of DAP to the substrate (in particular, cellulose pulp). The solvent, which for the DAP consolidant is water, has a negligible impact (less than 0.1 %) in all the categories. For the ACD, HT and EUT indicators, as introduced in section 3.2, the impact of the DAP treatment is almost entirely related to the release of ammonia as a by-product of the consolidation process (eqs. (2) and (3)).

For the nanolimes (Fig. 4b), the environmental footprint of the consolidating treatment is dominated by the organic solvent in which the lime nanoparticles are dispersed (i.e., ethanol), which constitutes 99.3 % by mass of the consolidant product. The evaporation of ethanol after the application of the product to the substrate is responsible for almost the entirety of the burdens in the POF indicator, while the production of ethanol is the main contributor to the impact in the other 5 categories. The production chain of the lime nanoparticles and their precursors contributes for less than 7 % of the impact in all the categories.

Conversely, for the ES system (Fig. 4c), the production of ethyl silicate itself is the main contributor to the environmental impacts, while the solvent (white spirit), constituting only 25 % by mass of the final product, shows minor contributions ranging from 3 % in the ACD indicator to 16 % in the RD indicator. A non-negligible share of impacts (up to 24 % in the RD category) is associated with auxiliary materials, namely the additional demand of white spirit for rinsing of excess product after application. Similarly to the nanolimes, the impacts in the POF category are almost entirely related to the evaporation of volatiles in the application and consolidation process: in particular, for about a quarter to the white spirit and for the rest to the ethanol released by eq. (1).

