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- Divisione di Chimica dell'Ambiente e dei Beni Culturali

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Programma Scientifico

Divisione di Chimica dell'Ambiente e dei Beni Culturali

Lunedì 11 Settembre 2017

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9:40 – 9:55	ABC/ANA/FIS OR02 Pamela Ferrari *Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks*
9:55 – 10:10	ABC/ANA/FIS OR03 Nicole Bonelli *Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in a polymeric network*
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11:55 – 12:10	ABC/ANA/FIS OR07 Elettra Barberis *Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects*
12:10 – 12:25	ABC/ANA/FIS OR08 Giuseppe Egidio De Benedetto *Provenance of Bitumen from different Apulian Bronze Age settlements through a biomarker based approach*
12:25 – 12:40	ABC/ANA/FIS OR09 Fantauzzi Marzia *From XAES signals to depth-profile reconstruction: the case of copper and copper alloys.*
12:40 – 12:55	ABC/ANA/FIS OR10 Marco Orlandi *Integrated approach for the chemical characterization of archaeological woods*

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17:50 – 18:00	ABC OR13 Sante Capasso *Clear evidence of the Macromolecular Structure of Humic acids*
18:00 – 18:10	ABC OR14 Lara Nobili *Accelerated tests to evaluate the combined effect of aggressive saline components of atmospheric particulate matter on corrosion and metal release of weathering steel*
18:10 – 18:20	ABC OR15 Caterina Marcoaldi *Analysis and detection of emergent contaminants in seawater by passive sampling*
18:20 – 18:30	ABC OR16 Giuseppe Mascolo *Removal of emerging organic pollutants in wastewater treatment plant effluents by an electrochemical process employing boron-doped diamond electrode*
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9:15 – 9:30	ABC OR19 Cristina Chiavari *B-IMPACT: a new project for the development of eco-friendly and non-hazardous outdoor bronze protective coatings*
9:30 – 9:45	ABC OR20 Alessandro Ciccola *Synthetic pigments, binder and light:* *a multitechnique study on degradation of contemporary art materials*
9:45 – 10:00	ABC OR21 Valeria Comite *The assessment of the carbonaceous component in black crusts damaging the stone surfaces of historical monuments*
10:00 – 10:15	ABC OR22 Jeannette Lucejko *A comprehensive study of the effects induced by brown rot fungi on archaeological waterlogged wood*
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12:00 – 12:15	ABC OR28 Giorgia Sciutto *A new MA-XRF system and an advanced methodological approach for the elemental characterization of panted surfaces: the exceptional case study of the Cimabue's masterpiece*
12:15 – 12:30	ABC OR29 Ilaria Serafini *The challenge of orchil dyes: advanced analytical techniques to discriminate the different lichen species*
12:30 – 12:45	ABC OR30 Esmeralda Neri *Life Cycle Analysis of a pyrolysis process applied to end-of-life tires*
12:45 – 13:00	ABC OR31 Mirko Volanti *LCA methodology: a case study of the industrial production of terephthalic acid from renewable sources*

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15:25 – 15:50	ABC/ANA KN02 Davide Vione *Photoinduced Processes in Surface Waters: A Photochemical Mapping of Sweden*
15:50 – 16:10	ABC/ANA OR01 Luca Carena *Application of an electro-activated glassy carbon electrode (GCE) to the analytical monitoring and photochemical studying of acetaminophen*
16:10 – 16:30	ABC/ANA OR02 Luca Rivoira *Removal and photodegradation of glyphosate herbicide from waters using a mesoporous substrate with adsorbent properties*
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17:30 – 17:50	ABC/ANA OR03 Sara Padoan *Characterization of ionic composition in the submicron fraction of urban aerosol.*
18:10 – 18:30	ABC/ANA OR04 Mirko Severi *Sea salt sodium record from Talos Dome (East Antarctica) as a potential proxy of the Antarctic past sea ice extent.*
18:30 – 18:50	ABC/ANA OR05 Roberto Udisti *A six-year record of size distribution and chemical composition of Arctic aerosol. Main results and future bi-polar perspectives.*
18:50 – 19:10	ABC/ANA OR06 Janeth Tafur Marinos *Effects of biomass, temperature and thermochemical process on PAH concentration in biochar*
19:10 – 19:30	ABC/ANA OR07 Ezio Bolzacchini *Particulate and gaseous indoor contamination at the Museum of "Last Supper" of Leonardo Da Vinci: results from one year of monitoring activity*

Keynote e Conferenze su Invito

- ABC/ANA/FIS KN01: Rocco Mazzeo, Department of chemistry, University of Bologna/Microscopy and Microchemistry Art Diagnostic Laboratory (M2ADL), Ravenna, Italy
- ABC/ANA/FIS KN02: Erika Ribechini, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124 Pisa, Italy
- ABC KN01: Raffaele Cucciniello, Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II,132 84084 Fisciano (SA), Italy
- ABC/ANA KN01: Antonio Marcomini, University Ca’ Foscari of Venice, Italy
- ABC/ANA KN02: Davide Vione, Department of Chemistry, University of Torino, Via P. Giuria 5, 10125 Torino, Italy
- ABC/ANA KN03: Alessandra Genga, Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, 73100, Italy.

Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces

Rocco Mazzeo[a], *Stjin Legrand*[b], *Giorgia Sciutto*[a], *Silvia Prati*[a], *Emilio Catelli*[a], *Paolo Oliveri*[c], *Koen Janssens*[b]

[a] *Department of chemistry, University of Bologna/Microscopy and Microchemistry Art Diagnostic Laboratory (M2ADL), Ravenna, Italy;* [b]*Department of chemistry, University of Antwerp, Antwerp, Belgium;* [c]*Department of Pharmacy-DIFARUniversity of Genoa, Genoa, Italy; rocco.mazzeo@unibo.it*

In the last decades, many research efforts have been devoted to the development of advanced non-invasive approaches for the examination of cultural heritage. However, up to now, too few attentions has been paid on the potentialities of the Macro Mid-Infrared total reflection (MA-FTIR) mapping analysis. Indeed, the infrared reflectance spectroscopy single point investigation has been largely applied in analytical studies of artworks due to its advantage of characterizing both organic and inorganic materials. On the other hand, the possibility to simultaneously obtained information on molecular composition and spatial distribution of constituents is of crucial importance for properly addressing conservation issues.

To this aim, the present research work was focused on the application of an advanced MA-FTIR mapping system for the study of altered bronze surfaces. Moreover, an *ad hoc* multivariate approach has been proposed for the interpretation of data.

A bronze sculpture exposed in the atmosphere deteriorates with time, developing a greenish/blackish layer mainly constituted of corrosion products. The formation of these corrosion products implies complex chemical, electrochemical and physical processes that strongly depend on the constituents of the surrounding environment. In addition, different acrylic resins, synthetic waxes and organic inhibitors may be commonly applied for short-term protection of outdoor bronze sculptures.

To the Authors knowledge for the first time Mid FTIR macro mapping analysis was performed on metal patinas, allowing the location of corrosion products and old coatings, and describing their interactions. The performances of the approach have been initially evaluated on standard bronze samples characterized by the presence of a green basic hydroxysulfate (brochantite) treated with different organic materials. Subsequently, the exceptional case of study of the bronze sculptures of the Neptune Fountain (Bologna, 16th century) has been investigated.

The instrument acquired hyperspectral cubes by scanning the metal surface without any contact, recording sequential total reflection single-point spectra. The big dimension of the data cubes obtained, as well as, the deformation of IR bands induced by specular reflection phenomena, may serious hampering the correct interpretation of the spectral features. Thus, a chemometric method, based on the use of the brushing procedure, was proposed to extract all the useful information embedded in a complex hypercube.

The high specificity of MA-FTIR mapping revealed important outcomes on the state of conservation of the monumental statue. In particular, it was possible to clearly describe well preserved areas in which wax and incralac resulted to be still present, describing their distribution and identifying zones affected by a more aggressive corrosion process.

GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the 16th to 17th century

Erika Ribechini[a], *Laura Blanco-Zubiaguirre*[b], *Ilaria Degano*[a], *Jacopo La Nasa*[a], *Javier García-Iñañez*[c], *Maitane Olivares*[b], *Kepa Castro*[b]

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The aim of this work is focused on the identification of the organic residues from ceramic vessels recovered from a deposit in Lekeitio (Basque Country, Northern Spain). These vessels are suspected to have been used by the Basque whalers in the period from 16th to 17th Century to store whale oil. Bearing in mind our aim, different analytical approaches based on chromatography and mass spectrometry (GC/MS and HPLC-ESI-qTOF) were used to study both fresh blubber and whale oil products and the archaeological substances in order to obtain chromatographic profiles and possibly detect highly diagnostic biomarkers. Two hydrolysis approaches were used in order to compare data and obtain as much information as possible; (i) microwave assisted direct hydrolysis of the ceramic samples and (ii) microwave assisted hydrolysis of previously solvent-extracted samples. On the other side, the study of solvent (chloroform:hexane (3:2 v/v)) soluble fraction was carried out by means of HPLC-ESI-qTOF. Preliminary results led to the identification of some interesting organic compounds in the hydrolysable and soluble aliquots from the ceramic vessel such as pristane, phytane, several saturated fatty acids, hydroxyacids and cholesterol along with triacylglycerols in the solvent soluble fraction. On the other hand, the obtained results for the fresh whale oil and blubber suggested a similar lipid profile to the ones obtained for the archaeological samples. The chemical results together with archaeological data seem to indicate the vessels were used to store whale oil.

A new passive sampler for atmospheric NO_x determination

Raffaele Cucciniello[a], *Rosa La Femina*[a], *Ilaria Zarrella*[b], *Concetta Pironti*[a], *Oriana Motta*[b], *Antonio Proto*[a]

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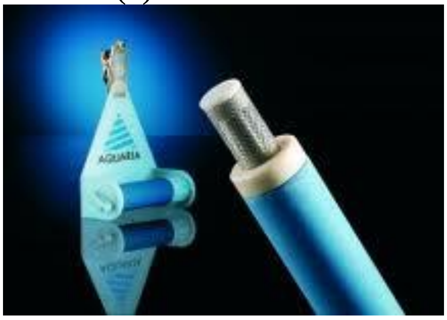
Atmospheric nitrogen oxides, NO and NO_2 (NO_x), are important polluting compounds, representative of gaseous emissions. NO_x concentrations are often used as a tracer of traffic related air pollution (1,2) and have been associated with adverse health effects and mortality in epidemiological studies.

Conventional NO_x measurements are typically conducted by using a chemiluminescence analyzers. Notwithstanding, a cost-effective alternative and simpler measurement technique for assessing air quality may be the use of passive devices (3).



De Santis and coworkers, to the best of our knowledge, have developed a passive sampler for NO_x ($NO + NO_2$) in the air by using an axial device and TEA/CrO_3 as reactive sorbent (4).

In this context, we were interested to search an alternative and environmentally friendly methods that could, on the one hand, collect NO and NO_2 simultaneously and, on the other, allow to overcome the environmental concerns related to the use of CrO_3 as substrate. In this paper, we report on the use of Na_2CO_3-impregnated silica as reactive substrate for atmospheric NO_x using a new passive sampler device.

The present study pursues three specific objectives:

- to explore new substrates for the simultaneous measure of NO to NO_2 overcoming environmental concerns connected to the use and disposal of CrO_3 as oxidant agent.
- to perform calculation of the diffusion sampling rate of the passive samplers.
- to perform validation experiments in the laboratory and in the outdoor environment, by the correlation of NO and NO_2 measured by passive samplers and with co-located chemiluminescence analyzer.

References

1. E. A. Riley et al. *Atmos. Environ*. (2016) 132, 229-239; **2.** B. Beckerman et al. *Atmos. Environ.* (2008) 42, 275-290; **3.** J. N. Cape *Critical Rev. Anal. Chem.* (2009) 39, 289-310; **4.** F. De Santis et al. *Anal. Bioanal. Chem.* (2002) 373, 901-907.

An integrated modelling approach to study the impacts of nutrients on coastal aquatic ecosystems in the context of climate change

Marco Pesce [a], Andrea Critto[a,b], Silvia Torresan[a,b], Monia Santini[b], Elisa Giubilato[a], Lisa Pizzol[a], Paola Mercogliano[b], Alberto Zirino[c], Ouyang Wei[d], Antonio Marcomini[a,b]

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Increase of atmospheric greenhouse gases (GHGs) due to anthropogenic activities is causing changes in Earth's climate. Global mean temperatures are expected to rise by 0.3 to 4.8 °C by the end of the 21st century, and the water cycle to be affected by changes in global atmospheric moisture. Coastal waterbodies such as estuaries, bays and lagoons, together with the ecological and socio-economic services they provide, could be most affected by the ongoing changes on climate being subjected to the combined changes in the physico-chemical processes of atmosphere, upstream land and coastal waters. Particularly, climate change is expected to alter phytoplankton communities by changing climate and environmental drivers such as temperature, precipitation, nutrient loadings and concentrations, and to exacerbate the symptoms of eutrophication events such as hypoxia, harmful algal blooms and loss of habitat. A better understanding of the links between environmental drivers and phytoplankton communities is necessary for predicting climate change impacts on aquatic ecosystems. In this context, the integration of climate scenarios and environmental models is a valuable tool for the investigation and prediction of phytoplankton ecosystem dynamics under climate change conditions. In the last decade, the impact of climate change on the environmental distribution and cycling of nutrients, including effects on aquatic ecosystems, prompted modeling studies at a catchment scale, mainly related to lake ecosystems. The further development of integrated modeling approaches to other types of waterbodies such as coastal waters can be a useful contribution to increase the availability of management tools for ecological conservation and adaptation policies. Here we present the case study of the Zero river basin (ZRB) in Italy, one of the main contributors of freshwater and nutrients loadings to the salt-marsh Palude di Cona (PDC), a waterbody belonging to the lagoon of Venice. To predict the impacts of climate change on nitrogen (N) and phosphorus (P) loadings of the ZRB and the consequent effects on the coastal phytoplankton community of PDC, we applied an approach integrating an ensemble of GCM-RCM climate projections, the hydrological model SWAT and the ecological model AQUATOX. Climate scenarios for the area indicated an increase of precipitations in the winter period and a decrease in the summer months, while temperatures show a significant increase over the year. The hydrological model SWAT predicted changes in water discharge and nutrient loadings of the ZRB, pointing out an increase in the winter period and a reduction during the summer months for both parameters. Simulations with AQUATOX predicted changes in water temperature, nutrient concentrations and N:P ratios, and consequent variations in the biomass and composition of phytoplankton in PDC, with major changes observed in the spring-summer period, where the abundance of warm-adapted species increases noticeably (1).

References

1. Pesce et al., 2017.

Photoinduced Processes in Surface Waters: A Photochemical Mapping of Sweden

Davide Vione[a], Birgit Koehler[b], Francesco Barsotti[a], Marco Minella[a], Claudio Minero[a], Lars J. Tranvik[b], Tomas Landelius[c]

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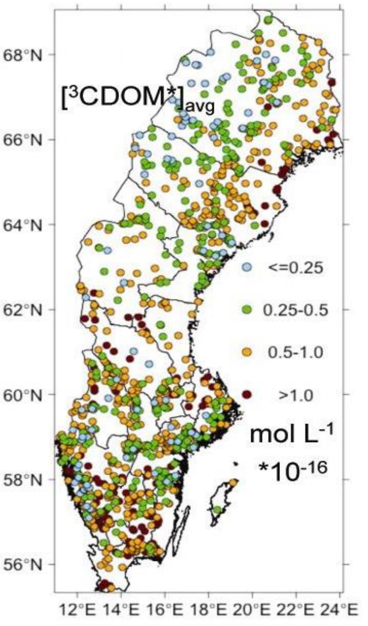
Photochemical reactions induce the self-depuration of surface waters, particularly against polar biorefractory pollutants that include many emerging contaminants (1). Photoreactions are divided into direct photolysis and indirect photochemistry. Direct photolysis involves sunlight-absorbing pollutants, and transformation is triggered by photon absorption. Indirect photochemistry takes place when sunlight is absorbed by naturally occurring compounds called photosensitisers (e.g., nitrate, nitrite and chromophoric dissolved organic matter, CDOM) to produce reactive transient species such as the hydroxyl ($^{\bullet}$OH) and carbonate ($CO_3^{\bullet-}$) radicals, singlet oxygen ($^1O_2$), and CDOM triplet states (^{3}CDOM*) (2,3).

We have recently modeled photochemical processes in surface waters (4), predicting the phototransformation kinetics of pollutants and deriving photochemical parameters from available time series of water chemistry. In the latter case, one can get insight into the impact of climate change over photochemistry (5). Here we show the application of photochemical modeling to data from a large geographic region. Based on a wide dataset that includes over 1000 Swedish lakes with their average depth, water chemistry and the incident sunlight irradiance, we could predict the steady-state [$^{\bullet}$OH], [$CO_3^{\bullet-}$], [$^1O_2$] and [^{3}CDOM*]. This is the first ever photochemical mapping of a country's inland waters.

The model results were validated by comparison of available field data with the predicted photochemical lifetimes of carbamazepine and ibuprofen in Lake Boren (6). Based on the photochemical map, and compared to temperate lakes, the CDOM-rich boreal lakes of Sweden are dominated by ^{3}CDOM* processes (except for the lakes located in the NW part of the country). In contrast, the efficient scavenging of $^{\bullet}$OH and $CO_3^{\bullet-}$ limits the importance of the relevant reactions. The ^{3}CDOM* processes are particularly effective towards the degradation of phenols, phenylurea herbicides and sulfonamide antibiotics (7). CDOM is a key photosensitiser in most Swedish lakes and strongly prevails over nitrate and nitrite. Climate change is expected to produce water browning in boreal lakes including the Swedish ones, due to export of light-absorbing organic compounds from soil to surface waters (8). Browning enhances the levels of CDOM, which is the ^{3}CDOM* precursor. Therefore, the importance of the ^{3}CDOM*-induced processes is expected to increase even more in the future, in Swedish lakes as well as in many other boreal areas.



Modelled steady-state [^{3}CDOM] in the 1048 Swedish lakes under study*

References

1. *Analytical Chemistry* 2011, *83*, 4614−4648; **2.** *Chemistry - A European Journal* 2014, *20*, 10590−10606; **3.** *Chemical Reviews* 2015, *115*, 13051−13092; **4.** *Environmental Science: Processes and Impacts* 2014, *16*, 732−740; **5.** *Science of the Total Environment* 2016, *541*, 247-256; **6.** *Environmental Science & Technology* 2015, *49*, 1646−1653; **7.** *Chimia - International Journal for Chemistry* 2007, *61*, 641−644. 8. *Global Change Biology* 2011, *17*, 1186−1192.

Primary and secondary carbonaceous species in PM10 and PM2.5 samples

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Carbonaceous PM is composed of a refractory component, commonly called elemental carbon (EC), and an organic fraction, called organic carbon (OC). Organic aerosols represent a large fraction of atmospheric aerosols. The organic fraction can include saturated and unsaturated aliphatic compounds, aromatic compounds, alcohols, ketones, aldehydes, carboxylic acids, amines, sugars, polyols, and organic sulfur compounds (2). Organic and elemental carbon were measured in daily PM10 and PM2.5 and 6 hours range time PM2.5 samples collected from September 2015 to October 2015 in a coastal rural site near Brindisi in the Apulia region (Italy), in order to determine factors affecting the carbonaceous aerosol variations. OC and EC were measured on Sunset Laboratory Thermal–Optical Carbon Aerosol analyser using NIOSH protocol.

Carbon content (total carbon TC) represented a considerable fraction for both PM10 and PM2.5. The highest values for both parameters were recorded when the winds blows from NE Europe and when Sharan Dust events have been recognized. The results show that OC and EC exhibited higher concentrations during the night hours, suggesting that stable atmosphere and lower mixing play important roles for the accumulation of air pollutants and hasten condensation or adsorption of volatile organic compounds.

Moreover, ATR-FTIR analysis were performed on some samples with the lowest and the highest OCsec and on samples characterized by Saharan Dust event. FTIR spectroscopy provides absorption peaks which can be identified and assigned to chemical bonds to identify functional groups in a complex sistem. The FTIR method is relatively simple and rapid and requires only small sample size. To our knowledge, there are only few examples of recent studies which are subjected to quantification or qualification of chemical species of aerosol samples. FTIR coupled with attenuated total reflectance (ATR) is a new technique developed recently. ATR FTIR analysis were carried out and it let identify organic functional groups included non-acid organic hydroxyl C-OH group (including sugars, anhydrosugars, and polyols, herein indicated as alcohol group), aromatic C=C-H group, aliphatic unsaturated C=C-H group, aliphatic saturated C-C-H group, non-acid carbonyl C=O group, carboxylic acid COOH group, and amine NH2 group. Among the inorganic ions, carbonates, sulfate, silicate and ammonium can be recognized.

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Comunicazioni Orali

Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces

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The development and characterization of a new family of water based gel-like systems containing hydroxypropyl guar gum (HPG) with borax as crosslinker are presented in this contribution. In the formulation glycerol is introduced as plasticizer, and its role is broadly investigated. The effect of the components on the structure, on the viscoelastic behavior of the system and on the activation energy related to the relaxation process has been investigated by means of rheology, Nuclear Magnetic Resonance (NMR) and Small Angle X-ray Scattering (SAXS) (1,2). Results indicated that the mechanical properties of the systems can be tuned by varying the amount of each component; ^{11}B-NMR and ^{1}H-NMR measurements highlighted the role of glycerol in the crosslinking mechanism, with the formation of a glycerol-borate complex. The characterization approach is used to identify the best formulation, in the view of a future application in the field of cultural heritage conservation, in particular for the cleaning of surfaces of historical and artistic interest (3). The main goal is to obtain a system adaptable to the roughness typical of surfaces of many artifacts. The best formulation was used for preliminary cleaning tests on a *stucco* artifact deriving from the decorations of *La Fenice* theatre, in Venice. The tests suggest a promising efficacy in selective cleaning of the surface and make these materials particularly interesting in the field of restoration.

Figure 1: On the left, Storage modulus values at Frequency=1Hz (■) and Crosslinked Borate Area obtained from NMR measurements (▲) are plotted against glycerol concentration. Pictures on the right show the *stucco* surface before (A) and after (B) the cleaning, with the comparison between the the HPG based system (1) and a wet cotton swab (2).

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Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks

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Chemical poly ethyl methacrylate (PEMA) organogels loaded with Diethyl Carbonate (DEC) were synthesized by means of radical polymerization (1, 2). These systems are specifically designed for the removal of degraded Pressure Sensitive Tapes (PSTs) from paper artworks, a very common issue in the field of manuscripts and drawings restoration. DEC, an organic green solvent, shows interesting swelling properties towards PSTs components; besides it is inert to most common inks and dyes, unlike other commonly used cleaning systems such as polar solvents and microemulsions (3).

Several organogels were obtained by changing reaction parameters; on the basis of macroscopic evaluations (e.g. mechanical properties, homogeneity), some systems were chosen for a deep physico-chemical characterization performed by means of different techniques. Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC), and gravimetric analysis were used to assess solvent content and uptake/release behaviour of gels; rheological analysis permitted the evaluation of their viscoelastic properties; Fourier Transform Infrared Spectroscopy (FT-IR) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) allowed to investigate the presence of unwanted residues in the exchange solvents and the effectiveness in the removal of PSTs. The penetration of DEC through the backing layer of PSTs and the swelling of the adhesive was investigated by means of Laser Scanning Confocal Microscopy (LSCM).

Cleaning tests on mock-up samples and real artworks were also successfully performed.

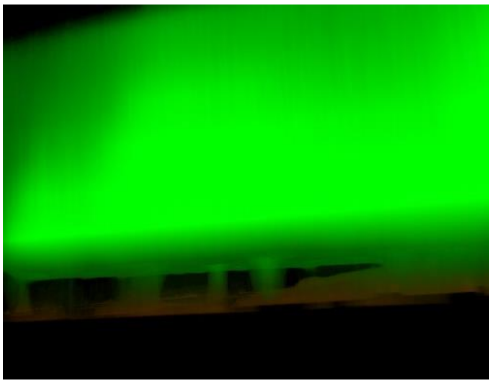

Fig. 1 – Laser Confocal image of a PEMA-DEC gel onto a PST sample: penetration of DEC (in green) through the backing up to the adhesive layer (in red)

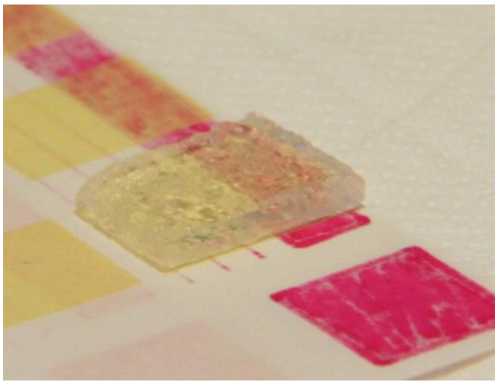

Fig. 2 – Application of a PEMA-DEC organogel for the removal of a Masking Tape from a mock-up sample

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Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network

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Nanosystems and confinement tools for the controlled release of a cleaning agent, e.g., hydrogels and microemulsions, have been used for several years for the treatment of delicate surfaces in art restoration interventions. However, notwithstanding the unprecedented achievements from an applicative point of view, a fundamental comprehension of their interaction mechanism is still lacking. In this study PVA hydrogels, obtained via freeze-thaw processes, are prepared as scaffolds for water-based nanostructured fluids for application in the cleaning of artworks: rheological, thermal, microscopic and scattering techniques showed that, depending on the number of freeze-thaw cycles, the hydrogels exhibit different physicochemical and viscoelastic properties, making them suitable for application in a broad range of cleaning issues. The gels have been loaded with an oil-in-water microemulsion and the diffusion of the microemulsion droplets inside the polymeric network has been investigated through Fluorescence Correlation Spectroscopy (FCS), demonstrating that the microemulsion is permanently kept inside the matrix and can freely diffuse in the network. In addition, we show that, when the gel-microemulsion system is put in contact with a layer of hydrophobic grime, a dynamic interaction between the microemulsion droplets and the underlying layer is established, leading to the solubilization of the hydrophobic molecules inside the droplets in the gel matrix. Thus, for the first time, through FCS, insights about the removal mechanism of hydrophobic grime upon interaction with cleaning agent embedded in the polymeric matrix, are obtained. Some examples of significant case studies treated with these innovative materials will be presented.

Nanocomposites for the consolidation and deacidification of cellulose-based artifacts

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A restoration method designed for the conservation of degraded fibrous-based artifacts should addressed the two main problems concerning these materials. Firstly, a mechanical reinforcement of artifacts is usually needed to ensure that the original material keeps its integrity. Moreover, pH buffering is required to prevent acidic degradation that is inherent to natural materials. (1)
It has been recently shown that these two issues are related. For instance, it takes less than 100 years for acidic compounds to induce a significant loss of mechanical properties in canvases based on natural materials. (2) The same degradation effect of acidic compounds is found in paper-based artworks, drawings and documents. In this regard, several deacidification methods have been proposed and proven efficient in hampering the degradation of cellulose. (3,4,5)

Research efforts have been recently devoted to the development of a nanocomposite material for the consolidation and concomitant pH adjustment of cellulosic works of art and artifacts that is one of the goal within the EU Project NANORESTART.
The use of nanocellulose, in combination with nanoparticles and cellulose derivatives, could ensure the consolidation of fiber-based materials using almost entirely natural materials. The choice of these materials is due to the high compatibility of the proposed treatments with the original fibrous support, which is essential from the conservation point of view.
Considering the high variability of cellulose-based artifacts, several different approaches were followed in order to provide conservators with a wide palette of tools that can be used on different works of art that are in need of both consolidation and deacidification treatments.
Nanocomposite materials were analyzed in order to gain more information about their structure and characteristics. Mechanical tests on not aged and aged reference samples were used to assess the consolidation efficacy of the proposed consolidation treatments before testing on real case studies.

