LIFE AQUEMFREE

LIFE13 ENV/ES/000488

LIFE-Aquemfree: In-Farm remediation by solar photocatalysis of agro-waste water

Isabel Garrido Martín

Athens, 17 January 2020

Región de Murcia
Consejería de Agricultura y Agua

Instituto Murciano de Investigación y Desarrollo Agrario y Alimentario imida

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Novedades Agrícolas

FECOAM

The project

Project ENV/ES/000488 LIFE-Aquemfree

Co-ordinator: IMIDA
Partners: Universidad de Murcia
Novedades Agrícolas S.A.
Federación de Cooperativas Agrarias de Murcia

48 months (01/07/2014 – 30/06/2018)

Total budget: 1.863.566 €

CE contribution: 911.356 €

LIFE13 ENV/ES/000488
LIFE-Aquemfree

Beneficiary:
Type of beneficiary
Regional authority

Name of beneficiary
Consejería de Agricultura y Agua
Comunidad Autónoma de la Región de Murcia

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Fulgencio CONTRERAS LOPEZ

Duration of project:
48 months (01/07/2014 – 30/06/2018)

Total budget in euro:
1,863,566.00

EC contribution in euro:
911,356.00

Themes: Environmental management: Cleaner technologies / Industry-Production: Agriculture – Fisheries / Risk management: Pollutants reduction / Water: Waste water treatment

Background

Murcia as a pilot Region

Contribution to Spanish production

25% vegetable production

60% lemon

60% table grape

50% melon

50% grapefruit

250.055 has

8.420 Tm PPP/year

90.000 m^3 waste water (360 l/ha)

Background

Agro-waste water

Tank rinse after treatments

Treatment remnants

Packaging rinse

Equipment and machinery cleaning

Average waste water in a farm 2.5 m^3/year

Background

Legal framework

The **Directive 2009/128/EC to achieve the sustainable use of pesticides** obliges Member States to *«…adopt the necessary measures to ensure that the* operations *by professional users and where applicable by distributors do not endanger human health or the environment»*

Background

Legal framework

Operations include:

- handling of packaging and remnants of pesticides
- disposal of tank mixtures remaining after application
- cleaning of the equipment used after application
- recovery or disposal of pesticide remnants and their packaging

Background

Available technologies 2012

HELIOSEC (Syngenta): The effluent is dehydrated and subsequently the waste is removed

PHYTOBAC (Bayer): The effluents are decomposed in the soil naturally by the effect of microorganisms in a closed system

Background

The problems to be tackled

Environmental: waste water management

Legal: Directive “sustainable use of pesticides”

Technical: no complete solution available

The project

Objective: 0 residue in water

Demonstrate an alternative, economic and ecological technique to degrade pesticide residues contained in wastewater produced on farms by remnants in containers and treatment tanks, rinsing tanks after use, cleaning machinery and equipment, etc. with innovative equipment installed in the farms

The project

- One first prototype of AQUEMFREE equipment installed and running in one pilot farm.
- 4 pilot pieces of equipment installed and running in four commercial farms.
- Operation Manuals for equipment and method procedures.
- Technical and socio-economic viability results.
- Governance recommendations for public authorities, both legal and financial instruments

Conventional processes: unable to eliminate persistent pesticides (reverse osmosis, adsorption, disinfection,..)

Advanced oxidation processes (AOPs): Generation of strongly reactive free radicals to react with recalcitrant organic compounds

Photochemical AOPs → solar or artificial light for generating $^{\bullet}OH$

Non-photochemical AOPs → other types of energy for generating $^{\bullet}OH$

Non-photochemical	Photochemical
Ozonization in alkaline media (O_3/HO^-)	Photolysis of water in vacuum ultraviolet
Ozonization with hydrogen peroxide (O_3/H_2O_2)	UV/H_2O_2
Fenton processes (Fe^{2+}, Fe^{3+}/H_2O_2)	UV/O3
Electro-oxidation	$UV/O_3/H_2O_2$
Electrohydraulic discharge-ultrassound	Photo-Fenton processes (Fe^{2+}, $Fe^{3+}/H_2O_2/UV$)
Supercritical water oxidation	**Heterogeneous photocatalysis**
Catalytic wet air oxidation	Sulphate radical-based

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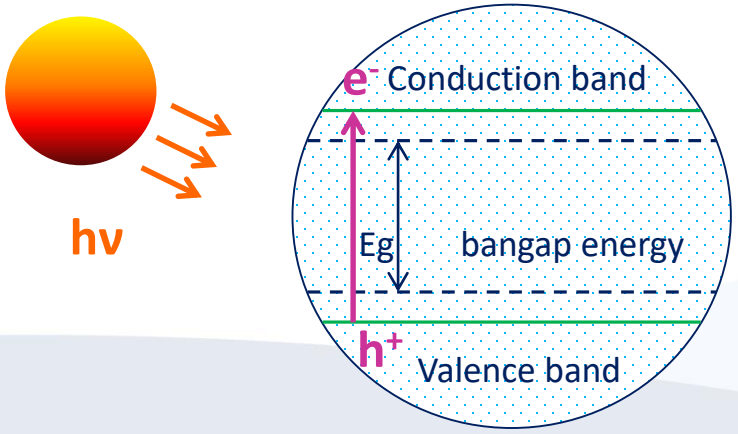
SOLAR PHOTOCATALYSIS

Radicals are formed by light radiation (photons)

$e^- + O_2 \rightarrow O_2^{\bullet -}$

$O_2^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH$



$TiO_2 + hv \rightarrow h^+ + e^-$

$h^+ + H_2O \rightarrow {}^{\bullet}OH$

Organic pollutants

↓

Intermediate products

$CO_2 + H_2O$ + inorganic salts

Photocatalyst: Semiconductor particulate material (TiO_2, ZnO,…)

- Photoactive
- Able to utilize visible/UV light
- Biologically and chemically inert
- Photostable
- Inexpensive
- Non-toxic

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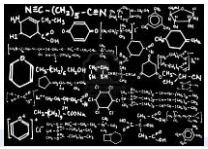
The process

