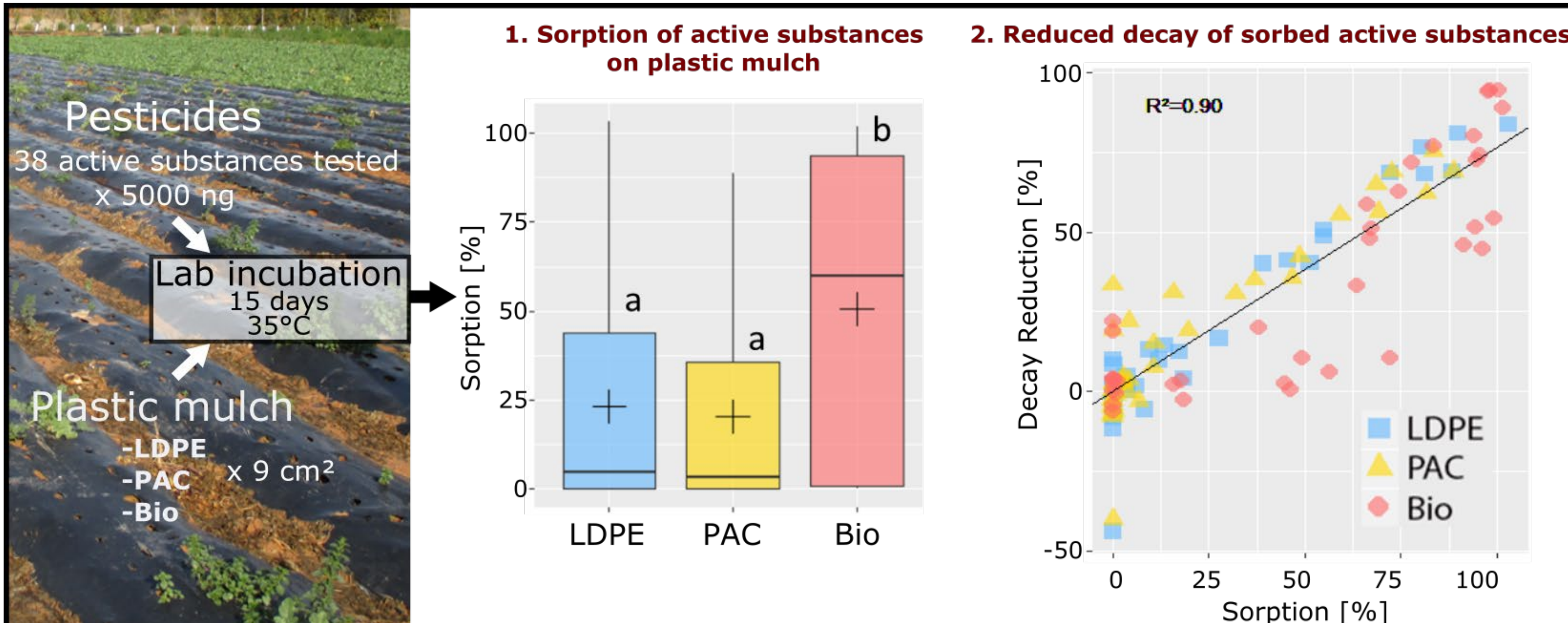
Interactions between agricultural mulching plastic debris and pesticides