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FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach

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Metal artifacts are among the most common materials in the Cultural Heritage field: alloys have been used in several fields of everyday life and their analysis can prove useful information about the technology of the ancient populations. In particular, coins are important for studying provenance, dating, minting and corrosion processes as well as provenance and stratigraphy of the archaeological sites (1,2).

In this work a set of Roman silver coins, dated back to the Antonini's period, has been analyzed using FIB-FESEM-EDX aiming to establish the used technique for the silvering and discriminating different mints. Recently, this approach was used as a complementary technique for the characterization of bronze coins (3) but this is the first application on Roman silver coins. The aim of this work is to investigate the microstructure and the composition of the alloy with a micro-invasive approach. Commonly to investigate the composition of the metal core are used invasive and destructive techniques, therefore the developing of methods with minimal damage on metal is of a great interest.

The study of Antonini's coins is also important as in that historical period Roman Empire underwent to a severe debasement which influenced coinage, so the surface silvering it is still an open question. Diocletian in the 294 A.D. introduced a complex alloy (Cu-Sn-Pb-Ag) with an Ag-rich surface patina of 2 µm. Some coins of the set show a very fine silvered surface with a core composition entirely made of Cu, whereas others have the composition made of Sn-Cu-Pb with a very low concentration of Ag. This technique has been joined with surface analysis (Raman spectroscopy, SEM mapping, voltammetry of microparticles (VMP) and electrochemical impedance spectroscopy (EIS)) for a deeper knowledge of the samples. The results showed the leaching of the Sn and Pb as well as of the Cu that formed several common products on the surface of the coins, *i.e*, Cu_2O, CuO, PbO, SnO. The presence of AgCl has been detected in several coins.

In conclusion, FIB-FESEM-EDX analysis provides information about the composition, structure and thickness of the metal patina as well as the composition and microstructure of the metallic core which in turn reflects the technology of minting. As a result, FIB-FESEM-EDX features yield information for the diagnostic, authentication, technologies and historical context in which the coins were fabricated. Such multi-analytical data allow us the possibility of screening the coins minting, obtaining significant differences between those minted in Roma and those minted in the Gallia.

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I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra

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Konrad Witz, tedesco di origine, ma attivo soprattutto in Svizzera fra il 1431 e il 1445 circa, è, per dirla con le parole dello storico dell'arte Jonathan Jones, "un gigante della pittura medievale che aspetta solo di essere scoperto". Le opere superstiti di questo artista sono davvero poche; fra queste sicuramente le più importanti sono le due tavole dipinte nel 1444 su entrambi i lati per l'altare maggiore della Cattedrale di Ginevra ed ora conservate nel Musée d'art et d'histoire de Genève (1). Il presente studio illustra i risultati della campagna diagnostica condotta, prima dell'intervento di restauro, sui materiali costitutivi, la tecnica esecutiva e lo stato di conservazione di queste opere. Le indagini scientifiche sono state condotte dapprima mediante tecniche strumentali non invasive, successivamente su microcampioni prelevati in modo mirato dopo l'acquisizione dei dati delle analisi preliminari.
Gli obiettivi delle indagini sono così sintetizzati:

- osservazione in situ della superficie delle opere mediante l'impiego di microscopia a bassi ingrandimenti, in luce visibile e UV, per osservare lo stato di conservazione della pellicola pittorica originale e differenziare le parti originali dalle eventuali ridipinture;
- analisi XRF in più punti delle superfici policrome per avere dati preliminari sulla composizione degli elementi chimici e orientare la scelta dei prelievi di campione;
- esame chimico-stratigrafico di campioni di materiale pittorico per documentare la composizione delle stratificazioni dei materiali costitutivi, dalla preparazione fino alle vernici superficiali, e avere così informazioni circa la tecnica esecutiva;
- identificazione delle cariche minerali negli strati preparatori e dei pigmenti nelle stesure pittoriche;
- riconoscimento, mediante test microchimici ed istochimici, delle classi di appartenenza dei leganti organici nelle varie stratificazioni;
- identificazione dei leganti pittorici mediante gascromatografia abbinata alla spettrometria di massa (GC-MS).

Una prima ricognizione delle superfici pittoriche delle quattro opere è stata effettuata mediante l'impiego di uno stereo-microscopio operativo con sorgenti di luce visibile e UV. Successivamente, sono state analizzate le superfici pittoriche mediante uno spettrofotometro portatile a raggi X (XRF). Sui dipinti sono state, inoltre, eseguite indagini radiografiche e riflettografiche all'IR per studiarne lo stato di conservazione e esaminare i dettagliati disegni preparatori. Una volta acquisite in situ tutte queste informazioni sono stati effettuati sedici microprelievi di materiale pittorico in zone ritenute maggiormente significative in relazione alle domande di conoscenza.
I test microanalitici impiegati sono stati finalizzati alla ricerca di sostanze proteiche, composti saponificabili e polisaccaridi. Le analisi rivolte all'identificazione dei leganti organici sono state condotte mediante microspettroscopia infrarossa a trasformate di Fourier e gascromatografia accoppiata alla spettrometria di massa (GC/MS).

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Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects

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During the last years, there has been a growing interest in the identification of proteinaceous material of cultural heritage and archaeological objects. Our group recently developed a new method for the non-invasive analysis of proteins material from precious and ancient artworks. The technique uses a functionalized film that extracts the proteins from the surface of the object. The extracted proteins are then analyzed by LC-MS/MS analysis using shotgun proteomics (1).

In this research, we will present the application of this method to several historical and archaeological samples. Moreover, we will discuss the analytical performances for the identification and quantification of proteins in complex matrixes.

In particular, we will present the developed protocol and the results obtained from the analysis of several artworks: a polychrome wooden altarpiece from the Maestro of Oropa, a polychrome sandstone capital, a rare polychrome alabaster, several wood medieval and renaissance panels (Pietro Gallo from Alba, Defendente Ferrari, Martino Spanzotti, Jean Bapteur, Gerolamo Giovenone) and a detached fresco from Antoine de Lonhy.

Moreover, through the use of this method we were able to identify the animal origin of an old precious manuscript from Domenico della Rovere (XIV century) as well as the binders from a rare sample of painted leather casket from Parisian manufactory (beginning of XIV century).

The analysis of the bottom of several greek vessels (Pyxis, Krater, Kylix cup and Kantharos) revealed the presence of animal origin proteins.

In conclusion, this study will report the first use of this non-invasive method for the characterization of proteins from ancient objects without the need to transport or sampling the artifacts.

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Provenance of Bitumen from different Apulian Bronze Age settlements through a biomarker based approach

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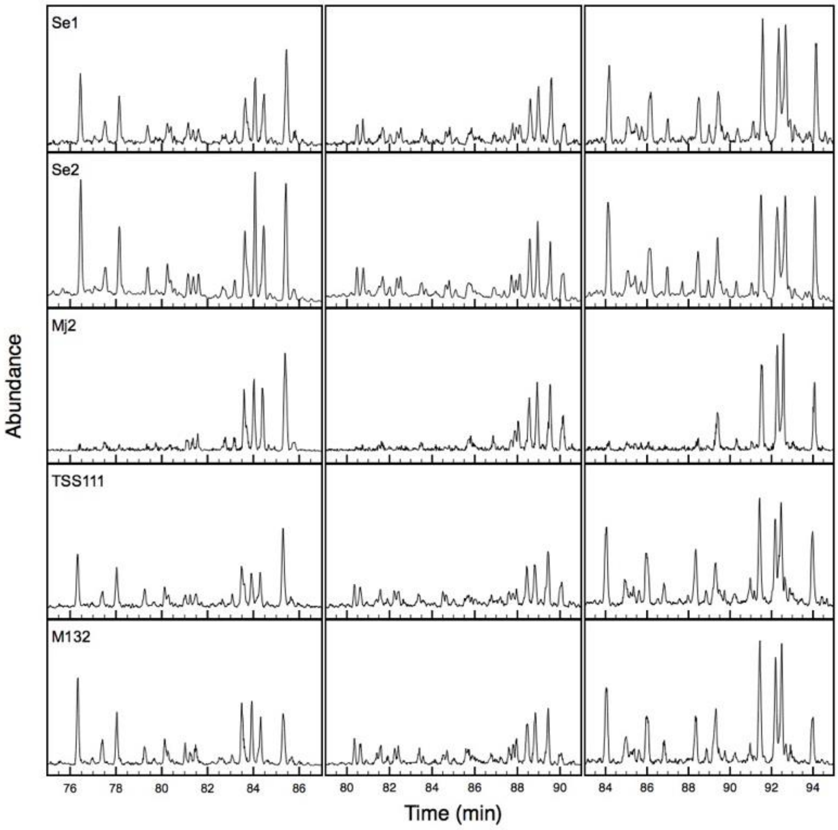
Bitumen has been used frequently in the Near East throughout history until modern times. Natural bitumen, found in solid or liquid form, was exploited and processed by ancient populations in Egypt, Mesopotamia and Syria for several uses such as to repair broken pottery, to waterproof containers or boats, to build the massive ziggurat temple mounds or to haft composite flint tools (1,2,3).

Together with the more widely studied and archaeologically important bitumen deposits in the Near East and Middle East (4,5), there are several seepages in Central Mediterranean which deserve more attention with respect to their exploitation and circulation in Antiquity. Evidence of bitumen use was found at several Apulian Bronze Age coastal sites (6), such as Otranto, Roca, Le Pazze (Lecce), Scoglio del Tonno (Taranto), Monopoli (Bari) and Torre Santa Sabina (Brindisi), but there are no archaeometric data about the relevant source(s).



Different bitumens from the central mediterranean sea region were studied as a possible source and analysed together with the archaeological samples using a geochemical, biomarker-based approach. The compositions of geological and archaeological samples were determined and provenance established. In the present communication, the relevant results will be described.

Acknowledgments

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From XAES signals to depth-profile reconstruction: the case of copper and copper alloys

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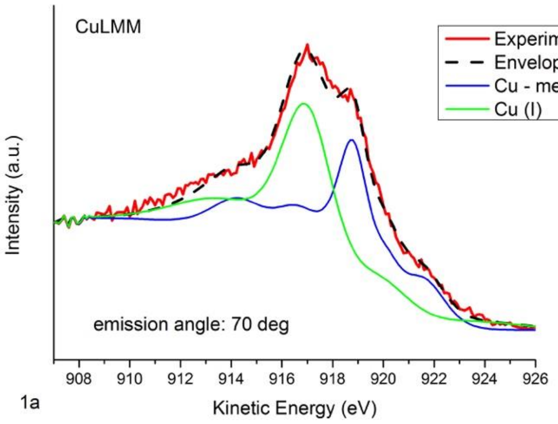
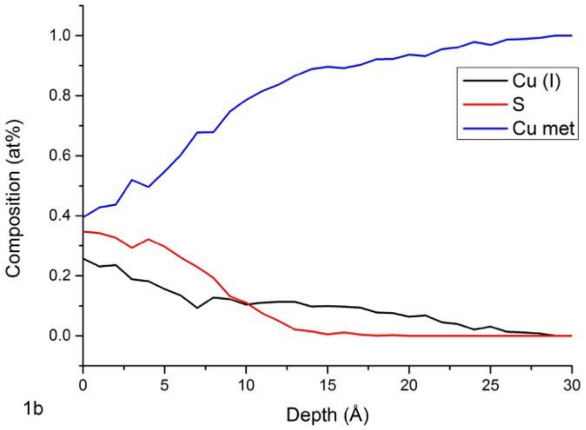
The analysis of the chemical state of co-existing copper and Cu (I) compounds by XPS is difficult since the Cu2p signal does not show any chemical shift. On the contrary the XAES signal $CuL_3M_{45}M_{45}$ allows distinguishing between Cu (0) and Cu (I) compounds. An analytical method starting from curve fitting of composed Auger induced CuLMM signals based on standards that permits quantifying the amount of copper and Cu_2O on the surface of brasses was developed and the thickness of the contamination and oxide nanolayers on the brass samples was determined by applying the three-layer model to standard XPS signals (1).
An alternative non-destructive way to reconstruct the in depth composition profile of a nano-layered surface by XPS involves the acquisition of angle resolved XPS spectra. An ARXPS experiment provides information on the intensities of the photoelectron signals vs emission angle: the higher is the emission angle, the more intense are the signals of the elements in the most external layer. To transform this ARXPS information in concentration vs depth, an iterative protocol based on the maximum entropy method (MEM) (2) can be applied.

In this work the depth profile of a S-functionalized copper sample, before and after rubbing in a tribometer was reconstructed applying MEM. The functionalization of copper with sulfur lead to the formation of Cu(I) – S bonds. The curve fitting of CuLMM (Figure 1a) allowed quantifying the % of Cu2p due to metallic copper and to Cu (I) in order to obtain the apparent concentration graph, which is the input for the MEM routine. The in depth distribution obtained is shown in Figure 1b.



1a



1b

Results obtained also on the in depth reconstruction of the oxide layer on the surface of brass alloys aged in buffer phosphate solution at pH 7 will be presented and discussed.

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Integrated Approach for the Chemical Characterization of Archaeological Woods

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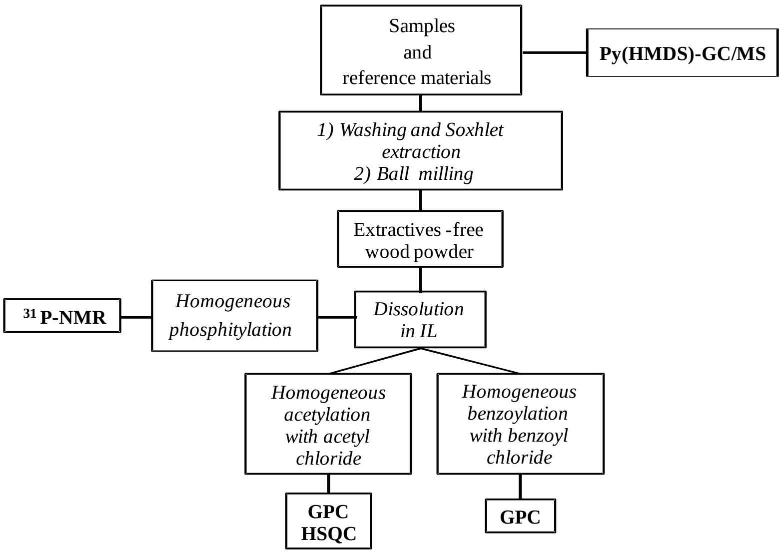
Wet archaeological wooden artefacts represent a conservation challenge still far to be solved, especially when archaeological wet wood has been previously treated with unstable materials and/or contain unstable inorganic salts which influence the degradation pathways. In order to evaluate the state of conservation of archaeological wet wood we have developed since 2007 an integrated analytical approach based on NMR spectroscopy, Py-GC/MS, and GPC analysis and applied on woods from the Site of the Ancient Ships of San Rossore (1,2,3) (Pisa Italy) and Vasa (4). Recently we have improved the analytical approach by dissolving archaeological wood into ionic liquids (ILs) as non-derivatizing solvents: in fact 1-allyl-3-methylimidazolium chloride ([amim]Cl) can provide a homogeneous reaction medium for derivatization of wood-based lignocellulosic materials. As a result, the functionalised wood developed an enhanced solubility in molecular solvents, thus enabling information about modifications of lignin, depolymerisation of cellulose and structure of lignin-carbohydrate complexes to be obtained by means of spectroscopic (2D-HSQC-NMR and ^{31}P-NMR) and chromatographic (Gel Permeation Chromatography) techniques. Py-GC-MS was used to investigate the degradation undergone by the lignocellulosic components on the basis of their pyrolysis products, without any pre-treatment of the samples [Figure 1].



The application of all these combined techniques provided a comprehensive characterisation of the whole cell wall of archaeological wood and the evaluation of its state of preservation. These analytical techniques were applied in an integrated way for the first time on archaeological wood from the Oseberg collection. High depletion of carbohydrates and high extent of lignin oxidation were highlighted in the alum-treated objects, whereas a good preservation state was found for the untreated wood of the Oseberg ship (Norway) (5).

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Assessment of nano-TiO_2 colloidal stability in aqueous media by analytical techniques and principal component analysis

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TiO_2 NPs are one of the most important inorganic materials which deserves careful investigation because of the high production and use in a wide range of applications and consumer products. In this framework, the colloidal stability assessment of TiO_2 NPs was performed varying in a controlled way the organic surface modifiers, electrolyte concentrations, pH and dispersion media. Functionalization was achieved by exploiting ligands with suitable geometries to get covalently linked to the TiO_2 NPs surface. Specifically, four catecholate derivatives (catechol, 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, dopamine hydrochloride), salicylic acid and polyethylene glycol (PEG) polymer were employed. Surface charge, hydrodynamic diameter and sedimentation velocity of the different NPs at two electrolyte NaCl concentrations (1 and 10 mM) were measured. The overall results were combined to obtain different dispersion stability classes, displayed by principal component analysis (PCA). The role of the organic modifiers on colloidal stability was highlighted, showing the influence exerted by NaCl concentration and pH. Under these conditions, 3,4-dihydroxybenzoic acid led to the most stable functionalized TiO_2 NPs dispersions. The study was further extended to organic and other aqueous media, i.e. ethanol, deionized water, and reference ecotoxicological media. Despite of the general destabilization observed in media with different ion valences and high salt concentrations (ionic strength up to 630 mM), an improvement of functionalized TiO_2 NPs colloidal stability was shown with respect to the pristine.

Thallium speciation in acid mine drainages, surface and tap water: A case study from northern Tuscany, Italy

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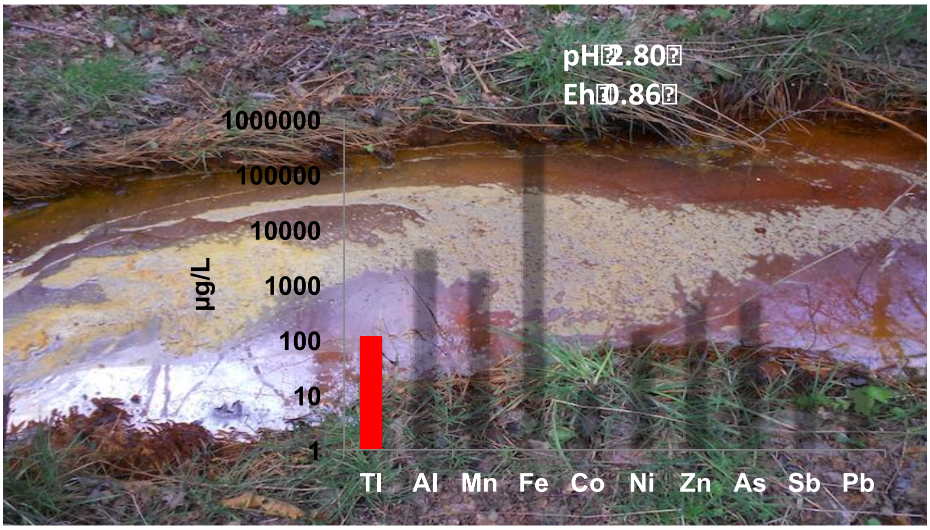
The increasing presence of thallium in the environment is attracting some attention because of its growing demand by modern high-technology industries. Thallium is more toxic than mercury, cadmium, copper, lead, and zinc, and its aquatic toxicity is apparently not affected by water hardness or humic acid concentration.

Tuscany (Italy) was one of the Italian regions that experienced a significant mining activity, which left a legacy of environmental problems related to acid mine drainages. The finding in 2014 of high Tl concentrations in drainages from abandoned mining districts located in the northwest of Tuscany (Valdicastello Carducci) posed some concern related to the potential dispersion of this element in the environment. The study of thallium redox speciation appears a way to understand its environmental behavior, since the valence state of thallium determines its toxicity, distribution and mobility.

In this work, the speciation of thallium in acid mine drainages, surface and tap water in the mining catchment of Valdicastello Carducci was first determined after separation with ion chromatography and online detection with ICP-MS. The method proposed for Tl speciation is simple, specific and fast (separation in less than 2 min). Thallium(III), considered the most unstable and toxic form of Tl, has been found in considerable amounts in drinking and river water, and it was also revealed in water samples collected in 2007.

Successively, adopting as model real water samples collected from a mine drainage and a river both rich in thallium, the distribution of aqueous Tl(I)/Tl(III) as a function of light exposure and solution properties was studied. The influence of sunlight and UV radiation, anions and organic acids was evaluated.

Beside the methodological advantages of the speciation method, our study offers a remarkable application on real samples from a thallium-contaminated area in Italy, which represents a unique possibility to investigate the behaviour of this interesting element. The study can provide an important scientific groundwork for the handling of thallium pollution.



Deposition of Airborne Pollutants on Plant Leaves and Role of Plant-Bacteria Interactions in Accumulation and Degradation Processes

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Phytoremediation has been shown to be an effective plant-based biotechnology for reducing and degrading indoor and outdoor airborne pollutants. Plants are known to scavenge significant amounts of air pollutants mainly by deposition on aboveground shoots. Leaf fall and runoff then transfer part of the adsorbed pollutants to soil and rhizosphere below. After uptake by roots and leaves, plants can metabolize, sequestrate and/or excrete air pollutants. Plant-associated microbes can help plants cope with stressful environments, but the extent to which they assist the removal of airborne contaminants in urban settings is yet poorly understood.

The main goal of the present project was an extensive and detailed characterization of the potential of the bacterial community in the phyllosphere/atmosphere to degrade airborne pollutants and to pose the basis for future successful applications of phytoremediation technologies to air pollution (1-3). Specifically, three sampling sites were chosen: two urban parks in Milano (MI) and Terni (TR), environmental hotspots, and Monte Martano (MM), a remote background site in Umbria. Five plant species (evergreen and deciduous) have been selected: *Cedrus deodara* (TR, MI, MM) *Platanus x acerifolia* (MI, TR), *Tilia x vulgaris* (MI, TR), *Magnolia grandiflora* (MI) and *Quercus ilex* (TR). Plant leaves were sampled twice each of the four seasons in 2016. Particulate matter (PM_{10}) was also sampled on a regular basis on all the sampling sites. Our aim was to characterize bacterial communities hosted by phyllosphere and atmosphere samples and to concomitantly quantify the leaf surface-adsorbed contaminants (polycyclic aromatic hydrocarbons, PAH, heavy metals, major ions). Moreover, the PAH degrading abilities and plant growth-promoting traits (PGPT) of culturable leaf-associated bacteria were assessed. Phyllospheric bacterial communities were taxonomically characterized by Illumina high-throughput sequencing of the V5-V6 hypervariable regions of 16S rRNA gene. Culturable bacteria (epi- and endo-phytes) were isolated on oligotrophic and copiotrophic media, identified through Sanger sequencing of 16S rRNA and screened for plant growth-promoting traits and ability to utilize PAHs. PAHs (39 chemical species) were extracted from leaf surface and analysed in HRGC-MS. Heavy metals have been characterized by ICP-AES and major ions by ion chromatography. The experimental database has been investigated with state-of-the-art statistical techniques.

We found that different plant species hosted specific bacterial communities. All communities were able to catch and degrade airborne pollutants, but specific patterns of activity varied among species. Most bacterial taxa were typical air-borne or plant-associated bacteria, albeit urban air pollutants are suspected to selectively reshape the composition of phyllosphere communities.

Detailed results will be discussed at the conference.

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Sito di monitoraggio in alta quota nelle Dolomiti Bellunesi (Col Margherita): sistema informatico per la gestione automatizzata dei dati meteo-climatici

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L'Istituto per la Dinamica dei Processi Ambientali (IDPA) del CNR gestisce un sito di misura di alta quota (Hight Altitude Station - HAS) in un'area remota a Col Margherita. La stazione di monitoraggio, accessibile dal passo San Pellegrino e dal passo Valles, situata nelle Dolomiti bellunesi a 2530 m sul livello del mare (latitudine 46° 22' 2.11" N, longitudine 11° 48' 23.03" E), è stata installata nell'estate del 2012 nell'ambito del progetto EU - FP7 Global Mercury Observation System (GMOS).

Per risolvere le problematiche legate alla gestione a distanza degli strumenti si è resa necessaria l'adozione di specifiche tecnologie hardware-software (IT) per l'acquisizione, gestione, trasmissione e validazione dei dati forniti dalla strumentazione automatica in dotazione alla cabina. Il sistema IT è stato progettato e sviluppato per permettere il controllo degli strumenti di misura di parametri chimico-fisici, della sensoristica meteo - climatica, delle telecamere interne/esterne della stazione.

Sviluppato su architettura Gnu-Linux, è stato utilizzato principalmente software Open Source. Sono stati integrati protocolli di comunicazione seriale per il controllo degli strumenti. L'acquisizione e la validazione dei dati viene gestita con LabView e Python. La sincronizzazione e il backup sono gestiti con Bash, crontab, scp e rsync. L'analisi statistica, la visualizzazione dei dati e la reportistica automatica sfruttano gli strumenti R, Shiny, Sweave e Latex.

Sono state considerate differenti soluzioni per la conservazione dei dati in rete (Cloud Storage) e per rendere fruibili i dati ad altri gruppi di ricerca, in accordo con gli standard Open Geospatial Consortium (OGC).

Attualmente il sito di misura è dotato di strumentazione meteo - climatica, di un analizzatore di mercurio atmosferico (TGM) e di ozono ed è in grado di integrare ai dati raccolti in automatico le misure di parametri chimico fisici ottenuti da campagne di monitoraggio hot-spot (inquinanti organici e inorganici nelle deposizioni atmosferiche, particolato atmosferico e neve).

L'obiettivo è realizzare la completa automazione dei processi di acquisizione, trasmissione, visualizzazione, validazione e produzione di report automatici dei dati misurati.

The Environmental Performance of Natural Defatting Products Used in the Leather Tanning Cycle

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The tanning industry in the EU is committed to a sustainable development at social and environmental level. The EU tanning sector is about 15-16% of the total EU leather industry, 700,000 Tons of leather and 1,800 companies mainly located in Italy (1,200-1,250) and Spain. It is fundamental to provide these industries with innovative and eco-friendly leathers that meet the EU quality standards. The crisis, which the leather sector is suffering from the reduction of internal demand and competition of low-wage third countries, is pushing for the introduction of new strategies, to address the market with innovative products and sustainable perspectives.

In recent decades, ethoxylated derivatives of fatty alcohols, vegetable oils and sugars have replaced the well-known chlorinated paraffins and alkylphenols, because of their toxicity. However, the production of ethoxylated alcohols, although profitable, may have a considerable environmental impact, since it is based on the consumption of petroleum, natural gas, animal fat and plant oils as primary raw materials.

This study, carried out under an European project (LIFE13 ENV/IT/000470 - Ecodefatting), aims to introduce new formulations in a view to reduce the environmental impact of the manufacturing processes (1). The new formulations include substances derived from natural products (lactose and citric acid) obtained in compliance with the REACH regulation (Regulation EC No 1907/2006).

The Life Cycle Assessment (LCA) methodology was applied from a "*cradle to the gate"* perspective and considering a laboratory scale production. The functional unit is the amount of the defatting agents obtained from the synthesis that is 3200g. The study was performed using the SimaPro 8.0.4 software and IMPACT2002+ impact assessment methods (2,3).

Primary data obtained from the experimental procedure were directly collected. The remaining data were obtained from specialized databases (Ecoinvent v3) and literature such as devices, machineries, plants, internal transports, ordinary maintenance operations and all data regarding installation, use and end of life steps. In addition, an environmental evaluation from the mere chemical point of view was also performed by means of the software EATOS (Environmental Assessment Tool for Organic Syntheses) (4). The use of EATOS allowed a first approximate quantification of the most impacting chemicals employed in the synthetic preparation of the degreasing product, while LCA methodology allowed to consider several further impact categories, including transportation and energy consumptions, thus realizing a more complete environmental assessment.

