SHORT REPORT OF THE SHORT-TERM SCIENTIFIC MISSION (STSM)

UNDERSTANDING THE SPATIAL HETEROGENEITY OF URBAN ALLOTMENT SOILS

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STSM date: from 22-06-2015 to 10-07-2015

ACKNOWLEDGEMENTS

I am grateful to COST Action TU1201 for providing me the opportunity to realize this Short-Term Scientific Mission with Béatrice Bechet in IFSTTAR.

I would like to thank to Béatrice Bechet for having received me, for all the support given, and for the total availability in carrying out analyses to soils. She has been extremely helpful in providing a framework for my STSM and warning me for very important questions.

I would also like to thank to Teresa Leitão for having encouraged me to apply myself for the STSM and for all the support that she has been giving to me over the past few months.

Finally, I have to say thank you to Nadège Coubriere by the full availability to help me in the laboratory and also to Maria José Henriques for her assistance during the sampling and for helping me in preparing the samples for transport to Nantes.

ABSTRACT

The short term scientific mission on understanding the spatial heterogeneity of urban allotment soils was developed in the IFSTTAR, Nantes, France. The soils of six urban allotment gardens of Lisbon were transported to Nantes and analysed using a portable X-ray fluorescence spectrometer (PXRF). The soils suffered a pre-treatment before being analysed, they were dried and then sieved into fine sand and coarse fractions. It was found that urban allotment gardens aren't very contaminated by comparison with Portuguese and Canadian regulations. Heavy metals like cadmium, mercury, lead, nickel or zinc have lower concentrations then thresholds. It's noteworthy that exists a contamination case with arsenic in one plot of LNEC's urban allotment garden, and the CRIL's urban allotment garden is, overall, the garden that has the greatest number of elements whose concentration exceeds the thresholds.

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1. INTRODUCTION

Most of the world population lives in cities, more specifically more than half of the world population, and the United Nations expect that two-thirds of the planet Earth will live in cities by 2050 (UN (United Nations) 2001). So, it's essential that cities become more and more sustainable. The sustainability concept isn't new, it appeared applied to cities in 1992 at the United Nations Conference on Environment and Development (Eco-92), in Rio de Janeiro, with a document called Agenda 21 (Howorth 2011) where the sustainable urban development concept was defined and further on reaffirmed in 2002 at the World Summit on Sustainable Development, in Johannesburg (Robert, Parris, and Leiserowitz 2005). Sustainable development is:

"…the development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland 1987)

Since 1992 that the sustainability concept has become more popular and, at this moment, it's a key factor in many situations. This concept can be applied to cities. A sustainable city has to incorporate the environmental dimension in its development, protecting the environment. In addition, two more dimensions exist: the social justice and the economic development (Buckingham-Hatfield and Percy 1999). The governmental authorities have to take into account these three dimensions for a good sustainable development. Therefore, an essential factor to obtain a sustainable city is to maintain or, if possible, to increase the green areas in cities. These areas, covered in green urban structure, join a wide number of ecologic functions beneficial for a lot of organisms in urban environment. Furthermore, the green areas are recreational and leisure spaces and a way to frame the urban structure. An example are the spaces where people grow food in the city. These space are known as urban allotment gardens. In cities all over the world the number of these gardens has increased, as well as the demand for them. In times of crisis the demand for these spaces tend to increase (Dubbeling, Zeeuw, and Veenhuizen 2010), given that growing its own food allows someone, who is going through a bad financial time, to save money at the market. According to Pinto (2007) the urban allotment gardens are an important environmental liberating, a supplement of family income and an important source of proteins and vitamins for humans, allowing a better use of the available resources in the interstitial spaces of urban ecosystems.
But not all points are positive: these agricultural spaces are inserted in urban areas so they are exposed to a lot of pollution sources: traffic emission (vehicle exhaust particles,

tire wear particles, weathered street surface particles, brake lining wear particles), industrial emission (power plants, coal combustion, metallurgical industry, chemical plant), domestic emission, weathering of building and pavement surface and atmospheric deposited (Wei and Yang 2010). These pollution sources are also a heavy metals source, which is toxic for plants, animals and human beings above certain quantities. Many researchers have showed urban soils contaminated with heavy metals (Kapungwe 2013, Wei and Yang 2010, Kabala *et al*. 2009, Singh and Kumar 2006), so it's important to evaluate the heavy metals concentration in soils/plants of urban allotment gardens. The soil is the support for plants, and some plants have the capability of accumulating the soil metals. The individual that consumes contaminated vegetables can have serious health problems, so the soil analysis is not only a study of its agricultural capacity but also an indirect study to food safety of the products grown in them. The analysis can be performed by various methods: instrumental neutron activation analysis (INAA), X-ray based techniques, laser-induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), total digestion, pseudototal digestion, single and sequential extraction, flame atomic absorption spectrometry (FAAS) and inductively-coupled plasma atomic emission spectrometry or mass spectrometry (ICP-AES, ICP-MS) (Alloway 2013).

In this Short Term Scientific Mission (STSM) the soils of six urban allotment gardens of the city of Lisbon were analysed by portable X-ray fluorescence spectrometry (PXRF) at Laboratory of Water and Environment (GERS department) of IFSTTAR, Nantes. The PXRF it's a non-destructive, fast and multi-element analyser methodology (Hou, He, and Jones 2004). The portable apparatus are more accessible and the researcher have the results faster than chemical methods, their limits of detection (LOD) are enough for the environmental monitoring for most of soil's elements, although the LOD of PXRF are worse than conventional XRF laboratory equipment and Inductively Coupled Plasma (ICP) technics (Shand and Wendler 2014).

2. URBAN AGRICULTURE

"Urban agriculture can be defined as the growing of plants and the raising of animals for food and others uses within and around cities and towns, and related activities such as the production and delivery of inputs, processing and marketing of products" (Veenhuizen and Danso 2007)

Urban agriculture is not a new concept, it has existed since medieval times (Howorth 2011). Food production is linked to the city's history from its origins. Before the industrial revolution there was not an efficient transport system neither sophisticated techniques to preserve food, therefore the population has to grow their own food near their home (Southall 1998). With the beginning of 20th century urbanization, through the constructions of highways, residential areas, railways and others infrastructures necessary for the growth of cities, the urban agriculture spaces have slowly disappeared. Only at the end of the 20th century the "Urban Agriculture" concept gained importance through political and government agencies, they recognized that agricultural practice in urban areas could have socio-economics benefits for the population (Howorth 2011). But it was not only the politicians who gave importance to urban agriculture, also researchers, urbanists and landscape architects have been giving a great importance to this activity, making an activity that was neglected into an activity with a great potential to create a form of sustainable livelihood. Thus, the urban agriculture is not only linked to research related to the natural sciences (agronomy, pollution and water and soil quality) but also to issues of social and economic nature (land transaction, rural flight and social integration), to urban planning and to issues linked to architecture. A factor that contributed to this change was 1960s' new environmental ethics, with an alternative lifestyle and a sense of self-sufficiency based on renewable energy (Matos and Batista 2013).

It is estimated that about 800 million people all over the world are, in some way, linked to urban agriculture, both in developed countries and in developing countries, producing approximately 15 % of food worldwide (predominantly fruit, vegetables, dairy and small livestock) (FAO 2014). The scale of urban agriculture in the world is well above the perception people have of this activity. For example, in Kenya and in Tanzania two in three urban families are connected to agriculture, in Taiwan more than half of all urban families are members of agricultural associations. The major Chinese cities produce about 90 % of their needs in vegetables through urban agriculture, Japan, Netherlands and Chile are examples of other countries where urban agriculture is well present in cities (Smit and Nasr 1992).

