applied sciences

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Degradation of Low-Density Polyethylene Greenhouse Film Aged in Contact with Agrochemicals

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Featured Application: Recycling plastic film used in agriculture for crop protection is currently hindered by contamination with agrochemicals. Experimental tests conducted confirmed that film mechanical characteristics weakened with aging, even if samples treated with double spraying followed slower degradative kinetics. The Carbonyl Index was confirmed as a useful aging indicator.

Abstract: Plasticulture is a technique widely affirmed throughout Europe and the rest of the world that employs plastic material for protecting agricultural cultivations, e.g., soil mulching, low/middle tunnel covering, and greenhouse farming. Because of their effects on the sustainability of agricultural production, these materials present serious environmental drawbacks. Even if plastic recycling is a consolidated technical solution, several obstacles hinder the mechanical recycling of film used in plasticulture. Mostly, the degradation of its mechanical characteristics, due to aging and simultaneous contamination with agrochemicals used for fighting plant disease and ensuring crop health, plays a major hampering role. In the present paper, the results of laboratory tests on agricultural PE-LD plastic film for greenhouse covering, artificially aged for different lengths of time and treated with two different agrochemicals (fungicide and anti-aphid), are presented. The contamination with agrochemicals resulted in a considerable reduction in mechanical properties throughout the usage phase even if in samples that underwent twofold spraying, slower degradative kinetics were observed. In conclusion, based also on the measured changes in the Carbonyl Index value, it is doubtful that this plastic film would be included in a mechanical recycling process.

Keywords: plasticulture; greenhouse covers; plastic film degradation; mechanical characteristics; agrochemical contact; agro-plastic recycling; Carbonyl Index

Citation: Picuno, C.; Godosi, Z.; Santagata, G.; Picuno, P. Degradation of Low-Density Polyethylene Greenhouse Film Aged in Contact with Agrochemicals. *Appl. Sci.* **2024**, *14*, 10809. https://doi.org/10.3390/app142310809

Academic Editor: Marco Carnevale Miino

Received: 22 October 2024
Revised: 17 November 2024
Accepted: 20 November 2024
Published: 22 November 2024

1. Introduction

The main sector in which plastic material is employed as a constructive element is agriculture. Indeed, in civil and industrial buildings, plastic material is usually used in non-structural ancillary finishing applications only, e.g., façade cladding, flooring, wall insulation, and door/window frames. In agriculture, plastic is a key component when used as a building closure material to grow cultivations, since it develops both a passive effect—by protecting them from adverse weather conditions—and an active effect—by valorizing the solar radiation, thus creating a better environment for the crops.

The market for agricultural plastic film for crop protection is mostly based on soil mulching and greenhouse farming [1]. According to the the latest estimation on a global scale [2,3], in 2021, the amount of plastics annually used in agricultural production was equivalent to 359 million tons, i.e., almost 3.5% of the global plastic production. Concerning protected cultivation under a greenhouse/tunnel, China covered around 2.8×10^6 hectares with plastic greenhouses, i.e., the largest area protected with plastic greenhouses in the

world that, together with Japan and Korea, accounts for about 80% of the whole area covered by greenhouses [4]. In Europe, in 2020, a total amount of 547,000 tons/year of agricultural films was put on the market [5], mostly for application as soil mulching, greenhouse covers, and livestock silage [6]. Agricultural plastic film—for crop protection, silage application, etc.—is mostly based on low-density polyethylene (PE-LD) or linear low-density polyethylene (PE-LLD) polymers and PE-LD/EVAC (ethylene-vinyl acetate) co-polymers, generally incorporating additives (up to 15%) and extruded with a thickness variable in the range of (20–250) μm [7].

Reducing the plastic footprint of agriculture requires more thorough research on the service life of plastic films and their compatibility with the Circular Economy concept [8–11]. Indeed, the use of plastics in agriculture causes major environmental impacts, such as those related to the handling of huge volumes of post-consumer material, particularly in regions with a delicate environment and consolidated tourism sector [12]. Macro-, micro-, and nano-plastics released by agro-plastics have the potential to contaminate soil, endangering human health, the environment, and food security as well [13–15].

Over recent years, there has been a notable increase in research and development focused on bio-based and biodegradable polymers (often, improperly named as "bio-plastics") as substitutes for fossil-based plastics, although they are still plastics. Despite representing only 0.5% of global plastic production, there is a noticeable bias in the scientific community about the development of bio-based plastic formulations over conventional petroleum-based plastics, having pros and cons in comparison with PE-LD [16]. Bio-based polymers are derived from renewable biomass resources. However, not all bio-based polymers are fully biodegradable. Bio-based and biodegradable plastics are still in development: the process of substitution of petroleum-based plastics by bio-based plastics, in view of their identified end-of-life and environmental impacts, is not currently reliable [17]. Therefore, given the importance of the preservation of agricultural soils against possible irreversible pollution by plastic material, the invocation of a principle of caution in their use appears to be at the moment unavoidable. We should strive for the consolidation of scientific knowledge on this subject—as in the case of several other fields of scientific knowledge, e.g., human vaccines.

A deeper comprehension of the obstacles to plastic's mechanical recycling potential is necessary to investigate new options for its usage in agriculture that have a limited adverse effect on the environment due to the transformation of post-consumer plastic material into a new, secondary product [18,19]. To overcome the primary obstacles to mechanical recycling, the main critical aspects to be investigated are those connected to the conditions in which plastics used in agriculture eventually lose their intended performance. Analyzing the most suitable conditions for removing plastic film after aging is therefore undelayable.

Greenhouse Plastic Film Aging

PE-LD film is commonly used as a greenhouse covering material because of its good mechanical properties, chemical resistance, and affordability. However, its chemical structure may be heavily impacted by weathering circumstances, which alters the film's mechanical and physical characteristics. The interconnection among the different aging factors of plastic material and its resilience to degradation phenomena remains a poorly investigated issue, which requires a suitable scientific approach, aimed at introducing innovative solutions, capable of enhancing the durability of a greenhouse plastic film.