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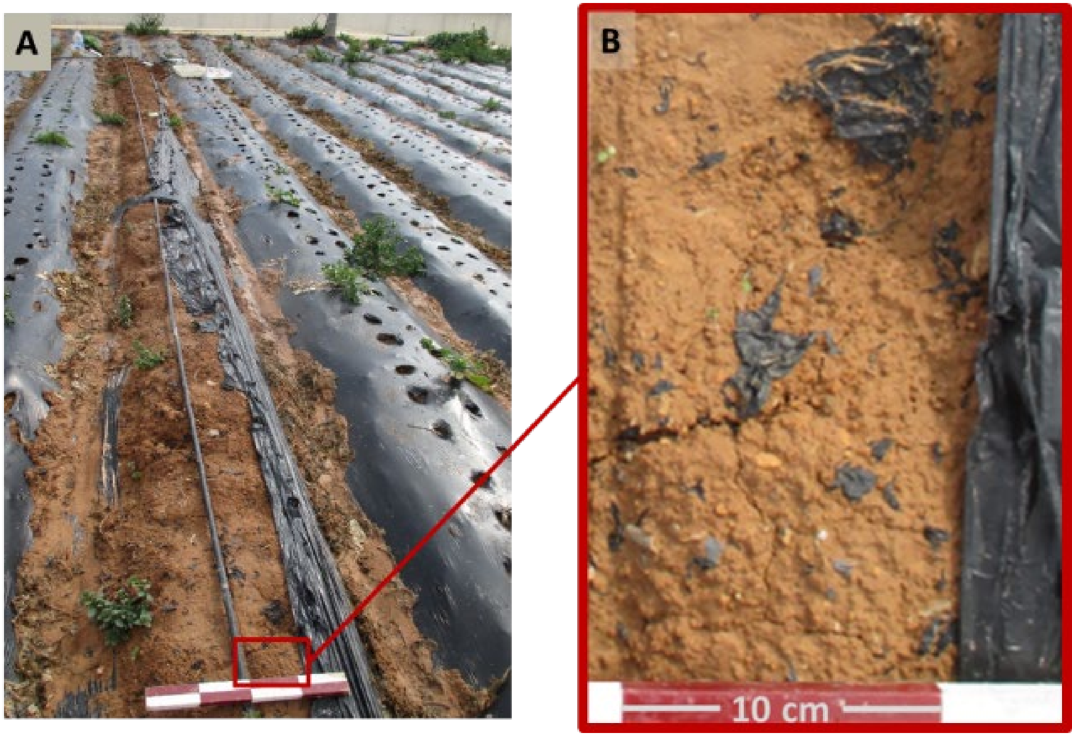
The European Commission estimated in 2016 that 100 000 tonnes of plastic mulch is used per year.



Plastic mulch is use to:

- Control weeds
- Increase soil temperature
- Decrease water evaporation

Light density polyethylene plastic mulch after harvest of Kohlrabi. The sides of the mulch film are buried into the soil making complete removal impossible and leading to debris accumulation over time.

Pesticides are widely applied in conventional agriculture and leave residues in the soil

Pesticides are mostly used in mixtures.

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Pesticide residues in European agricultural soils – A hidden reality unfolded

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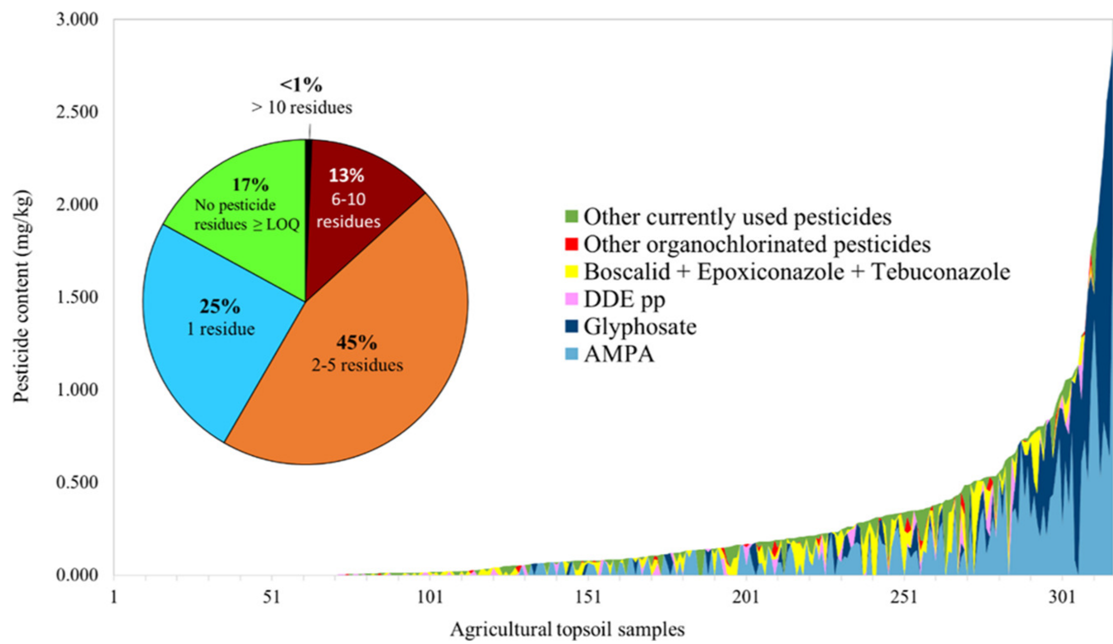