In contrast to rural agriculture, urban agriculture is fully integrated in the urban system through the use and reuse of urban natural resources (Mougeot 2000). In addition to urban agriculture there is also a type of agriculture which is found on the border between urban and countryside or suburban areas with low population density, this is the peri-urban agriculture (Matos and Batista 2013). According to Mougeot (2005), the most important characteristic that distinguishes urban agriculture of another type of agriculture isn't so much its location, but the fact that it constitutes a part of the urban economy and of the ecological and social system. So the urban agriculture uses urban resources (land, work, organic waste and water), produces for citizens, it is strongly influenced by urban conditions (policies, land competition, markets and urban prices) and, finally causes impact in urban system (effects on food security, poverty, ecology and health). The urban agriculture can be present in different areas of cities in different forms, such as: urban allotment gardens, urban landscaping with fruit trees, farms, plantation of medicinal and/or ornamentals plants, grow vegetables along the roads, occupation of empty urban lots and grow food at home in, for example, balconies, rooftops and courtyards (Pinto 2007). Most urban agriculture practitioners are involved is this activity as a livelihood (Freeman 1993), using urban agriculture to get fresh food. These families can direct their income to buy other essential products for Human diet. But the urban agriculture objectives have been changing and the focus is not only alimentation. The urban agriculture has been stimulated by urban sustainability, by the increase of food prices, by the impoverishment of some social groups and by an increased awareness of consumers about the origin of their food (Draper and Freedman 2010; Guitart, Pickering, and Byrne 2012). This activity is often characterized by: being close to markets, present high competitiveness for land, be located in a limited space, use organic residues namely solid organic residues and waste waters, present a low degree of organization, its products being mainly perishable and present a high degree of specialization (Matos and Batista 2013).

The main environmental problems in urban areas are the poor air quality, the heat island effect, floods, low ecological biodiversity, a stream of waste increasing and excessive carbon emissions (Knizhnik 2012). Many of these problems can be solved through the fomentation of urban agriculture, according to Cook, Lee, and Perez-Vazquez (2005) the benefits of urban agriculture based on the following areas:

- Social (leisure, fomenting local groups, therapy for individuals with special needs, rehabilitation of youngsters);
- Environmental (renewal of abandoned urban spaces, diversification of the usage of urban land, increase of biodiversity, preservation of the water, soil and air cycle, reduction of the carbon footprint);

- Human (promotion of sociability through the encouragement of personal qualities such as altruism, the improvement of the quality of life through social interaction, health benefits through physical exercise, better food quality and bigger diversity);
- Economical (stimulus of the local economies, creation of employment and wealth, directly or indirectly);
- Emotional (due to the pause that it can provide to the monotonous and gray everyday of the citizens, allowing them to realize the real dimension of time).

In literature there are many authors who share the same opinion about the urban agriculture benefits (Vásquez-Moreno and Córdova 2013; Pearson, Pearson, and Pearson 2010; Twiss *et al*. 2003; Putegnat 2001; Brown and Jameton 2000; Deelstra and Girardet 2000).

In short, the benefits more frequently reported concerning urban agriculture, in the literature reviewed are:

- Reduces food transport distance, thus saving energy and reducing food prices;
- Reduces the heat island effect;
- Contributes for the conservation of green spaces and urban soils;
- Provides habitats for several species and contributes for local genetic diversity;
- Improves the physical and mental health of citizens;
- Works as a strategy for halting the urban sprawl;
- Improves the food security of cites.

Urban agriculture also has disadvantages, one of the biggest being restrictions the lack of space in cities (Deelstra and Girardet 2000), and another well documented problem is the contamination of soils and vegetables with some pollutants. The urban pollution has being the potential to reduce the yield and the nutritional quality of vegetables (Jäger *et al*. 1992).

2.1 URBAN SOILS

The soil formation is the result of complex biogeochemical processes involving numerous abiotic and biotic factors, acting together. The soil is the interface with the atmosphere, lithosphere, hydrosphere and biosphere (Schwartz *et al*. 2013), so it is a media with huge importance in our world. For the soil formation the degradation and weathering of parent

rock is necessary, generating, through dissolution, oxidation and hydration, a wide range of minerals which form the soil skeleton. The proportion of these soil minerals defines the soil type (Schwartz *et al*. 2013). Unlike the original parent rock, the soil is a full of life environment, dynamic, very reactive and constantly evolving (Lavelle and Spain 2005). The soil has many functions, for example: it is the physical and nutritional support for plant growth, it is the habitat for soil organisms including organic matter decomposers, it acts as a filter for water and also serves to support human diets ((Gobat, Aragno, and Matthey 2010; Vannier 1979).

The soil is comprised by a solid phase and also a gaseous (soil pores) and liquid phase. The solid phase is known as soil matrix and contains the mineral and organic materials. The gaseous phase is termed soil atmosphere and the liquid phase represents the soil water with dissolved substances, it is also known as soil solution (Costa 1975). Thus, we can conclude that soil has four essential functions (Varennes 2003):

1. Supports plant growth, providing the environment for the development of the roots and providing water and nutrients for plants.
2. Recycles waste and dead tissues of animals and organisms, becoming the elements of these materials available again.
3. Provides ecological niches where millions of organisms live, from small mammals to fungi and bacteria.
4. Controls the water movement and its quality in watersheds.

Urban areas are an ecosystem dominated by human beings, giving us the opportunity to study the anthropogenic influence on soil. The urban soils are very altered due to the anthropogenic activities, such as: compression by heavy equipment, topsoil removal, atmospheric deposition of toxic compounds, heavy metal contamination, intensive application of fertilizers and chemical pesticides and contamination due to transports and industry (Pouyat *et al*. 2010; Lohse *et al*. 2008). According to Park *et al*. (2010) the anthropogenic disturbance on urban soils can be seen in two different ways:

- The first one is related with initial urban development. Typically, these perturbations are drastic, involving modifications on soil profile, removing or adding soil, compaction and introduction of vegetation.
- The second one is related with less drastic perturbations, but still harmful. These forms of disturbance include the changes from chemical inputs, such as atmospheric deposition, fertilizers and chemical pesticides applications and precipitation runoff that can be contaminated due to urban activities.

The green urban structure of cities includes cemeteries, green along traffic, all parks, gardens and urban allotment gardens. The soils of urban allotment gardens are very similar morphologically and functionally to agricultural soils. However they differ from the

last one in management, composition and use from the last ones. In fact, the uses of urban soils vary quite often to adapt the spaces to the needs (Putegnat 2001). As the cities are constantly changing, the urban soils suffer with these changes.

One important thing to do in urban soils is to evaluate their quality. According to Doran and Parkin (1994), the soil quality is defined as the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality and promote plant and animal health. The soil contamination is a real problem in many cities (Heinegg *et al*. 2002), they can be contaminated with, for example, heavy metals (Kapungwe 2013), polycyclic aromatic hydrocarbons (PAHs) (Tang *et al*. 2005) and polychlorinated biphenyl (PCB) (Wilcke et al. 1999). There are several problems associated with soil contamination, plants can uptake these contaminants that will generate health problems if Humans consume them. Another problem is the accidental ingestion of contaminated soil particles. The accidental ingestion can be derived from badly washed hands, inhalation of dusts and eating unwashed or badly washed food (Abrahams 2002). I have been referring contamination of urban soils, but it is important to distinguish between “contamination” and “pollution”. A contamination case means that one or more substances have accumulated. In normal cases, these substances wouldn’t be in soil or at least would be at a lower level. On other hand, a pollution case means that the presence of these substances can affect the living organisms (Varennes 2003).