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Aerosols along vertical profiles: an overview of ten years of research from Italy to the North Pole

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The knowledge of vertical distribution of particulate pollution is fundamental in understanding the interplay between chemical and dynamical processes occurring within the atmosphere which finally reflects on the impact of atmospheric pollution on human health and climate change.

At this purpose from 2005 vertical profiles measurements were carried out using a unique sampling platform consisting of a tethered balloon (4.5 m diameter) equipped with an instrument package of: 1) a micro-Aethalometer AE51 (Magee Scientific), 2) a 1.107 Grimm OPC (0.25-32 µm, 31 size classes), 3) a cascade impactor (Siuotas SKC), 4) Tedlar bags for VOC, 5) a miniaturized nanoparticle detector (miniDiSC) and 6) a meteorological station (LSI-Lastem),

Tethered balloon measurements were conducted both over Italy (2005-2016; Po-Valley, Central Italy, Alpine Valley) and over Svalbard (2011-2012; Ny-Ålesund, 1200 far from North Pole) along different seasons winter, spring and summer. In addition to these, tower building based sampling activities of PM_{10} and $PM_{2.5}$ were carried out in the centre of Milan.

Aerosol samples were analysed using ion chromatography (Dionex ICS-90 and ICS-2000), GC-MS (Agilent 6850 and 5973), SEM-EDS (Philips XL30).

The aims of the aforementioned campaigns were to determine the aerosol chemical composition with height in relationship with size distribution data in order to investigate the aerosol dynamics across the Planetary Boundary Layer (PBL) as driver for important feedbacks on human exposure to PM (ground-level concentrations) and on climate change (feedbacks induced by the atmospheric heating and aerosol vertical location).

All the collected data (Italy and Svalbard) indicated the top of PBL as a clear transition in aerosol chemical composition, concentration and size distribution.

On the Italian side, coarse particles experienced a lower atmospheric mixing than fine particles due to settling processes, leading to a decrease with altitude of crustal components (i.e. Ca^{2+}, silicates); at the same time, fine particles experience an increase of their size together with secondary aerosol components (i.e. ammonium nitrate), sphericity, and correlation among fine aerosol sizes. This pattern evidenced recurrent ageing dynamics (condensation/coagulation) (1). In this respect, experimental results were coupled with modelling activity (WRF-Chem) (2), clearly showing that secondary aerosol formed in upper aerosol layer is of great importance as may contribute up to 25-40% to ground level concentrations on an hourly basis affecting human exposure.

Moreover, a ground-level layer of black carbon (BC; from +16.1% to +34.2%) was evidenced in according with a ~30% higher content of polycyclic aromatic hydrocarbons with respect to the whole PBL. BC also revealed a marked concentration drop across the PBL (from -48.4±5.3% up to -69.1±5.5%) resulting in a heating rate characterized by a vertical negative gradient (from -2.6±0.2 K day^{-1} km^{-1} up to -8.3±1.2 K day^{-1} km^{-1}) able to promote a negative feedback on the atmospheric stability (3).

On the Svalbard side, results allowed to describe for the first time the seasonal phenomenology of vertical aerosol properties allowing to discover a springtime low-altitude secondary aerosol formation (enriched in sulfates) never observed before in that area (4).

Most important, the mid-latitude (Italy) – North Pole (Svalbard) comparison of vertical behaviour of BC allow to experimentally interpret the modelling explanation of the Arctic Amplification (double heating compared to the globe).

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Radioactivity in Domitia coastal area (Southern Italy): a multidisciplinary approach

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Aim of this work is the radioactive characterization of two Campanian coastal environments, in particular down drift the river discharges, that had never been examined before, in order to investigate the distribution vs depth of natural (^{238}U, ^{232}Th, ^{226}Ra, ^{40}K) and anthropogenic (^{137}Cs, ^{239}Pu, ^{240}Pu) radionuclides and their handling in the coastal environment. Samples were collected down-drift the Garigliano river mouth, to understand if the Garigliano Nuclear Power Plant (GNPP) located near the edge of the river, could represent a source of contamination. For comparison, an analogous coastal site has been chosen southward, down-drift the Volturno river, far enough from the GNPP, otherwise contaminated (1). Natural and anthropogenic gamma emitters were analyzed by γ-Ray Spectrometry. Moreover, stratigraphic and sedimentological characterization has been carried out on the cores first by identifying their sedimentary pattern, the fossil content and by their description in stratigraphic logs, then by wet-sieving and selection of mollusca shells for ^{14}C dating by AMS (Accelerator Mass Spectrometry). In order to investigate the mineral composition, we have adopted the WAXRD (Wide Angle X-Ray Diffraction) technique. Since sandy matrices had never been analyzed before in our laboratory, except for soils and concrete (2), with only a scarce literature existing about their treatment, a new protocol (3) was realized by us to detect the anthropogenic ^{239}Pu, ^{240}Pu. This method can be simplified in two phases: the pre-concentration phase and the column separation. In the first phase, the sample is sieved, dried, combusted, leached and concentrated through steps of iron precipitation, centrifugation and washing. The second phase comprises: i) an anion-ion exchange resin for the extraction of Pu with other impurities, ii) its purification with the TEVA® Resin and iii) its detection by ICP-MS. As experimentation, this procedure has been extended by us, also to the analysis of samples by AMS: a part of the solution obtained after the final treatment is subjected to another cycle of iron precipitation and washing~~s~~ to reduce the volume, subsequently, it is dried and baked at 800°C for 8 hours and analyzed by AMS. This multidisciplinary approach has provided new important insights on the sedimentary evolution of the two deltaic strand plains studied, as well as on the detection and interpretation of the radionuclide content in coastal sandy matrices. The consistent presence of natural radionuclides is due to the volcanic and sedimentary rocks; ^{137}Cs does not contribute to the contamination of the coastal areas; the analytical procedure adopted to extract anthropogenic Pu by sand with ICP-MS is applicable to AMS detection. The ratio is set in the typical range of the global fallout (the Chernobyl accident), allowing the GNPP to be excluded from the contamination of the coast.

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Single particle characterization of particulate matter: Source apportionment

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An air environment includes solid and/or liquid particles in a variety of elements and shapes and gas component. Short-term and long-term exposure to elevated concentrations of these aerosol particles is associated with a number of adverse health effects as for example lung cancer, inflammatory lung disease, respiratory diseases, cardiovascular diseases and premature death. The aerosol particles are emitted by a wide variety of emission sources and can be transported over vast distance. Therefore, to devise a means of control, it is important to monitor the pollution level of particulate matter and to discover the type of emission sources by receptor model. The conventional source apportionment methods are based on bulk chemical analysis and require the specification of emission sources and information on the elemental composition of particles from each of the emission sources. In this work, we applied individual particle analysis to sources apportionment of particulate matter using scanning electron microscopy coupled with energy dispersive analysis (SEM-EDS) (1). This approach is based on the hypothesis each aerosol particle can deliver unique information about its emission source. Based on the morphology and chemical composition determined by scanning electron microscopy and energy-dispersive X-ray microanalysis, the particles were classified into the following fourteen groups: alumosilicates, silicates, calcium sulfates, sulfate-silicates mixtures, carbonaceous particles, soot, biological particles, sea salt, iron oxides, iron mixtures, metal oxides, secondary particles, fluoride and calcium carbonates. The particle groups observed in the present work can be assigned to different emission sources. Source apportionment based on properties of individual particles is especially helpful for discrimination of industrial emissions originating from high temperature processes from a natural soil component (2). The following source categories were distinguished and apportioned: soil, industry, secondary, soot, carbonates, calcium sulfates, sea salt and other.

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Quanto mercurio nelle acque minerali naturali della Campania?

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Il mercurio (Hg) è un inquinante ubiquitario prodotto da sorgenti antropiche e naturali, con effetti negativi sugli ecosistemi e sulla salute umana. La provenienza di questo metallo pesante oltre ad essere locale e regionale è anche transfrontaliera. Per tale motivo nel 2013, attraverso la Convenzione di Minamata, 140 paesi (di cui 26 dell'Unione Europea) hanno sottoscritto il Trattato che fissa la riduzione e il controllo dell'impiego di Hg in prodotti e in processi industriali e artigianali (1) per garantire la protezione dell'ambiente e della popolazione. Una volta immesso nell'ambiente il Hg, attraverso processi batterici naturali, viene trasformato in mono-metil-mercurio (MeHg) in ambienti acquatici. Il MeHg è il più tossico dei composti organo-mercuriali e data la sua elevata liposolubilità va incontro a bio-accumulo e bio-magnificazione (2). Oltre che con gli alimenti, il Hg può essere assunto con l'acqua, anche se in misura inferiore (3). Studi condotti su scala internazionale hanno evidenziato che monitorare le concentrazioni dei macro-elementi caratteristici, di metalli tossici e di specie indesiderate nelle acque in bottiglia permette di valutare non soltanto la qualità dell'acqua, ma anche lo stato di salute delle falde e di comprendere la geochimica delle acque sotterranee (4). Nelle pubblicazioni più recenti sono stati forniti dati relativi a numerosi parametri chimici e metalli pesanti, ma tali lavori sono privi di informazioni sui livelli di Hg (4, 5), in quanto i valori ottenuti sono risultati inferiori ai limiti di quantificazione del metodo analitico impiegato.

Figura 1 - Acque in bottiglia in laboratorio.

Figura 2 - CV-AFS.

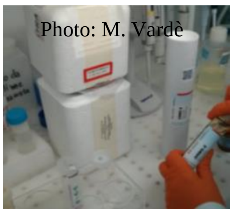

Figura 3 – CRMs.

Un totale di 19 differenti acque minerali provenienti da acquiferi della Campania e reperite sul territorio nazionale, sono state analizzate per valutare l'eventuale presenza di mercurio (Fig. 1). Prestazioni analitiche ottimali, in termini di controllo di possibili interferenze e limite di rilevabilità, sono state ottenute impiegando la spettrometria di fluorescenza atomica a vapori freddi (CV-AFS), consentendo la determinazione del mercurio totale a sub-ppt (Fig.2). Questa specifica tecnica strumentale unita alle accortezze adottate nella metodica analitica, l'impiego di matrici certificate e la partecipazione a circuiti di inter-comparazione internazionale (Fig.3) si sono dimostrate idonee per la rigorosa valutazione delle concentrazioni di mercurio, altrimenti non raggiungibili con strumentazione come AAS e ICP-MS. I risultati presentati in questo lavoro indicano che i livelli di Hg sono ampiamente al di sotto dei limiti legislativi e dunque l'assunzione di Hg in ultra-tracce con le acque minerali naturali non pone rischi per la salute umana.

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Efficiency improvement of the TiO_2 – ZnO NPs photocatalytic coupled system supported on a persistent luminescence material

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Heterogeneous photocatalysis is applied to several research areas, especially for environmental applications; among these, water remediation and wastewater bleaching are important fields the scientific research is focusing on. TiO_2 and ZnO (NPs) are the most preferable materials, due to their excellent chemical stability, high carrier mobility, environmental sustainability, high photocatalytic efficiency, nontoxicity and low cost for massive synthesis. However, TiO_2, as much as ZnO, are limited as sunlight-driven photocatalysts, due to their large band gap (ca. 3.2 eV for both), which requires, for photo-activation, photons with energy at least equal to the band gap; hence, the UV light source is mandatory (UV represents only 5-8% of the solar spectrum). A possible way to overcome this limitation is using a supporting material, capable to emit a proper radiation in order to activate "internally" the photocatalyst. It was reported as supporting the photocatalyst onto a persistent luminescence material (PeLM) increased the general efficiency and allowed the photocatalytic process to occur even in the darkness. In fact, the PeLM is able to be charged with both natural and artificial radiation and, glowing in darkness, provides the necessary photons to the catalyst (1). The coupled system has potential application in the removal of organic emerging pollutants, being particularly effective in the treatment of contaminated water by pharmaceutically active compounds and in turbid wastewater like olive mill vegetation waters. Both the matrixes are characterization by poorly biodegradable products. The capability to work also in darkness is significant in the reduction of electric energy consumption, resulting, in principle, to be an energy neutral technique for water purification and pollution control. The coupled system was obtained through a solid state synthesis: amorphous TiO_2 powders (synthesized *via* sol-gel technique), ZnO powders (2) and PeLM powders (prepared *via* solid-state synthesis) were mixed in water under magnetic stirring for 30 minutes, dried in oven at 105 °C for 12 hours and eventually subjected to a thermal treatment at 350°C for 1 hour. Several samples were prepared, by varying the weight ratio between the reagents powders, and characterized by means of XRD, SEM, BET. The photocatalytic activity was evaluated using a methylene blue solution. The best catalysts were then tested on a turbid solution of olive mill wastewater and an aqueous solution contaminated with pharmaceuticals compounds, e.g. the fluoroquinolone antibiotic Ofloxacin.

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Thermal processing alternative of biomass residue for biochar applications

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Efficient and innovative valorization of digestate from anaerobic digestion (AD) is one of the key issues for the development of sustainable biorefinery schemes based on bioenergy and bioproducts. Digestate contains several nutrients that should be returned to the fields, but its exploitation in agriculture sometimes constrained by to various factor, such as risk of N leaching and water eutrophication (see "Direttiva Nitrati"). Thermal treatment through pyrolysis or hydroprocessing can be considered as an alternative pre-treatment step to stabilize the solid digestate from AD. Carbonized (and thus sterilized) solid digestate is an easily transportable high added-value product, also called biochar. The present study reports on the results of two digestate carbonization experiments carried out in distinct processes at lab and pilot-scale: conventional carbonization (slow pyrolysis, SP) and hydrothermal carbonization (HTC). The digestate was obtained by a 1 MWel plant located in Italy, and derived from the anaerobic digestion of agro-industrial residues and herbaceous biomass. The sample was characterized by proximate and ultimate analysis, determining macroscopic parameters such as moisture content, ash, volatile substances and higher and lower heating value and elemental composition (CHNS), including inorganics. In order to process the feedstock in the slow pyrolysis reactor, the digestate was dried at 75 °C for 48 hours in order to reduce its high water content (76.2% w/w w.b.). Preliminary ThermoGraviMetric (TGA) allowed the determination of the devolatilization behavior and the solid residue (27.8% w/w d.b. at 900°C).

The slow pyrolysis was carried out in a batch stirred reactor, under a 10 l/min N2 flow, at an average heating rate of about 7 C°/min, and the maximum process temperature of about 500 °C was maintained for 1 hour.

Due to the high water content of the digestate, HTC is a very promising process for the direct utilization of these wet feedstocks, without any pretreatments, differently from pyrolysis that requires very dried material at inlets. HTC represents a very innovative technology, capable of directly exploiting wet feedstock by avoiding the energy-intensive step of drying. HTC experiments were performed in a micro reactor in batch mode at 10% w/w biomass to water ratio, investigating different reaction temperatures (200-250°C) and residence times (0.5-3 h). Mean heating rate ranged between 33.5 to 43.0 °C/min.

The products obtained from the slow pyrolysis and hydrothermal carbonization of digestate were characterized and compared in terms of ultimate, proximate and BET analysis. Furthermore, the HTC aqueous phase was analyzed by means of gas chromatography and HPLC techniques.

In the HTC experiments the carbon content of the char and its yield showed an opposite trend: by increasing reaction severity, in terms of temperature and residence time, the yield decreased and the carbon content increased. As far as the slow pyrolysis process is concerned, its yield was substantially lower than the HTC cases, thus indicating a higher carbonization degree, as confirmed by the analysis of the product

In addition, other specific analyses were also carried out, comparing the obtained chars with the current Italian and international product standards in order to assess their potential commercialization and limits as a potential amendment in agriculture, with benefit for the entire AD chain.

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Catalytic oxidation of trichloroethylene over mayenite: Influence of the preparation method on the catalytic activity

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Trichloroethylene (TCE) is a chlorinated solvent that belongs to the class of dense non-aqueous phase liquids, and it is an ubiquitous environmental pollutant (1). Thermal and catalytic routes were investigated as valuable techniques to TCE complete destruction (2). The activity of mayenite in the catalytic oxidation of chlorinated organic compounds was recently investigated obtaining interesting results (3). In this work mayenite was synthesized by different routes namely ceramic (Cer), Sol-gel (Sg) and hydrothermal (Hydro). The synthetized catalysts have been evaluated for the oxidation of trichloroethylene by monitoring the conversion as function of the temperature (light-off curve). Experiments were carried out at atmospheric pressure in a fixed bed reactor.

As shown in Tab.1, Mayenite prepared by the Hydrotermal method showed better performance (T_{50}= 350 °C, T_{90}= 500 °C) in absence of water than the other mayenites. The effect of water vapor on the TCE catalytic oxidation was also investigated. The results showed that the addition of water to the feed stream did not alter the activity observed except for mayenite prepared by the ceramic route. These differences in catalytic activity could be explained by the different surface area of the catalyst. Mayenite prepared by Hydrotermal route presents the highest surface area (MayeCer = 11.7 m^2g^{-1}; MayeSg= 2.0 m^2g^{-1}; MayeHydro = 35.5 m^2g^{-1}) and the highest activity. In literature its proposed that the activity of the mayenite is related to the presence of $O^{2-}$and O_2^{2-} anions sites that favour the total oxidation of TCE (4). It seems that the mayenite synthetized by the hydrothermal method has a good combination of surface area and redox properties that explain the great activity of this material in the TCE oxidation reaction.

T	Blank	Maye Cer	Maye Hydro	Maye Sg
150	0	0	0	0
200	0	0	6	0
250	0	0	11	8
300	0	4	17	10
350	0	18	48	31
400	0	30	85	54
450	0	51	87	57
500	0	75	93	70
550	10	85	100	86

Tab. 1 TCE conversion in dry conditions for Ceramic Mayenite, Hydrotermal Mayenite, Sol-gel Mayenite ([TCE]= 1000 ppm, 400 mL/min, 0.7 g of catalyst)

As conclusion, we can state in order to obtain an active catalyst for the TCE oxidation, we need a combination of oxidative properties and high surface area. Those can be obtained preparing a mayenite with the hydrothermal route due to lowest temperatures used in this method for the preparation of the catalyst. Moreover except for Ceramic mayenite, it was showed that the presence of water did not increase the activity of the materials.

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Clear evidence of the Macromolecular Structure of Humic acids

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The Humic substances (HS), a class of compounds obtained from biological decomposition of the organic matter, play an important role in the environment. They are the main fraction of the soil organic matter, and are of paramount importance in sustaining plant growth. HS are responsible for the structure and physico-chemical properties of soil and are involved in the majority of soil surface phenomena. In function of their solubility in water, they are divide in umina, humic acids (HA) and fulvic acids. HA are the fraction soluble at neutral and alkaline pH and are the main carriers affecting the mobility of pollutants in the environment. Because of their role, HS have been object of many scientific reports about their chemical structure and adsorbing property. They have aromatic structures and alkyl chains with a diversity of functional groups, notably carboxyl, phenol, hydroxyl, and quinone groups. In water HA molecules tend to aggregate giving colloids (1). Self-assembly increases with concentration, at low pH and in the presence of metal ions. Because of this and of the wide mass distribution of HA, an accurate determination of the molar mass of these compounds is a difficult task. Despite the large number of scientific reports, their molecular mass still remains unclear and is the object of an intense current debate in literature. Same researchers have suggested in recent years that HA consist of small unites that are held together by weak intermolecular forces (2): a supramolecular assembly.

This communication deals with a study on the molecular structure on three samples of HA: a) extracted from leonardite (3) a vitreous mineraloid product formed by natural oxidation of lignite and mined in many countries; b) extract from compost (3); c) a commercial sample, obtained from the decomposition of dead plants and supplied by Alfa Aesar (Germany). The molecular structure was investigated by treatment with the monocarboxylic acids, dialysis experiments and size-exclusion chromatography (SEC). SEC experiments at low pressure gave chromatograms with a broad peak, with an elution volume at the maximum height of the peak very close to that of the globular protein bovine serum albumin, molar mass = 66.5 kDa. The pattern of the chromatogram did not vary with HA concentration, and second-run chromatograms of single eluted fractions showed relatively sharp peaks. Moreover, HA molecules were retained by dialysis membrane with cut-offs of 6 - 8 kDa. From these data, it seems that the HA in the samples analysed have a canonical macromolecular structure rather than being a supramolecular aggregate of relatively small molecules, as recently proposed.

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Accelerated tests to evaluate the combined effect of aggressive saline components of atmospheric particulate matter on corrosion and metal release of weathering steel

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Weathering steel (WS) is a low-alloy steel which naturally develops a protective patina of corrosion products on the surface after its atmospheric exposure. The composition, stability and consequently the protective ability of the patina is strongly affected by exposure and climatic conditions, as well as by the presence and amount of atmospheric contaminants (1,2). Among them, particulate matter (PM) may interact with the exposed material enhancing its aesthetic decay and corrosion (3), with consequent release of alloying elements in the environment.

In a previous work (4) the effects of the main anionic constituents of PM (chlorides, nitrates and sulphates) on WS corrosion were studied by means of an accelerated ageing test, characterized by alternated immersion of samples in solutions with different concentrations of the single selected species. That work provided interesting information about the effect of single salts, which acted on metal corrosion with different mechanisms and kinetics, and laid the basis for a more detailed study aimed at evaluating a more realistic situation, where these species can interact and possibly produce synergistic effects in the corrosion process.

For this purpose, new wet&dry ageing tests were set up and performed using different mixtures of Cl^-, NO_3^- and SO_4^{2-}. The concentrations of each species in the mixtures ranged between 1.5 and 35 mg L^{-1}, to simulate the exposure to both mild and quite aggressive environments, and the composition of the solutions was selected through multivariate techniques (Design of Experiment). WS corrosion in presence of the different mixtures of Cl^-, NO_3^- and SO_4^{2-} was examined by analyzing corrosion rate and alloying metal release both in dissolved and particulate fractions. The study of the effects of the considered salts depending on their ratios in the different solutions appears very interesting if considering the modifications in the composition of atmospheric depositions due to present changes in air quality.

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Analysis and detection of emergent contaminants in seawater by passive sampling

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The aim of this study is to assess the performance of POCIS (Polar Organic Chemical Integrative Sampler) passive sampling for the analysis of diuron and some sulfonamides in seawater, with a critical evaluation of the analytical method of detection and quantification by UPLC-QTof. Monitoring by passive sampling (PS) is based on mass transfer due to the different chemical potentials of analytes between a given environmental compartment and the collection medium inside a dosimeter. POCIS samplers are used to sample polar hydrophilic compounds with octanol/water partition coefficients logKow<3. Two configurations are used for sampling different classes of contaminants, spanning a wide range of polarity ($0.05 \leq \log K_{ow} \leq 2.68$): pharmaceutical-POCIS (pharm-POCIS) and pesticide-POCIS (pest-POCIS). The sorbent in POCIS samplers is usually based on polystyrene divinylbenzene combined with active carbon in the case of pest-POCIS, or Oasis™ HLB sorbent in pharm-POCIS.

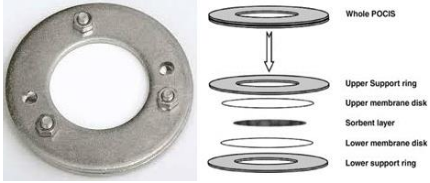

Fig.1 POCIS sampler

Pest-POCIS and pharm-POCIS laboratory calibrations have been conducted to calculate the sampling rates (Rs) of 7 polar contaminants (5 sulfonamides, diuron and trimethoprim), commonly found in seawater. Calibrations have been conducted in parallel in a double synthetic marine water system with two blank tests. Samples of water were taken at regular intervals and extracted by SPE (Oasis-HLB), until complete exhaustion. At the end, the POCIS samplers were analyzed and results were comparable to the expected values. Environmental application took place in the Gulf of La Spezia.

A selective and sensitive method has been developed for the determination of the Rs's for diuron and some sulfonamides. The results of the study allowed to obtain a fast, efficient and sensitive method of determination, able to comply with the Environmental Quality Standards (EQS) established for this analytes in the Water Framework Directive. Passive sampling is very appealing for the determination of time-weighted average concentrations and the response time of the sampler can be chosen according to the desired length of the sampling period. The main advantage of passive sample collection/enrichment technology lies in the considerable simplification of sample collection *in situ*, and it seems to be a valuable complement to generally applicable dynamic methods. Extensive laboratory calibration of POCIS samplers were performed and kinetic uptake studies were carried out without analytically complex procedures, ensuring the general applicability of the approach. Samplings from La Spezia showed that POCIS samplers compared very well with the traditional discrete sampling.

Removal of emerging organic pollutants in wastewater treatment plant effluents by an electrochemical process employing boron-doped diamond electrode

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Various studies over recent years have proved the increasing occurrence in effluent of wastewater treatment plants (WWTP)of several contaminants of emerging concern (CECs), which are not completely removed by the common technologies employed in conventional WWTP. CECs found at highest levels (ng L^{-1} to µg L^{-1}) are pharmaceuticals, artificial sweeteners, pesticides, flame-retardants, plasticizers and perfluoroalkyl substances (1,2).

The main objective of this study was to investigate an electrochemical treatment based on a boron-doped diamond (BDD) electrode, as an advanced oxidation process (AOP) for the removal of several CECs from effluent of WWTP with enhanced performance in terms of efficiency and applicability (3).

Electrochemical treatments were performed with a CONDIAPURE® system using a DIACHEM® electrode stack in a flow through cell (CONDIAS GmbH, Germany), in both synthetic water and real secondary effluent. The electrode stack was composed by two BDD cathodes and one BDD anode and in situ oxidation was performed with four anode/cathode pairs applying a total current of 0.4 A. A total of 10 L of solution with the target organic pollutants was circulated through the reactor at a flow rate of 18.5 L/min.

The removal of a mixture of CECs (iopromide, carbamazepine, diclofenac, erythromycin, benzotriazol, sulfamethoxazole, caffeine, gabapentin, metoprolol, phenythoin, primidone, venlafaxine, TCEP) by the investigated electrochemical system was primarily assessed in synthetic model water spiked with the target contaminants at concentration in the range of 2-5 µg L^{-1}. Removal below limit of quantification (LOQ) was achieved for all tested compounds after 200 min of treatment. Decay follows pseudo first order kinetics and kinetic constants (k) of 0.07 min^{-1} for sulfamethoxazole and diclofenac and in the range 0.03-0.01 min^{-1} for the other CECs were obtained, being TCEP the pollutant with slowest kinetics.

Afterwards, the secondary effluent of the municipal WWTP Garching (Germany) was employed as a real water matrix which revealed the occurrence of several CECs (including the mixture of selected compounds listed above) at concentration levels between 20 ng L^{-1} and 20 µg L^{-1}. The electrochemical treatment of the effluent was performed under the same conditions employed with the spiked synthetic water. Results demonstrated removal below LOQ for all the target CECs after 300 min with lower degradation rates than in the spiked synthetic water solution ($k \leq 0.01\ min^{-1}$).

The detection of transformation products of investigated CECs was performed by UPLC-QTOF/MS/MS, by employing a non-target analysis approach which was based on accurate MS and MS/MS data and open source databases and software.

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Chemical characterization of freshly emitted steel plant fumes by chemical and spectroscopical methods

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Atmospheric aerosols, emitted by both anthropogenic and natural sources, affect the climate system and the human health in many ways (1). Aerosol chemical composition can be very complex because of the multi-compounds emission at the source and the mixing and ageing processes that can happen during its permanence in the atmosphere. Industrial processes can emit many different compounds, and some of them are particularly relevant in terms of harmful potential for human health, such as heavy metals and PAHs, and climate impact, like iron and light absorbing carbon containing compounds (black carbon). Iron speciation, in particular, is a rising topic in aerosol research because it helps to determine the harmful potential of Fe-bearing particles and also their impact on oceanic and Amazonian rainforest productivity (2). In this frame, a characterization of the aerosol at the source is useful to understand which types of compounds are emitted, to trace them through their transport in the atmosphere and to assess the single source contribution to the total aerosol composition.