3 plastic mulches tested

- Low Density Polyethylene **(LDPE)** Fully saturated polymer of hydrocarbons
    - Highly resistant
- Pro-oxidant Additive Containing **(PAC)** LDPE with additive to enhance oxidation and photo-degradation
    - Tend to accumulate when buried in the soil
- Biodegradable **(Bio)**
    - Polybutylene adipate terephthalate
    - Supposedly degradable by soil microorganisms

38 pesticide active substances (AS)

- 17 insecticides
- 15 fungicides
- 6 herbicides

Commonly applied with plastic mulching in South-east Spain

Active substances tested:

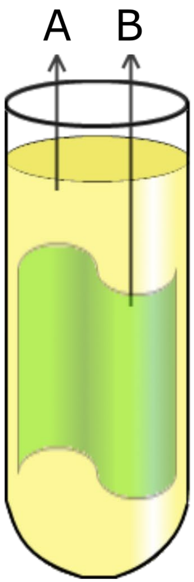
Active substance	LOQ [ng/mL]	Category
Ametoctradin	2.5	fungicide
Azadirachtin	2.5	insecticide
Azoxystrobin	0.125	fungicide
Boscalid	0.125	fungicide
Chlorantraniliprole	0.125	insecticide
Chlorpyrifos	1	insecticide
Clorimuron-ethyl	0.125	herbicide
Cyflufenamid	0.125	fungicide
Cyfluthrin	2.5	insecticide
Lembda-cyhalothrin	2.5	insecticide
Cymoxanil	1	fungicide
Cypermethrin	2.5	insecticide
Deltamethrin	2.5	insecticide
Difenoconazole	0.125	fungicide
Dimethomorph	0.125	fungicide
Emamectin	0.125	insecticide
Fenhexamid	0.5	fungicide
Flonicamid	0.125	insecticide
Fluazinam	5	fungicide

Active substance	LOQ [ng/mL]	Category
Flufenoxuron	0.125	insecticide
Fluopicolide	0.125	fungicide
Imidacloprid	0.125	insecticide
Indoxacarb	0.125	insecticide
Kresoxim-methyl	5	fungicide
Linuron	2.5	herbicide
Metalaxyl	2.5	fungicide
Metrafenone	0.125	fungicide
Metribuzin	2.5	herbicide
Oxyfluorfen	0.25	herbicide
Pendimethalin	1	herbicide
Pirimicarb	0.125	insecticide
Propamocarb	0.25	fungicide
Propyzamide	2.5	herbicide
Pyraclostrobin	0.125	fungicide
Spinosyn-A	0.125	insecticide
Spinosyn-D	0.125	insecticide
Spirotetramat	0.125	insecticide
Thiacloprid	0.125	insecticide