Lastly, for the treatment based on acrylic resin (Fig. 4d), the main

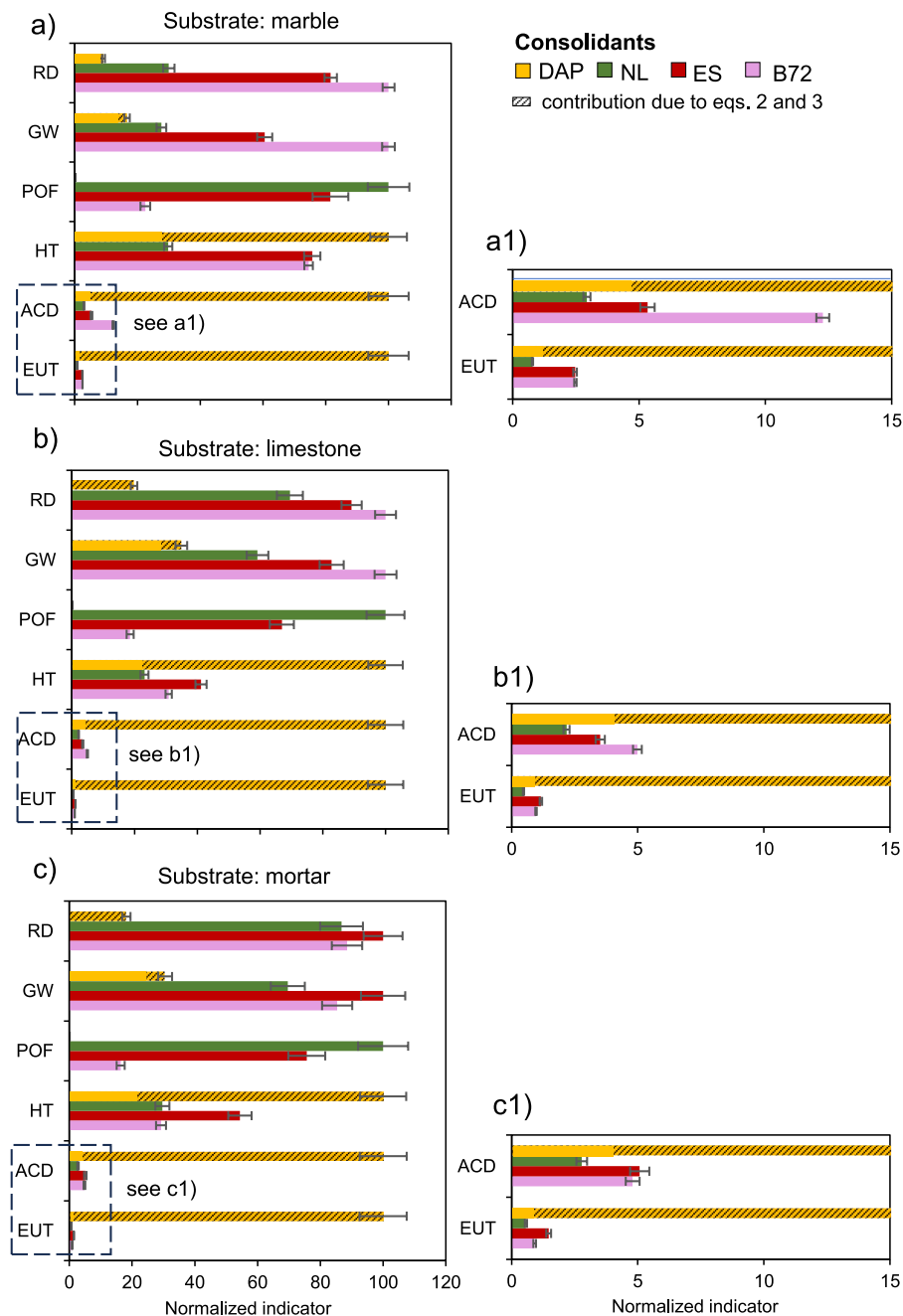


Fig. 3. Environmental impact of the alternative consolidants in the selected impact categories for application to: a) marble, b) limestone, c) mortar. For DAP, the contribution to impact associated with the decomposition of ammonium carbonate is hatched. Internal normalization is adopted.

contributor to impacts is acetone, both as component of the product (solvent for the resin beads) and as rinsing agent for the removal of excess product from the substrate. The production of the acrylic resin Paraloid B72® is responsible for a minor share of impacts, up to 13 % in the ACD category. Again, more than 99 % of the burdens in the POF category are associated with the evaporation of the solvent after application.

The findings of Fig. 4 allow identifying the main environmental hotspots of the four consolidating treatments. Generally speaking, the need for organic solvents is a key critical aspect for NL, B72 and in part ES. Organic solvents dominate the impacts both in the core application and consolidation process, as they are released as volatile compounds potentially contributing to photo-smog, and in the upstream production

chain, as they constitute most of the product mass and typically entail energy-intensive synthesis routes [81]. The DAP treatment does not present these types of impact, using water as solvent. On the other hand, the release of ammonia after application, a consequence of its consolidation mechanism, is the main hotspot identified for the DAP product. In this regard, it should be mentioned that the formulation considered in this study (3 M DAP) is basically the most concentrated one proposed in the literature: the higher the DAP concentration, the higher is the amount of NH_3 released in the atmosphere and hence the higher the HT, ACD and EUT impacts. Use of alternative formulations of the treatment with lower DAP concentrations have been proposed in the literature (e. g., adding 10 vol% ethanol allows to use effectively a 0.1 M DAP concentration, thanks to the boosting effect of alcohol on the phosphate ions

