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Almost ten years of plasters residue analysis in Italy: activity areas and the function of structures

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Abstract

Plasters are porous materials that absorb the substances with which they come into contact. When activities are carried out on floors, the substances used and produced by the activities are poured onto them and absorbed. The chemical analysis of the residues preserved in plastered archaeological floors can therefore provide information on the use of space and the function of structures. In this paper we show a synthesis of the results of the analyses of Roman and Medieval buildings with plastered floors found in Italy, which allowed to identify the traces of different activities such as food production, preparation and consumption, as well as toilet activities. Spot tests aimed at identifying the presence of phosphates, fatty acids and protein residues have been used to analyse the plaster samples. The results were plotted in a GIS environment and maps were generated to understand the distribution of the chemical residues. Gas chromatography-mass spectrometry (GC-MS) has been carried out on specific samples to better identify the organic residues.

Key words: Residue analysis; human activities; plasters; food; Roman; Medieval.

Introduction

Plasters are porous materials that absorb the substances which come in contact with them. When activities are carried out on floors, the substances used and produced by these activities are poured on the floors and absorbed by them (Barba, 1986, 2007). For instance, when a person cooks, there is a close relationship between the dirt in the kitchen and this daily activity - things fall and everything gets dirty. Also, when candles are lighted in a church, the wax melts and falls down. The same situation was true in the past: when people prepared and consumed food, killed animals, made offerings to the gods, washed themselves, the surfaces on which they carried out these activities got dirty.

The chemical residues are absorbed where the activities were actually carried out and cannot be moved from one place to another, as it happens with other archaeological materials such as ceramics or lithics (Barba, 1986, 2007). Therefore, the study of the distribution patterns of the chemical residues preserved in archaeological floors allows for the identification of activity areas (Binford, 1983; Flannery and Winter, 1976; Manzanilla, 1986) and provides information on the use of space and the function of structures (Barba, 2007; Barba and Lazos, 2000; Barba and Ortiz, 1992; Barba et al., 1995; Middleton, 2004; Middleton and Price, 1996; Middleton et al., 2010; Milek, 2012; Ortiz and Barba, 1993; Pecci, 2009a; Pecci et al., 2010, 2013a, 2013b; Salisbury, 2013; Wells, 2004; Wells and Moreno Cortes, 2010; Terry et al., 2004). Although many years of research have shown that also beaten earthen floors absorb the residues left by human activities, plastered surfaces are ideal to be studied (Barba, 2007).

Many investigations have been carried out in different parts of the world in order to identify traces of human activities and to understand the use of space. These investigations have involved the study of different archaeological and ethnoarchaeological contexts, from single rooms and buildings, to the whole site. Ethnoarchaeological and archaeological studies have demonstrated that the chemical compounds in floors do not have a random distribution and that there is a close relationship between certain types of human activities and the chemical enrichment of floors (Barba, 2007; Barba and Lazos, 2000; Barba and Ortiz, 1992; Barba et al., 1995; Middleton et al., 2010; Milek, 2012; Ortiz and Barba, 1993; Pecci, 2009a; Pecci et al., 2013a, 2013b; Salisbury, 2013; Wells and Moreno Cortes, 2010; Terry et al., 2004). The quantity and quality of the residues impregnated in the floors depends on the type of activities carried out and on their duration. The activities that can actually be detected and interpreted are those either repeated frequently or that have generated a considerable amount of residue (Barba and Lazos, 2000).

Recently, also the analysis of the organic residues preserved in the vats of production installations has been implemented in order to understand which was the substance produced (usually oil, wine or fish sauces) (Pecci, 2007; Pecci et al., 2013a, 2013b).

In this paper we show a synthesis of the results of the analyses of Roman and Medieval buildings with plastered floors or vats found in Italy that were analysed at the Archaeometry Laboratory of the Archaeology Department of the University of Siena (2002-2009). The analyses allowed to identify in different rooms, patterns typical of food production and preparation activities carried out in kitchens, production installations, and the identification of activities related to bathrooms and thermae.

All the samples were analysed using spot tests developed in Mexico (Barba, 2007; Barba et al., 1991) aimed at identifying the presence of phosphates, fatty acids and protein residues. Some samples were also analysed to identify the presence of carbonates and the pH level in the samples. Gas chromatography/mass spectrometry (GC/MS) analyses have also been carried out on specific samples in order to better identify the organic residues (Middleton et al., 2010; Pecci et al., 2013). This technique has been extensively used to study the contents of ceramic vessels (Evershed, 2008; Garnier, 2007; Pecci, 2009b; Regert, 2011), but it has been useful also to understand the traces left by human activities on the floors of buildings and in production installations (Barba et al., 1996; Middleton et al., 2010; Pecci et al., 2013a, 2013b, 2013c).

Materials and methods

Sampling

Analyses for this study were carried out on samples taken from different rooms and structures, such as the kitchens of the medieval monastery of San Vincenzo al Volturno (Isernia, Southern Italy), a Late Medieval building at

Castel di Pietra (Gavorrano, Grosseto, Central Italy), a Roman *domus* at Populonia (Livorno, Central Italy) and the Garum workshop at Pompeii (Naples, Southern Italy). Moreover, the results of the analysis of a possible oil production mill, a production vat and a cellar at Donoratico (Livorno, Central Italy), as well as a room belonging to the thermae and the *lavatrina* of the *domus* at Populonia are presented here.

The description of the different buildings and rooms will be presented in the Results paragraph.