LOQ : limit of detection

Materials and Methods

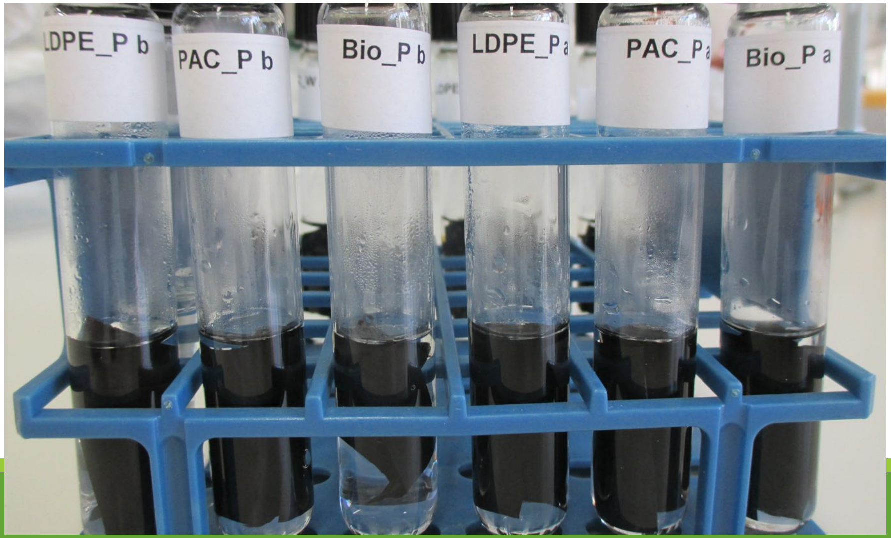
Incubation in glass tubes at 35°C for 15 days in a laboratory oven



3x3 cm² plastic square : either LDPE, PAC or Bio

5 mL incubation solution : either with or without a mixture of 1000 ng/mL of each active substance in 10% acetonitrile and 90% distilled water

↑ Pesticides extraction and analysis in the soultion (A) or plastic (B)



Pesticides extraction :

- 5 mL of distilled water and 10 mL of acetonitrile containing 1% acetic acid (Molbet al. 2008)
- Ultrasonic bath and shaking for one hour (Nerín et al. 1996)
- phase separation with 1 g of sodium acetate and 4 g of magnesium and centrifugation

Pesticides determination adapted from the QuEChERS (Quick Easy Cheap Effective Rugged Safe) approach (Anastassiade et al. 2003) :

- LC-MS/MS system (TQ-S coupled to Aquity UPLC, from Waters Milford, MA, USA)
- Calibration curve of nine fortified blanks (0, 0.125, 0.25, 0.5, 1, 2.5, 5, 10, 25 ng mL^{-1})
- Blank fortified at 5 ng mL^{-1} every 10 measurements
- Peaks integration with MassLynx™ (Version 4.1, Waters)
- Limit Of Quantification (LOQ) : lowest calibration level inside the linearity range (deviation of back-calculated concentration from true concentration within ± 20%) and an ion ratio within ± 30% of the average of calibration (EuropeanCommission 2017)

Measurement :

m_i = mass of active substance initialy in the solution
$m_{solution}$ = mass of active substance extracted from the solution after the incubation
$m_{plastic}$ = mass of active substance extracted from the plastic after the incubation

Calculation :

$$\text{Sorption} = \frac{m_{plastic}}{m_i}$$

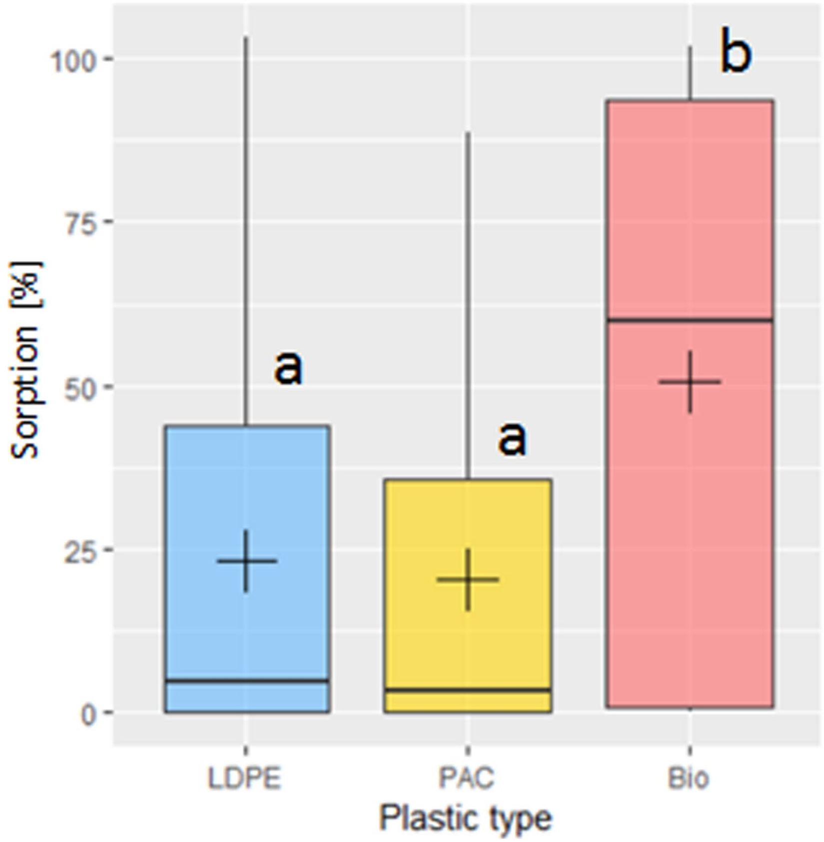
$$\text{Recovery} = \frac{m_{plastic} + m_{solution}}{m_i}$$

