INNOVA-MED CONFERENCE

Innovative processes and practices for wastewater treatment and re-use in the Mediterranean region

8-9 October 2009, Girona, Spain

Scientific Committee

THURSDAY, 8. October 2009

8.30 Bus transport from the Carlemany hotel

8.45 – 9.15 Registration

9.15 – 9.30 Welcome and Introduction

9.30 – 9.45 Damià Barceló
ICRA, Girona, and IDAEA-CSIC, Barcelona, Spain
Problems and needs of sustainable water management in the Mediterranean area

Session 1: Innovative wastewater treatment

Chair: T. Knepper

9.45 – 10.15 Sixto Malato Rodríguez
CIEMAT – Plataforma Solar de Almería, Spain
Advanced technologies for wastewater treatment

10.15 – 10.45 Anuska Mosquera
Universidad de Santiago De Compostela, Spain
Emerging technologies for urban and industrial wastewater treatment

10.45 – 11.30 Poster session/Coffee break

11.30 – 12.00 Amadeo R. Fernández-Alba
University of Almeria, Spain
Evaluation of ozone waste water treatments and studies evaluating the reuse of treated effluents

12.00 – 12.30 Josef Hagin
Grand Water Research Institute (GWRI), Technion – Israel Institute of Technology, Israel
Advanced membrane wastewater treatment: Palestinian – Jordanian – Israeli project

12.30 – 13.00 Rafik Karaman
Faculty of pharmacy, Al-Quds University, Jerusalem, Palestine
Efficiency of the membrane technology in terms of pharmaceutical removal from wastewater

13.00 – 15.00 Lunch

Session 1: Innovative wastewater treatment (continuation)

Chair: S. Malato

15.00 – 15.30 Paola Verlichi,
ENDIF - Engineering department in Ferrara, Italy
Treatment and treatability of hospital wastewaters

15.30 – 16.00 Inmaculada Ortiz
University of Cantabria, Santander, Spain
Advanced regeneration processes for water reuse

16.00 – 16.30 Pilar Fernández Ibáñez
CIEMAT – Plataforma Solar de Almería, Spain
Disinfection of water by advanced technologies using solar energy

16.30 – 17.00 Poster session/Coffee break

Chair: A. Fernandez-Alba

17.00 – 17.30 Thomas Egli
EAWAG, Dübendorf, Switzerland
What happens during "Sodis"? A deeper insight into cellular damages caused by sunlight

17.30 – 18.00 Isabel Oller Alberola
CIEMAT – Plataforma Solar de Almería, Spain
Decontamination of industrial wastewater by advanced oxidation processes coupled with biotreatment

18.00 – 18.30 Discussion

18.45 Bus transport to the Carlemany hotel

21.00 Joint dinner (Carlemany hotel)

FRIDAY, 9. October 2009

9.00 Bus transport from the Carlemany hotel

Session 2: Occurrence of contaminants and analytical aspects

Chair: M. Fürhacker

9.30 – 10.00 Thomas P. Knepper,
EFF, Idstein, Germany
Occurrence and fate of contaminants in semi-arid areas

10.00 – 10.30 Subhi Saman
Palestinian Water Authority, Palestine
Normalization of trace metals in sediments as anthropogenic pollutants and determination of enrichment factors at wadi Al-Qilt, West Bank, Palestine.

10.30 – 11.30 Poster session/Coffee break

Chair: O. Zimmo

11.30 – 12.00 Adrian Covaci,
Toxicological Center, University of Antwerp, Belgium
Sewage epidemiology: Using wastewater to estimate cocaine consumption at national level.

12.00 – 12.30 Wolf von Tümpling
Helmholtz Centre for Environmental Research – UFZ, Magdeburg, Germany
Self cleaning potential of surface waters according to pharmaceuticals - Possibilities and limits

12.30 – 13.00 Mohamed Tawfic
Suez Canal University, Ismailia, Egypt
Wastewater treatment facilities, and life cycle analysis
A Sustainability Perspective

13.00 – 15.00 Lunch

Session 3: Water reclamation and reuse

Chair: M. Tawfic

15.00 –15.30 Maria Fürhacker
BOKU-University, Vienna, Austria
Challenges and solutions for waste and waste water reuse

15.30 – 16.00 Raquel Iglesias Esteban
Centro de Estudios Hidrográficos del CEDEX, Madrid (España
Water reuse in Spain: Data overview and costs estimation of suitable treatment trains

16.00 – 16.30 Mohamed Rejeb
INGREF Tunisia
Treated wastewater reuse for sustainable water resources management in Mediterranean countries

16.30 – 17.00 Redouane Choukrallah
IAVCHA, Agadir, Morocco
Actions towards sustainable and safely use of treated wastewater in agriculture: Morocco experiences

17.00 – 17.20 Lluís Sala
Consorci de la Costa Brava, Girona, Spain
Water reclamation and reuse in Costa Brava (1989-2009): Lessons learned and practical contributions

17.20 – 17.45 Coffee break

Session 4: Wastewater management and reuse in the Mediterranean countries: Experiences and constraints

Chair: R. Choukrallah

17.45 – 18.15 Omar Zimmo
Birzeit University, Palestine.
Overview of wastewater management practices in Mediterranean countries

18.15 – 18.45 Eleftheria Kampa
Ecologic, Berlin, Germany
Constraints to wastewater treatment and reuse of wastewater and sludge in Mediterranean Partner Countries

18.45 – 19.30 Discussion

19.30 End of Conference

19.45 Bus transport to the Carlemany hotel

Posters

1.
THE ROLE OF pH ON SULFAMETHOXAZOLE REMOVAL BY WALNUT SHELLS

S. Teixeira[1], C. Delerue-Matos[1], L. Santos[2]
[1]REQUIMTE/Departamento de Engenharia Química, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal
[2]LEPÆ/Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

2.
REGENERATION OF PAPER MILL WASTEWATER WITH FENTON AND PHOTO-FENTON PROCESSES

Maria N. Abellan, David Galí, Mertixell DelaVarga, Julia García-Montaño, Miren Blanco*, Amaia Martínez*, Arrate Marcaide*
LEITAT Technological Center, R&D Department, Passeig 22 de Juliol, 218 - 08221 Terrassa (Barcelona) Spain.
* TEKNIKER Technological Center, Avda. Otaola, 20-Apdo.-P.O. Box 44 – 20600 Eibar (Guipuzkoa) Spain

3.
FENTON AND BIOLOGICAL-FENTON COUPLED PROCESSES FOR TEXTILE WASTEWATER TREATMENT AND REUSE

José Blanco, Maria N. Abellan, David Galí, Meritxell DelaVarga, Julia García-Montaño, Francesc Torrades*
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* Departament d'Enginyeria Química, ETSEIA de Terrassa, Universitat Politècnica de Catalunya, C/Colom 11, E-08222, Terrassa (Barcelona) Spain.

4.
ADVANCED OXIDATION PROCESSES WITH ZEOLITES TO REMOVE GASOLINE COMPOUNDS FROM WATER

Gonzalez-Olmos R., Kopinke F.-D., Georgi A.
Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering, Permoserstrasse 15, D-04318 Leipzig, Germany

5.
MERCURY REMOVAL UNDER CONTINUOUS FLOW CONDITIONS

L. Carro, J.L. Barriada, P.Lodeiro, R. Herrero and M.E. Sastre de Vicente
Departamento de Química Física e Ingeniería Química I, Facultad de Ciencias, Universidad de A Coruña, Alejandro de la Sota 1, 15008, A Coruña (Spain).

6.
PHYSICOCHEMICAL ASPECTS ON THE REDUCTION OF Cr (VI) LEVELS IN SOLUTION USING BRACKEN FERN BIOMASS

M López-García, P. Lodeiro, R Herrero and M.E. Sastre de Vicente
Departamento de Química Física e Enxeñería Química I. Facultade de Ciencias. Universidade de A Coruña, Alejandro de la Sota 1,15008. A Coruña , Spain.

7.
PHOTOCATALYTIC OXIDATION OF 17α-ETHINYLESTRADIOL UNDER SIMULATED SOLAR LIGHT IN AQUEOUS TiO_2 SUSPENSIONS

Zacharias Frontistis[1], Nikolaos. P. Xekoukoulotakis[1,2*], Evroula Hapeshi[2], Despo Fatta-Kassinos[2] and Dionissios Mantzavinos[1]
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[2]Department of Civil and Environmental Engineering, School of Engineering, University of Cyprus, 75 Kallipoleos Str. 1678, Nicosia, Cyprus

8.
REMOVAL OF EMERGING POLLUTANTS IN CONVENTIONAL TERTIARY TREATMENT SYSTEMS AND REED BEDS.

Víctor Matamoros[1], Josep Mª Bayona[2] and Victòria Salvadó[1]
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[2]Environmental Chemistry Dpt. IIQAB-CSIC, jordi Girona, 18. E-08034 Barcelona, SPAIN

9.
TRANSPORT AND TRANSFORMATION OF PHARMACEUTICALS, ESTROGENS, AND OTHER ANTHROPOGENIC WASTE INDICATORS THROUGH WASTEWATER-TREATMENT PROCESSES

Edward T. Furlong1, James L. Gray1, Patrick J. Phillips2, Kathleen Esposito3, Beverly Stinson3, and Dana W. Kolpin4
1U.S. Geological Survey, Denver, Colorado
2U.S. Geological Survey, Troy, New York
3 Metcalf and Eddy, Inc., New York, New York
4 U.S. Geological Survey, Iowa City, Iowa

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MULTI-WALLED CARBON NANOTUBES FOR ELECTROCHEMICAL SENSING OFTHE ANTIBIOTIC CIPROFLOXACIN IN WASTEWATER

E. Manuela Garrido[1], Jorge Garrido[1], Fernanda Borges[2], Christopher Brett[3]
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[3] Department de Chemistry, Faculty of Sciences and Technology, University of Coimbra, 3004-535 Coimbra, Portugal.

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CLEAN-UP STRATEGIES IN THE DETERMINATION OF SEVERAL THERAPEUTIC CLASSES OF PHARMACEUTICALS IN WASTEWATER SAMPLES BY LC-MS/MS AND THEIR IMPACT ON RECEIVING SURFACE WATERS

M.A. Sousa[1,2], C. Gonçalves[1,2], E. Cunha[1] and M.F. Alpendurada[1,2 *]
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[2] IAREN – Water Institute of the Northern Region / Rua Dr. Eduardo Torres, 229 / 4450-113 Matosinhos, Portugal

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PHOTO-ASSISTED TREATMENT OF MICROCONTAMINANTS IN SEWAGE WASTE-WATER FOR WATER REUSE

Bruno Souza*, Samanta Pereira, Angel Cruz, Renato F. Dantas, Marcia Dezotti, Carme Sans, Santiago Esplugas
Departament d'Enginyeria Química, Universitat de Barcelona. Martí i Franquès 1, 08028, Barcelona, Spain.

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NEW RECEIVING WATER BODY FOR A LARGE WASTEWATER TREATMENT PLANT IN A SENSITIVE AREA IN NORTHERN ITALY: REFITTING WITH NATURAL SYSTEMS AND WATER REUSE

Verlicchi P., Galletti A., Masotti L.
Department of Engineering University of Ferrara, Via Saragat 1 I-44100 Ferrara Italy

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UV-A AND SOLAR DRIVEN CATALYTIC REMOVAL OF OFLOXACIN PRESENT IN SEWAGE INTENDED FOR REUSE

Hapeshi E.1, Michael I.1, Michael C.1, Xekoukoulotakis N.P.2, Mantzavinos D.2 and Fatta-Kassinos D.1
1Department of Civil and Environmental Engineering, School of Engineering, University of Cyprus, 75 Kallipoleos Str. 1678, Nicosia, Cyprus
2Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR 73100 Chania, Greece

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ALTERNATIVE BIOLOGICAL TREATMENT FOR DEGRADING MICROPOLLUTANTS IN WATER USING LIGNINOLITIC FUNGI

Blánquez P., Caminal G*., Cruz C., Gabarrell X., Marco-Urrea E., Sarrà M., Vilaplana M., Vicent T.
Grup de Recerca Consolidat (2009 SGR 656)
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PRESENCE OF DICLOFENAC AND ITS HUMAN METABOLITES IN WWTP AND EVALUATION OF THEIR TOXICITY

Victoria Osorio[1], Sandra Pérez[1], José Luís Abad, Marinel·la Farré, Damià Barceló[1]
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LINKING EFFLUENT DISCHARGES, RIVER FLOW AND MEASURED ENVIRONMENTAL CONCENTRATIONS OF EMERGING CONTAMINANTS IN THE LOW LLOBREGAT RIVER (NE SPAIN)

D. Barceló[a,b], A., M. López de Alda[a], M. Petrović[a,c], A. Ginebreda[a], S. Pérez[a], C. Postigo[a], M. Köck[a], R. López[a], R. Brix[a], A. Munné[d], L. Tirapu[d]
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18.

REMOVAL OF ANTHELMINTIC DRUGS AND THEIR PHOTODEGRADATION PRODUCTS BY NF/RO – LABORATORY SCALE STUDY

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CHARACTERIZATION OF PRODUCED WATER FROM COALBED METHANE PRODUCTION WITH EMPHASIS ON ORGANIC CONSTITUENTS RELEVANT FOR TREATMENT

Katharine G. Dahm, Pei Xu, Dean Heil, and Jorg E. Drewes
Environmental Science and Engineering Division of the Colorado School of Mines in Golden, Colorado, USA.

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MULTI-RESIDUE METHOD FOR TRACE LEVEL DETERMINATION OF PHARMACEUTICALS IN SOLID SAMPLES USING PRESSURIZED LIQUID EXTRACTION FOLLOWED BY LIQUID CHROMATOGRAPHY/QUADRUPOLE-LINEAR ION TRAP MASS SPECTROMETRY

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DETERMINATION OF MULTI-CLASS PHARMACEUTICALS IN WASTEWATER BY FULLY AUTOMATED ON-LINE SPE-LC-MS/MS

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PREFACE

This final Conference of the European Union (EU) funded coordination project INNOVA-MED entitled: **Innovative processes and practices for wastewater treatment and re-use in the Mediterranean region** is being organized in Girona, Spain in collaboration with Catalan Insititute for Water Studies (ICRA) and Catalan Water Agency (ACA).

In the course of the Conference, 23 lectures and 21 posters will be presented, being the principal topics (i) innovative wastewater treatment, (ii) water reclamation and reuse, (iii) wastewater management.

We expect that this Conference will bring novel information concerning the occurrence of contaminants in arid and semi-arid regions, innovative treatment technologies and practices in wastewater reuse, presenting experiences from different Mediteraniean countries. Several good practice examples will be presented discussing constraints and possible solutions. The Conference aims to be a valuable piece of information thus supporting the local authorities and the different stakeholders in Mediteraanean countries in overcoming key constraints to treatment and reuse of wastewater and sludge.

Finally, we would like to thank the participants in this Conference, including lecturers and poster presentations for their contributions to the scientific programme. In addition, we would like to thank the local organizers from ICRA for their support and warm welcome.

Wishing you a very successful and enjoyable Conference in Girona.

D. Barceló and M. Petrovic
October 2009

PROBLEMS AND NEEDS OF SUSTAINABLE WATER MANAGEMENT IN THE MEDITERRANEAN AREA

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The Mediterranean Sea is the largest semi-enclosed European sea, characterized by a narrow shelf, a narrow littoral zone and a small drainage basin especially in the northern part. Today, 82 million people live in coastal cities in 21 countries on the Mediterranean rim and by 2025 there will be an estimated 150-170 million. Today the southern Mediterranean countries account for 32 per cent of the region's population; by 2025 that is expected to have reached 60 per cent. Even though the population growth is slowing down in the area, this will still mean an increase in environmental pressure in the immediate future, especially because the rise in population will be mainly concentrated in the countries in the southern and eastern Mediterranean. The important level of human activity in coastal areas is also leading to serious pollution problems, caused by the large quantities of industrial and urban waste that are produced and discharged in the sea with a low capacity for self-decontamination and a slow water renewal cycle. Seasonal population pressures are also very high. Over 100 million tourists visit Mediterranean beaches and cities every year and this number is expected to double by 2025. In order to cater for this booming business, natural habitats have been replaced by modern resorts and the extra pollution generated is often dumped untreated into the sea, threatening the equilibrium of entire ecosystem of the region.