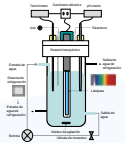
2014 → **2018**

1. Ex-ante analysis and selection of pilot farms

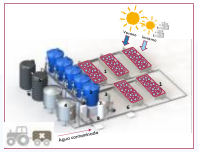


2. Selection of phytosanitary products

3. Fine-tuning of analytical metodology



4. Optimization at laboratory scale



5. Essays at field scale in pilot plant

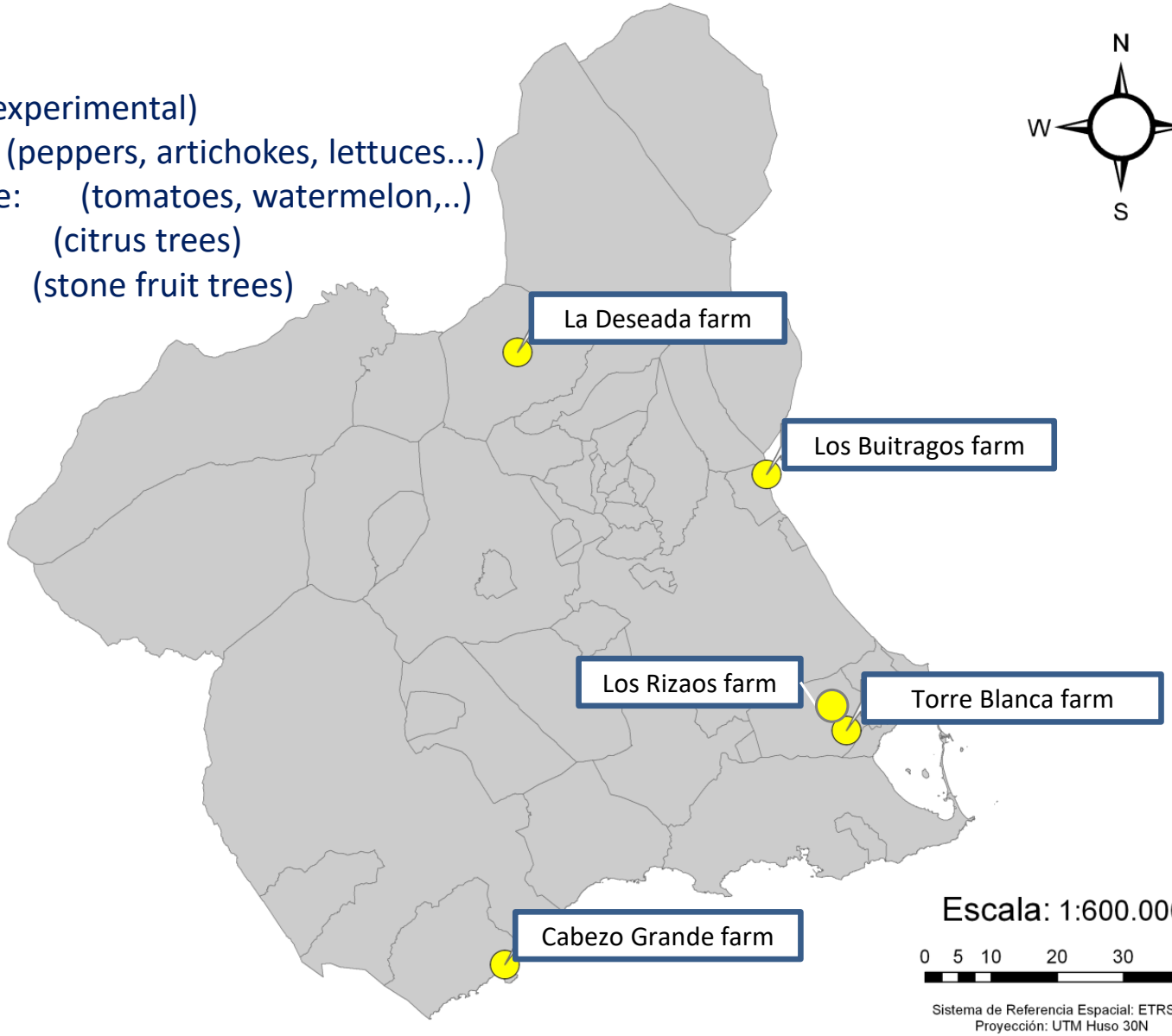
6. Prototypes installed in 4 farms and essays performed in real conditions

7. Analysis of results and socio-economic assessment

8. Reporting and dissemination of results

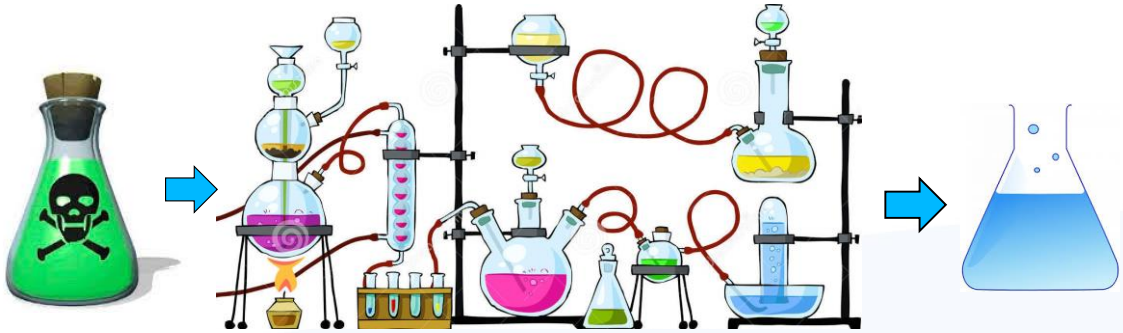
The farms

- → Torre Blanca (experimental)
- → Los Rizaos: (peppers, artichokes, lettuces...)
- → Cabezo Grande: (tomatoes, watermelon,..)
- → Los Buitragos: (citrus trees)
- → La Deseada: (stone fruit trees)