$$\text{Decay} = 1 - \text{Recovery}$$

$$\text{Decay reduction} = \text{Decay without plastic} - \text{Decay with plastic}$$

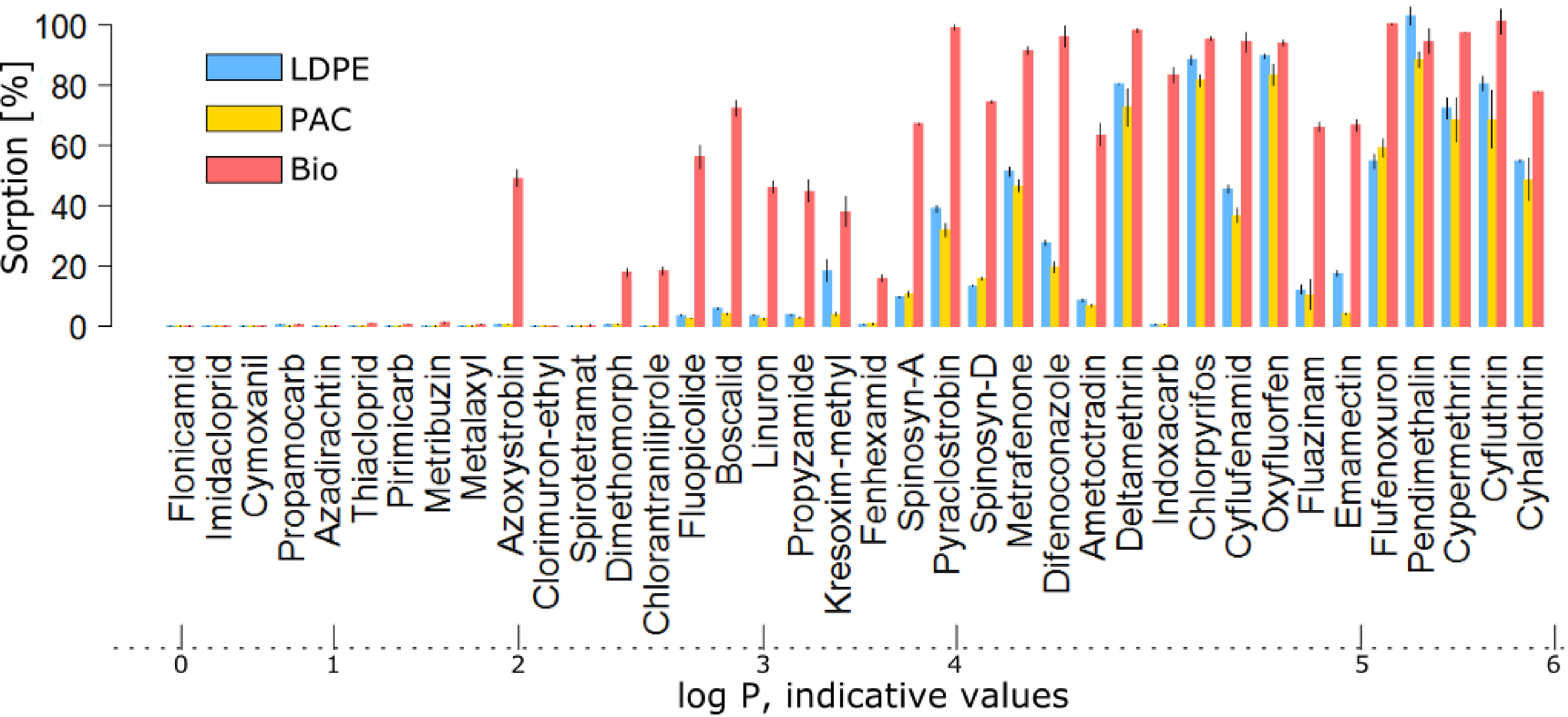
Average sorption on the 3 plastic mulches :