The regions included in the Mediterranean basin are amongst the world areas most suffering of water scarcity in addition to the pollution of freshwater resources. It is estimated that 30 million Mediterranean people live without access to clean drinking water (see Figure 1).

The degree of pressure on water resources, expressed through the *exploitation index of renewable natural resources* (volume of annual abstraction on renewable natural water resources / annual average volume of available renewable natural water resources, expressed as a percentage), and its projection to 2025 is shown in Fig. 2. Tensions on the resources are expected to be particularly high in Egypt, Israel, Libya, Palestinian Territories and in the Spanish Mediterranean catchment areas (index at 75% or higher), as well as in Malta, Syria, Tunisia and in some catchments of Morocco (index between 50 and 75%).

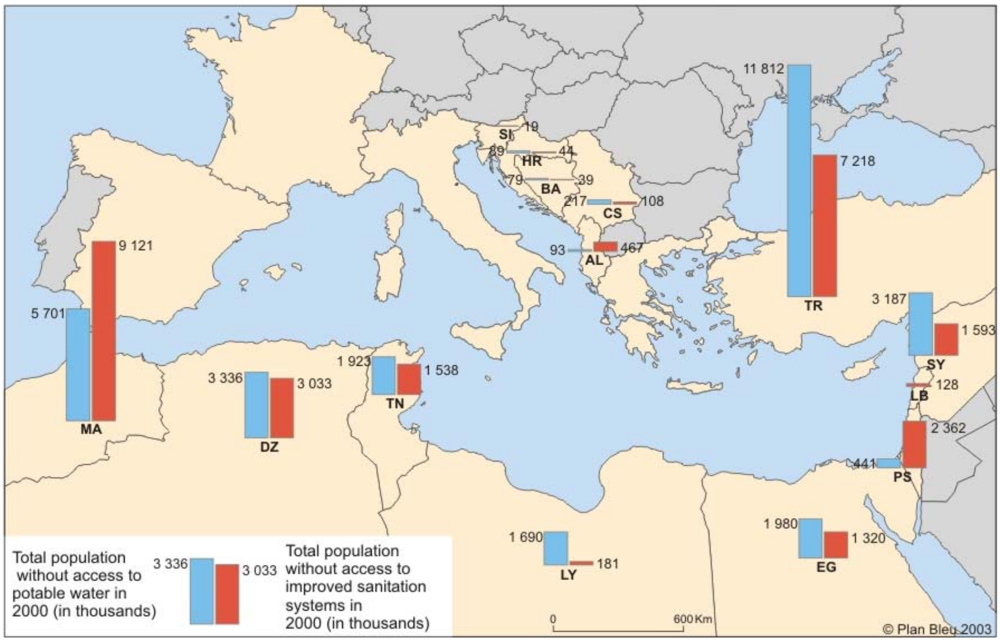

Figure 1. Access to safe drinking water and sanitation (source: *UN-SDMI,OMS-Unicef, 2003)*

Understanding water scarcity and the way to cope with scarcity is not just a matter for water managers or scientists. Water scarcity has a direct impact on citizens and economic sectors that use and depend on water, such as agriculture, tourism, industry, energy and transport. Water scarcity and droughts also have broader impacts on natural resources at large, through negative side-effects on biodiversity, water quality, increased risks of forest fires and soil impoverishment. Ultimately, the shortage of available water may not only have effects on water quality, but also on the ecosystems' integrity, and may result in economic and social disarrangements.

The increased pressure on water resources will cause additional effects on aquatic ecosystems, with some direct and indirect effects. This is particularly relevant since freshwater ecosystems deliver relevant services to human societies. The effects on watersheds are commonly focused upon streams and rivers. Hence there will be affects on morphology (incision, channel simplification), chemistry (higher nutrient and pollutant concentrations) and biological communities (lower diversity, arrival of invasive species, lower efficiency of biological processes). Regional climate models provide a series of consistent high resolution scenarios for several climate variables across Europe. Analyses in Mediterranean watersheds consistently suggest that the climate will be significantly hotter and drier, especially in summer. It is foreseen that this will influence both the fate and behavior of pollutants.

Since, it is evident that the physical, socio-economic and environmental limits of supply-based policies have been reached future scenarios includes implementation of a number of policies based on improved water demand management and policies aimed to increase exploitable potential through improved water and soil conservation, and increased recourse to the artificial replenishment of water tables in arid areas. Alternative scenario (see Figure 3.) accounts for potential savings in agriculture (including reutilization of wastewater, reduction of transport losses and increase in efficiency in irrigation), industry (increase in recycling rate); domestic water (reduction of transport losses and leaks).

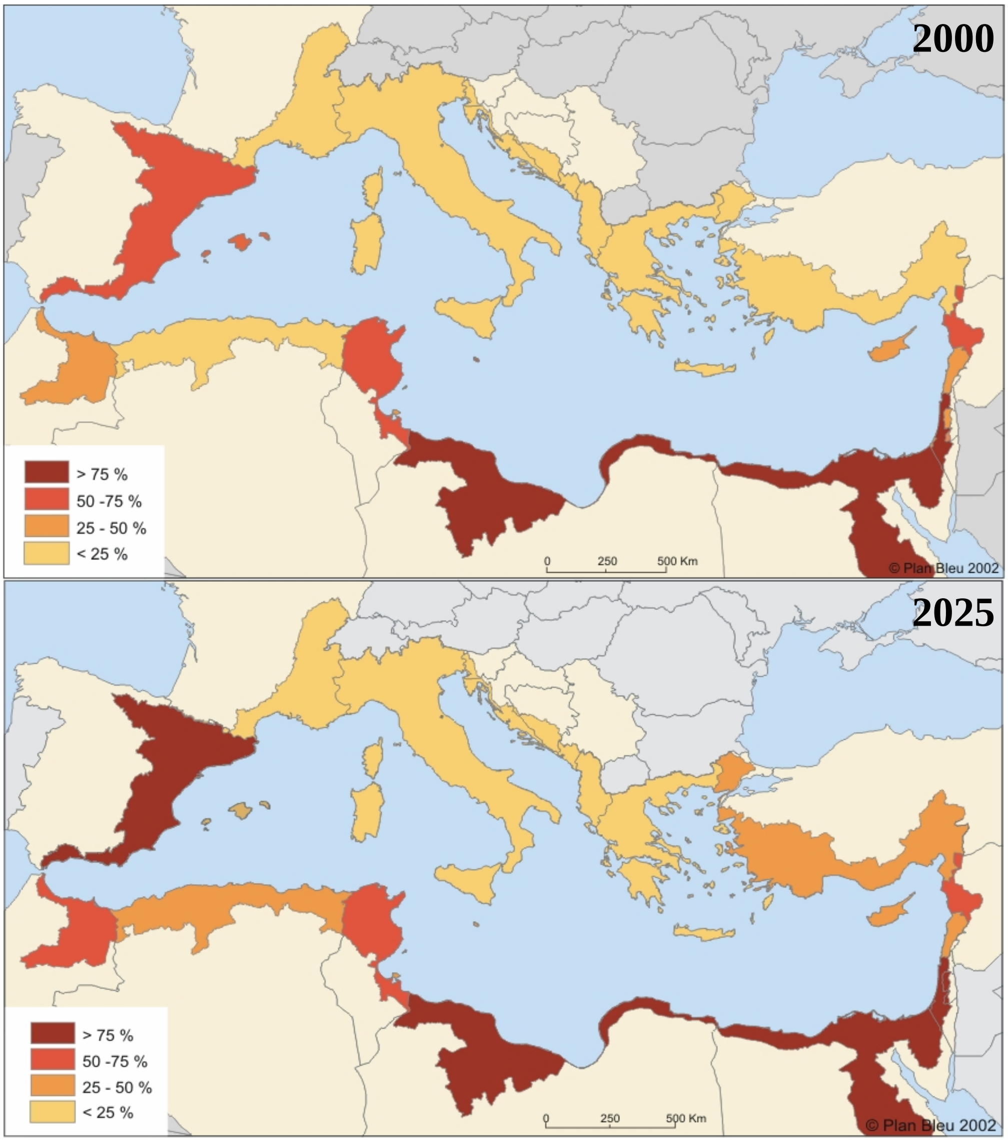

Figure 2. Exploitation indices of renewable natural water resources (source: Plan Bleu, UNEP – Regional activity centar. Environment and development in the Mediterranean.)

Analyzing potential alternatives and needs indicates that there is not a single and easy solution for water scarcity because multiple causes (or stressors) require multiple solutions. Several options need to be applied when considering the existing resources. In particular for the scenario of climate change, increased demand and decreasing resources must be considered. These options need to consider the delicate coupling between social and natural systems, where each has their share. Both improved technologies and upgraded water management practices are necessary in all sectors where water is used (e.g. agriculture, manufacturing or tourism). It is essential that the full economic and environmental costs be considered in evaluating the alternatives, where conservation of resources and their quality *at the source* could also be included. The use of decision support systems may be helpful in integrating the multiple actors, as well as in optimizing drought management and mitigation measures.

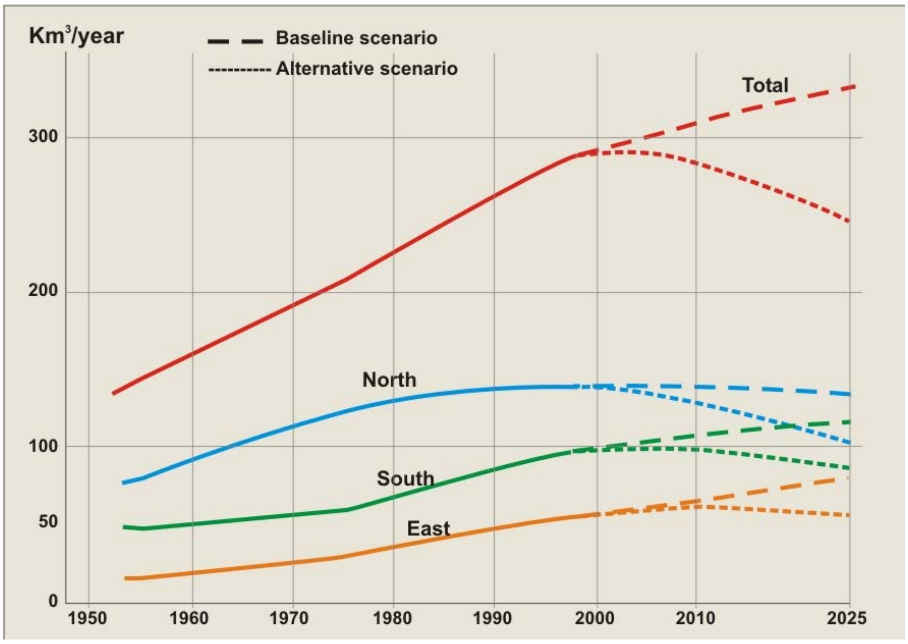

Figure 3. Total water demand of Mediterranean sub-regions (evolution 1950-2000 & baseline and alternative projections 2000-2025) (source Source : Plan Blue)

More relevant options are:

- Working for a culture of water-saving and efficiency is essential. This requires an active public awareness from citizens and economic sectors. Potential savings can be stabilized into the future and these savings extended to domestic and agricultural needs. Developing water savings in irrigation, within general planning for the economical needs of the whole territory, is essential.

- Valuing ecosystem services can provide a framework for understanding that societal needs and natural capital are not separated. Public education is critical to achieve the goal of compatible use of water resources and the conservation of our natural heritage.

- Improvement of wastewater treatment quantitatively and qualitatively. Any choice of treatment technology performed should rely on those not entailing excessive costs and providing the best environmental practice and option. Furthermore new and innovative control strategies could be adopted in order to improve the biological process performance and reach a proper water quality and energy consumption. Adoption of new technologies for wastewater treatment. Consider in combining different technologies (biological and physico-chemical) in a single wastewater treatment plant according to the different effluent characteristics .

- Reuse of sewage waters can be considered as an adequate water source for urban, tourism and agricultural uses. With proper treatment, sewage water can even be used for drinking water. There exist several techniques adequate for the improvement of chemical and microbiological quality that could help to provide these uses. The solutions are linked, however, to available energy; this sometimes becomes the critical limitation. Public perception also needs to be improved when this source of water is considered. It is expected that 190 Mm^3 of reused waters could be available by 2015 in Catalonia.

- Desalination is a current option to obtain water resources that could provide a source of water that could be considered as independent of potential changes in climate. However, energy needs and costs are high. Consequently, desalination should not be considered the only option.

- Use of ground waters requires adequate protection of aquifers. Overexploited aquifers affect available water for surficial aquatic ecosystems and may create problems of subsidence and salt water intrusion. Recharging aquifers requires good chemical and microbiological quality of the waters. Some techniques to improve the water quality of underground waters exist, even at the large scale. Recovered ground water wells can provide additional resources (up to 25 Mm^3 in Catalonia which could be raised to 90 Mm^3 during extreme droughts).

ADVANCED TECHNOLOGIES FOR WASTEWATER TREATMENT

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One of the most pervasive problems affecting people throughout the world is inadequate access to clean water and sanitation. Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods of purifying water at lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. In both developing and industrialized nations, a growing number of contaminants are entering water supplies from human activity: from traditional compounds such as heavy metals to emerging micropollutants such as endocrine disrupters and nitrosoamines[1]. Increasingly, public health and environmental concerns drive efforts to decontaminate waters previously considered clean. More effective, lower-cost, robust methods to disinfect and decontaminate waters from source to point-of-use are needed, without further stressing the environment or endangering human health by the treatment itself. Conventional methods of water disinfection and decontamination can address many of these problems. However, these treatment methods are often chemically, energetically and operationally intensive, focused on large systems, and thus require considerable infusion of capital, engineering expertise and infrastructure, all of which precludes their use in much of the world. Furthermore, intensive chemical treatments (such as those involving ammonia, chlorine compounds, hydrochloric acid, sodium hydroxide, ozone, permanganate, alum and ferric salts, coagulation and filtration aids, anti-scalants, corrosion control chemicals, and ion exchange resins and regenerants) and residuals resulting from treatment (sludge, brines, toxic waste) can add to the problems of contamination and salting of freshwater sources.

AOPs can be broadly defined as redox methods which are based on the intermediacy of reactive oxygen species, such as hydroxyl radicals, $^{\bullet}OH$, superoxide radical anions, $O_2^{\bullet-}$, and perhydroxyl radicals $HO_2^{\bullet}$, to convert harmful organic and inorganic pollutants found in air, water and soil to less hazardous compounds. The most widely used AOPs include ozonation, electrochemical oxidation, Fenton's and photo-Fenton's reagent, heterogeneous semiconductor photocatalysis, wet air oxidation, and sonolysis, among others[2]. A brief description of these technologies is given below.