The worsening of a plastic's visual perception, as well as of its mechanical performance, radiometrical properties, physical characteristics, or chemical structure, is in general referred to as its "degradation". The Ultraviolet (UV) component of solar radiation is, within atmospheric conditions, the primary element that contributes to the rapid deterioration of agricultural plastics [20,21]. Additionally, other variables may play a considerable role. These include temperature and the relative humidity of the internal air; mechanical stress imposed by wind, rain, hail, and snow or related to the installation (stretching) phase; interaction with air's oxygen/dust, atmospheric pollutants, and rainwater; interactions

with supporting structures or agricultural soil; exposure to agrochemicals, etc. Describing, measuring, and controlling plastic degradation are all problems made more difficult by several environmental, chemical, and technological aspects [22,23]. When the primary mechanical characteristics of an agricultural plastic film—mainly, its percentage elongation at break—fall below 50% of the original measure when new, the material is considered as having reached the end of its service life. Indeed, this value is generally considered as the indicator that this material has finished its working life and has to be removed before its mechanical characteristics become so poor that its removal and further mechanical recycling could be impossible. Therefore, the primary recycling attributes consist of having adequate mechanical characteristics, in comparison to the plastic material when it was new.

In order to characterize the deterioration of a PE-LD film, Briassoulis et al. [24] examined the quantitative criteria that may be used, coming to the conclusion that the variance in the percentage elongation at break is the primary determinant of the final evaluation of a greenhouse plastic film's degradation. This is how weathering conditions—particularly sunlight, in the 290–400 nm range—alter a PE-LD film's chemical structure and, consequently, its mechanical and physical properties. Dehbi et al. [25] conducted some experimental tests using artificial and natural aging in Northern Algeria at four different greenhouses, simulating conditions of temperature and UV-A radiation, in order to comprehend the mechanisms of natural and artificial aging processes of a triple-layer film made of PE-LD used as greenhouse cover. Mechanical characteristics significantly decreased with aging, according to the data, and this might be due to the structural alteration of the plastic film. The results revealed that the maximum loss of yellow-color additives occurred after 2981 h under the natural aging process and after 2440, 1096, 1340, and 121 h under the four considered artificial aging conditions, respectively.

Several research studies agreed on how the degradation process of PE-LD films used as greenhouse covers involves a wide number of interrelated phenomena, including chemical deterioration brought on by interactions with air pollutants and agrochemicals, photodegradation brought on by reactions aided by UV light, and ultimately mechanical degradation brought on by bond ruptures brought on by mechanical stress [26,27]. Nonetheless, a variety of strategies may be implemented to protect polymers from the damaging effects of UV radiation, e.g., the addition of UV absorbers, which may enhance the resistance of polymeric materials to aging. Some other studies [28] analyzed the key theories explaining the impact of UV radiation on polymer decomposition and the testing procedures for assessing the aging properties of polymeric materials while elucidating the current and suitable methods for enhancing the UV resistance of polymers by means of additives and UV absorbers, able to prolong their lifetime.

The simultaneous impact and interactions between aging and pesticides on plastic greenhouse film have been so far the subject of a few scientific studies. However, rather than focusing on the implications for the material's end-of-life phase, these studies primarily addressed the fluctuations that occur in its technical qualities. Through laboratory analysis and open-field trials, all of these studies have indeed explicitly looked at how aging affects the mechanical strength and radiometric properties of plastic film used for greenhouse covering, rather than their post-consumer recycling properties. Briassoulis [29] examined the combined effects of accelerated aging on PE-LD greenhouse film, by using UV light and an aggressive herbicide (Vapam). The basic characteristics of aging were examined over a short period of time using an unstabilized film. Changes in a few of the film's mechanical properties before and after aging were used to gauge the procedure. A revised artificial aging process that was intended to more accurately resemble the weathering of PE-LD greenhouse film was eventually launched. Briassoulis et al. [30] also looked at a number of experimental multilayer films that were subjected to accelerated aging in conjunction with agrochemicals. They observed that agrochemicals speed up the negative effects of UV-A radiation on PolyAmide (PA) and Ethylene-Vinyl alcOHol (EVOH) layers, leading to the early breakdown of the barrier layers, thus further jeopardizing the mechanical strength and durability of the overall film. This study concluded that the stabilized multilayer

films exhibit longer lifetime depending on the level of stabilization (1% or 2%), but PA and EVOH are not recommended as barrier layers in agricultural films since, when UV-A radiation and agrochemicals combine, they negatively affect both mechanical properties and photo-degradation behavior.

Schettini and Vox [31] conducted some experimental studies to assess the effects of solar radiation and pesticide contamination on the physical characteristics of PE-LD films. Both the new films and samples obtained at the conclusion of several experiments were subjected to radiometric testing. To examine the relative efficacy of the stabilizing systems, a laboratory examination of the absorption of some pollutants was performed on the samples collected at the conclusion of the field exposure. These authors concluded that, during the six months of experimental field testing, the radiometric properties of the films in the solar and Photosynthetically Active Radiation (PAR) wavelength ranges were not significantly changed by the combined impacts of agrochemicals and natural weathering. Rather, differences of as much as 70% of the initial measure in the Long-Wavelength InfraRed (LWIR) range were noted for the stabilized films.

Further analyses that aimed to explain the aging mechanism and the effect of UV combined with agrochemicals have been more recently conducted by some authors [32], who investigated the most suitable strategies based on nano-micromaterials, able to provide thermal radiation insulation, preserving heat and energy in greenhouses, without worsening visible light transmittance. These authors reviewed also the radial and thermal properties of greenhouse covering materials; thus, they focused on fillers, colorants, reinforcing agents, and additives, as both compounds based on graphene and fullerene and phase-transition materials (PCMs). They finally found that these materials could control the microclimate, reduce CO_2 emissions, use less energy, and increase agricultural productivity.

The present paper presents the results of an extension of a prior study on greenhouse PE-LD plastic film [33], whose objective was to critically evaluate the impact of non-natural aging factors, such as the plastic film's contact with agrochemicals under UV light, from the standpoints of reusability and recyclability. In order to better understand how exposure to agrochemicals causes films to deteriorate and obtain information that will be helpful for their subsequent mechanical recycling, these initial tests have been now expanded and further examined, by involving here also repeated agrochemical spraying on the PE-LD plastic film.