~23% LDPE and PAC mulches
~50% for Bio mulches



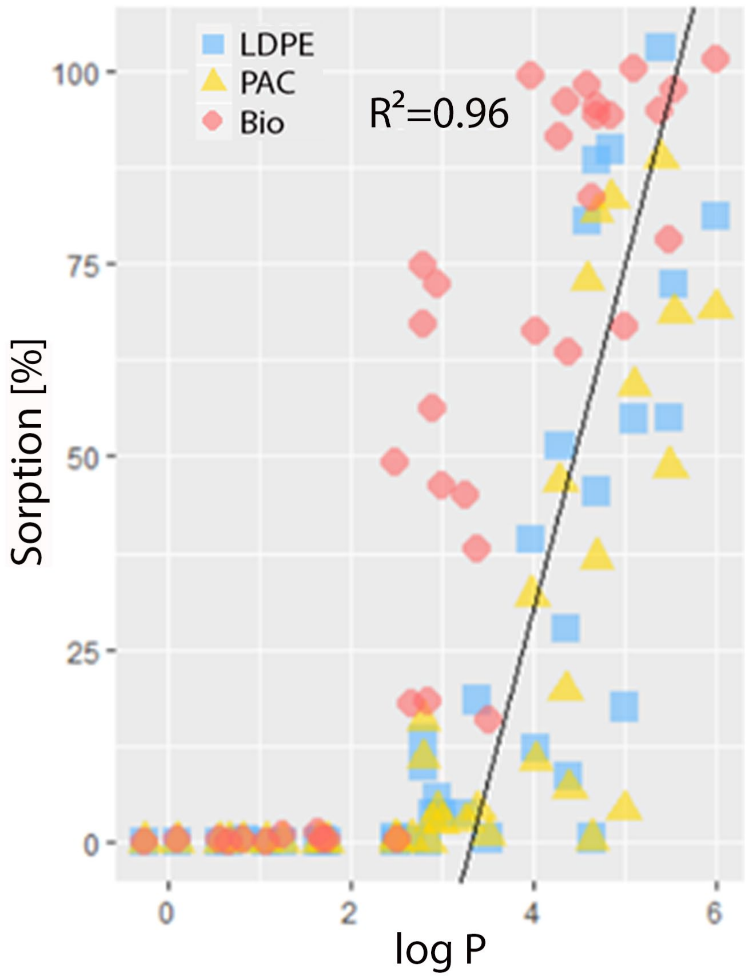
Sorption [%] on each type of plastic: LDPE (blue), PAC (orange) and Biodegradable (red)
The box plot (horizontal lines) represents sorption for at least 25%, 50% and 75% of the active substances. The vertical black lines represent the minimum and maximum values. The cross is the mean sorption for all active substances. Different letters indicate significant differences among plastic types after a Kruskal-Wallis comparison at $p < 0.05$

Different sorption behavior for all active substances:



Mean sorption [%] for each active substance on LDPE (blue), PAC (orange) and Biodegradable (red) plastic mulch. Black lines at the top of each column represent the measurement ranges (min and max). Active substances are ordered according to increasing **log P** (octanol-water partition coefficient at pH 7, 20°C)

