ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 5, Issue 6, November 2016

Analysis of Pesticides: a First Study toward a Smart Analysis

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Abstract*— In this paper we propose to evaluate the amount of a specific set of pesticides/herbicides from the evaporation or desorption of harmful molecules from the soil. The aim of this work is focused on the definition of reliable pattern that can be detected by disposable gas sensors in order to create a robust gas sensor network for a real time monitoring of vast agricultural areas. As first results we discussed a new automatic procedure for pesticides analysis implemented to define a comparing table to be matched by the as sensors responses. In particular, we analyzed two common pesticides (Chlorpyrifos and Pendimethalin) by measuring their desorption from fibers placed in contaminated soil for different times.

***Index Terms*— pesticides monitoring, solid phase micro extraction (SPME) measurements, gas chromatograph/mass spectrometer (GC-MS).**

I. INTRODUCTION

A large number of pesticides have been widely used to improve the agricultural productivity [1]. However, their application should be minimized owing to its harmful effect on the environment [2-6]. The usage of high amount of pesticides pollutes the food chain and is highly hazardous to the human health [7-8]. Therefore it is important to monitor the pesticide amount in the crops and in the environment in real time to ensure the good quality of the products thus increasing the level of food security [9-12], or to control the presence of pesticide residues in soil devoted to biological production.

Classical analytical methods for determination of pesticide residues are often laborious, time-consuming, expensive, require large amounts of toxic organic solvents and usually involve many steps, leading to loss of some analytes. Additionally, they require very expensive equipment such as gas or liquid chromatography [13-15]. Therefore, the reduction of time and costs of this kind of measurements is strongly recommended.

The Italian Ministry of Foreign Affairs funded a project addressed to satisfy this need [16]. In this project we want to develop a low–cost system based on gas sensors [17] capable to monitor in real time the pesticides that release residues in air. The system shall be able to communicate with other sensor probes in order to create a sensor network able to produce a map of the measured compounds. Since the application is related to extended agricultural areas, the sensing system should exploit disposable devices based on low cost materials. Moreover, another mandatory requirement of the system is the possibility to detect the pesticides residues both qualitatively and quantitatively, from the analysis of the evaporated fraction or desorbed products of the analytes in air. This goal will be reached by using gas sensors and developing a gas sensors network able to map in real time the soil quality in.

The project is actually carried out by the group of Prof. Fabio Leccese of the Science Department of the University of “Roma Tre” with the group of Dr. Rada Đurović-Pejčev from the Institute of Pesticides and Environmental Protection in Belgrade and supported by others research group such as the Institute for Microelectronics and Microsystems (IMM) of the Italian National Research Council (CNR) and some small and medium enterprises (SMEs) of the Rome Area. The expertise of these teams are strongly complementary and this collaboration can favor the development of a new class of low cost devices for the control of food quality and soil contamination. The first results of this research activity is shown in this paper. In particular, the first problem faced was to define a reliable measurement procedure in laboratory that could permit a significant comparison with a real operative scenario. Within this context, the first step was the definition of a little set of pesticides usable for the experiment; the second was the definition of a correct experiment design. For the first step, we consider some characteristics such as availability on the world market, diffusion on the world market, cultures on which the pesticides are used molecules size and pesticides evaporation rate. Once chosen the pesticides, we defined an experiment design by using standard instrumentation to highlight the possibility to obtain valuable data from measurements made in air.

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II. MATERIAL AND METHODS

A. Evaluation of the Pesticides

In order to evaluate a significant procedure for our investigation, the first step of our activity has been focused on the definition of a limited set of pesticides. Some practical rules have guided our choices:

- Availability on the market: the chemical compound must belong to a well-known class of substances typically commercialized in the different countries.
- Diffusion: a pesticide/herbicide widely used is, at the same time, easy to recoup on the market and probably used for a large variety of crops even if it is not the best product available in the market.
- Presence of the active principle at least in the two markets where the research groups are located (Italy and Serbia) to ensure the usage of the same substance for the experiments. Obviously if the molecule is available in Italy, it can be purchased also in the rest of the European Union.
- Pesticide vapor pressure: since the final goal of the project is related to the usage of gas sensor, it is crucial to choose the molecules with the highest probability to evaporate or desorb.
- The similarity of the inert substances present in the purchasable commercial products with the active principles inside in Italy and in Serbia.

