AGROCHEMICAL PLASTIC PACKAGING WASTE DECONTAMINATION AND RECYCLING: PILOT TESTS IN ITALY

P. PICUNO*, Z. GODOSI**, C. PICUNO***§ AND K. KUCHTA***

* *University of Basilicata – SAFE School, via dell'Ateneo Lucano, n.10, 85100 Potenza (PZ), Italy*

** *Civil Engineer, Freelance Consultant, via Nicolò Giudice, n.1, 70010 Cellamare (BA), Italy*

*** *Hamburg University of Technology – Institute of Environmental Technology and Energy Economics, Harburger Schloßstraße, 36, D-21079 Hamburg, Germany*

§ Corresponding Author: caterina.picuno@tuhh.de

The contribution to programming and executing this research should equally be shared among the Authors

SUMMARY: Agriculture, one of the main economic pillars in Europe, plays a growing important role towards the environmental sustainability of the extra-urban land, in which the agricultural activities may proactively contribute to control and regulate the whole ecological conditions. Modern agriculture currently needs big quantities of agrochemicals, which are necessary for the growth and protection of crops and animals. These agrochemicals are commercially distributed to consumers in many types of containers. The most widely used among their packaging solutions usually employ plastic material (*e.g.*, containers for liquid pesticide; sacks for granular fertilizer; *etc.*). This material, after the use of the agrochemical, needs to be decontaminated, before being entrained in a recycling process. In the present paper the main results coming from a EU-funded international project are reported, with specific reference to the pilot station that was realized in Italy with the aim to implement and test a codified system for the decontamination of these plastic containers for agrochemicals. The experimental tests were supported by relevant laboratory analysis, which have confirmed that the "*triple rinsing*" system – traditionally employed by farmers for washing and decontaminating these containers - may be effective only under some conditions. Triple-rinsing by farmers has indeed lead to an only partial decontamination of the plastic containers, if farmers did not follow an appropriately triple-rinsing protocol, or did not triple-rinse the containers immediately after their emptying.

Proceedings CRETE 2018, Sixth International Conference on Industrial & Hazardous Waste Management
Chania – Crete – Greece; 4 – 7 September 2018
ISSN: 2241-3146

1. INTRODUCTION

Agriculture is one of the main economic pillars in Europe, mostly in its southern area which, lying close to the Mediterranean Sea, benefits from better local weather conditions and more sunny days, then playing a traditional role which has contributed to a legacy rooted into the history of the whole European continent. Agriculture plays indeed also a growing important role on the current quality of life of European citizens and their dietary habits, as well as towards the environmental sustainability of the extra-urban land, since it safeguards the rural landscape, proactively contributing to regulate and control its whole ecological framework. In the early sixties, to increase the agricultural productivity worldwide, new varieties of plants, called "*hybrid*" have been introduced, more receptive to the nutrients, faster maturation, and can grow in every season, allowing more crops throughout the year. At the same time, an increase in the use of heavy machinery, a wide and extensive diffusion of plastic materials and a massive use of agrochemicals made their entrance in agriculture.

The agricultural plastics have been garnering greater attention in recent years because these materials have become ubiquitous in all sectors of agriculture. Plastics are substituted for the longer lasting materials previously used — *e.g.*, concrete, glass, ceramic, metal, *etc.*— because they are often less costly, safer to use, and improve production efficiency (Picuno P., 2014). Modern agriculture currently needs also big quantities of agrochemicals, which are necessary for the growth and protection of crops and animals. The term “agrochemicals” usually covers a broad range of pesticides, including insecticides, herbicides, and fungicides. However, it may also comprise synthetic fertilizers, hormones and other chemical growth agents, and concentrated stores of raw animal manure. Pesticides not only may harm living target organisms, but often remain as residues in food, soils, ground-waters and even the air, so affecting the agro-ecosystem as well as the human health. Overall, pesticides were recently recognized as one of the six world's worst pollution problems affecting human health. Even though gaps in the current data on the issue make it difficult to be precise about the scale and trends of the problem in Europe, there is evidence that the pesticide issue is serious and growing. According to Eurostat, the total quantity of pesticides sold, expressed in active ingredient (a.i.) reported for 2015 for n.25 countries was approximately 385,000 tons. Spain, France, Italy and Germany are the major consumers, consuming nearly 60% of the total of plant protection products in EU (Briassoulis et al., 2014).