A total of 36 samples were taken from the San Vincenzo al Volturno kitchen, following a regular grid of 1x1 m, and 9 samples from the fireplace (Figure 1). At Populonia, 6 samples were taken from the kitchen floor (room D2) of the domus, following a regular grid of 1x1 m, and 2 samples from the hearth (Figure 2). At Pompeii the kitchen floor was sampled following a grid of 30x30 cm, recovering 46 samples, while 7 samples were collected from the cooking surface of the oven (Figure 3). To verify the

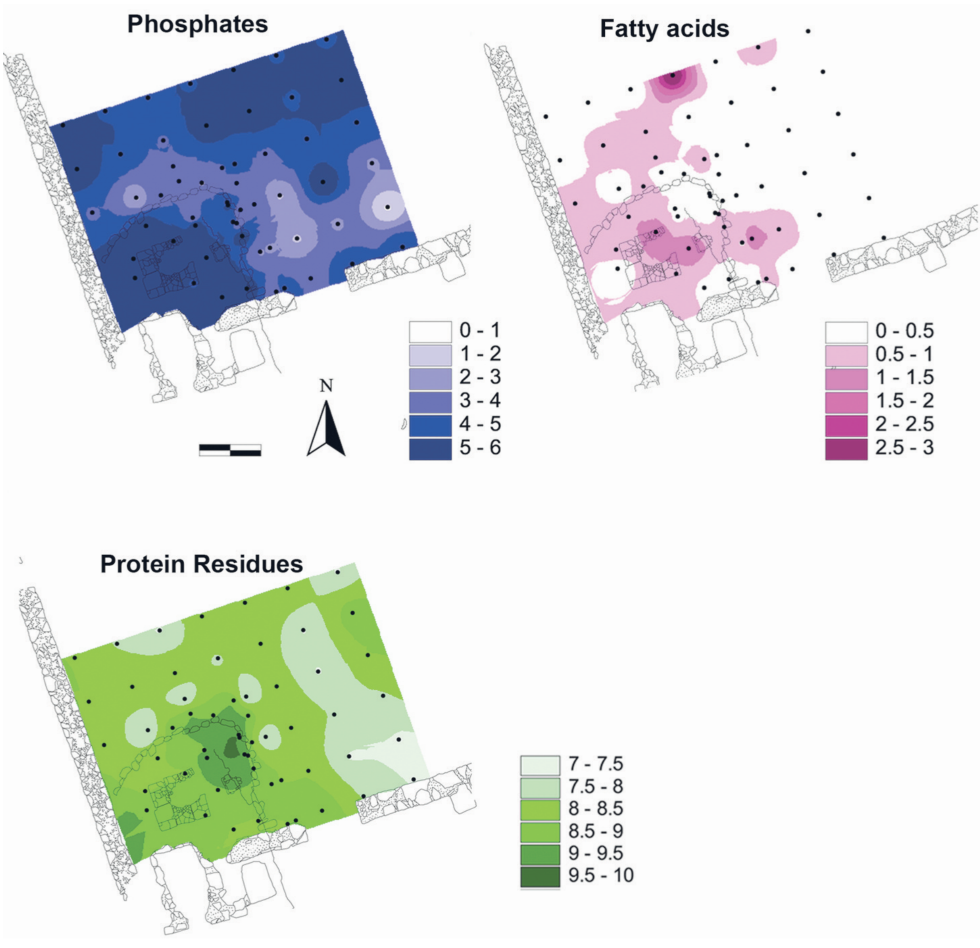

Figure 1. Kitchen of San Vincenzo al Volturno. The distribution maps of phosphates, fatty acids and protein residues are shown. The spots indicate the sampling points.

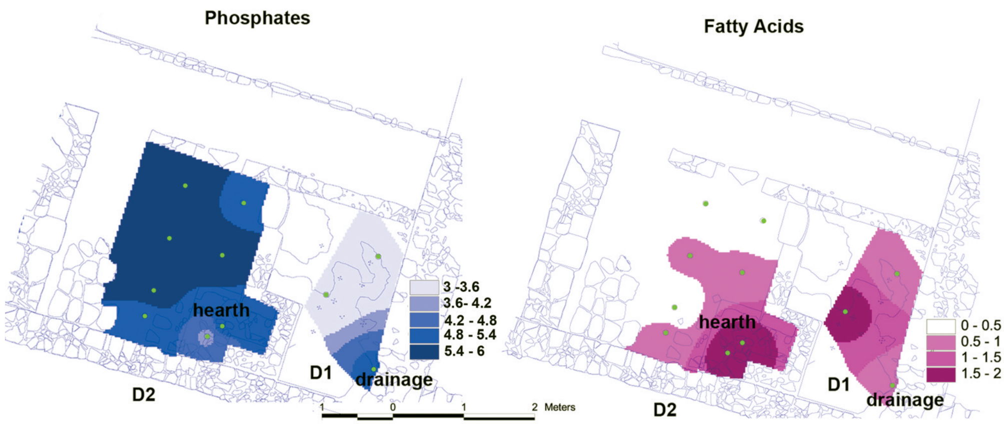

Figure 2. Kitchen (D2) and lavatrina (D1) of the domus at Populonia. The distribution maps of phosphates and fatty acids shown. The spots indicate the sampling points.

possibility of studying the traces of human activities also in materials different from plastered floors, at Castel di Pietra, 92 samples were taken from the beaten earthen floor of a room, probably used as a kitchen, most of which were recovered in the corners of a grid of 50 x 50 cm. Moreover, 8 samples were collected from a hearth, contemporary to the floor, and 9 samples from the older tile hearth, corresponding to the most ancient occupation of the room (Figures 4 and 5). The hearths are made of tiles joined with plaster.