In this work, we characterized steel production emissions from the Thyssen Krupp (TK-AST) plant in Terni, Central Italy. This plant is located inside the urban area and its emissions are clearly detectable in the urban aerosol composition (3). We investigated the composition of aerosol emitted by two smelters and two converters. The samples were taken inside the chimney stacks of the plant in order to avoid mixing with other types of aerosol and atmospheric processing.

Both chemical composition and mineralogy were investigated by means of several analytical techniques such as Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Ion Cromatography (IC), Gas Cromatography (GC) and X-ray diffraction (XRD). Moreover, a detailed study on iron speciation was performed by means of selective leaching experiments and X-ray absorption spectroscopy (XAS). Chemical analysis shows very high emissions of Fe, Ca and fluorides and evidence some differences between the different plant sections also in alkanes profile and PAH distribution. XRD analysis show three main phases, two slightly different magnetite phases and one calcite. The predominance of spinel oxide iron structure is remarkable also in the XAS results, but a different Fe^{2+}/Fe^{3+} ratio has been observed compared to the pure magnetite structure. Leaching experiments show a high predominance of the residual insoluble fraction, attributable to spinel oxides, among the others accordingly with mineralogical results, while the contribution of the other fractions is highly variable amongst the different plant portions.

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Exploitation of agro-residues in designing of silicate materials

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Up to now, the agro-industrial sector is an important resource for the global economy, with very different production realities (milk and derivatives industry, slaughtering of animals and production of cold cuts, manufacturing and processing of fruits and cereal, etc.). Each type of agro-residue often contains a lot of high value-added substances that constitute a new raw material for possible applications of commercial interest. In this work, we report some case studies related to the possibility of exploiting some agro-wastes and by-products (rice husk ash, sawdust, grape seeds, cherries seeds, sugar cane ash, sludge from beer wastewater treatment plant, animal bone flour or flour ash, corn cob and olive pomace) in silicate materials (sintered and vitrified) useful for both building and agronomic sector. Ceramic bricks were obtained by introducing rice husk ash, RHA, (mainly constituted by amorphous silica and together with low amount of tridymite and cristobalite phases), (up to 20 wt%) as silica source or sawdust, grape and cherries seeds (up to 10 wt%) as pouring agents in clays mixtures. The introduction of RHA into brick bodies influences the sintering behavior, it did not affect the linear shrinkage%, while water absorption% values showed an increase as RHA content increases. From the mechanical point of view, samples with up to 5 wt% resulted satisfactory (12 MPa) comparing to the industrial limit (10 MPa). Sawdust, grapes and cherries seeds, due to their organic substances content, during their combustion, bring an energetic support in the bricks firing phase and act as pore forming agent. Grapes and cherries seeds also maintain the mechanical properties of the fired brick, showing modulus of rupture around 21–23 MPa with a weight reduction of 3–10% with respect to the standard one.

Spherical pellets of lightweight aggregates were prepared by mixing different percentages (up to 15 wt%) of sludge from beer wastewater treatment plant, animal bone flour, corn cob and olive pomace in two different clay-based mixtures and thermal treated at 900 and 1000°C for 1 hour. Technological parameters such as bulk and absolute density, total porosity, water absorption, pH and electrical specific conductivity were determined in order to test their potential use in agriculture. Animal bone flour ash was also used to formulate glass and glass-ceramic fertilizers, with a low and controlled solubility in water of macro nutrient elements useful for plants as P and K. From the preliminary results, it is possible to hypothesize poring effect in the realization of lightweight aggregates for different application fields such as lightweight substrate/soil for agricultural use, as pH corrector for acid soils, because they showed pH between 8-9. On the other hand, further tests were conducted by adding to these mixes (clay-poring agent) 10 wt% of animal bone flour ash or a fertilizer glass-ceramic (P_2O_5+K_2O > 12wt%) or calcined olive pomace. In order to verify the nutrients release of the functionalized lightweight aggregates, tests following European and Italian rules using citric acid solution (2%vol) and distilled water were performed. The results highlighted that mix containing the bone ash releases more amount of nutrient in a short time (30 min) on the contrary the compositions containing the fertilizer glass showed a high release at longer time (21 days). This aspect is important from the environmental point of view because the slow release can avoid the leaching by rain of nutrient elements and their concentration in groundwaters.

B-IMPACT: a new project for the development of eco-friendly and non-hazardous outdoor bronze protective coatings

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The B-IMPACT (Bronze-IMproved non-hazardous PAtina CoaTings) project, funded within the European M-ERA.Net consortium, aims at developing innovative eco-friendly and non-hazardous protective coatings for the protection of bronze surfaces exposed to the outdoor environment (http://www.b-impact.eu, info@b-impact.eu). This project, started in March 2015 and ended in April 2017, was coordinated by the Slovenian National Building and Civil Engineering Institute and involves academic partners (University of Toulouse (F); University of Bologna and University of Ferrara (I), together with industrial partners for bronze production (Livartis d.o.o. and Geida d.o.o. (SLO)) coating formulation (Pylote SAS and C2M Aurochs Industrie (F)) and toxicity assessment (Ecamricert SRL (I)).

Two different bronze alloys, supplied by the artistic foundry Livartis, have been considered as substrates: a modern silicon bronze (Cu-3Si-1Mn) used in contemporary art, artificially black patinated with K_2S ("liver of sulphur"), and a historical quaternary bronze (Cu-6.5Sn-4Zn-2Pb), patinated by artificial ageing in conditions which closely simulate outdoor exposure (runoff and stagnant rain conditions). The performance of protective coatings has been assessed by electrochemical tests in artificial acid rain and, in the case of the most promising ones, by severe accelerated ageing involving environmental parameters (rain runoff, UV radiation ...). Both the exposed surfaces (coated vs. uncoated) and the ageing solutions have been characterized, in order to quantify the protective efficiency of the coatings and their ability to limit metal release during exposure. Specific toxicity tests addressed the compliance of coatings with European health and safety regulations. After validation at the bench scale, the feasibility of the best coatings at the upscale level was assessed by industrial partners. The main results concerning the behaviour of the best performing coatings obtained by the B-IMPACT project will be presented.

Synthetic pigments, binder and light:
a multitechnique study on degradation of contemporary art materials

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The characterization of ageing of contemporary synthetic binders constitutes an open field in cultural heritage research: the recent and industrial origin of these materials, the unknown interactions with pigments and additives and the less controlled exposition conditions of contemporary art represent important factors to investigate.

In this perspective, this study, part of a PhD project, is aimed to characterize the UVB degradation of an emulsion acrylic binder through spectroscopic –reflectance, FTIR, 1D and 2D-NMR- and spectrometric –ESI-MS- techniques: this approach provides optical and chemical information on the total variation of polymeric species. The focus is directed to the influence of synthetic organic pigments on the ageing process: as assessed for the traditional inorganic pigments (1), organic pigments can play a role on the surface and bulk degradation of polymeric binders (2) and this can be very important for the differential ageing of pictorial films.

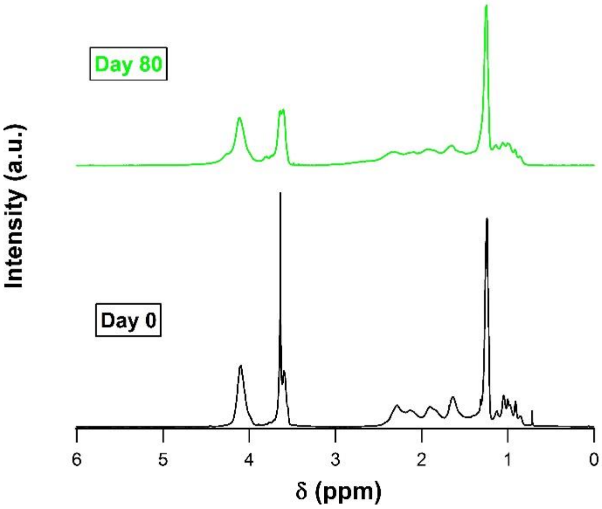

Figure 2: comparison of ^{1}H-NMR binder spectra before and after the ageing process.

The information of this study is related to the ageing of street art samples, whose characterization is gaining a major attention during the last years (3). In fact, street artworks are subjected to aggressive environmental conditions, and the knowledge about their conservation characteristics can result fundamental, even in the perspective of restoration debate about validity of street art conservative operations.

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The assessment of the carbonaceous component in black crusts damaging the stone surfaces of historical monuments

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The issue of conservation of the monumental heritage is mainly related to atmospheric pollution that causes the degradation of stone surfaces. Black crusts can be formed as a result of different chemical and physical reactions between the stone surface and environmental factors (such as gaseous pollutants and aerosol particulate matter, PM). These black layers present on the stone monuments reflect the composition of the aerosol particulate matter to which the surfaces are exposed. In particular elemental carbon (EC, also known as black carbon, typically emitted by combustion processes) is the PM component responsible for the characteristic black color of the crusts where it is embedded together with calcium sulphate due to the conversion of calcium carbonate, the main constituent of the stone. Organic carbon (OC) represents the other carbonaceous component of PM and it is present in the black crusts, too. It is of both primary or secondary origin and is linked to numerous sources (traffic, heating plants, biomass burning, etc.).

A deep knowledge of the crust composition in terms of OC and EC optical properties is mandatory in order to get information on the sources responsible for the surface darkening.

OC/EC in PM samples are generally quantified by a reference method (TOT, Thermal Optical Transmittance) not suitable for the analysis of these components in the crusts.

A new approach for OC/EC quantification (1,2) based on a thermal protocol and including CHN and TGA analyses, has been here proposed. The method validation has been performed analyzing suitable reference standard samples prepared by mixing different chemical species in order to simulate the composition of the black crusts present on the monument surfaces.

In addition, the characterization of OC optical properties with UV-visible spectrometry has been performed, to understand the role of light absorbing carbon (i.e. brown carbon) on surface stone darkening. The chemical composition of OC was further investigated with Fourier Transform infrared spectrometry (FT-IR) to identify the contribution of the different organic functional groups to the ageing/browning of stone surfaces.

This research aims to get a new simple method for the evaluation of the carbonaceous component of the black crusts which are formed on carbonate stone surfaces. The protocol has been applied to some real samples of black crusts of different provenance.

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A comprehensive study of the effects induced by brown rot fungi on archaeological waterlogged wood

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The archaeological site of Biskupin (Poland) is a prehistoric settlement dating to the 8th century BC, situated on a marshy island. Excavations started in 1934 and a considerable amount of wooden artifacts was found sunken in the water of the lake. Unfortunately, during many years of archaeological excavations, wooden remains deposited in the trenches were exposed to degradation process and underwent decomposition. Among the main causes of wood degradation, fungi and bacteria were the most destructive ones.

The chemical effects induced by fungi and bacteria on wood are not well known or studied. For this reason, we present here a study of a set of wood samples (Pinus sylvestris) buried in the Biskupin site, reproducing the burial conditions of the original archaeological wood. The samples were then removed from the burial environment after 4, 6, 8 and 10 years of deposition in two monitoring stations (wet peat and lake water). After removal from the burial, the samples were exposed to laboratory controlled attack by a brown rot fungus Coniophora puteana. The final aim was to evaluate the effects of fungal activity on the wood substrates with different degrees of natural degradation. The study is part of an experimentation designed to evaluate the short-time effects of the in situ conservation strategy adopted for the Biskupin archaeological woods.

Various techniques were used to assess the physical and chemical degradation of the wood. Physical properties, such as moisture content and conventional density were determined on the basis of the mass of absolutely-dry wood and the volume of the sample in the state of maximal saturation. An attempt to distinguish between the morphological changes induced by the fungal attack and by the exposure to the burial environment itself was carried out through scanning electron microscopy (SEM) examination of the transverse, radial longitudinal and tangential longitudinal sections of the samples The chemical state of preservation was evaluated by using infrared spectroscopy (FTIR) and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) with in situ silylation. All the results were compared with those obtained for reference materials, including sound pine wood and contemporary and archaeological pine wood attacked by Coniophora puteana.

Carbon Isotope Ratio in Carbonates and Bicarbonates determined by ^{13}C NMR Spectroscopy

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This study focused on the innovative use of ^{13}C NMR spectroscopy for the bulk carbon isotope ratio determination, at the natural abundance, of inorganic carbonates and bicarbonates. Isotope Ratio Mass Spectrometry (IRMS) represents the method of choice for analyses at the natural abundance due to the relative high accuracy (0.1‰) and sensitivity (up to 0.01‰).

However several analytical methods, alternative to IRMS, have been designed and applied for the δ^{13}C analysis, such as mid-infrared laser spectroscopy, non-dispersive infrared spectrometry (NDIRS) and Fourier Transform infrared spectrometry (FT-IR), which offer the advantage of being less expensive and complex.(1)(2)

In the past, NMR spectroscopy has been mainly used to measure the ^{13}C position-specific isotope ratio monitoring (irm-^{13}C NMR) of organic molecules with high precision. The first part of the present study was dedicated to the optimization of spectral parameters for the ^{13}C NMR analysis, necessary to enhance the precision and accuracy on δ^{13}C determinations. Indeed, it was analyzed the influence of relaxation time (T_1), the presence of relaxation agent, the pulse intervals (D_1) and the use of an internal standard on the determination of the δ^{13}C of several carbonates and bicarbonates, comparing the results with those previously determined by means of IRMS.

The determination of ^{13}C/^{12}C ratio of carbonates and bicarbonates (≈50-100 mg) was performed with a precision of the order of 1 ‰ in the presence of a relaxation agent such as $Cr(acac)_3$ and $CH_3{}^{13}COONa$ as internal standard. The sample was prepared by dissolving $CH_3{}^{13}CO_2Na$, sample and $Cr(acac)_3$ in D_2O. Isotope carbon composition of bulk sample was evaluated using linear calibration that is obtained out using two carbonates (Cs_2CO_3 and K_2CO_3) and two bicarbonates ($NaHCO_3$ and NH_5CO_3) with a correlation coefficient r^2=0.9987. The method was applied to water soluble inorganic carbonates and bicarbonates and then extended to insoluble carbonates by converting them to Na_2CO_3 following a simple procedure, without observing isotopic fractionation. By this way the ^{13}C NMR spectroscopy can be also successfully applied for the characterization of the ^{13}C/^{12}C ratio in several different fields such as cultural heritage and geological studies.

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Characterization and study of the behaviour of acrylic paint films subjected to artificial ageing: the case of *Edelwachs* acrylic emulsion

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The aim of the present work is to study and evaluate the stability of Pigrol *Edelwachs*® (*Tikkurila GmbH*, Germany). This product, sold as an aqueous emulsion of acrylic copolymers and wax, is generally used as wood protective, but the iconographer Fabio Nones (Trento-1961) has been experimenting its use as an innovative medium for painting. Widely used by Nones and his students, *Edelwachs* has never been studied neither from a compositional point of view nor regarding its stability over time. Its composition was studied by chromatographic (Py-GC / MS) and spectroscopic (FTIR-ATR) techniques that have been commonly applied to characterize acrylic and waxy products (1-3). Based on the results obtained, a combination of methacrylate (MA), methylmethacrylate (MMA), nbutylacrylate (nBA), nbutylmethacrylate (nBMA) monomers was detected, while the waxy component appears to have a microcrystalline nature. Mock-up paints, according to Nones' technique, were prepared by dispersing in *Edelwachs* five inorganic pigments previously characterized using the FTIR-ATR and XRF techniques. The stability to sedimentation of the pure product and of the obtained paints was evaluated by analytical centrifugation tests: the results highlighted that *Edelwachs* is a stable emulsion. To study the stability of *Edelwachs'* films, the mock-ups were subjected to accelerated ageing by photo-catalytic treatments (UV-A and UV-B mix), treatments at low (5-6 °C) and high temperatures (50-100 °C) and exposure to high relative humidity values (HR 85%). As reported in literature (4-6), it is known that these ageing conditions could be potentially critical for acrylates. The effects of the artificial ageing were monitored over time by optical microscopy techniques, colorimetric and VIS-reflectance spectrometry, FTIR-ATR analysis, contact angle measurements and weight variations. The paints show a good stability for all treatments considered, especially those containing titanium white. Thanks to TG-DSC analysis, the main exothermic/endothermic processes and the glass transition temperature (Tg) of the different paints were evaluated before and after ageing: it was observed that the ageing conditions applied may have different effects on the paints depending on the nature of the pigment and the pigment/binding ratio. Moreover, a multi-analytical characterisation of real samples taken from Nones' artworks was carried out. The works, painted out between 2001 and 2016, allowed us to evaluate the characteristics of the naturally aged paints. The morphology of the real samples was observed through optical and electronic microscopy. The composition was studied using FTIR-ATR and SEM-EDS techniques.

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Multianalytical study for the restoration of a gypsum sculpture of Galleria d'Arte Moderna (GAM) of Milan

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Diagnostic and monitoring are crucial steps in the field of cultural heritage preservation. In particular, diagnostic is usually aimed at characterizing materials and at assessing the state of conservation and degradation processes that affect the artworks.

Given the complexity and heterogeneity of the constituent materials, as well as the possible presence of restoration materials from previous interventions, a multi-analytical approach is generally followed, as it can provide more complete results. In addition, the close collaboration between restorers and conservation scientists is always highly desirable in order to tackle efficiently the conservation issues.

In the occasion of the exhibition "*100 Anni. Scultura a Milano 1815-1915*" at the Galleria d'Arte Moderna (GAM) of Milan, an extensive diagnostic campaign has been conducted on selected artworks prior to their display.

A multi-analytical and micro-invasive approach has been adopted. Preliminary observations, documentation and characterisation of the surfaces has been performed on site by non-invasive techniques. Diagnostic on micro-samples was then performed to precisely characterize the materials, the stratigraphic structure, and to investigate specific deterioration patterns.

Morphological and colorimetric analysis were carried out by means of digital optical microscopy and of spectrophotometric analysis in visible light (colorimetry), both performed *in situ* in a totally non-invasive way. Laboratory analysis on micro-samples were carried out by means of Fourier Transform infrared spectroscopy (FTIR), Raman spectroscopy and scanning electron microscopy coupled with EDX (SEM-EDX) on fragments and polished cross-sections.

The present work is focused, in particular, on the study of the gypsum statue "La Maddalena" by Pompeo Marchesi, which presented a peculiar deterioration pattern. The results of the diagnostic activity clarified the nature and extent of the degradation. Moreover, through the analysis of the stratigraphy, the residual presence of altered finishings due to past restoration interventions was identified. By following an integrated and collaborative approach, the information gathered during the diagnostic activity supported the selection and setup of the conservation methodologies of the restorers for the treatment of the artwork.

Fully biodegradable novel bio-based organogels for the cleaning of artworks

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The cleaning of paintings, which is generally devoted to the removal of aged varnishes, still represents one of the most delicate and potentially hazardous interventions for the safety of operators and the treated surface. Indeed, the most common approach is based on the use of volatile organic solvents applied by cotton swabs. However, this cleaning method has several drawbacks such as the fact that wet procedures do not preserve the health of the restorers and generate wastes. In addition, the solvent may diffuse into the porosity of the underneath layers causing phenomena like swelling and leaching that leave the paint surface brittle with loss of mechanical strength.

In the last years, even if an increased attention has been devoted to the proposal of more healthy products to guarantee the safeguard of the operators, few attentions has been devoted to the development of green methods, which foresee the use of renewable and biodegradable materials.

On these bases, the present research work was aimed at developing fully green novel bio-based organogels for the cleaning of artworks. In particular, different gel formulations were proposed for the cleaning of paintings and of metal surfaces.

The gels were based on poly-3-hydroxybutyrate (PHB) as gelling agent and the formulation were varied with the use of different green solvents.

γ-valerolactone (GVL), ethyl lattate (EL) and dimethyl carbonate (DMC) were selected as active agents in the removal of varnishes from oil paintings and water sensitive paint layers, such as tempera. In particular, the tested gels are completely water free so that they can remove surface varnishes applied on hydrophilic paint layers without affecting them.

Recently, new green gels were also formulated to remove protective organic coatings applied during past restoration on bronze objects. In these cases, the use of less polar solvents (methyl levulinate (ML) allowed the cleaning of aged complex mixtures containing oils and natural and synthetic waxes.

An ad hoc analytical protocol was set up for the evaluation of the performances of the new methods in comparison with the traditional ones.

The gels were tested on painting mock-ups and then validated on real artworks. Encouraging results were obtained on exceptional case studies, such as on the Cimabue masterpiece *The Majesty of Santa Maria dei Servi"* (XIII) located at the Chiesa Santa Maria dei Servi in Bologna (Italy) and on the bronze pulpit (XV) attributed to Donatello and located at San Lorenzo church in Florence (Italy).

Particulate matter and material decay: analysis of dry deposition on horizontal and vertical surfaces exposed through the "Deposition Box" system

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Airborne Particulate Matter (PM), after its removal from the atmosphere through wet and dry mechanisms, can physically/chemically interact with materials and induce premature decay.

In this contest, the effect of dry depositions is a really complex issue, especially for outdoor materials, because of the difficulties related to the collection of atmospheric deposits repeatable in terms of mass and homogeneously distributed on the entire investigated substrate.

To overcome these problems, a new sampling system, the "Deposition Box", was designed, built and validated. The sampler consists of a 50x50x20 cm box, covered by a pitched roof which eliminates the variability induced by removal mechanisms (i.e. winds and rainfalls) in classical outdoor expositions; on the bottom of the box, a fan standardizes the air exchange rate (30 h^{-1}) across the box, ensuring a continuous sampling of ambient air and quite calm conditions inside the box and allowing the deposition to occur.

In the present work, four surrogate materials (Aluminium, Regenerated Cellulose, Cellulose Nitrate and Acetate) with different porosities and surface features were exposed in the urban-marine site of Rimini (Italy). Two mechanisms of PM deposition were differentiated and investigated by analyzing samples exposed both in horizontal (diffusion + gravitational mechanism) and in vertical (diffusion mechanism) positions. Colourimetric measurements were performed on surrogate materials before and after the exposure to quantify the surface soiling due to PM deposition. Beside the mass, the water-soluble fraction of PM has been also characterized by Ion Chromatography (IC) and Atomic Absorption Spectroscopy (AAS). Morphological and dimensional characterization were also performed on particles collected on rounded sheets of adhesive tape mounted on SEM stubs (sampling area: 1.13 cm^2) and exposed both in horizontal and vertical positions.

The promising outcomes suggest that "Deposition Box" can represent an affordable tool to study different PM deposition fluxes and mechanisms on materials and a useful collecting device for the preparation of surfaces for further analyses, aimed at deepening the topic of building and heritage materials decay.

Fig.1: The inner and the external features of Deposition Box during the exposures of surrogate surfaces.

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A new MA-XRF system and an advanced methodological approach for the elemental characterization of panted surfaces: the exceptional case study of the Cimabue's masterpiece

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Chemical maps related to the distribution of elements within a painted surface may provide important information both on the characterization of painting materials and on the definition of proper conservation actions. Indeed, in the recent years, an increasing interest has been devoted to the development of compact macro-XRF systems, establishing the technique as one of the most powerful non-invasive method for the characterization of artworks. In addition, MA-XRF scanners allow the investigation of large painted surface and a reliable documentation with a reduced acquisition time and costs.

However, the big dimension of the data matrix obtained may hamper the correct evaluation of the results. Thus, specific methodological strategies should be defined and followed to collect and extract all the useful information embedded into hyperspectral cubes.

To this aim, the present research work was focused on the evaluation of an advanced, last-generation MA-XRF system: the CRONO scanner developed by XGLab SRL. The instrument is composed of a main XRF unit and of a motorized stage system to implement the scanning. The excitation source is a Rh tube with adjustable maximum voltage (up to 50kV). The X-ray excitation light is collimated to 0.5, 1 or 2 mm, software selectable and a 50 mm^2 Silicon Drift Detector. The speed modulation permits to scan the investigated surfaces varying acquisition time, spatial resolution and spectral quality (S/N ratio), according to type of information required.

The experimental workflow proposed has been applied on an exceptional case of study: the “Madonna Enthroned with the Child and Two Angels” by Cimabue (1240 – 1302), disclosing new reliable knowledges on the masterpiece. The XRF acquisitions allowed a detailed visualization of elements ascribable to pigments used by the artist and a precise localization of several retouched areas. Moreover, a particular attention was addressed to the characterization of the throne decorations. Indeed, elements, such as Cu, Pb, As, Au and Ag were identified, suggesting the use of different execution techniques and pointed out new questions on the originality of some decorative paint effects.

The challenge of orchil dyes: advanced analytical techniques to discriminate the different lichen species

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Orchil can be considered one of the most intriguing dyes, known during the history of art.

Puh or *phukh* was the name, given by Akkadians and Hebrews, to a purple dye obtained by a "plant", probably the lichen (1). Cited also in *Naturalis Historia* by Pliny for its wonderful violet color, it was also described as "more beautiful than purple from shellfish" by Theophrastus (1). This detail is particularly important, because the prosperity of orchil is almost referable to its property of miming shellfish purple (1). Some sources refer that orchil production was lost in the Mediterranean Sea at the end of Roman Empire and was rediscovered only at the end of Middle Age, thanks to a Florentine merchant, Federigo Rucellai, who, by chance, observed the preparation of violet purple color from the lichen, in the Levant (1). Described in different historical texts during the centuries, its use is well attested until the synthesis of first synthetic dye: the mauveine, which can be considered its synthetic alter ego. The commercialization of this dye has led to disuse of orcein dye.

However, even if the great numbers of citations in the historical texts should bring to many evidences in historical textiles, few research papers are able to demonstrate the presence of orchil dye. The main cause of difficulty in finding orchil dyes is its very high photo-instability (2). This induced a rapid degradation and only few residual molecules of orchil can be observed in textiles manufactures.

In the last years, scientific investigations have been conducted, focusing on optimization of non-invasive (such as UV-Vis fluorimetry) and micro-invasive (such as SERS on fiber) techniques and of proper analytical conditions in HPLC-MS to confirm the presence of phenoxazone compounds (2-5).

Furthermore, under the name of orchil several species of lichens, not only *Roccella tinctoria* DC. (one of the most famous) can be counted: at least 60-70 species of lichen are able to produce phenoxazone compounds after a treatment in ammonia.

Taking into account these evidences, the present work is focused on a multi-analytical approach, as a powerful tool to develop a secure protocol for the detection of orchil dye. Furthermore, it would investigate the possibility of discriminating among the different species of lichens, such as *Roccella tinctoria* DC., *Lasallia pustulata* L., *Ochrolechia tartarea* L.

Starting from SERS on fiber analyses, on the yarns dyed with the different lichen species, the research has been conducted applying a new extraction protocol from dyed yarns (6) and the residue obtained has been used for a separation through HPTLC. Then, HPTLC-SERS spectra have been acquired for each spot on TLC plates and this information has been got together with those obtained from HPTLC-MS experiments. This would led to the identification of main phenoxazone compounds, in charge of the colour, but also secondary compounds which, probably, could be identify as markers, useful to distinguish among the several lichen species.

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Life Cycle Analysis of a pyrolysis process applied to end-of-life tires

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The "Sustainability Report 2015" of Ecopneus states that the total collection of end of life tires (ELT) in 2015 amounted to 247966 tons and of these 246128 tons were managed through mechanical and thermal treatments because ELT represents both an important resource of materials (especially rubber, 40% in weight, and steel) and of energy. For this purpose, the goal of the work has been the assessment of the environmental impacts of a novel pyrolysis process of ELT, designed by the company Curti s.p.a. and the comparison with alternative valorization and/or disposal scenarios. It is important to outline that Curti plant is different from the other already on the market because it only needs a simple pre-treatment step (1) for ELT.