2. Materials and Methods

Monolayer PE-LD plastic film, extruded through blow-extrusion technology into a nominal thickness of 200 μm (density: 0.92 g/cm^3), typically used for covering greenhouses, was examined in this study. Samples from this film, having dimensions 420 mm × 200 mm, were obtained, so as to get ten specimens from each sample type, to be subjected to tensile and spectro-radiometrical tests.

These samples were initially spray-coated alternatively using two different agrochemicals, largely used by greenhouse farmers in Southern Italy, i.e., the anti-aphid insecticide EPIK SL VITHAL (active ingredient: *Acetamiprid* 50 g/L-producer: Ital-agro srl) [34] and the fungicide CUMETA FLOW (active ingredients: *Metalaxil-m* 1.85%, copper hydroxide sulfate 15.40%, producer: Diachem S.p.A) [35]. These two agrochemicals were sprayed on one side of the plastic film as they were, by using a nebulizer spraying at a distance of 30 cm from the film surface.

Then, the spray-coated films were artificially aged for 2/4 weeks at 20 °C, RH 60%, and UV radiation 1000 W m^{-2}, in a chamber for artificial aging (CO.FO.ME.GRA SolarBox 3000e) at the Laboratory of Rural Buildings and Agro-Forest Land Planning—Material Testing Section—of the University of Basilicata (Italy).

The duration of this artificial aging process was chosen to simulate an aging period in an open field in Southern Italy (i.e., Apulia Region—Province of Bari), where a total of about 4850 MJ m^{-2} (116 kLy) of solar energy has been measured to come on average every

year. Given that the aging chamber's bulb emits energy with a power of 1000 W/m^{-2}, this figure roughly equates to eight weeks of artificial aging, i.e.,:

$$8 \text{ weeks} \times 7 \text{ days/week} \times 24 \text{ h/day} \times 3600 \text{ s/h} \times 1000 \text{ W m}^{-2} = 4838.4 \text{ MJ m}^{-2}$$

Therefore, the two- and four-week testing periods of artificial aging roughly correlate to three and six months of natural aging exposition, respectively.

These conditions for conducting the tests were chosen for the present research because there is no specific ISO/ASTM standard dedicated to the aging of greenhouse PE-LD films. Some relevant standards would be used to assess the degradation and performance of these films, but they provide general guidelines for testing plastics and accelerated aging, so their adaptation to the specific requirements of a greenhouse PE-LD film and agrochemical exposure conditions appears quite difficult.

The spraying of these two agrochemicals was repeated halfway through the aging period, i.e., after 1 week (in the case of the total aging duration of 2 weeks) and after 2 weeks (in the case of the total aging duration of 4 weeks), so as to simulate the ordinary conditions employed by farmers to protect their crops against plant diseases. The untreated PE-LD film samples, both unaged (N0) or aged for 2 weeks (N2) and 4 weeks (N4), were analyzed too, as reference samples.

The following samples with their identification codes—based on the type of used agrochemical (A for anti-aphid, F for fungicide), weeks of artificial aging (0, 2, 4), and "yes" or "no" halfway repetition of agrochemical spraying (y, n)—were analyzed (Table 1): (N0), (N2), (N4); (A2n), (A4n), (A2y), (A4y); (F2n), (F4n), (F2y), (F4y). For example, the sample (F4y) is PE-LD film sprayed with fungicide (F), aged four weeks in the artificial aging device (4), and halfway sprayed (y).

Table 1. Classification of analyzed PE-LD films.

Contamination	Not Contaminated	Contaminated with Anti-Aphid		Contaminated with Fungicide	
		New Halfway Spraying		New Halfway Spraying	
Aging Time		No	Yes	No	Yes
0 weeks	(N0)	---	---	---	---
2 weeks	(N2)	(A2n)	(A2y)	(F2n)	(F2y)
4 weeks	(N4)	(A4n)	(A4y)	(F4n)	(F4y)

After the aging process, all samples were subjected to tensile tests by using a Galdabini PMA10 Universal testing machine (Figure 1) equipped with a 5 kN load cell, located at the University of Basilicata, Italy (DAFE Department—Laboratory of Rural Buildings and Agro-Forest Land Planning—Material Testing Section), at 20° room temperature and 45 ± 5% RH.

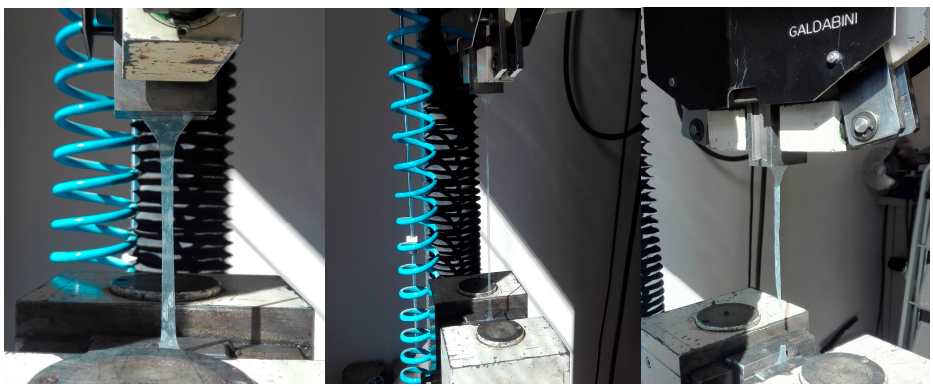

Figure 1. Tensile tests on greenhouse plastic film.

Ten specimens from each PE-LD film sample were cut with a die-cutter, whose dimensions are reported in Figure 2, in accordance with the Italian UNI 8422 Standard [36]. Each film's thickness was measured five times at random points, so as to calculate the average value.

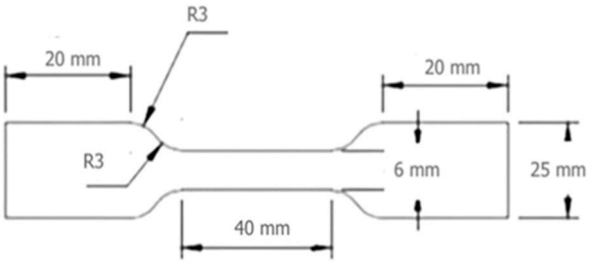

Figure 2. Dimensions of specimen for tensile test on greenhouse plastic film.