As I have seen, the urban allotment gardens constitute one of the urban soils uses. In the next subchapter I will address the thematic of urban allotment gardens, specifying for the Lisbon case.

2.2 URBAN ALLOTMENT GARDENS – LISBON CASE

The implementation of urban allotment gardens in Portugal is a slightly recent phenomena unlike most of Northern European countries (Rodrigues *et al*. 2014). It was in Lisbon were the first forms of urban agriculture emerged, responding to social changes that were related to migrations and immigration movements towards the city during 1960’s and 1970’s (Matos and Batista 2013) . During this time, plots of vacant land were occupied, and improvised, clandestine and illegal allotments emerged. In the past decade, the number of urban allotment gardens in Portugal have increased due to the effort of municipalities and stakeholders to create areas for this activity and legalize and provide better conditions to the existing ones *(*Rodrigues *et al*. 2014). The urban allotment gardens are responding to new needs for leisure and occupation, reconnecting people to land, countryside and nature. For these reasons, but also because of budget

constraints, urban allotment gardens are being offered as an alternative way of open space with reduced maintenance, which provide sustenance and opportunities for recreation, fostering social cohesion and well-being (Dunnett and Qasim 2000). The urban allotment gardens also have educational and pedagogical benefits, where the knowledge can be shared inter-generationally and citizens can learn practices of growing food (Rodrigues *et al*. 2014)

Urban allotment gardens, as has been seen, are one of the main ways to practice agriculture within city. An allotment is characterized as a small agricultural plot where are grown food, such as vegetables, greenery or fruit trees, but it's also possible cultivate non-food products, such as ornamental or medicinal plants. If these products (food or non-food) are produced within urban system, then this activity is called urban allotment garden (Pinto 2007). The soils of urban gardens are thus specific agricultural soils, localized in urbanized environments and subjected to an intensive agriculture. The urban allotment gardens are placed in areas that have a high biological value because of their moisture characteristics and deeper soil. Plus, the frequent mobilizations and incorporations of organic matter increase the level of microbial life soil and contributes significantly for the maintenance of food webs.

In Portugal a national policy for urban allotment gardens has not yet been developed. This activity is often planned and managed by public or private entities at a local level. Some cities have created programmes to encourage their implementation and in some cases they are integrated in the green infrastructure, or allocated under the land use category of "production and recreational zones" (Rodrigues et al. 2014). This is the case of the municipality of Lisbon, where the urban allotment gardens are found in "production and recreational" zones of Municipal Master Plan (MMP) of Lisbon. The categories of allotments covered by the MMP are social allotment gardens, recreational allotment gardens and pedagogical allotment gardens. Lisbon City Council with the introduction of urban agriculture intends to:

- Contribute to greater environmental sustainability of the city at various levels, namely maintaining ecosystems, contributing to an improvement of microclimate, improving soil quality by organic correction and appropriate cultural mobilizations and improving water systems by increasing soil permeability;
- Contribute to the supply of fresh food in urban centres;
- Contribute to an improvement in public health;
- Value landscape and environmentally urban areas by spatial organization of indefinite use areas;
- Value culturally by general awareness of the population to ancient production systems, approaching city population to rural areas;

- Sensitize all citizens from different social strata for the importance of fresh food and for the nutritional and economic advantages of organic farming.

I mentioned that Lisbon's urban allotment gardens covered by MMP are social, recreational and pedagogical allotment gardens, but what are the main objectives of each one?

Social allotment gardens

The social gardens are used by families or individuals. Their main objectives are to satisfy food needs of individuals/families with few monetary resources. These allotments are intended, therefore, for food production for self-consumption and sometimes, if there is surpluses, to sell the products in local markets with the objective of improve farmer/family incomes.

Recreational allotment gardens

The recreational allotment gardens are also used by families or individuals, its main objectives are the leisure and recreation of users. Users of these type of allotment gardens see in this type of activity an opportunity to improve their quality of life, since they have the chance to escape to city stress and day-to-day work with an approach to rural world.

Under this classification, it also exists community allotment gardens, which are for collective use of residents groups and have as purpose the leisure, recreation and environmental education of communities. They also serve to increase contact among people from the same neighbourhood, by exchanging experiences, thereby increasing social cohesion.

Pedagogical allotment gardens

The aim of these allotment gardens is the environmental education through natural sciences, work and socialization in the garden. They are intended mostly to younger people in order to have, from an early age, a strong environmental awareness of the benefits that agriculture can have. Users can also acquire knowledge about crop cycle, collaborating in agricultural activities necessary for the proper development of allotment gardens. Usually these gardens are inserted in so-called "pedagogical farms" where besides horticultural aspects the people may have contact with many rural traditions.

In the beginning of this subchapter was mentioned that the vacant land plots were occupied during the 1960's and 1970's. In fact, Lisbon's unregulated allotment gardens

reached 300 ha between 1970 and 1987, between 1987 and 1995 this area reduced to approximately 100 ha and stabilized (Cabannes and Raposo 2013). Since 2007, there is a municipal program that is converting several areas in allotment parks. These allotment parks, apart from spaces dedicated to agriculture, also have lawned areas, playgrounds, kiosks, fitness equipment and cycle paths. The first two parks were inaugurated in 2011 – "Quinta da Granja" and "Jardins de Campolide" – and in 2012 was opened another one – "Parque Hortícola de Telheiras Nascente". In 2013 Lisbon City Council created five more parks – "Quinta de Nossa Senhora da Paz", "Parque Bensaúde", "Parque dos Olivais", "Parque Vale de Chelas" and in the surrounding of "Cerca da Graça". Last year the "Parque Hortícola da Boavista" and "Hortas do Casalinho da Ajuda" were inaugurated. In total, in 2014, the city has 10 allotment parks, serving over 400 families. The Lisbon City Council will open more parks, two of them will be in the areas of National Laboratory of Civil Engineering (LNEC) and Psychiatric Hospital of Lisbon (CHPL) ("Parques Hortícolas Municipais" 2015). Currently there are already allotment gardens in these areas, but they are not regulated by Lisbon City Council.

For my STSM I sampled the soils in some of these gardens. As it will be seen later, the allotment parks used were: "Quinta da Granja", "Parque Vale de Chelas" and allotment gardens of LNEC and CHPL. In addition to these allotment gardens, the soil of one non-regulated allotment garden in the edge of a motorway was also sampled. Below are displayed the photographs of sampled urban allotment gardens. For more photographs see the appendix 1.

Figure 1 - Urban allotment garden of Granja antiga

Figure 2 - Urban allotment garden of Granja nova

Figure 3 - Urban allotment garden of Vale de Chelas

Figure 4 - Urban allotment garden of LNEC

Figure 5 - Urban allotment garden of CHPL

Figure 6 - Urban allotment garden of CRIL

2.3 RISKS ASSOCIATED WITH URBAN AGRICULTURE

Urban agriculture is part of an urban environment, therefore it is subject to all urban pollutants. The most important and best documented urban pollutants in the literature are heavy metals, PAHs and PCBs. All of these pollutants can be found in urban environments and therefore in urban allotment gardens. In turn, these elements in urban allotment gardens can be found in soils as well as in vegetables. In this STSM I will focus only on heavy metals.