As for the production structures, 16 samples were taken from the mortar used to coat a mill at Donoratico (Figure 6) and 16 from the plastered floor of the corresponding room. 4 samples were taken from the bottom of a vat (made of lime mixed with broken ceramic shards or tiles) and

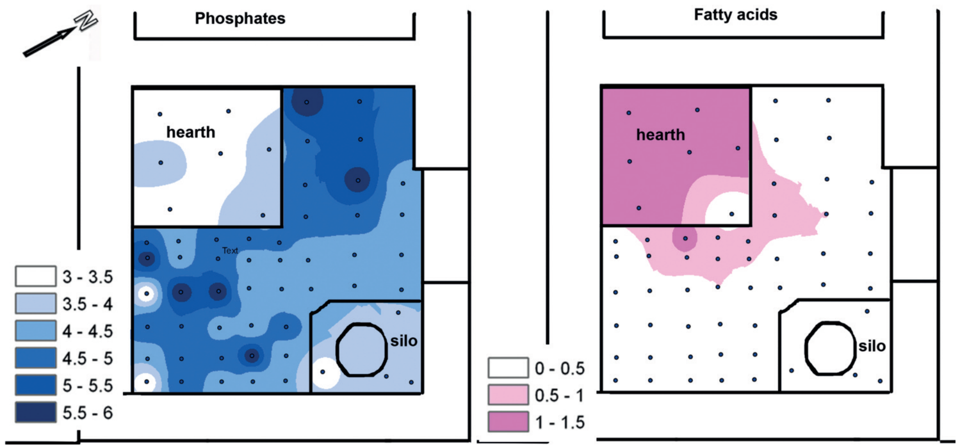

Figure 3. Kitchen at Pompei. The distribution maps of phosphates and fatty acids shown. The spots indicate the sampling points (modified from Pecci and Domínguez, in press).

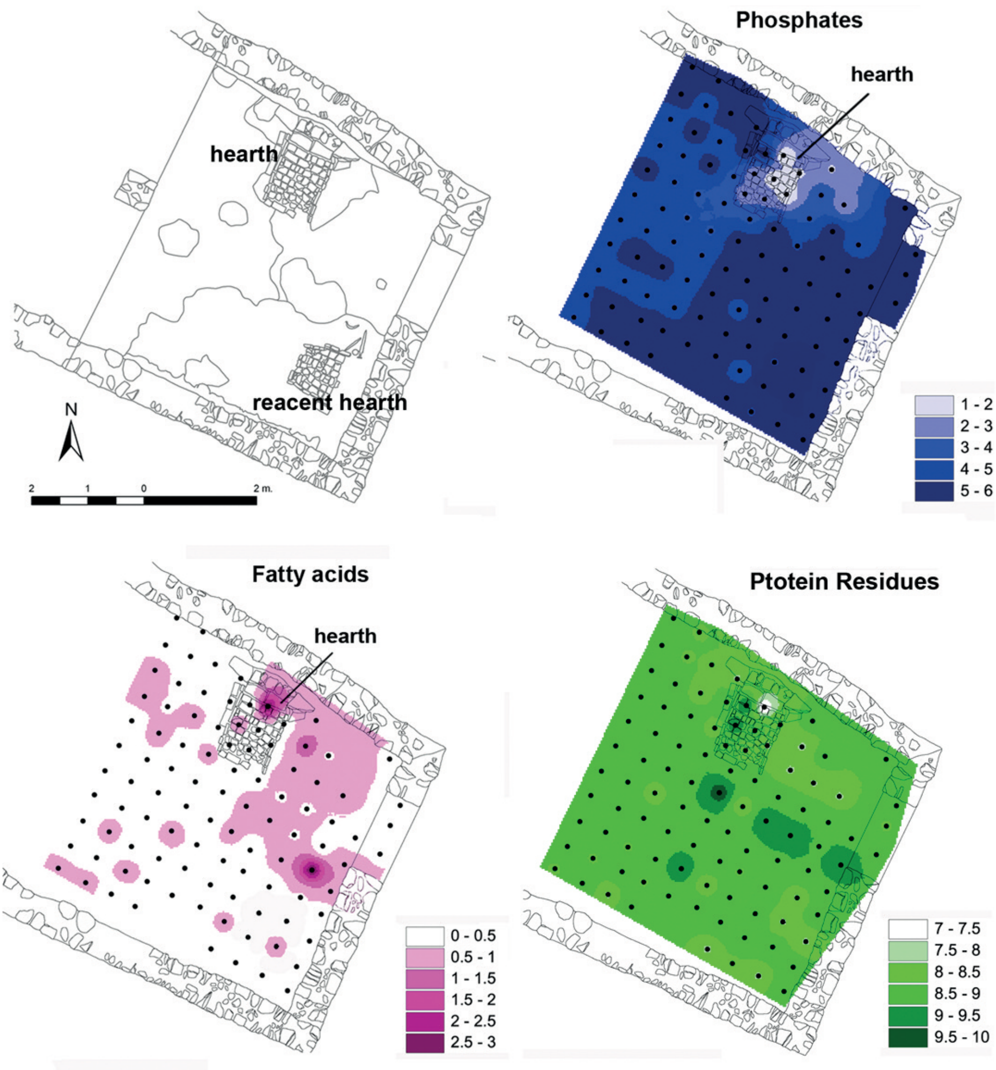

Figure 4. Room at Castel di Pietra. The distribution maps of phosphates, fatty acids and protein residues are shown. The spots indicate the sampling points (modified from Pecci et al., 2009).

71 samples were taken from the floor of a cellar at the same site (Figure 7).

At Populonia, samples were taken from the lavatrina of the domus (Figure 2). Here, due to the poor conservation of the floor, which was made of *opus signinum* (broken ceramic sherds or tiles, mixed with lime) and marble tesserae, only 3 samples were collected. 18 samples were taken from the floor of a room belonging to the thermal complex at the same site. Here, samples were taken only from the sides of the room, because in the center the floor was damaged. To avoid to

