Extensive analytical evaluation of advanced tertiary treatments for water reuse purposes

Ana Agüera

Department of Analytical Chemistry
University of Almería


Analytical Chemistry Dpt.
Pesticide Residues Research Group
University of Almería

Analytical evaluation of water treatment processes (1999-2012)

ELSEVIER

Catalysis Today 54 (1999) 353–367

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Photocatalytic degradation of pesticide pirimiphos-methyl
Determination of the reaction pathway and identification of intermediate products by various analytical methods

Jean Marie Herrmann [a], Chantal Guillard [a], M. Arguello [a], Ana Agüera [b], Ana Tejedor [b], Luis Piedra [b], Amadeo Fernández-Alba [b,*]

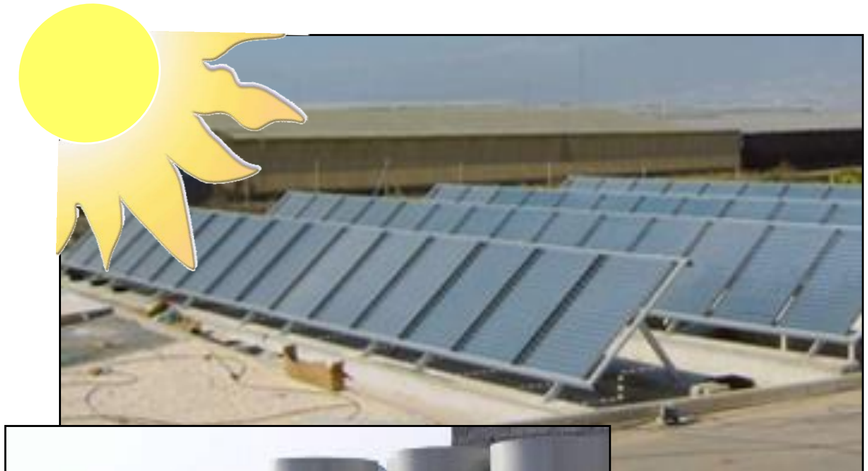
[a] CNRS Photocatalyse, Catalyse et Environement, Ecole Centrale de Lyon BP 163, 6913 Ecully Cedex, France
[b] Pesticide Residue Research Group, Faculty of Sciences, 04071 Almería, Spain

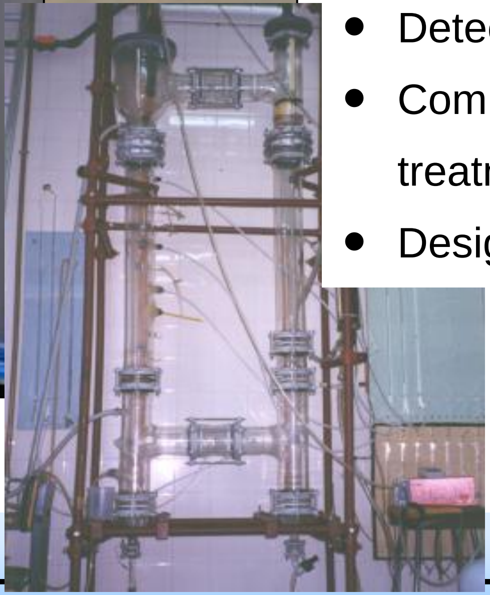
Pesticide Residues Research Group
University of Almería

Solar Treatment of Water Research Group

Plataforma Solar de Almería (CIEMAT)

Analytical evaluation of water treatment processes (1999-2012)

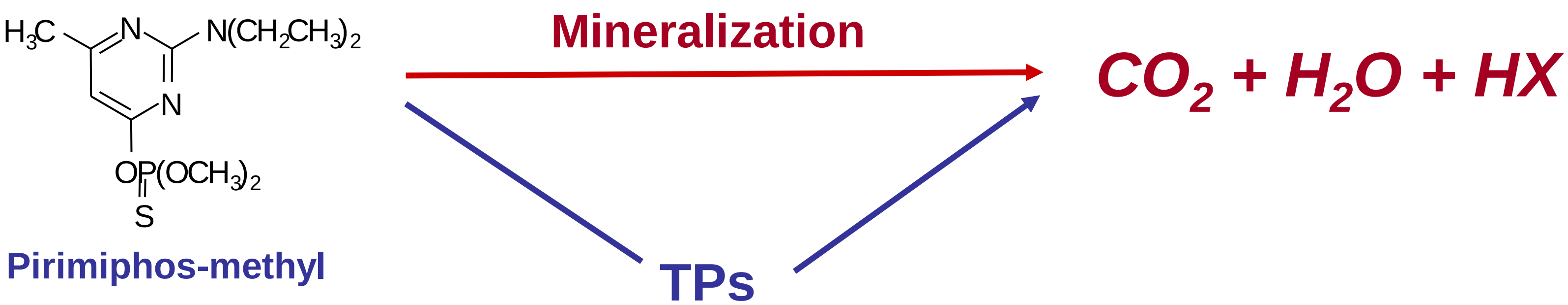


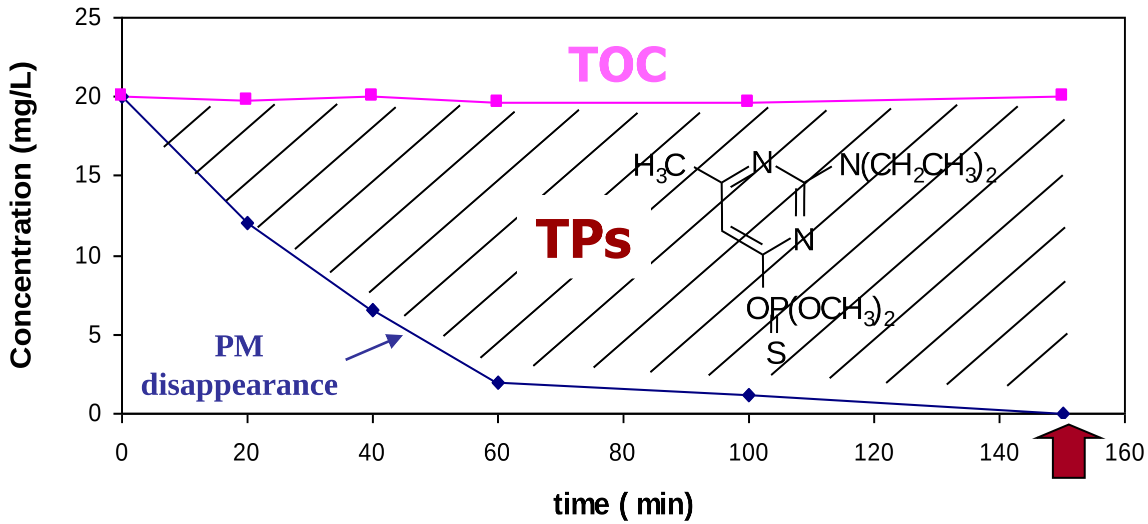


OBJECTIVES

- Understanding of degradation mechanisms: identification of TPs
- Combination of chemical and toxicological analysis: interpretation of toxicity and biodegradability results
- Detection of undesirable compounds
- Comparison of efficiency of different treatments: applicability as tertiary treatments
- Design and optimization of the process

UNDERSTANDING OF DEGRADATION MECHANISMS: IDENTIFICATION OF TPS



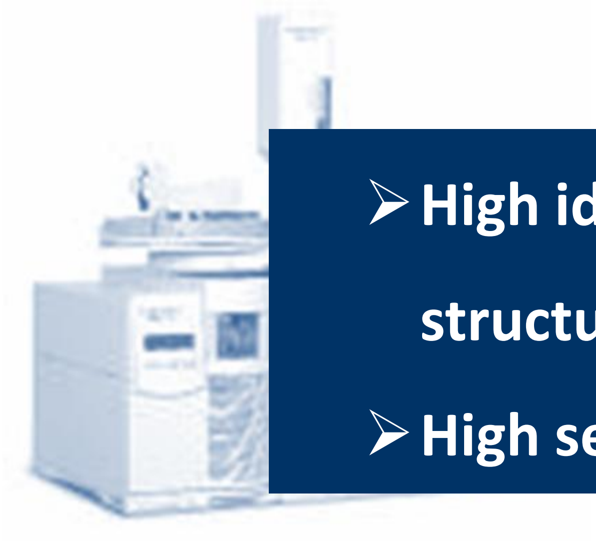


DIFFICULTIES:

- Large amount of unknown compounds
- Different physical-chemical properties
- Wide range of concentrations
- Absence of analytical standards for an accurate identification/quantification

Ana Agüera
University of Almeria

IDENTIFICATION OF TPs: ANALYTICAL REQUIREMENTS



- High identification capability: structural information
- High sensitivity in "full-scan"

GC-MS

- ✓ non polar compounds
- ✓ volatile compounds
- ✓ thermally stable

LC-MS

- ✓ polar compounds
- ✓ low volatility
- ✓ thermally unstable

Ana Agüera
University of Almeria

IDENTIFICATION OF TPs: ANALYTICAL REQUIREMENTS

LC-TOF-MS

Accurate mass measurements

Elemental composition of parent and fragment ions

Very high sensitivity in "full-scan"

Low concentration intermediates

No limitations in the type and amount of compounds that can be simultaneously analyzed

Complex reaction mixtures

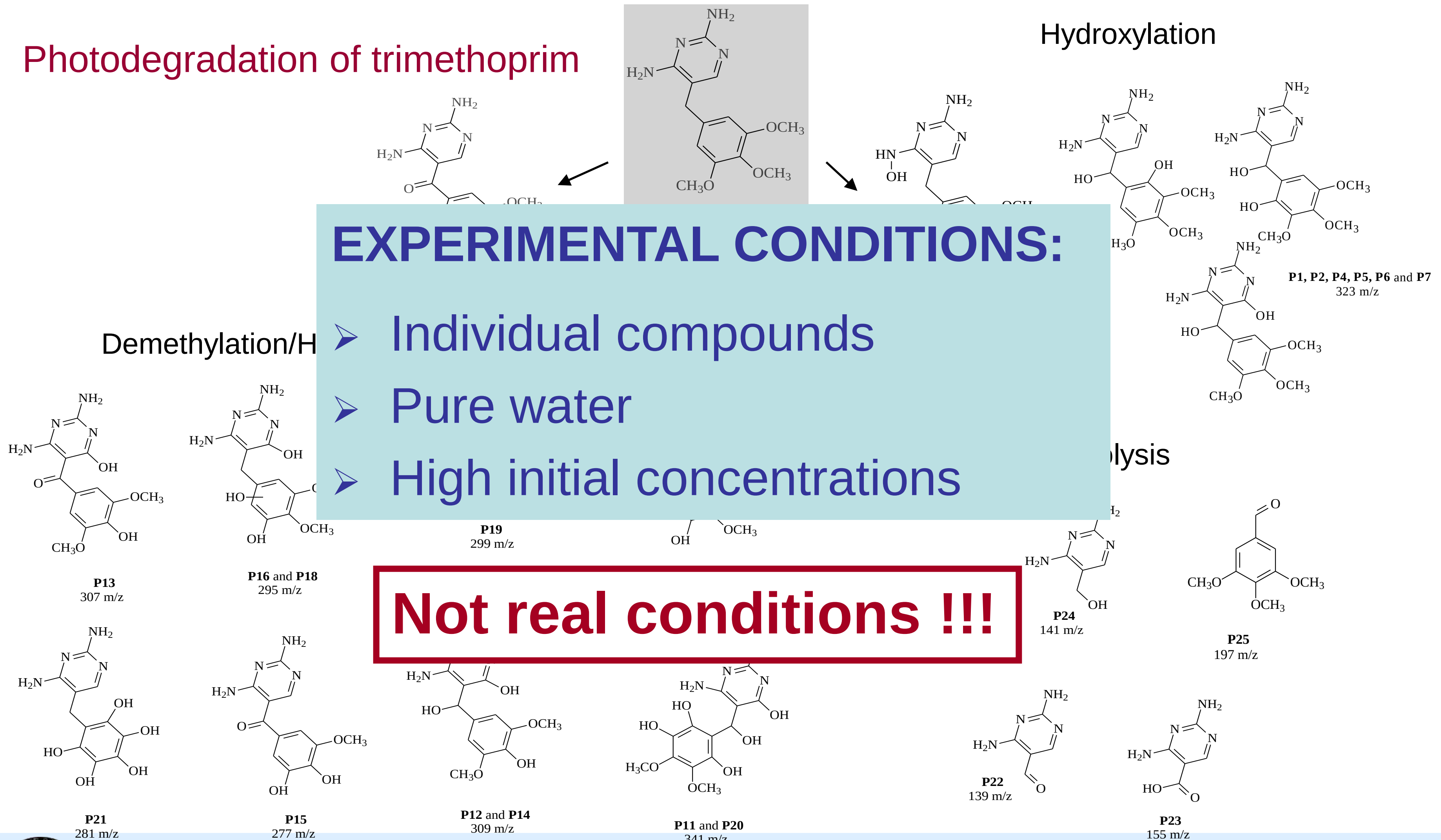
LC-QTOF-MS/MS → **Increased structural information**