Preparatory Actions

Optimisation of the photocatalytic process



- PPPs: 42
- Photocatalysers: TiO_2 and ZnO
- Results: High degradation levels

42 SELECTED ACTIVE INGREDIENTS

Formulación comercial	Ingrediente activo	Fórmula molecular	Pm	Log Kow a pH 7, 20°C	Presión de vapor a 25°C (mPa)	Índice GUS	Solubilidad agua a 20° (L^{-1})
Epik 20 %	Acetamiprid	$C_{10}H_{11}ClN_4$	222,7	0,8*	$1,7x10^{-4}$	0,94	2950
Borneo 11 %	Etoxazol	$C_{21}H_{23}FNO_2$	359,4	5,52	0,007	0,25	0,07
Jalisco 10 %	Hexitiazox	$C_{17}H_{21}ClN_2O_2S$	352,9	2,67	$1,3x10^{-3}$	0,03	0,1
Atominal 10 %	Piriproxifen	$C_{20}H_{19}NO_3$	321,4	5,37	$1,3x10^{-2}$	-0,27	0,37
Spintor 48 %	Spinosad-A	$C_{41}H_{65}NO_{10}$	732,0	4,01	$3,0x10^{-5}$	-	235*
Spintor 48 %	Spinosad-D	$C_{42}H_{67}NO_{10}$	746,0	4,53	$2,0x10^{-5}$	-	0,332
Movento 15 %	Espirotetramat	$C_{21}H_{27}NO_5$	373,5	2,51	$5,6x10^{-6}$	-1,12	29,9
Envidor 24 %	Espirodiclofen	$C_{21}H_{24}Cl_2O_4$	411,3	5,83	$3,0x10^{-4}$	-0,42	0,05
Courage 20 %	Imidacloprid	$C_9H_{10}ClN_5O_2$	255,7	0,57	$4,0x10^{-7}$	3,76	610
Steward 30 %	Indoxacarb	$C_{22}H_{17}ClF_3N_3O_7$	527,8	4,65	0,006	0,13	0,2
Apolo 50 %	Clofentezin	$C_{14}H_8Cl_2N_4$	303,2	3,1	$1,4x10^{-3}$	-	0,002
Flash 5 %	Fenpiroximato	$C_{24}H_{27}N_3O_4$	421,5	5,01	0,01	-1,0	0,023
Stroby 50 %	Kresoxim Metil	$C_{18}H_{19}NO_4$	313,4	3,4	$2,3x10^{-3}$	-0,09	2,0
Furabel 10 %	Penconazol	$C_{13}H_{15}Cl_2N_3$	284,2	3,72	0,366	1,36	73
Arius 25 %	Quinoxifen	$C_{15}H_8Cl_2FNO$	308,1	4,66	0,012	-0,93	0,047
Rufast 7,5 %	Acrinatrina	$C_{26}H_{21}F_6NO_5$	541,4	6,3	$4,4x10^{-5}$	-1,10	0,002
Decis 1,5 %	Deltametrina	$C_{22}H_{19}Br_2NO_3$	505,2	4,6	0,0000124	-4,26	0,000
Switch 25 %	Fludioxonil	$C_{12}H_6F_2N_2O_2$	248,2	4,12	$3,9x10^{-4}$	-2,67	1,8
Calypso 48 %	Tiacloprid	$C_{10}H_9ClN_4S$	252,7	1,26	$3,0x10^{-7}$	0,14	184
Actara 25 %	Tiametoxam	$C_8H_{10}ClN_5O_3S$	291,7	-0,13	$6,6x10^{-6}$	3,82	4100
Atemi 10 %	Ciproconazol	$C_{15}H_{18}ClN_3O$	291,8	3,09	0,026	3,10	93
Switch 37,5 %	Ciprodinil	$C_{14}H_{15}N_3$	225,3	4	$5,1x10^{-1}$	1,11	13
Score 25 %	Difenoconazol	$C_{19}H_{17}Cl_2N_3O_3$	406,3	4,36	$3,3x10^{-5}$	0,90	15,0
Ridomil Gold 46,5 %	Metalaxil(-M)	$C_{15}H_{21}NO_4$	279,3	1,71	3,3	1,71	2600
Flint 50 %	Trifloxistrobin	$C_{20}H_{19}F_3N_2O_4$	408,4	4,5	$3,4x10^{-4}$	0,19	0,61
Plenum 50 %	Pimetrozina	$C_{10}H_{11}N_5O$	217,2	-0,19	$4,2x10^{-3}$	0,65	270
Sencor 70 %	Metribuzin	$C_8H_{14}N_4OS$	214,3	1,65	0,121	2,57	1165
Titus 25 %	Rimsulfuron	$C_{14}H_{17}N_5O_7S_2$	431,4	-1,46	$8,9x10^{-4}$	3,23	7300
Altacor 35 %	Clorantraniliprol	$C_{18}H_{14}BrCl_2N_5O_2$	483,2	2,86	$6,3x10^{-9}$	4,22	0,88
Signum 26,7 %	Boscalida	$C_{18}H_{12}Cl_2N_2O$	343,2	2,96	0,00072	2,66	4,6
Systhane Forte 24 %	Miclobutanil	$C_{15}H_{17}ClN_4$	288,8	2,89	0,198	3,30	132
Signum 6,7 %	Piraclostrobin	$C_{19}H_{18}BrClN_3O_4$	387,8	3,99	$2,6x10^{-5}$	0,06	1,9
Oberon 24 %	Espiromesifen	$C_{23}H_{30}O_4$	370,5	4,55	$7,0x10^{-3}$	-0,30	0,13
Fenos 24 %	Flubendiamida	$C_{23}H_{22}F_7IN_2O_4S$	682,4	4,14	0,1	3,98	0,029
Karate Zeon 10 %	λ-cihalotrin	$C_{23}H_{19}ClF_3NO_3$	449,9	5,5	0,0002	-3,28	0,005
Clorex 48 %	Clorpirifos Etil	$C_9H_{11}Cl_3NO_3PS$	350,9	4,7	1,43	0,17	1,05
Teppeki 50 %	Flonicamida	$C_9H_6F_3N_3O$	229,2	-0,24	$9,4x10^{-4}$	0,16	5200
Ortiva 25 %	Azoxistrobin	$C_{22}H_{17}N_3O_5$	403,4	2,5	$1,1x10^{-7}$	2,65	6,7
Bravo 72 %	Clortalonil	$C_8Cl_4N_2$	265,9	2,94	0,076	0,62	0,81
Goal 24 %	Oxifluorfen	$C_{15}H_{11}ClF_3NO_4$	361,7	4,86	0,026	0,26	0,116
Stomp LE 33 %	Pendimetalina	$C_{13}H_{19}N_3O_4$	281,3	5,2	1,94	-0,41	0,33
Kerb Flo 40 %	Propizamida	$C_{12}H_{11}Cl_2NO$	256,1	3,3	0,0267	1,80	9
Alverde 24 %	Metaflumizona	$C_{24}H_{16}F_6N_4O_2$	506,4	4,6	$2,32x10^{-8}$	-1,05	0,001