The tensile tests were carried out at a crosshead rate of 200 mm min^{-1}. Maximum strength (MPa) and percentage elongation at break (%) were measured to express the results.

With the use of a Jasco FT-IR spectro-radiometer (Jasco Global, Ikeja, Nigeria), the radiometrical properties of the plastic film were examined as well. The absorbance was measured in the wavelength range of 5380–6060 nm (1650–1859 cm^{-1}), which corresponds to the infrared region frequencies linked to the presence of functional carbonyl groups and allows for the evaluation of changes in the material's Carbonyl Index (CI) over time, which was calculated by the following equation:

$$CI = \varepsilon \frac{A^t - A^0}{S}$$

where

CI = Carbonyl Index, %;
A^t = absorptivity of the Carbonyl Index in the range 5380–6060 nm at time t, %;
A^0 = absorptivity of the Carbonyl Index in the range 5380–6060 nm at time 0, %;
ε = molar attenuation (absorptivity) coefficient, m;
S = film thickness, m.

The ability to determine the material's aging through the assessment of the CI [37]—defined as the absorptivity at the peak 1713 cm^{-1} (corresponding to a wavelength of 5838 nm) [21,38]—is an intriguing application, derived from the laboratory spectro-radiometrical tests. Indeed, the CI is a useful parameter, which aids in assessing how aged a plastic film is, since, when exposed to external weather conditions, the concentration of carbonyl groups—which are lacking in the virgin polymer—increases, changing the absorptivity in the 5380–6060 nm range and peaking in the sub-range of 5715–5850 nm [39]. A higher CI is therefore an indicator of degradation occurring, with an increase in the absorption intensity in the wavenumber range of the carbonyl groups, usually being indicative of photo-oxidation mechanisms [40]. The CI, however, also possesses some drawbacks, with uncertainty levels connected to the sensitivity to sample preparation, limited information on degradation mechanisms, some potential interferences from other functional groups, the dependence on baseline correction, limited applicability to highly oxidized samples, etc. Taking into consideration these limitations helps researchers to make informed decisions about the application and interpretation of this important parameter, which remains a valuable tool for assessing polymer oxidation, particularly when used in conjunction with other investigation techniques.

3. Results

Table 2 shows the results obtained by the tensile tests. Maximum strength [MPa] and percentage elongation at break [%] are reported in terms of average value and relevant bi-lateral confidence interval (95%).

Table 2. Results of tensile tests.

PE-LD Film	Maximum Strength [MPa]	Elongation at Break [%]
(N0)	26.00 ± 0.95	716.06 ± 22.79
(N2)	24.64 ± 0.91	687.44 ± 23.89
(N4)	20.18 ± 1.95	580.87 ± 46.41
(A2n)	20.75 ± 2.16	601.16 ± 49.29
(A2y)	21.93 ± 2.54	639.46 ± 59.15
(F2n)	16.30 ± 3.89	402.33 ± 182.78
(F2y)	21.61 ± 3.04	617.55 ± 78.51
(A4n)	13.80 ± 1.49	452.04 ± 129.48
(A4y)	18.53 ± 2.28	501.79 ± 92.76
(F4n)	10.01 ± 1.66	51.06 ± 17.24
(F4y)	16.11 ± 2.86	396.47 ± 135.39

The same values are reported in Figure 3, in terms of a bar chart displaying the mechanical property average value, positioned in the middle of its respective error bar, so as to show data visually, facilitating their interpretation.

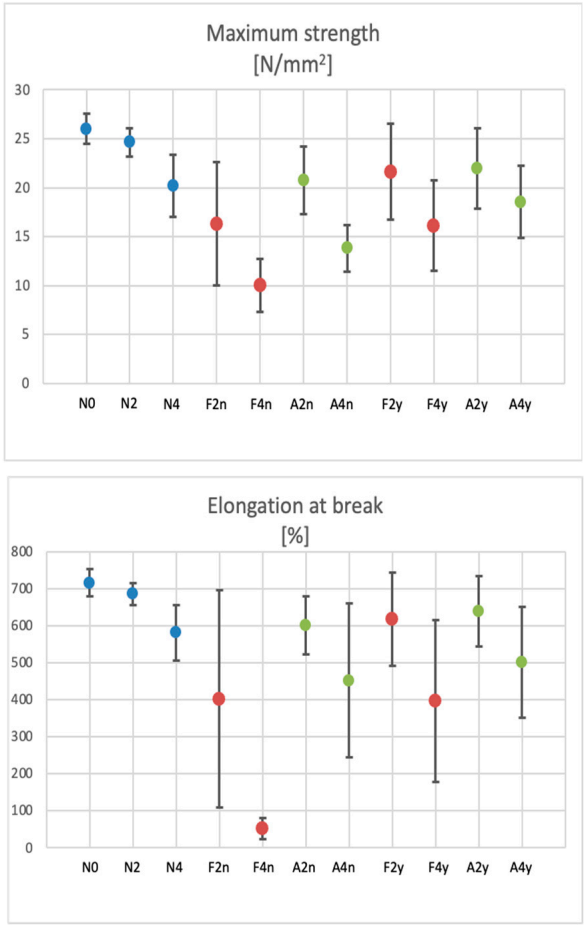

Figure 3. Bar chart based on data in Table 2, displaying the average value of maximum strength and elongation at break, positioned in the middle of the respective error bars. Different colors in this Figure 3 are referred to the different agrochemical that has been sprayed, i.e.,: RED = Fungicide; GREEN = Anti-aphid; BLUE = No spraying.

Figure 4a,b show the results of the mechanical tests, expressed in terms of maximum strength [MPa], respectively, for the samples treated with agrochemicals only once (i.e., at the beginning of the test) and the corresponding samples, undergoing two spray-coating

treatments. Figure 5a,b show the corresponding results, referring to the elongation at break. In all of these figures, both maximum strength and elongation at break are expressed as a percentage change over time, in relation to the same parameter when the material was new (i.e., for which, the original value was assumed to be equal to 100%).