The sources of heavy metals' contamination in urban environments can be geogenic or anthropogenic. Between these two sources, the anthropogenic one is the major cause of concern, due to economic development and increased levels of human's activity. It is important keep in mind that high concentrations of heavy metals in urban soils may affect people's health. Among the adverse effects on public health from excessive concentration of heavy metals stand out: poisonings in the short-term and oncological diseases in the long term if there is prolonged and growing concentration in the food chain (Pinto and Ramos 2008). In fact, for most people, the primary route of exposure to toxic components is through food intake (Calderón *et al*. 2003). That's why it is also very important to study the uptake of heavy metals by vegetables because these elements can accumulate in the edible portion of crops consumed by Humans. After being present

in Human body heavy metals are easily accumulated due to their non-biodegradable nature and long half-life times for elimination (Guo *et al*. 2012).

In subchapter "2.1 Urban Soils" it was reported that one of the several problems associated with soil contamination is the accidental ingestion of contaminated soil particles. This exposure route is most significant for children due to the time they spend outdoors, getting to mouth objects or their hands that may have been in contact with contaminated soil. Abrahams (2002) analysed data from several studies about the amount of ingested soil by children in various age groups and concluded: the children aged 1-4 years ingest 9-96 mg d^{-1}, children aged 6-12 years ingest only 25 % of the amount of soil consumed by the previous age group and children over 12 years don't ingest more than 10 % of the amount ingested by children aged 1-6 years. Adults only ingest an average of 10 mg d^{-1}.

3. X-RAY FLUORESCENCE SPECTROMETRY

It was in 1895 that Wilhelm Röntgen discovered X-rays. X-rays are a form of electromagnetic radiation, as are radio waves, infrared radiation, visible light, ultraviolet radiation and microwaves (Lucas 2015).

X-ray fluorescence (XRF) spectrometry is a widely-used technique for routine determination of the major elements as well as trace elements. The use of XRF spectrometers for elemental analysis became widespread in the 1950's early 1960's. The researchers who had led to this technique is now possible were, firstly Barkla who observed the X-ray emission spectra and then Moseley, who established a relationship between the frequency (ν) and the atomic number of each element (Z) by a law:

$$\nu = K(\mathrm{Z} - \sigma)^2$$

where K and σ are both constants that vary with the spectral series. It was this discover that made possible the use of this technique (Jenkins, Gould, and Gedcke 1995).

The analysis per XRF is a method based on measuring the intensity of the characteristic X-rays emitted by elements in sample, when excited by electromagnetic waves. The XRF spectrometry is a non-destructive and quick method that analyse simultaneously several elements, this method has been being developed to be included in portable devices (Hou, He, and Jones 2004). In my STSM the analysis of the soil samples were performed using a portable XRF spectrometer (PXRF). During the last 10 years the PXRF devices have been developing quickly (Weindorf, Bakr, and Zhu 2014), gaining popularity among the scientific community through publishing several papers about various themes: pH determination (Sharma *et al*. 2014), soil texture (Zhu, Weindorf, and Zhang 2011),

identification of soil horizons (Weindorf *et al*. 2011), identifying contaminants in the soil (Hürkamp, Raab, and Völkel 2009), analysis of plant nutrients (McLaren, Guppy, and Tighe 2011) and it was also used in agronomy applications (Paltridge *et al*. 2012).

3.1 PRINCIPLES OF X-RAY FLUORESCENCE

An atom is formed by a nucleus around which the electrons gravitate. These electrons are located in different orbits – K, L, M and N – that have well-defined energy levels. When samples are excited by a primary beam of X-rays, interaction of X-rays photons with atoms causes the ionisation of inner shell orbital electrons. As the inner shell electron is ejected the atom becomes unstable, so one outer shell electron occupies the empty place. This transition releases energy in the form of X-ray photons originating the fluorescence phenomenon which are specific of each element (Sharma *et al*. 2015), the energy involved in this transition can be measured and corresponds to the energy difference between the two orbitals. The devices measure the intensity of the characteristic fluorescence radiation of each element.

For all XRF spectrometers the analytical scheme can be divided into four phases (Jenkins, Gould, and Gedcke 1995):

1. Excitation of sample's atoms by bombardment with high-energy photons;
2. Selection of a characteristic emission line of an element by wavelength dispersive spectrometer or an energy dispersive spectrometer;
3. Detection and integration of the characteristic photons to give a measure of the intensity of the characteristic line emission;
4. Conversion of the intensity of the characteristic line emission to a value of element concentration using an appropriate calibration procedure.

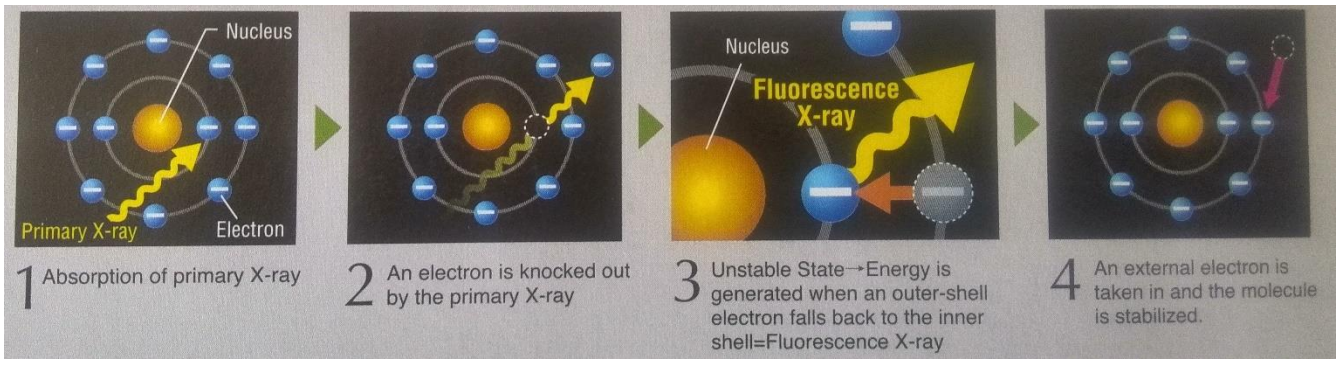

Figure 7 - Illustration of the phenomenon of fluorescence (source: Thermo Scientific equipment catalog)

4. METHODOLOGY

4.1 SOIL SAMPLING

The soil sampling was made on June 17th in six urban allotment gardens of Lisbon:

- UAG regulated by city council:
  - "Quinta da Granja" that was divided into two zones – old part ("Granja antiga") and new part ("Granja nova");
  - "Parque Vale de Chelas";
- Private UAG:
  - UAG of National Laboratory of Civil Engineering (LNEC);
  - UAG of Psychiatric Hospital of Lisbon also known as "Júlio de Matos Hospital" (CHPL);
- Non-regulated UAG:
  - UAG of CRIL. CRIL means internal ring road of Lisbon and is a motorway with an average car traffic of 75 000 vehicles per day (Silva, Ramos, and Lourenço 2010).