Ozone, O_3, is a strong oxidant that is able to react through two different reaction mechanisms, called direct and indirect ozonation[3]. Thus, ozone can directly react with certain functional groups of organic compounds found in water and wastewaters, such as unsaturated and aromatic hydrocarbons with substituents such as hydroxyl, methyl and amine groups, through 1,3 dipolar cycloaddition and electrophilic reactions, giving rise to degradation products. On the other hand, ozone decomposes in water to form $^{\bullet}OH$, which are stronger oxidizing agents than ozone itself, thus inducing the so-called indirect ozonation. Ozone decomposition in water can be initiated by the hydroxyl anion, HO^-, and thus indirect ozone oxidation is favored at alkaline pH conditions. Treatment performance is enhanced if ozone is combined with ultraviolet irradiation, hydrogen peroxide or with iron or copper complexes that act as catalysts, thus generating additional $^{\bullet}OH$. Homogeneous oxidation with the Fenton's reagent involves the use of ferrous, Fe(II) or ferric, Fe(III) ions in the presence of hydrogen peroxide via a free radical chain reaction mechanism, which produces $^{\bullet}OH$. It is considered to be a metal-catalyzed oxidation reaction, in which iron ions act as the catalyst. Process efficiency is closely related to the solution pH, whose optimal values are between 2 and 4, as well as the COD:H_2O_2:Fe ratio in the feed[4]. Moreover, efficiency may be enhanced in the presence of UV irradiation as more $^{\bullet}OH$ are produced in the so-called photo-Fenton reaction. Heterogeneous semiconductor photocatalysis using TiO_2 as photocatalyst involves the illumination of an aqueous TiO_2 suspension with irradiation with energy equal to or greater than the band gap energy of the semiconductor, thus generating valence band holes and conduction band electrons[5]. Holes and electrons may either undesirably recombine liberating heat or make their separate ways to the surface of TiO_2, where they can react with species adsorbed on the catalyst surface. Valence band holes can react with water and the hydroxide ion (i.e. under alkaline conditions) to generate .OH, while electrons can react with adsorbed molecular oxygen reducing it to $O_2^{\bullet -}$, which, in turn, reacts with protons to form peroxide radicals.

- **H_2O_2/Fe^{2+} (Fenton):** $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$
- **H_2O_2/Fe^{2+} (Fe^{3+})/UV (Photo-Fenton):** $Fe^{3+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet}$
- **$TiO_2/h\nu/O_2$ (Photocatalysis):** $TiO_2 \xrightarrow{h\nu} e^- + h^+$; $h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$

- **O_3/H_2O_2:** $H_2O_2 \xleftrightarrow{H^+} HO^- + O_3 \rightarrow O_2 + HO_2^-$; $HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$; $HO_2^{\bullet} \Leftrightarrow H^+ + O_2^{\bullet -}$; $O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -}$; $O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet}$; $HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2$; $HO^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2$
- **O_3/ UV:** $O_3 \xrightarrow{h\nu} O^1(D) + O_2$; $O^1(D) + H_2O \longrightarrow H_2O_2$; $H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet}$
- **H_2O_2/UV:** $H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet}$

Figure 1. AOPs including those which can be driven by solar irradiation

Electrochemical oxidation over anodes made of graphite, Pt, TiO_2, IrO_2, PbO_2, several Ti-based alloys and, more recently, boron-doped diamond (BDD) electrodes in the presence of a suitable electrolyte has been employed for the decontamination of various organic-containing effluents, including pharmaceutical and endocrine disrupting compounds. Two mechanisms are responsible for organic matter electrochemical oxidation, namely: (a) direct anodic oxidation where the pollutants are adsorbed on the anode surface and destroyed by the anodic electron transfer reactions and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, ozone and hydrogen peroxide, among others[6].

The use of AOPs for wastewater treatment has been studied extensively, but generation of

UV radiation by lamps or ozone production is expensive. So, future applications of these processes could be improved through the use of catalysis and solar energy. Therefore, research is focusing more and more on those AOPs which can be driven by solar irradiation, photo-Fenton and heterogeneous catalysis with UV/TiO_2. Since 1990 there has been a clarification of the kind of solar technology, which should be involved, in solar AOPs[7]. For many of the solar detoxification system components, the equipment is identical to that used for other types of water treatment and construction materials are commercially available, being specific concerning the photoreactor. Photocatalytic reactors must transmit UV light efficiently because of the process requirements. Common materials that meet these requirements are fluoropolymers, acrylic polymers and several types of glass. Borosilicate glass has good transmissive properties in the solar range with a cut-off of about 285 nm. With regard to the solar reflecting/concentrating materials, aluminium is the best option due to its low cost and high reflectivity in the solar UV spectrum on earth surface. There is a category of low concentration collectors, called Compound Parabolic Concentrators (CPCs), which constitute a good option for solar photochemical applications. The light reflected by the CPC is distributed all around the tubular receiver so that almost the entire circumference of the receiver tube is illuminated. They can make highly efficient use of both direct and diffuse solar radiation, without solar tracking.

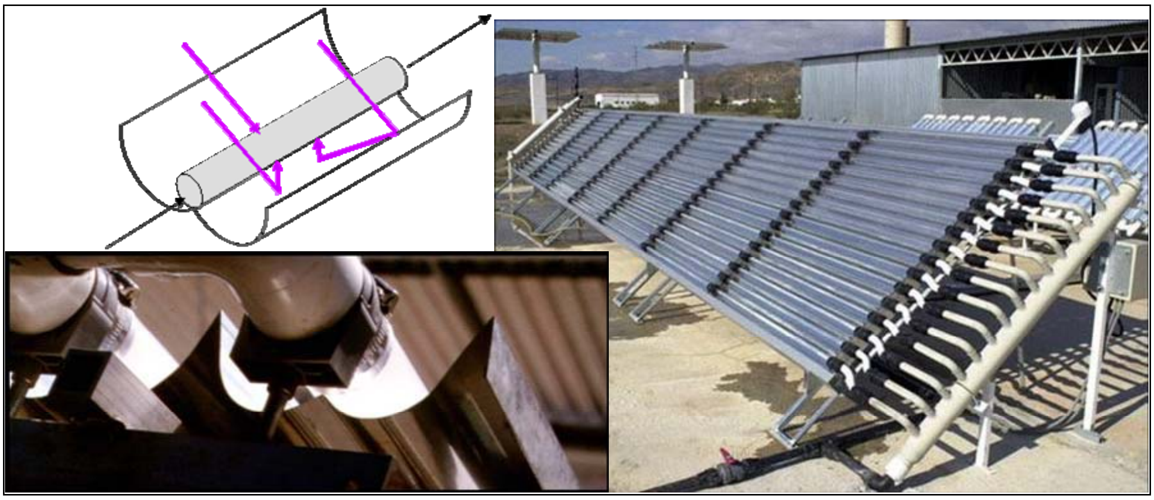

Figure 2. Details of a compound parabolic concentrator.

TOC (or COD) as a general parameter of wastewater treatment should always be known. Toxicity and biodegradability of wastewaters are very often related but not always. As a general rule one should test both parameters when dealing with real wastewaters. Knowledge of toxicity of the wastewater, as evaluated by a battery of different bioassays, should be necessary always. When the TOC, biodegradability and toxicity are determined, one should follow the subsequent decision path when applying AOPs:

1. If the wastewater is biodegradable a biological pre-treatment should be performed (unless legal discharge limits are already fulfilled, which is an unlikely case for industrial wastewater), because classical biological treatments are, at present, the cheapest and most environmentally compatible option. Then, after this biotreatment, the effluent quality has to be checked if further treatment is necessary or if the effluent can be safely disposed of in agreement with the legal discharge limits established.

2. If the wastewater is not biodegradable and TOC is high (>100mg/L) AOP pre-treatment before biotreatment should be envisaged. After the treatment the effluent quality has to be checked, to decide if it complies with legal requirements for effluent discharge.
3. If the wastewater is not biodegradable, TOC is low (<100 mg/L) but toxicity is high, one should design the appropriate AOP treatment for reducing the toxicity, but without a subsequent biotreatment, because such a low TOC would not produce pre-treated effluent (this means, with lower TOC) suitable for a biotreatment. Very often this wastewater could be disposed to the environment after the AOP treatment or, which is more convenient, to a public sewage treatment system for polishing it.
4. If the wastewater is not biodegradable, TOC is low (<100 mg/L), toxicity is low, but other physical-chemical legal requirements are not met, also an AOP treatment without subsequent biotreatment should be envisaged. After the AOP treatment the effluent quality has to be assessed before discharge.
5. If the wastewater is not biodegradable, TOC is low (<100 mg/L), toxicity is low and all legal requirements for discharge are met, the wastewater can be safely discharged.

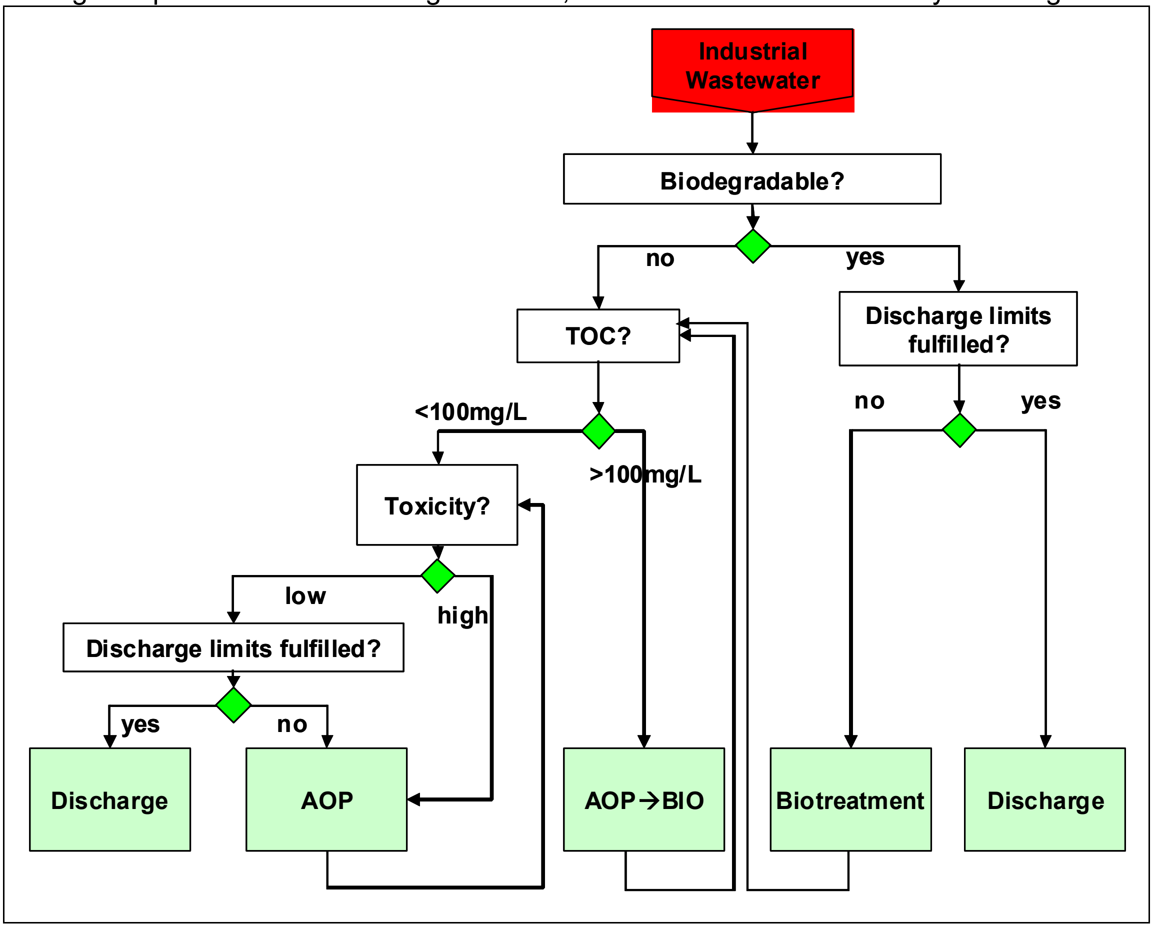

Figure 2. Decision scheme for selecting the appropriate treatment train when applying AOPs.

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EMERGING TECHNOLOGIES FOR URBAN AND INDUSTRIAL WASTEWATER TREATMENT

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1.- Technologies based on aerobic granular biomass

Biological wastewater treatment is often accomplished by means of conventional activated sludge systems. In general, activated sludge has relatively poor settling characteristics with values of sludge volumetric index (SVI) around 100-200 mL/g VSS and settling velocities lower than 1 m/h. The interest in applying aerobic granular systems is mainly related to the compactness of its design in comparison to conventional activated sludge wastewater treatment systems.

Experiments performed at laboratory scale indicated that, in aerobic granular reactors, organic matter removal efficiencies ranged between 80 and 98%, while nitrogen removal efficiencies were slightly lower (70 - 95%). The physical properties of the aerobic granular biomass showed values of SVI lower than 60 mL/g VSS, densities larger than 10 g VSS/L and mean feret diameter (D_{feret}) that ranged between 1.0 and 3.5 mm. These results obtained at laboratory scale showed the potential of the aerobic granular technology to treat wastewaters from industrial and municipal origin (Adav et al., 2008). However most of these previous studies for the cultivation of aerobic granules were based on the use of synthetic feeding while information associated with urban or industrial wastewater is more limited (Arrojo et al, 2004, Figueroa et al., 2009). In general a pre- or post-treatment is recommended to fulfil the disposal requirements when important suspended solids concentrations are present (de Bruin et al., 2004).

The first pilot research project using the aerobic granular technology was performed in The Netherlands using the Granular Sequencing Batch Reactor (GSBR) in the so called Nereda™ system in order to demonstrate the applicability of the aerobic granular sludge technology for the treatment of municipal wastewater (de Bruin et al., 2005). Two SBRs units with a height of 6 m and a diameter of 0.6 m were operated in parallel treating wastewater at a flow rate of 5.0 m^3/h. The formation of aerobic granules took few weeks, and exhibited a SVI of 55 mL/g VSS. The reactor was designed for the simultaneous organic matter, nitrogen and phosphorous removal. Successful start up in a pilot-scale sequencing batch reactor seeded with aerobic granules precultured in a small column reactor was achieved.

In spite of the recent intensive research carried out in the aerobic granulation field, there is still lack of information about some aspects which could limit the widespread use of aerobic granulation in wastewater treatment:

a) Most of the works were carried out at laboratory scale and only a few at pilot scale. Scale-up of granular systems leads to a modification of the hydrodynamic conditions which are very important in order to promote the formation and stability of aerobic granules and though further information is required in this particular issue.

b) Little information is available regarding the application of aerobic granular technology to the treatment of low-strength domestic wastewater which is expected to difficult or lengthen the granulation process. Thus, it is necessary to know the effects of the low COD loads on the integrity of the granular structures.

c) In industrial practice, a similar strategy than the used for the fast and easy start-up of UASB reactors would be carried out by seeding anaerobic granules directly into the reactor. This significantly would reduce the time required for start up.

d) The aerobic granular process has a great potential to be coupled to anaerobic processes, pre-treatment/reverse osmosis processes, and others for utilizing its advantage of high biomass retention and tolerance to toxic compounds.

2.-Advanced technologies based on Anammox processes

The removal of nitrogen from wastewater is generally carried out by the conventional processes of nitrification and denitrification. However these processes are not suitable to treat wastewater with a low COD/N ratio which requires addition of an external organic carbon source. Autotrophic nitrogen removal can be achieved by the combination of the partial nitrification to nitrite of half of the ammonium in the influent and a subsequent ANaerobic AMMonium OXidation (Anammox process) step. Both processes can be carried out in a two-units configuration (i.e., Sharon and Anammox) or in a single-unit configuration (this process has been given different names: CANON / OLAND / Deammonification). During partial nitrification, around 50% of the NH_4^+-N is oxidised to NO_2^--N by Ammonium Oxidizing Biomass (AOB). Subsequently, the Anammox process converts ammonium together with nitrite (electron acceptor) directly to N_2 in the absence of organic carbon source.

The combination of partial nitrification and Anammox to treat wastewaters with high nitrogen content and without organic matter gives some advantages compared to the conventional nitrification-denitrification process: 1) The oxygen requirements are 60% lower; 2) No organic matter must be added; and 3) Sludge production is only 15% compared to the conventional processes. This low sludge production reduces the management costs but makes the start-up of Anammox reactors quite long. For this reason, systems with high biomass retention capacity must be used.