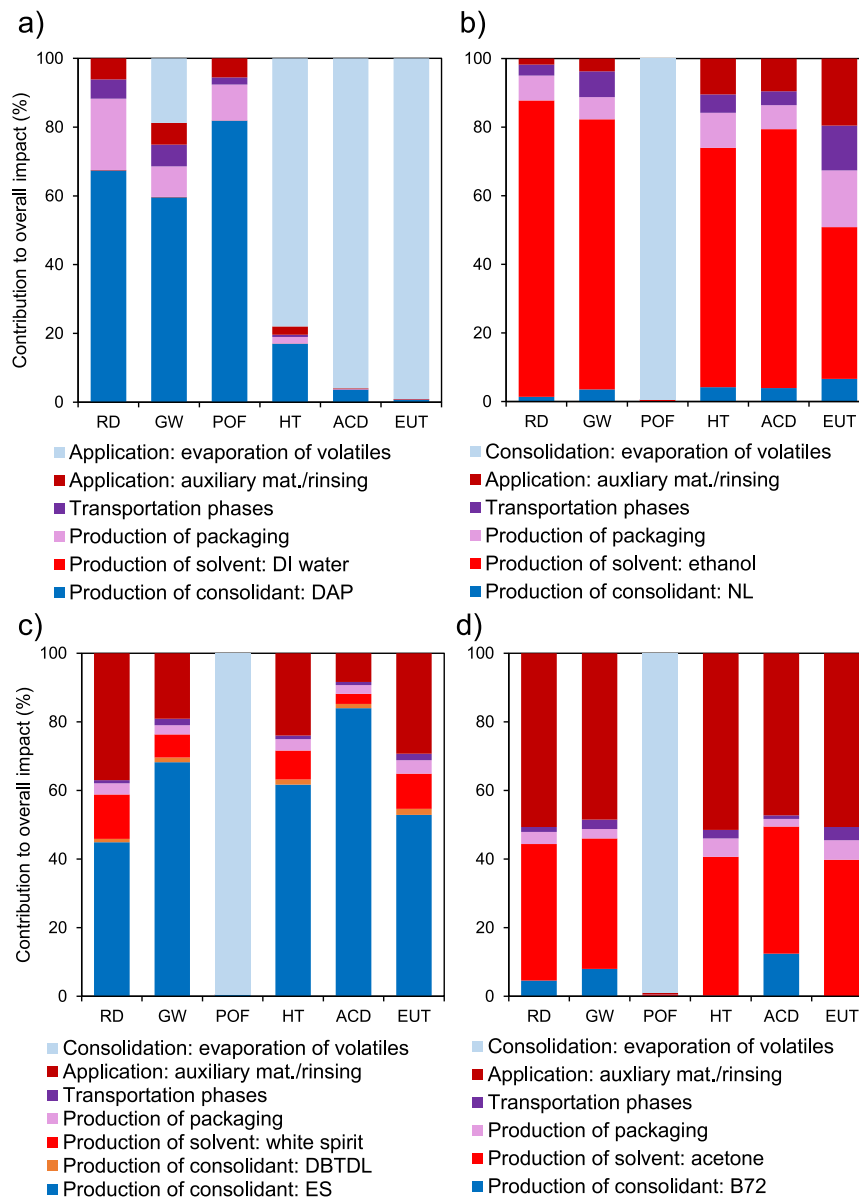


Fig. 4. Contribution of the life cycle stages to the overall impact for the four consolidants: a) DAP, b) NL, c) ES, d) B72. Substrate: limestone.

reactivity [82]) and may help improve the environmental performance, though the consolidating performance may be diminished [45]. Future work will be dedicated to identifying the formulations that guarantee the optimal trade-off between environmental performance and consolidating ability, following the approach of analysis discussed in section 3.3. To offer a preliminary evaluation of the impact that using a different concentration of the active principle may have on the reported LCA results, for each consolidant a more diluted concentration was also taken into account, as reported in Fig. S11 of the SI. For the diluted concentration, no data on the actual consolidating ability were collected experimentally and the comparison is only performed for the case of application until apparent refusal. As shown in the figure, whereas the dilution of DAP provides a significant reduction of the acidification impact owing to the reduced amount of volatilized ammonia, the dilution of products for which the impacts are mainly driven by the solvent offers much more limited environmental advantages.

4.4. Global life cycle impacts for the “performance-based” scenario

If the consolidating ability of the various treatments is taken into

account according to the results of section 3.1, then it is possible to compare the environmental impact of the four consolidants for the same level of mechanical strengthening. As an example, in Fig. 5 the consolidating ability is plotted against the global warming indicator, assumed as a reference single parameter. Analogous plots are presented for the photochemical smog formation and acidification categories in section S2 of the SI.