Samples were taken at one depth (0-5 cm) to study the anthropogenic inputs because the topsoil layer has, almost entirely, the contamination that came through anthropogenic inputs, while the deeper soil layers contain mostly concentration which had natural origin (Facchinelli, Sacchi, and Mallen 2001) or was leached by the infiltration of precipitation. In each urban allotment garden 3 plots were chosen, and in each one of these plots the soil was collected from 3 different points. The soils were collected with a plastic spade due to the possibility of residual contamination through metal materials. In total 18 bags were collected, and transported, by plane, to IFSTTAR (The French Institute of Science and Technology for Transport, Development and Networks), in Nantes, France. Before the transport, the soils were dried at 40 ºC at LNEC laboratory during two days.

From now on all the work described was performed in IFSTTAR.

4.2 SOIL ANALYSIS

First of all, a plan of what could be done with the soil samples was done, by Béatrice Bechet and me. The following tasks were decided to be performed:

1. Sieve the soil samples into two fractions – < 2 mm and > 2 mm;
2. Milling the < 2 mm fraction for analysis in the PXRF spectrometer;
3. Analyse the soil samples with PXRF spectrometer;

4. Sieve the < 2 mm fraction into > 250 μm, [250 – 63] μm, < 63 μm;
5. Analyse the previous fractions with PXRF spectrometer;
6. Select a sample of each UAG to analyse by ICP techniques.

1. <u>Sieve the soil samples into two fractions - < 2 mm and > 2 mm</u>

Before sieving the soils, they were dried again, due to temperature differences experienced in the plane's baggage compartment. This time they were air dried during two days. The soil samples were sieved with a 2 mm mesh (Figure 8), obtaining two fractions - the fine sand fraction (< 2 mm) and the coarse fraction (> 2 mm) (Figure 9). Each fraction was put into separate bags, properly identified with laboratory reference, Portuguese reference and fraction. Each bag was weighed and its weight registered. The sieving process was carried out using an hotte and I was using rubber gloves to do the sieving to prevent any contamination. The equipment was washed between each sieving first with tap water and then with deionized water.

Figure 8 – Sieving process. On the left the sample before sieving, on the right the same sample after sieving

2. <u>Milling the < 2 mm fraction</u>

For the PXRF analysis the < 2 mm fractions have to present a fine texture in order to facilitate the penetration of X-rays. So the milling process was carried out using the following equipment: Pulvérisette 6, SPRITCH. For each sample 50 g of soil was put into a bowl with 6 balls for 3 minutes at 400 rpm, the bowl was put inside the equipment. The milled soil was transferred to plastic vials. Between each milling the bowl was cleaned with sand and 10 mL of water with 6 balls inside during 15 seconds at 400 rpm.

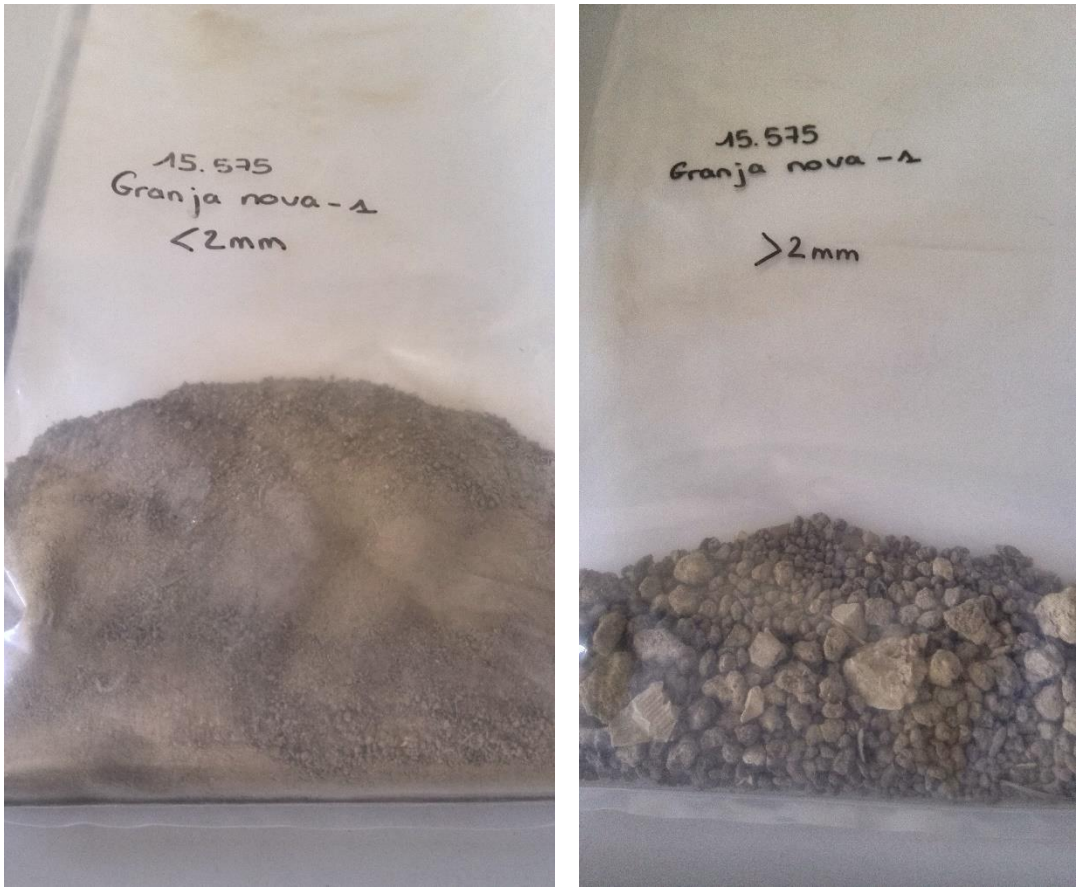

Figure 9 - fine sand fraction (< 2 mm) on the left and the coarse fraction (> 2 mm) on the right

3. Analyse the soil samples with PXRF spectrometer

The samples that were analysed were those which were put in vials, so the milled < 2 mm fraction. The equipment used was the Thermo Scientific Niton Xl3t goldd. All the samples were analysed using two modes – mineral and soil mode – these modes are characteristic of the equipment. For both modes the samples were analysed during 120 seconds, performing three repetitions.

4. Sieve the < 2 mm fraction into > 250 µm, [250 – 63] µm, < 63 µm

This task was done to better understand in which fraction contamination is allocated, analysing then these fractions by PXRF spectrometry. The equipment used to shake the sieves was the Analysette 3, FRITSCH. It was made a dry sieving to obtain the > 250 μm, [250 – 63] μm and < 63 μm fractions, each sieving lasted 5 minutes and the shake amplitude was 2,0 mm. The division of fractions and the washing of sieves are the same as done in point 1.

All the photographs of the used equipment are in appendix 2 and the limits of detection of the PXRF spectrometer in appendix 3.

In my stay at IFSTTAR were these tasks that were performed, the other tasks (points 5 and 6) will be performed by the laboratory technique and then the results will be sent to me. So I can't present all results in this short report. The remaining results will be presented in the longer scientific report.

5. RESULTS AND DISCUSSION

After sieving the soil samples between fine sand fraction and coarse fraction, the results of weighing the fractions are presented in appendix 4 as well as the percentages corresponding to each fraction. To facilitate comparison between different urban allotment gardens a graph was made gathering the three plots of each UAG, so the chart values are the mean values.