Group 1	Group 2	Group 3	Group 4	Group 5
Acetamiprid	Imidacloprid	Acrinatrina	Clorantraniliprol	Lambda-cihalotrin
Etoxazol	Indoxacarb	Deltametrina	Flubendiamida	Clorpirifos-etil
Hexitiazox	Clofentezin	Tiacloprid	Pimetrozina	Flonicamida
Piriproxifen	Fenpiroximato	Tiametoxam	Espiromesifen	Metaflumizona
Spinosad	Kresoxim-metil	Ciproconazol	Boscalida	Azoxistrobin
Espirotetramat	Penconazol	Ciprodinil	Piraclostrobin	Clotalonil
Espirodiclofen	Quinoxifen	Fludioxinil	Microbutanil	Oxifluorfen
		Difeconazol	Rinsulfuron	Pendimetalina
		Metalaxil(-M)	Metribuzin	Propizamida
		Trifloxistrobin		

Group 1: mainly for citrus fruits

Group 2: mainly for vineyards

Group 3: mainly for fruit trees

Group 4: mainly for tomatoes

Group 5: in many vegetable crops

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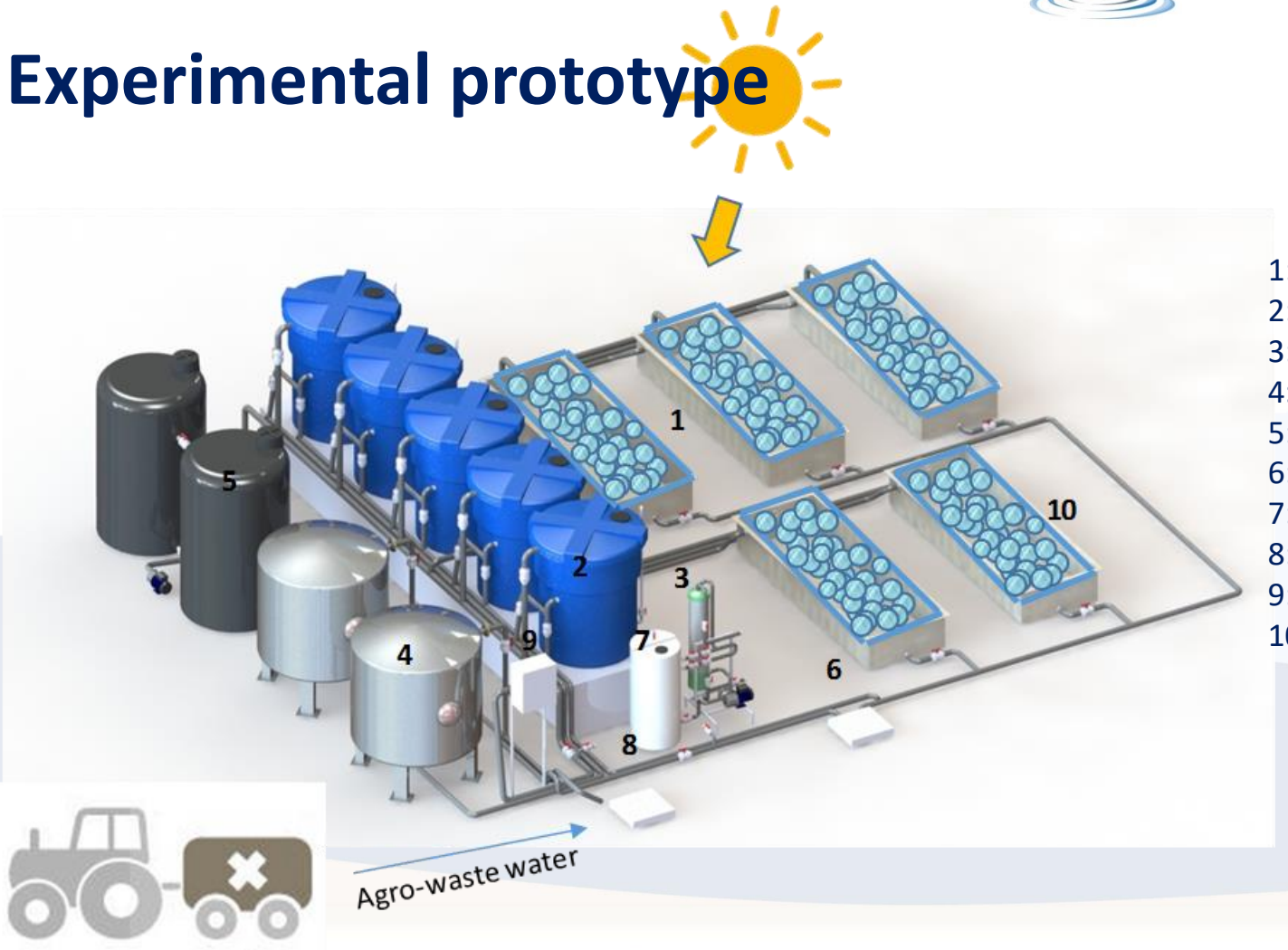
Experimental prototype



1: Reaction tanks
2: Water storage tanks
3: Ultrafiltration membrane
4: Sand filter
5: Post-treatment storage tanks
6: Electrical pump
7: Filtering water storage tank
8: Water inlet
9: Control unit
10: Polyethylene film

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Experimental prototype

Cleaning platform

Experimental prototype

➢ 5 Storage tanks

➢ 5 treatment ponds

Experimental prototype

LIFE AQUEMFREE

DESCONTAMINACIÓN EN FINCA DE AGUAS RESIDUALES
CON PRODUCTOS FITOSANITARIOS PROCEDENTES DE REMANENTES,
ENJUAGUES Y LIMPIEZAS MEDIANTE FOTOCATÁLISIS SOLAR.

