# Effects of cleaning procedures on the long-term corrosion behaviour of bronze artefacts of the cultural heritage in outdoor environment

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## Abstract

The cleaning of metallic artworks is a crucial step for their preservation. Cleaning operations generally aims at removing deposits, corrosion layers and all the non-stable and potentially reactive phases formed as a consequence of the interaction of the metal with the environment. Thus, all secondary-formed compounds and layers that can undermine the overall preservation of the artwork, both from the aesthetic and the corrosion point of view, should be removed. On the other hand, superficial stable patinas contributing to the artistic and historic value of the objects and that may provide protection to the metallic surface should be preserved. The optimal cleaning procedure should be able to promote a long-term improvement of the corrosion resistance of the surfaces. Therefore, the long-term monitoring of the corrosion behaviour of the cleaned surfaces with electrochemical techniques could provide valuable information for the selection of the optimal methodology. In this work, five cleaning procedures have been applied to five bronze sculptures. The cleaned surfaces have been characterised following a multi-analytical and non-invasive approach and the long-term evolution of their corrosion behaviour has been monitored by means of on-site non-invasive Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) measurements for more than 2 years.

## Keywords

Long-term monitoring; cleaning; outdoor bronze; cultural heritage; atmospheric corrosion; electrochemical techniques

## Acknowledgements

The authors are grateful to Fonderia Artistica Battaglia for the fundamental support and collaboration to this research, and to Maria Agnese Zappa for her precious contribution to the experimental activity.

## Introduction

Bronze is a quite durable copper alloy in moderately aggressive environments. For this reason, it has been widely employed in architecture and in sculpture, especially for outdoor applications. The composition of the patina constituted by corrosion layers on bronze surfaces results from the interaction between the metal substrate and the environment. In outdoor conditions, the first formation of a reddish-brown layer of cuprite is followed by the development of different additional compounds: copper basic sulphates, like antlerite and brochantite, can be found on bronzes exposed in urban environments, whilst copper hydroxychlorides (atacamite and paratacamite) usually form in chloride-rich environments (Graedel, Nassau, and Franey 1987; Lins and Power 1994; Skennerton, Nairn, and Atrens 1997; Strandberg 1998; Leygraf and Graedel 2000; Odnevall Wallinder and Leygraf 2001; Scott 2002; Chiavari et al. 2007; Robbiola et al. 2008; Odnevall Wallinder et al. 2014; Goidanich et al. 2014; Letardi et al. 2016; Pan et al. 2016; Albini et al. 2017; Catelli et al. 2018; ). The exposure environment and the resulting patina composition strongly affect also the corrosion behaviour of the metallic surfaces. In particular, bronze average corrosion rates reported for surfaces during the first year of exposure are 0.5-1.0 μm/y in urban environment (Stöckle et al. 1998; Laguzzi, Luvidi, and Brunoro 2000; He, Odnevall Wallinder, and Leygraf 2001; Odnevall Wallinder and Leygraf 2001; FitzGerald et al. 2006; Tidblad et al. 2016; Chang et al. 2019) and of 0.5-1.5 μm/y in marine environment (Stöckle et al. 1998; Laguzzi, Luvidi, and Brunoro 2000; FitzGerald et al. 2006; Odnevall Wallinder et al. 2014; Tidblad et al. 2016; Chang et al. 2019) corresponding to C2 (low corrosivity), and C3 (medium corrosivity) environments, according to the BS EN ISO 9223:2012 standard (2012). However, the presence of corrosion layers formed over the surface in some cases may lead to a general decrease of the corrosion rate with time (Odnevall Wallinder and Leygraf 2001; Stöckle et al. 1998; Bartuli, Cigna, and Fumei 1999; Laguzzi, Luvidi, and Brunoro 2000; Chang et al. 2019; FitzGerald et al. 2006). Therefore, depending on the features of each artwork and on the specific conservation history (exposure environments over time, previous cleaning or protective treatments performed), different conservation conditions and corrosion behaviours of the surfaces can be observed. In particular, the presence of chloride-rich corrosion products formed in specific conditions can be associated to particularly critical degradation phenomena (e.g. *bronze disease* (Scott 1990)). In addition, severe corrosion mechanisms can be activated in presence of galvanic coupling of the bronze with more noble metals (e.g. in case of gilded bronzes (Bartuli, Cigna, and Fumei 1999; Goidanich et al. 2011)).

Cleaning is a fundamental yet challenging step in the conservation of metallic works of art. The need for cleaning emerges when the original aesthetic features of the exposed surfaces are compromised and no longer properly recognizable. Moreover, cleaning becomes necessary for the selective removal of all the compounds that can be destabilising for the metallic surface and harmful for the overall conservation of the artefacts. The optimal cleaning procedure should be carefully selected according to the specific requirements of minimum invasiveness, selectivity and gradualness (Strandberg and Johansson 1996; Degrigny 2004, 2007), especially considering the intrinsic irreversible nature of such operation. Besides the metal substrate, also the artistic and natural patinas contribute to the historic and aesthetic value of the artworks and therefore they should be properly preserved, especially as they can be protective with respect to the metallic surfaces. Cleaning should selectively remove only the layers of atmospheric particulate deposits and the surface layers that have lost cohesion and adherence, that are hygroscopic or containing highly reactive corrosion products , (Scott 2002; Degrigny 2004, 2007).

The most effective cleaning procedure for each case should be defined after an appropriate diagnostic activity and according to the specific conservation state of the artefact. So far, no comprehensive guidelines are available in the literature for the cleaning of metallic artworks (Degrigny 2004; Palomar et al. 2016). The experience of conservators and, when available, the indication of the artists always play a very important role within this process, and are quite often leading factors in the definition of the most suitable methodologies, particularly considering aesthetical features. As previously discussed, from the corrosion point of view the intervention should be aimed at removing destabilizing products to reduce the corrosion rate. However, a temporary and short-term increase in the corrosion rate following the intervention is a possible side-effect of the cleaning operations due to the short-term reactivation of the treated surfaces. Such effect should be carefully investigated to evaluate the actual corrosion behaviour before and after cleaning during an adequate monitoring period.

The assessment of the protectiveness and corrosion behaviour of the corrosion layers and patinas are also not supported by standardized and shared guidelines. The efficacy and the overall effects of the cleaning treatments are usually evaluated through changes in the surface appearance and morphology (Matteini et al. 2003; Degrigny 2004; Sansonetti et al. 2015; Letardi et al. 2016; Palomar et al. 2016), or by investigating the variation in the composition of the patina upon cleaning (Dajnowski 2008; Buccolieri et al. 2013; Buccolieri et al. 2014; Letardi et al. 2016). Moreover, electrochemical techniques are also used to evaluate the corrosion behaviour after cleaning. In particular, Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) have proved to be powerful tools to perform on-site non-invasive measurements and monitoring campaigns , and they have been widely used for the study of patinas and protective treatments (Bartuli, Cigna, and Fumei 1999; Costa 2002; Ramírez Barat and Cano 2015; Letardi et al. 2016; Grassini et al. 2016; Gulotta et al. 2017; ). In some works such techniques have been also adopted for the evaluation of cleaning methodologies (Matteini et al. 2003; Marcelli 2004; Letardi et al. 2016; Sansonetti et al. 2015). In these cases, a general decrease of the corrosion resistance of the surfaces was actually measured immediately after the cleaning, with consequent reactivation of corrosion processes. However, long-term monitoring data on the effects of cleaning methodologies from the corrosion point of view are not available. As a consequence, it is still not possible to determine whether or not the reactivation of the surface can be considered a temporary phenomenon, nor its evolution over time. This is mostly due to the fact that it is usually difficult to access the artworks once the intervention is finished. In addition, the interventions on metallic artworks are frequently concluded with the application of a protective coating, which masks the actual contribution of the cleaning on the corrosion behaviour of the surfaces. Thus, it is hardly ever possible to perform monitoring over the long-term period, mainly for practical and logistic reasons. The correlation among long-term effects of different cleaning procedures and initial surface conditions could provide relevant indications for the selection of the optimal methodology .