After a deep market analysis, Table 1 summarizes the obtained results:

TABLE I. ACTIVE PRINCIPLE AND COMMERCIAL PRODUCTS AVAILABLE IN ITALY AND IN SERBIA

Active Principle	Commercial Products (Name, Producer, Format)	Used for	Used against
Tefluthrin [18]	Force (Syngenta - micro granules); Force 20 CS (Syngenta – capsules in suspension); Microsed Geo (Euro TSA – granules); DIASTAR MAXI (Chimiberg – granules); Underline 0.2 G (Chimiberg – granules); Teflustar (Chimiberg – granules); Geaterstar (Diachem – granules)	Sugar Beet, Wheat, Corn, Sorghum, Rape, Sunflower, Soybean, Tomato, Eggplant, Carrot, Celery, Turnip, Cabbage, Cauliflower, Lettuce, watermelon, fennel, Bean, Green Bean, Pea, Potato, Horticultural and ornamentals, turfs of: golf courses, sports fields, ornamental lawns	Chaetocnema t., Atomaria l., Scutigerella i., Tipula spp., Agriotes spp., Bibio h., Delia spp., Melolontha m., Agrotis spp., Diabrotica spp.., Chaetocnema t., Ceutorhynchus p., Psila rosae, Millipede, Centopede, Sphenophorus spp., Amphimallon solstitialis, Mole cricket
Chlorpyrifos [19]	Cyren 7.5 GR (Cheminova – granules); Cyren 44 Ec (Cheminova – concentrated liquid); Thitan 7.5 GR (Chimiberg – granules); Poker 7.5 (Gowan – granules); Nufos 7.5 G (Cheminova – granules); Zelig GR (Adama – granules); Vebi Clorpirifos 7.5 G (Vebi – granules);; Dursban (Dow – liquid); Rotiofen gold (Adama – liquid); Terial 40 L (Dow – liquid); Cator (Dow – liquid); Piridane 480 (Dow – liquid); Pychlorex 48 EC (Dow – liquid)	Apple, pear, quince, medlar, loquat, peach, nectarine, Vine Wine, Vine table, Mandarin, Clementine, Corn, Strawberry, Tomato, Eggplant (open field), potato (in open field), Rape, Palm.	Codling moth, Tortricids embroiderers, Cydia and Scale insects, Aphids, Cacopsylla apple, Asian bug, Miridi, Anarsia, Thrips, Fruit fly, Moths, Leafhoppers, Metcalfa, Borer, Noctuids, Colorado beetle, Meligete, Red palm weevil.
Bifenthrin [20]	Bifenax (I.N.D.I.A. – liquid); Bifenase (I.N.D.I.A. – aerosol); Roris (Linfa – liquid); Permecid (Kollant – liquid); Badogel (Linfa – gel); Bixan (Orvital – gel)	greenhouse ornamentals and cotton	Aphids, Worms, Ants, Gnats, Moths, Beetles, Earwigs, Grasshoppers, Mites, Midges, Spiders, Ticks, Yellow Jackets, Maggots, Thrips, Fleas, and Termites

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Pendimethaline [21]	Click Duo (Sipcam – liquid); Most Micro (Sipcam – liquid); Stomp Aqua (Basf – liquid); Stomp 330-E (Basf – liquid); Activus EC (Adama – liquid); DOST 330 EC (Genera - liquid); Stomp 2G (Basf – granules); Gramilane G (Diachem – granules); Ready Germiplus (Everris – granules); Penthium EC (Adama – liquid); Ordagro EC (Adama – liquid); Cripton EC (Adama – liquid); Stopper P (Adama - liquid); Sharpen 40% SC (Sharda – liquid); Sharpen 33% EC (Sharda – liquid); Pendiphar (Sharda – liquid); Penny (Sharda – liquid); Pendiwin (Sharda – liquid); Optimist 330 EC (Sharda – liquid); Pendicol 33 EC (Sharda – liquid).	Leafy Lettuce; leafy brassica (mustard greens, kale); alfalfa and grass hay; fresh legumes/dry pulses; citrus; tree nuts; carrot/other root and tuber; bulbs: onion; dry and green onion; asparagus; leeks; celery, celeriac	Between the graminacee: Alopecurus myosuroides, Apera spica-venti, Digitaria sanguinalis, Echinochloa crus-galli, Panicum dicothomiflorum, Poa annua, Setaria spp and Sorghum halepense. Between the dicotyledons: Amaranthus spp, Anagallis arvensis, Capsella bursa-pastoris, Cardamine hirsuta, Cerastium arvense, Chenopodium album, Fumaria officinalis, Heliotropium europaeum, Mercurialis annua, Myosotis arvensis, Papaver rhoeas, Portulaca oleracea, Ranunculs repens, Solanum nigrum, Sonchus arvensis, Spergula arvensis, Stachys annua, Thlaspi arvense, Urtica urens, and Viola spp.