From the plots in Fig. 5, a couple of general observations can be made. On the one hand, there are cases of treatments with lower consolidating ability and higher GW emissions than the possible alternatives (e.g., for marble: NL and ES with respect to DAP), suggesting poor performance from both consolidation and environmental point of view. In these cases, the rankings on both technical and environmental dimensions are in agreement. On the other hand, there are cases of treatments with similar GW indicators (e.g., for limestone: ES in the lowest amount and DAP in the intermediate amount) but with very different consolidation abilities (appreciably higher for DAP than for ES). In these cases, including in the analysis the consolidation performance clearly provides a more complete picture than the simple information on GW impact provided by Fig. 3 to support the selection of the

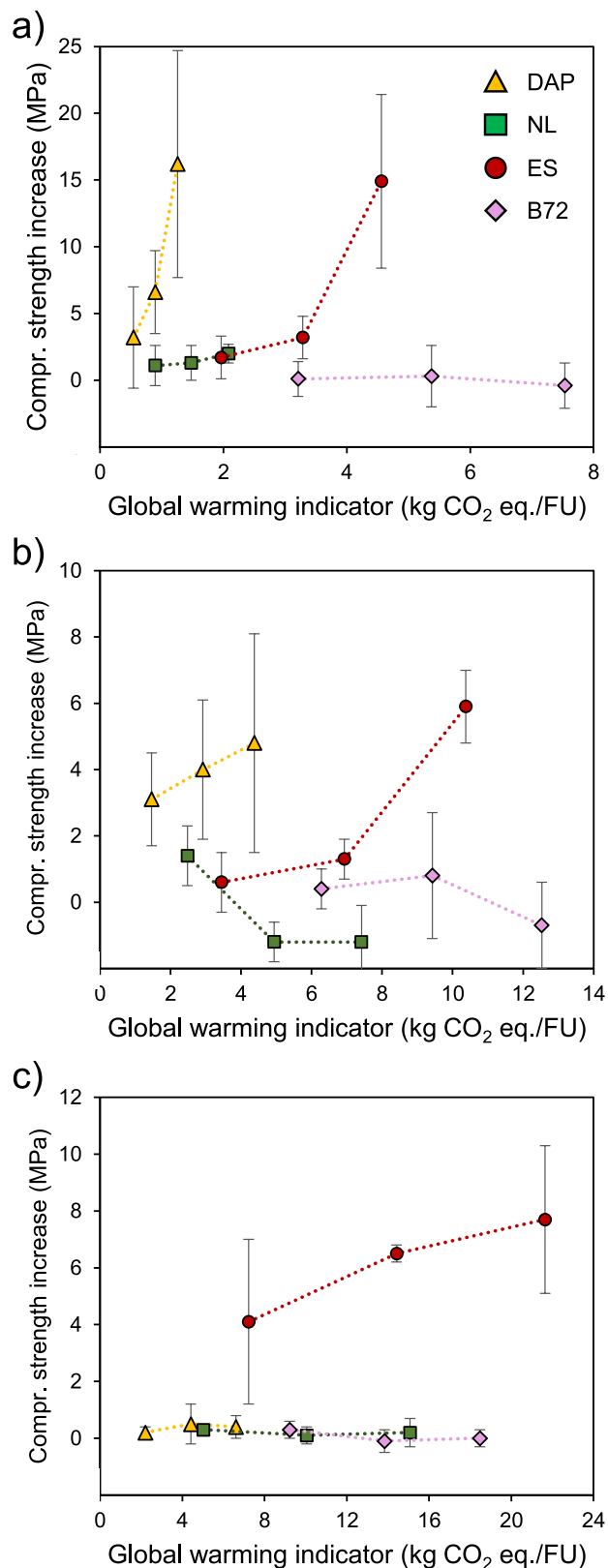


Fig. 5. Comparison of the consolidating performance and the global warming indicator for the four consolidants applied to: a) marble, b) limestone, c) mortar.

best consolidant for the application.