MS/MS spectra

Ana Agüera
University of Almeria

UNDERSTANDING OF DEGRADATION MECHANISMS: IDENTIFICATION OF TPs

Photodegradation of trimethoprim



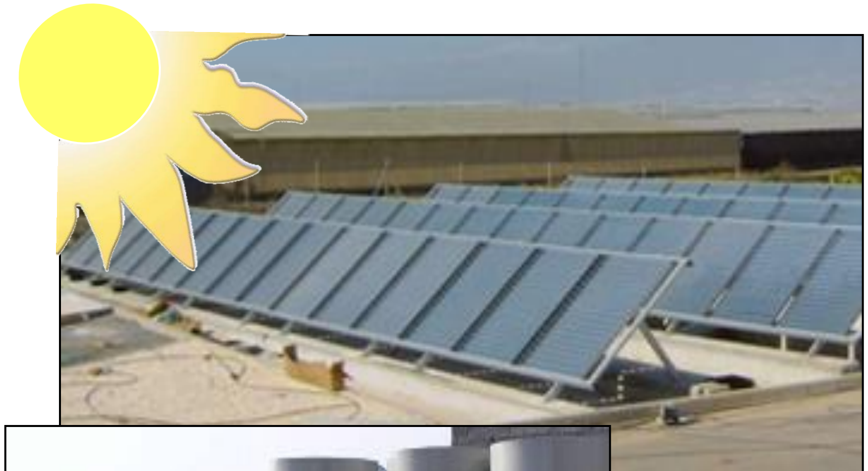
EXPERIMENTAL CONDITIONS:

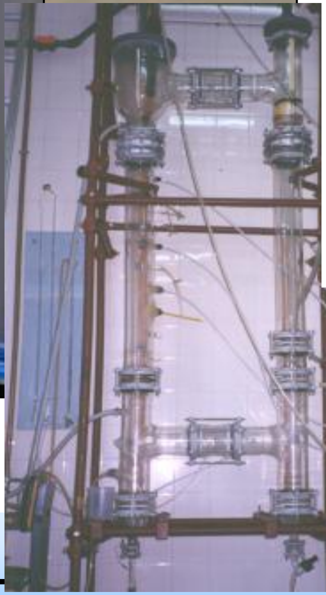
- Individual compounds
- Pure water
- High initial concentrations

Not real conditions !!!

Ana Agüera
University of Almeria

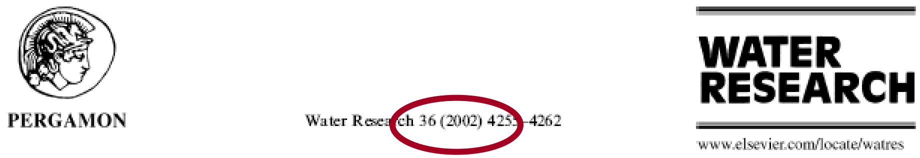
Analytical evaluation of water treatment processes (1999-2012)





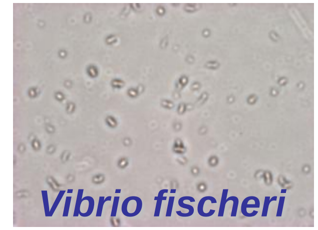
OBJECTIVES

- Understanding of degradation mechanisms: identification of TPs
- Combination of chemical and toxicological analysis: interpretation of toxicity and biodegradability results
- Detection of undesirable compounds
- Comparison of efficiency of different treatments: applicability as tertiary treatments
- Design and optimization of the process


PERGAMON
Water Research 36 (2002) 4255–4262
WATER RESEARCH
www.elsevier.com/locate/watres

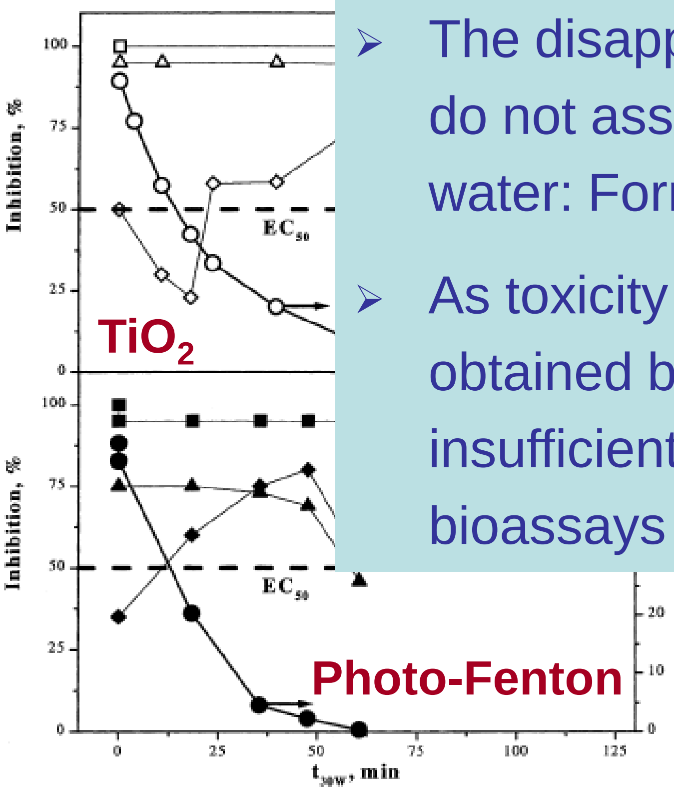
Toxicity assays: a way for evaluating AOPs efficiency

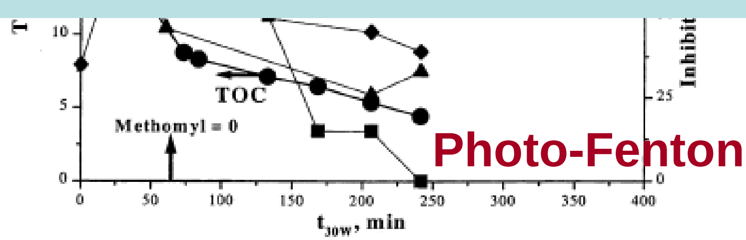
A.R. Fernández-Alba[a], D. Hernando[a], A. Agüera[a], J. Cáceres[b], S. Malato[b,*]



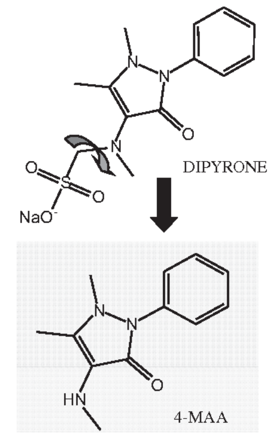
CONCLUSIONS:

- The disappearance of the target compounds do not assure the detoxification of treated water: Formation of toxic TPs
- As toxicity is a biological response, the values obtained by a single toxicity assay can be insufficient. Consequently, a battery of bioassays is recommended.