The four products shown in table 1 had the request characteristics. In order to make the first measurements as soon as possible, between these active principles, a further selection was made on the base of the immediate availability on the shops in Italy and in Serbia. The results was to buy products based on chlorpyrifos and pendimethaline.

B. Materials

Pesticides chosen for the study were chlorpyrifos and pendimethalin. In the optimization experiments, analytical standards of pure compounds were used (Dr Ehrenstorfer, Germany) (Table 2). Stock standard solutions containing 1 g/dm^3 of each pesticide were prepared in acetone, and the working standard solutions were prepared weekly by diluting the individual stock solutions with acetone. In the experiments with soil samples, commercial products of pesticides were used. In particular, for chlorpyrifos, Pyrinex 48 EC [22] that consists 480 g/l of chlorpyrifos as active substance and Dost 330 EC [23] for pendimethalin (330 g/l of pendimethalin) were used.

TABLE II. PHYSICO-CHEMICAL PROPERTIES OF STUDIED PESTICIDES [24,25]; M_R, MOLECULAR WEIGHT; S_W, WATER SOLUBILITY; H, HENRY'S CONSTANT

Pesticide	Chemical class	M_r (g/mol)	S_w mg/dm	H Pa m^3/ mol
Chlorpyrifos	organophosphorus	350.6	1.4	0.676
Pendimethalin	dinitroaniline	281.3	0.33	2.728

C. Design of experiments

A typical scenario of the use of the pesticides foresees that a farmer, using the suitable machines, sprinkles the pesticides on plants and soil.

At this point, the first challenge was related to the simulation of a real scenario but also to use a classical instrumentation to get reliable data and to compare these measurements with the future results obtainable with the gas sensors. For this reason, we decide to sprinkle with the chosen substances under test, an uncontaminated soil sample collected in Serbia. The soil was air dried and sieved (2 mm) before the use. Then, starting from the contaminated soil, we collected the pesticides by using standard fibers immersed in a hole formed in the soil sample. Fig. 1 shows the sequence of the steps followed for the solid phase micro extraction measurements.

ISSN: 2319-5967
ISO 9001:2008 Certified
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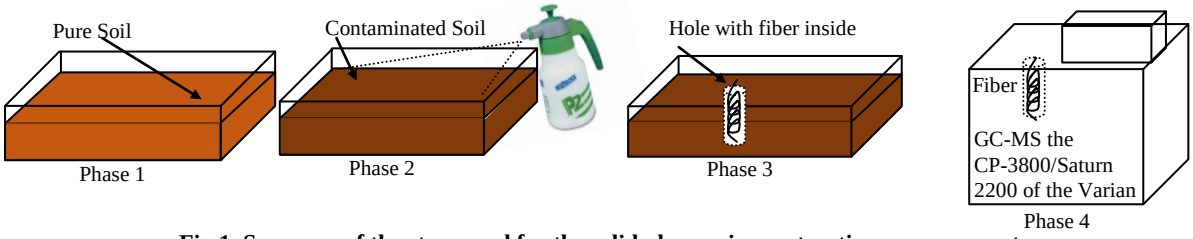

Fig 1. Sequence of the steps used for the solid phase micro extraction measurements.