Up to now these processes were applied to the return sludge line of municipal wastewater treatment plants (WWTPs). However, the actual configuration of WWTPs could even be changed, by the implementation of these processes, in order to achieve more compact and energetically efficient systems. Siegrist et al., (2008) reported that, with the application of partial nitrification/Anammox processes, WWTP are coming closer to energy autarky. With the introduction of separate digester liquid treatment the denitrification efficiency in the biological main treatment can be reduced without reduction of the overall nitrogen removal of the whole plant. This allows increasing the HRT of the primary clarifier to improve biogas production in the anaerobic digester and significantly reduce the aeration energy for BOD removal and nitrification.

Anammox based processes were successfully applied at full scale (Abma et al., 2007) but only applied to effluents with temperatures ranging between 30-40 ºC since this is the optimum range of temperature for Anammox bacteria. However, at laboratory scale, some works showed that Anammox processes could be successfully operated at temperatures around 20 ºC (Dosta et al., 2008). In fact, the CANON process was recently started up and operated at temperatures around 20 ºC removing ammonia loading rates up to 0.45 kg NH_4^+-

N/(m^3·d) (Vázquez-Padín et al., 2009a) which makes this process an interesting alternative to treat the effluents of the psycrophilic anaerobic digesters. Even higher nitrogen removal rates, up to 1.1 kg N/(m^3·d), were reached using a Granular SBR (Vázquez-Padín et al., 2009b) in order to obtain high sludge retention times to overcome the slow growth rate of Anammox bacteria.

Under a practical point of view, single-unit systems for partial nitrification-Anammox are preferred because they exhibit larger nitrogen removal rates (smaller reactors) and lower N_2O emissions than two-units systems although the latter are more flexible and stable to influent fluctuations (Kampschreur et al., 2008). The potential advantages of Anammox processes make them suitable to treat polluted ground water or to remove nitrogen compounds from aquaculture systems with recirculation.

3.-Hybrid biofilm suspended biomass Membrane Bioreactors

The use of small-suspended carriers or Integrated Fixed-film Activated Sludge (IFAS) is often used for increasing the capacity of conventional activated sludge (CAS) plants. The development of a biofilm onto the carrier increases the biomass concentration, the bioreactor capacity and the solid retention time of the biological system. These characteristics make feasible to apply higher organic and nitrogen loading rates (OLR and NLR, respectively) than in CAS. Hybrid suspended biomass-biofilm systems that relies in settlers for biomass separation have a main drawback, the settleability of the sludge decreases at high OLR (Ødegaard *et al*., 2000), which limits the loading rate that could be applied to hybrid systems.

The use of a support for promoting biofilm grow in Membrane Bioreactors (MBR) might be a good alternative for treating wastewater at high loading rate, and even an oportunity for reducing fouling in the membrane. Hybrid Biofilm-Suspended biomass MBRs were developed by the University of Santiago de Compostela (European patent EP 1484287 B1). Oyanedel *et al*. (2005) found that heterotrophs in this kind of reactors grew mainly in suspension as suspended heterotrophs have competitive advantage over fixed heterotrophs on COD. This favoured the development of biofilm with high nitrifying activity. Specific ammonia oxidation activity of the biofilm, was around 0.8 g N/g-protein·d (around 0.4 g N/g-VSS·d) and was not affected by the applied OLR. It is feasible to operate simultaneously at high ammonia loading rate (ALR) of 0.75 kg N/m^3·d, referred to the reactor volume, and organic loading rate (OLR) of 3.6-6.5 kg COD/m^3·d. Moreover, the obtained effluents presented a very good quality in terms of COD and suspended solids. This technology was tested in the laboratory and at pilot plant scale for treating industrial wastewaters from a tannery and a fish canning factory, with high nitrogen and organic matter content (Oyanedel *et al* 2003, Artiga *et al* , 2007, Artiga *et al.* 2005)

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EVALUATION OF OZONE WASTE WATER TREATMENTS AND STUDIES EVALUATING THE REUSE OF TREATED EFFLUENTS.

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Availability of water of good quality is a critical issue, since it represents an essential component for sustainable socio-economic development. Water quality damage, mainly a consequence of anthropogenic activities, and water deficit are cause of social concern and demand prompt actions. The aim of EC Water Framework Directive [1] is to achieve good ecological water status in terms of the presence of chemicals from human activity. In this connection, increasing water scarcity enhances wastewater reuse, which is specially geared to the large amount of effluents from Sewage Treatment Plants (STPs) that currently are discharged to surface bodies. According to the European Environment Agency, Spain is considered as a water-stressed country [2], and is the European country with the highest reuse potential, with a maximum of 2000 hm^3/year, a figure an order of magnitude above the current situation [3].

Among the reasons why wastewater reuse has not received appropriate attention up to date, the potential effects in human health and the environment trace contaminants, such as priority pollutants, pharmaceuticals and personal care products (PPCPs), etc., must be highlighted. It has been demonstrated by many studies [4] that these compounds escape conventional wastewater treatment, thus entering the environment via treatment effluent from STPs.

The presence of micropollutans, even in very low amounts, severely endangers the reuse of treated wastewater. Therefore, effective tertiary treatment technologies are needed in order to ensure that reclaimed wastewater is safely used. Available technologies for wastewater reclamation include from simple sand filtration until advanced oxidation processes and reverse osmosis.

Advanced Oxidation Processes (AOPs), involve the generation of hydroxyl radicals and other strong oxidant species that are able to degrade compounds characterized by high chemical stability or by strong difficulty towards complete mineralization [5]. These technologies involve different methods for the generation of hydroxyl radical. They include Fenton systems, ozonation, homogeneus ultraviolet irradiation, heterogeneous photocatalysis using semiconductors, radiolysis and a number of electric and electrochemical methods. The choice of the most suitable technology or combination lies on the quality required for the reclaimed water.

Ozonation is an attractive and a well established technology for wastewater reuse purposes [6,7,8]. We studied the ozonation of pharmaceuticals in wastewater from the secondary clarifier of urban and domestic STPs by using alkaline ozone and a combination of ozone and hydrogen peroxide. Alkaline ozonation achieved only a moderate degree of mineralization essentially concentrated during the first few minutes; but the addition of hydrogen peroxide eventually led to a complete mineralization [7]. **Table 1** shows the concentrations found in the effluent used for ozonation treatments. The concentration of individual pharmaceutical compounds ranged from 3 to 2100 ng/L and represented a total charge of 10 µg/L. The Table includes data from intermediate samples analyzed after different processing times in conditions of alkaline ozonation and with injection of hydrogen peroxide.

Table 1. Evolution of the concentration of pharmaceuticals compounds (ng/L) determined in a STP a function of processing time when treated with O_3/H_2O_2 and O_3/HO^-.

Compound	**O_3/H_2O_2**					**O_3/HO^-**				
Time (min)	**0**	**5**	**10**	**20**	**30**	**0**	**5**	**10**	**20**	**30**
4-Methylamino-antipyrine (4-MAA)	22	<5	<5	<5	<5	22	<5	<5	<5	<5
Antipyrine	20	<16	<16	<16	<16	21	<16	<16	<16	<16
Atenolol	849	8	<6	<6	<6	717	<6	<6	<6	<6
Bezafibrate	139	<8	<8	<8	<8	126	<8	<8	<8	<8
Carbamazepine	65	2	<1	<1	<1	61	2	<1	<1	<1
Carbamazepine epoxide	18	<18	<18	<18	<18	18	<18	<18	<18	<18
Ciprofloxacin	741	70	44	50	49	572	6	6	9	10
Codeine	329	<10	<10	<10	<10	351	<10	<10	<10	<10
Diazepan	3	<3	<3	<3	<3	3	<3	<3	<3	<3
Diclofenac	369	<1	<1	<1	<1	216	<1	<1	<1	<1
Erythromycin	126	<99	<99	<99	<99	120	<99	<99	<99	<99
Fluoxetine	54	15	3	<3	<3	135	<3	<3	<3	<3
Gemfibrozil	608	<0.1	<0.1	<0.1	<0.1	618	<0.1	<0.1	<0.1	<0.1
Hydrochlorothiazide	1300	15	<2	<2	<2	1470	<2	<2	<2	<2
Indomethacine	47	<4	<4	<4	<4	40	<4	<4	<4	<4
Ketoprofen	346	<105	<105	<105	<105	335	<105	<105	<105	<105
Ketorolac	40	<3	<3	<3	<3	42	<3	<3	<3	<3
Mefenamic acid	85	<3	<3	<3	<3	71	<3	<3	<3	<3
Mepivacaine	5	<2	<2	<2	<2	5	<2	<2	<2	<2
Metoprolol	18	<14	<14	<14	<14	16	<14	<14	<14	<14
Metronidazole	212	<17	<17	<17	<17	188	<17	<17	<17	<17
N-acetyl-4-amino-antipiryne (4-AAA)	2100	<100	<100	<100	<100	2065	<100	<100	<100	<100

Compound	O_3/H_2O_2					O_3/HO^-				
Time (min)	**0**	**5**	**10**	**20**	**30**	**0**	**5**	**10**	**20**	**30**
Naproxen	389	<24	<24	<24	<24	334	<24	<24	<24	<24
N-formyl-4-amino-antipiryne (4-FAA)	1096	<33	<33	<33	<33	1029	<33	<33	<33	<33
Ofloxacin	565	33	<33	<33	<33	464	<33	<33	<33	<33
Omeprazole	181	<6	<6	<6	<6	164	<6	<6	<6	<6
Propanolol hydrochloride	30	<4	<4	<4	<4	27	<4	<4	<4	<4
Ranitidine	297	<153	<153	<153	<153	224	<153	<153	<153	<153
Salbutamol	6	<4	<4	<4	<4	5	<4	<4	<4	<4
Sotalol	13	<12	<12	<12	<12	12	<12	<12	<12	<12
Sulfamethoxazole	150	<15	<15	<15	<15	117	<15	<15	<15	<15
Trimethoprim	69	<29	<29	<29	<29	59	<29	<29	<29	<29

The data showed that after 5 min, removal efficiencies were over >99% for most compounds irrespective of the use or not of hydrogen peroxide. Only fluoroquinolones and fluoxetine were relatively resistant to ozonation with removal in the 90–95% range. The total concentration of the analyzed pharmaceuticals after 10 min reached, for the most unfavourable conditions less than 0.5% of the initial load. The ozonation of pharmaceuticals is very rapid, both in the presence and in the absence of hydrogen peroxide, a result due to the very large second-order kinetic constants for the reaction of most pharmaceuticals with ozone. In the absence of hydrogen peroxide, a TOC decay of about 15% was obtained after 1 h, from which most part (∼ 80%) took place during the first five reaction minutes. On the other hand, by injecting pulses of hydrogen peroxide (0.15 mL of H_2O_2 30% w/v in a 5-L reactor every 5 min), the degree of mineralization reached an average over 90%.

We studied also the occurrence and removal of emerging contaminants, mainly pharmaceuticals, personal care products and some metabolites, by using different ozone doses [6]. **Table 2** shows the evolution of the concentration for samples taken during ozonation up to a reaction time of 15 min and the amount of ozone required for a given degree of removal. The last right column of Table 2 shows the dose of ozone required for the complete removal (no detection) of a given compound or to achieve certain removal efficiency in cases where ozonation was unable to get complete oxidation in less than 15 min corresponding to a dose of ozone of 0.34 mmol/L of wastewater.

Table 2. Removal of pollutants contained in wastewater during ozonation. The ozone doses are those required to reach concentrations below the limit of quantification (LOQ[a]) in treated samples.

Ozonation time (min)	LOQ[a]	0	2	4	6	10	15	Ozone doses for remotion	k_R (M^{-1} s^{-1})
3-(4-methylbenzylidene) camphor	39	55	50	65	39	72	54	Not removed	
4-aminoantipyrine	19	58	–	–	–	–	–	<50 μM	
4-methylaminoantipyrine (4-MAA)	2	389	–	–	–	–	–	<50 μM	
Antipyrine	8	30	16	–	–	–	–	<90 μM	
Atenolol	3	911	655	265	24	–	–	<220 μM	
Azithromycin	12	235	–	–	–	–	–	<50 μM	
Benzophenone-3	33	123	89	100	102	119	119	Not removed	
Bezafibrate	4	115	72	67	37	15	4	Still detected at 340 μM	3260 ± 780
Carbamazepine	1	106	17	2	–	–	–	<130 μM	
Carbamazepine epoxide	9	32	23	19	13	–	–	<220 μM	
Ciprofloxacin	5	522	334	28	–	–	–	<130 μM	
Citalopram hydrobromide	2	60	31	4	–	–	–	<130 μM	
Clarithromycin	5	39	–	–	–	–	–	<50 μM	
Codeine	5	378	–	–	–	–	–	<50 μM	
Cotinine	12	100	61	54	48	38	28	28% remained for 340 μM	680 ± 29
Diclofenac	1	433	–	–	–	–	–	<50 μM	
Diuron	1	100	60	46	25	6	1	Still detected at 340 μM	3890 ± 200
Erythromycin	10	72	16	–	–	–	–	<90 μM	
Ethylkexyl methoxycinnamate	15	234	274	322	231	214	204	Not removed	
Famotidine	14	1045	–	–	–	–	–	<50 μM	
Fluoxethine	2	17	–	–	–	–	–	<50 μM	
Furosemide	82	840	–	–	–	–	–	<50 μM	
Galaxolide	23	1486	749	552	178	196	173	83% for 340 μM	
Gemfibrozil	1	332	50	18	19	15	15	95% for 340 μM	
Hydrochlorothiazide	1	707	461	199	–	–	–	<130 μM	

Ozonation time (min)	LOQ[a]	0	2	4	6	10	15	Ozone doses for remotion	k_R (M^{-1} s^{-1})
Indomethacine	2	37	–	–	–	–	–	<50 μM	
Ketoprofen	2	162	156	102	68	18	3	Still detected at 340 μM	3040 ± 770
Ketorolac	2	533	165	–	–	–	–	<90 μM	
Lansoprazole	9	337	162	84	32	–	–	<220 μM	
Lincomycin	3	12	–	–	–	–	–	<50 μM	
Loratadine	1	29	18	7	2	–	–	<220 μM	
Mefenamic acid	2	59	–	–	–	–	–	<50 μM	
Metoprolol	3	27	17	5	–	–	–	<130 μM	
Metronidazole	3	113	73	85	56	14	3	Still detected at 340 μM	3100 ± 780
Musk xylene	3	89	92	95	89	98	91	Not removed	
Musk ketone	36	123	125	140	95	105	76	38% for 340 μM	
N-acetyl-4-aminoantipyrine (4-AAA)	50	8605	2419	101	–	–	–	<130 μM	
Naproxen	12	109	–	–	–	–	–	<50 μM	
N-formyl-4-aminoanttipyrine (4-FAA)	17	1776	471	21	–	–	–	<130 μM	
Nicotine	4	81	12	10	13	10	14	Still detected at 340 μM	
Norfloxacin	8	38	56	–	–	–	–	<90 μM	
Octocrylene	16	114	115	113	81	95	91	20% for 340 μM	
Ofloxacin	3	3594	276	18	11	9	10	Still detected at 340 μM	
Omeprazole	3	1015	231	7	–	–	–	<130 μM	
Primidone	5	80	86	65	40	–	–	<220 μM	
Propanolol	2	32	7	–	–	–	–	<50 μM	
Propyphenazone	2	23	–	–	–	–	–	<90 μM	
Ranitidine	2	111	3	–	–	–	–	<90 μM	
Sulfamethoxazole	8	95	39	19	15	–	–	<220 μM	
Sulfapyridine	12	50	–	–	–	–	–	<50 μM	