The packaging solutions for commercially distributing agrochemicals to consumers usually employ many types of plastic containers - *e.g.*: containers for liquid pesticide; sacks for granular fertilizer; *etc.* - composed by a polymer or copolymer or coated polymer. This plastic material, after the use of the agrochemical, needs to be decontaminated, before being entrained into a material recycling process. In the present paper, the main outcomes of an internationally-funded European Project are reported, along with the results coming from a more recent analysis of the decontamination process.

2. THE DISPOSAL OF AGROCHEMICAL PLASTIC PACKAGING WASTE

The implementation of the principles of circular economy are leading governments, enterprises and individuals to embrace practices that favor the reuse of materials. In case of plastic material, the pre-separation of polymeric material on the basis of its composition, followed by cleaning and conditioning, may enable a large amount of these materials to be returned to the production system. Traditionally, farmers have unfortunately recklessly dumped plastic waste into the environment, burned them, or buried them. Such practices directly contribute to environmental contamination and pose a public health risk (Briassoulis et al., 2010). After some decades of increasing use, the problem of disposal is ever more difficult to ignore. Several studies indicate that most agricultural plastics which are burned or buried on-farm, create fire hazards, clogging water channels, and releasing high levels of polluting emissions. Agricultural plastics are dispersed across the rural landscape, bulky, and often contaminated with debris (*e.g.*, dirt, pebbles, vegetation, chemical residues, moisture), limiting their suitability and value for re-processing (Briassoulis et al., 2013).

A systematic approach aimed to the proposal of a suitable solution for the collection and disposal of Agricultural Plastic Waste (APW) has been proposed by a EU-funded Project (Labelagriwaste project, 2009), that has proposed and implemented at pilot scale an holistic environmentally sound waste management scheme able to minimize the costs and maximize the revenues by transforming the agricultural plastic waste streams into labelled guaranteed quality commodities freely traded in an open market. The labelling management scheme proposed has been designed to be technically feasible, economic and able to satisfy the geographic diversity and the various technical requirements of the major stakeholders throughout Europe, including farmers, plastics producers and recyclers, as well as industrial facilities utilizing alternative fuels for energy production. In the framework of the same LabelAgriWaste project, some experimental investigations have been performed about the possibilities of producing through mechanical recycling of post-consume agricultural plastic film, new plastic film (Picuno et al., 2012) or rigid profiles produced by mixing plastic film with some additives, *e.g.*, glass fibers (Dimitrijevic et al., 2013).

The mismanagement of Agrochemical Plastic Packaging Waste (APPW) constitutes a major environmental problem, resulting in pollution of soil, air and water resources and compromising the agricultural products safety, the protection of the environment and public health. Mismanagement of the APPW is reported in many countries of the world. Due to lack of education and guidance in the proper management of small quantities of pesticide-related waste, hazardous chemicals are often left lying around in rural and urban areas, whereas the reuse of contaminated empty containers for domestic purposes, which has been frequently identified in many developing areas, is another major health risk (Damalas et al., 2008). Some schemes for the management of APPW have been established in a few European countries, as in Germany (Pamira, 2018), France (Adivalor, 2018) and Spain (Sigfito, 2018). However, these schemes are incompatible with each other, while in most cases they are not combined in a synergistic way with the management of other APW categories to optimize use of resources, increase efficiency and reduce cost. Thus, for example, the French system *Adivalor* considers and handles the triple rinsed containers of agrochemicals as non-hazardous waste, while the Spanish system *Sigfito* considers them as hazardous waste and handles them in an analogous way. The French system *Adivalor* also collects agricultural plastic films. In many other European countries, mostly those characterized by an intensive agricultural production (Italy included), no schemes exist for the management of APPW, with serious negative consequences for the environment and public health (Briassoulis et al., 2014).