IN-FARM REMEDIATION OF AGRO-WASTE WATER
WITH PESTICIDES FROM REMNANTS, CLEANING
AND RINSE BY SOLAR PHOTOCATALYSIS.

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Surveys: "No liquid in excess"

TiO_2 P25 Degussa/oxidant

Oxidant

Summer tests: July-August 2015

Winter tests: November-December 2015

800 liters of water

100 ppb of each pesticide

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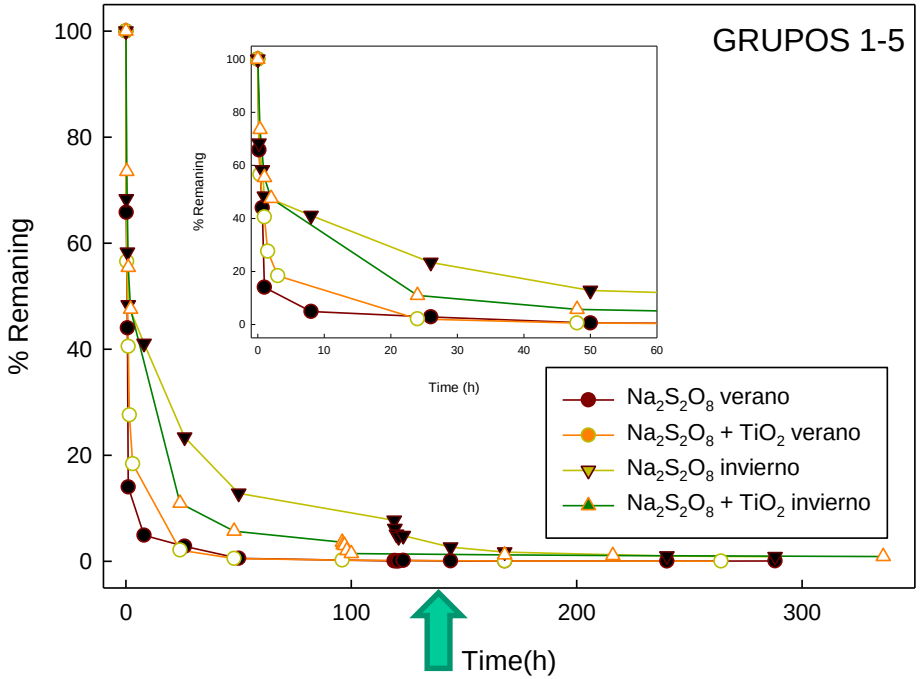
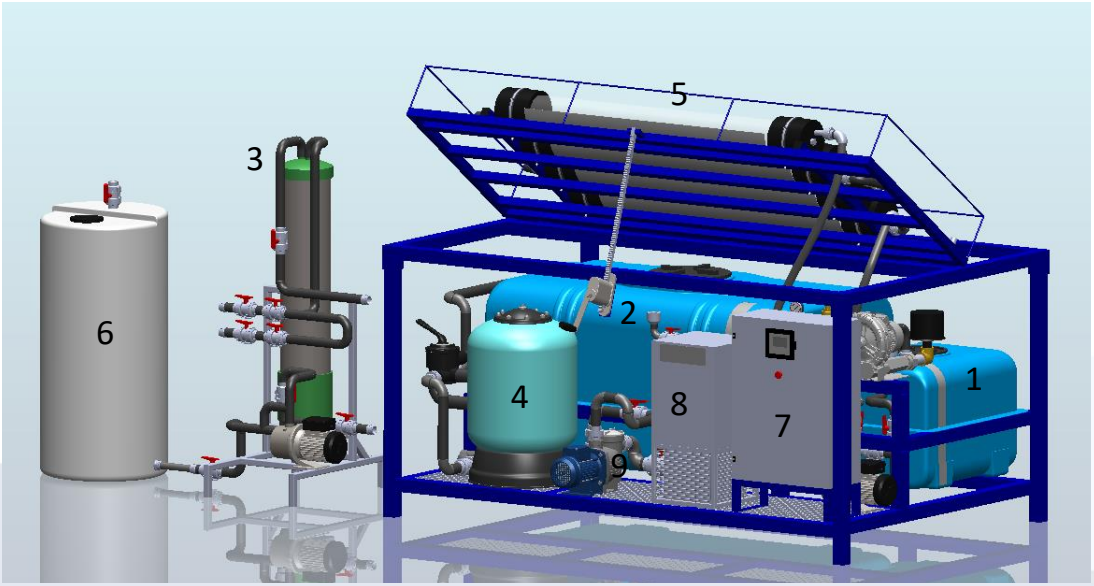
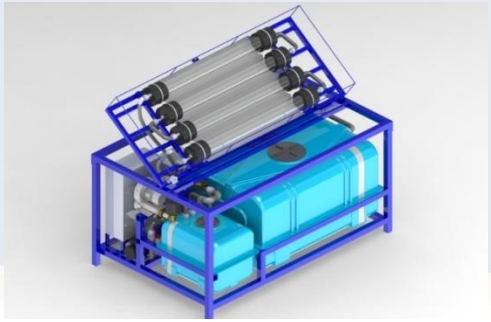


5 days: nearly total degradation

Pilot plants at commercial farm scale



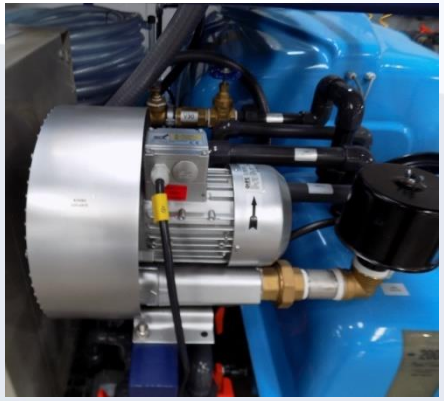
1: Reaction tank (200 L)
2: Storage tank (1000 L)
3: Ultrafiltration membrane
4: Sand filter
5: Photoreactor module with four borosilicate tubes (75 L)
6: Filtering water storage tank
7: Control unit
8: Cooler
9: Centrifugal pump