The case of mortar is exemplificative of the interplay between the consolidation and environmental metrics. If a compressive strength increase in the range 0.2–0.5 MPa (+10 % compared to the untreated weathered substrate) is the preservation target, then DAP, NL or B72 could be chosen as equally effective, but the various treatments imply significantly different GW burdens. Therefore, the GW indicator can be used to screen between the three options. If very significant strength-ening (e.g., a compressive strength increase of more than 4 MPa) is the target of the restorer, then only ES is a suitable option, but this comes at the price of a significantly higher GW footprint.

Also for the other impact categories, the joint analysis with compressive strength improvement allows to better discriminate between alternatives, as presented in the charts in section S2 of the SI. Considering acidification, the impact of DAP stands out owing to ammonia emissions, but the other consolidants show similar burdens. If compressive strength increase is factored in, ES is a preferred choice compared to NL and B72. Conversely, considering smog formation, DAP is clearly superior on both the environmental and consolidation metrics, apart from the case of lime mortar in which only the ES treatment reaches a compressive strength increase higher than 4 MPa, but at the cost of a significantly higher POF footprint.

5. Discussion and limitations

Comparing the findings of the “recommendation-based practice” scenario in Fig. 3 and the “performance-based” scenario in Fig. 5, it is evident that the quantification of the consolidating ability adds an important factor to the analysis. As the philosophy of comparative life cycle assessment is centered around the concept of functional unit (ISO 14040 [42]), the evaluation of the environmental impact of consolidants for cultural heritage shall be based on a clearly identifiable performance indicator of the product analyzed. Hence, comparing the impacts of the amount of product that is needed to fulfil a given performance target, i. e., to obtain a certain increase in mechanical properties (“performance-based scenario”) is advisable, as portrays a scenario of purpose-driven use of the consolidants, with clear advantages in terms of resource conservation and emission reduction. By converse, the use of the amount of product corresponding to apparent refusal in defining the reference flow (“recommendation-based practice”) provides a representation of the current practice. It shall be noted that the comparison based on 1 L of consolidant product (as typically done in the literature) misses both the above definitions of performance characteristics and may bring to misleading results with reference to practical applications of consolidating materials.

Here, for limestone and marble, DAP and ES exhibited similar consolidation performance, thus confirming the relative results between the “recommendation-based practice” and the “performance-based” scenarios. Conversely, in the application to lime mortar, the “performance-based” analysis evidenced a trade-off between consolidation ability and GW footprint, as ES stood out in the former while resulting the worst option for the latter. The opposite situation was highlighted for NL, whose low consolidation performances outbalance the good GW score evidenced in the “recommended practice” scenario. Generally speaking, the study underlines that a fully aware interpretation of the LCA results needs to take into proper account the choice of the functional unit.

Furthermore, clear and unambiguous definition of the reference functions of the consolidants would support the development of benchmarking methods for materials [83] and facilitate the integration of the environmental aspects in multi-criteria decision frameworks for the selection among alternative conservation treatments [23].

Here, the increase in compressive strength was taken as a sole representative parameter for the assessment of the consolidating ability, as it is a commonly adopted parameter to evaluate the performance of a consolidant [17,22]. Other mechanical parameters (such as tensile

strength, drilling resistance or abrasion resistance) may be adopted as well, but they all share the limitation of requiring destructive testing, which cannot be performed onsite on real monuments. Relatedly, laboratory tests might require trade-offs between the representativeness of the tested specimens and the practical constraints imposed by test protocols. For example, in this study the need to have a material suitable for handling for the laboratory tests influenced the mix design of the mortar samples.

A possible alternative is the use of non-destructive tests conducted onsite, such as ultrasonic measurements [84], although the consolidating abilities assessed by ultrasounds and by destructive tests may differ, depending on the type of substrate, its pore system, the nature of the consolidant and its ability to chemically or physically bond to the substrate [39]. Despite the aforementioned limitations and the known difficulty of transferring laboratory test results to real situations onsite [85], the adoption of model systems like those considered in this study appears as a useful tool to obtain simplified but still reliable indications before the actual application onsite.