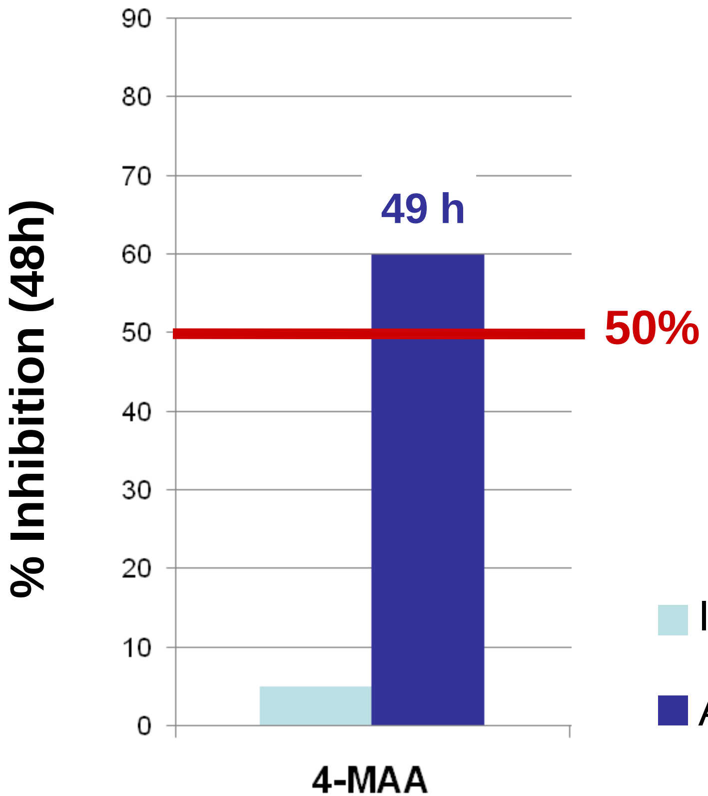




DETECTION OF UNDESIRABLE COMPOUNDS



Toxicity evolution of a 4-MAA solution during photolysis

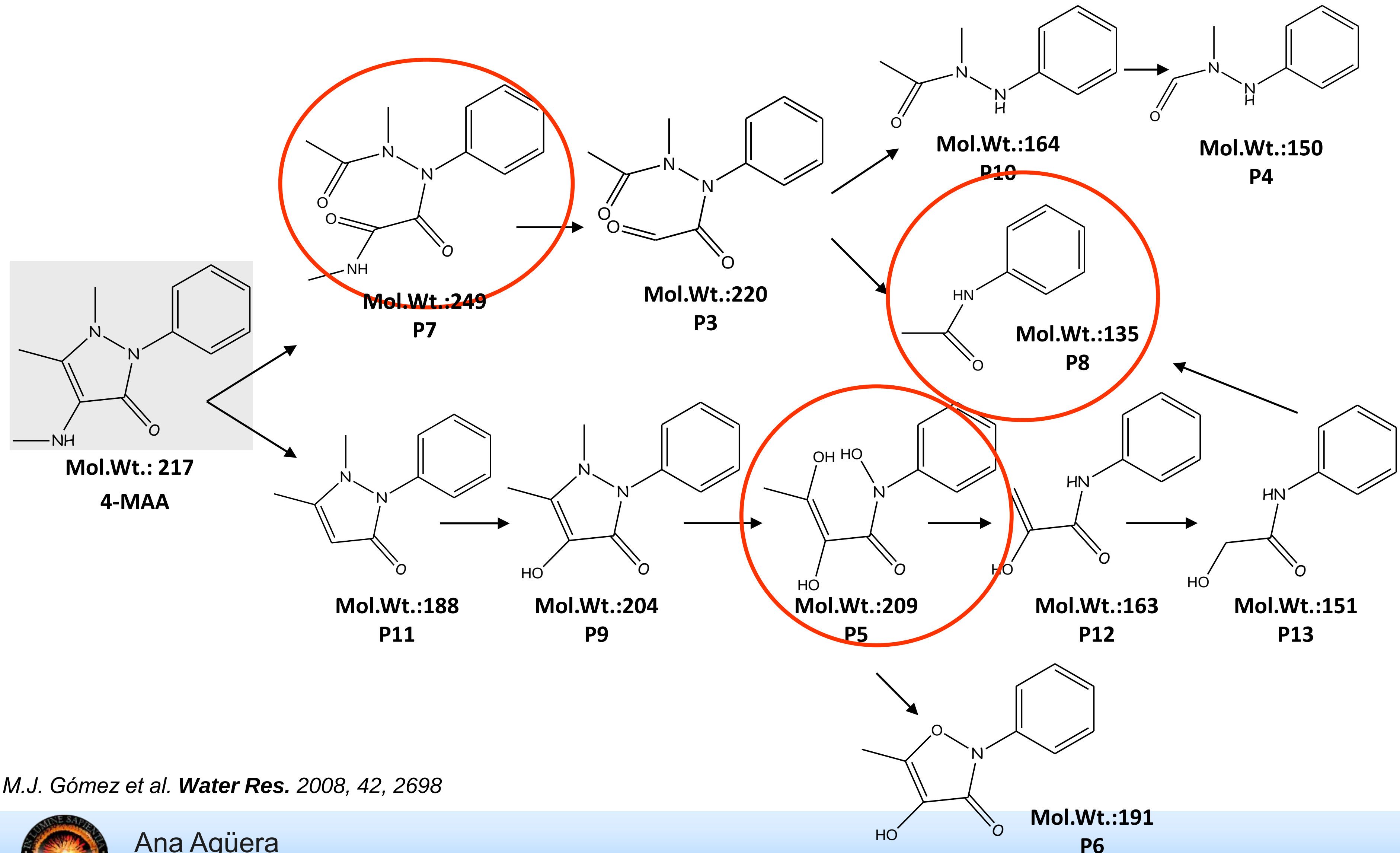


ACCUTE TOXICITY TEST

Daphnia Magna

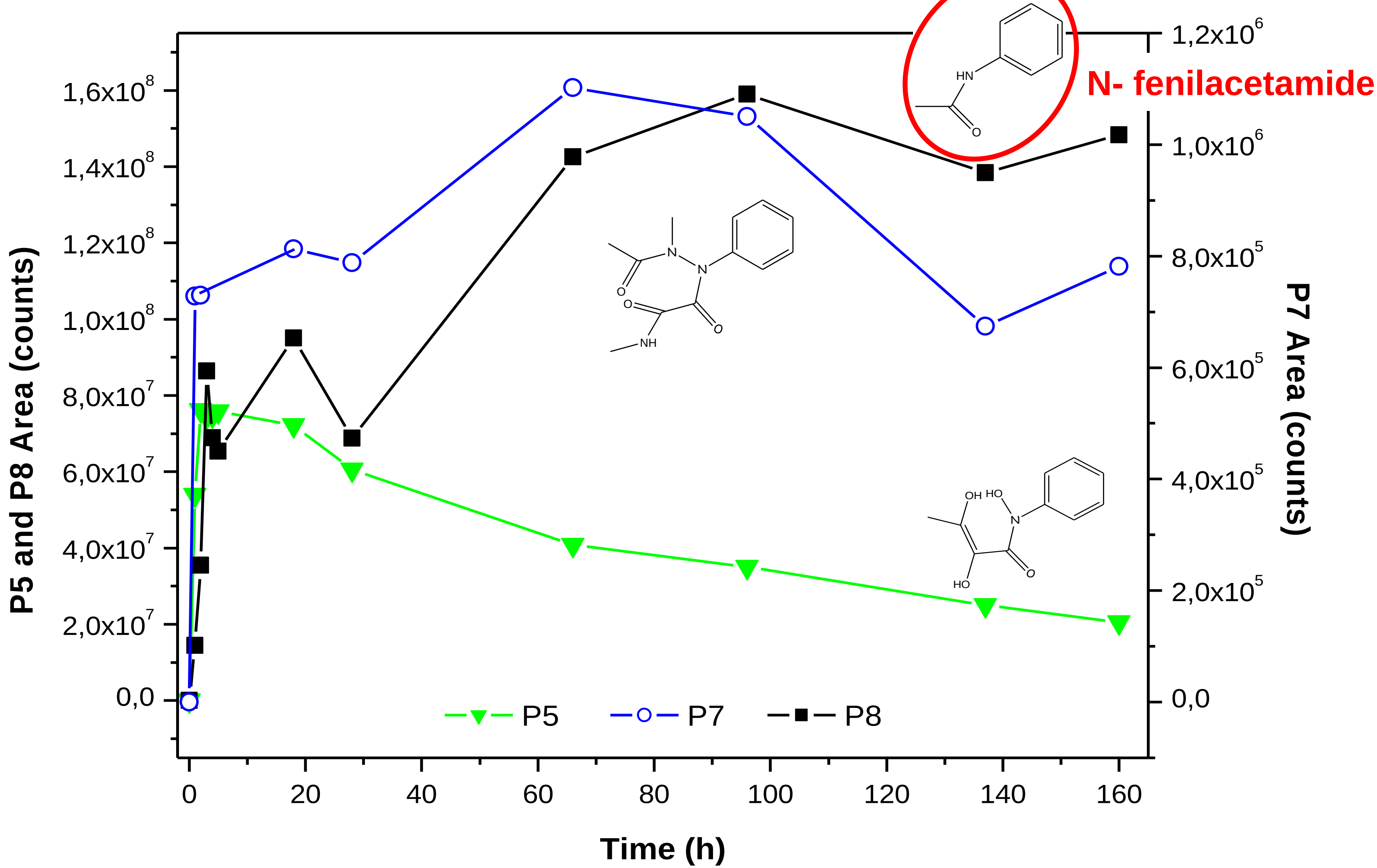
Ana Agüera
University of Almeria

4-MAA PHOTODEGRADATION PATHWAY



M.J. Gómez et al. **Water Res.** 2008, 42, 2698

TIME EVOLUTION OF THE MAIN TPs OF 4-MAA UNDER UV-TREATMENT



Ana Agüera
University of Almeria

N- fenilacetamide or Acetanilide

Log in / create account

Article Talk Read Edit View history Search

WIKIPEDIA
The Free Encyclopedia

Main page
Contents
Featured content
Current events
Random article
Donate to Wikipedia

Interaction
Help
About Wikipedia
Community portal
Recent changes
Contact Wikipedia

Toolbox
Print/export
Languages
العربية
□□□□□
Deutsch
Español
Français
Italiano

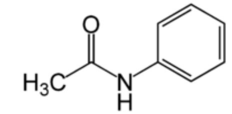
Thank you for protecting Wikipedia.
(We're not done yet.)

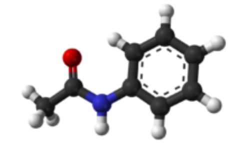
Acetanilide

From Wikipedia, the free encyclopedia

Acetanilide[5] is an odourless solid chemical of leaf or flake-like appearance. It is also known as **N-phenylacetamide**, **acetanil**, or **acetanilid**, and was formerly known by the trade name **Antifebrin**.

Acetanilide





IUPAC name [hide]
N-phenylacetamide
N-phenylethanamide

Identifiers

Contents [hide]

Preparation and properties [edit]

Acetanilide can be produced by reacting acetic anhydride with aniline:

$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

The preparation used to be a traditional experiment in introductory organic chemistry lab classes,[6] but it has now been widely replaced by the preparation of either paracetamol or aspirin, both of which teach the same practical techniques (especially recrystallization of the product) but which avoid the use of aniline, a suspected carcinogen.

Acetanilide is slightly soluble in water, and stable under most conditions.[4] Pure crystals are plate shaped and colorless to white.

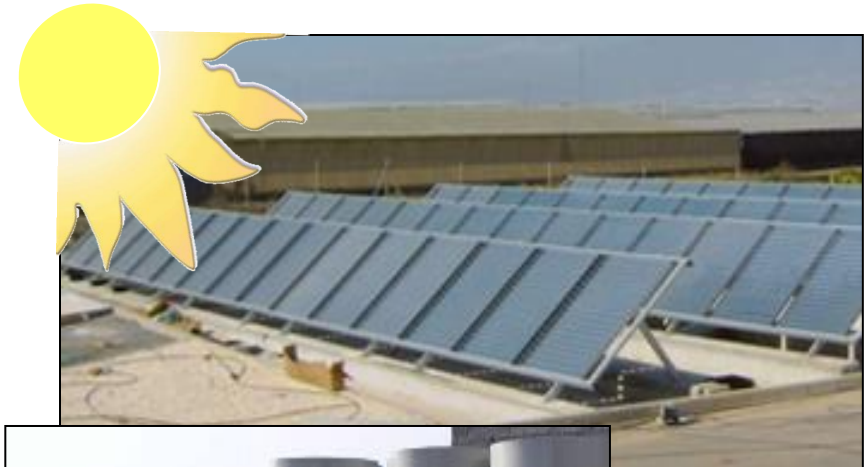
Applications [edit]

Pharmaceutical use

Acetanilide was the first aniline derivative serendipitously found to possess analgesic as well as antipyretic properties, and was quickly introduced into medical p
and P. Hepp in 1886.[8] But its (apparent) unacceptable toxic effects, the most alarming being cyanosis due to methemoglobinemia, prompted the search for sup
phenacetin.[9] After several conflicting results over the ensuing fifty years, it was established in 1948 that acetanilide was mostly metabolized to paracetamol (US
that it was the paracetamol that was responsible for the analgesic and antipyretic properties.[10][11][12][13] The observed methemoglobinemia after acetanilide adr
of acetanilide that is hydrolyzed to aniline in the body.[note 1] Acetanilide is no longer used as a drug in its own right, although the success of its metabolite – par

Ana Agüera
University of Almeria

Analytical evaluation of water treatment processes (1999-2012)



OBJECTIVES

- Understanding of degradation mechanisms: identification of TPs
- Combination of chemical and toxicological analysis: interpretation of toxicity and biodegradability results
- Detection of undesirable compounds
- Comparison of efficiency of different treatments: applicability as tertiary treatments.
- Design and optimization of the process

Real conditions !!!

Ana Agüera
University of Almeria

CHARACTERIZATION OF URBAN WASTEWATER EFFLUENTS

INCOMPLETE REMOVAL

EMERGING CONTAMINANTS

Rapid

Sensitive

Selective

Broad range of compounds

Accurate confirmation

Ana Agüera
University of Almeria

CHARACTERIZATION OF WASTEWATER EFFLUENTS: MULTIRESIDUE METHODS

Antibiotics
1. Metronidazole
2. Sulfamethoxazole
3. Trimethoprim
4. Ciprofloxacin
5. Cefotaxime
6. Ofloxacin
7. Erythromycin
8. Tetraciclyne
9. Norfloxacin
10. Clarithromycin
11. Lincomycin
12. Sulfamethazine
13. Sulfapyridine
14. Sulfadiazine
15. Sulfathiazole
16. Azithromycin
17. Simvastatin

Analgesic/ Anti-Inflammatory
18. Acetaminophen
19. Indomethacine
20. Fenoprofen
21. Codeine
22. Mefenamic Ac.
23. Ibuprofen
24. Ketorolac
25. Naproxen
26. Diclofenac
27. Ketoprofen
28. Propyphenazone
29. Urbason

Contrast media
30. Iopromide
31. Iopamidol

Beta Blockers
32. Atenolol
33. Propranolol
34. Sotalol
35. Metoprolol
36. Nadolol

Antihistamines
37. Famotidine,
38. Lansoprazole
39. Ranitidine
40. Omeprazole
41. Loratadine

Diuretics
42. Furosemide
43. Hydrochlorothiazide

Antidepressants
44. Fluoxetine
45. Paroxetine
46. Venlafaxine
47. Citalopram
48. Amitriptyline
49. Clomipramine

Lipid regulators
50. Fenofibrate
51. Bezafibrate
52. Gemfibrozil
53. Pravastatin
54. Mevastatin
55. Simvastatin