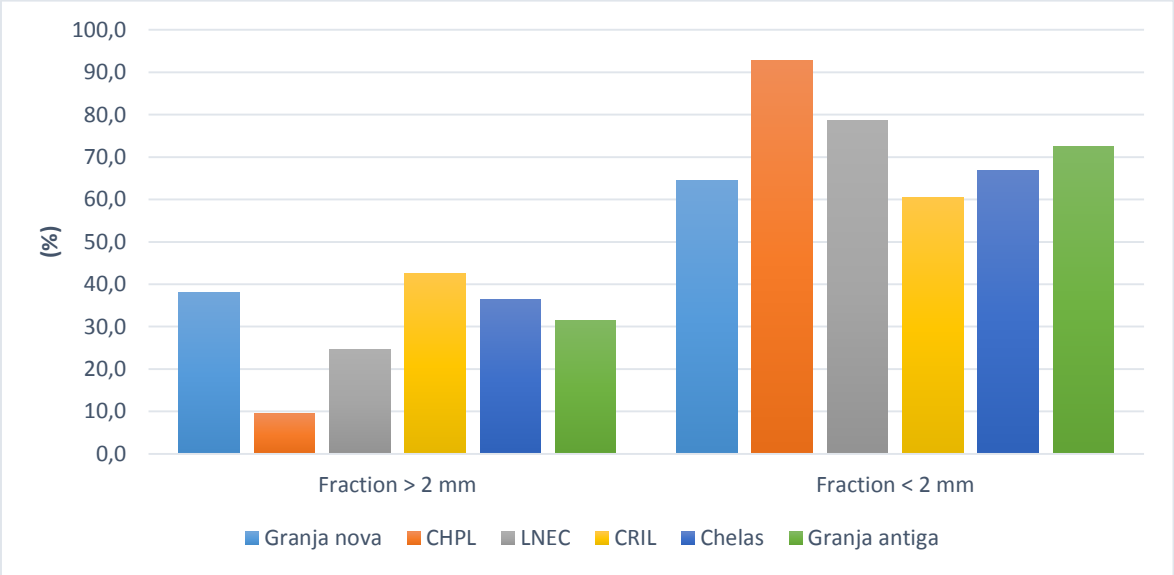

Figure 10 - Percentage of fine sand and coarse fraction for each urban allotment garden

Through the analysis of the figure 10 we have concluded that the samples with coarser elements are: CRIL and Granja nova. On the other hand the sample that presents a higher percentage of fine sand fraction is: CHPL. The soils of CRIL allotment garden

present a lot of construction materials and solid objects from the surrounding roads (see figure 6 to better understand the surroundings), including pieces of mosaics and bricks.

After the sieving the soils were analysed by PXRF spectrometer. To find out if the values are within legal limits I have used two documents, one of them is part of the Portuguese law and the other is part of Canadian law. In Portugal the only governmental document that has heavy metals limits to soils is the Ordinance n.º 176/96 (2nd series) of October 3rd, Ministries of agriculture, rural development and fisheries and environment. This ordinance regulates the concentration of heavy metals in the soils that will receive sludge, the amount of heavy metals in sludge for agricultural utilization as fertilizer as well as the maximum amount of heavy metals that can be introduced annually in the soil. The Portuguese legislation only provides values for cadmium, copper, nickel, lead, zinc, mercury and chromium to the following pH ranges: $pH \leq 5.5$; $5.5 < pH \leq 7.0$; $pH > 7.0$. For elements not covered by this ordinance the Portuguese government recommends the use of Canadian legislation, more specifically the Soil, Ground Water and Sediment Standards for use under Part XV.1 of the Environmental Protection Act (2011). This documents has an exhaustive list of elements and their limit values.
The limit values for the analysed elements in my STSM are listed in table 1, note that for some elements neither document has limit values.

After the analysis of the soils by PXRF spectrometer, a table was constructed with all concentration values for each element. The table in appendix 5 is the result of data processing, it was made by the mean of three repetitions. With this data the following boxplot was constructed, to facilitate the visualization of dispersion of elements concentrations. The box plot only shows the elements for which there are limit values, where the red line represents those thresholds, and also only the elements that have enough concentration values to represent a good box plot (i.e. the elements with most of values below the limit of detection are omitted).

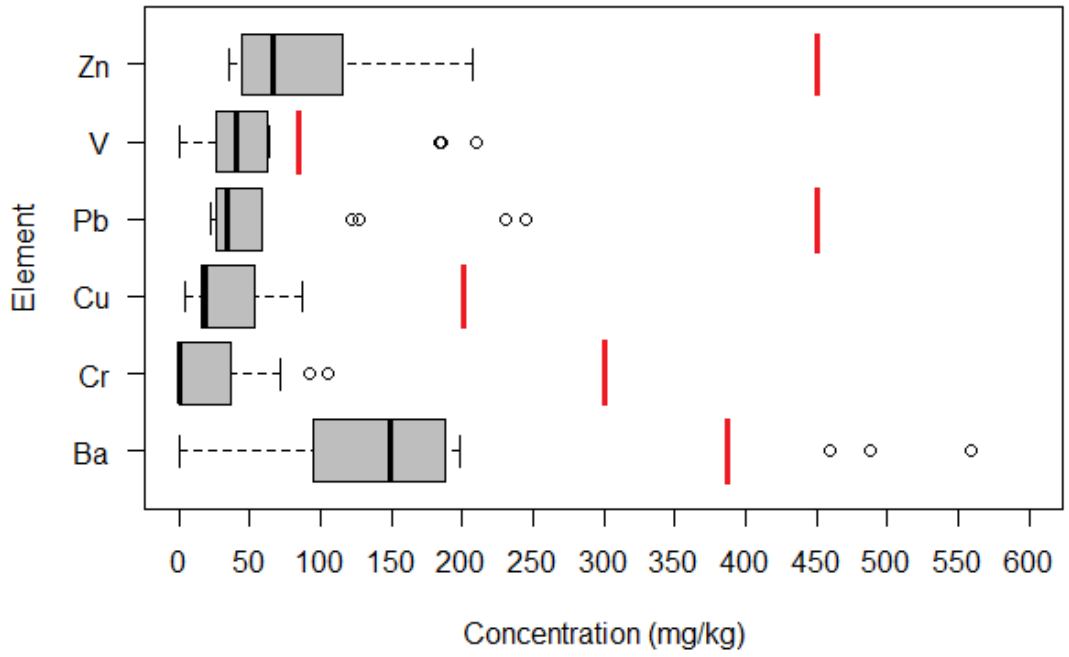

Figure 11 - Concentrations of some elements in soil samples

Looking to figure 11 and appendix 5, we can conclude that some concentrations are above the thresholds. I will group the discussion of the concentration values by element, but I will only consider those with threshold:

- Arsenic:

For this element the maximum permitted concentration is 11 mg kg^{-1}, analysing the appendix 5 it can be seen that all samples are below the limit of detection (LOD) except one – "MJH LNEC" – which has the concentration of 18.13 mg kg^{-1}.

- Barium:

Barium was found in almost all samples, but always below the threshold. Only the UAG of CRIL shows evidence of contamination with concentrations above 390 mg kg^{-1}, this can be seen at figure 11. At the others sites the mean concentration is, approximately, 150 mg kg^{-1}.