Alongside the mechanical improvement, also other parameters need to be taken into account when selecting a consolidant, such as the compatibility with the substrate (e.g., to avoid an undesired color change after treatment) and the durability (e.g., to avoid that the mechanical benefit is lost too quickly or, even worse, that the consolidating intervention itself actually *accelerates* the deterioration of the substrate, because of physical-mechanical incompatibility between the consolidant and the substrate). The durability of the consolidating treatment also determines how often a product needs to be applied, which in turn influences the treatment sustainability in the long term. All these aspects are currently being investigated in our research [39] and future work will be dedicated to the incorporation of durability considerations in the life cycle assessment of consolidating products.

Nonetheless, the joint evaluation of the mechanical strengthening action and the environmental impact of consolidants proposed in the present study represents a relevant first step towards an integrated assessment of technical performance and environmental sustainability. Clearly enough, as mentioned in section 2, the desired level of increase in mechanical properties and hence the necessary amount of consolidating product can only be defined case-by-case in these kinds of application (depending on the specific characteristics of the substrate, its level of deterioration, the specific type of consolidant, the application method, etc.). Hence, due attention shall be paid in the extending the numerical results of the current study to specific cases where the application of consolidants significantly differs (e.g. in terms of consumption) from the cases analyzed here. Nevertheless, the outcomes of the current study shall be considered as i) a contribution to establish a systematic approach to the quantification of sustainability aspects in consolidation of cultural heritage, and ii) an example of typical results from the evaluation of a diversified range of combinations of consolidants and substrates, covering the most common consolidating products and three types of carbonate substrates with different chemical-mineralogical composition, open porosity and pore size distribution.

6. Conclusions

A comparative LCA on consolidants for application onto built cultural heritage was performed to assess the environmental profile of an innovative treatment based on diammonium hydrogen phosphate (DAP) against three established commercial alternatives. For each consolidant, experimental tests on model substrates allowed determining the amount of product required to reach the condition of apparent refusal or to achieve a certain degree of consolidating performance. Thanks to the experimental campaign, it was thus possible to set up a comparative LCA according to two alternative definitions of the functional unit (the “recommendation-based” scenario and the “performance-based” scenario).

The results evidence that the production chain for the DAP treatment presents appreciably lower environmental impacts than those of the commercial alternatives. As shown by the contribution analysis, the environmental advantage of the DAP-based treatment is mainly related to the absence of organic solvents in its formulation. Conversely, in the life cycle stage of application and consolidation process, the substitution of commercial consolidants with the DAP treatment induces a burden shift: the application of nanolimes, ethyl silicate or acrylic resin has the side effect of the volatilization of the respective solvents, potentially contributing to photochemical ozone formation, while the application of DAP entails the release of ammonia, a substance that can contribute to the acidification and eutrophication of environmental media. Improvements in the formulation of the DAP-based treatment should be directed towards the minimization of ammonia emissions, e.g., by optimizing the concentration of the DAP solution.

More generally speaking, as the application of LCA to the field of conservation is relatively new, the present work had also the methodological objective to advance the discussion on the definition of the most suitable functional units for comparative LCA of conservation materials. As the actual practice in the use of stone consolidants in conservation works is extremely varied, the two alternative criteria of application until apparent refusal and application up to a certain degree of consolidating performance were proposed as possible references for a standardized comparison between consolidants. In particular, the joint evaluation of the consolidating ability and the environmental performance (e.g., in charts such as those presented for the increase in compressive strength vs. the global warming indicator) appears especially useful to support practitioners in the selection of the best overall treatment for their conservation project.

CRedit authorship contribution statement

Alessandro Dal Pozzo: Writing – original draft, Software, Methodology, Data curation, Conceptualization. **Giulia Masi:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Enrico Sassoni:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization. **Alessandro Tugnoli:** Writing – review & editing, Supervision, Resources, Project administration, 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.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.buildenv.2023.111153>.

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