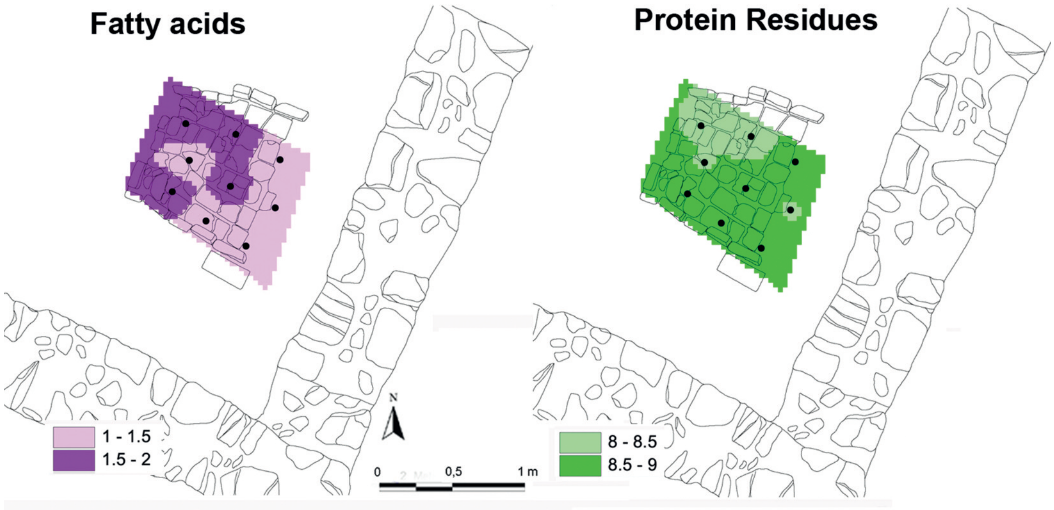

Figure 5. Older hearth at Castel di Pietra. The distribution maps of fatty acids and protein residues are shown. The spots indicate the sampling points (modified from Pecci et al., 2009).

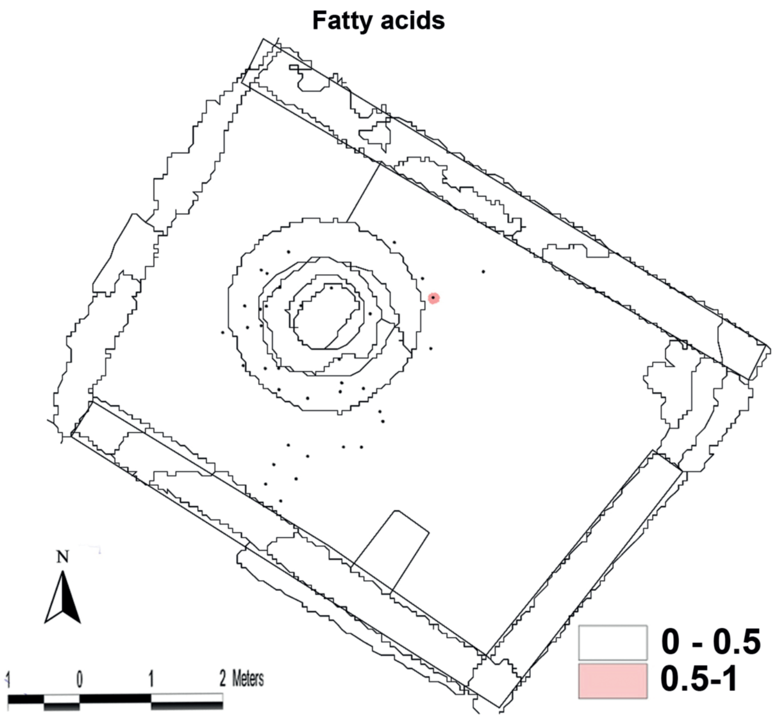

Figure 6. Mill at Donoratico. Sampling points and the distribution maps of fatty acids are shown. In the upper part of the figure there are the chromatograms of two samples, showing the absence of residues.

damage the floor in *opus spicatum*, samples were recovered where there were existing breaks at a distance of approx. 1 m (Figure 8).

When the sampled surfaces were made of broken ceramic sherds or tiles mixed with lime, samples were recovered with a scalpel and only the lime was analysed, to avoid contamination eventually caused by the residues present in used ceramics. In the other cases, samples were obtained from the floors of the studied room by drilling holes of around 1.5 cm diameter.

Samples were taken from the whole layer of the floors, therefore their deepness varied depending on the floor studied.

In general, samples were taken at the intersections of a regular grid covering the rooms. Nevertheless, sometimes it was not possible to exactly follow the grid, due to the presence of archaeological structures, floor conservation etc., as it often happens in archaeological sampling (Wells, 2010).

A total of 11 samples were analysed with gas chromatography-mass spectrometry (GC-MS). All of them come from Donoratico: 4 from the mill and the floor of the corresponding room, 2 from the vat and 5 from the cellar.

Methods of analysis

All the samples were ground to a fine powder and analysed at the Archaeometry Laboratory of the Medieval Area of the Archaeology Department of the University of Siena, using spot tests developed in the Institute of Anthropological Research, UNAM, in Mexico City, where this type of analyses was developed and firstly used (Barba, 2007; Barba et al., 1991). These spot tests