For the solid phase micro extraction (SPME) measurements, we used the 100 µm polydimethylsiloxane (PDMS), 85 µm polyacrylate (PA) and 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibers (Supelco, USA). As detection device, we used a gas chromatograph/mass spectrometer (GC-MS) the CP-3800/Saturn 2200 of the Varian (Australia). A 30 m x 0.25 mm x 0.25 µm, VF-5ms column (Varian) was used. The thermal desorption of analytes from SPME fiber was conducted according to previously established optimal conditions for injector port (7 min at injector temperature of 270 ^{0}C) [26]. The GC was programmed as follows: initial temperature was 120 °C, then increased to 170 ^{0}C at 8 ^{0}C/min and held for 4.5 min, increased to 270 °C at 9 °C/min and held for 6.5 min. Helium was used as the carrier gas and its flow rate was 1.1 ml/min.

The ion trap mass spectrometer was operated in the electron impact/selected ion monitoring (EI/SIM) mode. The ion trap and transfer line temperatures were set to 220 °C and 250 °C, respectively. One specific pesticide ion was selected for detection and quantification, while the second one was used for confirmation. The ions inspected were 314 (258) for chlorpyrifos and 252 (191) for pendimethalin.

In order to determine the optimum condition for SPME measurements (sorption of pesticides on fiber coating), three different SPME fibers were tested as well as different time of their exposure to pesticides under study. Optimization was done using 2.5 ml of aqueous solution containing 100 µg/l of pesticides studied. The tested SPME fibers were placed in the gas phase above the solution for sorption, and after the appropriate time they were put in the injector port of GC-MS for pesticides desorption.

Efficiency of previously optimized SPME method was tested in the analysis of soil samples contaminated with the same pesticides. Soil samples (250 g) were fortified with commercial products (separately for each pesticide) and placed in the flowerpot. The applied doses were the maximal recommended doses for each product (8 l/ha and 6 l/ha for Pyrinex 48 EC (480 g/l of chlorpyrifos) and Dost 330 EC (330 g/l of pendimethalin)), respectively. These doses were equivalent to 3.2 mg (chlorpyrifos)/kg (soil) and 1.65 mg (pendimethalin)/kg (soil).

After 24 h and 7 days of soil contamination with pesticides, the SPME measurements were performed. In both cases, it was made a little hole in the middle of flowerpot where SPME fiber was exposed for sorption of pesticide. After the previously established optimum time of SPME fiber exposure, the fiber was transferred into GC-MS injector for desorption.

D. Results and discussions

Different experimental parameters that could affect SPME measurements i.e. sorption of pesticides on SPME fibers were optimized using spiked water samples.

Optimization was done by a well-structured approach including the choice of a most suitable SPME fiber, and determination of optimal time for sorption.

Time dependence of the amount of pesticides desorbed by the fibers was investigated at intervals ranging from 30 to 120 min. The results indicate that for both pesticides and the fibers 120 minutes were a sufficient time interval for obtaining large signals (see figure 2). As can be seen, the best sorption efficiency for both pesticides was achieved using PDMS fiber, so this fiber type was chosen for additional measurements.

Efficiency of the method previously optimized for SPME of aqueous solutions, was tested in the analysis of soil samples contaminated with commercial products of pesticides under study. At this purpose, the fibers have been inserted in a hole of the soil to absorb the pesticides. The results obtained after 24 h and 7 days of soil contamination with pesticides are presented in the Fig. 3. The obtained results showed that both pesticides are measurable in the gas phase.

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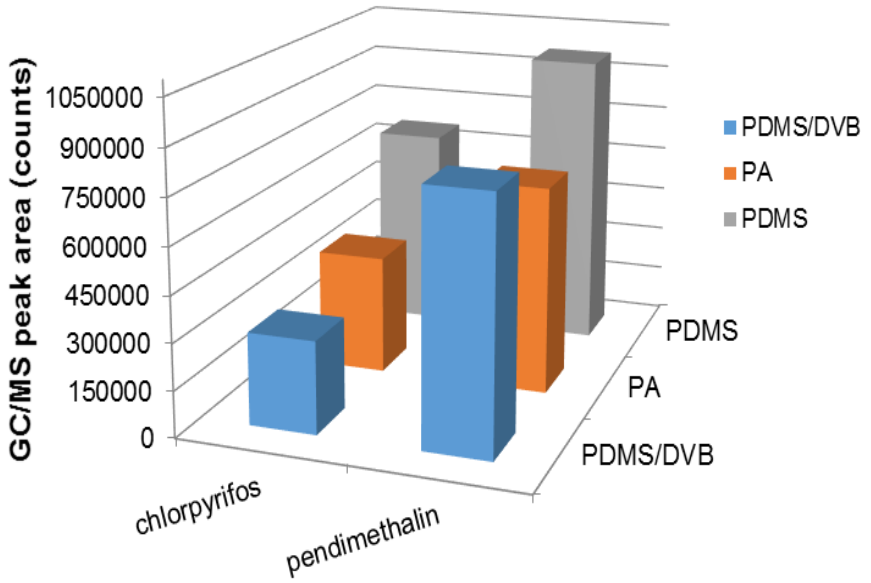