Sympathomimetics
56. Salbutamol
57. Terbutaline

Antiepileptic Psychiatric drug
58. Carbamazepine
59. Diazepan
60. Primidone

Antineoplastics
61. Ifosfamide
62. Cyclophosphamide
63. Tamoxifen

Anesthetics
64. Mepivacaine

Coricosteroides
65. Methylprednisolone

Anti-Infective
66. Clotrimazole

UV Filters
67. Benzophenone-3
68. Camphor
69. Cinnamate
70. Octocrylene

Flame retardant
71.TCPP oekanal

Metabolites
72. 4-Acetoaminoantipyrine
73. 4-Formylaminoantipyri
74. 4-Methylaminoantip
75. 4-Dimethylaminoan
76. 4-Aminoantipyrine
77. Paraxanthine
78. Carbamaz.10,11-epox
79. Antipyrine
80. Fenofibric Acid
81. Clofibric acid
82. Cotinine
83. Salicilic acid

Pesti

Disinfectants
ylol
ne

Plastic additives
92. Bisfenol-A

>120

Fragances
98. Celestolide
99. Phantolide
100.Traseolide
101.Galaxolide
102.Ketone
103.Tonalide
104.Musk xilene
105.Musk ketone

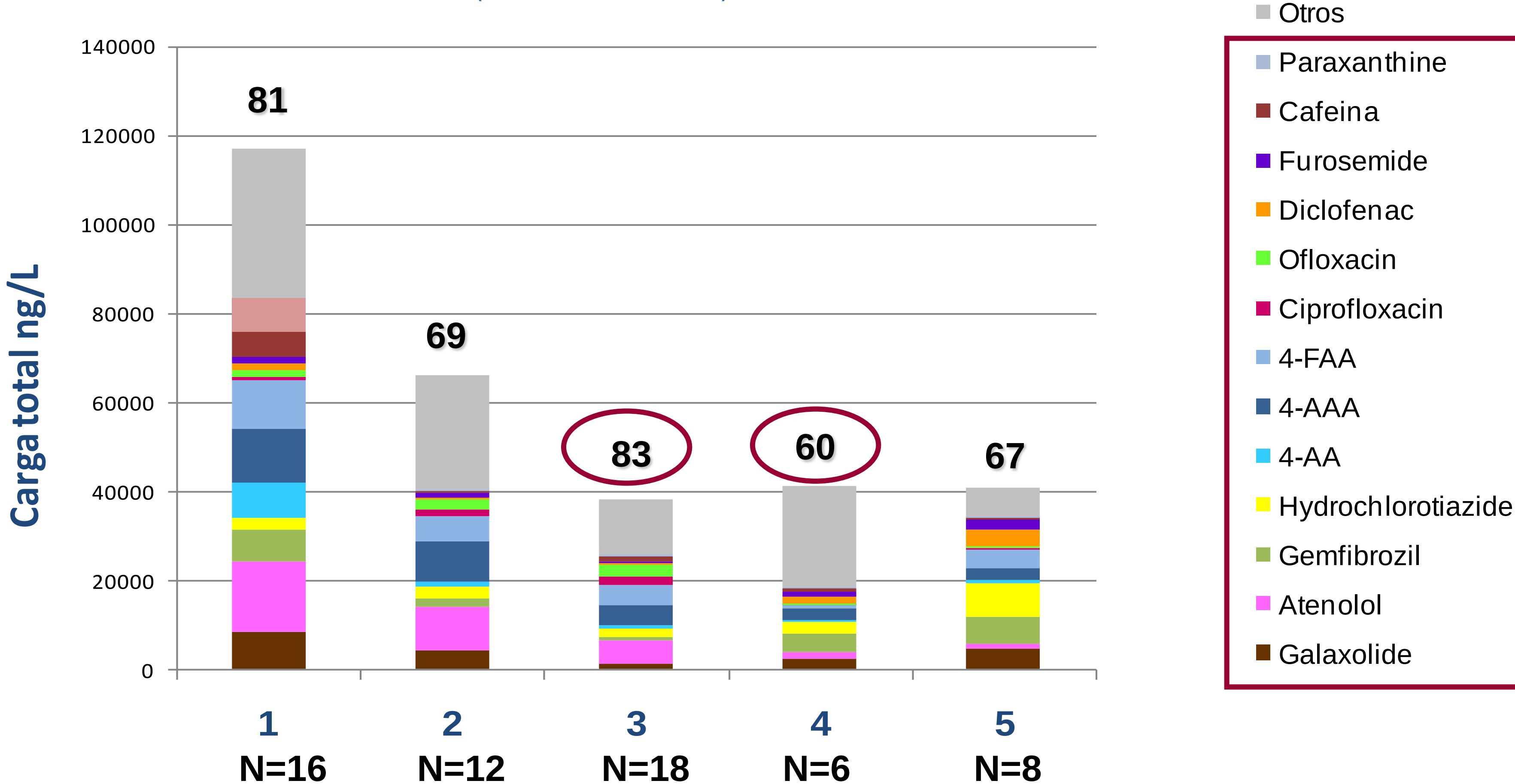
Antioxidants
106.BHT

PAHs
107.Acenaphtene
108.Acenaphtilene
109.Anthracene
110.Benzo[a]anthracene
111.Benzo[a]fluoranthene
112.Benzo[a]pyrene
113.Benzo[k]fluoranthene
114.Crysene
115.Fluoranthene
116.Fluorene
117.Naphtalene
118.Phenantrene
119.Pyrene

Ana Agüera
University of Almeria

CHARACTERIZATION OF URBAN WASTEWATER EFFLUENTS

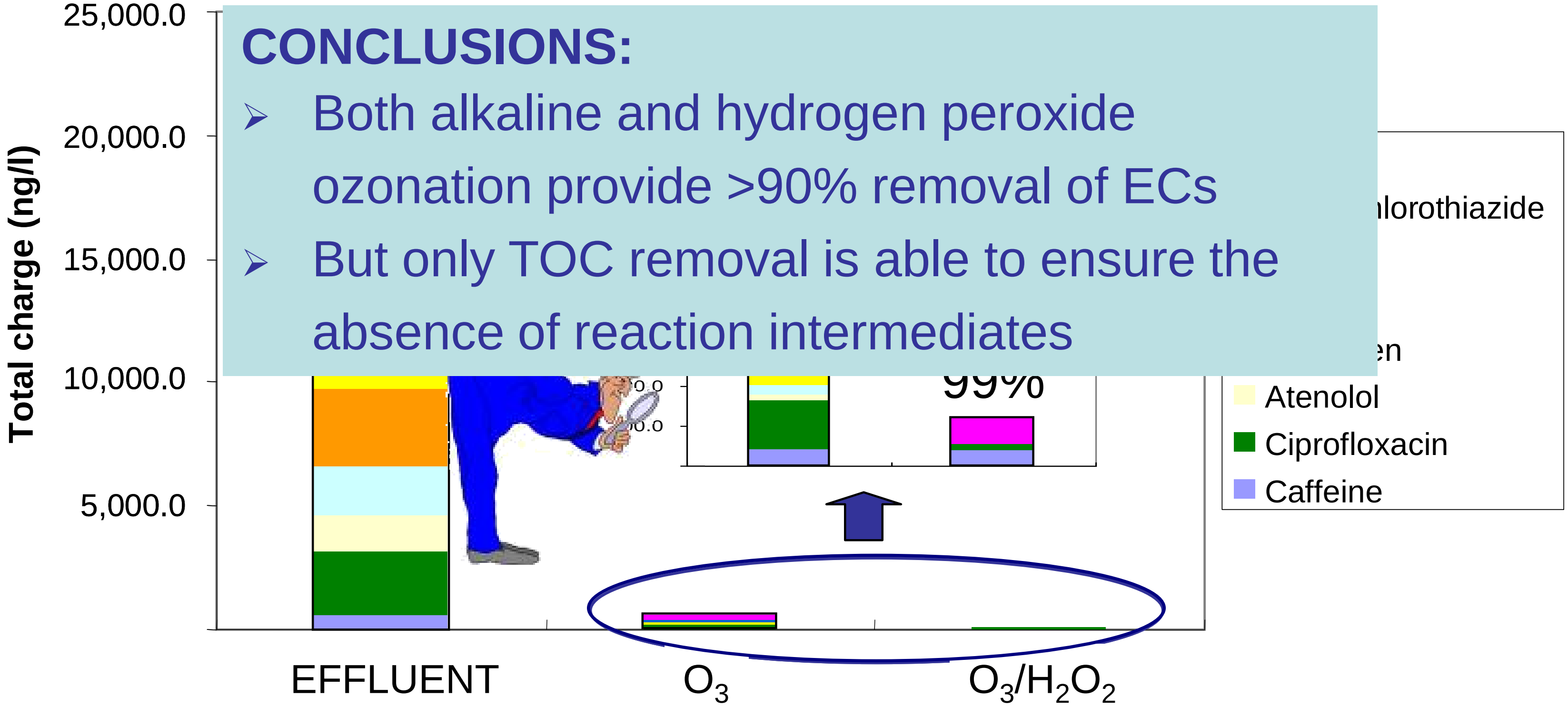
1.- ALMERIA- El Ejido (urbana/agrícola)
2.- MADRID- Alcalá de Henares (urbana)
3.- MADRID- Alcalá de Henares (urbana/industrial)
4.- CANTABRIA- Vuelta Ostrera (urbana)
5.- BARCELONA- Baix Llobregat (urbana)



Ana Agüera
University of Almeria

COMPARISON OF TREATMENTS EFFICIENCY IN REMOVING ECs

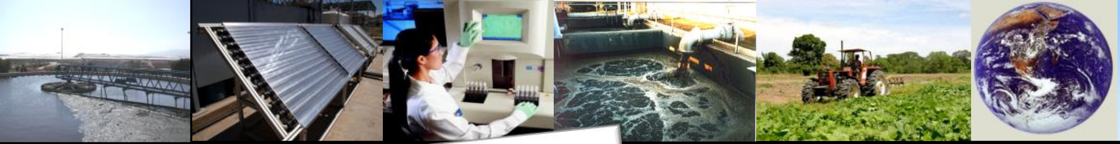
APPLICABILITY AS TERTIARY TREATMENTS



CONCLUSIONS:

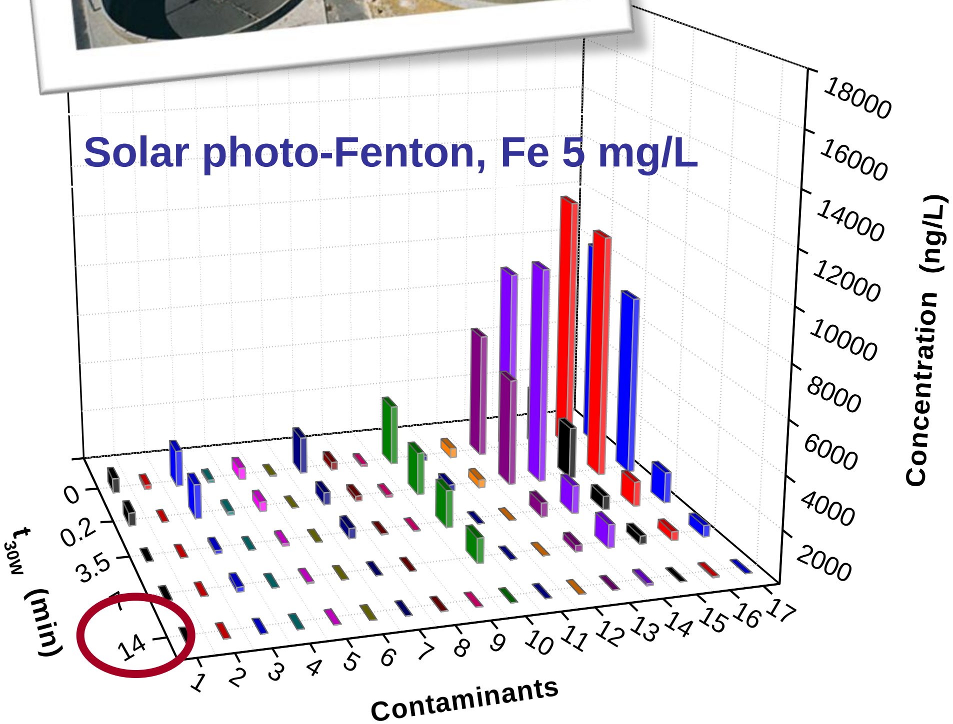
- Both alkaline and hydrogen peroxide ozonation provide >90% removal of ECs
- But only TOC removal is able to ensure the absence of reaction intermediates