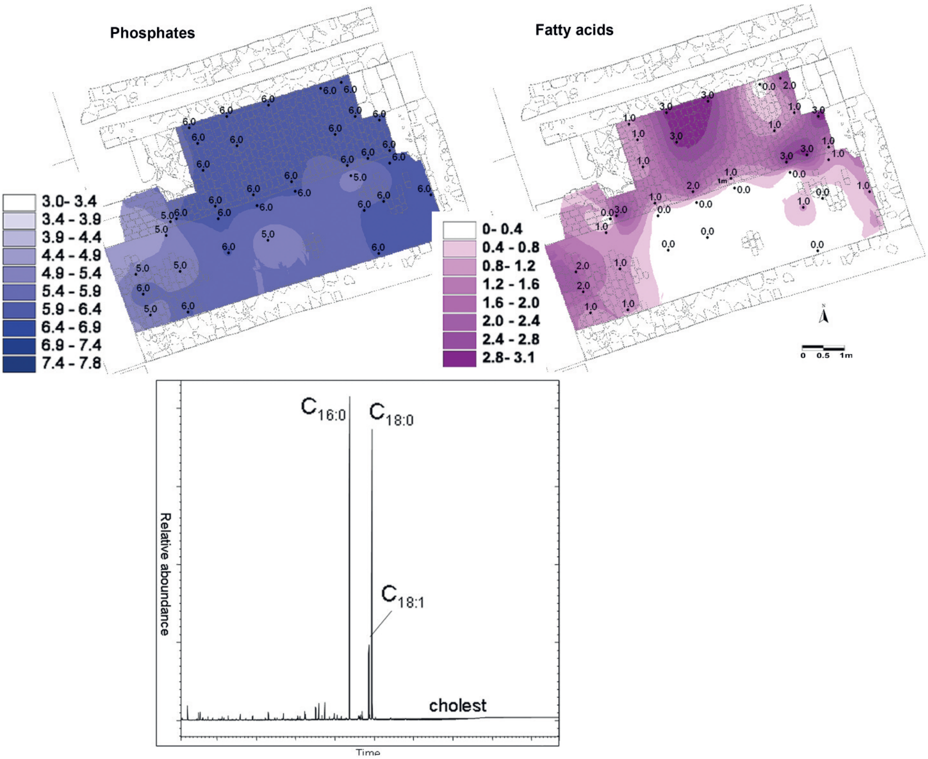

Figure 7. Cellar at Donoratico. Sampling points and the distribution maps of phosphates and fatty acids are shown. In the right part of the figure the chromatogram of one of the samples analysed is shown.

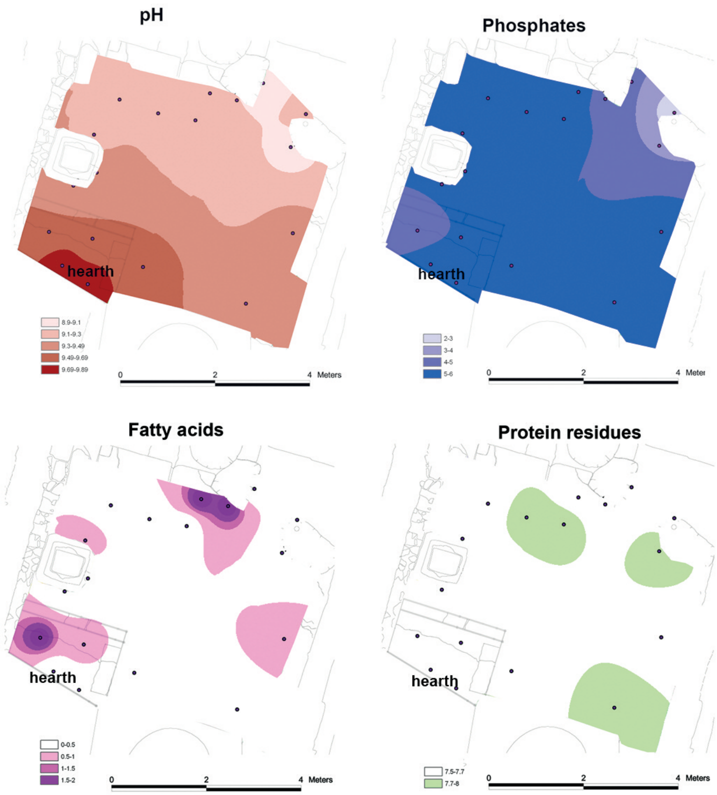

Figure 8. Room attached to the thermal baths at Populonia. The distribution maps of pH, phosphates, fatty acids and protein residues are shown. The spots indicate the sampling points.

have also provided good results in the analyses of activities carried out in the Mediterranean area and in India (Middleton et al., 2010; Pecci, 2009a; Pecci et al., 2013a; Rondelli et al., in press).

Following the methodology developed in Mexico, one sample was analysed for each sampling point. The method used for the analyses is published in Barba (2007) and is reported below.

Phosphates are extracted from the sample using an acid solution to react with ammonium molybdate and produce a yellow phosphomolybdate. Through the reduction reaction with ascorbic acid, it changes to blue molybden compounds. The amount of phosphates in the sample is related to the intensity of the blue colour produced on the filter paper. Once the colour has been fixed with sodium citrate solution and the filter paper has dried, colours are classified by identifying intervals using numbers between 0 and 6. For the procedure, 0.005 g of the powdered sample is placed on the center of a Whatman No. 42, ashless filter circle (45 mm). Two drops of chemical A (a solution of 5.0 g of ammonium molybdate dissolved in 35 ml of 5 N hydrochloric acid and diluted to reach 100 ml with distilled water) are placed on the sample. After 30 seconds, two drops of chemical B (0.5 g of ascorbic acid dissolved in 100 ml of distilled water) are added. Two minutes after the reaction begins, several drops of chemical C (one part of sodium citrate is dissolved in two parts of distilled water) are added, covering the entire sample to stop the reaction (Barba, 2007).

To extract fatty acids, 0.1 g of the powdered sample is placed into a test tube. Two mL of chloroform are added. The solution is heated for 1 minute, until the chloroform is reduced to half. The supernatant is then transferred to a watch glass and two drops of 28.7% ammonia are added. After 1 minute, two drops of 30% hydrogen peroxide are added. If fatty acids are present, bubbles of oxygen produce a foam in a solution of ammonium soaps obtained by the saponification of fatty acids. The foam will start to form and will not disappear. The difference in quantity and stability of the foam is compared using a scale from 0 to 3 (Barba, 2007).

In the Protein Residues test, the amino groups are decomposed by an alcaline reaction producting ammonia gas. For this procedure, 0.01 g of the powdered sample is placed in a test tube. Add 0.01 g of calcium oxide and some drops of distilled water. After cleaning the rim of the tube, two strips of pH-indicator paper are placed on the rim. The test tube is then heated for approximately 1 minute, until the indicator paper turns color by the NH3 vapors. The darker the color, the more protein residues are present. The pH scale values are used to indicate the amount of protein; values of 7.0 - 7.5 indicate no presence of protein residues (Barba, 2007).