2.1. The AGROCHEPACK Project

In response to these serious problems, the European Project "*Design of a Common Agrochemical Plastic Packaging Waste Management Scheme to Protect Natural Resources in Synergy with Agricultural Plastic Waste Valorization* – AgroChePack" (AgroChePack Project, 2013), funded by the European Territorial Cooperation MED Programme (2G-MED09-015) has been implemented, with the aim to develop an integrated, efficient, environmentally friendly and economically viable management system for the management in Europe of APPW. This new system has been designed in order to transfer *know-how* from existing schemes and promoting synergy with other similar schemes previously proposed for the management of other non-hazardous agricultural plastic waste (*e.g.*, plastic film for greenhouse, tunnel, mulching; pipe/tapes for irrigation; *etc.*). This new integrated APPW management scheme has been piloted in five EU countries (Greece, Italy, Cyprus, Spain and France).

The analysis conducted in the framework of the AgroChePack Project have shown that overall, and considering the present legal limits established for pesticides, the recycling of the polymeric packages that have contained pesticides is feasible after a "*triple rinsing*" procedure. The hazardousness analysis of the triple rinsed containers collected from the pilot trials confirmed the laboratory experiments results, suggesting that the appropriate application of the triple rinsed technique of the containers by suitably trained farmers ensures their decontamination and their characterization as non-hazardous waste according to the EWC provisions. The triple rinsing of empty bottles removes most of the pesticides, achieving levels below legal limit; this removal has been demonstrated for all cases with one exception. However, for some pesticide/polymer combinations, the significant amount of pesticide that persists within the polymer could be later released during recycling or reuse. Depending on the future use of these polymers, besides being legally feasible, the product obtained after the recycling process has not to introduce risks (Briassoulis et al., 2014).

3. MATERIALS AND METHODS

In Italy where, as in other Countries, an APPW management scheme has not been established yet, it is necessary to develop appropriate environmentally friendly solutions. A previous analysis was performed to assess the current situation within the Apulia Region (Southern Italy), that was selected for performing the pilot tests. A mapping of APPW generation - collecting information on cultivations (main species, cultivated areas and their localizations), plastic material and agrochemical products used to estimate APPW streams (quantity, temporal and spatial distribution, problems experienced with specific disposal solutions applied, *etc.*) and on farmers' knowledge about the environmental damage caused by poor waste management - has been performed. This analysis has be taken as a basis for the realization of a pilot plant (Figure *1*), which was designed for the pilot implementation of the AgroChePack project.

Figure 1. The Agrochepack Pilot Station at Cellamare (Italy)

Specific pilot tests were performed during the AgroChePack Project, aimed to critically assess the possibility to implement the European Crop Protection Association - ECPA's policy on Container Management Strategies (CMS), consisting essentially in three different rinsing options:

- Triple-rinsing;
- Pressure rinsing (Figure 2);

• Integrated rinsing.

Basing on the results obtained in this Pilot station, some experimental tests were conducted in the laboratory of the Institute of Environmental Technology and Energy Economics of the Hamburg University of Technology (Germany), in order to evaluate the effect of photo-oxidation on the inner surface of a pesticide container as well as to compare the absorption rate of the pesticide within the polymeric matrix of a not-aged and an aged container.

Figure 2. Triple rinsing at the Agrochepack Pilot Station at Cellamare (Italy)

3.1. Samples preparation and decontamination procedure

Two identical PE/PA6 pesticides bottles with a 0,75 l volume were subject to decontamination according to the triple-rinsing procedure described in the “Guidelines for small containers” outlined as a result of the AgroChePack Project (AgroChePack Project, 2013). The bottles contained the herbicide Axial® Pronto 60 by Syngenta having the following active ingredients: 60 g/l Pinoxaden, 15 g/l Cloquintocet-mexyl and other co-formulants with reported limited hazardousness. One of the two bottles was filled for one third of its volume and, prior to decontamination, it was subject to artificial accelerated weathering in order to simulate thermo-oxidative degradation (Gulmine et al., 2003; Pfennig et al. 2016).