Life Cycle Analysis methodology (LCA) has been so applied to determine the most critical stages of the process under study, assessing the environmental benefits arising from the recovery of materials and energy and the greater or lower impact compared to the mechanical or thermal technologies already on the market, choosing the boundaries of the system "from gate to gate", taking into account treatment processes, materials recovery and disposal of waste water\residues, and as functional unit (FU) 1 ton of ELT treated by the Curti plant.

First, a comparison between different pretreatment scenarios performed in other recovery processes, has been performed, taking into account: single cut, grinding, crushing and pulverization. After, the whole environmental impact of the pyrolysis plant managed by the company Curti s.p.a. has been analysed. Then, pyrolysis process has been compared to other scenarios of recovery of energy: the management of 1 ton (FU) of ELT has been compared also for cement plant and waste to energy process (2). Lastly, the comparison of different scenarios of material recovery with the pyrolysis process has been realized. The different scenarios realized have been analyzed through three different method of analysis: first using the ReCiPe analysis method, considering five impact categories at midpoint level: climate change, human toxicity, particulate matter formation, fossil fuels depletion and metal depletion; three categories of damage were also considered: human health, ecosystem quality and resources depletion. Then, the environmental assessment step has been completed using also the Cumulative Energy Demand (CED) and the Global Warming Potential (GWP) methods, to investigate potential impacts in terms of energy demand and of CO_2 equivalent emission. Considering only the pre-treatments, the pyrolysis process has an environmental impacts equal to 1/3, 1/10 and 1/20 compared with grinding, crushing and pulverization, especially in terms of climate change and fossil depletion. The analysis of Curti pyrolysis process showed that the avoided impact due to the recovery of carbon black, steel and oil fuel exceeds widely the impact generated by the process. Compared to other energy-recovery scenarios, a greater advantage results for the pyrolysis process. Then, comparing it to other materials recovery scenarios, a huge influence is given by the different options of recovery considering which materials actually they replace, considering a full recovery of metals and rubber (to replace the synthetic rubber) or intermediate options: this second scenario would bring to a greater gain from the environmental point of view for the Curti pyrolysis technology.

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LCA methodology: a case study of the industrial production of terephthalic acid from renewable sources

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The scope of the present study is to investigate the environmental sustainability of different routes of terephthalic acid (TA) production from renewable sources in order to identify which of the selected pathways has the lowest environmental load. The comparison was performed between five different production processes: GEVO® (1), BioForming® (2), TA from DMF and acrolein (3), TA from HMF and ethylene (4), and an alternative pathway from p-cymene (5). The first two are already set at industrial level, while the others are still under development. All scenarios needed to build the synthesis routes were therefore modeled in order to obtain, starting from biomass, the production of terephthalic acid. Among those investigated, four ways provide for the formation of p-xylene, subsequently oxidized to terephthalic acid through the Amoco® process, while the last is proposed as an alternative because it uses p-cymene as a precursor to obtain the molecule of interest. In order to do it the methodology LCA (Life Cycle Assessment) has been used as a scientific tool of analysis and evaluation of the potential impacts of each scenario. LCA is a method of analysis which allows the evaluation of the environmental weights associated with the entire life cycle of a product or a process, through the identification and quantification of energy and material flows in input and in output from the system under consideration. LCA studies may consider all aspects related to the life cycle of the system using an approach "from cradle to grave" or limited (as in this case) to its production phase ("from cradle to gate"), imagining a uniformity of the destiny (use and disposal) for the downstream stages. The potential impacts are evaluated by comparison with CED method (Cumulative Energy Demand), that analyze the needs of direct and indirect resources expressing the result in energetic terms, and ReCiPe method, which divide the environmental loads in intermediate categories of impact (midpoint level), that can be grouped into categories of damage to the receptor (endpoint level). The results of the analysis show that for all scenarios the principally responsible categories for the impacts are those that are directly related to the production and cultivation of the starting biomasses. The main category associated with the major contribution is the *Agricultural land occupation*. This tendency is connected to the bio-based nature of the processes, therefore we also included in the assessment the following categories: *Natural land transformation*, *Freshwater eutrophication*, *Terrestrial acidification* and *ecotoxicity*, but these show more marginal responsibilities. Among the investigated scenarios the process from DMF and acrolein is the one that presents the worst results in environmental terms for all the comparisons made, while the alternative pathway from p-cymene turns out to be the most promising. The reason of this result is due to the fact that we consider a waste biomass for the production of p-cymene (orange peels), instead a dedicated culture as for the other scenarios.

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Application of an electro-activated glassy carbon electrode (GCE) to the analytical monitoring and photochemical studying of acetaminophen

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The occurrence of emerging contaminants in surface waters, such as pharmaceuticals and personal-care products, is an environmental issue of high concern due to the toxic effects on ecosystems and humans (1). *Waste Water Treatment Plants* (WWTPs) are usually not able to remove these compounds from wastewater because they are water soluble and biorefractory. Therefore, emerging contaminants are often released in water bodies. As far as pharmaceuticals are concerned, antibiotics, analgesics and anticonvulsionants are usually detected in surface waters (2). In these environments, xenobiotics can undergo both abiotic and biotic degradation. Among abiotic pathways, direct and indirect photochemical reactions can be key degradation processes. Direct photolysis occurs when the xenobiotic absorbs the solar light and undergoes subsequent chemical transformations. In contrast, indirect photolysis is triggered by *Photochemically Produced Reactive Intermediates* (PPRIs) that react with xenobiotics. The main PPRIs are $HO^{\bullet}$, $CO_3^{\bullet -}$, excited triplet states of Chromophoric Dissolved Organic Matter ($^3CDOM^*$) and $^1O_2$. They are formed upon absorption of solar light by photosensitizing compounds, such as CDOM, nitrate and nitrite (3). Usually, photochemical reactions act as self-depuration processes in water bodies, but they can also induce formation of harmful photodegradation products. Luckily, the photochemical fate of xenobiotics (half-life times and photoproduction of intermediates) can be modeled, and thus foreseen, by knowing or measuring the relevant photoreactivity parameters (e.g., reactions rate constants and photoproducts formation yields) and by using suitable photochemical models (4). Therefore, the monitoring of xenobiotics concentration in both WWTPs influents/effluents and surface waters, and the understanding of the photochemical fate of these compounds, are important tools to assess the human impact on aquatic environments.

Acetaminophen (also known as paracetamol, hereafter APAP) is a widely used analgesic drug usually detected in surface waters (2) at concentrations up to 10 $\mu g\ L^{-1}$ (5). In this work, we have focused on the use of *Differential Pulse Voltammetry* (DPV), with a recently implemented electrochemically activated glassy carbon electrode (aGCE) (6), for the monitoring of APAP in the surface waters of the Po river basin, in the province of Turin (Piedmont, Italy). In order to confirm the reliability of the electrochemical response, we have compared DPV results with those obtained with *High Performance Liquid Chromatography* hyphenated with *High Resolution Mass Spectrometry* (HPLC-HRMS), commonly used to quantify pharmaceuticals. Furthermore, DPV with the aGCE was used to assess the photochemical degradation of APAP, and the relevant kinetic results were compared to those obtained in a previous work with a standard experimental methodology (7). The purpose is to make it possible to monitor the APAP photodegradation, and the formation of photoproducts, in real-time by developing an adequate electrochemical set-up.

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Removal and photodegradation of glyphosate herbicide from waters using a mesoporous substrate with adsorbent properties

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Nowadays, a large amount of pesticides is used worldwide and many of these substances penetrate the soils, polluting water resources. Among these compounds, glyphosate is a non-selective herbicide recently classified as a probable carcinogen for humans (Group 2A). Conventional water treatment techniques are not effective in its removal, therefore the scientific community is exploring new approaches for the removal of glyphosate from aquatic systems.

In this work, we evaluate the adsorption and degradation properties towards glyphosate of a mesoporous silica-based support, encapsulated with iron oxides and functionalized with (3-aminopropyl)triethoxysilane ($SBA\text{-}15\text{-}FexOy\text{-}NH_2$). Results demonstrate the excellent adsorption performance of the $SBA\text{-}15\text{-}FexOy\text{-}NH_2$ towards glyphosate. Indeed, the adsorption is very fast and reaches equilibrium during the first 10 minutes of contact. Through the adsorption isotherms, the maximum monolayer coverage capacity (98 mg/g) was obtained. The adsorption properties of $SBA\text{-}15\text{-}FexOy\text{-}NH_2$ were also studied in the presence of high concentration of PO_4^{3-} (40 mg/L), a potential competing ion frequently present in water resources. Results indicate that the material keeps unaltered its adsorption performance, while at the same time removing PO_4^{3-} from the aqueous solution.

The presence of Fe in the substrate was intended to trigger photodegradation reactions; in particular, photo-Fenton reactions were studied at pH 3.0 and 6.5 under UVA and UVB irradiation. The most effective method was UVB irradiation at pH 6.5; these conditions allowed the successfully degradation (90%) of the previously adsorbed glyphosate. Worth noting it was observed the retention of the glyphosate by-products on the $SBA\text{-}15\text{-}FexOy\text{-}NH_2$ sorbent, thereby preventing the release of additional molecules into the aqueous matrix. It was shown that the photo-Fenton treatment regenerates the material and makes it possible to carry out at least three adsorption-degradation consecutive cycles, without any loss in performance.

Finally, the adsorption and photodegradation capabilities of the material have also been verified on a Po river water sample, thus showing the possible application of the sorbent even in matrices that are affected by high amounts of possible interfering species (e.g. organic matter).

The study here presented is part of a PhD research program.

Characterization of ionic composition in the submicron fraction of urban aerosol

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Atmospheric particles are polydisperse, varying the diameter of more than four orders of magnitude: from some nanometers (nm) to tens or hundreds of micrometers (µm) (1). Particle size is one of the most important parameters to monitor particles' behavior in the atmosphere because it indicates the type of source and influences transport and deposition processes. Particle size distribution and concentrations of ionic species are quantified to determine their potential sources of input, chemical evolution and transport (2).

The main aim of the present work was to investigate the particle size distribution of ionic compounds (Cl^-, Br^-, I^-, NO^{3-}, MSA, SO_4^{2-}, PO_4^{3-}, C_2-oxalic acid, C_2-glycolic acid, C_2-acetic acid, C_3-malonic acid, cis-usC_4-maleic, trans-usC_4-fumaric, C_4-succinic acid, αC_7-benzoic acid, C_5-glutaric acid, hC_4-malic acid, C_6-adipic acid, C_7-pimelic acid, Na^+, NH_4^+, K^+ and Mg^+) in urban aerosol collected at Venice. We used 120 MOUDI^{TM} II sampler that permitted to separate particles in 12 dimensional fractions starting with a diameter greater or equal to 18 µm to a diameter below of 56 nm. The sampling was carried out during the 2016 spring season between March and May.

The determination of anionic compounds was performed using ion-chromatography coupled to mass spectrometry (IC-MS), while cationic species were determined through capillary ion chromatography with conductometry (2).

The concentration of ionic compounds in the aerosol samples represented the highest percentage of aerosol mass concentration. The study of the ionic composition and their particle size distribution in the analyzed samples has allowed to identify different sources, as well as marine input and anthropogenic contribution.

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Sea salt sodium record from Talos Dome (East Antarctica) as a potential proxy of the Antarctic past sea ice extent

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Sea-ice represents a powerful phenomenon exerting a strong influence on the oceanic, biological and climatic systems and, given its importance, it is a focus in environmental research. The expansion and retreat of Antarctic sea-ice is one of the most striking seasonal changes affecting the Earth today, effectively increasing by two fold the surface area of Antarctica. Despite an unknown exact mechanism, sea-ice plays a critical role in the polar amplification of climate change and, therefore, it is important to predict changes in sea ice under the future conditions of an ongoing climate change. A better understanding of the links between sea-ice and climate and a real improvement of the models requires a large series of long observational datasets. Antarctic sea ice has shown an increasing trend in recent decades, but with strong regional differences from one sector to another of the Southern Ocean. The Ross Sea and the Indian sectors have seen an increase in sea ice during the satellite era (1979 onwards). Here we present a record of ssNa$^+$ flux in the Talos Dome region during a 25-year period spanning from 1979 to 2003, showing that this marker could be used as a potential proxy for reconstructing the sea ice extent in the Ross Sea and Western Pacific Ocean at least for recent decades. After finding a positive relationship between the maxima in sea ice extent for a 25-year period, we used this relationship in the TALDICE record in order to reconstruct the sea ice conditions over the 20th century. Our tentative reconstruction highlighted a decline in the sea ice extent (SIE) starting in the 1950s and pointed out a higher variability of SIE starting from the 1960s and that the largest sea ice extents of the last century occurred during the 1990s. Our findings were also compared to other ice core reconstructions of Antarctic past sea-ice extent.

A six-year record of size distribution and chemical composition of Arctic aerosol. Main results and future bi-polar perspetives.

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The Arctic regions are among the areas most sensitive to present climate changes; through connections involving ocean, atmosphere, biosphere, lithosphere and cryosphere, they respond to, amplify, and drive changes elsewhere in the Earth system, so that understanding their role the climate-environmental feedback processes is essential to set reliable predictive climate models. In particular, the atmospheric aerosol strongly interacts with the climate forcings through scattering and absorption of the solar irradiation and as sources of cloud condensation nuclei. Although these processes are well known, the quantitative and qualitative (the sign of the climate forcing) of the aerosols in the Polar Regions is affected by a large uncertainty, yet. The main uncertainties include the relative cloud/snow surface albedo and the scarce spatial coverage of size distribution and chemical composition of aerosol at high latitudes. To improve our knowledge on the size distribution, the atmospheric load and the chemical composition of the Arctic aerosol, continuous measurements and sampling campaigns are ongoing since 2010 in two Arctic sites: Thule (North Greenland) and Ny Alesund (Svalbard Island, Norway). At Thule, 24-h samples are all-year-round collected at daily or every other day resolution. Contemporaneously, “summer” (March to September) aerosol was annually sampled at Ny Alesund. In the latter site, aerosol was collected by several systems (PM10 samplers, multi-stage impactors (4- and 12-stage Dekati samplers) and on different substrates (Teflon filters, quartz filters, polycarbonate and Teflon membranes). Besides, shorter measurement and sampling campaigns were carried out by using a tethered balloon, up to about 1.000 m altitude, to study the effect of the PBL dynamics on the aerosol atmospheric load and chemical composition. Filter chemical analysis includes: ions composition (inorganic anions and cations and selected organic anions, including light carboxylic acids and MSA), elemental composition (by PIXE analysis), main and trace metals (including Rare Earth Elements - REEs, by ICP-HR-MS), Pb isotopic ratios (by ICP-QMS) and Elemental/Organic Carbon fractions (EC/OC, by Sunset thermo-optical analysis). Besides, continuous measurements of particle size-distribution (TSI-SMPS and TSI-APS; 6 nm – 20um; 10 min resolution), Black Carbon (by Particle Soot Absorption Photometry – PSAP) and natural radioactivity (Rn progeny, by FAI PBL Monitor) were carried out during the sampling periods at Ny Alesund. Here we report the most relevant results up to now obtained and the future perspective both concerning Arctic and Antarctic aerosol, in the framework of three PNRA (Progetto Nazionale di Ricerche in Antartide) projects recently approved and funded. In particular, the use of specific chemical markers (such as nss-sulfate for anthropic Arctic Haze, REEs elements for dust, MSA for biogenic emissions, selected heavy metals for local and long-range anthropic sources) allowed studying the changes in sources intensity and atmospheric transport efficiency for aerosol reaching the Arctic regions. Sulfate source apportionment was performed to evaluate the contribution of sea spray, continental dust, biogenic emissions and anthropic activities to the sulfate global budget. MSA was used to understand the complex interactions among sea ice dynamics, chlorophyll blooms and marine primary productivity. Lead isotopic composition and REEs composition were used in identifying the continental source of dust and anthropic pollutants. Finally, a relationship between marine biogenic emissions and nucleation events was found by particle size distribution in the nanometric mode.

Effects of biomass, temperature and thermochemical process on PAH concentration in biochar

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Biochar is the solid carbonaceous material produced by the pyrolysis of biomass for a variety of applications in the agro/environmental field (1). The thermochemical processes of biomass also produce a variety of organic compounds including PAHs, highly harmful compounds to man and to the environment.

The effects of biomass, temperature and type of process (pyrolysis and gasification) on 16 US EPA PAH concentration in biochar were investigated. To this end, 47 biochars were analyzed for their PAH content. 38 of them were produced in laboratory furnace, in highly controlled pyrolysis conditions, from 11 biomasses of which 7 were of wood (beech, chestnut, pine, poplar, spruce pine, commercial conifer, and pruning from fruit tree and grape vine) and 4 of grass (thistle, giant cane, rice straw and miscanthus leaves). The temperatures of pyrolysis were 350, 550, 750 and 1000 °C. In addition, 6 biochars were produced in industrial plants of pyro-gasification or pyrolysis. These plants were fueled with six of the biomasses used in the laboratory pyrolysis (spruce pine, conifer, pruning, thistle, giant cane and rice straw). Finally, 2 biochars (named STG and SPG), produced in a small experimental plant of gasification, and a biochar commercially available were considered. For the latter the production conditions were not known.

Examining the sum of the concentrations of 16 PAHs (Σ_{16}PAH) of each laboratory biochar, it can state that the type of biomass (wood or grass) does not affect the Σ_{16}PAH, but this Σ_{16}PAH depends on single biomass. Although the highest Σ_{16}PAH values related to the type of biomass were found at 350 °C for wood biochars and 550 °C for grass biochars. The Σ_{16}PAH at the highest temperatures studied (750 and 1000 °C) were always lower than values of the other temperatures. Other interesting considerations that can be made concern single PAHs trapped on biochar at 350, 550 and 750 °C. For instance, all 16 PAHs were present at 550 °C except acenaphthene, and naphthalene and phenanthrene were found to be the most common and abundant PAHs. The process (pyrolysis or gasification) influences on the concentration of PAHs in biochar, however, the design of the reactor used and the working temperature are also important. The fact that the produced gas passes through or not the char bed to exit from reactor is an important factor. The lab. pyrolysis, in which the produced gas is continuously brought away by inert gas, gave biochar with Σ_{16}PAH lower than pyro-gasification, in which the syngas passes through the char bed. For example, Σ_{16}PAH were 455 and 3989 μg/kg for lab. pyrolysis and ind. pyro-gasification biochars, respectively. In this study the ind. pyro-gasification biochars were generally characterized by PAHs that did not include those with MW > 228 uma, unlike the biochar from ind. pyrolysis that contained 15 of the 16 US EPA PAHs. Considering the TEC (toxic equivalent concentration) values, the ind. pyro-gasification biochars investigated are suitable for their potential use as soil amendments.

In conclusion, it can be said that to produce biochar with lower PAH content is necessary choose the suitable parameters concerning the feedstock, temperature, process and design of the reactor.

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Particulate and gaseous indoor contamination at the Museum of "Last Supper" of Leonardo Da Vinci: results from one year of monitoring activity

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Atmospheric particles and gaseous pollutants can affect cultural heritage, especially the most fragile, such as The Last Supper of Leonardo da Vinci. During the centuries, The Last Supper became a case in establishing the extent of the issue of environmental conditions for the preservation of the Leonardo's masterpiece. The Leonardo's painting is protected by a filtering system (1). Previous indoor studies in the Last Supper museum were aimed to the indoor/outdoor penetration of particulate matter (2). Uncertainties concerning the particles dynamics and the gaseous contamination still persist. At this purpose, a specific experimental setting was developed allowing to perform continuous, high-time resolution, monitoring activity: a novelty in the field of conservation of cultural heritage.

Measurements (March 2016-April 2017; 1 min time res) were conducted using a combination of: 1) Aethalometer (AE-33, Magee Scientific, 7-λ), 2) condensation particle counters (TSI 3787), 3) an optical particle counters (Grimm 1.107), 4) a low volume sampler (Mega system) 5) a custom developed rotating impactor, 6) a real-time NH_3-NO_x-O_3 detector (Environment spa) and 7) passive and active CO_2, samplers were used in order to determine the isotopic ratio $^{13}C/^{12}C$ ($\delta^{13}C$) using a newly developed method (3). A Ca-based sorbent, $CaO/Ca_{12}Al_{14}O_{33}$, 75:25 w/w, was used for passively collecting atmospheric CO_2, and an Ascarite®-based sorbent for the active sampling; the collected CO_2 was desorbed from the substrate with acid treatment and directly analysed by non dispersive infrared spectroscopy (NDIRS).

Whereas particles concentrations reached the low level reported in previous studies (1), the high time resolution showed their diurnal cycle: the total number concentration reached a value of 20.7 ± 0.1 cm^{-3} (BC was 8 ± 1 ng m^{-3}) during night and then increased with visitors up to 167.8 ± 3.3 cm^{-3} (BC was 37 ± 4 ng m^{-3}) during daytime. These values remained however far from outdoor pollution levels ($\sim1\text{-}2{*}10^4$ cm^{-3} and $\sim1000\text{-}2000$ ng m^{-3}) highlighting the efficiency of the filtering system. The impact of visitors was also confirmed by CO_2 data that revealed a decreasing $\delta^{13}C$ values with increasing the number of visitors. The results on the isotopic composition of CO_2, correlated to the variation of atmospheric CO_2 concentration, permitted to follow the anthropogenic impact in the different areas of museum and were used such as a non-invasive marker to detect the air circulation and to improve the filtering system operations.

The diurnal cycle of primary and secondary particles was also investigated obtained using the apportionment of particle concentration based on N/BC ratio (4). A secondary particles peak in the afternoon (up to 300 m^{-3}) was observed. Also the NH_3 concentration peaked in the afternoon reaching a double concentration than that observed during night-time.

Moreover, the chemical composition of collected PM samples showed a mass fraction of NH_4NO_3 of 7% inside the museum that, compared with the external value of 30% highlighted the volatilization and decomposition of NH_4NO_3. The presence of ammonia became a driver of new particle formation.

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Comunicazioni Poster

Supporting the development of sustainable nano-based formulations for the restoration of modern and contemporary works of art

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Currently there is a lack of methodologies for the conservation of modern/contemporary artworks, many of which will not be accessible in short time due to extremely fast degradation processes. In this context, the application of nanotechnology already showed promising results and more solutions are currently being explored in the frame of the NANORESTART (NANOmaterials for the REStoration of works of ART) H2020 project. In particular, the project aims at developing nano-based formulations to ensure long term protection and security of modern/contemporary cultural heritage, taking into account environmental and human risks, feasibility and materials costs. Specifically, it focuses on: (i) tools for controlled cleaning, such as highly retentive gels for the confinement of enzymes and nanostructured fluids based on green surfactants; (ii) the strengthening and protection of surfaces by using nanocontainers, nanoparticles and supramolecular systems/assemblies; (iii) nanostructured substrates and sensors for enhanced molecules detection. To support the developers of new materials in designing safer and sustainable products, a four steps strategy was designed and is currently adopted in the project. First, a list of potential ingredients (along with their Material Safety Data Sheets) is collected for each proposed innovative formulation together with its composition (as ranges of percentage in weight for each ingredient). This allows to apply the self-classification approach included in the EU Classification, Labelling and Packaging (CLP) regulation with the aim to classify each formulation according to a set of human health and environmental hazards and to advise the material developers about weight thresholds that should not be exceeded in order to avoid specific hazards. Secondly, information on conventional counterparts already in the market (including their Safety Data Sheets) are collected to prioritize the most promising new formulations: on these products physico-chemical characterization in environmental and biological media as well as (eco)toxicological testing are performed. Toxicity tests are carried on according to internationally standardized testing protocols (ISO and OECD) and EU REACH regulation requirements [e.g. in vitro: SOS-ChromoTest and UMU-ChromoTest; in vivo: MicrotoxTM, microalgae (Pseudokirchneriella subcapita) and Daphnia magna]. Physico-chemical characterization includes spectroscopic and light scattering techniques [Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), analytical centrifuge (Dispersion Analyser) and Dynamic Light Scattering (DLS)]. Estimated toxicity are then compared to the results of the self-classification approach in order to identify possible nano-specific hazards. Results support the third step, when environmental impacts along the life-cycle of the formulations are assessed (in particular in application and post-applications stages). Finally, in the fourth and last step, environmental impact assessment results are combined with technical (e.g. stability, compatibility, re-treatability), economic (e.g. market price) and social (e.g. ethical) criteria in order to derive a conclusion on the overall sustainability of the innovative nano-based products.

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Portable Infrared Spectroscopy for the Non-invasive Analysis of Cultural Heritage Objects

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Infrared spectroscopy has been widely employed for the characterization and study of cultural heritage materials. But most FTIR spectrometer are located in laboratory and the analysis can be performed only on small samples, when a sampling is possible. Several in-situ infrared spectrometers have been used for the investigation of artworks. In this research, the performances of a portable infrared spectrometer will be presented together with some case study and applications. In particular, use of the diffuse reflectance infrared Fourier transform (DRIFT) device will be discussed and our recent results on the development of an infrared library database collection for the non-invasive identification of canvas grounds and colorants will be presented (1). The DRIFT spectroscopy has been also tested for the non-invasive characterization of a watercolor from Graham Vivian Sutherland (2). Moreover, we will show the use of ATR-FTIR spectroscopy for the characterization of the best consolidation treatment for the restoration of the rubber artwork "Presagi di Birnam" from Carol Rama (3). Lastly, a study on the degradation plastic materials used in contemporary art has been carried out performing an artificial accelerated ageing in solar box and the chemical-physical alterations were monitored through the new portable instrument (4).

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Aspetti giuridici e tecnologici nella valorizzazione dei materiali di scarto

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Gli sforzi verso l'attuazione effettiva del principio dello sviluppo sostenibile in un contesto concorrenziale sempre più ampio ed a più velocità hanno portato in primo piano il tema della potenzialità dei processi di valorizzazione dei materiali di scarto e, più in generale, dell'uso di sostanze alternative alle materie prime tradizionali. I sistemi premiali (anche in termini di competitività) per le produzioni a ridotto impatto ambientale, unitamente alla crescente sensibilità per il c.d. ciclo di vita del prodotto, hanno comportato una crescente sensibilità dei mercati verso settori in cui l'obiettivo della prevenzione della produzione di rifiuti diventa una voce primaria nei *business plan*. Tale processo coinvolge stakeholders con competenze e priorità estremamente diverse, circostanza che, se da un lato comporta la possibilità di creare sinergie estremamente positive, dall'altro a volte rischia di frenare l'attuazione sul piano industriale dei processi innovativi volti alla valorizzazione della materia.

In particolare, l'esigenza di una regolazione comune che l'Europa cerca di soddisfare, unitamente alle specificità nazionali irrinunciabili ed alle peculiarità di ogni singolo progetto, rendono ad oggi la sperimentazione e, soprattutto, lo sfruttamento a livello industriale dei risultati dell'innovazione tecnologica tutt'altro che agevoli. L'esempio dei materiali di scarto è emblematico. Da un lato, infatti, l'obiettivo della riduzione, a monte, della produzione dei rifiuti, comporta la creazione, sul piano spesso prima giuridico che tecnologico, di categorie teoriche di incerta applicazione (si pensi al caso dei sottoprodotti); dall'altro lato, la possibilità di valorizzare i rifiuti mediante processi di recupero innovativi rischia di trovare un freno nei procedimenti autorizzativi finalizzati al controllo preventivo sull'attuazione di tali processi a livello imprenditoriale. I conflitti tra i diversi interessi che vengono in considerazione (ambientali, economici, sanitari, pubblici, collettivi, diffusi …) rischiano, in un contesto tecnologico globale sempre più dinamico, di creare un potente freno allo sviluppo della sinergia tra il mondo dell'industria e quello della ricerca.