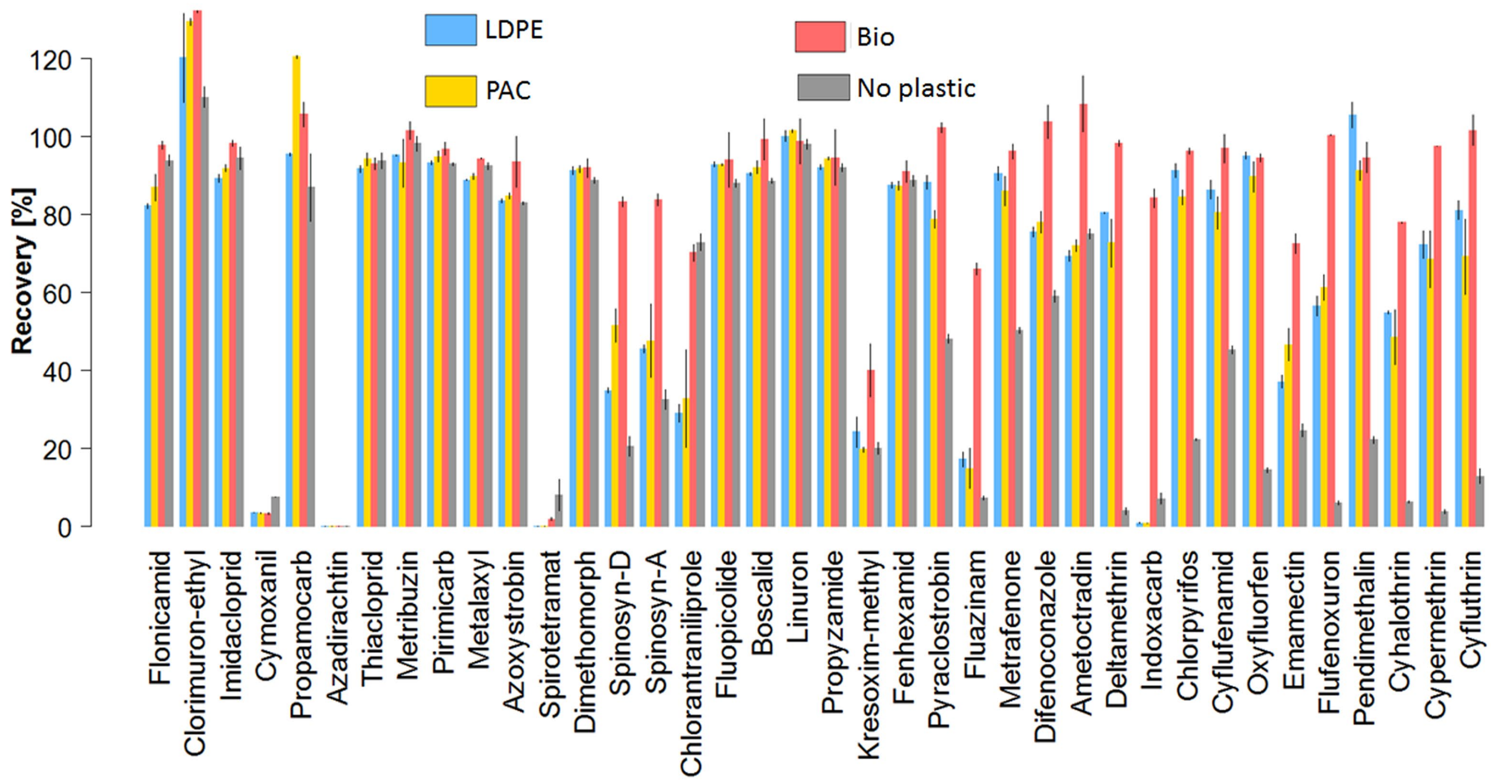
Sorption behavior is linked to the log P of the active substances.



Sorption [%] of active substances on LDPE, PAC and Bio mulch as a function of the active substances log P (octanol-water partition coefficient).