The aim of the present work was to assess and compare the long-term effects of five cleaning procedures, selected among the most widely employed in conservation field, from the corrosion pointof view . The cleaning methodologies include: i), mechanical removal by micro rotary tool and scalpel; ii) cleaning with nonpolar solvents; iii) combined mechanical and solvents cleaning (application of a poultice followed by scalpel cleaning); and iv) laser cleaning. Solvents cleaning and mechanical methodologies were selected as being generally time consuming and cost-effective, which are both fundamental requirements for the treatment of small-scale and diffused heritage. Laser cleaning was selected as it is reported in literature as a promising and highly selective cleaning methodology for metallic artworks (Matteini et al. 2003; Siano and Salimbeni 2010; Buccolieri et al. 2013; Sansonetti et al. 2015;). These methodologies have been tested on bronze sculptures hosted at the *Cimitero Monumentale* of Milano (Italy). This site is located in a highly polluted area of the city and it hosts a wide variety of valuable works of art dated back to the XIX Century. After a preliminary survey conducted on more than 60 objects, 5 sculptures representative of the most varied state of conservation observed, have been selected for the study. The cleaning procedures have been implemented and carried out by the conservator-restorer. The corrosion behaviour of the surfaces after cleaning has been monitored for a period of around 2 years by means of on-site electrochemical measurements (LPR and EIS). During the monitoring period, the cleaned artworks have been exposed in different conditions to evaluate their effects on the evolution of the corrosion behaviour.

The electrochemical monitoring of the artworks was supported by a multi-analytical diagnostic strategy for the preliminary characterization of the materials, the assessment of the state of conservation, and for the evaluation of the effects of the cleaning methodologies. In particular, the bronze surfaces have been characterized before and after cleaning by in situ digital microscopy and visible-light reflectance spectrophotometry to evaluate the results of the adopted procedures from the aesthetic, colorimetric, and microstructural point of view. Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) of micro-samples have been employed to characterize the chemical composition of the corrosion layers and to evaluate the presence of any residual protective treatments from previous interventions. FTIR analysis have been performed also after cleaning intervention, to verify the effects of the cleaning procedures on the composition of the patina. Scanning Electron Microscopy coupled with micro-analysis (SEM-EDX) has been performed to characterize the bulk alloys composition and to investigate the surfaces before cleaning.

## Materials and Methods

### *Artworks*

Five bronze sculptures hosted at the *Cimitero Monumentale* of Milano were selected from a larger variety of artefacts to be restored (more than 60), in order to be representative of the most common deterioration patterns  observed . In particular, three bas-relief plates, *Donna Villarubia* (DV), *Lastra Sorio* (LS) and *Tondo Pitter* (TP) and two *tuttotondo* sculptures, *Donna Novi* (DN) and *Putto* (PU) were selected (Fig. 1).
In Tab. 1 the average dimensions of the sculptures are listed; in Tab. 2 the semi-quantitative evaluation of the compositions of the bulk alloys of the artworks obtained by SEM-EDX measurements is reported.


**Fig. 1** Selected artworks: DV) Donna Villarubia; LS) Lastra Sorio; TP) Tondo Pitter; DN) Donna Novi; PU) Putto

**Tab. 1** Dimensions of the selected artworks. For Donna Novi and Putto a general indication of the height is reported; for Tondo Pitter the diameter is given

| *Donna Villarubia* | *Lastra Sorio* | *Tondo Pitter* | *Donna Novi* | *Putto* |
| --- | --- | --- | --- | --- |
| 40x60 cm | 63x52 cm | 32 cm (ø) | 110 cm (height) | 68 cm (height) |

**Tab. 2** Composition of the bulk alloys of the studied artworks [wt%]

| | **Cu** | **Zn** | **Sn** | **Pb** |
|---|---|---|---|---|
| *Donna Villarubia* | 83.47 | 7.48 | 6.48 | 2.57 |
| *Lastra Sorio* | 84.59 | 4.71 | 8.84 | 1.86 |
| *Tondo Pitter* | 84.02 | 5.31 | 7.89 | 2.77 |
| *Donna Novi* | 75.33 | 6.16 | 5.14 | 13.36 |
| *Putto* | 86.87 | 6.65 | 5.71 | 0.77 |

Only limited historical information are available about the analysed sculptures. All of them were realized between the second half of the XIX century and the beginning of the XX century. According to the Cemetery registers, *Donna Villarubia*, *Tondo Pitter*, *Donna Novi* and *Putto* were exposed outdoor in unsheltered conditions, while *Lastra Sorio* was located in one of the open-air galleries of the Cemetery in a semi-sheltered environment.

<u>Cleaning methodologies</u>

The five cleaning procedures are detailed below.

- Controlled mechanical cleaning of the surface corrosion layers by means of micro rotary tool
- Controlled mechanical cleaning by means of scalpel;
- Cleaning based on a series of nonpolar solvents in cellulose pulp poultice applied in close succession according to increasing volatility (white spirit, ethyl and isopropyl alcohol, cyclohexane and acetone);
- Combined mechanical and solvents cleaning through the application of white spirit in a cellulose pulp poultice, followed by scalpel cleaning;
- Laser cleaning, by means of an El.En. Eos Combo s/n RQ6B2201B instrument, equipped with a 1064 nm laser. A setup with a 5Hz frequency and a 600 mJ of energy was selected after preliminary cleaning tests and was applied on all the laser treated areas. No wetting agents were employed.

The first four procedures were tested on separate areas of *Donna Villarubia*, *Lastra Sorio*, *Tondo Pitter* and *Donna Novi* that showed similar features from the compositional and electrochemical point of view after preliminary tests.

The scalpel cleaning was the only methodology applied on *Putto*, as it granted a higher selectivity with respect its delicate finishing layer.

Laser cleaning was tested only in the final phase of the experimentation since the laser equipment was available only for a short time. Thus, this cleaning methodology was tested only on three artworks (*Tondo Pitter, Donna Novi* and *Donna Villarubia*).

<u>Characterization methods</u>

*The in-situ* documentation of the surface morphology has been performed with a portable digital microscope Dino-Lite Premiere AM7013MT, with variable magnification from 50x to 200x. *In-situ* visible spectrophotometry measurements (25 per area) have been performed with a portable reflectance spectrophotometer Minolta CM-2600d using a Xenon light source in the spectral range of 400-700 nm, CIE standard illuminant D65, CIE standard colorimetric observer 10°, reference colour system CIE L*a*b*. Both portable microscopy analysis and spectrophotometric measurements have been performed before and immediately after the cleaning treatments.

Powder micro-samples have been collected from the surfaces before and after cleaning of all the statues for the laboratory investigations and a micro-fragment was collected from *Putto* before cleaning.

The compositional characterization of the powder samples was performed by Fourier Transform Infrared spectroscopy (FT-IR), using a Thermo Nicolet 6700 spectrophotometer with DTGS detector with detection range between 4000-400 $cm^{-1}$, after dispersing the powders in KBr pellets. FT-IR analysis have been performed both before and after the cleaning of the surfaces.

Bulk alloys and powder samples of all the sculptures and the micro-fragment of *Putto* have been analysed in Scanning Electron Microscopy coupled with microanalysis using an ESEM Zeiss EVO 50 EP in extended pressure equipped with an Oxford INCA Energy 200 - Pentafet LZ4 spectrometer. The analysis were performed directly on the micro-samples, and for *Putto*also on a polished cross-section prepared by embedding the metal fragment into bi-component epoxy resin (MA2 Mecaprex).

The mineralogical characterization of the samples have been performed by XRD analysis with a X-ray diffractometer Philips PW1830, Bragg-Brentano and Thin Film geometry and copper anticathode (Kα1 radiation with wavelength λ = 1,54058 Å).