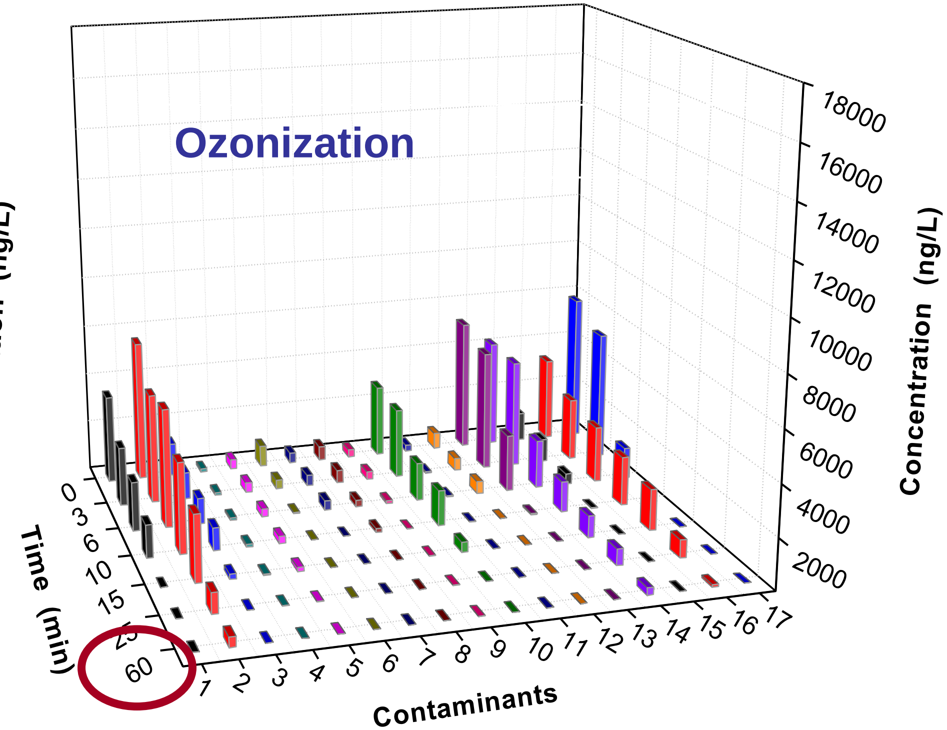
Ana Agüera
University of Almeria



COMPARISON OF TREATMENTS EFFICIENCY IN REAL CONDITIONS

> 90% removal of micropollutants





1-Bisphenol A; 2-Ibuprofen; 3-Hidroclorotiazide; 4-Diuron; 5-Atenolol; 6-4-AA; 7-Diclofenac; 8-Ofloxacin; 9-Trimethoprim; 10-Gemfibrozil; 11-4-MAA; 12-Naproxen; 13-4-FAA; 14-ΣC; 15-4-FAA; 16-Caffeine; 17-Paraxanthine).

COMPARISON OF TREATMENTS EFFICIENCY IN REAL CONDITIONS

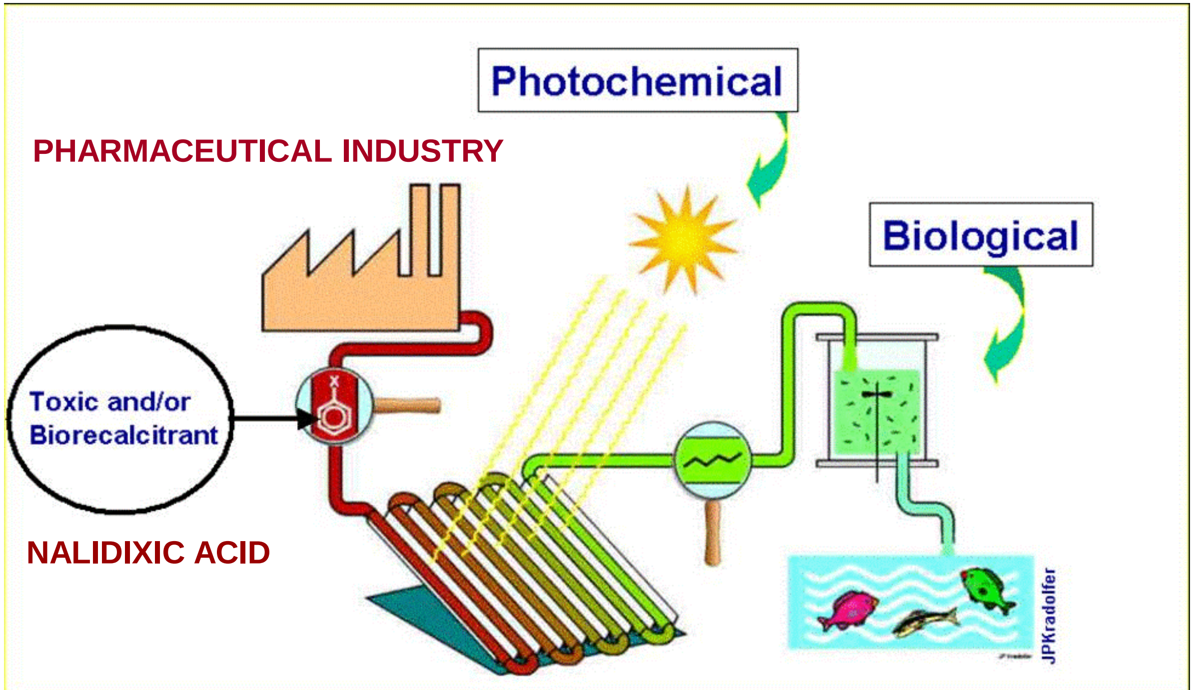
ECONOMICAL STUDY

Costs of solar photo-Fenton and ozonation tertiary treatments for 90% and 98% elimination of micropollutants

	Solar Photo-Fenton €/m³		Ozonation €/m³	
	90%	98%	90%	98%
Reagent	0.04	0.074	0.16	0.22
Labour	0.03	0.05	0.05	0.05
Electricity	0.004	0.01	0.035	0.042
Investment	0.09	0.15	0.78	0.90
Total	**0.164**	**0.284**	**1.025**	**1.212**

DESIGN AND OPTIMIZATION OF PROCESSES

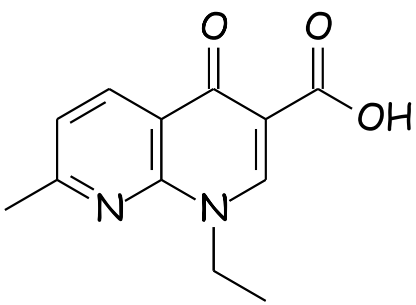
TREATMENT OF INDUSTRIAL EFFLUENTS



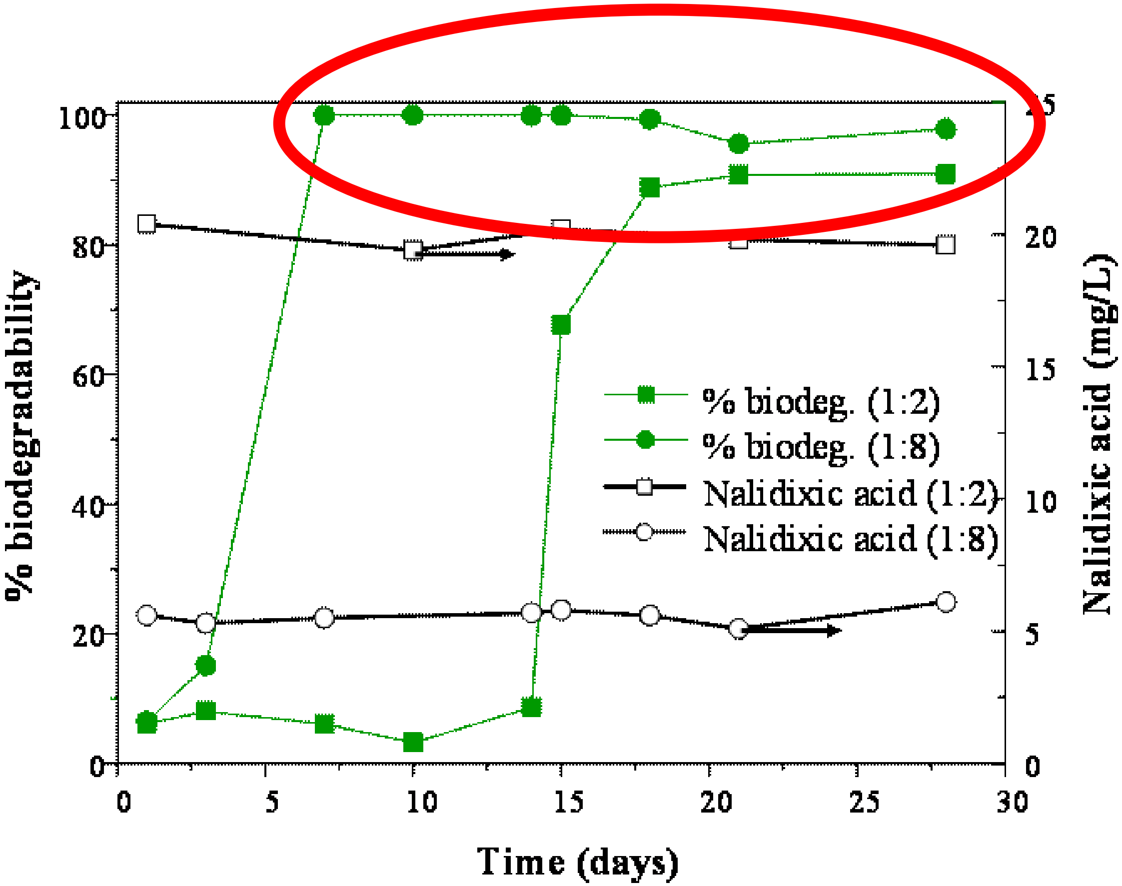
Industrial Wastewater → Photo-Fenton → Biological treatment → Reclaimed Water