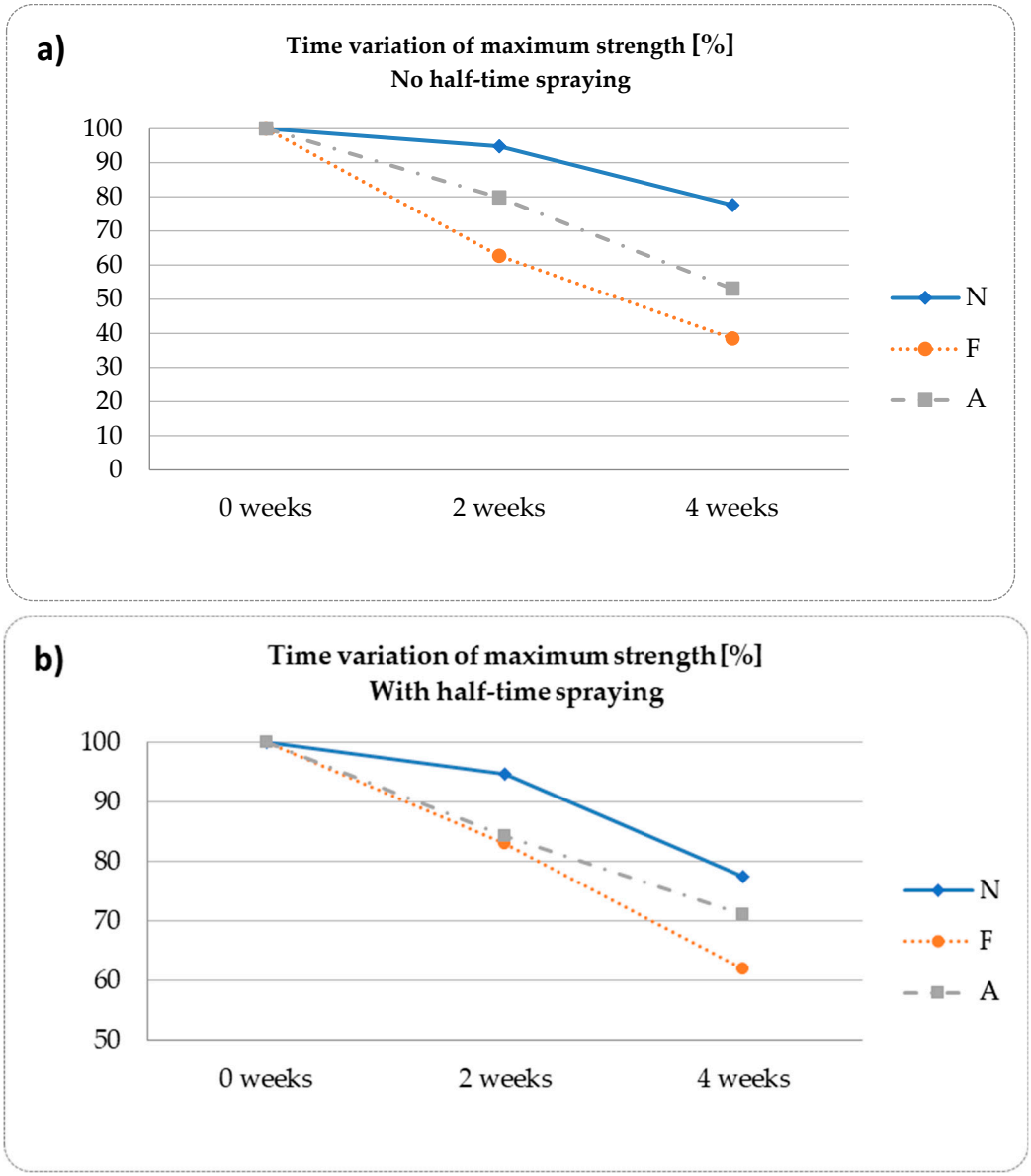

Figure 4. Ratio of aged/unaged film for each time interval of maximum strength for (**a**) virgin and after only one spray-coating samples—(N0), (N2), (N4); (A2n), (A4n); (F2n), (F4n)—and (**b**) virgin and after two (one halfway) spray-coated samples—(N0), (N2), (N4); (A2y), (A4y); (F2y), (F4y).

These results evidenced the same trends underscored in the "n" based samples, although slower kinetics of mechanical behavior decay could be observed. Hence, the repeated application of agrochemicals could have probably protected the film surface from the formation of radical groups responsible for chain scission, inhibiting the oxidative reaction with the air and slowing down the PE degradative phenomena [26]. A specific case seems to be attributed to plastic film F4n, which considerably lost its mechanical properties—mainly, its elongation at break. This is probably due to an enhanced effect on the time of the fungicide that had been sprayed, which considerably worsened the level of reliability of the same percentage elongation at break value, even after only two weeks of artificial aging.