*__Electrochemical measurements__*

In situ electrochemical measurements for the characterization of the stability and reactivity of the patinas, and for the monitoring of their evolution after cleaning were performed with a portable potentiostat Ivium Technologies CompactStat with Ivium® software, employing the ContactProbe proposed by Letardi (Letardi 2004). A three electrode configuration with AISI316L stainless steel counter and pseudo-reference electrodes was adopted. The polarization resistance value (Rp) has been obtained from both LPR and EIS measurements. In particular, the Rp from EIS measurements was calculated as the difference of the modulus |Z| at low and high frequencies (Zhang et al. 2002; Nishikata, Zhu, and Tada 2014). LPR measurements were performed after 10 minutes of open circuit potential monitoring, varying the potential of ±10 mV with respect to $E_{corr}$, and with scan rate of 10mV/min. For the EIS measurements the following setup have been adopted: frequency range between 100 kHz and 10 mHz, with ±10 mV with respect to $E_{corr}$. At least two repetitions of LPR and EIS analysis have been performed on each studied area. The Rp values reported in the following have been obtained as the average of all Rp values, measured both by EIS and LPR analysis on each area.

The electrochemical characterization of the surfaces has been performed in several steps, before and after the cleaning treatments, as reported in Fig. 2, in order to monitor the evolution of the surfaces when exposed to different environmental conditions. During the conservation treatments the statues were all kept in laboratory. Then, approximately 12 months after cleaning, all of them except for *Donna Novi* were moved outdoor in non-sheltered conditions and where monitoring continued. After about 1 year of exposure outdoor and 2 years after the cleaning, *Donna Villarubia* and *Tondo Pitter* were moved back to the laboratory. *Donna Novi* remained indoor all the times since it became part of an exhibition.

At least three repeated measurements were performed on each cleaned area during each phase of the monitoring.

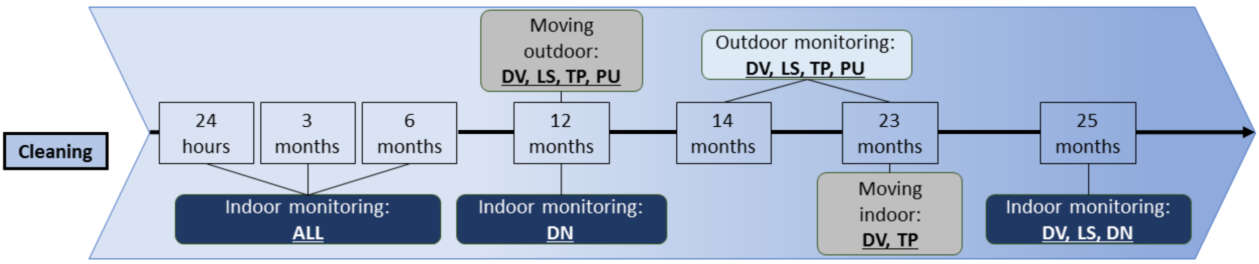



**Fig. 2** Timing of the different phases of electrochemical monitoring of the artworks after cleaning of DV) Donna Villarubia; LS) Lastra Sorio; TP) Tondo Pitter; DN) Donna Novi; PU) Putto

## Results and discussion

*Characterisation of conservation conditions before cleaning*

Both *Donna Villarubia* and *Lastra Sorio* were characterized by the presence of extensive scaling of the most superficial corrosion layer. In particular, *Donna Villarubia* was characterized by a dark, apparently thin and smooth corrosion layer that presented a quite uniform colour, but limited adherence to the underlying ones (Fig. 3a).

*Lastra Sorio* presented a light green, thick and powdery superficial layer, prone to scaling (Fig. 4a). The removal of the outermost layer revealed the presence of a more compact grey-blueish patina. The corrosion layers of *Lastra Sorio* appeared quite different in terms of colour, adhesion and coherence compared to the other studied artworks, possibly because it was the only artefact exposed in a semi-sheltered environment for several years.

*Putto* was characterised by a dark surface layer that appeared poorly adherent to the substrate and quite homogeneous in colour except for some light green areas all over the surface (Fig. 5a).

*Donna Novi* was characterised by the presence of a smooth and hard external layer of corrosion products with a dark green colour and waxy appearance (Fig. 6a).

After preliminary cleaning tests on *Donna Novi* and *Putto*, a goldish surface was revealed under the outermost layers. In order to investigate its nature, a micro-fragment was taken from *Putto* and its cross section was analysed by SEM-EDX (Fig. 7). The goldish finishing was obtained by applying on the metallic surface (Fig. 7, layer *a*) a *porporina* layer (Fig. 7, layer *b*) made of small brass laminas up to 100 µm wide, with an approximate thickness of less than 1 µm. The *porporina* finishing was completely covered by a superficial layer of corrosion products of some tens of µm (Fig. 7, layer *c*), which appears not strongly adherent to the surface and partially cracked.

*Tondo Pitter* was completely covered by a black and rather uniform layer of waxy substances, probably due to a past restoration or maintenance interventions. Such layer covered the patina and it altered dramatically the aesthetic of the sculpted details. Observation with portable microscope highlighted the presence of discontinuities on the superficial waxy layer (Fig. 8a).

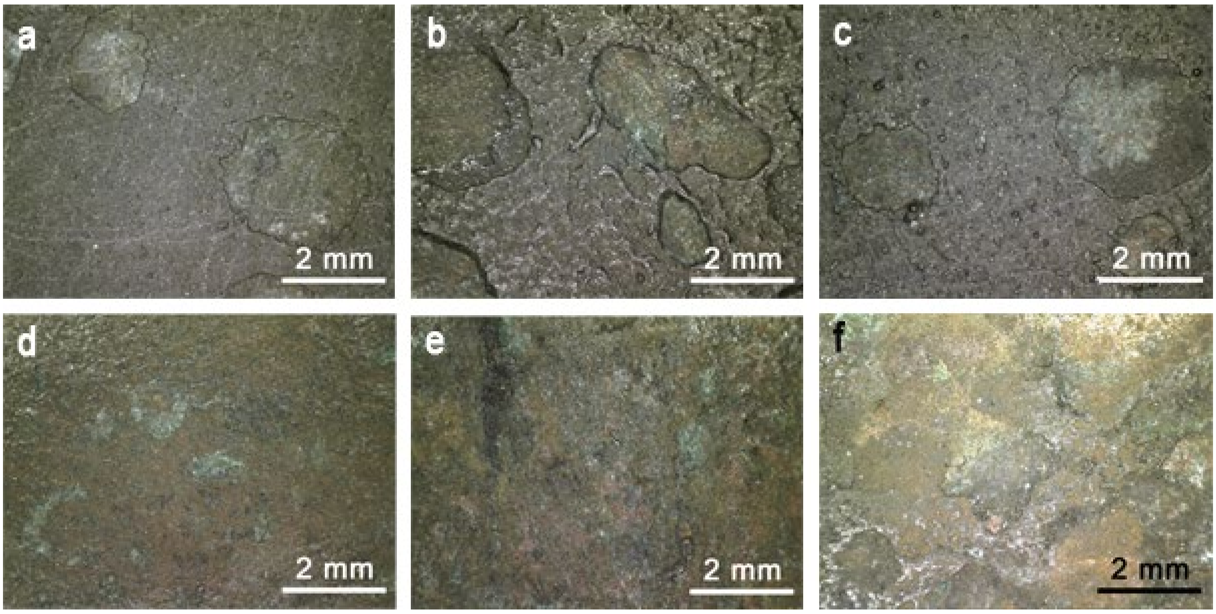



**Fig. 3** *Donna Villarubia*: images in portable digital microscopy. a) Uncleaned surface; b) surface cleaned by micro rotary tool; c) surface cleaned by nonpolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel; f) surface cleaned by laser