DESIGN AND OPTIMIZATION OF PROCESSES

INDUSTRIAL WASTEWATER CHARACTERIZATION



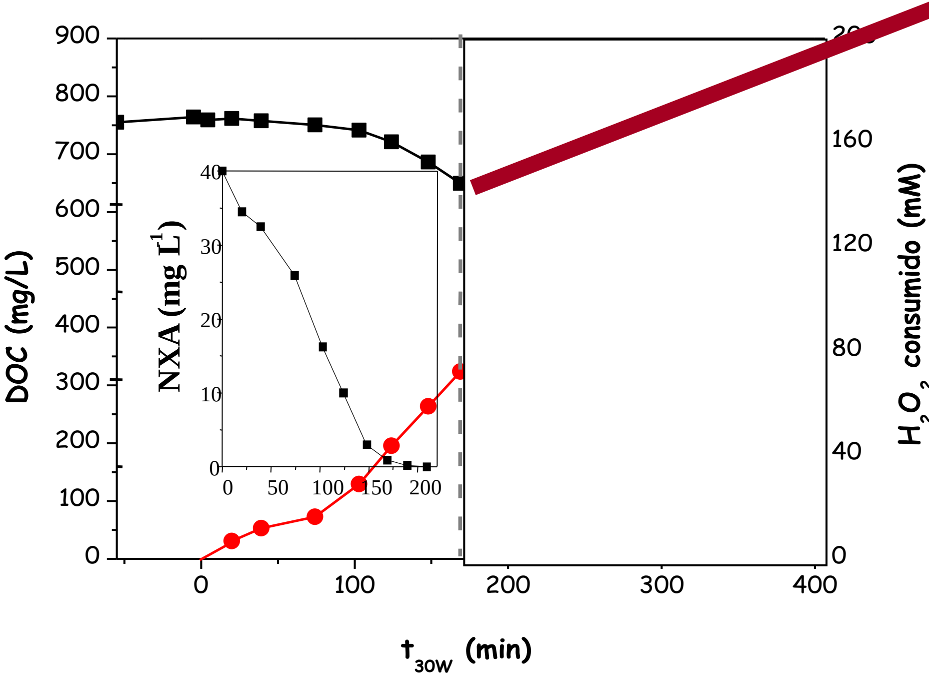
Nalidixic acid



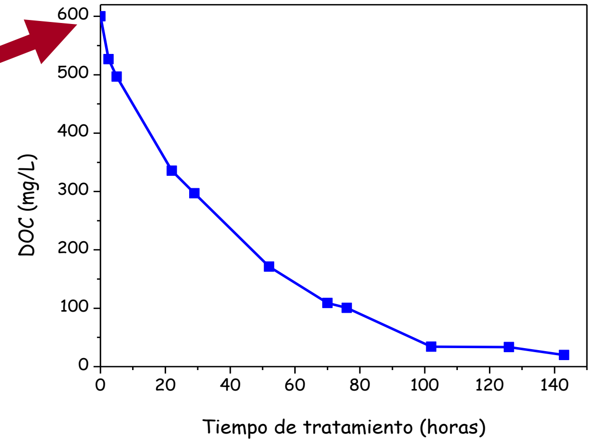
Ana Agüera
University of Almeria

DESIGN AND OPTIMIZATION OF PROCESSES

Photo-Fenton Treatment

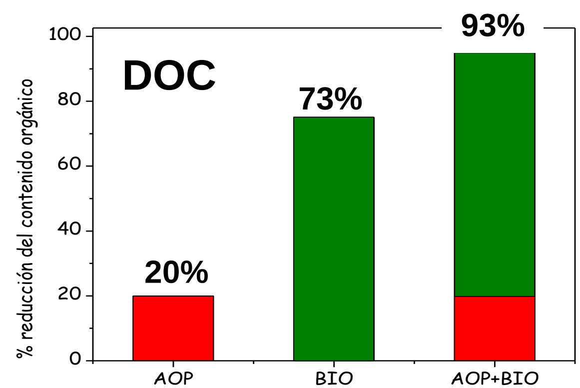


Biological Treatment



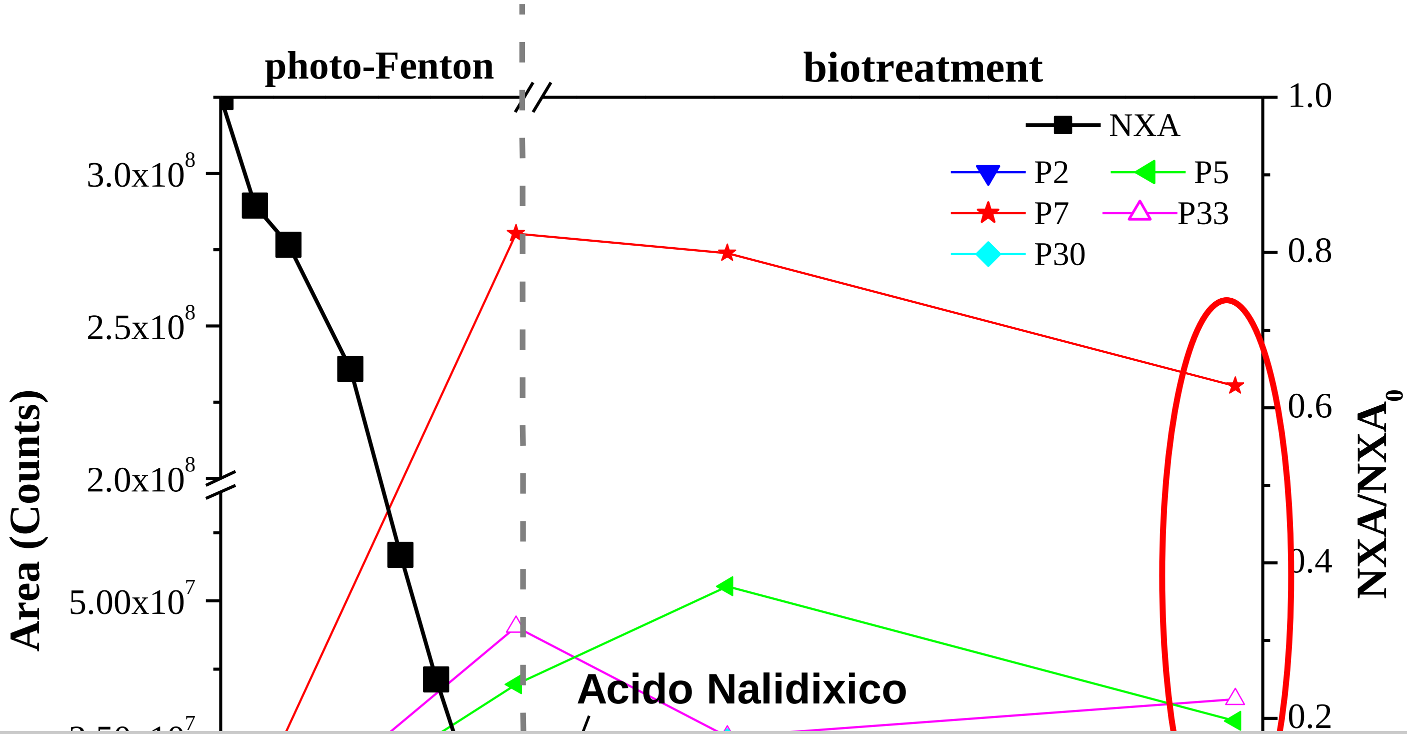
Initial sample

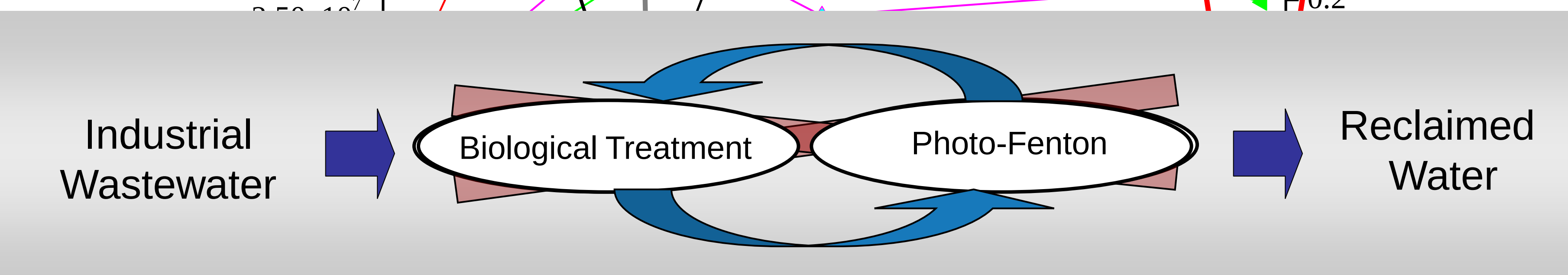
Final sample



DESIGN AND OPTIMIZATION OF PROCESSES

PHOTO-FENTON + BIOTREATMENT

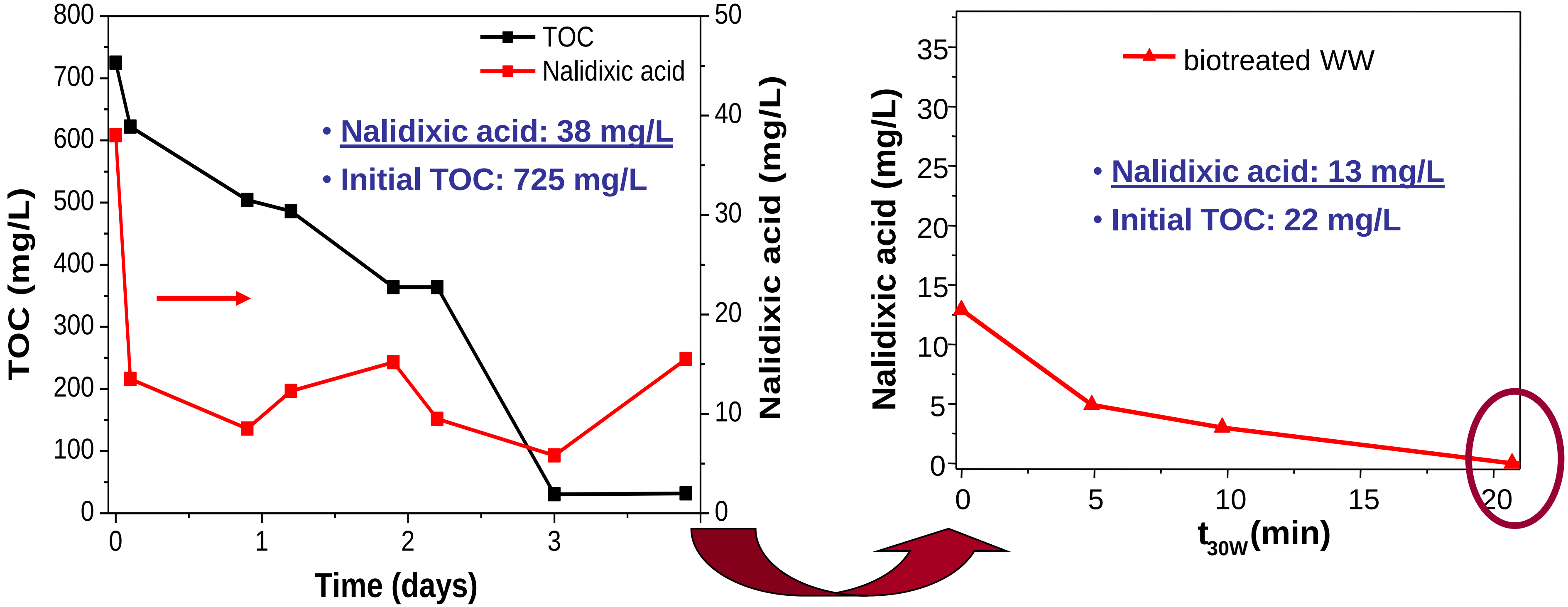




DESIGN AND OPTIMIZATION OF PROCESSES

Biological Treatment

Photo-Fenton Treatment

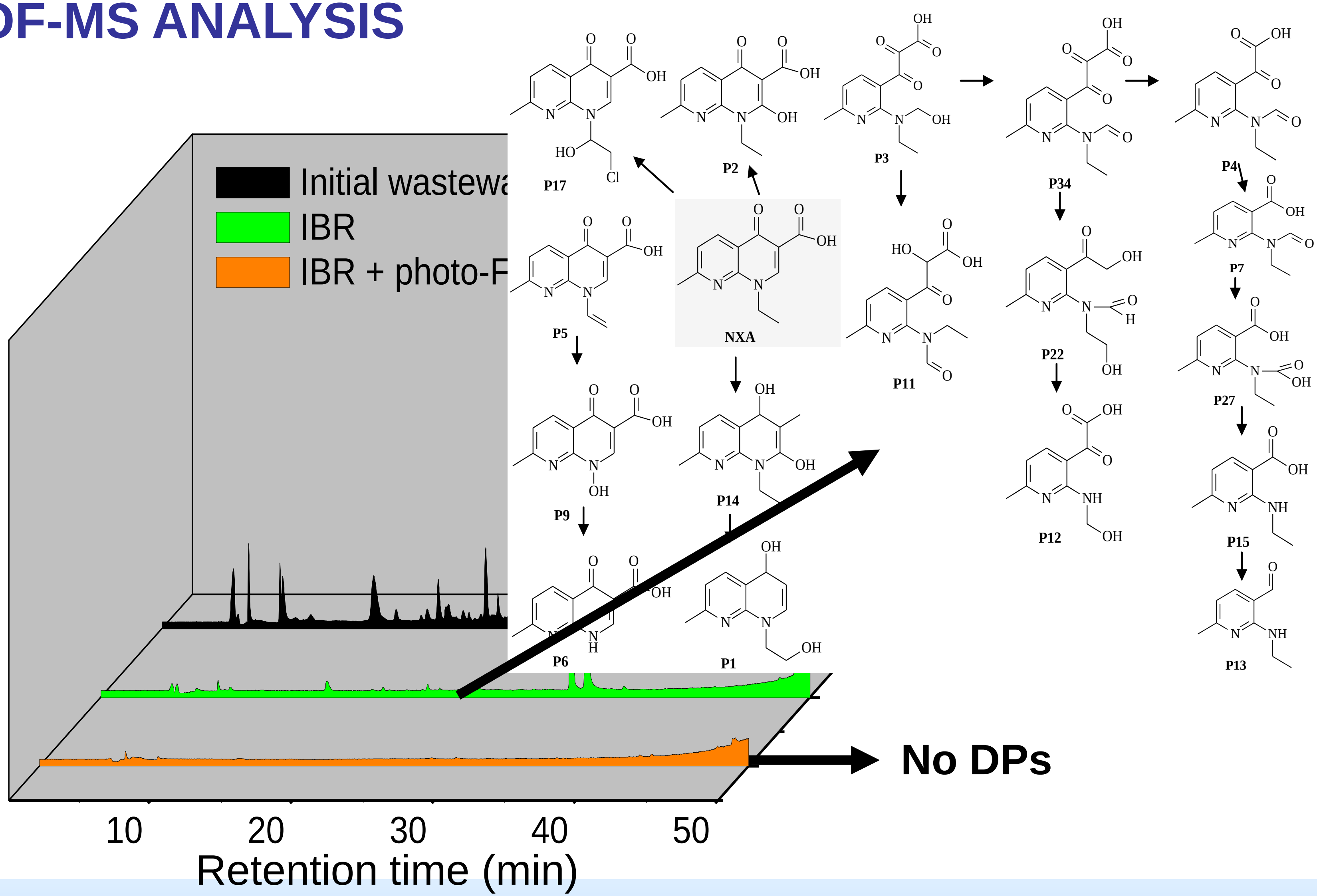


- 96% TOC removal
- Nalidixic acid persists (~15 mg/L)