The aging was performed in two steps: firstly, the herbicide container was heat-treated under an oven temperature of 55 °C for 96 h. Then, the same was transferred for 16 h into a UV irradiation box equipped with 13 multi-directional LEDs with a power of 39 W each, under a 400 nm wavelength and a temperature of 55 °C. Afterwards, both bottles, were completely emptied and triple rinsed as specified in the Guidelines with deionized water. A fourth washing was necessary because of insufficient clarity of the cleansing water.

3.2. Extraction of pesticides

A possible absorption of agrochemicals in the plastic matrix of the containers was investigated by extracting the remaining pesticide using a mixture of solvents. Although a standardized extraction procedure is not yet in place, several authors have tried to find common grounds for the extraction of different types of pesticides from containers of different polymeric blends (Briassoulis et al., 2014; Eras et al., 2017). For this work, the procedure described by Eras et al. (2017) was applied with some changes related to the specific nature of the pesticide and to the particular purpose of this work.

For both bottles the top and the bottom parts were discarded. The aged bottle was cut at the level of the pesticide prior emptying: this served with the sole purpose of evaluating the different superficial degradation of the polymer aged in contact and not in contact with the pesticide. These two parts as well as the not-aged bottles were cut in two halves each for replicates. Each half was cut into 1cm x 1cm pieces and of these, few pieces were kept for surface degradation analysis. Afterwards, the pieces of each half of the two bottles were stored into four borosilicate glass bottles with ISO screw caps. The solvent used was a 50:50 mixture of acetone and methanol and the procedure is as described in Eras et al. (2017) with the exception of: i) in order to accelerate the extraction, the glass bottles were placed on a shaker for one hour, instead of utilizing an ultrasonic bath; ii) the number of subsequent extractions was stopped at two.

3.3. Characterization

At first, the samples were analyzed by means of HPLC-UV, GC-FID and GC-MS methods. However, the possible sensitivities were not sufficient and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) was used to analyze the active ingredients´ concentrations in water and in the solvent mixture after the extraction steps.

The samples´ surface was coated with a 15 nm layer of gold by sputtering using a Baltec SCD 050 sputter coater, and then they were inserted in a Zeiss Leo Gemini 1530 with a voltage of 15 kV for analysis. Photomicrographs were taken with a magnification of 100-f and 1000-fold.

4. RESULTS AND DISCUSSION

4.1. Decontamination procedure

According to the composition of the pesticide, the concentration thresholds for its hazardousness were evaluated on the basis of the *Globally Harmonized System of Classification and Labelling of Chemicals* on its last version, listing the classification criteria and the hazard communication elements by type of hazard (United Nations, 2017). The concentrations resulting after the triple rinsing procedure, both of the single active ingredients and of the mixture, were considerably lower than the concentration thresholds set for all the statement codes attributed to the contaminants.

As expected, no substantial difference was recorded between aged and not aged container as result of triple rinsing procedure. Adsorption into the polymeric chain is expected and was investigated as well. However, the instability of Pinoxaden in LC-MS/MS hindered the analyses. Consequently, further research is envisaged to be done.

4.2. Inner surface structure

The effect of ageing is evident already from a low magnification (Figure): the inner surface of the polymer shows an increased roughness in case the container is aged in contact with the pesticide (Figure 3.c)). In addition to this, a higher magnification (1000-fold as shown in Figure) reveals a degradation pattern that differs whether the container is a) not aged; b) aged not in contact with the pesticide and c) aged in contact with the pesticide. Specifically, after ageing small hollows in the surface of the polymer occur, independently from the contact with the pesticide. However, ageing the polymer in contact with the pesticide, not only produces the above-mentioned hollows and increased roughness, but it also causes pesticide contaminants to crystallize.