Table 1 - Legislated limit values for the analysed elements

ELEMENT	Ordinance n.º 176/96	Soil, Ground Water and Sediment Standards for use under Part XV.1 of the Environmental Protection Act
	(mg kg^{-1})	(mg kg^{-1})
Aluminium (Al)	-	-
Arsenic (As)	-	11
Barium (Ba)	-	390
Bismuth (Bi)	-	-
Calcium (Ca)	-	-
Cadmium (Cd)	4	1
Cobalt (Co)	-	22
Chromium (Cr)	300	160
Copper (Cu)	200	180
Iron (Fe)	-	-
Mercury (Hg)	2	1,8
Potassium (K)	-	-
Magnesium (Mg)	-	-
Manganese (Mn)	-	-
Molybdenum (Mo)	-	6,9
Nickel (Ni)	110	130
Phosphorus (P)	-	-
Lead (Pb)	450	45
Antimony (Sb)	-	7,5
Selenium (Se)	-	2,4
Silicon (Si)	-	-
Strontium (Sr)	-	-
Titanium (Ti)	-	-
Vanadium (V)	-	86
Zinc (Zn)	450	340

- Cadmium:

Cadmium is an element whose concentration is below the LOD for all samples, so this element doesn't need specific concern by local authorities.

- Cobalt:

The threshold for this element is 22 mg kg^{-1}. There are only two plots with concentrations above the threshold all other are below the LOD. These plots are “Granja nova – 1” and “CRIL – 1” with 90.97 and 210.44 mg kg^{-1}, respectively.

- Chromium:

This element was only measured in Granja nova and CRIL allotment gardens, for the remaining sites the concentration is below the LOD. The maximum measured value was 105 mg kg^{-1} in “CRIL – 3” and the minimum was measured in “Granja nova – 3” with 35.44 mg kg^{-1}.

- Copper:

All measured values are clearly below the threshold, 200 mg kg^{-1}. The highest values are found in CRIL and Granja antiga, with mean values of 54.21 and 67.25 mg kg^{-1}, respectively. For all other urban allotment gardens the concentration of copper in soils is very similar.

- Mercury:

As well as cadmium, mercury also has all measurement below the LOD.

- Molybdenum:

The concentration of this element doesn’t vary too much between plots, the range is [2.76, 4.48] mg kg^{-1}, being this values lower than the threshold. For Granja nova, CHPL and Chelas all plots have values below the LOD.

- Nickel:

Nickel concentration is lower than LOD in all urban allotment garden, except the CRIL’s urban allotment garden. At this location the mean value between the three plots is 93.69 mg kg^{-1}, which is a lower value that the threshold.

- Lead:

Lead is one of the most analysed element in urban environments, sometimes with concentrations higher than recommended. The threshold for lead is very different if we use the Portuguese legislation (450 mg kg^{-1}) or the Canadian legislation (45 mg kg^{-1}). If we use the Portuguese legislation, all concentration values are below the threshold. On

the other hand, if Canadian legislation was used there are some value above the threshold: two plots in CHPL, one plot in LNEC and all plots in Granja antiga. Surprisingly, CRIL's allotment garden has lower values than Granja antiga. Granja antiga is the furthest allotment garden of pollution sources.

- Antimony:

This element have all measurements above the LOD, its threshold is 7,5 mg kg^{-1}.

- Selenium:

The threshold for selenium, according to Canadian legislation, is 2.4 mg kg^{-1}. Analysing the appendix 5 we can conclude that almost all samples show a concentration above the threshold, although the difference to the limit is small. In Granja antiga wasn't obtained selenium concentrations in any of the three plots.

- Vanadium:

After analysing vanadium boxplot in figure we can conclude that some plots have concentrations above the threshold. These plots 11 are all localized in CRIL's allotment garden, the mean value of vanadium at these plots is 193.03 mg kg^{-1}.

- Zinc:

The soil samples of all urban allotment gardens have zinc concentrations below the threshold of 450 mg kg^{-1}. The maximum measured value is 207.89 mg kg^{-1} in "Granja antiga – 2", the minimum is 34.82 mg kg^{-1} in "Granja nova – 3" and the mean value is 85.99 mg kg^{-1}.

6. CONCLUSION

First of all, it's important to say that the results will be analysed in depth in the longer scientific report. In this short report I only analyse superficially the results. I tried to give an idea of heavy metals and remaining elements distribution through urban allotment gardens. So we can conclude that the urban allotment garden with more concentration values above the elements threshold is CRIL, showing contamination with barium, cobalt, selenium and vanadium. For the longer scientific report will be analysed the geology of each allotment park, to better understand if the measured values have natural or anthropogenic origin. In addition, will be also analysed the influence of each element in human's health.

This short term scientific mission in IFSTTAR was very helpful for me at personal level as well as professional level. What has been learned will be very important for the conclusion of my master's thesis. I realized that it's important to reflect about urban locals where is acceptable the introduction of urban allotment gardens, urban planners have to take into account several factors for the proper functioning of these parks. It is recommended to perform an early environmental assessment of urban allotment gardens, in order to identify possible problems of contamination and urban pollution.

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APPENDICES

APPENDIX 1 Photographs of sampled urban allotment gardens

Figure 12 - Slope cultivated in the CRIL's urban allotment garden

Figure 13 - Another perspective of the CRIL's urban allotment garden

Figure 14 - Plot sampled in Granja antiga

Figure 15 - Overview of a part of the Granja allotment park

Figure 16 - Plot sampled in Chelas

Figure 17 - Greenhouses in the CHPL allotment garden

APPENDIX 2 Equipment used for soil analysis

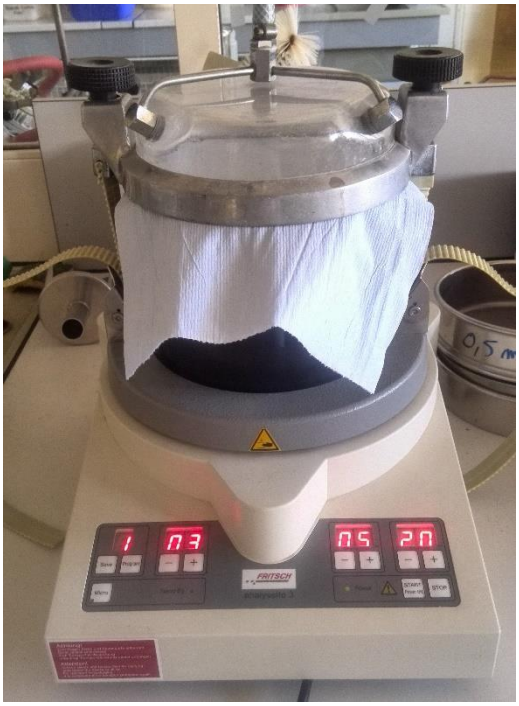

Figure 18 - At the top, from left to right, equipment used for sieving and Pulvérisette 6, SPRITCH. Below, from left to right, Thermo Scientific Niton Xl3t goldd and Analysette 3, FRITSCH

APPENDIX 3 Limits of detection of PXRF Thermo Scientific Niton Xl3t goldd

Element	LOD (*ppm)*
Ca	40
Sc	10
Ti	30
V	15
Cr	25
Mn	25
Fe	30
Co	20
Ni	25
Cu	15
Zn	8
As	5
Se	3
Rb	2
Sr	3
Zr	4
Mo	4
Ag	10
Cd	7
Sn	13
Sb	10
Ba	45
Hg	5
Pb	4
Th	5
U	5
S	250
K	75