- Total removal of Nalidixic acid and TPs

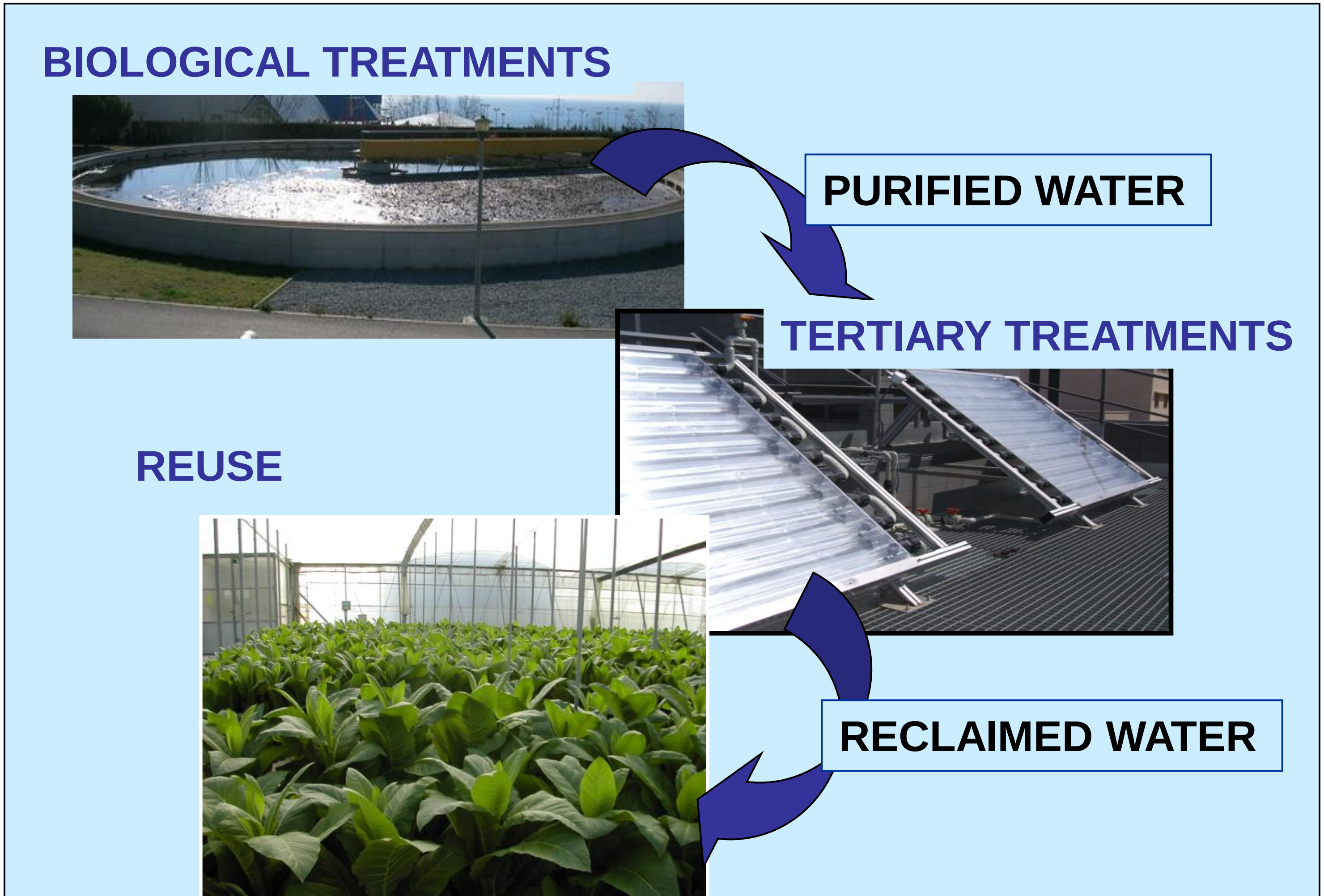
Ana Agüera
University of Almeria

LC-TOF-MS ANALYSIS



Ana Agüera
University of Almeria

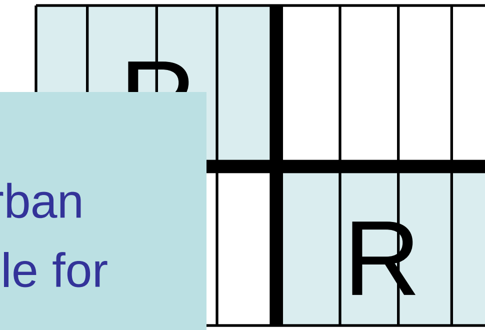
ANALYTICAL EVALUATION FOR REUSE PURPOSES



Reuse of treated urban wastewater (secondary treatment) in industrial crops (tobacco) to obtain products of interest in industry

CONCLUSIONS:

- From productive point of view, the use of urban wastewater (secondary treatment) is feasible for industrial crop irrigation
- The content of N and P in WW is higher: lower dose of fertilizers



RIGATION

on (kg·m^{-2})

Compounds of market value

- % Hydrosoluble proteins
- % Sugars
- % Starch
- % Nicotine
- % Solanesol

Ana Agüera
University of Almeria

11 Compounds

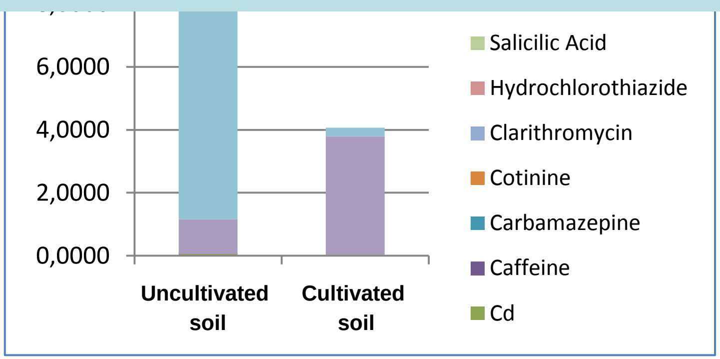
Accumulation of contaminants in the soil

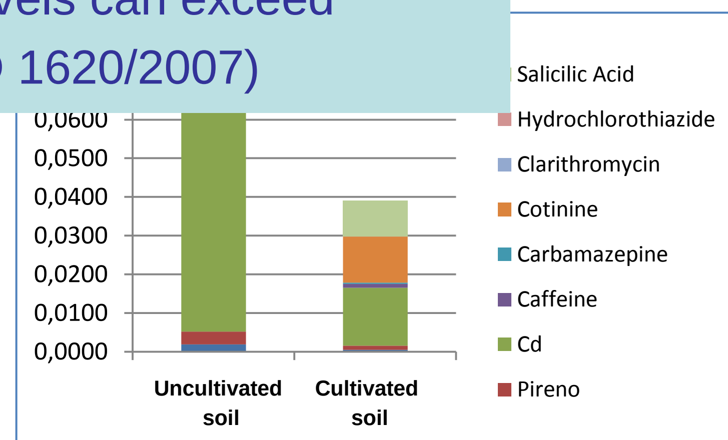
Compounds		Concentration (mg/kg)	
		Uncultivated	ivated soil
Priority pollutants			3.1450
			.0600
			.0033
			.0019
Emerging contaminants			.0003
			.0010
			.0001
			.0007
			1.0938
			.0017
			-

CONCLUSIONS:

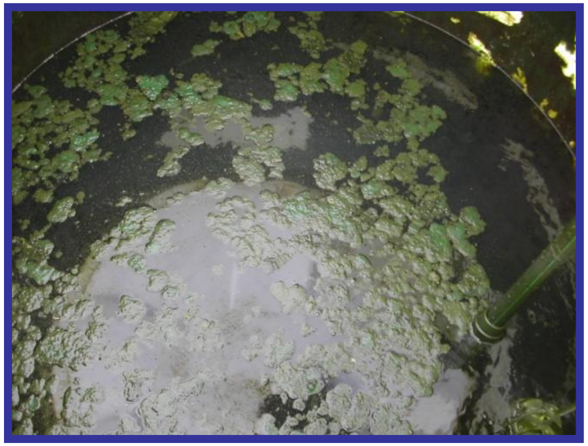
- Organic pollutants and heavy metals were detected in the soil, so control is necessary to prevent their accumulation in soil and groundwater contamination.
- The cultivation extracted contaminants of the soil. Industrial crops reduce the risk of accumulation of contaminants in soil, leaching and groundwater contamination and pose no risk to the consumer
- E. coli and suspended solids levels can exceed maximum allowable values (RD 1620/2007)

OMS
Maximum tolerable concentration in soil
Cadmium: 4 mg·kg^{-1}
Lead: 84 mg·kg^{-1}





Aditionals technical difficulties



Shutter of the irrigation system

Limited storage capacity

Frequent maintenance
of the filters

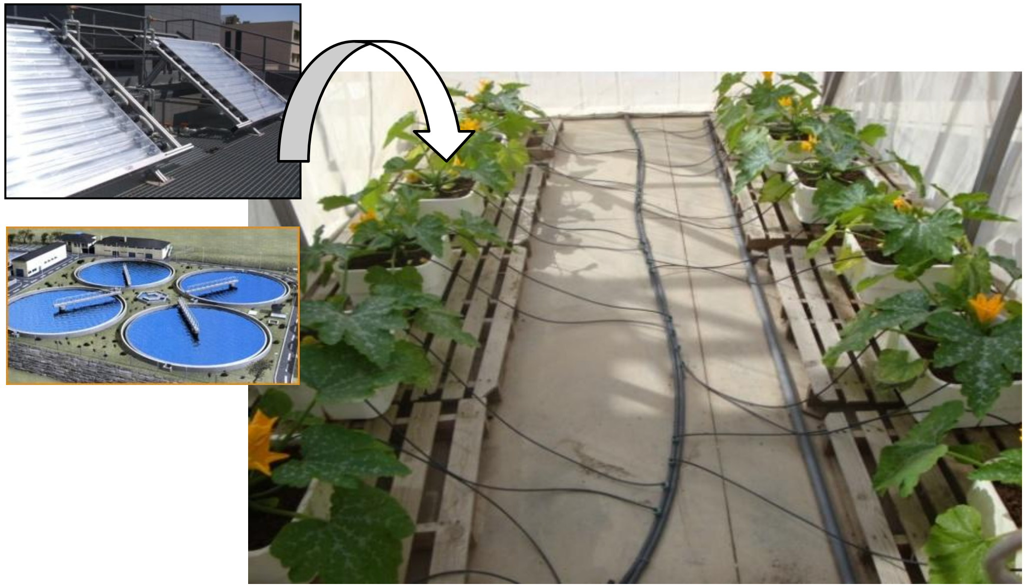
Need for additional treatment !