➢ **Sand filter**

➢ **Tanks**

➢ **Photoreactor module**



➢ **Centrifugal pump**

➢ **Control unit**

Pilot plants at commercial farm scale

1st LOS RIZAOS

TiO_2 P25 Degussa/oxidant

Oxidant

Summer tests: July-August 2016

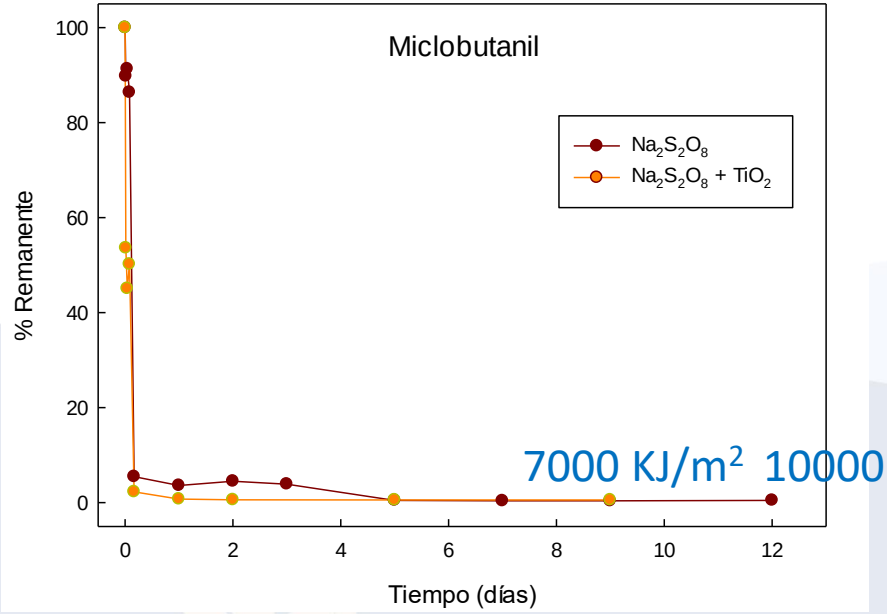
200 liters of water

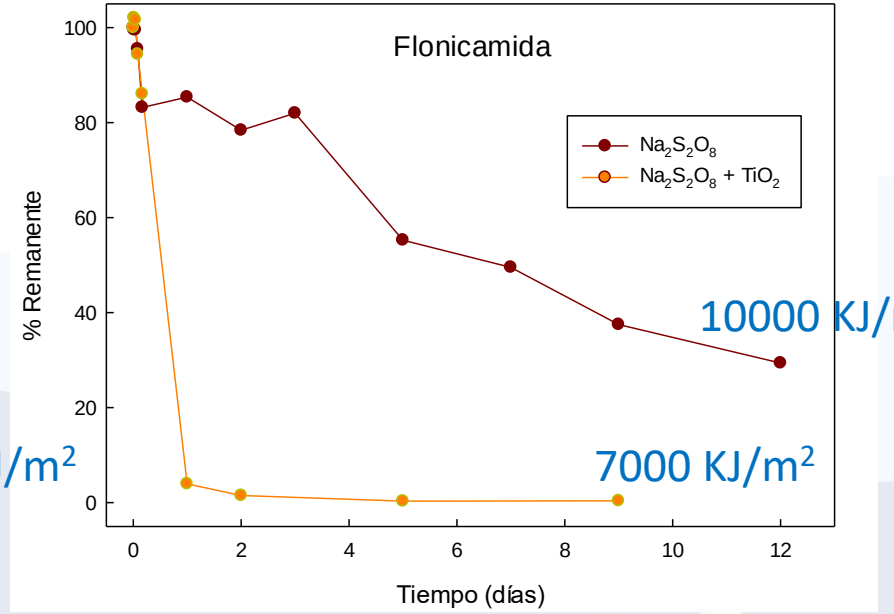
100 ppb of each pesticide

Pilot plants

Optimisation of the process

13 most recalcitrant compounds





Pilot plants

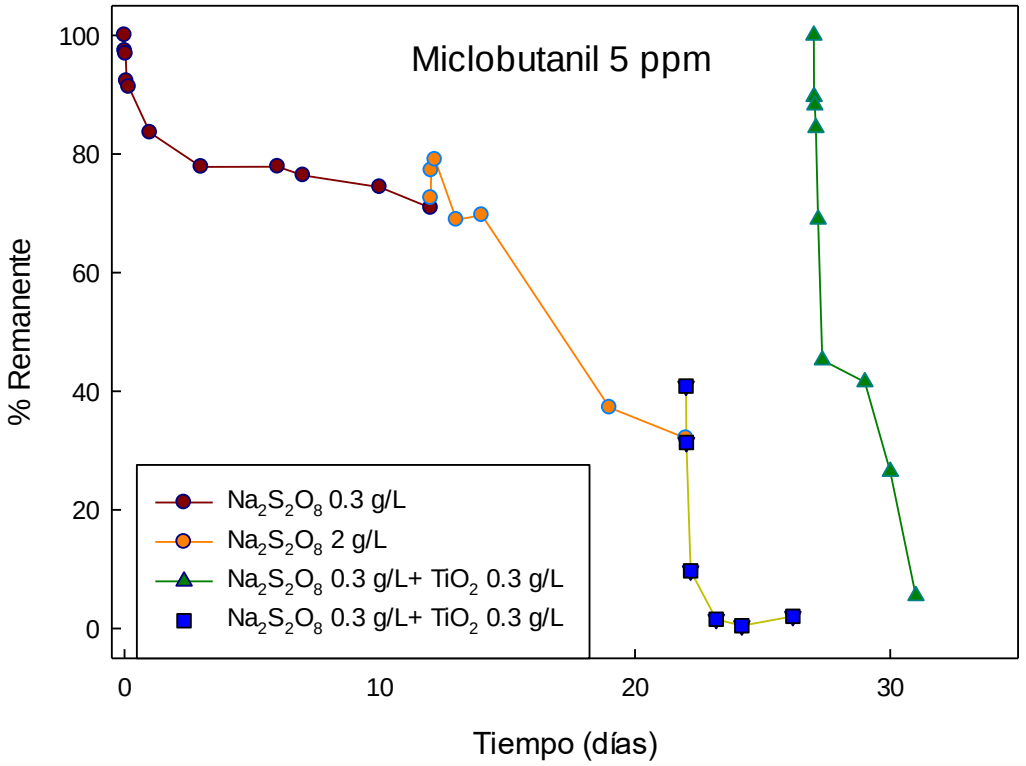
Los Rizaos farm

High concentrations of pesticides (ppm).