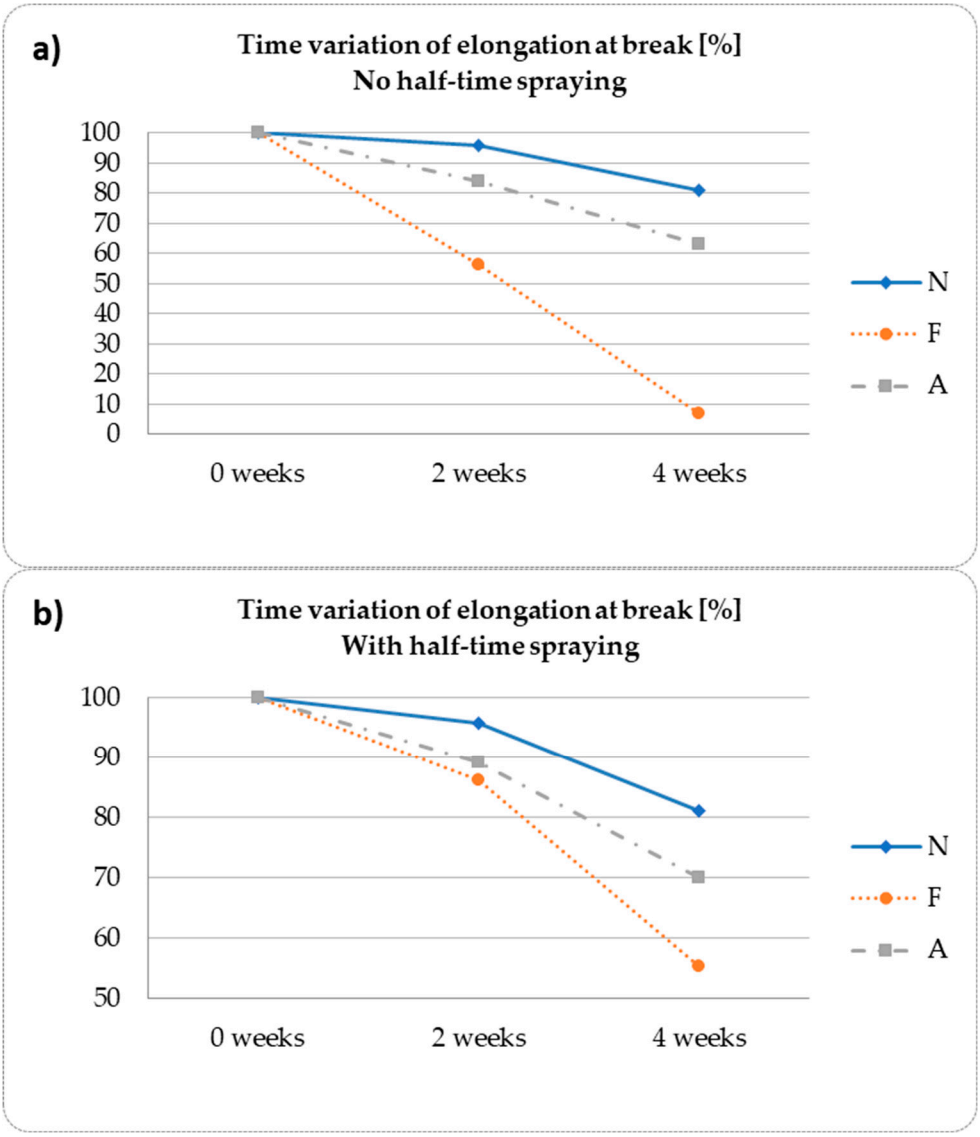

Figure 5. Ratio of aged/unaged film for each time interval of elongation at break for (**a**) virgin and after only one spray-coating samples—(N0), (N2), (N4); (A2n), (A4n); (F2n), (F4n)—and (**b**) virgin and after two (one halfway) spray-coated samples—(N0), (N2), (N4); (A2y), (A4y); (F2y), (F4y).

Finally, in terms of CI (see Table 3), the results confirmed the material's trend to quickly break down, when exposed to contact with fungicide or anti-aphid.

Table 3. Carbonyl Index percentage change during the aging period.

Artificial Aging Time	PE-LD Film		
	(N)	(A)	(F)
0–2 weeks	+31.3%	+16.1%	+21.4%
0–4 weeks	+28.5%	+26.0%	+42.4%

More specifically, the CI of the untreated sample, after the first rapid worsening, underwent a weak decrease, likely associated with cross-linking reactions occurring between the carbonyl end chains of depolymerized macromolecular segments. This outcome suggests that degradation mechanisms (mostly, chain scissoring) take place during the first period of aging, mainly influenced by the formation of carboxyl and double bond terminal groups, as widely reported in the literature [41]. Indeed, the reactive terminal groups,

like carbonyl ones, can provide cross-linking reactions, thus reducing their concentration. However, after four weeks of aging, the CI values of the agrochemical-sprayed samples noticeably increased. This outcome confirms the previous hypothesis of the photo-catalytic degradation of the agrochemicals, mainly fungicides, responsible for faster PE polymer chain scission (Norrish reactions) according to mechanical performance [42].

4. Discussion

From these results, it is worth highlighting a significant effect of the deterioration of the mechanical properties of the film, due to the likely synergistic effect induced by both the agrochemicals and the artificial aging. In particular, the samples treated with the fungicide are much more affected by the worsening of mechanical performances. This result could be correlated to specific interactions and reactions occurring between Metalaxil-m and polyethylene during UV-accelerated weathering. Although a detailed description of the chemical phenomena is outside of the current paper's aim, it is possible to hypothesize that the active fungicide, whose structure is made of [N-(2,6-dimethylphenyl)-N-(methoxy-acetyl)-DL-alanine ester], shows chemical functional groups sensitive to redox-photocatalytic processes, able to generate a series of active radicals, strongly contributing to the photodegradation Norrish reactions of polyethylene, leading to the scission of the main chain [41,42]. Differently from the fungicide, the acetamiprid—whose chemical structure is typical of a chloronicotinyl compound including monochloropyridine, a nitrile, and a carboxamidine—follows different photodegradation mechanisms, strongly correlated to the specific environment. It is particularly enhanced in a water environment, due to the presence of pyridine and double and triple carbon nitrogen groups [43].

It is also worth highlighting that the mechanical properties of all the samples treated with double fungicide and insecticide spraying follow slower degradative kinetics, as shown in Figures 4 and 5. It is likely that the higher concentration of both active compounds provides a thicker coating on the PE surface, thus preserving the polymer from the faster degradative phenomena. This outcome is significant since the double treatment supports an improved action of both compounds, which protects the PE-LD film from the fast photodegradation phenomenon. This occurrence could be taken into consideration both to enhance the action of the functional compounds and to preserve the mechanical performances of the polymer matrix for longer times.

Nevertheless, after four weeks of film permanence in the aging chamber (equivalent to about six months of real aging conditions on a greenhouse located in Southern Italy, at least in terms of global energy received), the PE-LD plastic film should be replaced, since, after coming into contact with a pesticide or fungicide, it has lost 50% of its "as new" elongation at break, thus its useful life may be considered as finished.

The impact of the contamination of the film material by these agrochemicals in the use phase is considerable. The effect on the material in the use phase reflects a consequent hindrance of the material, from a recycling perspective. Indeed, as the material enters the recycling stage, its chances of becoming a closed-loop recycled material are rather low. When PE-LD film comes into touch with the fungicide, this behavior is particularly evident. As shown in Figure 5b, the material has almost entirely lost its mechanical properties, after four weeks of artificial aging. Further reprocessing through mechanical recycling would be therefore impossible, since the material becomes brittle and fragmented. This is especially important when taking into account the extra breakdown mechanisms that thermo-mechanical processes cause in polymers during mechanical recycling [44,45].