The pH (Hydrogen Potential) is a routine test for soils and uses a combined electrode connected to a pH meter. For the procedure, 0.01 g of the sample is mixed with 5 ml of distilled water in a test tube. After shaking well and waiting about 20 minutes, have the reading on display (Barba, 2007).

The scales used are semi-quantitative (0 - 6 for phosphates, 6 - 12 for protein residues and 0 - 3 for fatty acids, while for pH the measured values are considered) (Barba, 2007), and do not correspond to actual quantities. However they allow determining the presence/absence and the relative abundance of the residues. Values above 9 of pH indicate the presence of ash. This suggests the activity of heating with fire, possibly for cooking. Protein residues are present in substances such as blood or meat; fatty acids indicate activities in which fatty materials are involved, such as animal or vegetable fats, like oils or resins used in cooking or incense burning, but can also be related to body washing. Phosphates indicate organic material waste and can be the result of biological deterioration of materials in time. They could also origin from the nature of the material surface analysed (i.e. for beaten earthen floors). However, when the floor matrix is homogeneous at the moment of its construction, the differential enrichment of the floor that can be observed, usually depends on the distribution and diversity of the activities carried out (Barba, 2007). In these cases, phosphates are usually present when food preparation and consumption, or ritual activities involving the offering of organic materials are carried out.

The results of the spot tests were plotted on the plan of the rooms studied using a Geographical Information System (GIS). They were then interpolated with Inverse Distance Weighting (IDW) and kriging methods. This permitted to obtain distribution maps showing the concentrations of each chemical compound in the floor. Although recent studies have shown the potentiality of different interpolation methods (Rondelli et al., in press), here the methods were only chosen depending on the dimension of the rooms and the sampling. IDW was chosen when small surfaces with an intensive sampling were studied, or when few samples were taken, since this method insists on the results obtained in the sampling points, and it has proven to be very useful for the study of small scale areas, while kriging was used in bigger areas (Pecci, 2005).

The distribution maps were then related to the other archaeological materials found on the floors during excavation, such as ceramics, lithics and biological material, in order to trace the spatial distribution of activities at intra-site level.

On the basis of the results obtained with the spot tests for the presence of fatty acids, some samples were also analysed with gas chromatography-mass spectrometry (GC-MS). The GC-MS analysis was aimed at identifying the origin of the lipids present in the samples and in particular to verify the vegetal or animal origin of the fats. For this, the total lipid extract was obtained by following the procedure described by Mottram et al. (1999), using 2 g of grounded sample and chloroform/methanol for the extraction.

GC-MS can also be used to identify the traces of wine residues in the samples, using a specific extraction method that involves an hydrolysis with KOH (Pecci et al., 2013c). Some of the samples analysed and reported in the "Food production" paragraph have been analysed following this procedure (Pecci et al., 2013c).

All the extracts were derivatised adding 25 µl of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Sigma-Aldrich) and heating at 70 °C for 1 h. The analyses were carried using a gas chromatograph CP3800 (Varian, Walnut Crick, CA, USA) equipped with a DB5 30 m, 0.25 mm (i.d.) - 0.25 µm film thickness fused silica capillary column, and a mass spectrometer Saturn 2000 (Varian, Walnut Crick, CA, USA) operated in the electron ionisation mode (70 eV). The mass range was scanned in the range of m/z 40-650. The GC oven temperature was held at 50 °C for 1 min, then it was raised at 5 °C/min up to 300 °C and held isothermally for 10 min.

Results

Food preparation activities

The first case studies presented here involve the analysis of rooms used as kitchens. Several examples of food preparation areas have been studied in Mexico (Barba, 1986, 2007; Manzanilla and Barba, 1990; Ortiz and Barba, 1993; Pecci et al., 2010); but no studies existed on Roman or Medieval kitchens in Italy until the results presented here were obtained. The kitchen of San Vincenzo al Volturno seemed to be a perfect case study to test the possibilities of application of the residue analysis of floors in this new context. The kitchen was a room of 9 square meters. In the south-western corner there was a big fireplace, made of bricks and clay. In the northern part there was a cooking platform, of which only four cavities - the firing chambers- were still in place. A drainage was found near the northern wall of the room, which was used to throw away the leftovers of meals and the garbage produced during the food preparation process (Carannate et al., 2008).

This part of the monastery was abandoned after the attack from the Arabs in 881, when a big fire took place and destroyed it. For this room the function of the space was known, thanks to the presence of the hearth, the ovens, and the abundant zoological remains, therefore it was ideal to identify the patterns that can be considered typical of food production and preparation activities carried out in kitchens (Pecci and Marazzi, 2006).

The results of the analyses show high values of pH in all the room, indicating the presence of ash. This can be related to the fire that consumed the area and that was recognized to be the 881 fire described in the Chronicum Volturnense, related to the Arab attack to the monastery. The evidence for this is the presence of charcoal fragments and ash in the floor. Phosphates were concentrated mainly on the hearth, next to it and in front of the ovens, suggesting they were related to the food preparation and consumption activities. Also high values of fatty acids and protein residues were present on the hearth (Figure 1). These concentrations suggest that the monks intensively used the fireplace, the area around it and the ovens for food preparation (Figures 9 and 10).

Another Medieval room probably used as a kitchen was excavated at Castel di Pietra

(Gavorrano - Grosseto) (Citter, 2009). Here two hearths were identified, related to two different phases of use of the room. As said above, the room floor is of beaten earth, but the hearths are made of tiles joined with plaster. One of the hearts is contemporary to the floor that was analysed, while the other one is older. This room was in use during the 14th century AD. During the excavation, it was hypothesized that the room had been re-used as a shelter for animals. The results of the analyses show that both the hearth and the corresponding floor level are rich in residues. In particular, the fatty acids are concentrated especially on the hearth (where the bricks show burnt traces) and around it, probably as a result of food preparation, as in the previous case study. The same goes for the protein residues. Other concentrations of fats are present in the room and suggest the performance of activities that make the floor 'dirty', probably also related to the preparation of food (Pecci et al., 2009) (Figure 4). The distribution of phosphates is more homogeneous. This distribution can be attributed in part to the nature of the beaten earthen floor (which in itself may be rich in phosphates, as demonstrated by the analysis of floor surfaces of ethnoarchaeological cases and Medieval huts at Grosseto and Donoratico - Pecci, 2009a), but it could also result from the use of the room as a stable, as suggested during the excavation, since feces are particularly rich in phosphates.