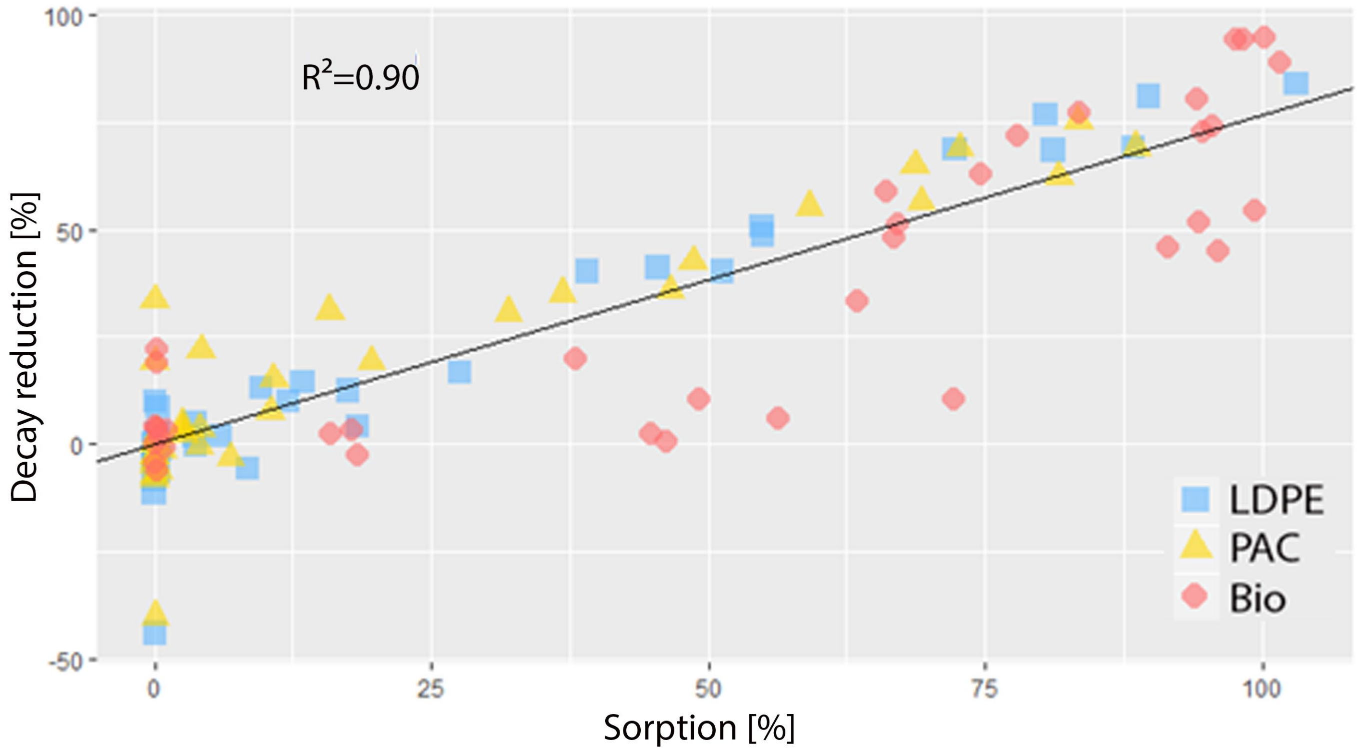
The black line is a regression calculated for sorption >0 : y=46x-150 ; R^2 = 0.96 ; $p<0.0001$

The recovery varies for all active substances and for the plastic used



Recovery [%] for each active substance with LDPE (blue), PAC(orange) and Biodegradable(red) plastic mulch and without plastic mulch (grey). Black lines at the top of each column represent the measurement ranges (min and max). Active substances are ordered according to increasing log P (octanol-water partition coefficient) from left to right

Decay reduction reduction is linked to the sorption behavior of the active substances.



Decay reduction [%] for active substances sorbed on plastics related to the sorption [%] of active substances for the three types of plastic, LDPE (blue square), PAC (orange triangle) and Biodegradable (red circle). The black line is the regression calculated for sorption >0 : $y=0.76x$; $R^2=0.90$; $p<0.001$

Limitations:

- Only one time measurement : No kinetic data
- Mixture of active substances: possible competitive sorption
- Medium not representative to the field conditions
- Concentration higher than applied concentration
- Not aged plastic used
- Only one type of biodegradable plastic

Need for research :

- Use of kinetic experiment
- Use aged plastic
- Test the sorption of pesticides plastic in different soil conditions
- Test different types of biodegradable plastics

Conclusion

- Active substances sorption ~23% on LDPE or PAC and ~50% on Bio
- Sorption on plastic may reduce the active substances decay

Thank you for you attention!