These findings appear to be consistent with the literature outcomes presented in the earlier sections, corroborating the existence of a correlation between the absorption intensity showed by a variation in the CI value, with the degradation of the plastic film. Since the Carbonyl Index acts as an indicator of the extent of degradation in the plastic films used in greenhouses, the main chemical reactions occurring during plastic UV aging responsible for its variation must be mentioned. The main degradation mechanisms (photo-oxidation,

thermo-oxidative degradation, photo-fragmentation, and cross-linking/chain scission) and the pivotal chemical reactions involved are detailed as follows:

(I) Photo-Oxidation

Initiation step. The initial step involves the absorption of UV light by the polymer, leading to bond cleavage and the formation of free radicals.

$$\text{R-H} + \text{UV}h\nu \rightarrow \text{R}\cdot + \text{H}$$

Propagation step. The free radicals react with molecular oxygen to form peroxy-radicals, which can then form hydroperoxides.

$$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$$

$$\text{ROO}\cdot + \text{R-H} \rightarrow \text{ROOH} + \text{R}\cdot$$

Decomposition step.

Hydroperoxides are unstable and decompose to form alkoxy and hydroxyl radicals, leading to the formation of carbonyl compounds.

$$\text{ROOH} \rightarrow \text{RO}\cdot + \text{OH}\cdot$$

$$\text{RO}\cdot \rightarrow \text{R}'\cdot + \text{R-C(=O)-R}''$$

Thus, in the photo-oxidation process, the general whole reaction can be resumed in

$$\text{Polymer} + \text{O}_2 + h\nu \rightarrow \text{Carbonyl-containing compounds} + \text{Other degradation products}$$

(II) Thermo-Oxidative Degradation

Initiation. Thermal energy causes the homolytic cleavage of polymer chains, forming free radicals.

$$\text{R-H} \xrightarrow{\Delta} \text{R} + \text{H}\cdot$$

Propagation and Decomposition. As occurs for photo-oxidation, the free radicals react with oxygen to form peroxy radicals and hydroperoxides, which decompose to form carbonyl compounds and double bonds.

$$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$$

$$\text{ROO}\cdot + \text{R-H} \rightarrow \text{ROOH} + \text{R}\cdot$$

$$\text{ROOH} \rightarrow \text{RO}\cdot + \text{OH}\cdot$$

$$\text{RO}\cdot \rightarrow \text{R}'\cdot + \text{R-C(=O)-R}''$$

$$\text{RO}\cdot \rightarrow \text{R-CH=CH-R} + \text{R}''$$

Thus, in the thermo-oxidation process, the general whole reaction can be resumed in

$$\text{Polymer} + \text{O}_2 + \Delta \rightarrow \text{Carbonyl-containing compounds} + \text{Alkenes} + \text{Other degradation products}$$

(III) Direct Bond Scission

Moreover, UV radiation can directly cleave bonds in the polymer backbone, forming smaller fragments that can further react with oxygen and each other to form carbonyl compounds and double bonds.

$$\text{R-R}' + h\nu \rightarrow \text{R}\cdot + \text{R}'\cdot$$

$$\text{R}\cdot + \text{O}_2 \rightarrow \text{R-C(=O)-R}''$$

$$\text{R}\cdot + \text{R}\cdot \rightarrow \text{R} = \text{R}$$

Thus, if direct bond scission occurs, the general whole reaction can be resumed in

Polymer + hν→Carbonyl-containing compounds + Alkenes + Smaller fragments

(IV) Cross-Linking and Chain Scission

During the first step of polymer decomposition, a cross-linking reaction could occur between free radicals formed during UV exposure and other polymer chains. In addition, the polymer chains can break, leading to the formation of smaller chains with terminal carbonyl groups and double bonds.

$$R\cdot + R'\cdot \rightarrow R\text{-}R'$$

$$R\text{-}CH_2\text{-}CH_2\text{-}R + h\nu \rightarrow R\text{-}CH\cdot + \cdot CH_2\text{-}R$$

$$R\text{-}CH\cdot + O_2 \rightarrow R\text{-}CHO$$

$$R\text{-}CH\cdot + R\cdot \rightarrow R\text{-}CH{=}CH\text{-}R$$

The general reactions involved in these processes can be resumed in

Polymer + *hν*→Cross-linked polymer + Alkenes + Smaller chains with carbonyl groups

All the previous schematized degradation mechanisms lead to aldehydes, ketones, carboxylic acids, and alkenes as primary oxidation products.

Formation of Aldehydes: $R\text{-}CH_2\text{-}R' + O_2 \rightarrow R\text{-}CHO + R'\cdot$

Formation of Ketones: $R\text{-}CH + O_2 \rightarrow R\text{-}C(=O)\text{-}R'$

Formation of Carboxylic Acids: $R\text{-}CHO + O_2 \rightarrow R\text{-}COOH$

Formation of Alkenes: $R\text{-}CH + R\cdot \rightarrow R\text{-}CH{=}CH\text{-}R$

Degradation mechanisms were therefore magnified by the combined effects of photo-oxidation from solar radiation with the chemical actions of the agrochemicals, altering the polymeric matrix structure. The rise in the concentration of carbonyl groups at the surface is directly correlated with the fluctuation of the absorbance value, measured at 1718 cm^{-1}, as a function of irradiation duration for the investigated materials. Dehbi et al. [32] found a strong correlation between the increase in CI and the decrease in PE-LD molecular weight, which occurs during photo-thermal degradation. The absorption band at 1713 cm^{-1} contained carbonyl groups, which are indicative of photo-oxidation processes. The quantity of products generated was in good agreement with variations in the carbonyl index and molecular weight. More low-molecular-weight compounds were produced as the photo-oxidation period increased. As a result of the enhanced oxygen availability at the surface layers, the oxidation of PE-LD materials produced a variety of carbonyl groups, including carboxylic acids, aldehydes, esters, ketones, and lactones. Due to the complexity of the occurring chemical photodegradation reactions, it is, however, very difficult to discern the real sequence of chain scissoring and end-group recombination in cross-linking reactions.