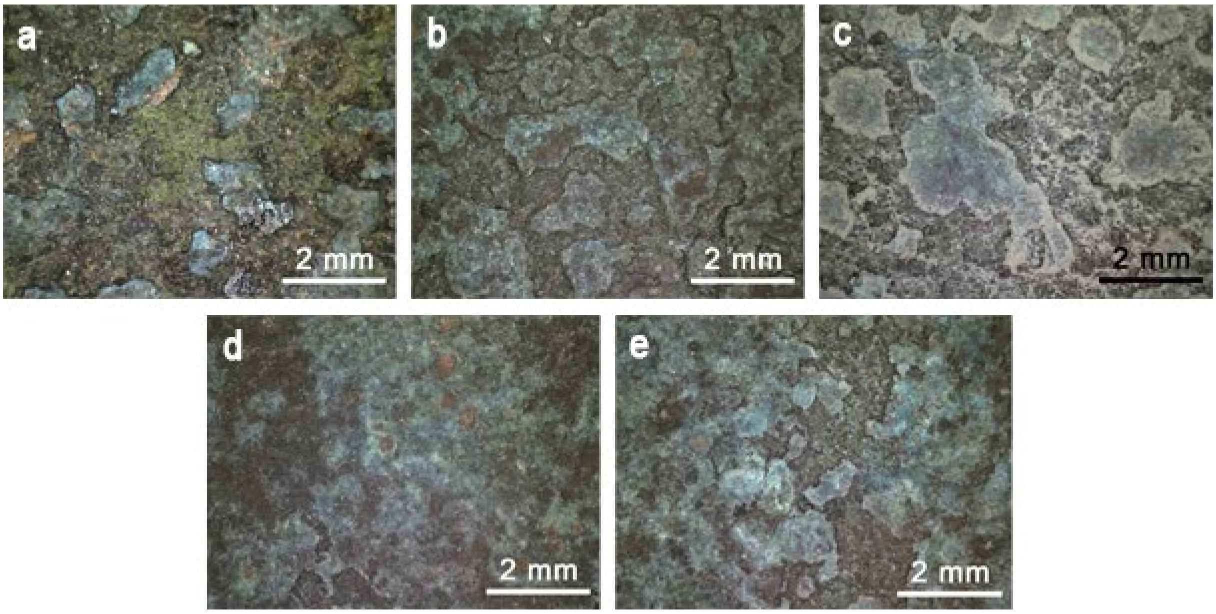



**Fig. 4** *Lastra Sorio*: images in portable digital microscopy. a) Untreated surface; b) surface cleaned by micro rotary tool; c) surface cleaned by nonpolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel

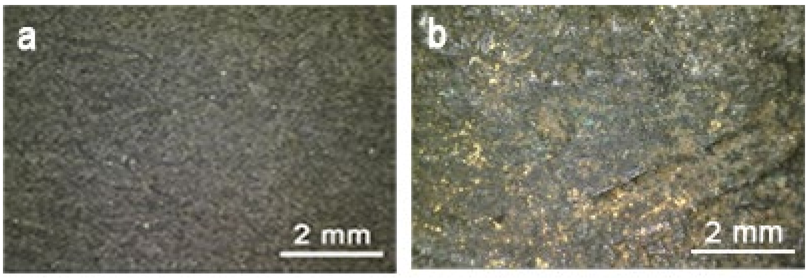



**Fig. 5** *Putto*: images in portable digital microscopy. a) Untreated surface; b) surface cleaned by scalpel

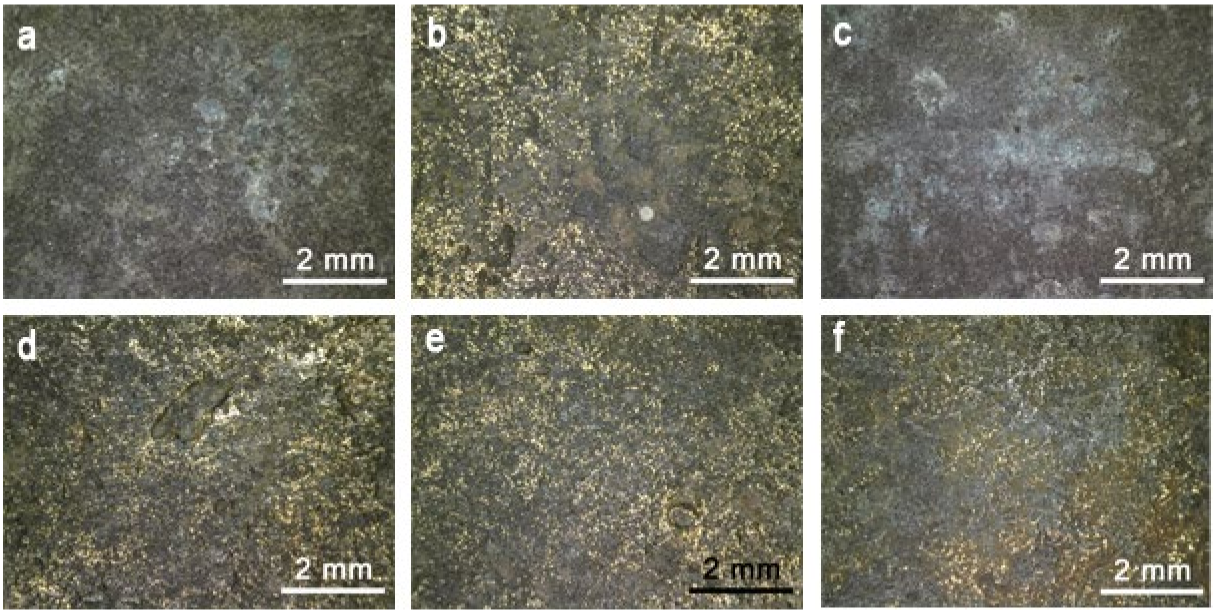



**Fig. 6** *Donna Novi*: images in portable digital microscopy. a) Untreated surface; b) surface cleaned by micro rotary tool; c) surface cleaned by nonpolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel; f) surface cleaned by laser

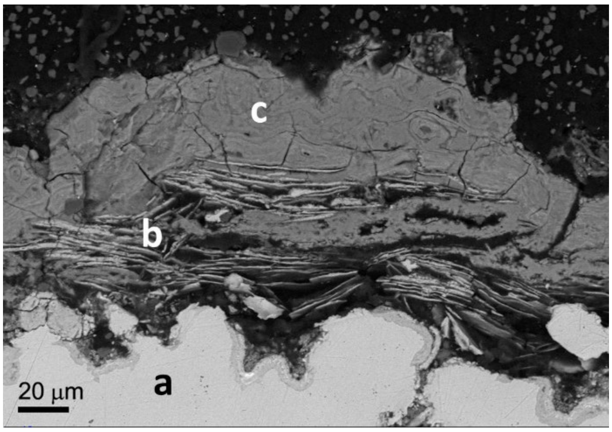



**Fig. 7** SEM image of the polished cross-section of Putto fragment showing: a) metallic substrate; b) *porporina* layer; c) superficial layer of corrosion products

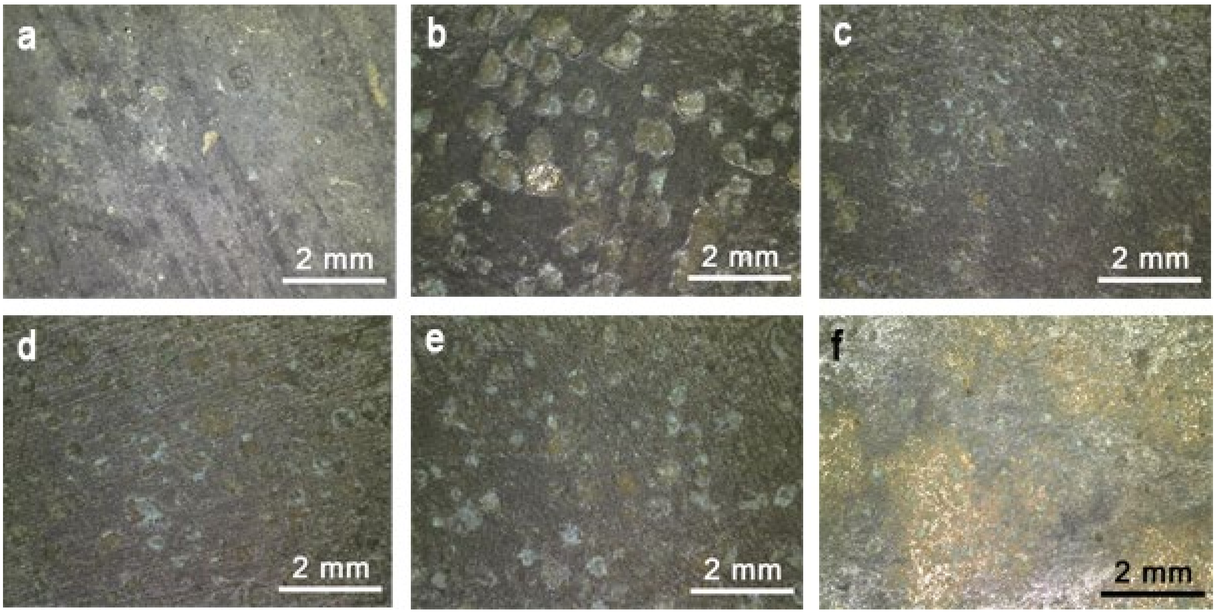



**Fig. 8** *Tondo Pitter*: images in portable digital microscopy. a) Untreated surface; b) surface cleaned by micro rotary tool; c) surface cleaned by nonpolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel; f) surface cleaned by laser