Figure 9. Fireplace at San Vincenzo al Volturno (after Pecci and Marazzi, 2006).

Figure 10. Ovens in the kitchen of San Vincenzo al Volturno.

The oldest brick hearth also presents abundant protein residues and fatty acids. These data indicate that the structure was probably used for the preparation of food. The abundance of residues compared to those in the newer hearth suggests a long-term use (Figure 5).

The patterns of enrichment in phosphates, fatty acids and protein residues of the hearths and the floor around them, identified at San Vincenzo al Volturno and Castel di Pietra, are true not only for Medieval kitchens, but can also be found in Roman kitchens. At Populonia, during the excavations carried out by the University of Siena (D. Manacorda, C. Mascione, E. Zanini), the University of Pisa (M.L. Gualandi) and the Soprintendenza Archeologica della Toscana, a Roman *domus* in use during the 2nd century BC was identified (Mascione et al., 2003). It was composed of three rooms, a kitchen (D2), with a hearth located in the wall that divided the kitchen itself from a bathroom (lavatrina) (D1), which was used at the same time to cook and heat the lavatrina, and a third room that was a service room (D3) (Mascione et al., 2003) (Figure 2). In the kitchen, the high pH values of the floor samples can be attributed to the dispersion of ash, not only on the fireplace, but also in the rest of the room (Pecci, 2003). Fatty acids have a high concentration on the hearth, and decrease around it, as it happens at San Vincenzo al Volturno. As for the phosphates, the high values of the floor samples can be explained both as result of food preparation activities carried out in the kitchen as well as by the fact that the material used in the kitchen floor is beaten earth mixed with lime, which might be already rich in organic matter before any activity is carried out.

Another example of Roman kitchen is the one studied in the framework of the Project "From Fishing to *Garum* at *Pompeii* and *Hercolaneum*" University of Cádiz (D. Bernal) and University Ca' Foscari of Venice (D. Cottica), in the so called Garum Workshop at Pompeii (Pecci and Domínguez, in press). Here, as well, the activity carried out in the room was known. However, the challenge of this work was to verify the possibility of performing these analyses in Pompeii, and to understand if the patterns of absorption of the floors were altered by the tremendous consequences of the Vesuvian eruption. The results of the analyses show that fatty acids and protein residues are higher on the surface of the oven, where the cooking activities were carried out (Figure 3) (Pecci and Domínguez, in press). This enrichment is very likely related to the spilling of substances during the preparation and mainly the cooking of the food. Fats in particular have the same pattern that has been observed above for the kitchens of San Vincenzo al Volturno and Populonia.

As for the phosphates, like for the Populonia kitchen, the high values of the floor samples compared to those of the oven surface samples, can be related to the building material. The surface of the oven and the one surrounding the silo are plastered surfaces in very good preservation conditions: here the relatively low values of phosphates of the oven could be related to the fact that phosphates are usually close to absent in well-made/preserved plastered floors and all the enrichment is to be attributed to the residues of the activities performed (Barba, 2007). Although the floor of the kitchen is plastered, the quality is lower than the surface of the oven and the one surrounding the silo, and the continuous walking around has probably damaged it. Nevertheless, it is possible that part of the phosphates enrichment in the floor around the hearth, is related to the falling of dirt produced by the food preparation and cooking activities.

Food production

As part of a long term research carried out at Donoratico for the analysis of the traces left by human activities in the framework of the project Castello di Donoratico carried out by R. Francovich and G. Bianchi at the site, several buildings were studied. Here we present few examples of this research, focusing on those buildings whose mortars and plasters were analysed.

In the so called Area 7000, a Late Medieval mill was excavated (Figure 11). Samples were recovered from both the mortar used to keep together the stones that covered the mill and the plastered floor around it, where it was preserved (Pecci, 2004; Middleton et al., 2010). In fact, ethnoarchaeological case studies have shown that oil production also leaves traces on the floors (Pecci et al., 2013b). The results of the spot tests show that there is no presence of fatty acids in the plaster of the structure or of the floor around it (Figure 6). Here, also GC-MS analysis

Figure 11. Mill at Donoratico (after Pecci, 2004).

was performed on four samples to verify the absence of oil traces. No residues related with oil, usually indicated by the presence of β sitosterol, and relatively high oleic acid were identified in the samples. Therefore, the structure probably was not used to produce olive oil but for grinding some substances that didn't leave fatty residues, such as flour. Another possibility is that the mill was built but never used. The GC-MS analysis of the extract aimed at identifying wine residues showed that no wine residues were present in the samples, either.

Another interesting result was obtained from the analysis of samples taken from the bottom of a Roman vat recovered at the site (Pecci, 2007; Pecci et al., 2013a). The application of GC-MS analysis to the vats of food production installations has revealed to be useful also in other Roman and Late Antique contexts in the Mediterranean area, and has helped to solve the problem of their function (i.e. in Lecce (Puglia) and Case Nuove (Tuscany), in Italy and in Son Peretó (Mallorca) and Plá de Ses Figueres, (Cabrera) in Spain) (Pecci et al., 2013a; Vaccaro et al., 2013). However, here we show the results obtained at Donoratico.The form of the vat, with a circular hole at the bottom was similar to oil and wine production vats (Brun, 2004), but no archaeological features were present that could suggest the actual function. Here the spot tests show absence of fatty acids, which were consistent with the absence of an oil content in the vat. The analysis of two samples with GC-MS confirmed that no fatty acids related with the presence of oil were present in the sample. On the contrary, the GC-MS analysis of the extract for the identification of wine residues, showed that tartaric acid, that is usually considered the marker of wine, together with other acids that are present in this substance, were present in the samples, suggesting that the vat was used for the production of this beverage (Pecci et al., 2013a).