Also in other farms

surplus of 10-50 LITERS

Real samples



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Finca Los Rizaos

Problem: high concentrations of pesticides (ppm)

Solution: Use of TiO_2 (ultrafiltration membrane)

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Farm: Los Rizaos
Crop: Vegetables and fruits
Pesticides found: 28
Imidachloprid, Dimethoate, Acetamiprid, Thiacloprid, Metalaxyl, Cyprodinil, Chlorantraniliprole, Dimethomorph, Triadimenol, Myclobutanil, Propyzamide, Fenpyrazamine, Difenoconazole, Indoxacarb, Metrafenone, Cyflufenamid, Abamectin, Triadimefon, Azoxystrobin, Clorpyrifos, Penconazole, Fludioxonil, Quinoxyfen, Cypermethrin, Pirimicarb, Bupirimate, Folpet, Chlorothaloni
Photocatalytic treatments: 20
Total volumen of agrowaste water treated: 3600 L
Total amount of pesticides treated: 238.6 g
Degradation percentage: 85.5%

Use of TiO_2

Farm: Cabezo Grande

Use of TiO_2

Crop: Vegetables and fruits

Pesticides found: 18

Pymetrozine, Acetamiprid, Thiacloprid, Spinosad, Chlorantraniliprole, Triadimenol, Spirotetramat, Propyzamide, Fluopyram, Difenoconazole, Indoxacarb, Pyriproxifen, Abamectin, Hexythiazox, Spiromesifen, Etoxazole, Methyl Clorpyrifos, Oxyfluorfen

Photocatalytic treatments: 10

Total volume of agrowaste water treated: 1800 L

Total amount of pesticides treated: 35.8 g

Degradation percentage: 83.3%

Use of Oxidant

Farm: Los Buitragos
Crop: Citrus
Pesticides found: 9
Spirotetramat, Abamectin, Hexythiazox, Etofenprox, Terbuthylazine, Clorpyrifos, Penconazole, Oxyfluorfen, Quinoxyfen
Photocatalytic treatments: 9
Total volume of agrowate water treated: 1620 L
Total amount of pesticides treated: 0.43 g
Degradation percentage: 97.8%

Farm: La Deseada

Crop: Stone fruits

Pesticides found: 15

Thiamethoxam, Imidachloprid, Acetamiprid, Cyprodinil, Cyproconazole, Fenhexamid, Myclobutanil, Difenoconazole, Trifloxystrobin, Abamectin, Hexythiazox, Etofenprox, Chlorothalonil, λ-cyhalothrin, Deltamethrin

Photocatalytic treatments: 11

Total volume of agrowaste water treated: 1980 L

Total amount of pesticides treated: 55.7 g

Degradation percentage: 82.4%

Use of TiO_2

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DESCONTAMINACIÓN EN FINCA DE AGUAS RESIDUALES CON PRODUCTOS FITOSANITARIOS PROCEDENTES DE REMANENTES, ENJUAGUES Y LIMPIEZAS MEDIANTE FOTOCATÁLISIS SOLAR.

IN-FARM REMEDIATION OF AGRO-WASTE WATER WITH PESTICIDES FROM REMNANTS, CLEANING AND RINSE BY SOLAR PHOTOCATALYSIS.

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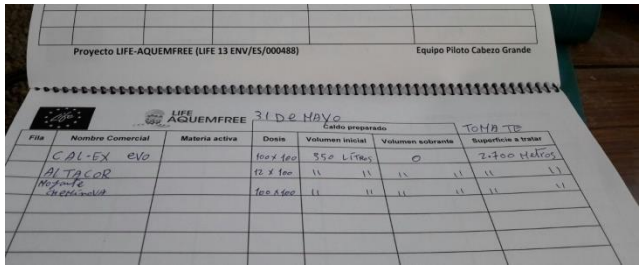


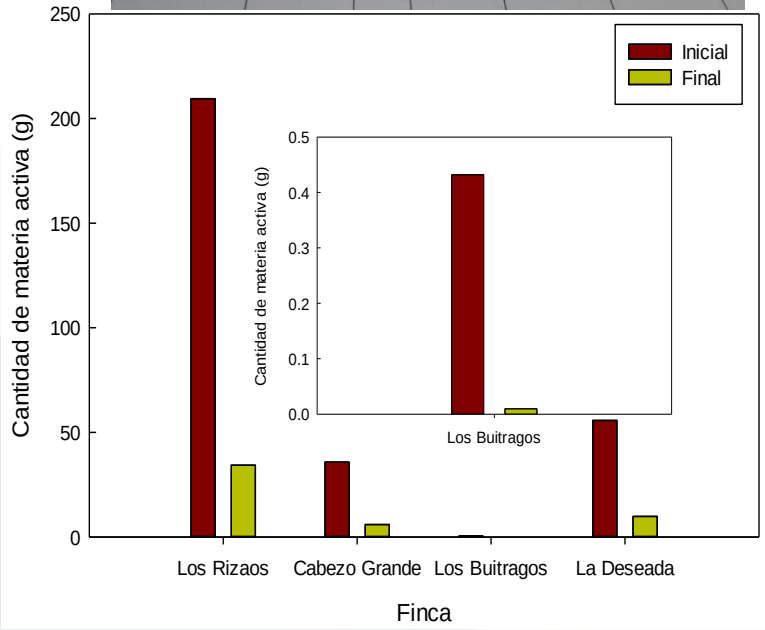
45 active ingredients photodegraded in 4 farms