Al fine di mostrare concretamente gli effetti di quanto sopra illustrato, verranno presentati alcuni casi studio riguardanti processi di valorizzazione di materiali di scarto la cui fattibilità tecnologica è stata verificata in laboratorio:

i) produzione di materiali da costruzione e di aggregati leggeri con funzione fertilizzante per uso agricolo a partire da materiali di scarto dell'industria agro-alimentare (gusci d'uova, cenere di lolla di riso, sansa d'oliva, semi d'uva, noccioli di frutta, cenere di farina d'animali, tutolo di mais);

ii) produzione di vetri, vetro-ceramici e geopolimeri a partire da materiali di scarto dell'industria inorganica (diverse tipologie di vetro di scarto, come da imballaggio, da lampade fluorescenti e da tubo catodico, scorie d'acciaieria, scorie da inceneritore di rifiuti solidi urbani).

Per ciascuno di questi casi, verrà condotta un'analisi approfondita sulla base della normativa vigente, in modo tale da mettere in luce le eventuali criticità di carattere giuridico-economico che potrebbero ostacolare, se non addirittura impedire, una trasferibilità a livello industriale dei processi in esame.

LCAs of different niche animal based food products: an overview

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Livestock constitutes the 9% of global greenhouse gases (GHG) emission (3057 Mton CO_2eq per year) (1), 54% of which are due to bovine livestock. Information on product supply chains is therefore fundamental to raise awareness of consumers on the environmental implications of their food choices. This study, promoted by the Slow Food Foundation (2), aimed at providing quantitative information on lifecycle of products in order to support their qualitative description. The method Life Cycle Assessment (3,4) (hereafter LCA) was used to estimate the potential environmental impacts (i.e. Carbon Footprint) due to the supply chain of different niche animal based food products: beef and pork meat, cheese and eggs. All the 7 farms under study were characterized by semi-wild breeding, slow growth, autochthonous races and auto-produced animal feed.

The system boundaries take into account the overall lifecycle of each product, from organic feed production to livestock management, product transformation and packaging. Biogenic emissions, due to enteric fermentation and manure management, were also included and evaluated by specific models (5,6).

Results from LCA of these products were very clear and always highlighted lower values than other conventional (industrial) productions (i.e. average value based on data from scientific literature (7). In particular, emissions for beef meat production are about 28% lower than European average values, 16% lower for pork meat, 74% lower for cheese and 37% lower for eggs. These differences are mainly due to the farm management e.g. breeding system in a semi-natural way, auto-produced feedstock within the farm and without the use of chemicals, re-use of livestock manure as fertilizer, machinery efficiency, small use of electricity in shed.

Outcomes demonstrate that analyzed breeding farms are well managed and clearly driven by a sustainable rationale. In general, not intensive breeding farms (e.g. semi-wild animals taken in grass-land and a limited time spent in cattle-shed) and organic feed (self-)production are good practices to mitigate carbon footprint and finally contribute to increase the overall quality of products. It is well known how products from breeding systems have high environmental impacts. Decreasing the consumption of these products, as a personal food attitude, is an obvious solution. Nevertheless, since these products are important for our nutrition, a desirable solution is also to choose higher quality food, such as products from Slow Food Presidia. The natural management of analyzed breeding farms allows for increasing quality and healthiness of food (besides good taste) and, as demonstrated above, also to mitigate environmental impacts and guarantee sustainability as prompted by the Slow Food Foundation.

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Hydrochemical and spatial analysis as tools to deciphrate groundwater flow: a case study in the central Alps

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The understanding of water flow in alpine catchment is a key issue in environmental analysis and planning, to have a clear concept of water distribution and availability and to monitoring water quality. So, although these settings are normally well supplied with precipitation and groundwater recharge, the water exploitation may represent a major challenge (1).

To understand water circulation there is the need to apply a multi-disciplinary approach, including a geological and geochemical understanding of the study area, the analysis of hydrochemical tracers, and statistical tools (as multivariate analysis and spatial analysis) to understand distribution of chemical variables and infer the possible groundwater flow (2).

In this study chemical analysis of water samples in a little catchment in the central Alps were statistically treated to understand similarities and dissimilarities between springs and to assess the possible groundwater circulation.

The study area analyzed includes two hydrological basins: the Ventina valley basin, principally alimented by the homonymous glacier, and the Pirola lake basin, alimented by atmospheric deposition and snow deposits. There are different lithologies in the two basins, because the Pirola lake is crosscutted by a fault separating metagabbros in the northern part (rich in minerals containing Mg, Ca, Al, K, Na) and serpentinites (containing elements as Mg, Fe, Ni, Cr, Cu) in the southern part (3).

Water samples were collected during summer 2014, 2015 and 2016. Chemical-physical parameters (pH, electrical conductivity and temperature) were directly measured on field using probes, and samples were collected to analyze for following analysis in laboratory for major ions (through ionic chromatography) and trace metals (through inductively coupled plasma-mass spectrometer). The collected data were then treated through multivariate statistics (using Principal Component Analysis and Cluster Analysis) and geostatistics (Moran's I for spatial autocorrelation and distribution mapping techniques) to observe differences and similarities to springs and model possible water circulation in the two basins. Moreover, the application of cluster analysis using different chemical variables show similarities in the different basins even if the underlying geology results different.

The results show that the distribution of different geochemical markers (as, for example, Ca/Mg ratio, K, Na), indicate similarities between springs of the two different basins, especially in the central area.

The interpretation of data suggests so a possible communication, probably in the deep aquifer, from the different basins, indicating so a possible recharge of the Ventina valley even from the Pirola lake, and a mixing of the shallow and deeper aquifer.

This study remarks the need to apply multidisciplinary integrated approaches to understand natural phenomena as the water flow, even in a small and apparently simple structured basin.

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nZVI encapsulated in biochar from olive mill waste: production, characterization and application in removing pollutants from wastewater

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The work is focused on the production of carbon-encapsulated zero-valent iron nanoparticles (CE-nZVI) from moist biomass waste and their application in the removal of organic and inorganic priority pollutants from wastewater.

The nanoparticles are produced by Hydrothermal Carbonization (HTC), a process where the solution is heated in a high-pressure reactor at low temperatures from olive mill waste (OMW, a carbonaceous waste from the olive oil industry, very common in the Mediterranean area). OMW directly reacts with iron(III) (from Fe(III) nitrate nonahydrate salt), heated at 200°C for 3 hours.

A post-treatment with nitrogen increases the ZVI content, which is actively involved in the removal of heavy metals and pesticides from wastewater. In this work, different conditions of post-treatment are studied. In general, the total iron content increases with the temperature of post-treatment because of the increasing degree of carbon carbonization (temperatures of 600°C, 700°C and 800°C for 3 hours are tested). However, both the ZVI content and the surface area of the nanoparticles increase till 700°C and then they start to decrease, probably because at 700°C carbon still has an amorphous structure but at 800°C the surface of the particles becomes more crystalline.

The second part of the project is about the application, at lab-scale, of CE-nZVI in removing 5 heavy metals and a pesticide from an aqueous solution.

Regarding heavy metals, a solution containing chrome, cadmium, nickel, copper and zinc (10 mg/L each) is used. Metal ions are removed by sorption and reductive precipitation, according to their standard potential with respect to the iron's one. Results show that the problem of the aging effect (1) is solved using CE-nZVI instead of the not-encapsulated ones. In fact, no re-dissolution of any element is observed even after 200 hours.

The results of tests carried out using just OMW biochar (without ZVI) confirm that the presence of iron is essential for the removal of heavy metals.

The effect on pesticides is evaluated by experiments on a 100 mg/L aqueous solution of of 2,4-dichlorophenoxyacetic acid (2,4-D), a herbicide used worldwide to control the growth of broadleaf weeds, carried out with and without H_2O_2 and in the presence and absence of UV light. The removal mechanism involves the Fenton reaction, which produces highly reactive hydroxyl radicals that rapidly and unselectively oxidize non-biodegradable compounds. Best removal results are obtained using samples with 0.2 nFe/nC which is the maximum ratio that can be reached in CE-nZVI synthesis. The presence of hydrogen peroxide is fundamental for the formation of radicals. UV light improves the removal efficiency (photo-reduction produces more iron(II), which reacts to produce radicals).

In conclusion, the environmentally sustainable and low-cost production of CE-nZVI can contribute to solve the waste disposal problem, and the positive results at lab scale are promising for a future use of these nanoparticles in real plants for wastewater treatment.

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Trace elements in a bioindicator and PM_{10}: are they correlated?

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The analysis of bark collected from the annual segments of the tree branches has shown an interesting potential as a natural archive, allowing to reconstruct the past deposition of the trace elements present in the atmosphere along a 10-15 year period (1). The results obtained are consistent with those reported in literature for different kinds of samples (e.g. particulate matter, dust, precipitation, aerosol, lichens).

Considering that part of the trace elements caught by the tree bark (and by other bioindicators) is associated to the particulate matter present in the atmosphere, the presented study aims to verify whether the PM_{10} values are correlated with the concentration of the trace elements measured in the bark of tree branches. In fact, data of PM_{10} have been collected during the last years in many cities, as the adverse effects of particulate matter on human health are well known (2).

What is rarely determined is the chemical composition of PM_{10}, although several recent studies have shown its relevance for health (3). Even when PM_{10} is analyzed, only the trace elements included in the legislative reference framework for air quality standards are measured.

In this work the concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn have been measured by ICP-OES on the bark of holm oak (*Quercus ilex* L.) branches (n=18) in the city of Genova. The annual segments (a total of 171 samples) cover the period from 2005 to 2016. These concentrations have been compared with the PM_{10} values measured by the monitoring stations managed by the Regional Agency for Environmental Protection (ARPAL).

Among the 10 elements investigated, significant correlations ($p<0.05$) with PM_{10} have been found for Cd, Ni, Pb and Zn, all elements having important effects on human health and often considered as produced by vehicular traffic.

The technique here described allows to obtain information about time periods or areas not covered by monitoring programmes and about trace elements never analyzed, because not considered important in the past.

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Advanced Diagnostic and Conservation: the case study of a chasuble dating from early 18th century

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The object of the study is a pink chasuble belonging to the ancient textile collection of the Palatine Chapel in Palermo, dating from early 18th century. It's a silky and metal polymateric artifact: gold and silver threads are embroidered or inserted in the fabric weaving (figure).

This kind of chasuble is called "Roman" and it's characterized by the presence of a central cross on the front and a central column on the reverse. These areas are made of embroidered satin while the rest of the artifact is made of a fabric called "lampas", probably a French production of the early 18th century, belong to the type of "lace fabrics".

The samples collected from an embroidered silk satin chasuble were analyzed using an innovative analytical approach. In the first phase of the work, a preliminary identification of the dyes present in the samples was performed through SERS on fiber analyses.

In recent years, surface-enhanced Raman spectroscopy (SERS) has emerged as a powerful alternative method for the study of organic colorants used in artworks. SERS is an ideal tool for the detection of dyes because it requires very little sample, enhancing Raman signals of analytes and quenching the typical fluorescence of organic compound. Generally, SERS analysis was performed on the extract of the sample and, only in the last few years, new SERS methods, based on direct SERS on fiber analysis without the need of extraction or hydrolysis pre-treatments, were developed (1). SERS on fiber methods result to be particularly interesting since strongly reduces the amount of sample required for dyes identification.

Then, in order to deepen the preliminary results obtained through SERS on fiber analyses, the dyes present in the samples were extracted using the innovative ammonia mild extraction method. The classic extraction methods were based on mixtures of organic solvent with acid (2,3,4). These methods imply the complete or partial hydrolysis of glycosidic compounds present in the samples, allowing only the identification of the main aglycones. The ammonia mild extraction method (5) was developed just for preserving the glycosidic compounds and then getting closer to the real molecule pattern involved in dyeing process. The results obtained allowed to identify the presence of several natural dyes (such as Madder, Brazilwood, Indigo, Quercitron and Saffron) and, only in one sample of a synthetic dye (Eosin), probably due to precedent restoration treatments.

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Mesoporous substrates with ion-exchange functionalities for the removal of sugar matrices

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Sugars can be present in food products as native components or as added components during production processes.

From an analytical chemistry point of view, the presence of sugars can make difficult the routine safety control of food products (e.g. analysis of pesticides or other contaminants), whereas from an environmental chemistry point of view, sugars contribute to the increase of the biochemical oxygen demand (BOD) of wastewaters of food industrial processes.

Analysis of contaminants in food products is usually preceded by a sample pre-treatment to eliminate matrix interference and to separate analytes of interest from other components. QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) technique is one of the most used approach in food analysis. In this technique, sugar interference is removed by d-SPE using a commercial sorbent named PSA (primary, secondary amine).

The aim of this work is to prepare mesoporous substrates that can be used both as alternative sorbents to PSA in analytical chemistry applications and as adsorption substrates for the removal of sugar contribution to BOD.

For this purpose, a SBA-15 substrate was functionalized with (3-aminopropyl)-triethoxysilane (APTES) and N-3-trimethoxypropylaniline. The adsorption behaviour of the synthesized sorbents was tested on three representative sugars: glucose, sucrose and fructose. The effect of initial sugar concentration (5000-350000 mg/L), of the pH (2.1-8.5) and of the solvent in which sugars are extracted (water and acetonitrile) on the adsorption recovery is shown for each of the sugar molecule. The performances of the synthesized sorbent are compared with those of commercial PSA. To quantify sugar adsorption and to test the efficiency of the materials in real matrices, ion chromatography with amperometric detection was used.

For both the extraction solvent tested, the best performances were obtained at pH 2.1, with a contact time of one minute: these conditions are compatible with those of the QuEChERS technique. The adsorption of sugars obtained for both the materials is 10% -30% higher than the adsorption obtained with PSA, thus suggesting a possible replacement of commercial PSA in the QuEChERS technique with the substrates proposed.

To verify the performances of the substrates in food matrices analysis, we applied QuEChERS extractions on strawberries intentionally contaminated with PAHs and PCBs. After extraction, PAHs and PCBs were analysed by GC-MS. Signal-to-noise ratio and method detection limits were calculated for samples treated with PSA and samples treated with new materials synthesized.

The suitability of the sorbents on the reduction of the organic load of industrial wastewaters was finally tested, simulating the typical composition of wastewater of soft drinks production. The two proposed materials show better performance than PSA: glucose, sucrose and fructose removal was about 90% for SBA-15 functionalized with N-3-trimethoxypropylaniline, 70% for SBA-15 functionalized with APTES and 60% for PSA.

Micro-invasive study of a 15th century Armenian manuscript: first identification of lac dye by means of HPLC-MS

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The possibility of analyzing small samples taken from paintings allows obtaining interesting information that could not be gained by means of non-invasive techniques. This is particularly true for illuminated manuscripts, which are fragile and precious artworks and for which sampling is therefore usually not allowed. In such cases the knowledge of the colourants used for the miniatures is forcedly confined to the results yielded by a poorly selective non-invasive analytical approach.

In the present case, a 15th century Armenian illuminated manuscript was subjected to a diagnostic study. The manuscript was made in a scriptorium at Aghtamar Island, in the Vaspurakan region of historic Armenia and the present investigation represents one of the few performed on ancient Armenian manuscripts. A selection was carried out in order to obtain samples from all hues present in the miniatures and 15 micro samples (mostly < 1 mm^2) were obtained. The samples size was still suitable for performing non-destructive measurements with UV-Visible diffuse reflectance spectrophotometry with optic fibers (FORS), in order to obtain preliminary information useful for addressing further analyses. After that, Raman spectroscopy, Surface Enhanced Raman Spectroscopy (SERS), SEM-EDX and HPLC-MS were used for a complete characterization of the samples.

The combination of molecular (Raman, SERS, FORS, HPLC-MS) and elemental (SEM-EDX) techniques allowed the identification of all the colorants used in the miniatures. Natural ultramarine blue, indigo, cinnabar, minium and orpiment were the main identified pigments. Green hues were rendered by a mixture of indigo and orpiment, the so-called *vergaut*. Of particular interest was the identification of iron-gall ink, which in this case has been used as a pigment in the black areas of the paintings.

As to red-pink areas, preliminary FORS analysis suggested the presence of dyes from scale insects such as kermes, Armenian cochineal, Polish cochineal or lac dye (Indian lac), whereas Mexican cochineal was excluded for historical reasons. This analysis, however, is not selective enough to distinguish among these colourants which belong to the class of anthraquinonic dyes. Despite the extremely small size of the available sample, upon hydrolysis with concentrated formic acid and HPLC-MS analysis it was possible to identify lac dye through the identification of laccaic acid A and B. Lac dye is obtained from *Kerria lacca*, a species native of Southeastern Asian countries, therefore its presence - and not that of Armenian cochineal - might seems unusual from the geographic point of view. Nevertheless, the exhaustive molecular characterization obtained here for the organic dyes is relevant as miniature paintings are very rarely analyzed with invasive techniques and such information is therefore almost totally lacking.

Interesting information was also obtained regarding later interventions on the miniatures. Raman analysis highlighted the presence of 20th century pigments such as phthalocyanine blue and Naphthol Red, clearly indicating contemporary restorations.

Morphochemical characteristics and mixing state of long range transported wildfire particles at Ny-Ålesund (Svalbard Islands)

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Wildfires are an important variable of climate change in the Arctic as a source of particles which are able to modulate the radiative forcing in the atmosphere and the albedo properties of snow and ice exposed surfaces besides serving as large sources of cloud condensation nuclei (1,2). Recent studies on the mineral chemistry and geochemical signature of aerosols sampled at ground level and along vertical profiles at the scientific Polar base of Ny-Ålesund, Svalbard Islands (78°55'30"N 11°55'20"E), have shown a significant contribution of biomass burning forest fire on this area especially in summertime (3,4). A prolonged and exceptionally intense air mass advection event transporting biomass burning aerosols generated in Alaska affected Ny-Ålesund in the mid of July 2015. This study is focused on the morphochemical characteristics and mixing state of individual aerosol particles collected during the event. To this aim aerosol samples were collected on nucleopore polycarbonate membranes using a DEKATI 12-stage low volume impactor and analyzed by scanning electron microscopy (SEM) coupled with image analysis, 3D surface reconstruction and energy-dispersive X-ray microanalysis (SEM-EDS). Results of SEM investigations depict a complex aerosol characterized by an external mixing between a main part of carbonaceous organic particles (tar balls – TBs - and organic particles - OPs), lower ammonium sulfate (AS) and minor potassium chloride (KC) and mineral dust (MD) amounts. The carbonaceous particles, in particular, are mostly in the accumulation mode size range with morphologies that range from spherical to slightly elongated. The organic particles show an internal mixing of low density organics and/or ammonium sulfate upon denser nuclei. Individual particle analyses were complemented by aerosol size distribution (Aerodynamic Particle Sizer, Scanning Mobility Particle Sizer) and optical (Particle Soot Absorption Photometer, nephelometer) measurements at ground level in order to retrieve the optical and radiative properties of the aerosol in the atmosphere and to predict the fate and behaviour of particles upon deposition at ground level. Individual particle analyses were also compared with bulk chemical analyses on daily sampling filters and back-trajectory analyses of the air mass movement in order to enucleate distinct sources of the aerosol during the long range transport (5).

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TiO_2-NPs supported on sepiolites: a photocatalytic tool for removal of emerging pollutants

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Heterogeneous photocatalysis can be applied to several research areas, especially for environmental applications; among these, water remediation and wastewater bleaching are important fields the scientific research is focusing on. Nanometric TiO_2 is one of the most preferable material, due to its strong oxidizing ability, excellent chemical stability, long durability and reusability, non-toxicity, low cost and high surface to volume ratio. Due to its small particle size, the use of bare TiO_2 is limited, indeed, because it is difficult to be recovered from the suspension medium. A possible way to overcome this limitation is using a supporting material for TiO_2 with similar chemical and physical properties, such as chemical stability, reusability, water insolubility and high surface-to-volume ratio (1). Due to its high adsorbent capacity, sepiolite was chosen as supporting material for undoped and N-doped anatase TiO_2. Starting from a sol-gel route, where 2-propanol, titanium tetraisopropoxide and water or an ammonia solution were mixed together (1:2:5, V/V) in order to obtain an amorphous gel of undoped TiO_2 or N-doped, respectively, a solid-state and a hydrothermal synthesis were performed to support the nanometric TiO_2 onto the sepiolite. A chemometric approach was adopted in order to find the best syntheses conditions among the variables investigated, which are reagents ratio, temperature and time. This coupled system has potential application in the removal of organic emerging pollutants, being particularly effective in the treatment of contaminated water with pharmaceutically active compounds, whose presence in the environment represents an increasing threat (2). Photocatalytic experiments were performed on the optimized samples on methylene blue and on Ofloxacin solutions (a fluoroquinolone antibiotic), under simulated solar light and reaching very high degradation values (figure 1).

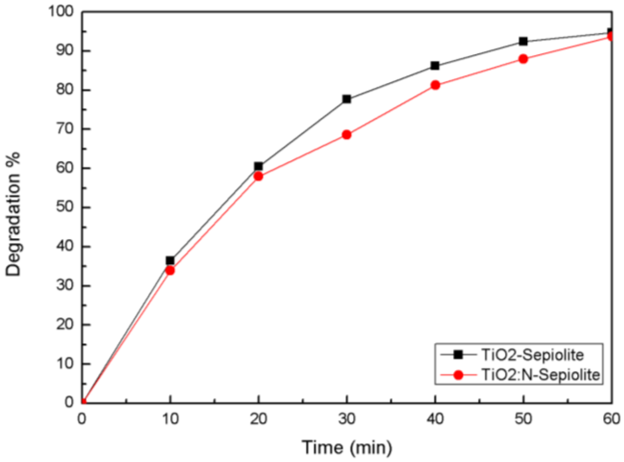

Figure1: Percentage degradation of TiO_2 and N-doped TiO_2 of an aqueous solution of methylene blue.

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Simultaneous determination of Chlorinated Priority Organic Pollutants (e.g. PCB, PBDE, PCDD, PCDF) in soil and sediments by Gas Chromatography-Tandem Mass Spectrometry

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Epidemiological studies show that exposure to specific persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) is strongly associated with negative interferences on endocrine systems and on alterations of reproductive physiology. Therefore, the determination of these compounds in the environment is of great importance from the ecotoxicological point of view. Accurate determination of PCDD/F, PBDE and PCB in complex matrices is a challenge because of their low expected concentrations in the range of ppb to sub-ppb. For the complexity of environmental matrices, analytical determinations often require long time periods of analysis and several stages of extraction/preconcentration, purification, etc in order to eliminate interferences. These procedures do not fit in extensive environmental monitoring programs, where it is necessary to analyze a large number of samples at a time not excessively long. In this paper, the official EPA methods (1,2) for chlorinated pollutant analysis has been evaluated and modified to provide a faster and more reliable alternative analytical method for simultaneous determination of interest compounds in soil and sediments with a single extraction.

Accelerated solvent extraction (ASE) has been used for simultaneous extraction of organic compounds. The most favorable extraction conditions proved to be n-hexane as the extraction solvent, temperature of 120 °C, pressure of 1500 psi and three static cycles in each case. Purification of the extract was accomplished by automated Power-Prep^{TM}/Sample Clean-up system. The analyses were then performed by using gas chromatography coupled to triple quadrupole mass spectrometry. Utilizing triple quadruple mass spectrometry under positive EI with multiple reaction monitoring (MRM) mode, greatly enhances the sensitivity and selectivity of detection, compared to selective ion monitoring (SIM) mode. The GC-QqQ(MS/MS) sensitivity, lower than that of GC-HRMS, is good enough (LODs in the down to low pg levels) to detect the normal concentrations of these compounds in environmental samples. The obtained analytical results demonstrate excellent recoveries for the various congeners, comparable to those of official methods and detection limits useful for the analysis of real matrices. The determination of these compounds in soils and sediments and the evaluation of the distribution of various congeners (fingerprint method) has allowed to obtain information on the origin of the contamination.

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Use of "mussel watch" experiments in biomonitoring of heavy metal and PAHs in a Site of National Interest

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Biomonitoring represents a useful tool for quantifying and clarifying the current status of environmental health, and indirectly assessing coastal water quality and changes in the environment, generally due to anthropogenic causes. In addition, it plays a key role in the formulation of protocols for vulnerable marine ecosystems, such as coastal and estuarine areas, transitional waters, influenced by various anthropic activities. Monitoring programmes use a great number of bioindicators - “sentinels organisms” - to detect temporal and spatial variation of marine contamination (1). As intertidal filter feeders, mussels accumulate heavy metals and organic pollutants in their tissues in proportion to the degree of environmental contamination. Bioconcentration factors depend not only by environmental conditions but also by physiological parameters such as the reproductive stage of organisms (2).

In order to evaluate metals and Polycyclic Aromatic Hydrocarbons (PAHs) bioaccumulation, mussel watch experiments were carried out using bivalve molluscs (*Mytilus galloprovincialis*) in contaminated areas of the Mar Piccolo of Taranto (Ionian Sea, Southern Italy), classified as “Site of National Interest" established by National Law 426 (1998) and included in the “National Environmental Remediation and Restoration Projects.”.

All mussels with 40-60 mm shell size were purchased from aquaculture farm located in a clean site on the Adriatic coast during the pre-spawning period in order to control seasonal variation due to mussel physiology (1).

Mussels were analyzed (T=0) and put into net cages that were suspended in the water column in two stations of the first Inlet in Mar Piccolo of Taranto. Every fifteen, mollusks were sampled by a scuba for a ten-week period, to carry out laboratory analysis.

The results showed the increase of PAHs and metals concentrations over time. For example, at the end of the exposure, mercury concentration, in molluscs increased by three times compared to baseline. Concerning ΣPAHs, after 5 week the concentration increased by about three times compared to T=0.

The obtained results have also made it possible to determine important correlations with the degree of contamination of marine sediments and to point out that resuspension phenomena of contaminated sediments in coastal areas can be a main source of contamination.

These data show that the “biota” (mussels in this case) is still a relevant target of exposure to some contaminants; for this reason, the biomonitoring activities are very important tools for human health and ecosystem risk assessment.

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Towards a closure of the European copper cycle: scenarios and environmental implications

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The scarcity of natural deposits has constrained Europe to import large amount of primary copper (Cu) forms to meet the domestic demand. In the recent years, warnings have risen up due to the risk of potential restrictions to the global primary Cu supply: ore grade decrease and a lack of potential substitutes can affect the future use of this metal (1,2). Consequently, the European Commission has promoted recycling as a central mean to secure raw material inputs to the European industry. To support the efforts of changing a respectable recycling rate (i.e., 60%) but far from perfect performance, we have explored four possible scenarios of Cu demand and supply to 2050 in the EU-28 and provided the related potentials for energy savings and climate change mitigation.

The study builds upon previous results (3) and applies linear regression analysis to compute the best fitting equations based on the major explanatory variables of Cu demand, including population, gross domestic product, the level of urbanization, and the time as explanatory parameter to capture the effect of time-dependent variables (e.g., technological development). The four scenarios model growth rates for the set of explanatory variables to 2050 according to their storylines (4).

The set of scenarios describes four possible futures, including (i) a future world driven by market forces in which per capita resource consumption continues to increase proportionally with those of the more developed countries (named Market World, MW); (ii) a scenario similar to the MW but in which a transition to a world more respectful of the environment is driven by government policies (Toward Resilience, TR); (iii) a world in which security is set as top priority and determines restriction of people migration and international trades (Security Foremost, SF); (iv) a world driven by the Sustainable Development Goals that determines more social, economic, and environmental equitability (Equitability World, EW), (4). The material flow model developed in (3) is used to simulate the generation of Cu scrap at end-of-life based on the expected future demand. Finally, we applied life cycle assessment to estimate the energy savings and carbon emission results associated to Cu recycling in the region. To this end, each scenario models developments in the energy inputs to Cu production and in the electricity production mix.