The compositional characterization of the surface of two artworks that resulted representative of the different conditions investigated, is reported In Fig. 9a-b. Fig. 9a shows the FTIR spectrum of a sample taken from *Donna Villarubia* before the cleaning, with the reference spectra of brochantite and antlerite. In Fig. 9b is reported the spectrum of *Tondo Pitter* before cleaning, with a reference spectrum of a typical microcrystalline wax. Both antlerite (peaks at 3570 cm$^{-1}$, 3485 cm$^{-1}$, 1156 cm$^{-1}$, 1110 cm$^{-1}$, 1072 cm$^{-1}$, 989 cm$^{-1}$, 887cm$^{-1}$, 850 cm$^{-1}$, 805 cm$^{-1}$, 755 cm$^{-1}$, 643 cm$^{-1}$, 645 cm$^{-1}$, 520 cm$^{-1}$, 490 cm$^{-1}$ and 465 cm$^{-1}$) (Catelli et al. 2018) and brochantite (3589 cm$^{-1}$, 3564 cm$^{-1}$, 3388 cm$^{-1}$, 3271 cm$^{-1}$, 1128 cm$^{-1}$, 1086 cm$^{-1}$, 989 cm$^{-1}$, 943 cm$^{-1}$, 875 cm$^{-1}$, 780 cm $^{-1}$ and 735 cm$^{-1}$, 630 cm$^{-1}$, 600 cm$^{-1}$, 512 cm$^{-1}$ and 486 cm$^{-1}$) (Catelli et al. 2018), copper hydroxy-sulphates normally found in urban environment, were detected on all the analysed surfaces. In addition, on *Donna Novi* and *Tondo Pitter* (Fig. 9b) visible peaks at about 2926 cm$^{-1}$ and 2850 cm$^{-1}$, and a double peak at 1472 and 1463 cm$^{-1}$ suggest the presence of organic compounds, probably constituted by microcrystalline wax (Catelli et al. 2018), often used as protective coating during maintenance interventions. The presence of brochantite and antlerite was confirmed also by SEM-EDX and XRD analysis on powders. The presence of deposits and dark particulate matter due to the interaction of the surfaces with the polluted environment of Milan, as well as the presence of residues of degraded protective treatments, conceals the typical green colour of these copper minerals. The environmental data and the concentration of pollutants recorded in Milan during the whole monitoring period are provided in table 3 (data from ARPA Lombardia-*stazione Marche* about 1 km far from *Cimitero Monumentale*). During the monitoring period 846 mm rain per year were measured (data from ARPA Lombardia-*stazione Rosellini*).

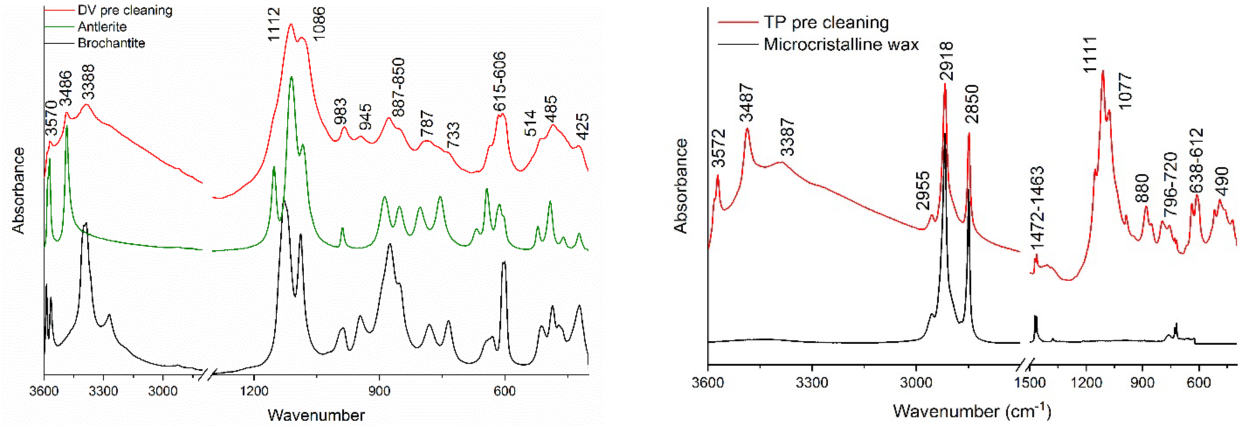



**Fig. 9** FTIR spectra of: a) Donna Villarubia before cleaning, with reference spectra of antlerite and brochantite; b) Tondo Pitter before cleaning, with reference spectra of microcrystalline wax

**Tab. 3**: Environmental data of Milan and concentration of pollutants, recorded about 1km far from *Cimitero Monumentale* (data from ARPA Lombardia-*stazione Marche*)

| | Temperature (°C) | Relative Humidity (%) | $NO_x$ (µg/m³) | $NO_2$ (µg/m³) | CO (µg/m³) | Benzene (µg/m³) |
|---|---|---|---|---|---|---|
| **Max.** | 37.3 | 99.6 | 1174.6 | 237.1 | 5.9 | 14.2 |
| **Min.** | 0.1 | 3.9 | 7.9 | 7.1 | 0.6 | 0.1 |
| **Average** | 15.4 | 60.1 | 134.9 | 64.0 | 1.0 | 2.3 |
| **Std. deviation** | 8.5 | 22.3 | 108.28 | 25.9 | 0.5 | 1.9 |

The results of the EIS and LPR measurements before cleaning are reported in Fig. 10, where polarization resistance (Rp) values (Fig. 10a) and |Z| values at low frequencies (Fig. 10b) are indicated. Both Rp values and |Z| at low frequencies are here reported to allow the comparison with the results reported in the literature. Both parameters are typically used to describe the corrosion behaviour of the surfaces, being both inversely correlated to corrosion rate (Gulotta et al. 2017; Goidanich et al. 2010; Bartolini et al. 1995; Letardi 2004; Letardi et al. 2016; Joseph et al. 2007; Sansonetti et al. 2015).

Four sculptures out of five (*Donna VIllarubia*, *Lastra Sorio*, *Donna Novi* and *Putto*) showed Rp values of the surfaces before cleaning around 10 Ω·m$^2$. *Tondo Pitter* is the only one showing a higher Rp value (80 Ω·m$^2$) probably due to the presence of the thick and dark waxy layer that apparently still provides some residual protection. In the case of *Donna Novi*, the organic residues present on the corrosion layers apparently do not provide any residual protection from corrosion. Considering the standard deviations of the Rp measurements, the distribution of values is quite homogeneous in all cases with the only exception of *Tondo Pitter*. This could be due to some limited discontinuities in the thick layer of wax, actually visible in the microscopic images of uncleaned areas (Fig. 8a). , The layer cannot therefore guarantee a uniform protection to the substrate. Overall, the measured Rp and |Z| at low frequencies values are in the range of 1-10 Ω·m$^2$ and $10^4$-$10^5$ Ω respectively. They are thus comparable with the typical data reported in the literature for non protected copper alloys exposed outdoor in not too aggressive environments (Gulotta et al. 2017; Goidanich et al. 2010; Bartolini et al. 1995; Joseph et al. 2007; Letardi 2004).