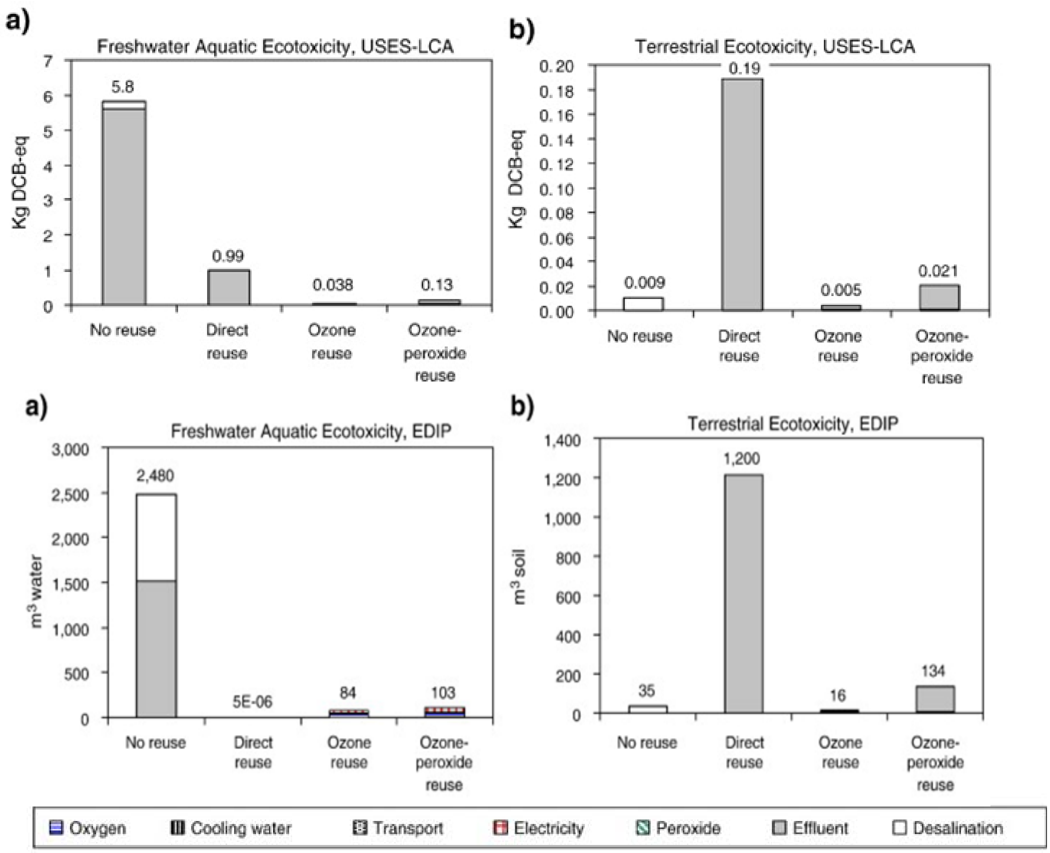
Ozonation time (min)	LOQ[a]	0	2	4	6	10	15	Ozone doses for remotion	k_R (M^{-1} s^{-1})
Tonalide	19	188	131	130	53	67	53	72% for 340 µM	
Triclosan	52	246	55	72	79	70	53	Still detected at 340 µM	
Trimethoprim	2	73	7	–	–	–	–	<90 µM	
Venlafaxine	6	179	127	21	–	–	–	<130 µM	

A group of 15 compounds rapidly disappear during the first 120 s on stream, with ozone doses <50 µM. These include codeine, diclofenac, indomethacin or naproxen. Antipyrine, erythromycin, ketorolac, norfloxacin, propanolol, ranitidine, and trimethoprim became completely removed for doses <90 µM. Carbamazepine, ciprofloxacin, citalopram hydrobromide, hydrochlorothiazide, metoprolol, omeprazole, venlafaxine and the two metabolites of metamizol, (4-AAA and 4-FAA), required <130 µM of ozone to disappear. Higher ozone doses area necessary to remove atenolol, lansoprazole, loratadine, primidone, sulfamethoxazole and diuron. Another group of four personal care products were completely refractory to ozone, not being removed at all after 15 min of reaction. These were the UV filters 3-(4-methylbenzylidene) camphor and ethylkexyl methoxycinnamate together with the sunscreen agent benzophenone-3 and the aromatic nitro musk xylene. Finally, certain compounds were removed in different extents using an ozone dose of 340 µM. From ketoprofen, metronidazole or ofloxacin, with removal efficiencies over 95% to the musk ketone and the UV filter octocrylene, with 38% and 20% removal respectively. It is interesting to point out than some compounds like diclofenac, indomethacin or the beta-blockers atenolol, metoprolol and propanolol, which are poorly removed in the activated sludge conventional treatment, exhibit large ozonation rates that allow their removal from wastewater using moderate ozone doses.

As an important part of this application, the development of a suitable analytical methodology is required; this allows an exhaustive chemical characterization of wastewater effluents and the evaluation of wastewater treatment processes. For this purpose, accurate and sensitive analytical instruments, based on Mass Spectrometry (MS) coupled to Chromatography (GC and LC), have to be used, which are capable of monitoring contaminant and its transformation product at trace level. Furthermore, the development of multiresidue methods, useful for the determination of a broad group of compounds of different physical-chemical characteristic, is required [8,9] – so as to obtain a correct chemical evaluation of the effluents as well as the characterization of “tracers” of the whole process. Afterwards it is relevant to characterize the endpoints of the treatments in a cost-effective way.

We assess the life-cycle environmental impact of urban wastewater reuse for agricultural purposes, putting special emphasis on the potential toxicity of priority and emerging pollutants present in the effluents to be reused [10]. The tertiary treatments assessed are ozonation and ozonation in combination with hydrogen peroxide, whereas desalination is chosen as the reference technology for water supply in a no-reuse scenario. **Figure 1** shows the life-cycle impact scores obtained for each scenario with the multimedia fate, exposure and effects model USES-LCA and EDIP97. From a freshwater ecotoxicity point of view (Fig. 1a), the worst scenario is not reusing wastewater, since all the pollutants in the WWTP effluent end up in the aquatic environment. If wastewater is instead reused, the impact is up to 2 orders of magnitude lower, due to the fact that the aquatic ecosystem no longer receives this pollution load, which is transferred to agricultural soil, and only a fraction of the initial pollution reaches freshwater through soil runoff, percolation, etc. The lowest impact on aquatic ecotoxicity corresponds to reusing wastewater after ozone treatment. With regard to terrestrial ecotoxicity (Fig. 1b), direct reuse is the worst option, since all the pollutants in the WWTP effluent are being emitted to soil. On the other hand, no direct pollution is being emitted to soil in the no-reuse scenario, as here water for irrigation comes from desalination, in which chemical pollutants have been assumed to be absent. The environmental impact of ozone-peroxide is higher than that of not reusing, but in the same order of magnitude, whereas the lowest impact is attributed to reuse after ozonation.

Fig. 1. Life Cycle Impact Assessment results per functional unit for toxicity-related impact categories, modelled with USES-LCA and EDIP97 models



In conclusion, results obtained suggest that scenarios involving wastewater reuse after tertiary treatment appear as preferable options from an integrated aquatic and terrestrial ecotoxicity perspective, since the no-reuse scenario involves a very high impact in aquatic ecotoxicity, whereas direct reuse performs similarly from a terrestrial ecotoxicity perspective. When tertiary treatments are compared to each other, it is observed that ozonation obtains lower toxicity scores than ozone-peroxide, although differences are small and at the same time uncertainty is high.

ADVANCED MEMBRANE WASTEWATER TREATMENT PALESTINIAN – JORDANIAN – ISRAELI PROJECT

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Introduction

Sustainable agricultural production is conditioned by irrigation with good quality water. However, agriculture is rapidly losing its share of such water. Recycling wastewater for irrigation is an important means of replacing the lost water and presents an environmentally acceptable way for its disposal.

Wastewater is currently used in the Middle East for irrigation. In the best scenario, secondary-treated effluent is used; in the worst, crops are irrigated with raw sewage.

Secondary treatment reduces levels of organic matter and biological activity in the effluent, but leaves some pathogens, toxic elements, and, most important, salts. The use of this effluent poses environmental and health risks, and in the more or less long range, it raises soil salinity and alkalinity to a detrimental level. Therefore, in order to ensure sustainability, implementing tertiary and quaternary effluent treatment is imperative.

The research group gained knowledge and experience in a completed project, supported by the USAID – MERC program, in operating membrane pilot plants for tertiary and quaternary treatment of secondary-treated effluent. The research project presented goes one step further by designing and operating an integrative wastewater treatment system yielding 6-8 m^3/hour of high quality water suitable for unrestricted irrigation of crops. Process engineering methods for minimizing membrane fouling and scaling and for reducing energy requirements are studied. Specifically, the performance of configurations of ultra filtration membranes is evaluated, and attention is paid to the removal of viruses, pharmaceuticals and endocrine disruptors.

Results of the current project, supported by the Peres Center for Peace and the USAID – MERC program, will provide guidelines for large-scale, economically feasible operation of wastewater treatment systems, and thus add a substantial amount of high quality water to regional resources. It is estimated that the process, if applied in the Jordanian – Palestinian – Israeli area, may yield 400-600 million cubic meters of water for unrestricted irrigation. An adequate supply of water to the entire region is a very significant component of creating and maintaining peace.

First Stage: Completed Part of the Project

Major conclusions from the first stage of our cooperative project:

Ultra filtration (UF) spiral-wound (SW) membranes tend to absorb organic substances inside the walls and form a cake layer causing fouling, which reduces the permeate flow rate. Cleaning procedures, backwash and flushing with acidic and alkaline solutions restored the flow rate, but not permanently. In one of the pilot plants, fouling caused almost complete clogging of the system using UF-SW membranes.

Precipitates and microorganisms block available pore space, resulting in reduced trans-membrane flux (1, 3). Membrane fouling can be reversed by backwashing and/or chemical cleaning, but it may also be irreversible, leaving permanent damage on the membrane (2, 4).

The cleaning of reverse osmosis (RO) membranes, which is rarely required, completely restored their performance.

Chemical cleaning using an anti-scaling solution for RO membranes and an anti-oxidant solution for UF membranes improved performance for several months.

Preliminary comparisons indicated that due to easier cleaning procedures, UF hollow-fiber (HF) membranes may have advantages over the UF-SW ones, and there may be an advantage to combining both kinds of UF membranes.

Chemical and biological analyses of permeates indicated that the UF membrane efficiently removes organic matter and microorganisms, but not salinity. The RO permeate is almost entirely free of ions. As an example, data from the BGU site are presented in Table 1. Heavy metals are removed adequately.

Table 1: Effluent analysis at three stages of treatment at the BGU Arad site.

Treatment Stage	BOD mg O_2/l	COD mg O_2/l	pH	Fecal Coliforms CFU/100ml	EC dS/m	N-NH_4 mg/l	PO_4 mg/l
Secondary effl.	105	640	7.8	7.2×10^5	1.81	41.9	25.8
UF permeate	2.0	106	7.7	4	1.78	52.1	7.8
RO permeate	0.1	1.4	6.2	0	0.11	3.0	0.8

In field experiments over several seasons, where an adequate amount of plant nutrients was applied, significant correlation was found between salt accumulation in the soil profile due to irrigation with effluents drawn from several stages of treatment and reduced crop yield. An example is given in Table 2.

Table 2: Crop yields, t/ha (a,b,c - LSD 5%) and EC (ds/m) at the BGU Arad site, irrigated with effluents from a stabilization pond (SP) and mixtures of UF and RO permeates.

Irrigation Water	Watermelon	Garlic	EC		
			Surface	30 cm	60 cm
SP	28 a	24 a	1.2	1.3	1.3
UF	36 ab	30 b	1.2	1.2	1.2
UF 70 + RO 30	34 ab	30 b	1.1	1.1	1.2
UF 30 + RO 70	44 bc	32 bc	1.1	0.9	1.0
RO	50 c	37 c	1.1	0.8	0.9

Correlation coefficients: garlic yield vs. EC at 30 cm; r = -0.92; melon yield vs. EC at 30 cm, r = -0.96; garlic yield vs. EC at 60 cm, r = -0.93; melon yield vs. EC at 60 cm, r = -0.99.

Reduced yield clearly correlates with increased soil salinity induced by irrigation water quality resulting from effluent treatment.

The NCARE team decided to use the treated wastewater in greenhouse flower production. Flowers grown in greenhouses, mainly for export, are a relatively high value crop and irrigation water is a minor input of the overall operational costs. Irrigation experiments were performed on roses, lilies, gladiolas and matthiolas. Measurements of plant development, yield and quality revealed the beneficial effect of membrane-treated effluents.

Furthermore, membrane treated water improved irrigation dripper performance.

The cost of membrane treatment was estimated by the BGU team to be $US 0.30-0.40 per 1 m^3 of clean effluent. This is based on their pilot system measurements and an energy cost of $US 0.06 per kW/h. In larger commercial systems, reduced costs may be expected.

Estimates calculated by the AQU and NCARE teams indicate a cost of about three times higher than the above. The calculations are based on performance of the pilot plants, which, during the study stages, suffered from fouling, expensive cleaning processes and membrane replacements.

Furthermore, AQU researchers indicate that introducing UF-HF membranes would reduce energy costs significantly and prevent irreversible UF-SW membrane fouling.

Second Stage: Current Part of the Project

Membrane Plant Construction and Operation, GWRI
Executed by Prof. Raphael Semiat, Prof. Carlos Dosoretz and Ing. Ilan Katz

Following an extensive literature review, computer modeling, and based on previous experience, a detailed design for the construction of the membrane plant, larger than a pilot plant, was prepared. The membrane plant was constructed in the Wolfson Faculty of Chemical Engineering at the Technion, and is in operation at the Carmel District Council secondary wastewater treatment site.

The membrane units, pumps and remote monitoring are installed in a closed container. Storage tanks are located outside the container.

The membranes installed are UF-HF Hydranautics, HYDRAcap60 and a two-stage RO Toray TML. A 20 micron filter, automatic disk pre-filter; means for reducing organic fouling and inorganic scaling are included.

A control unit monitors pump operation, backwash cycle, tank filling, pressure, temperature, flow rate and electrical power consumption. A data logging unit and remote (cellular) connection enable control and monitoring in real time.

A high water recovery ratio is expected.

Performance of UF and RO units is monitored continuously: water recovery, RO concentrate precipitation, process stability, membrane hydraulics, flow, pressure, temperature, membrane rejection of TOC, TN, COD, turbidity, EC, pH, alkalinity, PO_4, SO_3, Ca, Mg, Na.

The residual brine is currently being returned to the secondary wastewater treatment pond. Several alternatives are available for its disposal. The brine may be collected in solar ponds for water evaporation and salt accumulation. Treatment processes for thickening, stabilization and dewatering that lead to environmentally friendly disposal are available.

Membrane Plant Construction, NCARE, Jordan
Executed by Dr. Ahmad Bulad and Dr. Luna Al Hadidi

The new membrane system will be installed at the Al-Ramtha NCARE research station near the wastewater treatment plant.

The secondary wastewater treatment plant, having a capacity of 3,000 m^3/day, employs the activated sludge-extended aeration method. The treated effluent is currently being used for irrigation. The salinity level of the effluent is approximately 2 dS/m. Average concentrations of E.coli, COD and BOD_5 are about 70 MPN/100ml, 77mg/l and 12 mg/l, respectively.

The new membrane plant is currently under construction. Its design is very similar to the one operated by GWRI.

Pilot Membrane Plant –Virus Removal, BGU
Executed by Mr. Oren Blonder, Prof. Gideon Oron and Dr. Yossi Manor (Sheba Medical Center)

A mobile membrane system containing UF-HF and RO modules, with a capacity of about 1.5 m^3/h pre-filtered through a disk filter with equivalent openings of around 100 mesh, was constructed. A control system for on-line monitoring of operating parameters, such as EC, trans-membrane pressure, flow rates, temperature, etc., was installed.

Removal of pathogens and viruses by the system was tested. The feed water had a concentration of 3×10^5 of fecal coliforms and 4×10^4 of entero cocci, which was reduced to zero in the final permeate.