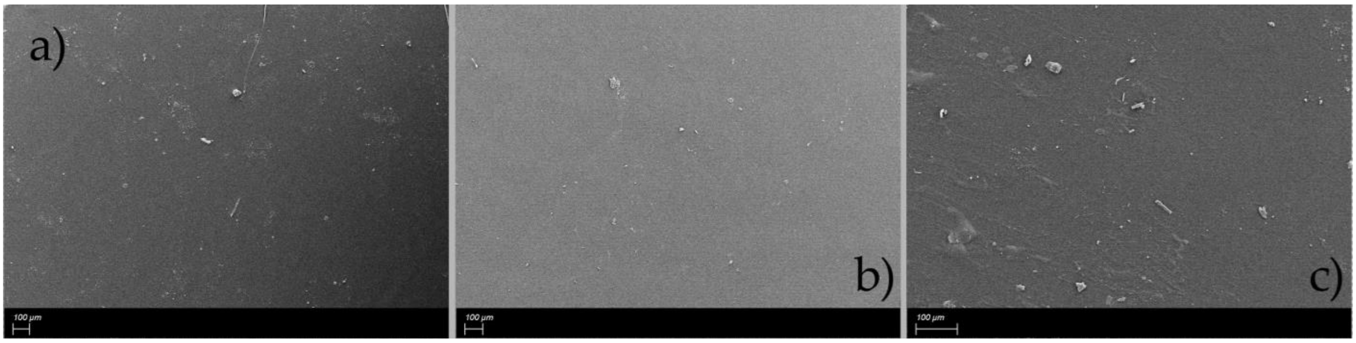

Figure 3. SEM pictures with 100-fold magnification. a) not-aged sample; b) sample aged not in contact with pesticide; c) sample aged in contact with pesticide.

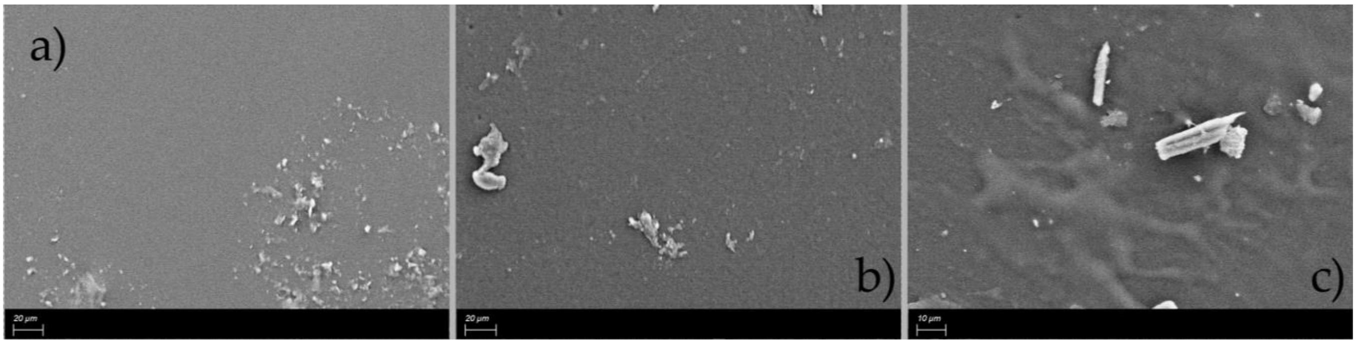

Figure 4. SEM pictures with 1000-fold magnification. a) not-aged sample; b) sample aged not in contact with pesticide; c) sample aged in contact with pesticide.

This degradation pattern mainly affects the effectiveness of the decontamination procedure. As a matter of fact, increased roughness a consequent crystallization of the pesticide contaminants onto the polymeric surface are likely to hinder the triple rinsing efficacy. The direct consequence is that, if the aged container is triple rinsed and treated as non-hazardous, it is delivered to a plastic recycling facility possibly causing contamination of the recyclate.

Nevertheless, the photo-oxidation times and settings which these containers are subject to, sensibly differ in reality from those tested for this paper, according to weather conditions and geographic location. Therefore, further research is foreseen in order to assess the influence of different weathering conditions on the polymer degradation.