The sculptures were classified into two groups according to the overall characterization data before cleaning. The first group includes those characterised by the presence of dark or light green areas formed by scaling or powder-like corrosion products with very limited presence of organic residues (*Donna Villarubia*, *Lastra*

*Sorio* and *Putto*). The second one includes the sculptures characterised by smooth and uniform dark or black surfaces, with detectable presence of wax residues (*Donna Novi* and *Tondo Pitter*). , A further distinction can be made between these two latter sculptures:  asthe residual waxy layer of *Tondo Pitter* still provide a modest residual protective efficacy while the one of *Donna Novi does not*.
These criteria guided the selection of the artworks for the laser cleaning: *Donna Villarubia* was representative of the first group of artworks; *Tondo Pitter and Donna Novi* were representative ofthe second, respectively with and without residual protection of the organic superficial layer.

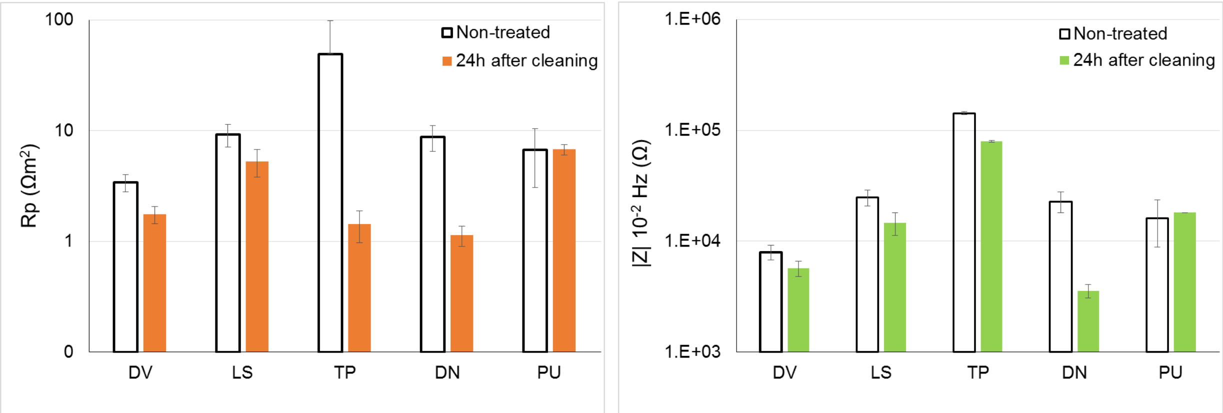



**Fig. 10** a) Rp values obtained both from LPR and EIS measurements, before and 24 hours after the cleaning; b) |Z| values at low frequencies before and 24 hours after the cleaning. The values are reported for all the studied artworks. White bars are referred to untreated areas; coloured bars report the average value of all cleaned areas for each artwork 24 hours after the cleaning intervention.

<u>*Characterization of the surfaces after cleaning*</u>

An evaluation of the five methodologies based on the surface morphology and colorimetric features  has been performed. In particular, the colour of the areas cleaned with micro rotary tool, laser and scalpel with or without poultice of *Donna Villarubia*, *Donna Novi*, *Tondo Pitter* and *Putto* shifted towards lighter and more red and yellow hues, due to the increase in L*, a* and b* values. *Lastra Sorio*,  showed a different behaviour with a variation towards more green and blue hues upon cleaning. Overall, the cleaning with solvents did not show any significant change in colour.
*In situ* microscopy clearly showed that the different cleaning procedure provided significantly different results on the two groups of statues. The mechanical methods were the most effective in removing the superficial deposits and corrosion layers as opposed to the solvents cleaning on all the studied sculptures. Among the mechanical procedures, the best result in removing the undesired products was  provided by the scalpel cleaning, either with or without preliminary application of the poultice. This was especially evident in the case of *Donna Villarubia* (Fig. 3d-e) and *Lastra Sorio* (Fig. 4 d-e) that were characterized by scaling, powdery and disaggregated corrosion layers, as previously discussed. On these two artworks the micro rot micro rotary tool ary tool (Fig. 3b-Fig. 4b) provided a less satisfactorily result, as it was not able to completely remove the rough, non-uniform and scaling patina that was indeed only flattened and spread over the surface. Scalpel cleaning was more effective in unveiling the underlying compact patina.
The cleaning with nonpolar solvents was poorly effective in all the studied artwork, including *Donna Novi* (Fig. 6c) and *Tondo Pitter* (Fig. 8c) that presented the highest amount of organic residues. In both cases the mechanical cleaning methods guaranteed the best results: they succeeded in removing the  waxy layer from *Tondo Pitter* as well as the dark green and quite hard layers from the surface of *Donna Novi*. In particular, regarding *Donna Novi*, all these methods worked similarly and were able to preserve the porporina layer (Fig.

6b-d-e). In the case of *Tondo Pitter*, the scalpel treatments, with or without poultice, provided the best result and brought to light a dark, compact patina (Fig. 8d-e).

The laser cleaning proved to be effective in removing both the smooth layers containing waxy residues and the inorganic non-coherent corrosion layers. On the other hand, this treatment was scarcely selective as it also removed some portions of the finishing patina that was supposed to be preserved. As a result, the metallic substrate was partially exposed, and the cleaned surface has an irregular appearence (Fig. 3f, Fig. 6f, Fig. 8f). It has to be noted that due to time constraints it was only possible to test a single experimental setup for the laser cleaning. Further investigation and tests with different instrumental parameters could lead to a more refined application of the methodology that could provide a more selective cleaning.

For the *Putto* statue only the scalpel cleaning was adopted (Fig. 5b). Based on the characterization of the artwork before cleaning, this statue was included within the first group of sculptures, as it did not present relevant amount of organic residues, for which the scalpel cleaning provided the best aesthetic results. The scalpel cleaning was also preferred to other mechanical procedures because of the presence of the *porporina*, as this methodology is moreselective with respect to the products to be removed. The scalpel cleaning allowed removing the dark incoherent corrosion layers rich in deposits, preserving the underlying *porporina* finishing layer (Fig. 11). In table 4 a summary of the information obtained from the microscopic observation of the surfaces before and after cleaning is reported.

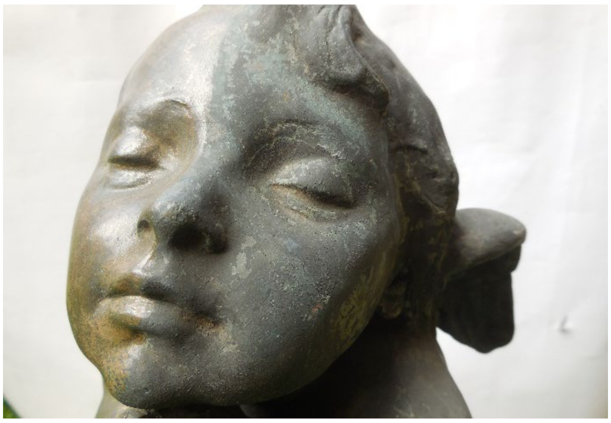


**Fig. 11** *Putto* during restoration. On the right portion of its face, the goldish finishing is visible after cleaning; on the left portion it is completely covered by corrosion layers

The efficacy of the cleaning methods in removing the waxy layers on the sculptures of the second group (*Donna Novi* and *Tondo Pitter*) has been also verified by FTIR analysis on powder samples taken from the cleaned surfaces. Among the methodology tested, the mechanical ones were the most effective in removing the organic compounds.