50 photocatalytic treatments

300 g of active ingredients in 90 hectolitres of accumulated waste water

250 g degraded

83 to 100% reduction of pollutant content*



*A longer photoperiod and pollutant dilution may increase performance

Región de Murcia
Consejería de Agricultura y Agua

Instituto Murciano de Investigación y Desarrollo Agrario y Alimentario imida

UNIVERSIDAD DE MURCIA

Novedades Agrícolas

FECOAM

Economical assessment

OBJECTIVE

To compare the current practices with the use of the pilot plants to assess the real viability conditions to implement the Aquemfree system

1. Cost structure

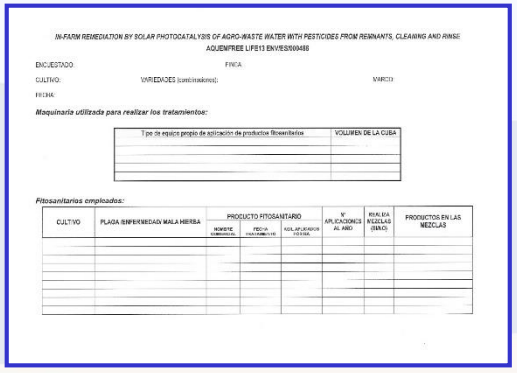
	Limón Fino		Limón Verna	
	Coste absoluto (€)	***Coste relativo (%)***	***Coste absoluto (€)***	***Coste relativo (%)***
Nave para aperos y cabezal	78	1,29%	78	1,31%
Cabezal de riego	160	2,64%	160	2,69%
Red de riego	90	1,48%	90	1,51%
Plantación	87	1,43%	76	1,28%
Material vario auxiliar	20	0,34%	20	0,34%
Embalse regulador	78	1,28%	78	1,31%
Coste del inmovilizado	***512***	***8,44%***	***502***	***8,45%***
Poda anual	523	8,63%	449	7,55%
Costes de maquinaria	698	11,52%	698	11,76%
Fitosanitarios	258	4,25%	258	4,34%
Fertilizantes	712	11,74%	747	12,58%
Herbicidas	61	1,01%	61	1,03%
Mantenimiento	93	1,53%	93	1,56%
Energía eléctrica	199	3,28%	189	3,18%
Personal fijo	1583	26,11%	1583	26,66%
Riego	1424	23,49%	1359	22,88%
Coste del circulante	***5552***	***91,56%***	***5437***	***91,55%***
Coste total (€)	***6.064***	***100,00%***	***5.939***	***100,00%***
Coste unitario (€/ha)	***6.064***		***5.939****	

* El coste unitario no incluye la recolección que suele ir a cargo del comprador

2. Equipment costs. Case 1 200L; Case 2 400L

Economies of scale: 32% reduction of index Investment/Volume
Significant reduction of treatment cost

3. Monitoring interviews to farmers



IN-FARM REMEDIATION BY SOLAR PHOTOCATALYSIS OF AGRO-WASTE WATER WITH PESTICIDES FROM REMNANTS, CLEANING AND RINSE
AQUEMFREE LIFE13 ENV/ES/000486

ENCUESTADO: FINCA:
CULTIVO: VARIEDADES (combinations): MARCO:
FECHA:

Maquinaria utilizada para realizar los tratamientos:

Tipo de equipo propio de aplicación de productos fitosanitarios	VOLUMEN DE LA CUBA

Fitosanitarios empleados:

CULTIVO	PLAGA /ENFERMEDAD/ MALA HIERBA	PRODUCTO FITOSANITARIO			Nº APLICACIONES AL AÑO	RIQUEZA N(U/L)AS (SI/NO)	PRODUCTOS EN LAS MEZCLAS
		NOMBRE COMERCIAL	FECHA TRATAMIENTO	KGS./L APLICADOS (TOTAL)			

Economical assessment

Territorial efficiency Aquemfree equipment 200

Citrus fruits: 159 has

Stone fruits: 160 has
Tomatoes in greenhouses: 63,6 has
Peppers in greenhouses: 53 has

Increase of production costs Aquemfree equipment 200

Citrus fruits: 0.236%
(E.g: increase of production cost of lemon fino of 6,064 €/ha is supposed to be 14.31 €/ha)
Stone fruits: 0.116 %
Tomatoes in greenhouses: 0.067 %
Peppers in greenhouses: 0.079 %

Territorial efficiency Aquemfree equipment 400

Citrus fruits: 318 has
Stone fruits: 320 has
Tomatoes in greenhouses: 127.2 has
Peppers in greenhouses: 106 has

Increase of production costs Aquemfree equipment 400

Citrus fruits: 0.163 %
Stone fruits: 0.111 %
Tomatoes in greenhouses: 0.047 %
Peppers in greenhouses: 0.055 %

Cost overrun is low in all cases

The larger the farm is, the lower is the running cost

The use of the system by a co-operative or similar with a bigger equipment (e.g. 800L) would decrease the use cost and increase the susceptible surface

Environmental assessment

LCA following the International Reference Life Cycle Data System (ILCD)

400L alternative is better than 200L for its lower material and energy inputs per treated litre

All ILCD impact categories are lower than current practices between 40 and 60%

The impact on Climate Change (equivalent CO_2) is reduce in 43%

Potential toxicity of treated waste water is between 84 and 100% lower considering human and water toxicity

Governance issues

Interest in promoting national legal changes to establish homologated systems

Promotion of including Aquemfree in the list of environmental actions in the operational program for Organisations of Producers (CAP)

Possibilities of funding through RDP measures

Promotion of “environmental marketing”

Conclussions and next steps

The innovative technology is efficient and viable (83 to 100%) using a renewable and endless energy source, in special in Mediterranean areas.

The economical and environmental assessment shows its viability

Possibilities of a new bussines model as a service for farmers

We are conducting research on safe use of treated water for irrigation

Use of Photocatalysis in other cases

LIFE AQUEMFREE

DESCONTAMINACIÓN EN FINCA DE AGUAS RESIDUALES
CON PRODUCTOS FITOSANITARIOS PROCEDENTES DE REMANENTES,
ENJUAGUES Y LIMPIEZAS MEDIANTE FOTOCATÁLISIS SOLAR.

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Thank you