Removal of viruses was tested by injecting one-liter doses of vaccine-strain polio virus into the feed water. These represent enteral viruses, which are among the most resistant to environmental conditions, and their average size of 23-27 nm is the smallest in the world of viruses. The UF-HF membrane removed the viruses at a level of five logs.

Membrane Technology for the Removal of Pharmaceuticals, AQU
Executed by Prof. Mustafa Khamis, Prof. Rafik Karaman and Prof. Omar Deeb

This part of the research aims at testing the efficiency of membrane plants in removing pharmaceuticals from wastewater. A detailed report is given in another presentation.

Membrane Technology for the Removal of Pharmaceuticals, GWRI
Executed by Ms. Shirra Gur-Reznik and Prof. Carlos Dosoretz

In view of the importance of removing pharmaceuticals and similar compounds from effluents, the work is performed in parallel at GWRI and AQU. Model compounds were used to test their rejection by membranes. Iodinated contrast media (ICM) spiked (1 mg/l) into tertiary effluents served as the main model compounds. Diatrizoate (DTZ), an ionic ICM was mostly used ($C_{11}H_9I_3N_2O_4$). In some cases, the anti-epileptic drug carbamazapine (CBZ) was used ($C_{15}H_{12}N_2O$). Both materials are usually found in secondary effluents: CBZ has a relatively low molecular weight (MW=236 Da) and low hydrophobicity (pK_{ow}=2.45); DTZ has a relatively high molecular weight (MW=614 Da) and intermediate hydrophobicity (pK_{ow}=3.51). Soluble organic matter was determined. Control experiments were carried out. The materials were tested on a background of tap water or distilled water and effluent with the addition of each of the model substances.

In the course of 24 hours, a practically complete rejection of DTZ occurred compared to an average organic carbon rejection of approximately 70%.

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EFFICIENCY OF THE MEMBRANE TECHNOLOGY IN TERMS OF PHARMACEUTICAL REMOVAL FROM WASTEWATER†

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Pharmaceuticals are a diverse group of chemicals that are designed to interfere with biological systems and have an important role in diagnosis, treatment, prevention the disease, health conditions, or functions of the human body (1). Pharmaceuticals are produced and used in increasingly large volumes every year (2). Personal care products (PCP) are defined as chemicals marketed for direct use by the consumer and having intended end uses primarily on the human body (1). They include cosmetics, bath additives, shampoo, skin care products, oral hygiene products, hair sprays, sun screens, hair dyes, deodorants, perfumes, soaps, fragrances, veterinary drugs, insect repellents and lotions. The expectations of the amounts of these products will continue to increase due to the increase in the standards of living as reflected by the improvement in the health care system and longer life expectancy.

The term endocrine disrupters (ED) refer, in general, to the synthetic chemicals and natural compounds that may affect the endocrine system that control the body's internal functions such as epinephrine and acetylcholine hormones that control sympathetic and parasympathetic nervous system, respectively. Both of these hormones affect heart rate, blood pressure. Many of these disrupters cause negative reproductive and developmental health effects for the human or animals and its offspring (3).

Although pharmaceuticals and endocrine disrupters have been detected in a wide variety of environmental samples including wastewater effluents, rivers, lakes, surface waters, groundwater and drinking water for decades, researchers have only recently begun to quantify their levels in the environment (4). With the development of new analytical technologies that result in the detection of minute traces of pharmaceuticals and other organic chemicals in the environment. These analytical methods become sufficiently sensitive to identify and quantify their presence in wastewater treatment plant (WWTP) effluents surface waters, drinking water, ground water. Pharmaceuticals and pharmaceuticals care products (PPCPs) are present in trace concentrations, generally in the range of mg/l to ng/l levels (5).

Pharmaceuticals undergo a number of enzymatic transformations (metabolism) in human tissues including liver, intestine, kidney, and lungs. The main part of metabolism occurs in liver (6). They are excreted, as a parent compound or an active metabolite in urine and feaces and reach WWTPs where they do not undergo further degradation to a satisfactory degree, so WWTPs play a key role in the introduction of pharmaceuticals into the environment.

Currently, intensive research is underway to investigate the effect of human and animal's medications on the environments. Daughton and Ternes (1) in their study concluded that the most frequently PPCPs found in environmental sample are acetaminophen, acetylsalicylic acid, betaxol, bezafibrate, biphenylol, bisoprolol, carazolol, carbamazepine and chlorophene. Studies on tertiary wastewater treatment plant effluents and nearby wells and creeks in the Sequim- Dungeness area of northwest Washington detected 16 compounds in wastewater samples. These compounds are acetaminophen, caffeine, carbamazebine, cimetidine, codeine, cotinine (is a metabolite of nicotine), diltiazem, hydrocodone, ketoprofen, metformin, nicotine, paraxanthine, salbutamol, sulfamethoxazole, trimethoprim and estrone. The concentration of these compounds was found to vary between 0.26 ng/l (estrone) to 200 ug/l (paraxanthine) (5).

Our study aims: (i) to identify the most popular drugs prescribed in Palestine and preparing a ranking list of these drugs. (ii) to test the performance of the membrane plants towards the removal of these drugs from synthetic wastewater.

In the first stage of this study we have evaluated the most popular drugs and household chemicals in Palestine by executing two different statistical methods: (a) preparing questioners together with visits and interviews of pharmaceutical companies, physicians, pharmacists and patients and (b) conducting a search on 5000 members of Kupat Holeem Klalit. The results of this study are summarized in Table 1.

Table 1: List of the top 20 most consumed pharmaceuticals in the West Bank area.

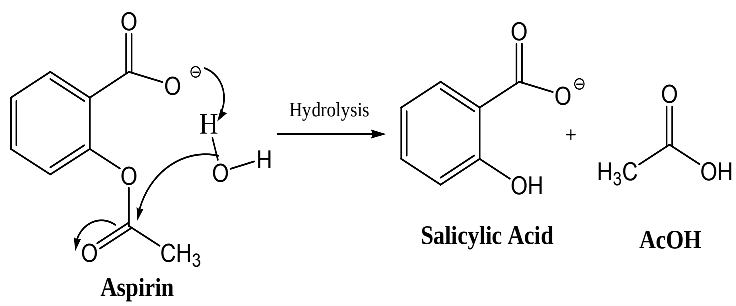
Drugs name Brand Name (Generic Name)	Uses
Vitacal+ D (Calcium + vit D) Cap	Calcium Deficiency
Disothiazide (Hydrochlorthiazide) Tab	Diuretic (hypertension)
Metformin (Metformin)Tab	(Diabetes)
Augmentin (Amoxycillin + Clav. acid)	Anti-bacterial
Zinnat (Cefixime) Tab	Anti-bacterial
Micropirin (Acetylsalicylic Acid) Tab	Anti-coagulant
Moxypen (Amoxycillin) Syr	Anti-bacterial
Fusid (Furosemide) Tab	Diuretic (hypertension)
Tribemin (Vit B1, B2, B6) Tab	Vit B Deficiency
Acamol (paracetamol) Tab	Anti-pyretic Pain killer
Ibufen (Ibuprofen) Tab	Anti-inflammatory
Ceforal (Cephalexin) Cap	Anti-bacterial
Normiten (Atenolol) Tab	Anti-hypertension
Omepradex(Omeprazole) Cap	Stomach ulcer
Simvastatin (Simvastatin) Tab	Lowering Cholesterol
Glibitic (Glipizide) Tab	(Diabetes)
Optalgin (Dyperone) Tab	Anti-pyretic Pain killer
Enalpril (Enalprilate) Tab	Anti-hypertension
Bezafibrate	Lowering Triglycerides
Amlodipine (Amlodipine) Tab	Anti-hypertension

Among the top twenty medicines that have been found to be frequently used in the West Bank and Jerusalem is the well know pain killer agent, aspirin. In addition to its uses as antipyretic and pain killer, aspirin (acetylsalicylic acid) is used once daily in low doses, 75 mg and 100 mg, as prophylactic medicine for the prevention of blood aggregation. The latter (blood aggregation) is the most common cause for heart attack among people over the age of

35.

As the first stage in testing the capability and the effectiveness of the membrane plants, kinetic experiments on aspirin have been carried out at various pH ranges. The kinetic results at room temperature reveal that aspirin undergoes hydrolysis to salicylic and acetic acids *via* a general base catalyzed process and the rate of the hydrolysis is first order and pH-independent. Chart 1 illustrates the mechanistic pathway and the kinetic behavior of aspirin, respectively. The kinetic studies suggest that the reaction rate in the presence and in the absence of sludge is similar with a value of $1.5 \times 10^{-4}\ s^{-1}$. It is worth noting that these results are in accordance with those obtained by Kirby and coworkers.
Simple mathematical calculations reveal that within 7 days most of the aspirin is hydrolyzed to salicylic acid.

Chart 1. **Mechanistic Pathway of the General Base Catalyzed Hydrolysis of Aspirin**



Since aspirin is not a stable chemical entity and undergoes a fast hydrolysis, our goal was to find a suitable method for removing the aspirin hydrolyzed products, salicylic and acetic acids. It is known that acetic acid has a low boiling point and it is expected that within a short time of its formation it will be evaporated. On the other hand, the solid un-volatile salicylic acid has to be removed by one of the well know filtration methods.

Studies are now underway to find the best method for the removal of salicylic acid.

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TREATMENT AND TREATABILITY OF HOSPITAL WASTEWATER. MANAGEMENT OF THE EFFLUENT OF A LARGE HOSPITAL SITUATED IN A SMALL TOWN - A CASE STUDY

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In the last years, increasing attention has been paid to the presence of *emerging pollutants* in wastewaters, surface waters and groundwaters (Daughton and Ternes, 1999; Heberer 2002, Barcelò 2003, Daughton 2004). Emerging contaminants correspond in most cases to unregulated pollutants, which may be candidate for future regulation depending on research on their potential health effects and monitoring data regarding their occurrence. They include surfactants, pharmaceuticals and personal care products (PPCPs), endocrine disruptors, illicit drugs, gasoline additive....

Referring to pharmaceuticals, large amounts of different compounds are used worldwide and, in the last decade, their sales are continuously increasing (Kummerer, 2001; Ternes and Joss, 2006). After administration, the active substances of medicaments are metabolized, but only to some extent. The unmetabolized active substances are excreted in urine and faecis as unchanged substances, as a mixture of metabolites or conjugated with an inactivating compound attached to the molecule (Halling-Sorensen et al., 1998), thus entering in the water cycle.

Hospitals are important sources for these compounds, but not unique. Residues of pharmaceuticals can be found in all wastewater treatment plant (WWTP) effluents, due to their inefficient removal in the conventional systems (Kummerer, 2001, Petrovic et al., 2003; Carballa et al., 2004, Onesios et al., 2009). A great variety of microcontaminants are present in hospital effluents resulting from diagnosis, laboratory and research activities from one side and medicine excretion by patients from the other side. They include active principles of drugs and their metabolites, chemicals, heavy metals, disinfectants and sterilizants, specific detergents for endoscopes and other instruments, radioactive markers, iodinated constrast media. Despite their specific nature, quite often, hospital effluents are considered of the same pollutant load of urban wastewaters (UWWs), so they are discharged into the sewer network, collected to a WWTP and cotreated with UWWs. Before immission into the municipal sewer, a chlorination is sometimes required for the whole hospital wastewater (HWWs) flow rate, sometimes only for the effluent from infectious disease wards (Emmanuel et al., 2003).

The common practice of cotreatment of hospital and urban wastewaters at a municipal WWTP is not considerated an adequate solution by many Authors (among them Altin et al, 2003, Pauwels et al., 2006, Vieno et al., 2007) because it is based on dilution of different discharges and it does not provide a segregation/separation of pollutants, in particular of emerging contaminants and toxic substances from the liquid phase which than is discharged into the environment.

The difficulties in removing micropollutants, in particular pharmaceuticals, from wastewaters are due to the fact that their concentrations are in the range 10^{-3}-10^{-6} mg L^{-1}, lesser than those of conventional macropollutants (BOD_5, COD, nitrogen and phosphorus compounds...). Moreover, they include a broad spectrum of compounds with great differences in the main properties which affect their behaviour and fate in the WWTP: solubility, volatility, adsorbibility, absorbibility, biodegradability, polarity and stability.

Municipal WWTPs were first built, then upgraded, with the principal aim of removing carbon, nitrogen and phosphorus compounds, as well as microbiological organisms: pollutants which regularly arrive at the WWTP in concentrations of the order of mg/L and at least 10^6 MPN/100 mL. Conventional treatments are not able to greatly remove also microcontaminants.

Moreover, HWW flow rates generally amount to only a small percentage of the total influent flow rate for co-treatment at a municipal WWTP. Consequently, dilution of HWWs with UWws will result in a decrement of the PhCs content in the final effluent (from $\mu g\ L^{-1}$ to $ng\ L^{-1}$), but not in their load, that is, the quantity released daily into the receiving water body. In this paper, a comparison between quali-quantitative characteristics of hospital and urban wastewaters is carried out, based on an in-depth literature review.

First water consumptions and wastewater production variation along the year are discussed for hospitals and urban settlements. Then chemical and physical characteristics of HWWs and UWWs are analized in terms of conventional macropollutants (BOD_5, COD, SS, nitrogen and phosphorus compounds, *E. coli*,...) as well as micropollutants (main pharmaceuticals, detergents, disinfectants).

An overview of the sustainable treatment options for HWWs is presented and finally the main outlines of a study carried out on the characteristics and adequate treatments of HWWs are reported. In particular the management of the effluent in a specific case study at the large hospital complex (900 beds), near Ferrara, Northern Italy, is examined through an evaluation and comparison of the design alternatives for its treatment and the main outlines of the final approved project are presented.

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ADVANCED REGENERATION PROCESSES FOR INDUSTRIAL WATER REUSE

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Mediterranean countries face water supply challenges due to water scarcity. Water reclamation, recycling and reuse address these challenges by resolving water resource issues and creating new sources of high-quality water supplies. Among others, industrial activities worldwide account for about a quarter of all water consumption and there is hardly any industry that does not use large amounts of water. Water standards related to industrial activities may vary in large range of parameters and limit values. In this context the future potential for regenerated treated water is enormous. This work reflects the big potential of advanced technologies to produce regenerated water offering specific solutions to industrial reuse needs.

Reuse of regenerated water in industrial activities

Industry accounts for about a quarter of all water consumption and there is hardly any industry that does not use large amounts of water. Much of the water used in industry is taken for public water supplies and has therefore been treated to potable standards. This means that it is often of better quality with respect to microbiological levels but still needs further treatment to reduce the mineral and organic contents according to the different specifications of use (Judd and Jefferson; 2005).

This high water consumption demands the use of new water sources apart from the natural and potable ones. The implementation of water-reuse concepts is becoming an important operational and environmental issue in the industrial sector (Hoinkis and Panten, 2008). Industrial use of water encompasses quantity and quality requirements that range from the use of large volume of low-quality water for cleaning applications to the use of high quality process water for manufacturing or boiler feed water, e.g. utility power plants are ideal facilities for reuse due to their large water requirements for cooling, ash sluicing, red-waste dilution, etc. Petroleum refineries, chemical plants and metal working facilities are among other industrial facilities benefiting form regenerated water not only for cooling, but for process needs as well, e.g. the viability of utilizing regenerated water in the electronics industry which requires water of almost ultrapure quality for washing circuit boards and other electronic components has been demonstrated (Gagliardo et al, 2002). On the other hand, the tanning industry can use relatively low-quality water. Requirements for textiles, pulp and paper and metal manufacturing are intermediate, e.g. the textile industry, of great importance in the Mediterranean region, uses 60-100 m^3/ton finished textile according to Li Rosi et al, (2007). Thus, the study of feasibility of industrial reuse of regenerated water must include an early stage on the definition of the needs of the potential users in order to determine the specific requirements for their specific duties to which the water is to be put

Reuse of secondary treatment wastewaters

One third of the water reclamation schemes rely on secondary treatment of municipal sewage. Municipal wastewaters are commonly treated by activated sludge systems that use suspended microorganisms to remove organics and nutrients, and large sedimentation tanks to separate the solid and liquid fractions. This level of treatment, fully revised in open literature (Metcalf and Eddy, 2003, Degremont, 2007), produces wastewater effluent that usually fulfils the requirement of cooling water in the industry, or irrigation water where the food crops are consumed after cooking (Russell, 2006). The conventional activated sludge technology is being substituted by the so called Membrane Bioreactors (MBRs), based on the combination of a suspended biomass reactor and separation step on porous membrane filtration. MBRs can produce high-quality effluent that is suitable for unrestricted irrigation and other industrial applications (Shannon et al., 2008). A MBR can also operate successfully where there are significant seasonal variations in load, for example tourist resorts- and can also be used to relieve overloading of existing sewage works (Hunter, 2007). Concerning countries with limited water resources, MBR technology Market is increasing considerably (Halalsheh, 2008, Cazurra, 2008).