**Tab. 4**: Summary of microscopic characterisation of cleaned and non-treated surfaces

| | *Before cleaning* | *Micro rotary tool* | *Nonpolar solvents* | *Scalpel (with or without poultice* | *Laser* |
|---|---|---|---|---|---|
| *Donna* | Dark, and smooth corrosion layer, prone to scaling, with uniform colour (Fig. 3a) | Not able to remove the scaling and non-adherent products (Fig. 3b) | Poorly effective (Fig. 3c) | Effective in removing the dark and scaling superficial layer. A compact and adherent dark patina | Both the superficial scaling patina and the underlying compact dark layer were removed, uncovering in some points the |

| | | | | | |
|---|---|---|---|---|---|
| | | | | was brought to light (Fig. 3d-e) | metallic substrate (Fig. 3f) |
| *Lastra Sorio* | Bright light green, thick and powdery corrosion layer, with evident scaling phenomena (Fig. 4a) | Not able to remove completely the scaling and non-adherent products (Fig. 4b) | Poorly effective (Fig. 4c) | Effective in removing the light green and uncoherent patina, exposing the underlying more compact bright green patina (Fig. 4d-e) | -- |
| *Putto* | Dark surface, quite homogeneous in colour, with light green areas (Fig. 5a) | -- | -- | Effective in removing both the dark and light green patinas, revealing the *porporina* finishing (Fig. 5b) | -- |
| *Donna Novi* | Dark green smooth and hard external layer, with waxy appearance (Fig. 6a) | Allowed removing dark green and hard superficial layer, revealing the *porporina* finishing (Fig. 6b) | Poorly effective (Fig. 6c) | Effective in removing hard dark green corrosion layer, revealing *porporina* finishing (Fig. 6d-e) | Removed the superficial hard dark green corrosion layer, revealing *porporina* finishing (Fig. 6f) |
| *Tondo Pitter* | Thick and apparently uniform black layer of wax. The aesthetic features of the sculptures were significantly altered (Fig. 8a) | Removed the black waxy layer in a non-uniform way (Fig. 8b) | Poorly effective (Fig. 8c) | Effective in removing the balck wax-based layer. A compact blueish patina was brought to light (Fig. 8d-e) | Both the black waxy layer and the underlying compact blueish patina were removed, exposing the metallic substrate in some points (Fig. 8f) |

*Long-term monitoring of the surfaces by in situ LPR and EIS*

The electrochemical measurements were performed to verify that the adopted cleaning procedures were not affecting the long-term corrosion behaviour of the surfaces . In addition, it could be valuable to establish if some of the selected cleaning methodologies could also have a beneficial effect from the corrosion point of view on a long-term perspective.

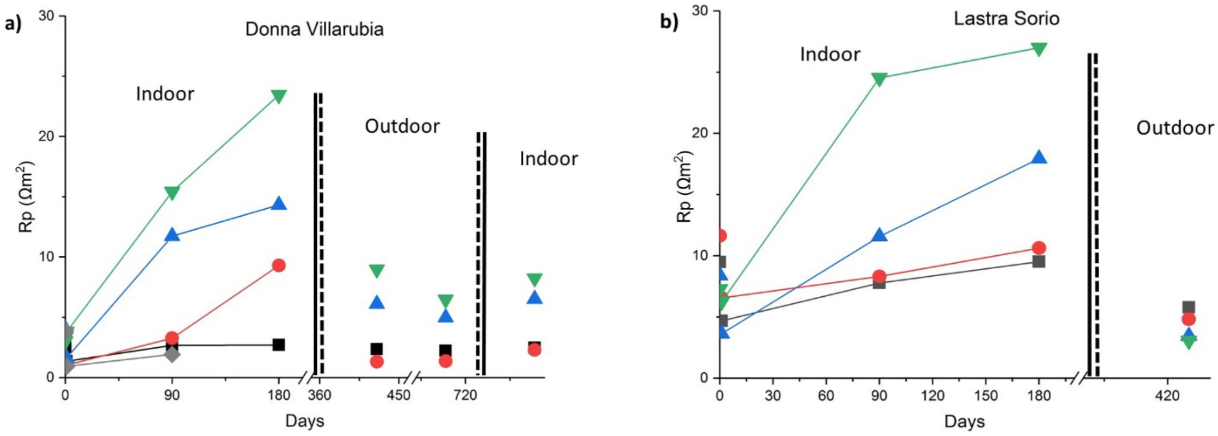
As it can be seen in Fig. 10, in the 24 hours following the treatment a general decrease in polarization resistance is recorded for almost all the analysed artworks and areas, irrespectively of the applied procedures,. This could be due both to the reactivation of the surface after the removal of the outermost layers, and, in case of *Tondo Pitter*, to the partial or complete removal of the residual coating of wax. The latter artwork actually showed the most relevant decrease in Rp values 24 hours after the intervention.

The evolution of the surfaces after the cleaning treatments was different for the two groups of artworks. Concerning the sculptures with negligible residues of wax before cleaning (first group: *Donna Villarubia*, *Lastra Sorio* and *Putto*, Fig. 12 a,b,e), a general increase in Rp values is observed for all the tested cleaning methodologies, as long as the artworks are kept indoor (6 months). In particular, the highest increase of the Rp value, and thus the highest improvement of the corrosion resistance of the surfaces, was observed on the areas cleaned by scalpel, with or without the application of the poultice. These cleaning methodologies were clearly effective in the removal of non-coherent, non-adherent and powdery corrosion layer, promoting the formation of a more stable and compact patina. This is a significant advantage for the surface from the corrosion point of view. Moreover, the slope of the first part of the graph (Fig. 12), representative of the first period of indoor storage, could suggest that keeping such condition for a longer period may result in an increased improvement of the corrosion resistance of the surface.

Considering the second group of statues, characterized by a relevant presence of wax residues before cleaning, different effects of the cleaning procedures were observed. In particular, for *Donna Novi* (Fig. 12c), which already showed lower Rp values before the cleaning treatments, after a first decrease of the Rp valuesno further variations of the Rp were observed in the subsequent months, even if this is the only statue kept stored indoor for the whole experimentation. *Tondo Pitter* (Fig. 12d), as mentioned beforeshowed the most dramatic decrease of Rp values 24 hours after cleaning (Fig. 10). In the following months, the same trend observed for the sculptures of the first group was observed, but it was not sufficient to compensate the loss of protective efficacy of the residual wax layer. Thus, even if an Rp increase of about 20 $\Omega\cdot m^2$ was observed, the initial Rp value of 80 $\Omega\cdot m^2$ was not recovered after 6 months of indoor storage. *Tondo Pitter*, moreover, is the only case for which the micro rotary tool cleaning proved to be the most beneficial from the corrosion point of view, providing the higher increase of Rp values in the 6 months of indoor storage.

The areas cleaned with laser presented some increase of Rp values three months after cleaning. Nonetheless, it  was scarcely effective compared to other tested methodologies

After the first period of indoor storage, some artworks were exposed outdoor (Fig. 2). This allowed verifying the evolution of the corrosion resistance of the surfaces in unsheltered outoor conditions. As it can be seen in Fig. 12a-b-c-e, the beneficial effect was completely lost in all cases. However, after one year the sculptures were relocated indoor and a further increase of the Rp values was observed, with values higher than those measured before the cleaning treatments. This behaviour can be an indication that the beneficial effect of cleaning and of the first year of indoor storage with consequent formation of a stable patina can be partially preserved by the surfaces even if exposed to an unsheltered outoor environment.