Under the influence of the UV-A component, plastics exposed to solar radiation undergo photo-degradation, which is thought to be a major factor in the fast deterioration of their characteristics and results in scissoring and cross-linking reactions, as well as oxidation. The results of photo-degradation are frequently vinyl, hydroxyl (OH), and carbonyl (C-O) groups. Numerous experimental studies with films exposed to UV radiation have demonstrated that the increase in carbonyl residues coincides with the worsening of mechanical performances, a decrease in molecular weights, and an increase in polymer crystallinity. The correlation of these aspects was empirically proven on PE-HD materials by Picuno C. et al. [46]. Through differential scanning calorimetry (DSC), FTNIR, and analysis

of the Melt Flow Index, these authors showed a strict correlation between the reduction in these parameters and the recyclability of the material, a characteristic that plays a crucial role in implementing the concept of the Circular Economy in agriculture [47]. In addition, a significant drop in the degraded film permeability to oxygen was proven by Briassoulis et al. [24,30], who showed that photo-degradation was also strongly dependent on thermal levels since it severely increased with temperature rising. In order to design the chemical formulation of the basic polymer and/or quantity and quality of its additives, it appears then possible to conclude that the results of this study are consistent with those obtained thus far in the international scientific literature. This confirms the need for further research aimed at developing an algorithm that could predict the useful lifetime of a plastic film, on the basis of the geographical location and relevant meteorological conditions, working conditions (agrochemical contamination, contact with frame steel, other environmental agents, etc.), type of cultivation, etc.

Finally, it should be mentioned that the aging of polyethylene (PE)-based materials utilized in agriculture, including greenhouse films, mulch films, and irrigation pipes, has garnered considerable attention, due to its environmental sustainability implications and the resultant production of microplastics (MPs). The degradation of these materials is significantly influenced by various environmental stressors, such as UV radiation, temperature fluctuations, mechanical stress, and chemical interactions with agrochemicals, like pesticides and fertilizers. Studies have shown that these factors contribute to the fragmentation of PE into microplastics, which poses a severe environmental challenge [48–50]. For instance, the photodegradation of low-density polyethylene (PE-LD) microplastics has been extensively studied, revealing that accelerated aging occurs under varying humidity and soil conditions, leading to significant material degradation [25]. Addressing these challenges requires innovative material design strategies that facilitate controlled degradation patterns. The concept of "design-for-recycling" is crucial, as it emphasizes the need for materials that can be effectively recovered and recycled before they fragment into microplastics [51]. Long-term field research is essential to evaluate how PE materials degrade under actual agricultural conditions, capturing the cumulative effects of solar radiation, seasonal variations, and interactions with agrochemicals [52]. Such research can inform the optimal timing for PE film recovery and recycling, thereby mitigating environmental impacts [52]. Furthermore, integrating suitable policies that promote regulated lifecycle management of PE materials can significantly enhance sustainability efforts in agriculture. By bridging innovative material design with effective policy frameworks, stakeholders can work toward reducing the environmental footprint of agricultural plastics [51,52]. The implementation of consolidated biodegradable alternatives and enhanced recycling processes can also play a pivotal role in addressing the accumulation of agricultural plastic waste, thus contributing to more sustainable agricultural practices [53,54].

5. Conclusions

The present investigation has contributed to the evaluation of the lifetime of an agricultural plastic film, assessing the combined effects of solar radiation and pesticide contamination on the technical properties of PE-LD greenhouse films and their potential to be transformed into a new secondary product. It has demonstrated that agrochemical by-products, whose breakdown was controlled by the active principles of the chemicals, as well as by the application technique and frequency, cause greenhouse films to degrade and lose part of their mechanical and physical qualities. However, the results here achieved have also shed light on the possibility that successive spraying may have not increased the aging mechanisms but rather contributed to their fixation. These results seem to fill a knowledge gap since they encourage further scientific research and technological development, aimed at the investigation of innovative solutions able to improve the durability of plastic films used in agriculture, as well as their post-consumer recyclability.

The practical implications of the results from the present research showed that, while UV radiation had the greatest effect on PE-LD films, the degradation of the films was

significantly influenced by the synergistic effects and relative significance of exposure to the two distinct agrochemicals. It is quite likely that mechanical recycling methods would have a detrimental effect on the viability of this material. In this regard, more investigation is needed on the material's capacity for recycling, the effects of the Melt Flow Index, and the modulation of melting and crystallization temperatures. It was determined that the Carbonyl Index fluctuation was a dependable measure of the plastic film's degree of deterioration, allowing for the determination of the ideal circumstances for its removal and transportation to mechanical recycling facilities.

A polymer's mechanical properties can deteriorate for a number of reasons, such as internal or included defects, the presence of additives that interact with the polymer and alter its primary structural characteristics, or the polymer matrix not being compatible with the additive, which prevents the proper load transfer from the matrix to the disperse phase. In this instance, it is anticipated that faster aging encourages the autocatalytic photodegradation of both compounds, which is the cause of the PE photodegradation activity and the decline in mechanical characteristics. According to the structural, molecular, and morphological examination of PE-LD, subsequent research would concentrate on the impact that various agrochemicals may have on the mechanical properties of greenhouse plastic film, taking into account both the impacts of aging and agrochemicals. More wide real tests should be performed in the field, in order to better understand the synergy of effects inducing the aging of PE, as laboratory conditions often fail to match real-world scenarios. An in-depth insight into all the effective aging parameters could therefore contribute to the definition of guidelines that can be used by the industry for implementing design-for-recycling protocols for agricultural plastic films, which will then be able to precisely define the characteristics of plastic films for agriculture, contributing to the future direction, pointing toward a more rational use of plastic materials in agriculture and to their efficient post-consumer recycling, thus contributing to a reduction in the plastic footprint of agriculture.

6. Patents

There are no patents resulting from the work reported in this manuscript.

Author Contributions: Conceptualization, C.P. and Z.G.; methodology, P.P.; validation, G.S.; writing—original draft preparation, P.P. and G.S.; writing—review and editing, C.P. and Z.G.; supervision, P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Acknowledgments: The mechanical and spectro-radiometric laboratory tests were carried out by Cosimo Marano, a member of the technical staff of the University of Basilicata's DAFE Department, to whom the authors express their gratitude.

Conflicts of Interest: Authors Caterina Picuno and Zoe Godosi were employed by the company DMTR Consulting. The remaining authors declare that the re-search was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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