Fig 2. Dependence of GC/MS analytical signal on type of SPME fiber, using the 120 minutes fiber exposure time.

Additionally, the obtained GC/MS peak areas indicate that amount of pendimethalin desorbed by PDMS fiber is something lower than chlorpyrifos. Considering that pendimethalin was characterized by higher Henry's constant than chlorpyrifos (Table 2), these results are unexpected. Possible explanation could be stronger adsorption of pendimethalin molecules on soil; this aspect will be investigated by further experiments.

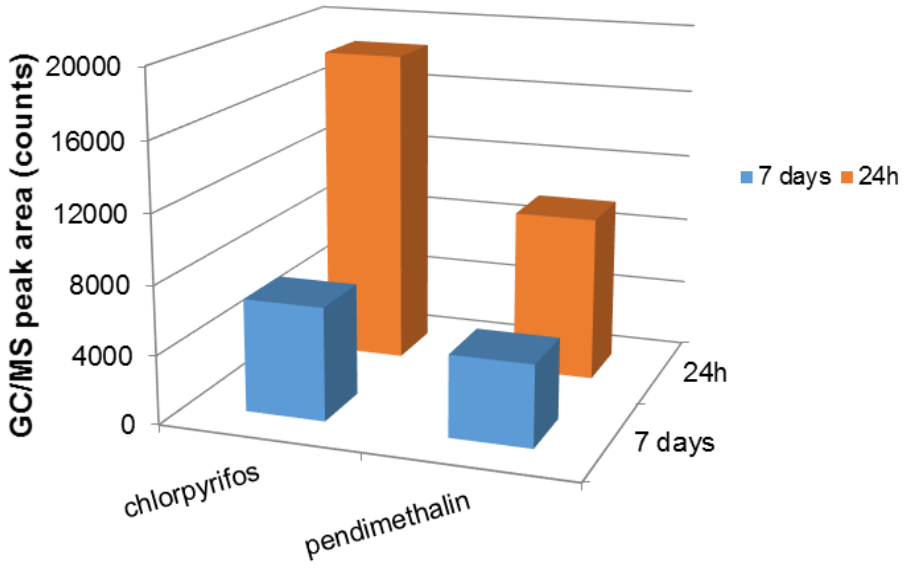

Fig. 3 GC/MS analytical signal after 24h and 7 days of soil contamination with pesticides, obtained by 120 minutes of PDMS fiber exposure in the hole made in soil.

II. DESIGN OF A NEW MEASUREMENT BENCH

To significantly simulate in laboratory the contamination and desorption of the pesticides a new tool has been designed and assembled. In fact, it must be taken into account that, in a real scenario, the sensors will be deployed at an average height of 1.5 m from the soil and they should not be directly exposed to the atmospheric agents such

ISSN: 2319-5967
ISO 9001:2008 Certified
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as rain for avoiding further devices deterioration. Moreover this testing structure needs to simulate the way in which the soil is contaminated by using a standard sprinkle at a fixed height. Finally, the system will be sealed in a cylinder and placed in a chemical bench to avoid possible contamination with the personnel that are performing the experiments. Fig. 4 shows the design of the structure of the new box for the measurement bench. On the top of the structure the array of gas sensors will be put to capture the gas fraction of the substances under test.