The results show that the current pattern of Cu production and consumption, as exemplified by the Market World scenario, is hardly sustainable in the long term: intensive inputs of primary Cu will be required and secondary Cu supply will represent only 45-50% of the demand, if recycling performance continues at the current levels. Aggressive recycling (i.e., 90% collection rate and 90% recovery rate) would likely improve the situation only by a little. The Equitability World is the only scenario that is highly positive even in case of stationary recycling rates. Prospects for environmental benefits follow the order EW > SF > TR > MW. Compared to the present demand (i.e., 2014), the resulting potentials for climate mitigation are expected to reduce the carbon footprint of Cu demand by about 25% to 42% depending on the scenario. Aggressive recycling would increase the benefits up to 35% to >60% for the EW. Energy savings are modeled to enhance by 5 to 10 times the present situation (i.e., ~40 TJ in 2014), should the ore grade decrease be confirmed. The study is part of the "QUEMC" project, which has received funding under the Marie Sklodowska-Curie grant agreement No 704633, and we expect that it can contribute significantly to the circular economy debate for strengthening guidance in the European climate strategies.

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Thermal stability and evolved gases investigations of all-inorganic lead halide perovskite $CsPbX_3$ (X= Cl, Br, I) nano-cubes for optoelectronic applications.

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The research of new optoelectronic materials is increasingly attracted on new quantum dots (QDs), the best nanocrystals (NCs), in terms of size, shape and composition, are binary and multinary (ternary, quaternary) metal chalcogenide (1). The all-inorganic lead halide perovskite, $CsPbX_3$ (X=Cl, Br, I), exhibit huge potential in various optoelectronic devices, due to the unique optical properties, i.e. size-dependent emission wavelength, narrow emission spectrum, and high luminescent efficiency. The practical advantage of $CsPbX_3$ NCs is the facile access to the visible spectral region *via* one-pot synthesis (2) as reported in Figure 1. The method allows to obtain monodispersed $CsPbX_3$ NCs having cubic shape and size around 10 nm. To date, the main studies are carried out to identify and improve the optical properties, in function of the influence of the thermal treatment on systems based on $CsPbBr_3$ nano-ink (3). Here we report a study about the stability of $CsPbX_3$ (X=Cl, Br, I) cubic nanocrystals performed through differential thermal analysis/thermogravimetry (DTA/TG) coupled with gas chromatography – mass spectrometry (GC-MS), in order to determine the degradation mechanism and the properties after an *in-situ* annealing.

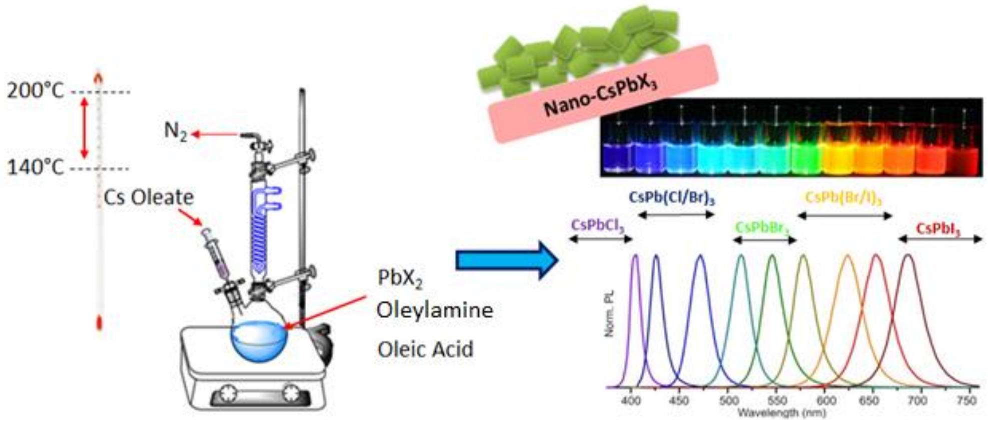

Figure 1.Scheme of one-pot synthesis of all-inorganic halide perovskite and relative optoelectronic properties (1)

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GOLENA BLU
Environmental improvement intervention in the industrial area of Tolmezzo Sud (UD) Technical-practical aspects, didactic purposes and growth for the territory

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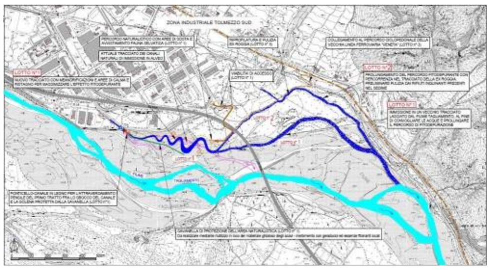
The project aims at improving the environmental situation in the industrial area of Tolmezzo Sud where the waste water is discharged by the consortium water treatment plant, before entering the Tagliamento River.

Over the last years the natural evolution of the riverbed, the alternating of lean and flood times (1,2,3,4) and the water coming from a local canal have led to the creation of a floodplain. This stretch of floodplain, affected by the discharged waste water, has assumed a wiggly configuration; thus slowing down the river flow speed and enhancing the favorable growth of typical wetland and cane plants which have self-depurative properties in themselves. The main aim of the project interventions is to amplify the natural situation that has recently emerged after the installation of the wastewater treatment plant. The proposed intervention, given the limited vital flow of the watercourse, includes:

- Increasing the twisted floodplain tract to expand the wet surface, active in the plant-based wastewater-treatment
- Growing additional plants with purifying effects and extending the vegetated surface for a boosted water purification (5)
- Raising awareness among the community of the environmental issues through the realization of a nature and educational trail within the naturalized area
- Disseminating the potential of mitigating measures
- Promoting the project TOLMEZZO - CITTA 'ALPINA 2017, with a concrete impact on the territory for the whole community and for the development of areas with strong anthropic pressure, by means of a reconversion of the river to its natural state.

Area of intervention Tolmezzo (UD)



Global project view “Golena Blu”

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Reproducibility and stability over time of silver colloidal pastes for Surface Enhanced Raman Spectroscopy (SERS) of natural dyes in ancient artworks

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Surface-Enhanced Raman Scattering (SERS) using noble metal nanometric surfaces represents an ideal analytical technique to detect and identify dyes in artworks (1), due to the dramatic enhancement of the Raman signals together with fluorescence quenching with respect to traditional Raman spectroscopies. Ag colloids are among the most popular SERS substrates employed in the detection of dyes in samples from the cultural heritage domain. One of the procedures to synthesize Ag substrates was proposed by Lee and Meisel and uses silver nitrate as Ag precursor and sodium citrate as reducing agent. The synthesis can be followed by an aggregation of the Ag nanoparticles through centrifugation of the colloid, obtaining the so-called 'silver colloidal pastes'. These pastes have been successfully used to obtain direct SER spectra of dyes from a number of materials, with the advantage of being effective in obtaining signals from very small samples without the need of complex preliminary treatments.

An inherent characteristics of the SERS technique is the variable intensity of the SER signals. Accordingly, the recent research activities of our group in the field of SERS analysis of dyes in archaeological and historical samples (2,3) evidenced a certain variability of the SERS response for different Ag paste batches. Moreover, for a same Ag paste batch, it has been highlighted that the SERS behavior is not constant over time. Furthermore, the synthesis procedure is relatively time consuming and cannot be realized on a very small scale. Thus, following the behavior of the Ag pastes over time would be very helpful in obtaining more controlled and reproducible results and in reducing any possible wastefulness. Considering all these factors, the synthesis of different Ag paste batches was carried out to evaluate: 1) the aging effect on the SER spectroscopic response of the pastes, by acquiring spectra on the same batch at different times (up to 10 weeks), 2) the reproducibility of the SER spectroscopic response of the pastes within the same batch (*intra-batch*) and among different batches (*inter-batch*) at the same aging time, 3) the use of an alternative synthesis procedure (by using ice at the end of the chemical reduction thermal step) and 4) the comparison of the spectroscopic response obtained on samples prepared with the same Ag paste at different aging times with those on the same sample prepared with the newly synthesized paste and acquired at the same aging times.

For considering the above reported points, we evaluated the spectroscopic response of the Ag pastes - as signals of Ag and citrate are normally obtained - and SER signals of a wool sample dyed with cochineal.

As expected, the overall results confirmed that it is not possible to obtain a completely predictable enhancement. Notwithstanding, they allow drawing some important conclusions. First of all, the results indicated that the paste efficiency reaches a maximum after some time from its synthesis. Moreover, they gave precious indications on the optimal sample preparation procedure and guarantee the analysis of the samples even after several weeks from the preparation.

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Cobalt beta zeolite catalyst for the trichloroethylene oxidation

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Trichloroethylene (TCE) is a halogenated aliphatic organic compound frequently detected as pollutant in the atmosphere and also in soils and groundwater (1). In the last years, several strategies have been developed for the removal of TCE including adsorption processes, phytoremediation and thermal incineration. Catalytic oxidation of TCE is an interesting alternative that permits to operate at lower temperatures (250–550 °C) with a drastic reduction of energetic costs (2). In the last years the activity of beta zeolite loaded with transition metals in the catalytic oxidation of trichloroethylene was evaluated (3). In this work Co-beta zeolite was prepared by pore volume filling method and it was tested for the total oxidation of gaseous TCE. Moreover the effect of water vapor (1.0 %) on the catalysts activity and selectivity was also investigated. Experiments were carried out in a fixed bed reactor (4).

Thermal oxidation, performed without catalysts, have shown a low TCE conversion under 600 °C.

On the other hand, when using Co-beta zeolite as catalysts for the TCE oxidation the conversion starts at 250 °C, achieving T_{50} and T_{90} respectively at 400 °C and 450 °C. Moreover the addition of water to the feed stream only slightly reduces the activity observed under dry air conditions. Product distribution in the TCE oxidation reaction for dry and wet conditions were reported in Figure 1a and 1b.

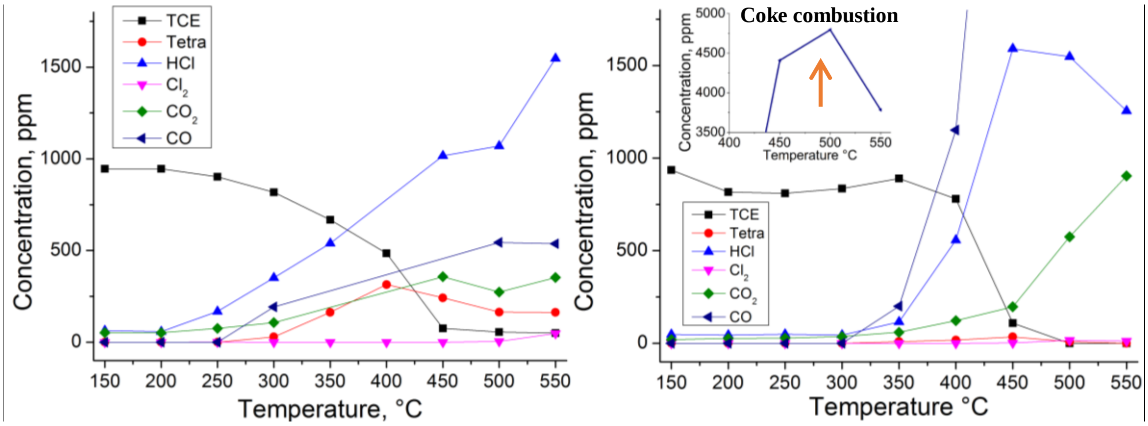

Fig. 1a/b Product distribution in the TCE oxidation reaction over Co beta zeolite for dry (right) and wet (left) conditions ([TCE]= 1000 ppm, 400 mL/min, 0.7 g of catalyst) .

Nevertheless, the presence of water vapor significantly increase the production of CO (inset shown in Fig. 1b). These results can be explained by a competitive absorption mechanism on the zeolite surface; due to its polarity, water competes for the absorption on the zeolite surface resulting in a lower oxidation activity of the catalyst and in an inhibition of tetrachloroethylene production. The last can be explained by a reduction of the zeolite acidity responsible of trans-chlorination reactions. From this work we can conclude that Co-beta zeolite is an active catalyst in the TCE oxidation of Moreover the presence of water vapor slightly reduce the catalyst activity being most significantly its influence in the selectivity of the reaction.

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Use-wear traces and wood tar residues on Funnel Beaker culture flint harvesting tools: a case study from south-west Poland

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Prehistoric harvesting tools made from lithic materials are easily distinguished amongst the archaeological assemblages. Lithic sickle inserts bear macroscopically visible traces of use. Cutting cereals causes edge rounding and highly reflected polish with flat topography cut through striations of various frequency (1). However, a location of polish and other associate traces show only which part of a lithic specimen served as a working edge, but the reconstruction of a complete sickle is not possible. More data, such as handles or residues of glue - wood tar or pitch - are necessary.

The technology of manufacturing adhesives for hafting arrowheads and projectiles had been known as early as in the Palaeolithic (2) and the Mesolithic (3). From the Neolithic European sites whole lumps of wood tar or post-production residues inside vessels or spoons are reported (4). The use of wood tar or pitch for hafting stone or bone tools by the Neolithic people is less documented. So far, no flint artefacts with macroscopically visible resinous substances are reported from SW Poland. The only proof of wood tar production in the Neolithic in this part of Poland are the remains of probably tar kiln with charred birch bark in the bottom (5).

Microscopic use-wear analyses of flint tools from the archaeological site Polwica-Skrzypnik in south-west Poland, dated back to the Funnel Beaker culture (TRB, late Eneolithic), revealed brawn or blackish substances on the surfaces of a few retouched blades. Specimens had been used for cutting cereals or other siliceous plants. The combined Fourier Transform infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS) study showed that dark substances are residues of wood tar or pitch - adhesives used for hafting. For the first time flint artefacts with macroscopically visible resinous substances are reported from this part of Poland. Resinous matter covers almost whole surface of tools. Location and distribution of use-wear traces clearly show that tools were used in longitudinal motion. Microscopic study together with residue analysis reveal the manner of use of the late Eneolitic sickles and the hafting mode

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ToF-SIMS technique applied to the study of organic and inorganic components in cultural heritage studies

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Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful method to investigate the surface composition of materials. Here we focus on the application of ToF-SIMS to study the inorganic components and the organic binders used in cultural heritage artworks (1,2). ToF-SIMS was applied to identify the pigments as well as the protein-based binders used in paintings of the 14 and 15th century on wooded panels and on walls. The results of ToF-SIMS, combined with those of other micro analytical techniques, allow to obtain a thorough characterization of the painting layers. Thanks to the spatial resolution of ToF-SIMS, it is possible to analyse, on the same sample, the priming and painting layers. A principal component analysis (PCA), based on the comparison of data of painting samples with those of artificially aged organic binders as references, is needed to characterize organic components in the painting layers. The ToF-SIMS analysis permitted to identify the organic binders present in the paintings and to study the ageing mechanisms of these protein-based matrices.

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Synthesis, characterization and applicative study of innovative materials for the conservation of cellulosic artefacts

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The interest of academia and industry for the use of renewable resources, in particular lignocellulosic biomasses, as an alternative to oil for the production of energy, fuels but also of new chemicals has grown in recent years. Moreover, focusing on the conservation of cultural heritage, the use of bio-based materials has further advantages like the compatibility, the affinity and the respect for the works of art, especially those made of the same chemical species that constitute the biomass (i.e. wood and paper) (1,2).

In this research new biopolymers and nanocomposites were synthesized using saccharides as feedstocks and their application in the conservation of cellulosic artefacts was studied. Saccharides were chosen as starting materials in order to introduce in the final products units with a structure similar to that of the cellulosic substrate and the synthetic methodologies were selected taking into account the principles of the Green Chemistry and the future application in the preservation of the cultural heritage. Allyl saccharide monomers were synthesized using allyl bromide to functionalize trehalose and glucose, obtaining products whose degree of functionalization varies according to the molar ratio between the reagents. The bio-based monomers were used for the synthesis of vinyl acetate copolymers, leading to the obtainment of final products that are soluble in acetone, but only partially soluble in water, according to the ratio between the comonomer units in the chains. In order to obtain water soluble products suitable to be used in the treatment of wood and paper and to prevent the hydrolysis of the vinyl acetate groups after the application on the degraded material, the vinyl acetate copolymers were hydrolysed to the correspondent vinyl alcohol copolymers, that were studied as consolidant for waterlogged archaeological wood. Real wooden samples were treated and the results were compared to those obtained using other bio-based oligoamidic products, which had been previously studied (2). The affinity of the products for wood and the reversibility of the treatments were evaluated together with some physical properties of the treated wood (i.e. maximum water content, basic density and volumetric shrinkage).

Finally, new nanocomposites between TiO_2 anatase nanoparticles and allyl saccharide/vinyl acetate copolymers were obtained by grafting the copolymers on properly functionalized nanoparticles. The nanocomposites were designed with the aim of obtaining new products with antimicrobial activity for the superficial treatment of cellulosic artefacts. An applicative study was performed to evaluate the antimicotic effect of the nanocomposites on recent wood against the attack of the fungus *Trametes versicolor*.

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LCA as suitable tool to improve industrial processes

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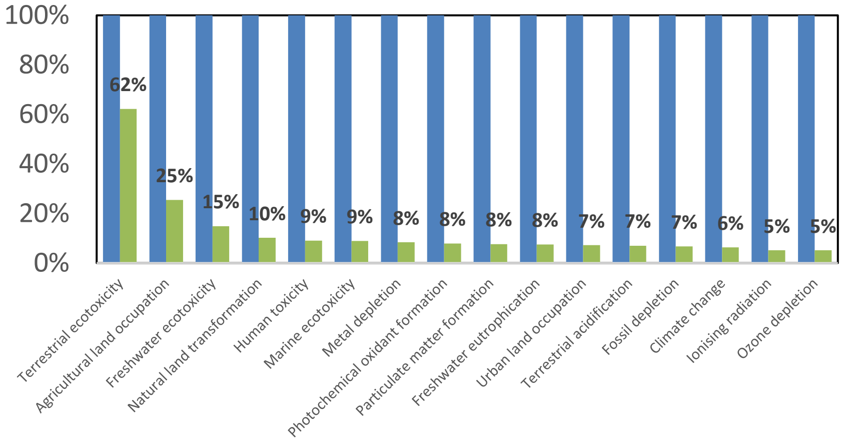
The production of daily life products such as food, feed, chemicals and pharmaceuticals involves large amounts of raw materials and energy (usually non-renewable) and generates waste with a negative impact on the environment. In this context, the research of new strategy and valid tools to reduce the overall impact of an industrial process seems to be essential. As matter of fact, industries are thus looking for alternative and sustainable technologies, able to reduce the amount of energy and water used and to minimize the fossil dependence. All actions aimed to enhance the greenness grade of the final desired products. Business model innovation and design, combine tools, methods and concepts such as creativity techniques, value network mapping, life-cycle assessment, and product-service systems. In this study, a Life Cycle Assessment (LCA) methodology was applied to support business model innovation and design sustainable strategies compared to the most consolidated alternative in the sector of detergents. An innovative product, a super concentrate pre-measured packets for floor cleaning and for daily maintenance of floors is counterposed to a traditional detergent and a LCA analysis is carried out to evaluate the environmental benefits as a consequence of its utilization. The results show that the smart product implies a resources usage (both renewable and non-renewable) lower than -92% if compared those used by the traditional product. In addition, a midpoint analysis carried out for the eighteen impact categories of the ReCiPe method shows a reduction trend from -38% up to -95% for the concentrated product (green in the figure below).



Non destructive characterization study of Picenes glass beads

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Studies carried out in the last decades defined that two main ethnic groups existed along the Italian Adriatic coast from the beginning of the Iron Age to the Romans conquest: Jalepigi and Sabelli, which were in turn divided into various tribes, including Picenes, living in the current coastal area of the Marche and of the northern Abruzzo regions between the 1st millennium B.C. and the 3rd century A.D.

The excavations of two Picene necropolises in Novilara (9th-7th century B.C, PU) and Matelica (9th-6th century B.C., MC) uncovered various grave goods including many colored glass, shell and bone-based beads.

A non-invasive characterization these beads has been performed by means of analytical techniques such as Reflectance and Raman spectroscopy and X-Ray diffraction.

Raman spectroscopy resulted particularly useful in the characterization of shell and bone based beads, displaying the typical spectra of calcite and Ca-phosphate, respectively, parallel reflectance spectroscopy gave information about the use of different chromophores in blue glass beads: as expected spectra of the darker samples contain the typical features of tetrahedral Co^{2+} ions, while data obtained from the two light blue beads available, coming from the Matelica necropolis, showed no traces of this metal but only the spectral profile deriving from the presence of Cu^{2+} ions. As known from literature, turquoise glass was commonly used during the Bronze Age, while cobalt started to be employed as a colorant during the Final Bronze Age in association with copper and then became the dominant metal to obtain dark hues due to its high colouring efficiency (1,2,3,4,5).

Both Reflectance and Raman Spectroscopy allowed the identification of hematite as the colouring agent of the only red bead available, coming from the Novilara necropolis. This is a very peculiar result, since no literature data have been reported so far, to the best of our knowledge, about the use of hematite in glassy beads dated to the Iron Age.

White and yellow samples were mainly studied by XRD: in both cases the use of traditional opacifiers such as Ca and Pb antimonates was demonstrated. Yellow samples in particular displayed the presence of lead pyroantimonate ($Pb_2Sb_2O_7$), whose diffraction peaks could be well distinguished over the broad glass structure; on the contrary, the collection of patterns from white samples, exhibiting a black surface decorative coating, gave results more difficult to be interpreted.

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Chemical investigations of bitumen from Neolithic flint flakes recovered from archaeological excavations in Central-Southern Italy

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The accessibility and distinctive chemical-physical properties of bitumen have made it one of the materials of choice since antiquity as adhesives, hydro-repellents, coating and sealing agents for the production of stone tools, ceramic vessels, ornaments and works of art. Bitumen belongs to the class of fossil materials formed by the evaporation of volatile components, polymerization and maturation reactions over geological timescale. This kind of fossil substance is particularly present in the Middle-Eastern region. Nevertheless, deposits of bitumen of different geological eras can be also found all over Europe. From a chemical point of view, bituminous materials are really complex mixtures of long-chain acyclic hydrocarbons, cyclic compounds such as hopanes and steranes, and aromatics. The composition of the bitumen varies depending on the area of origin, this means that the chemical characterisation of an archaeological bitumen can allow us not only to draw hypotheses on the possible function of tools/objects from which the bitumen is sampled, but also to obtain information on the geographical origin of the bitumen.

This paper will present the most important results regarding the characterization of bituminous residues sampled from Neolithic flint flakes recovered from archaeological excavations in Abruzzo and Puglia (Italy). Because of the chemical complexity of such organic substances, analytical procedures based on gas chromatography and mass spectrometry (GC/MS, Py-GC/MS) and on thermal analysis (TGA also coupled with IR detector, EGA-MS) have been chosen. The analytical protocol has been optimized and primarily tested in the study of bituminous materials (used as reference materials) from rocks and sediments of Central-Southern Italy, and subsequently used to characterize the archaeological bituminous materials recovered from the Neolithic stone tools.

Oli siccativi: approccio multi-analitico per l'identificazione di finger-print su campioni non trattati

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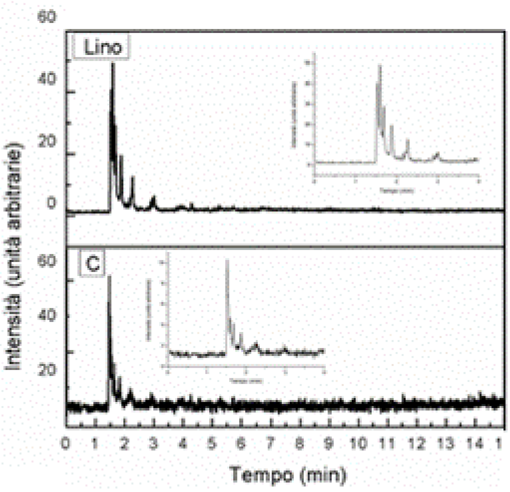
L'obiettivo di questa ricerca è stata l'identificazione, mediante analisi termica e termogravimetrica (DTA/TG) accoppiata alla gas cromatografia e spettrometria di massa (GC-MS) di *finger-print* caratteristici degli oli siccativi. Attualmente il riconoscimento di questo genere di leganti avviene basandosi sul rapporto tra le quantità di acido palmitico e acido stearico presenti (Tabella 1) (1) e le analisi hanno di norma necessità di un pretrattamento iniziale del campione (2,3).
/

	OLIO DI LINO	OLIO DI NOCE	OLIO DI PAPAVERO
P/S	1,1-2,4	2,3-3,6	3-7

Lo studio si è focalizzato sui principali oli siccativi di uso artistico: oli di lino, di noce e di papavero (4,5). Questi sono stati invecchiati artificialmente a 40°C in atmosfera di O_2 per un mese e quindi analizzati con le tecniche sopra citate. In particolare da 35° a 600°C con rateo di riscaldamento di 5°C/min in atmosfera di He (20 ml/min) con la contemporanea analisi dei gas evoluti. Sono state eseguite sia analisi con colonna mantenuta in isoterma, che corse cromatografiche in punti risultati particolarmente interessanti al fine di poter discernere in modo più accurato le molecole rilasciate dai campioni. Interessanti risultati si sono ottenuti investigando le specie rilasciate intorno a 400°C, identificando molecole riconducibili ai diversi oli. La metodica è quindi stata applicata su campioni derivanti da opere reali, un dipinto su tela (XIX secolo) e uno su tavola (XV secolo) riuscendo a discriminare non solo la componente organica derivante dagli oli (Figura 1) ma anche la componente "grassa" derivante dai leganti proteici. Per queste ragioni, la tecnica accoppiata DTA/TG – GC/MS potrebbe essere considerata una nuova metodologia nello studio e nella diagnostica dei Beni Culturali.



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Biodiesel from transesterification of waste vegetable oils by means of heterogeneous biocatalyst

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The traditional methods for biodiesel production include the use of alkaline catalysts, like potassium hydroxide and sodium hydroxide, since they are cheap, easy to handle, to transport and store, or solutions of sodium methoxide and potassium methoxide in methanol, which are preferred for continuous-flow processes.

However, alkaline catalysts involve high temperatures, undesired by-products formation and difficulties in glycerol recovering. The post-treatments required could thus affect the energy and environmental benefits of using biodiesel.

For these reasons, research aims at identifying alternative and innovative solutions, including enzymatic catalysis: enzymes operate at low temperatures, pressures and controlled pH, while maintaining low energy consumption and high selectivity.

In the present work, we verified the feasibility of producing biodiesel through the transesterification of waste vegetable oils using as catalyst a lipase (enzyme) obtained from Solid State Fermentation (SSF) of agro-food by-products. In order to ease the catalyst recovery at the end of the reaction, the lipase was adsorbed on two different types of waste glass: funnel glass from Cathode Ray Tube (CRT) (PbO=12-25% wt) and packaging glass from urban collection (PbO≈5%wt).

Waste glasses were firstly ground and sieved in order to obtain 180-300 µm particle size. Subsequently, they underwent a series of chemical treatments, which can be distinguished into surface cleaning by means of acidic and basic solutions (Treatment A and B) and silanization (C) using two different silanizing agents: chlorotrimethylsilane (shorter -CH_3 chain) and tributylchlorosilane (longer -CH_3 chain).

Lyophilized lipase (150 U/g) was dissolved in phosphate buffer (pH 7) in order to obtain a lipase solution with 2 U/ml. The enzyme was immobilized on the solid carriers by adsorption keeping the glass grains in contact with the lipase solution in the following conditions: 230 rpm, T=30°C, 22 hours. The transesterification reaction of waste vegetable oils was carried out by means of the heterogeneous catalyst (lipase adsorbed onto glass grains) using methanol as reagent and cyclohexane as solvent in the following conditions: 250 rpm, T=30°C, 24 hours. In order to calculate the reaction yield, nonadecanoic acid was added as standard. Methyl esters were detected by means of GC-MS analysis.