APPENDIX 4 Table with the results of weighing the soil fractions

Sample reference	Total weight (g)	Fraction > 2 mm		Fraction < 2 mm		Total (%)
		g	%	g	%	
Granja nova - 1	604,1	146,4	24,2	466,7	77,3	101,5
Granja nova - 2	571,1	271,9	47,6	321,6	56,3	103,9
Granja nova - 3	826,7	351,0	42,5	496,5	60,1	102,5
CHPL - 1	532,7	54,8	10,3	488,3	91,7	102,0
CHPL - 2	606,3	35,2	5,8	583,5	96,2	102,0
CHPL - 3	634,8	76,8	12,1	574,8	90,5	102,6
F LNEC	709,8	195,7	27,6	537,0	75,7	103,2
MJH LNEC	806,0	186,4	23,1	640,5	79,5	102,6
TL LNEC	699,1	159,2	22,8	564,1	80,7	103,5
CRIL - 1	743,2	290,2	39,0	477,2	64,2	103,3
CRIL - 2	769,1	366,1	47,6	427,1	55,5	103,1
CRIL - 3	811,6	333,5	41,1	502,1	61,9	103,0
Chelas - 1	715,3	214,7	30,0	523,9	73,2	103,3
Chelas - 2	695,5	285,6	41,1	433,5	62,3	103,4
Chelas - 3	723,3	275,3	38,1	470,3	65,0	103,1
Granja antiga - 1	583,5	181,0	31,0	426,5	73,1	104,1
Granja antiga - 2	599,0	227,7	38,0	395,2	66,0	104,0
Granja antiga - 3	654,4	165,9	25,4	511,8	78,2	103,6

APPENDIX 5 Results of PXRF analyse to soil

	Al	As	Ba	Bi	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn	Mo	Ni	P	Pb	Sb	Se	Si	Sr	Ti	V	Zn
	g/kg	mg/kg	mg/kg	mg/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg	g/kg	mg/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg	g/kg	mg/kg	mg/kg	mg/kg	g/kg	mg/kg	g/kg	mg/kg	mg/kg
Granja nova-1	26,71	<LOD	175,35	13,28	12,03	<LOD	90,97	36,58	18,65	23,09	<LOD	17,11	<LOD	311,81	<LOD	<LOD	1,16	22,77	<LOD	5,28	193,15	46,61	5,48	64,02	41,75
Granja nova-2	26,30	<LOD	197,62	11,52	15,84	<LOD	<LOD	40,51	20,89	23,48	<LOD	16,52	<LOD	253,49	<LOD	<LOD	1,07	25,55	<LOD	3,17	199,50	55,14	5,83	62,39	45,28
Granja nova-3	25,88	<LOD	134,38	<LOD	9,52	<LOD	<LOD	35,44	32,32	19,97	<LOD	14,42	<LOD	219,69	<LOD	<LOD	1,44	22,27	<LOD	3,99	199,59	49,22	5,17	50,27	34,82
CHPL - 1	11,80	<LOD	<LOD	8,92	33,37	<LOD	<LOD	<LOD	19,00	10,21	<LOD	13,57	<LOD	62,03	<LOD	<LOD	1,88	48,26	<LOD	<LOD	129,32	59,40	2,33	<LOD	132,08
CHPL - 2	14,32	<LOD	<LOD	9,35	15,95	<LOD	<LOD	<LOD	18,14	10,53	<LOD	15,47	<LOD	70,15	<LOD	<LOD	1,46	37,04	<LOD	3,78	158,28	47,24	2,84	<LOD	70,49
CHPL - 3	12,99	<LOD	<LOD	0,00	27,64	<LOD	<LOD	<LOD	15,17	10,41	<LOD	14,90	<LOD	87,71	<LOD	<LOD	1,71	58,46	<LOD	<LOD	135,61	55,82	2,55	<LOD	136,33
F LNEC	29,32	<LOD	96,68	<LOD	27,79	<LOD	<LOD	<LOD	4,50	15,91	<LOD	22,70	<LOD	124,41	<LOD	<LOD	1,34	33,82	<LOD	2,20	219,94	68,36	2,71	25,83	63,14
MJH LNEC	24,46	18,13	<LOD	<LOD	11,17	<LOD	<LOD	<LOD	13,19	10,05	<LOD	23,09	<LOD	79,38	2,76	<LOD	1,18	33,56	<LOD	3,61	247,35	43,97	2,19	26,44	47,50
TL LNEC	23,01	<LOD	167,81	<LOD	21,63	<LOD	<LOD	<LOD	16,24	11,61	<LOD	21,35	<LOD	105,96	2,76	<LOD	1,42	121,86	<LOD	<LOD	183,03	48,80	2,78	28,31	51,57
CRIL - 1	25,75	<LOD	458,88	<LOD	49,37	<LOD	210,44	71,39	53,23	82,84	<LOD	9,06	<LOD	1501,8	<LOD	84,32	2,21	33,09	<LOD	3,67	127,22	476,00	17,82	184,82	93,24
CRIL - 2	32,35	<LOD	558,57	<LOD	40,39	<LOD	<LOD	92,44	55,84	94,32	<LOD	9,14	<LOD	1645,9	<LOD	101,13	2,55	23,72	<LOD	<LOD	141,15	435,68	21,69	209,89	115,08
CRIL - 3	29,51	<LOD	487,85	14,41	45,53	<LOD	<LOD	105,00	53,55	87,09	<LOD	8,59	<LOD	1578,8	3,86	95,62	2,20	25,84	<LOD	<LOD	131,00	437,49	17,88	184,38	75,43
CHELAS - 1	25,42	<LOD	94,26	16,56	13,76	<LOD	<LOD	<LOD	17,48	15,10	<LOD	21,03	<LOD	133,95	<LOD	<LOD	1,19	34,03	<LOD	3,59	186,84	43,23	3,31	38,46	43,37
CHELAS - 2	27,68	<LOD	116,99	16,97	10,31	<LOD	<LOD	<LOD	12,56	16,16	<LOD	21,99	<LOD	107,12	<LOD	<LOD	1,10	37,39	<LOD	3,36	193,33	40,96	3,15	39,79	44,23
CHELAS - 3	28,22	<LOD	150,82	13,65	20,85	<LOD	<LOD	<LOD	14,98	18,61	<LOD	19,81	<LOD	108,76	<LOD	<LOD	1,07	29,09	<LOD	3,60	180,08	63,03	3,20	42,04	38,42
Granja - 1	25,79	<LOD	147,91	11,10	24,73	<LOD	<LOD	<LOD	51,92	21,47	<LOD	20,49	<LOD	250,39	3,31	<LOD	2,91	126,43	<LOD	<LOD	197,43	91,23	3,95	44,35	192,19
Granja - 2	19,70	<LOD	187,37	<LOD	52,78	<LOD	<LOD	<LOD	87,13	21,89	<LOD	18,29	<LOD	308,34	4,48	<LOD	3,62	244,47	<LOD	<LOD	183,03	139,80	3,72	44,63	207,89
Granja - 3	19,30	<LOD	157,62	<LOD	65,08	<LOD	<LOD	<LOD	62,72	16,64	<LOD	17,67	<LOD	204,50	<LOD	<LOD	2,98	230,32	<LOD	<LOD	183,69	115,86	3,02	<LOD	114,94