Reuse of regenerated waters

More often, some kind of tertiary treatment is required to meet the industry or irrigation standards, especially when disinfection is needed. This step is known as water regeneration. Typical tertiary treatment proposed in the literature (Lazarova et al, 2001) is composed of the following stages: low pressure membrane filtration (e.g. MF) followed by disinfection stage and finally high pressure membrane filtration (e.g. RO). Industrial quality standards and regulations for regenerated water reuse limit the presence of pathogens. Disinfection may be achieved by means of i) chemical agents, e.g. chlorine and its compounds, ozone, hydrogen peroxide, various alkalies, ii) physical agents, e.g. heat or sound waves and iii) radiation, e.g. ultraviolet irradiation (MEDAWARE, 2005, Leong et al, 2008) and more recently advanced oxidation processes (AOP) such as electrochemical disinfection (Polcaro et al, 2007).

Low pressure membrane processes of microfiltration (MF) and ultrafiltration (UF) are used for the removal of turbidity, pathogenic microorganisms and organic matter. Microfiltration (MF) refers to filtration processes that use porous membranes to separate suspended particles with diameters between 0.1 and 10 μm. Ultrafiltration (UF) uses a finely porous membrane to separate water and microsolutes from macromolecules and colloids. The average pore diameter of the membrane is 10-1000 A range (Baker R.W., 2004). MF and UF are mostly employed as pretreatments for wastewater desalination using reverse osmosis (RO) (Pearce, 2008). MF/UF systems for pretratment comprise 35-40% of all pre-treatment installations and they are expected to replace over 80% of the existing conventional/other pre-treatment systems by 2012. These treatments are also the favourite technologies on sewage for the removal of suspended solids, particles, bacteria and parasites.

Microfiltration (MF) presents high efficiency eliminating turbidity and suspended solids but the MF effluent does not present standard characteristics for reuse in most industrial applications. So MF is usually used as UF pre-treatment.

Ultrafiltration (UF) is increasingly used as a complete or intermediate water purification technique. Compared to conventional treatments UF offers several advantages such as: superior quality of treated water, a much more compact system, easier control for operation maintenance, fewer chemicals and less production of sludge (Abdessemed et al., 1999). UF membranes are attractive as a pre-treatment prior to RO for regeneration of secondary treated sewage effluent, because permeate qualities are high and constant despite widely changing raw water quality (Kim et al., 2002). UF is very efficienct for removing different parameters, e.g. a noticeable elimination of suspended solids and turbidity is achieved; metals like Fe, Zn, Al, Cr, Cu and Mn are significantly eliminated; microbial pollution is totally eliminated; Faecal coliforms, total coliforms, faecal streptococcus, protozoan cysts (Giardia and Cryptosporidium), and even viruses are totally removed by ultrafiltration (Alonso et al, 2001; Qin et al, 2004; Ravazzini et al., 2005); reduction in the concentration of organic matter occurs when the organic fraction is mostly in suspended form. No clear effect is produced concerning inorganic salts abatement and consequently conductivity values are not affected by this treatment.

Avoiding and mitigation of fouling related problems has become one of the most important targets whenever membrane processes are considered in water regeneration research and development. A commonly used approach to mitigating fouling is feed pre-treatment to remove/modify the components with high fouling potential (Shon et al, 2006). The most usual pre-treatment method in order to improve low pressure membrane performance includes pre-filtration (MF) or ohers like chemical coagulation and anion exchange resins (Fan, 2008). Chemical coagulation is widely used as a simple and effective means for the removal of particulates, colloids and high molecular weigh organic materials form water and wastewater. (Chen et al., 2007). However three are some cases where coagulation has had negative effects on membrane performance (Shorney et al., 2001, Shon et al, 2005) Anion exchange resin has been used as a means of improving membrane performance by removing a significant faction of organic matter from drinking water sources (Fabris et al, 2007) but few applications have been reported where anion exchange resins are used in wastewater treatment (Fan et al, 2008).

When high quality water is required, an additional step apart from MF/UF treatment is necessary. High pressure membrane technologies, nanofiltration (NF), membrane pore size 0.001 μm, and reverse osmosis (RO), membrane pore size 0.0001 μm, appear as potential treatments which allow the obtention of high quality water. RO results demonstrate the capacity of this technology for reducing and eliminating several parameters such as TDS, alkalinity, hardness, TOC, BOD_5, anions like chloride, nitrate, and phosphate, and different metals, for instance calcium, magnesium, chromium and iron in order to achieve ultrapure water quality for specific industrial applications (Kim et al., 2002).

Advanced oxidation processes (AOPs) have emerged as valuable tertiary treatments allowing not only inactivation of a wide spectrum of pathogens but also the removal of a great number of the so-called emerging pollutants such as pharmaceutical and personal care products that are not totally removed during conventional treatment remaining in the wastewater effluents (Ternes and Joss, 2006). Among different alternatives electrochemical oxidation with born doped diamond electrodes (BDD) has been reported to be effective on eliminating a wide spectrum of microorganisms although disinfection mechanisms have not been yet clearly identified (Rychen et al., 2003; Polcaro et al., 2007).

Considering the high variability in the wastewater sources, the specific standards of the different industrial activities and broad possibilities that are technically available according to the sate of the art, a combination of different centralised or decentralised technical solutions can be applied to reach the specific objectives when considering the local water cycle. The issue is not the availability of technology but the vision, experience and institutional infrastructure needed to recognize and implement reuse solutions. Representative examples of the R&D in reclamation strategies with industrial reuse purposes being developed in countries suffering some grade of water scarcity will be described

DISINFECTION OF WATER BY ADVANCED TECHNOLOGIES USING SOLAR ENERGY

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Introduction

Bad quality of drinking water or its inadequate treatment appears as one of the biggest foreseeable causes of death at early age in the world. This is because water is one of the main ways to diseases transmission. According to the World Health Organisation, contaminated water for human consumption is responsible for about five million deaths per year in the whole planet, being also a fatal risk factor for children. Every eight seconds a child dies of a disease related to water contamination. And this problem is not limited to developing countries. Even in OCDE countries, very often there are outbreaks of water contamination diseases. Disinfection methods based on chloride addition are the most used. For that purpose chloride is used in gas or diluted, acting efficiently against viruses and bacteria. However these methods generate highly toxic by-products, such us trihalomethanes and other carcinogenic compounds. The bactericidal effect of the solar radiation was firstly reported by Downes and Blunt in 1877. The ultraviolet range of the solar spectrum that reaches the terrestrial surface is limited to wavelengths superior to 290 nm. The instantaneous solar irradiation in a certain location depends on the solar height and can vary a factor from 2 to 100. Of all the solar radiation that reaches the Earth surface, less than 10% is UV light, of which only one small part is useful for water disinfection. In spite of it, there are many works of water treatment contaminated with organic compounds and microorganisms based on the exclusive use of the solar radiation. Its capacity has been demonstrated to eliminate a great amount of organic and pathogenic organisms avoiding toxic by-product generation typical of the conventional technologies. The bacterial decontamination rate by solar radiation is proportional to the intensity of radiation and the temperature and inversely proportional to the depth of the water, due to the dispersion of the light in it. The amount of radiation attenuated by this effect depends on the range of wavelengths, for example, between 200 and 400 nm the reduction does not attain 5% per meter of depth and to superior wavelengths it can reach up to 40%/m [1]. The most destructive wavelengths for the forms of microbial life are those of the near UV-A spectrum (320 to 400 nm), whereas the spectral band from 400 to 490 nm is the least harmful. Whereas differences in the speed of inactivation of bacteria to temperatures between 12 and 40 ºC are negligible, when the temperature raises until 50ºC the bactericidal action is accelerated in a factor of 2, probably due to the synergetic effect between radiation and temperature [1].

The recent studies on solar disinfection done at the Plataforma Solar de Almería facilities are focused on the study of the influence of different parameters on both processes for water disinfection, solar disinfection and solar photocatalytic disinfection. The targets used for these studies vary from a model coliform bacteria (like *E. coli*), oocysts of *Cryptosporidium*, up to resistant spores of wild strains of phytopathogenic fungi (like *Fusarium* spp.). These research works were carried out in different real sunlight conditions under cloudy and clear sky, with low and high ambient temperatures, using immobilized and suspended photocatalysts, and using several configurations of solar photoreactors (flow versus static systems, low versus high volumes of water treated per batch, under different concentration factors and surface area of the solar collector used). Turbid real waterand natural underground water were used to validate our results as well [2-12].

Research activities and applications

The European Union International Cooperation (INCO) has recently sponsored two different projects with the aim of developing a cost effective technology based on solar photocatalysis for water decontamination and disinfection in rural areas of developing countries (SOLWATER and AQUACAT projects). Both projects explore development of a solar reactor to decontaminate and disinfect small volumes of water. Field tests with the final prototypes were carried out in 2005 to validate operation under real conditions. Similar tests have been performed in photoreactors installed in Argentina, Egypt, France, Greece, Mexico, Morocco, Perú, Spain, Switzerland and Tunisia.

Among the recent projects that are being carried out in the Plataforma Solar de Almería, it is important to remark the SODISWATER project (http://www.rcsi.ie/sodis/), founded by the European Commission (VII FP). The strategic objective of this project is the development of an implementation strategy for the adoption of solar disinfection of drinking water (SODIS technique) [10,11] as an appropriate, effective and acceptable intervention against waterborne disease for vulnerable communities in developing countries without reliable access to safe water, or in the immediate aftermath of natural or man-made disasters.

The SODIS technique is highly effective against a broad range of pathogens such as Escherichia coli, Vibrio cholerae, Salmonella typhimurium Shigella dysenteriae Type I, Pseudomonas aeruginosa, Candida albicans, Fusarium solani, and the trophozoite stage of Acanthamoeba polyphaga. The biocide effect of sunlight is due to optical and thermal processes and a strong synergistic effect occurs at temperatures exceeding 45 ºC [11]. In addition to direct UV killing, sunlight is absorbed by photosensitizers present in the water that then react with oxygen producing highly reactive oxygen molecules such as hydrogen peroxide and superoxide dismutase which exert a disinfecting effect. Although SODIS has been evaluated for a small number of viruses the efficacy of SODIS against many viral, protozoan and helminthic pathogens with important relevance to Sub-Saharan Africa and developing countries in general, remains uncertain.

On the other hand, solar photocatalysis is at present one of the most successful applications of solar photochemistry. Hydroxyl radicals formed in the presence of water are highly reactive and attack the external cell wall provoking finally the cell death or inactivation. Solar photocatalytic disinfection is a promising method, which could be applied to an irrigation water treatment process in order to destroy phytopathogens avoiding drawbacks of common disinfection methods. Among the most important and general diseases of such hydroponic cultures, several fungal species like *Pythium, P. parasitica, olpidium bornovanus, Fusarium oxysporum* f.sp. *radiciscucumerium*, and other microorganisms, causes significant loses in greenhouse cultivations. The damage originated by these microorganisms increases its severity when recirculation hydroponic cultures are employed. These pathogenic microorganisms are difficult to control once they have entered the agricultural system. Various chemical fungicides (ethridiazol, furalaxyl, methalaxyl, benomyl, copper oxalate or oxyquinoline sulfate) have been tested for pathogen control but have turn out to be phytotoxic in soil-less cultures. Chlorine, a universal disinfectant, has provided disparate results and often shows phytotoxicity. The application of surfactants for controlling *Olpidium bornovanus* and incorporation of 5–7% sodium hypochlorite in the irrigation water, have demonstrated limited success. Therefore, non-chemical methods of pathogen control in hydroponic cultures, based on solar photochemical processes could offer a very attractive innovative solution.

The FITOSOL project (coordinated by PSA-CIEMAT) aims to eliminate phytopathogens in water through photocatalytic processes: application for the water disinfection and reuse in recirculation hydroponic cultures (http://www.psa.es/webesp/projects/fitosol/index.html). Within this project it has been already proven the feasibility of photocatalytic inactivation of different phytopathogenic microorganisms at lab and pilot plant scale, and under real conditions using solar radiation as a natural source of UV photons [3-7]. As a result of lab-scale studies, a new prototype of solar photoreactor has been designed and constructed at the facilities of Plataforma Solar de Almería (Fig. 1).

Figure 1. Picture of the CPC solar photoreactor constructed for photocatalytic disinfection of water contaminated with agricultural pathogens (PSA facilities, Spain).

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WHAT HAPPENS DURING "SODIS"? A DEEPER INSIGHT INTO CELLULAR DAMAGES CAUSED BY SUNLIGHT

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Availability of safe drinking water is a key health issue in developing countries; over 1.2 billion people are at risk because they lack access to save drinking water (WHO/UNICEF, 2005). In many parts of the world the UV part of sunlight can be employed for disinfection purposes: 6 hours of exposure to the sun of hygienically unsafe drinking water in PET bottles results in a several log-fold inactivation of diarrhoea-causing bacteria, protozoa and viruses (Wegelin et al., 1994; Malato et al., 2009). Solar disinfection (SODIS) is a simple and cheap method that is based on easily available and low-cost tools. Its impact on health has been documented in several epidemiological field studies, e.g., in India, where a total of 40% of diarrhoeal diseases and 50% of diarrhoea episodes were prevented by the use of SODIS (Rose et al., 2006). Over 2 million people are already using the method (URL 1) and SODIS is now included in the list of recommended methods for household drinking water disinfection by the World Health Organization and United Nations Children's fund (WHO/UNICEF, 2005). However, the exact mechanism of inactivation of microbial pathogens is not yet known and, therefore, this method still meets scepticism and is often rated as being too simple a technique to work safely. In the past years our research group has studied the mechanisms of inactivation of enteric bacteria by sunlight to supply a basis for broad acceptance of this elegant drinking water disinfection method. The results of our work are outlined below.

Disinfection methods like SODIS are normally assessed with living test microorganisms; frequently, the enterobacterium *Escherichia coli* is used as a model organism. However, an important point often overlooked is that microbial resistance to stress varies significantly with growth and cultivation conditions. Therefore, we have initially tested the sensitivity of *E. coli* MG1655 to three physical stresses that the cells experience during SODIS in field and laboratory experiments: sunlight, artificial UVA light, and mild heat (Berney et al., 2006a). Generally, fast-growing cells were more sensitive to all stresses than slow-growing cells. Experimental evidence suggests that stress sensitivity of *E. coli* is correlated with the intracellular level of the alternative sigma factor RpoS. Stationary phase cells were most resistant to stresses and this was true for *E. coli*, *Salmonella typhimurium*, *Shigella flexneri* and *Vibrio cholerae*. *S. typhimurium* was the most and *V. cholerae* the least resistant of the tested enteric strains (Berney et al., 2006b).