Results confirmed the feasibility of the process: methyl esters typical of biodiesel (Hexadecanoic acid, methyl ester and 9-Octadecenoic acid (Z)-, methyl ester) were detected in all the samples containing lipase adsorbed on packaging glass for urban collection. CRT glass was less performing as support for lipase, since two samples containing this kind of glass didn't give any transesterification products. The reason could be the high level of PbO of this glass (12-25% wt), but further analyses should be carried out in this regard.

Further investigations could concern: i) the use of higher lipase concentrations to increase the reactions yields (the current ones are <1%), ii) the use of alternative supports to glass (e.g. porous geopolymers); iii) LCA study of the process; iv) the use of methanol obtained from pyrolysis of cellulosic materials (pruning residues, dried legumes).

Application of laser technology in cleaning metal threads of ancient liturgical vestment (chasuble)

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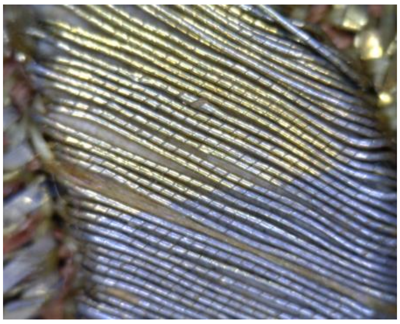
This paper focuses on the laser cleaning of metallic threads present as decoration on an ancient liturgical vestment using a Nd:YAG laser radiation in the visible region of the spectrum (532 nm). The chasuble, dating from early 18th century, belongs to the ancient textile collection of the Palatine Chapel in Palermo. This cleaning method, rarely used in the past on historical textiles, ensured a quick removal of the thick layer of oxidation and organic deposits present on the metal surface, providing the safety conditions for the artifact. The laser cleaning treatment revealed the ancient splendor of the chasuble and it was once again visible the richness and variety of decorative form, materials and techniques used for its production.

The (ICP–OES) analysis, carried out for the recognition of metal alloys, identified different composition for metallic yarn inserted on the perimeter area than those embroidered on the central area which have all similar composition. They are also applied three different kind of perimeter gallons in metallic yarns made on frame. On the chasuble there are a total of 11 different types of metal yarns, variables for construction technique, size, and surface appearance. The gold effect is obtained by applying a superficial gold layer on a silver alloy yarn.

The tests were carried out on different kind of thread, selecting small areas of 5 X 5 cm size. The average of the laser application time was 1 minute, while keeping a constant frequency of 10 Hz and changing the fluence in relation to the thickness of the oxidation layer.

The surface on which the laser runs has been previously moistened by applying a thin layer of water with a brush in order to contain the thermal spike, lowering the surface temperature. Humidification also facilitated the dirt removal due to the effect of the water vaporization. It was also used non-acidic small cardboard masks in order to protect the surface from the relapse of micro and nano-particulate redeposit that can attach the treated areas in case of prolonged irradiation (which would accelerate the reactivity) (1,2).



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Protective effect of linseed oil varnish on archaeological wood treated with alum.

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The Viking Age wood artifacts recovered in the early 1900s from the Oseberg mound and treated with alum, are today highly degraded, a condition attributed to the effects of the alum-treatment and of the reactivity of alum and derived salts (1). Some of the artefacts from the Oseberg collection which were treated with alum were also coated by linseed oil. Although the linseed oil did not fully penetrate the wood in many cases, these artifacts appear to be in better physical condition than those not treated with linseed oil.

In order to assess the effect of the presence of linseed oil on wood preservation, alum treated wood coated with linseed oil was investigated. The fragment was sampled at different depths from the surface. Three analytical techniques, giving relevant information about the molecular composition and state of preservation of both archaeological wood and aged linseed oil, were adopted: gas chromatography coupled with mass spectrometry (GC-MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and high-performance liquid chromatography coupled to electrospray ionisation and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-ToF).

Specifically, Py(HMDS)-GC/MS allowed to assess the state of preservation of the main wood components in the presence of linseed oil and the alum treatment, while GC-MS and HPLC-ESI-Q-ToF were used to perform the lipid characterization and to investigate the lipid degradation and oxidation processes.

The results showed that although the wood was highly depleted of carbohydrates (2), it was better preserved with respect to those artefacts not coated with linseed oil. Results from GC-MS and HPLC-ESI-Q-ToF together with those from Py-GC/MS suggested that the linseed oil played a mitigating role towards wood degradation. The behavior of the lipid material, more oxidized on the wood surface than at depth, suggested that selective oxidation of the oil over the wood components led to a better preservation of the material.

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The weight of food on the environment: an emergy evaluation of Italians' diet

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Consumption of food represents 16% of Italian families' expenses. But what is the environmental cost of producing the food we consume? This can be estimated by emergy evaluation (1), accounting for the solar energy (directly and indirectly) required for the production of goods.

Since food component is showing an increasing relevance concerning its impacts, this study is aimed at highlighting the dietary habits of Italians from an emergy perspective. To this aim we have collected data to make an emergy database of food produced and consumed in Italy. In particular, we carried out emergy evaluations of the top 50 food products consumed by Italian citizens. For most of these products, since data were not available, ex novo emergy evaluations have been performed. Comparing the ideal food pyramid (2) with the one resulting from the calculation of the emergy per unit mass we have seen that the food that should be consumed more frequently (located at the bottom of the food pyramid), has a higher efficiency in the transformation from direct and indirect solar energy to food mass. The emergy per unit mass calculated in this research are then used to estimate the emergy flow necessary to support the current weekly Italian food diet. The optimum average dietary energy requirement suggested by the Italian Health Ministry is set at 14000 kcal per week. An ideal diet should also be as much as possible varied and nutritionally balanced, i.e. based on the consumption of food groups, as illustrated by the food pyramid as graphical representation of the "Mediterranean diet". A comparison between the current Italian diet and an ideal Mediterranean, vegetarian and carnivore diets has been then performed.

Results of this research have demonstrated that the emergy of diets can vary as a wide range of values and that the ideal Mediterranean diet seems to be a good tradeoff between low emergy requirements and diversity of food. In fact, in absolute terms, the vegetarian diet shows the lowest emergy per week (3.53×10^{13} sej), very close to the Mediterranean one (3.74×10^{13} sej). On the contrary the carnivore diet shows the highest emergy requirements (5.81×10^{13} sej), around 55% higher than the vegetarian diet. The current Italian diet shows a requirement 10% higher than the emergy flow with respect to the Mediterranean diet, although the composition of the current Italian diet, is moving away from the Mediterranean one.

This study shows the relevance of a proper education on food and diets both from the health and an environmental view point since about 20% of the overall emergy supporting an average Italian (expressed in sej yr^{-1} $person^{-1}$) is related to food provision (3).

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Effects of environmental parameters biomonitoring polycyclic aromatic hydrocarbons in the air by *Salix matsudana* leaves.

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Persistent organic pollutants (POPs) encompass many organic contaminant classes that show high persistence, susceptibility for long-range transport (LRT), and potential for biomagnification in food chains (1,2). Air is an efficient medium for the global dissemination of persistent organic pollutants (POPs). Epidemiological studies investigating the health risks related to air pollution suggest that ambient air pollution (including polycyclic aromatic hydrocarbons, PAHs) may be responsible for increased rates of diseases like lung cancer (3, 4). Air pollution is an important environmental problem that can result from both human and natural actions. To reduce pollution levels and minimize harmful effects on human health, it is necessary to improve air monitoring and provide useful information to the communities. Recently, biomonitoring methods using passive plant samplers may offer a practicable low cost alternative, especially in terms of high spatial resolution and time-averaged data series (5, 6). In this study, seasonal distribution characteristics of PAHs in *Salix matsudana* leaves covering its annual life cycle were carried out in order to evaluate plant leaf response sensitivity on air pollution. *Salix matsudana* leaves were collected throughout different development phases of plant leaf inclusive of bud break to fallen leaves, covering from spring (May) to autumn (November). Simultaneously, particle and gas samples were collected using a high volume air sampler. Seven different PAHs were determined from three types of samples. The leaf area and lipid content changed from season to season: both parameters increased rapidly during the spring season, maintained a stable state in summer season, while lipid content dramatically decreased in autumn season. Except spring season, total PAHs showed similar seasonal trends between plant leaves and air samples, with correlation coefficients equal to 0.74 and 0.56 in summer and autumn season, respectively. In this work, it has been demonstrated that climate changes, such as rainfall and air mass movement, influence the daily concentrations of PAHs in leaf. Furthermore, PAH composition profile in leaves and air phase have been correlated by principal component analysis.

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Development of a qualitative and quantitative analytical method for the characterization of mixtures of free fatty acids and metal soaps in paint samples

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Until the 18th century, the paint production was at the basis of the activities in artists' ateliers: pure raw materials were purchased and then the paints were prepared according to traditional and sometimes secret recipes. From the XX century onwards, as a results of the scientific and technological industrial advancements, artists' oil paints were increasingly produced on an industrial scale: respect to the traditional oil paint media, the ingredients of industrial paints were modified to produce different working proprieties such as viscosity, drying rate, and color. In the modern oil formulations metal soap are commonly introduced as surfactant additives to facilitate the dispersion of pigments into the medium: dispersing agents were added to paints since the 19th century, and aluminum and zinc stearates were patented as dispersion agents and widely used after 1920. Metal soaps have the tendency to aggregate, and they may lead to the formation of inclusions, which can sometimes form lumps or protrusions on the paint surface, or can migrate from a paint layer to an adjacent one. Moreover, the presence of metal soap, can lead to an alteration of the speed of the hydrolysis processes involving the polymer network, leading to a deterioration of painting and painted surfaces (1).

The quantification of fatty acid metal carboxylates is often difficult, especially in mixture with free fatty acids. Different analytical methods based on gas chromatography/mass spectrometry (GC/MS) and infrared spectroscopy (FTIR) have been applied for the evaluation of metal carboxylates, but commonly their amount and type is determined together with free fatty acids or after specific sample pretreatment procedures.

In this work, we present the application of a new qualitative and quantitative analytical approach based on the use of GC/MS for the complete characterization of mixtures of free fatty acids and metal carboxylates in paint samples (2).

In this new method, we combined two silylation reactions directly on the same paint sample in order to derivatize in two different analytical steps the carboxylic and the carboxylate groups.

In the first step 1,1,1,3,3,3-hexamethyldisilazane (HMDS), that did not show affinity with the metal soap carboxylate groups, was applied for the derivatization of the fatty acids, while N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was applied for the silylation of the metal carboxylate.

The combination of this two derivatization procedures on the same paint sample allowed us to discriminate and quantify free fatty acids and metal carboxylates directly on the paint sample without any sample pretreatment.

This new analytical approach was successfully applied to characterize the chemical composition of paint samples.

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Early Medieval Globular Amphorae from Torcello: Microscopy, Porosity and Chemical Analyses for the Study of Production Techniques

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This work aims to study the production techniques, such as firing temperature, on selected globular amphorae fragments uncovered during the 2012-13 archaeological excavation at Torcello, Venice. Particle packing, microstructure, porosity and morphology, as well as chemical-mineralogical composition of ceramic matrix, are correlated with native material composition and firing temperature (1,2). Considering these physical and chemical properties, the samples were investigated and the results obtained through Mercury Intrusion Porosimetry (MIP), Scanning Electron Microscope (SEM-EDX) and Fourier-Transform Infrared Spectroscopy (FT-IR) were compared.

We considered some selected fragments of Early Medieval Globular amphorae, dating from the 7th to the 10th century, excavated in the 2012-13 archaeological excavation in Torcello (one of the first settled island on the northern Venetian lagoon) (3).

The samples are rich in SiO_2 and Al_2O_3 with varying amounts of CaO, Fe_2O_3, MgO, K_2O and TiO_2. Calcite was detected in some sherds, indicating Ca-rich raw materials and low-firing temperature. The presence of carbonate-rich clay promotes high porosity over 600°C, as a result of CO_2 exhaust. Decomposition of calcite begins at $T>650°C$ and the phase disappears at $T>850-900°C$. Hence, the presence of calcite in ceramic fired at $T>900°C$ could be due to a secondary calcite, formed from a reaction between CaO and silicates (4). Porosity results obtained by MIP allowed an estimation of the open porosity and pore size distribution of meso and macropores. Furthermore, a comparison between the MIP results and those obtained by digital image analyses of SEM micro-photographs, was evaluated.

The combined use of chemical and physical techniques has outlined the information about the raw materials and the technological–productive aspect. We have collected new data in order to estimate the firing temperature of the ceramic samples.

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Monoalkyl glyceryl ethers production in the presence of homogeneous and heterogeneous acid catalysts

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Monoalkyl glyceryl ethers (MAGEs) are valuable chemical compounds with different industrial applications, such as the formulation of additives (for fuels, lubricants, printing inks etc.), detergents, polymers, pharmaceuticals, antiseptic and antimicrobial creams. (1)

In this work, we report the synthesis of MAGEs by ring opening reaction of glycidol (2,3-epoxy-1-propanol) with alcohols in in the presence of both homogenous and heterogeneous acid catalysts.

The use of glycidol as starting material to produce such valuable chemicals seems to be very promising since it can be obtained through the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant. (2)

Recently we have studied the etherification of glycidol with different alcohols (ethanol, methanol, 2-propanol, 1-butanol, 1-pentanol, 1-octanol, and benzyl alcohol) in the presence of Lewis acid based catalyst such as metal chlorides and triflates. (3)

The experiments were carried out at 80°C and alcohol/glycidol moles ratio of 9 using different alcohols (methanol, ethanol, 2-propanol, tert-butanol, 1-butanol, 1-pentanol, 1-ottanol and benzyl alcohol) as nucleophiles. Results show that $Bi(OTf)_3$, $Al(OTf)_3$, $Fe(OTf)_3$ are able to catalyze the reaction of glycidol with alcohols at 80°C in 1 h using a catalyst loading of 0.01 % in moles. In the light of these results we have synthesized the corresponding heterogeneous catalysts using mesoporous silica as support.

The heterogeneous triflates have shown the same activities of the corresponding homogeneous one in terms of conversion (95%, 75% and 70% in 1 h respectively for Al, Bi and Fe) and selectivity (>90%) to MAGEs. However, a loss of catalytic activity was observed during the first reuse. Moreover, we have tested other heterogeneous catalyst such as sulfonated mesoporous silica, sulfonated activated charcoal and functionalized polymeric resins. The best results were obtained by using Nafion NR50, a perfluorinated ion-exchange polymer. This catalyst was stable under the investigated experimental conditions also after four subsequent reaction cycles.

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Nano-Cathedral project: experimental results from the evaluation of the performance protective treatments and insight into their interaction with stone materials

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The EU-funded Nano-Cathedral project is about the design, laboratory evaluation and on-site testing of innovative nanomaterials for the conservation of historic stone architecture. The nanomaterials are to be applied for *consolidation* or *protection* purposes on a selection of six lithotypes of five different European cathedrals and of a monument of contemporary architecture. The ultimate goals are first and foremost to build up a systematic knowledge of the characteristics of nano-structured products that are most relevant to their effectiveness in the treatment of different natural stones and also to promote an integrated European-wide approach to the use of innovative materials in the field of cultural heritage conservation (1).

Our research activity in the frame of the project is currently aimed at:

- implementing a laboratory protocol for the evaluation of the performance protective treatments on the selected lithotypes and their combined response towards environmental exposure;
- investigating the interaction between nanomaterials and lithotypes.

The protective treatments under study fall into three different categories: *photocatalytic* treatments, *biocidal* treatments and a *purely water-repellent* nanopolymer.

Concerning the first aim of the research, a characterization of about 60 stone specimens was carried out for each of the six lithotypes *before* and *after* the application of the treatments, including measurements of capillary water absorption, water vapour permeability, static contact angle and colour change. As regards the characterization of photocatalytic activity, we have worked so far on an optimization of the Rhodamine discolouration test on stone specimens and planned to carry out further tests on the treatments in their liquid form. The data obtained so far allowed us to fully characterize the performance of six nanomaterials, highlighting very clearly the differences among them if applied on different lithotypes. Regarding the interaction between nanomaterials and lithotypes, we are obtaining promising results from an electrokinetic technique, the streaming potential analysis, which provides an insight into the modification of stone properties after the application of the treatments and the chemical affinity between treatments and lithotypes. As future activity, all treated specimens will undergo an artificial ageing procedure in order to predict their response towards environmental exposure.

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Ageing of mono-azo and β-naphthol red and yellow synthetic organic pigments in painting matrices and textiles

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In the second half of the 19th century, chemical synthesis established and quickly developed. The new synthetic organic pigments (SOPs) quickly replaced the traditional natural organic dyes (extracted by vegetal and animal sources) due to their cheapness, great range of bright nuances and wide availability. Hundreds of these SOPs have been used for a variety of applications and exploited in the artistic field. The introduction of ready-to-use tube colours radically changed the way in which artists approached painting and SOPs have, since then, become the most important group of pigments used in modern art (1). Among the several classes of synthesized SOPs, β-naphthols, belonging to the class of azo pigments and obtained by coupling reactions, were considered the first successfully used in textile dyeing and printing (2). Nevertheless, the fastness proprieties of most of the azo dyes were not tested sufficiently before their introduction on the market and the absence of information about the miscellaneous additives used by paint manufactures in the commercial formulations resulted in a general lack of knowledge of the chemistry of these species in modern artworks.

This work aims to study the degradation and fading processes due to ageing and oxidation of some β-naphthol and mono-azo SOPs, not much investigated until now, such as the orange and red pigments Pigment Orange 5 (PO5), Pigment Red 3 (PR3), Pigment Red 53 (PR53), Pigment Red 49:2 (PR49:2), Fast Red AV and the yellow pigments and dyes Naphtol Yellow S (NY), Martius Yellow (MY) and Pigment Yellow 1 (PY1). Methods based on High Pressure Liquid Chromatography coupled with Diode-Array, Fluorescence or Mass Spectrometric Detectors (HPLC-DAD-FD-MS) were developed and optimized considering the chemical features of these SOPs and exploiting their high fluorescence. A novel C18 solid silica core column (Poroshell 120 EC-C18) was tested for the optimization of the analytical methods. The target compounds were studied both as pigments (e.g. casted on glass slides dispersed in isopropanol, or in more complex media constituted by linseed oil and white inorganic fillers) and as dyes on wool yarns. These mock-ups were naturally or artificially aged in order to study the degradation products and in some cases also the relative kinetics. The results allowed us to understand if and how the matrix influences SOPs' degradation rate and the formation of the different intermediates and end-products. Moreover, the differences between the degradation profiles of the different pigments belonging to the same class (β-naphthol) or to a different one (mono-azo) have been evaluated and some hypotheses about the degradation pathways have been formulated.

The analyses carried out so far provide preliminary results that will be further investigated analyzing extremely aged mock-ups and historical paint samples. Nevertheless, this work adds a missing piece of information to the little-known topic of the degradation of modern pigments. The final results of this study will eventually help restorers and curators to prevent or slow down deterioration processes and choose the most suitable procedures for preserving artworks.

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Orcein dyes and its synthetic alterego, the mauveine dyes: a threshold of a complete change

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Orchil dyes is one of the most fascinating dye in the art history. Considered as the "first" synthetic dye in the history, due to the treatment that the lichen should have been subjected to, in order to obtain the chromophores, it has been widespread used during the centuries, even if its detection in artworks is strongly compromised by its low photo-stability (1,2). As happened for other natural dyes, the discover of reaction for producing synthetic dye has led to their replacement with the synthetic alteregos. Furthermore, the mauveine, the real first synthetic dye in history, can be easily considered the alterego of orchil, due to a similar violet issue given to the yarns. Obviously, it is not easy to understand how much time the textile dye industry employed to spread in economic and social portrait of 20th century. For this reason, the *abito da passeggio* of Donna Concetta Tomasi di Lampedusa can be considered a precious historical proof, which can furnish several information about this matter. The multi-analytical approach applied to the study of dyes employed for the historical dress started from SERS on fiber analyses, which allowed hypothesizing the simultaneous presence of orcein and mauveine dyes (fig. 1). Thus, it has been chosen a selective extraction protocol for both dyes, followed by mass spectrometric analyses. In particular, the application of the new mild extraction technique, suitable for natural dyes, (3) allowed confirming the presence of orcein, albeit in a small amount. Furthermore, MALDI-ToF and HPLC-MS (fig.2) analyses confirm that it was used simultaneously with its synthetic alter ego, the mauveine, testifying its widespread diffusion in all over the Europe in only ten years, ready to completely replace the natural dye.

In particular, the identification of mauveine derivatives and their relative proportions can give additional important information, for what concerns the preparation of mauveine dyes and can be considered diagnostic for the synthetic recipes followed by the dyes industries in that period (4).

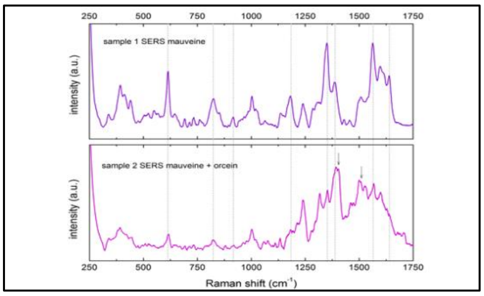

Fig. 1. SERS on fiber spectra performed on sample from the dress.

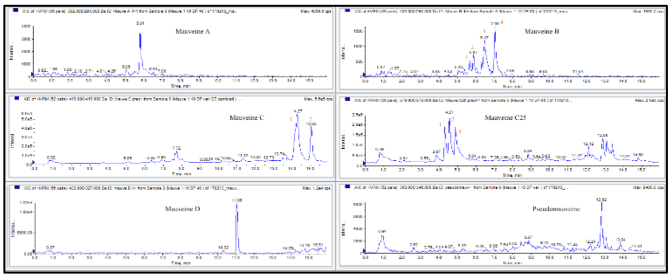

Fig 2. HPLC-MS of mauveine extract from the dyed yarns.

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Nuovo metodo per la pulitura di affreschi da sali solubili

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I dipinti murali rappresentano un inestimabile valore del patrimonio artistico mondiale, in quanto sono testimonianza di una tecnica molto antica. Essendo strettamente legate al supporto murario le pitture parietali risentono delle problematiche del supporto, come movimenti che generano crepe, infiltrazioni e risalita capillare dal terreno. Quest'ultimo problema, legato alla risalita capillare, può dare origine ad un ulteriore fenomeno di degrado: la manifestazione di efflorescenze saline sulla superficie delle pitture e all'interno del paramento murario.

Questo studio è incentrato su una nuova tecnica per la rimozione di sali solubili da affreschi e materiali porosi e la sua comparazione con le metodiche ad impacco note nel campo del restauro. La tecnica innovativa, basata sul brevetto dell'Università degli Studi di Genova (1) ha portato alla rimozione, su campioni opportunamente trattati, del 100% di sali in 60 minuti, mentre gli impacchi di polpa di cellulosa hanno rimosso il 20% in 120 ore. Per questo studio sono state utilizzate due specie saline note: NaCl e Na_2SO_4. Quest'ultimo è molto dannoso per i manufatti porosi a causa della pressione di idratazione e quella cristallizzazione a cui è soggetto (2,3). La fase di idratazione genera un forte aumento di volume (circa 314%) e il passaggio da fase anidra (detta thenardite) a fase decaidrata (4). Inoltre le condizioni climatiche come T e RH sono i principali fattori che innescano questo continuo meccanismo di cambiamento di fase; i materiali porosi soggetti a ripetuti cicli sono destinati a essere irrimediabilmente distrutti.

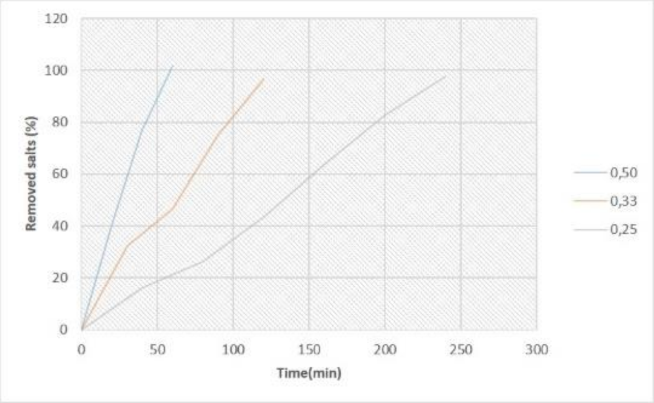

Fig.1. Rimozione di sali con differenti velocità di aspirazione.

Il grafico mostra come una portata di flusso di 0.50 m^3/min permetta di rimuove totalmente i sali in 60 minuti. La comparazione con i metodi ad impacco ha dimostrato che la nuova metodologia può essere utile per l'estrazione dei sali solubili dai supporti porosi e le due tecniche possono essere impiegate insieme.

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Study of calcium alkoxides as new solution for the consolidation of decayed limestone

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Limestone with different porosity are extensively used as a sculptural and architectural stone in artistic-architectural field. However, the combined action of several physical, chemical and biological factors, causes the weathering of stone leading to loss of surface and in-depth cohesion (1,2,3).

A novel consolidating product, calcium ethoxide, has been recently proposed during the European NANOMATCH project for the treatment of carbonate stones (4). In fact, this compound, dissolved in an organic solvent, reacts in presence of humidity and CO_2 to give in situ $CaCO_3$ and alcohols, leading to the filling of micro-fissures and reconsolidation of decayed stone (5). The carbonation process can follow two different reaction pathways: insertion of CO_2 molecule between Ca-O bond or insertion of H_2O molecule. The purpose of this research is the evaluation of carbonation process pathways of calcium ethoxide diluted in different organic solvent and the study of the consolidation effect of these new products on limestone widely employed within Italian Cultural Heritage, compared with a reference product.

Preliminary results regarding: variation of porosity (MIP), changing in mechanical and physical characteristics – drilling resistance measurement, ultrasound velocity, permeability test - and observation of treated surface – scanning electron microscopy - are here reported and discussed.

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Petroselli Chiara	ABC OR03
Petroselli Chiara*	ABC OR17
Picascia Antonio	ABC PO23
Picone Marco	ABC PO01
Pini Martina	ABC OR05
Pironti Concetta	ABC KN01
	ABC/ANA OR07
Pironti Concetta*	ABC OR23
	ABC PO23
Pizzol Lisa	ABC/ANA KN01
Poggi Giovanna	ABC/ANA/FIS OR01
Poggi Giovanna*	ABC/ANA/FIS OR04
Pojana Giulio*	ABC PO24
Postorino Paolo	ABC OR29
Pozzi Andrea	ABC PO05
Prati Silvia	ABC OR28
	ABC/ANA/FIS KN01
Prati Silvia *	ABC OR26
Profumo Antonella	ABC OR10
	ABC PO12
Proto Antonio	ABC KN01
	ABC OR12
	ABC OR23
	ABC PO23
	ABC PO34
	ABC/ANA KN03

Volpin Stefano	ABC/ANA/FIS OR06
Wei Ouyang	ABC/ANA KN01
Zangrando Roberta	ABC/ANA OR03
Zarrella Ilaria	ABC KN01
	ABC PO23
Zattini Giorgio	ABC OR30
Zborowska Magdalena	ABC OR22
Zelano Vincenzo	ABC/ANA OR06

Zendri Elisabetta	ABC PO33
	ABC PO39
Zhao Xiangai	ABC PO31
Zielinski Tymon	ABC PO11
Zirino Alberto	ABC/ANA KN01
Zoia Luca	ABC/ANA/FIS OR10
Zuena Martina	ABC PO33
Zuena Martina*	ABC PO39