Finally, at Donoratico, a cellar room of the 12th century, characterized by a small channel that leads directly outside the site defensive wall, was also analysed (Figure 12). It had a floor made of tiles, kept together by a lime mortar (Pecci, 2004; Middleton et al., 2010). The presence of the channel suggested that the room was used to get rid of the waste. The results of the spot tests show that phosphates are abundant all over the surface and that fatty acids are mostly concentrated on the northern half of the room. Here five samples were selected for the GC-MS analysis in order to clarify the origin of the residues. No traces of coprostanol and cholestanol were identified in the samples. They are considered to be the markers of feces (Bull et al., 2003) and have been identified in other samples analysed with GC-MS at the Laboratory (Buonincontri et al., 2007). and their presence could have been consistent with the use of the room as a stable. Oil markers, were not identified either. Instead, the presence of cholesterol and

Figure 12. Cellar at Donoratico (after Pecci, 2004).

Figure 13. Hams stored in Sardinia. Traces of the fat left by the ham can be observed on the wall.

high stearic acid ($C_{18:0}$), suggest the presence of animal origin fats in the samples (Figure 7) (Middleton et al., 2010). This suggests that the room was a food storage or production area. The study of modern cellars has shown that animal origin products such as ham, salami or cheese release some fat, while they are stored (Figure 13) and this fat can have enriched the room floor. Therefore the cellar could have been used either to produce or store animal origin products.

Other daily activities

At Populonia, in the same *domus* that was already described, a room, interpreted as a *lavatrina* (D1), was excavated (Mascione et al., 2003). The lavatrina could have served as a bathroom where people washed themselves, and/or as a latrine. Here the floor is made of broken ceramic sherds mixed with lime, but due to the bad conservation of the floor only 3 samples were recovered. The analyses results show a concentration of phosphates in the south-east area where a drainage channel is located. These phosphates could be related to the dirt produced by feces and suggest the use of the drainage for the latrine (Figure 4). The fatty acids could instead be related with bath activities (Pecci, 2003). In fact, ethnoarchaeological studies have shown that the fat of the body, during the washing can fall on the floor and be absorbed (Barba and Ortiz, 1992; López Varela et al., 2006).

At the same site, a room, which was probably in use during the end of the 2^{nd} and the 1st century BC, as a service room to the thermal bath, was excavated (Mascione et al., 2003). On the south-west of the room there is a structure, probably a hearth, where a layer rich of ashes was identified. The high levels of pH in the hearth samples are therefore related to the presence of the ashes (Figure 8). There are no protein residues on the hearth or the floor. Fatty acids are present in two of the samples of the hearth and on the northern part of the room (Pecci, 2003). The absence of protein residues suggests that the hearth was not used for the cooking of food, but possibly for the heating of the room or of water to be used in the thermal baths. The fatty acids concentration on the hearth could be the result of the burning of wood particularly rich in resin, while the one present in the floor at the opposite side of the room, could be related to activities carried out in the structure located to the north or to the use of vegetable oils for the body care, a common practice in Roman times.

Discussion and conclusion

The chemical analysis of the residues allowed to identify patterns that are characteristic of certain types of human activities, such as food production and preparation, and activities related with body care. In most cases, the analyses have provided results that confirm the interpretations of the function of rooms already proposed at archaeological level, allowing to understand the spatial distribution of activities. This is true in particular for the food preparation areas in the kitchens. Here, the fatty acids identified can be related to the animal fats cooked in pots and pans, or that dripped from a grid placed on the hearths, and possibly to the oil used for cooking food. The concentration of protein residues and phosphates in these areas are also related to the preparation of food while the dispersion of high levels of pH is often to be attributed to the presence of ash in the samples.

Sometimes the analyses allowed to suggest functions for rooms and structures different from the one proposed at archaeological level, or for which there were no archaeological features that could suggest an interpretation, such as in the cases of the mill and the vat at Donoratico. As for the food production structures, spot tests have provided good hypotheses on the food produced, but the use of GC/MS on selected samples was crucial to confirm the function of the structures.

In general, it is very important to take into account the material of the samples, as, for instance, phosphates can be influenced by the presence of earth in the floors and high levels of pH can be found in lime plastered floors. This is why the residues spatial distribution needs to be considered for the interpretation of the results.

The chemical analysis of floors could also be applied to the study of ritual areas, where the spilling of offerings make the floors "dirty", as Mexican case studies have shown (Barba, 2007; Barba et al. 1996; Getino and Ortiz, 1997; Pecci et al., 2010) and a test in a Roman villa at Massaciuccoli (Livorno, Central Italy) has suggested (Pecci and Cau, 2012).

Some limitations exist in the use of these analyses. For example, using spot tests it is possible that different activities can leave the same traces. i.e. butchering or cooking will enrich the floors with fats, protein residues and phosphates. The same can be true for ritual activities that involve the offering of food, blood or incenses that on the whole, are rich in phosphates, protein residues and fatty acids. Sometimes performing more specific analyses such as GC/MS allows to solve some of these problems, as shown in the paper, but this is not always the case. The differentiation among the possible activities can be done only by relating the chemical concentrations/absence to the archaeological context.

Another important issue is that porous surfaces absorb all the liquids with which they come in contact Therefore, in the cases in which the same area is used to perform different activities, or there is a re-use of the space, the analyses will identify the residues of the sum of all the activities performed and the results will be more complicate to interpret.

To face these problems, it is always important to remember that chemical analyses of floors must not be considered as an isolated tool, but must be related with all the data that come from the whole study of the archaeological site and that a strong integrated approach to the site is fundamental.

In general, chemical analyses of floors may have an interesting application for the intra site analysis and, used in combination with other techniques, constitute an effective archaeological tool for discerning ancient living patterns.

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