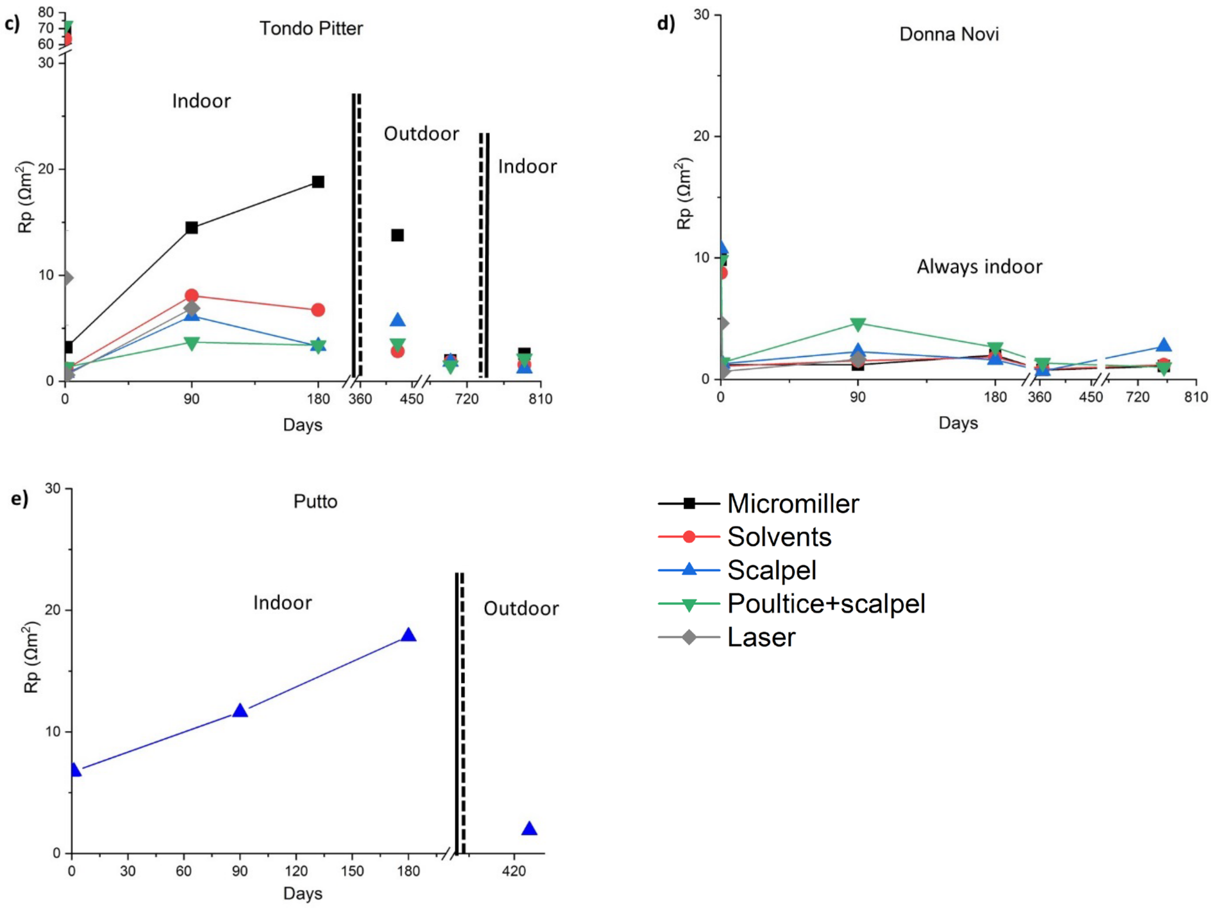



**Fig. 12** Mean Rp from EIS and LPR. a) Donna Villarubia; b) Lastra Sorio; c) Tondo Pitter; d) Donna Novi; e) Putto. Areas between solid lines: periods of indoor storage; areas between dashed lines: periods of outdoor exposition

<u>*Selection of the cleaning methodologies*</u>

Based on the obtained results, it was possible to select the optimal cleaning methodology for each studied sculpture. For two of the artworks (*Donna Villarubia* and *Lastra Sorio*) the scalpel cleaning was the optimal solution from both the aesthetical and the corrosion point of view. The scalpel method was then selected also for *Putto*, which presented a surface finishing similar to the one of *Donna Novi*, and it guaranteed good aesthetic results and an improvement in the corrosion resistance of the surfaces when the statue was stored indoors. The micro rotary tool was disregarded for *Tondo Pitter* due to aesthetic issues and the cleaning was finally performed by scalpel. In all these cases the cleaning by means of scalpel proved to be suitable also thanks to the small dimensions of the sculptures. For *Donna Novi*, the largest artworks among the studied ones, the micro rotary tool was chosen being the less time-consuming methodology and considering that all the mechanical procedures provided an acceptable aesthetic result, even if none of themled to an improvement of the patina stability after cleaning,.

## Conclusions

The results reported in this work showed that a long-term electrochemical monitoring could provide additional and valuable information for the design and management of a cleaning intervention.

It was confirmed that a general reactivation of the surfaces occurs after cleaning. However, the long-term corrosion behaviour can highly differ depending on the selected methodology. It was demonstrated that the results obtained with different cleaning procedures are strongly dependent on the initial surface conditions, which, in turn, are related to the conservation history of the artwork and to the past exposure conditions. For the surfaces characterised by scaling or powder-like corrosion products with very limited presence of organic residues, the scalpel cleaning proved to be the best option from both the aesthetical and the corrosion point of view.Scalpel cleaning also allowed the stabilization of the patina, and the consequent improvement of its protectiveness and reduction of the corrosion rate, when followed by the exposure to indoor environment. The preservation of the surfaces could be improved by delaying the application of the protective treatments , if it is possible to store the cleaned artwork in non-aggressive environment. The results suggest that an intermediate storage period indoor between cleaning and protection could actually promote the stabilization of the surface and maximise the benefits of cleaning. Further studies are needed to define the optimal time and conditions for the stabilization of the surfaces in connection to the storage environment of the artefacts, the surface conditions after the cleaning, and the protective system to be applied. Moreover, additional research should be focused to better understand the effect of the application of a coating immediately after the cleaning on the corrosion behaviour of the surfaces. In addition, the feasability of short-time monitoring campaigns should be investigated, in order to meet the needs of time sustainability of the restoration activity.

**Conflict of Interest**: The authors declare that they have no conflict of interest.

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**Figure captions**

**Fig. 1** Studied artworks: DV) Donna Villarubia; LS) Lastra Sorio; TP) Tondo Pitter; DN) Donna Novi; PU) Putto

**Fig. 2** Timing of the different phases of electrochemical monitoring of the artworks after cleaning

**Fig. 3** *Donna Villarubia*: images in portable digital microscopy. a) Non cleaned surface; b) surface cleaned by micro rotary tool; c) surface cleaned by apolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel; f) surface cleaned by laser

**Fig. 4** *Lastra Sorio*: images in portable digital microscopy. a) Non treated surface; b) surface cleaned by micro rotary tool; c) surface cleaned by apolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel

**Fig. 5** *Putto*: images in portable digital microscopy. a) Non treated surface; b) surface cleaned by scalpel

**Fig. 6** *Donna Novi*: images in portable digital microscopy. a) Non treated surface; b) surface cleaned by micro rotary tool; c) surface cleaned by apolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel; f) surface cleaned by laser

**Fig. 7** SEM image of the polished cross-section of Putto fragment showing: a) metallic substrate; b) *porporina* layer; c) superficial layer of corrosion products

**Fig. 8** *Tondo Pitter*: images in portable digital microscopy. a) Non treated surface; b) surface cleaned by micro rotary tool; c) surface cleaned by apolar solvents; d) surface cleaned by scalpel; e) surface cleaned by poultice and scalpel; f) surface cleaned by laser

**Fig. 9** FTIR spectra of: a) Donna Villarubia before cleaning, with reference spectra of antlerite and brochantite; b) Tondo Pitter before and after cleaning, with reference spectra of microcrystalline wax

**Fig. 10** a) Rp values obtained both from LPR and EIS measurements, before and 24 hours after the cleaning; b) |Z| values at low frequencies before and 24 hours after the cleaning. The values are reported for all the studied artworks. White bars are referred to non-treated areas; coloured bars report the average value of all cleaned areas for each artwork 24 hours after the cleaning intervention.

**Fig. 11** *Putto* during restoration. On the right portion of its face, the goldish finishing is visible after cleaning; on the left portion it is completely covered by corrosion layers

**Fig. 12** Mean Rp from EIS and LPR. a) Donna Villarubia; b) Lastra Sorio; c) Tondo Pitter; d) Donna Novi; e) Putto. Areas between solid lines: periods of indoor storage; areas between dashed lines: periods of outdoor exposition

**<u>Author contribution</u>**

All authors contributed to the study conception and design.

Material preparation was performed by Bruna Mariani.

Data collection and analysis were performed by Chiara Petiti, Sara Goidanich and Davide Gulotta.

The draft of the manuscript was written by Chiara Petiti. All authors commented on previous versions, read and approved the final manuscript.

Lucia Toniolo and Sara Goidanich supervised the whole research and writing activity.