5. CONCLUSIONS

From the results that were obtained by the pilot tests at Project level, it could be concluded that all containers rinsed at the AgroChePack pilot stations under supervision were decontaminated according to the limits for non-hazardous waste set by the legislation, while those triple-rinsed by farmers on their own responsibility (*i.e.*, outside the pilot station) were only partially decontaminated. One of the most evident limit of the triple rinsing method has revealed indeed that farmers in some cases do not appropriately triple rinse the containers or, mainly, they do not triple rinse them immediately after the use of the agrochemical.

Triple rinsing a plastic container much time after its emptying, or that has been partially used and which has remained much time half-used, results in fact into the formation of hollows and into an increase of roughness of the polymer surface, as well as into the crystallization on the empty internal side of the plastic container of chemical elements which are not removed even through an appropriate triple rinsing procedure.

REFERENCES

Adivalor, http://www.adivalor.fr/, last access: 31 May 2018

Agrochepack Project. Design of a Common Agrochemical Plastic Packaging Waste Management Scheme to Protect Natural Resources in Synergy with Agricultural Plastic Waste Valorization. Programme Interreg MED, Contract No. 2G-MED09-15, 2010–2013. http://www.agrochepack.aua.gr., last access: 31 May 2018.

Briassoulis D., Hiskakis M., Scarascia Mugnozza G., Picuno P., Delgado C., Dejean C. *Labelling Scheme for Agricultural Plastic Wastes in Europe.* Quality Assurance and Safety of Crops & Foods 2010, (2), 93-104.

Briassoulis, D.; Babou, E.; Hiskakis, M.; Scarascia-Mugnozza, G.; Picuno, P.; Guarde, D.; Dejean, C. Review, Mapping and Analysis of the Agricultural Plastic Waste Generation and Consolidation in Europe, Waste Management & Research 2013, 31(12), 1262-1278.

Briassoulis, D.; Hiskakis, M.; Karasali, H.; Briassoulis, C. Design of a European agrochemical plastic packaging waste management scheme – Pilot implementation in Greece. Resources, Conservation and Recycling 2014, 87, 72-88.

Damalas C.A.; Teilidis, G.K.; Thanos, S.D. Assessing farmers' practices on disposal of pesticide waste after use. Science of the Total Environment 2008, 390, 341-345.

Dimitrijevic, A.; Sica, C.; Picuno, P.; Scarascia-Mugnozza, G. Using the glass fibres in recycling agricultural plastic waste. Poljoprivredna Tehnika (Agricultural Engineering - Scientific Journal) 2013, 38, 31-38.

Eras, J.; Costa, J.; Vilarò, F.; Pelacho, A.M.; Canela-Garayoa, R.; Martin-Closas, L. Prevalence of pesticides in postconsumer agrochemical polymeric packaging. Science of the Total Environment 2017, 580, 1530-1538.

Gulmine, J.V.; Janissek, P.R.; Heise, H.M.; Akcelrud, L. Degradation profile of polyethylene after artificial accelerated weathering. Polymer Degradation and Stability, 79, 385–397.

Labelagriwaste Project. Labelling Agricultural Plastic Waste for Valorising the Waste Stream. Programme FP6 RTD CRAFT-Collective Research, 2006–2009, Contract No. 516256-2. http://www.labelagriwaste.aua.gr, last access: 31 May 2018.

Pamira, http://www.pamira.de/, last access: 31 May 2018.

Picuno, P.; Scarascia-Mugnozza, G.; Sica, C.; Dimitrijevic, A.; Laviano, R. Experimental tests and technical characteristics of regenerated films from agricultural plastics. Polymer Degradation and Stability 2012, 97, 1654-1661.

Picuno, P. Innovative Material and Improved Technical Design for a Sustainable Exploitation of Agricultural Plastic Film. Polymer - Plastics Technology and Engineering 2014, 53(10), 1000-1011.

Pfennig, L.; Kuchta, K.; Prette, A.; Fiore, S. Evaluation of LDPE and ABS degradation by means of NIR spectroscopy. Proceedings CRETE 2016, 5th International Conference on Industrial & Hazardous Waste Management.

Sigfito, http://www.sigfito.es/, last access: 31 May 2018

United Nations, Globally Harmonized System of Classification and Labelling of Chemicals, Seventh revised edition, New York and Geneva, 2017