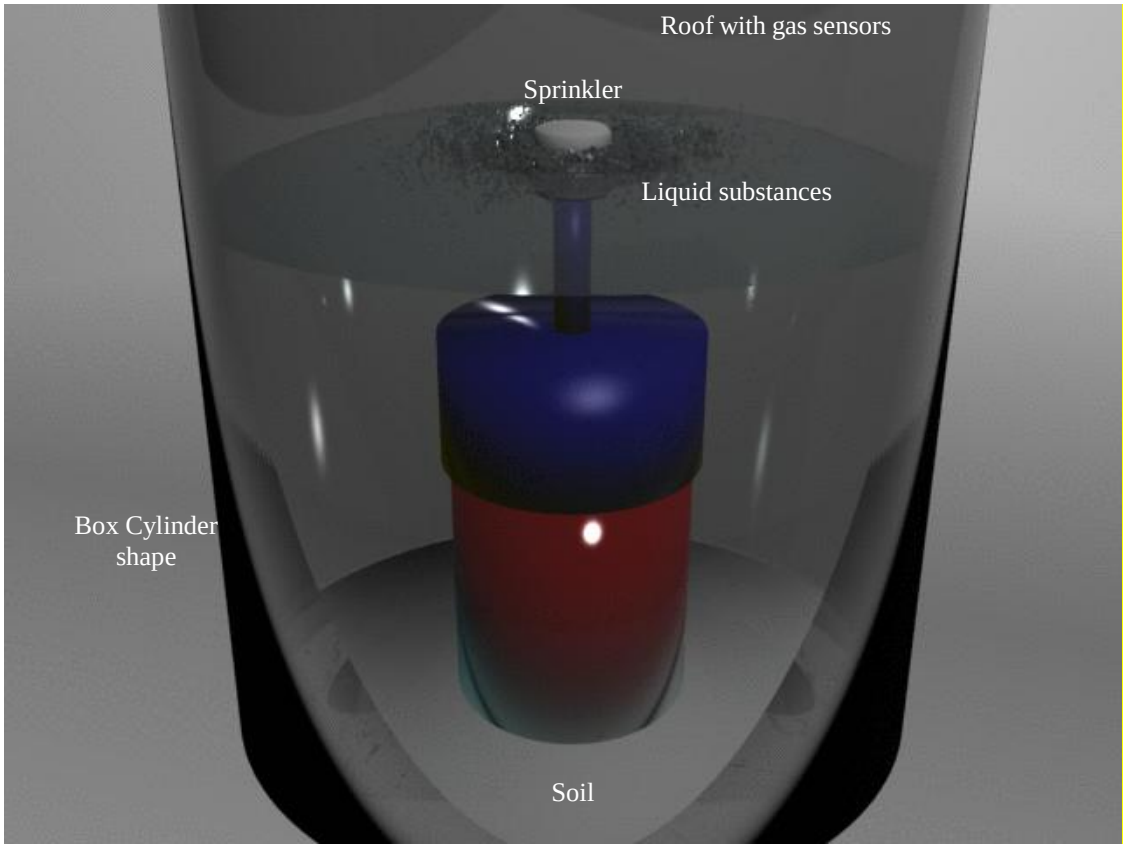

Fig. 4 Design of the new box for the measurements of pesticides in laboratory by using the gas sensors.

III. CONCLUSION

This paper shows the definition of a preliminary procedure to demonstrate the possibility to measure pesticides amount from their evaporation in order to exploit the implementation of low-cost and disposable gas sensors. The results allowed us to imagine and design a new box for simulating the desorption of specific molecules from the soil in laboratory. In this system, the substances can be sprinkled in absolute safety at a fixed height and a set of gas sensors housed in an overlying cap can detect the amount of molecules dispersed in the soil. This technology could represent a valuable improvement especially for the monitoring in real time of large agricultural areas to guarantee the minimal usage of these substances or to prove the production of real biological food.

ACKNOWLEDGMENT

This study is inserted in the general context of the research called “Smart Monitoring of Pesticides in Farming Areas” and has been partially realized with the contribution of the Italian Ministry of Foreign Affairs (in Italian “Con il contributo del Ministero degli Affari Esteri e della Cooperazione Internazionale, Direzione Generale per la Promozione del Sistema Paese”). This Activity last has been recognized as a research project of particular relevance selected within the frame of the executive programmed of scientific and technological cooperation between the Italian Republic and the Republic of Serbia for the years 2016-1018 by the “Italian Ministry of Foreign Affairs”.

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