Ana Agüera
University of Almeria

Reuse of reclaimed urban wastewater by solar photo-Fenton in horticultural crops: zucchini

Irrigation water:

T1: Purified water by secondary treatment
T2: Reclaimed water by solar photo-Fenton



PILOT PLANT

Ana Agüera
University of Almeria

Reuse of reclaimed urban wastewater by solar photo-Fenton in horticultural crops: zucchini

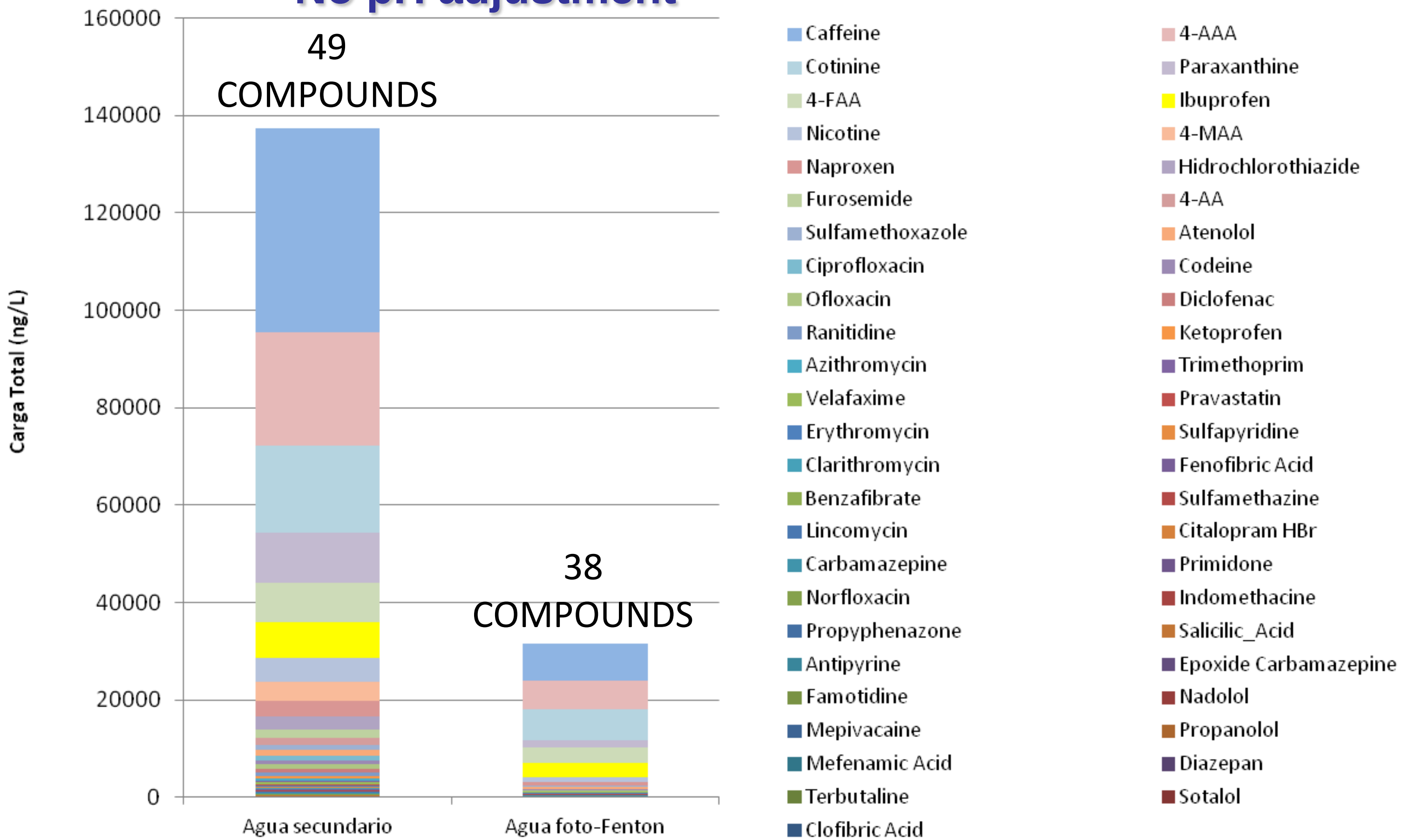
Solar photo-Fenton pH=3 → pH ↑

1. The treatment was effective in the removal of contaminants
2. An early damage was observed in the crop

	T1	T2
C.E.(25 ºC) mmhos/cm	1,55	3,66
Sales Totales g/l	1571	**3727**
Sulfatos mg/l	203	**1141**
Cloruros mg/l	543	**1068**
Sodio mg/l	265	**675**
E. Coli UFC/g	<10	10

Reuse of reclaimed urban wastewater by solar photo-Fenton in horticultural crops: zucchini

No pH adjustment



Ana Agüera
University of Almeria

Reuse of reclaimed urban wastewater by solar photo-Fenton in horticultural crops: zucchini

ANALYSIS OF SUBSTRATE

Sustrato (µg/kg)*		
Compuestos	**T0**	**T1**
4-AAA	32,55	24,09
4-FAA	9,21	1,54
Atenolol	5,48	0,04
Cafeína	1,36	1,29
Carbamazepina	0,91	0,74
Mepivacaina	0,11	0
Nicotina	4,13	0
Trimetoprim	2,67	1,07
Velafaxime	1,56	0,54

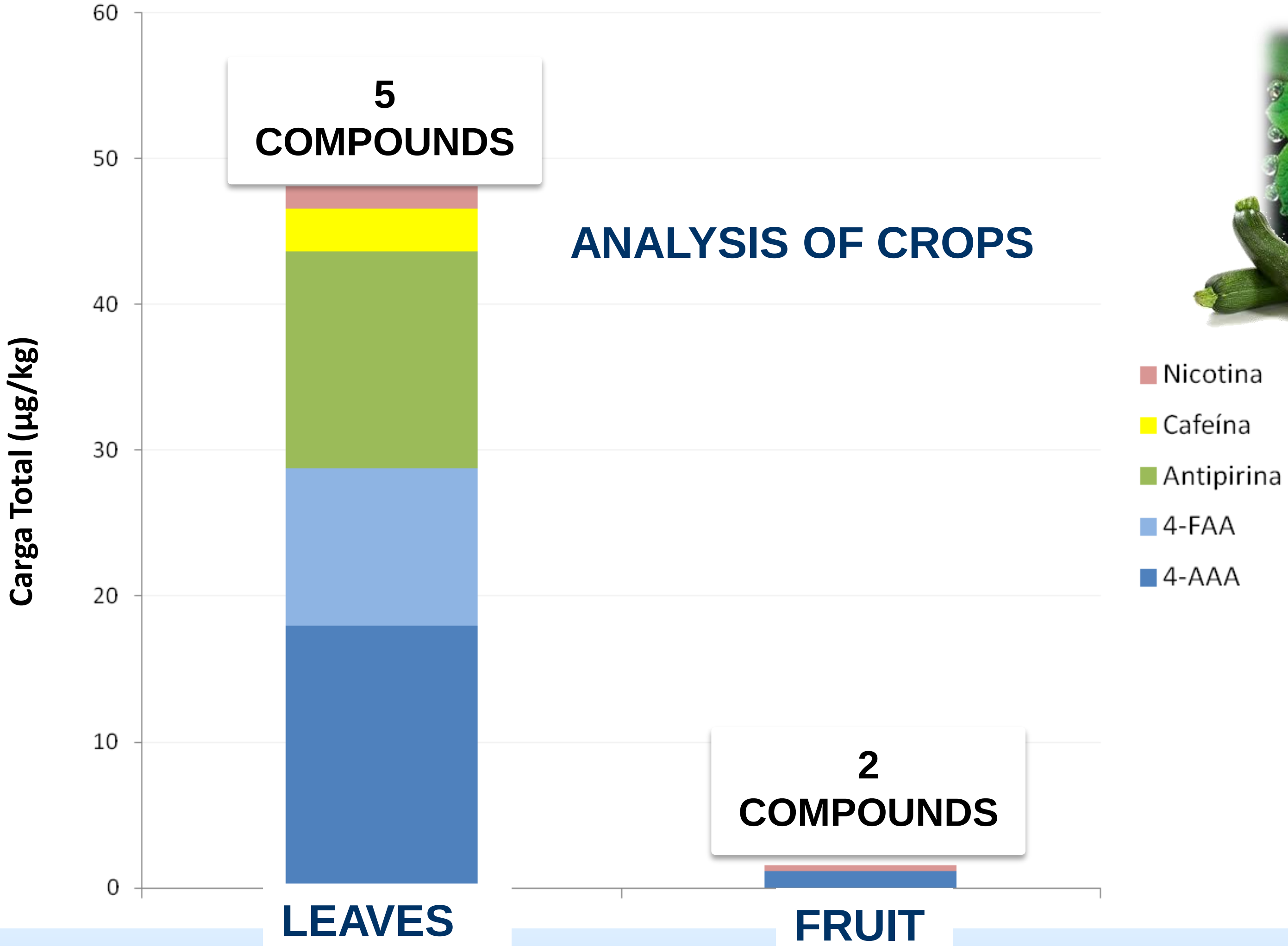
T0→ SECONDARY TREATMENT
T1→ MILD PHOTO-FENTON

9 COMPOUNDS

7 COMPOUNDS

Ana Agüera
University of Almeria

Reuse of reclaimed urban wastewater by solar photo-Fenton in horticultural crops: zucchini



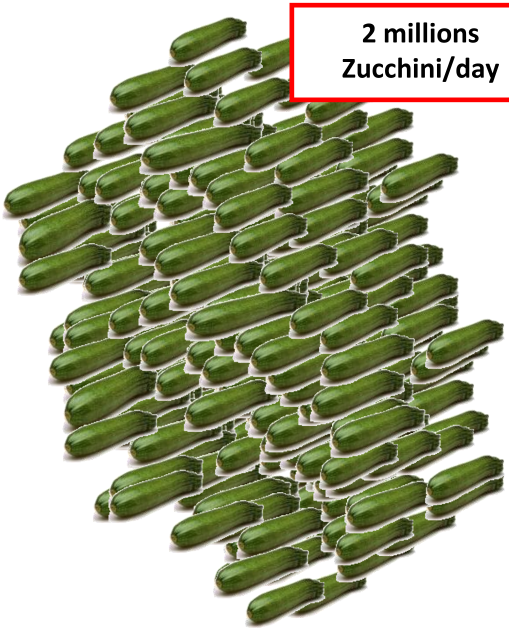
Ana Agüera
University of Almeria

Maximum concentrations in zucchini

Compound	Concentration (µg/kg)
4-AAA	1,17
Nicotine	0,38

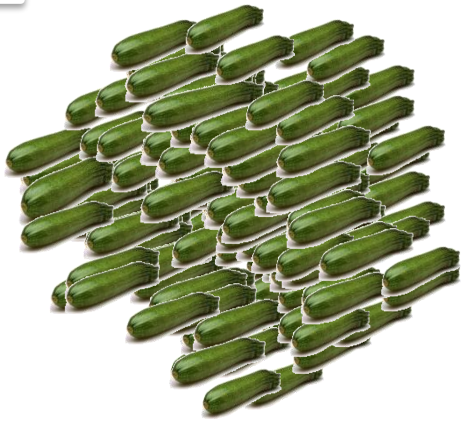
Dosis max. Dipirona: 6 g/día

2 millions Zucchini/day



Cigarrillo: 0.5 mg

6500 zucchini



Ana Agüera
University of Almeria

Ana Agüera
University of Almeria

THANK YOU !

- **Field experiments are required**
- **The design of the treatments must be adjusted to necessity in order to reduce cost**
- **Efficient control of the technologies applied**

Ana Agüera
University of Almeria