A first better insight into the processes of cell injury and death of *E. coli* during solar disinfection was obtained by combining a range of different methods (Berney et al., 2006c). Flow cytometric methods for viability/activity determination, combined with classical cultivation assays and ATP levels were measured in cells that were exposed to either sunlight or artificial UVA light. A UVA light dose of <500 kJ/m^2 (corresponding to ca. 2 hours of sunlight) was already sufficient to lower the proton motive force, such that efflux pump activity and ATP synthesis decreased significantly. The results strongly suggest that cells exposed to >1500 kJ/m^2 solar UVA radiation were no longer able to repair the damage and recover. In summary, the results with this combination of methods give a good picture of the "agony" of *E. coli* cells when it is stressed with sunlight. Similar results were obtained with *S. typhimurium* and *S. flexnery* cells (Bosshard et al., 2009a).

When growing in continuous culture, *E. coli* cells can adapt to continuous UVA irradiation at low fluences (Berney et al., 2007). A subsequent transcriptome analysis was performed during transient growth inhibition and in the UVA-adapted state (Berney et al., 2006d). The results indicated that UVA-light induces the stringent response and the up-regulation of the synthesis of various amino acids. Also several SOS response genes were up-regulated, indicating DNA damage.

Recently, we have identified proteins as the early (and probably most important) targets of inactivation of sunlight at the molecular level (Bosshard et al., 2009b). Damaged (carbonylated) proteins were found by an immunological method and tandem mass spectrometry (LC-MSMS) allowed to identify damaged proteins. This information was complemented with activity measurements of selected enzymes. We observed an increase in protein carbonylation reproducibly at the very early state of irradiation (already after a light dose of 250 kJ/m^2; for comparison, one full day of solar irradiation corresponds to about 2500-3000 kJ/m^2). A massive accumulation of protein aggregates was found in irradiated cells after about 1000 kJ/m^2. Some 73 out of 200 of the most abundant proteins of *E. coli* aggregated in the light. Target proteins included enzymes involved in translation, TCA cycle, transport, transcription, glycolysis, DNA-repair, protein folding, respiration and ATP synthesis. Enzyme assays after irradiation experiments confirmed these results. As an example, F_0F_1-ATPase activity decreased rapidly during irradiation (after about 1000kJ/m^2). The first targets seem to be proteins in the cytoplasmic membrane.

These results lead to the conclusion that the primary reason for pathogen inactivation by sunlight during SODIS is caused by damage of various proteins (and not DNA), presumably largely by free radical formation in oxidative stress that is closely associated with the respiratory chain. Central metabolic pathways are then blocked by this protein damage and this leads to cell death. Recovery from such very diverse damage seems very unlikely because the damaged proteins are prone to degradation and have to be re-synthesized, which requires much energy and building blocks. Therefore, SODIS is a save way to improve microbial water quality.

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DECONTAMINATION OF INDUSTRIAL WASTEWATER BY ADVANCED OXIDATION PROCESSES COUPLED WITH BIOTREATMENT

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Introduction

Nowadays a continuous increase concern on alternative water reuse technologies development in southern Europe as well as in the Mediterranean Countries mainly focused on agriculture and industrial activities have arisen. One of the major threats to water quality is chemical pollution such as heavy metals, solvents, dyes, pesticides, etc. Chemicals enter the aquatic medium in several different ways, either dumped directly such as industrial effluents, or from wastewater treatment plants (WWTP) that do not fulfill their obligations. They may also enter the water indirectly through the use of plant health products, such as biocides and fertilizers, in agriculture. Therefore, in order to develop measures for the elimination of these substances, it is essential to systematically analyze their sources and the pathways leading to surface water pollution.

Each of the various physical, chemical and biological processes developed for wastewater treatment has its own limitations inherent in its applicability, effectiveness or cost. In this context, conventional biological processes do not always provide satisfactory results, especially for industrial wastewater treatment, since many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment [1, 2]. Therefore, the only feasible option for such biologically persistent wastewater is the use of advanced technologies based on chemical oxidation.
These technologies are generally classified into:

Chemical oxidation for complete mineralization is generally expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete chemical degradation, and furthermore, they all consume energy (radiation, ozone, etc.) and chemical reagents (catalysts and oxidizers) which increase with treatment time [3]. One attractive potential alternative would be to apply these chemical oxidation processes in a pre-treatment to convert the initially persistent organic compounds into more biodegradable intermediates, which would then be treated in a biological oxidation process. Studies have long been showing that the biodegradability of a waste stream changes when subjected to prior chemical oxidation.
Ideally, chemical pre-treatment should be highly selective for those less biodegradable wastewater fractions, leaving the more biodegradable species intact for later biological treatment. Unfortunately, the prevailing mechanism by which most of the AOPs degrade organic pollutants is by forming hydroxyl radicals which are highly reactive but not at all selective.
Sometimes the effect of prior chemical oxidation is insignificant or even harmful to the properties of the original effluent, even though it is conceptually advantageous. There are several reasons for this, the most common of which are:

- Formation of stable intermediates which are less biodegradable or more toxic than the original molecules.
- Lack of selectivity during chemical pre-treatment.
- Poor selection of treatment conditions. For example, excessive pre-oxidation can lead to generation of an effluent with too little metabolic value for the microorganisms.
- No action is taken to eliminate the excess oxidant and/or catalyst used in determining oxidation schemes. Compounds such as ozone and hydrogen peroxide (both known as disinfectants), metals, metal oxides and metal salts (catalysts in many processes), are normally toxic to microorganisms.

These limitations underline the need to establish a step-by-step research methodology which takes these effects into account. Detailed studies are therefore necessary to find out how operating conditions affect the original properties of the pre-treatment stream (contact time, oxidant and/or catalyst type, dose and toxicity, temperature, etc.). Such studies must employ analytical tools to infer the reaction mechanisms, pathway and kinetics, evaluate the effect of the chemical pre-treatment on biodegradability, and various techniques for determining biodegradability and toxicity [4].

Advanced strategy for hazardous industrial wastewater treatment

When industrial wastewaters contain organic pollutants, which are toxic or non-biodegradable to common microorganisms impeding their treatment in conventional biological systems, chemical oxidation treatment by means of Advanced Oxidation Processes is a possible alternative. The major drawback of AOPs is their operating costs; therefore, research is focusing more and more on the combining AOPs/biological treatment systems [5-7]. In these integrated systems, AOPs are usually employed as a pre-treatment to enhance the biodegradability of wastewater containing recalcitrant or inhibitory pollutants, although in some specific cases they could be employed as a post-treatment option.
In this context, a new technology focused in the combination between photo-oxidative and biological processes for successfully treat different non-biodegradable industrial wastewaters, has been developed. This technology includes a general strategy which permits to define the best treatment option for a recalcitrant industrial wastewater. It covers four main steps in order to decide whether the Advanced Oxidation Process (AOP) must be applied alone, or if it must be integrated to an aerobic biological treatment according to the technical and economical point of view:

- Step 1: Check if wastewater is potentially treatable by AOP (Photo-Fenton, heterogeneous photocatalysis: TiO_2, ozonation, etc.) and/ or biological treatment.
- Step 2: Selection of a treatment strategy as a function of wastewater characteristics (only AOP, AOP-Biological process, Biological process-AOP, only biological process).
- Step 3: Develop and optimize a coupling strategy (if AOP-Biological process or Biological process-AOP was chosen in Step 2).
- Step 4: Economic study.

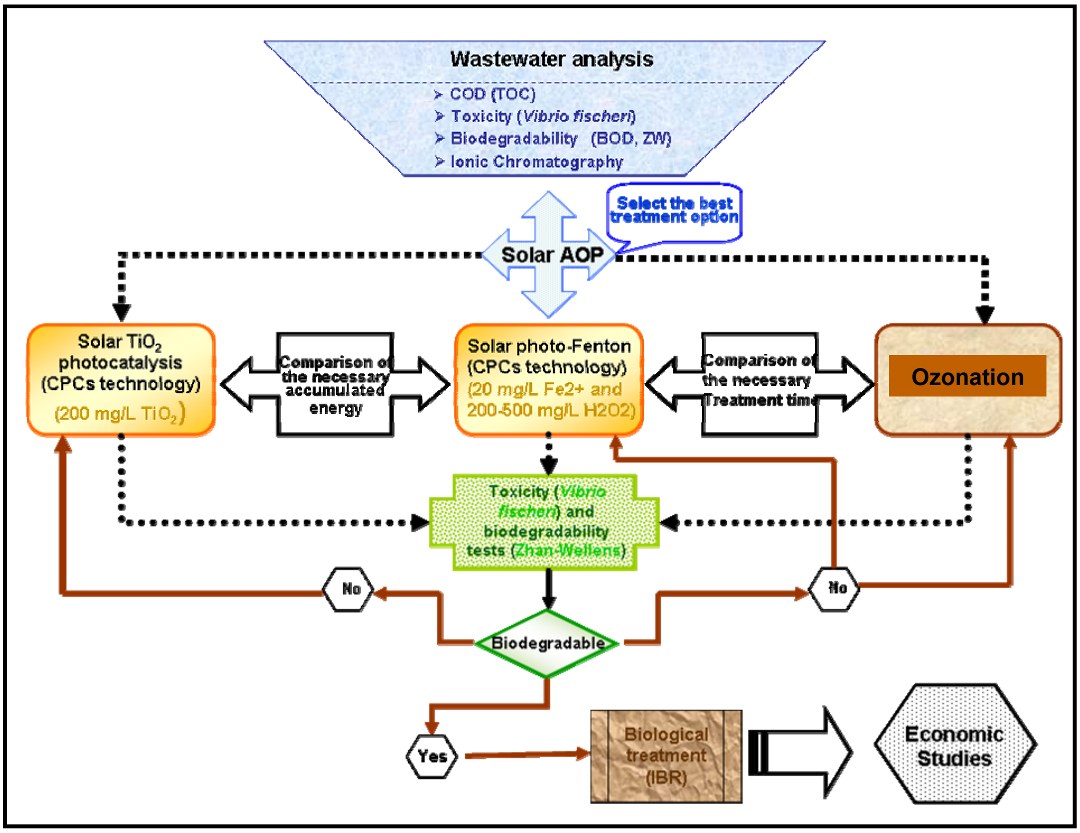

Figure 1. Diagram of the different steps involved in the advanced oxidation strategy for hazardous industrial wastewater treatment.

Integrated systems: research and applications

In this communication several examples of the integrated technology application for the treatment of different types of industrial wastewater are presented: pharmaceutical wastewater and wastewater containing emerging contaminants or pesticides. These experiments have been developed in the frame of several European and national projects:

INNOWATECH Project under the Sixth Framework Program, within the "Global Change and Ecosystems Program" (Contract nº: 036882): European project which the main objective is to investigate, assess and significantly enhance the potentiality of promising technological options (i.e., technologies, processes and concepts) for the treatment of industrial wastewater with the specific aim to provide tailor-made solutions to end-users for a wide range of wastewaters.
Recently two parallel activities have been developed in the PSA: in one hand the application of the combined systems: solar photo-Fenton/aerobic biological process and aerobic biological process/solar photo-Fenton for successfully treat a pharmaceutical wastewater containing a non biodegradable compound (nalidixic acid, a quinolone antibacterial agent) and characterized by an organic charge of 775 mg/L and around 4 g/L of NaCl. On the other hand, a pre-industrial scale plant based in this integrated technology has been designed and erected in a company that collects plastic pesticide containers for recycling. Containers are

shredded and washed producing water contaminated with pesticides. This real wastewater has been successfully treated in a 150 m^2 solar collector field combined with an immobilized biomass reactor (2700 L treated in 30 hours of continuous operation).

FOTOBIOX Project (CTQ2006-14743-C03-01/PPQ): National Research project which overall objective is to study in detail new technologies for combining solar photocatalysis and biological oxidation for the treatment and reuse of water polluted by persistent non-biodegradable toxic compounds.
Recently, the evaluation of the main parameters involved in the detoxification of water containing a commercial pesticides mixture by photo-Fenton [8], and its combination with an aerobic biological treatment at pilot plant and pre-industrial scale have been performed in the PSA. From this study it has been concluded that photo-Fenton stage is able to enhance real and simulated wastewater biodegradability after total degradation of the active compounds. Moreover, this partially oxidized effluent can be completely treated in an immobilized biomass reactor with a global efficiency of 96% in terms of mineralization (initial DOC of 500 mg/L): 40% accomplished by the solar photo-Fenton process and 56% by the biological treatment.

TRAGUA Project (CSD2006-00044): National Research project which main objective is to take benefit of 24 research groups experience on different areas in order to completely undertake the reuse of treated urban wastewaters coming from the Wastewater Treatment Plants.
The standard quality that must fulfill the reusable water demands is to be free of toxic, endocrine-disrupting compounds or non-biodegradable substances (pharmaceuticals, hormones, pesticides, etc.). For this purpose, Solar photo-Fenton process has been applied as a pre-treatment step for attaining the degradation of 15 emerging contaminants (ECs) at low concentrations (100 µg/L) in simulated and real effluent of municipal wastewater treatment plant with photo-Fenton at unchanged pH and Fe = 5 mg/L in a pilot-scale solar CPC reactor. Toxicity analyses have been also performed during the photo-Fenton treatment.

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OCCURRENCE AND FATE OF CONTAMINANTS IN SEMI-ARID AREAS

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Legislation in Europe

Since 2000 the Water Framework Directive (WFD) has been in place as the main European legislation to protect the water resources and water environment of Europe. It requires managing the river basin so that the quality and quantity of water does not affect the ecological services of any specific water body. Viewing rivers as integrated systems, this EU framework aims to achieve good chemical and biological water status and to restore every river, lake, groundwater, wetland and other water body across the community to a "good status" by 2015. The ecological status is based on biological criteria, supported by chemical, physico-chemical and hydromorphological elements.

The chemical status refers to defined pollutants, such as the priority substances for which environmental quality standards are proposed. The European Commission adopted a proposal for a new Directive to protect surface water from pollution on 17 July 2006 [1], which will set limits on concentrations in surface waters of 41 dangerous chemical substances (including 33 priority substances and 8 other pollutants) that pose a particular risk to animal and plant life in the aquatic environment and to human health.

Additionally, there is a growing concern about possible ecotoxicological importance of various classes of emerging contaminants in wastewaters and receiving ambient waters.

The priority hazardous substances are identified, taking into account the precautionary principle, relying in particular on the determination of any potentially adverse effects of the product and on a scientific risk assessment [2].

The objective of the Drinking Water Directive (DWD; 98/83/EC) is to protect the health of the consumers in the European Union. In the DWD a total of 48 microbial and chemical parameters must be monitored and tested regularly. The parametric values of the DWD are based on the scientific knowledge available and the precautionary principle (e.g. pesticides) has also been taken into account. There is also concern on endocrine-disrupting chemicals but at present no parametric values are established.

The Groundwater Directive (2006/118/EC) sets underground water quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater only for chemical parameters in response to the requirements of the Water Framework Directive (WFD).

For emission limitation the Urban Wastewater Treatment Directive (UWWT 91/271/EEC) aims to protect the environment from the adverse effects of urban, and from certain industrial sectors, wastewaters discharges and concerns the collection, treatment and discharge of domestic wastewater, mixture of wastewater and wastewater from certain industrial sectors. The main focus of this directive is the prevention of eutrophication or oxygen depletion and the monitoring of the performance of treatment plants and receiving waters is consistent with that goal.

The IPPC Directive (96/61/EC) is about minimising pollution from various industrial sources [3]. Among the others specific regulation (2004/850) on **persistent organic pollutants**, limitation in the production and use, is also to be considered: "*The Community is seriously concerned by the continuous release of persistent organic pollutants into the environment. These chemical substances are transported across international boundaries far from their sources and they persist in the environment, bioaccumulate through the food web, and pose a risk to human health and the environment. Further measures need therefore to be taken in order to protect human health and the environment against these pollutants*".

The increasing extent and level of municipal wastewater treatment in Europe in the past decades has significantly improved the quality of surface waters, even though obligations set for the European Union are not equally fulfilled by all its members. Oxygen depletion is now largely under control in many places. Phosphate concentrations in European rivers have been regulated and eutrophication of lakes and coastal waters has been reduced as a result even if problems remain. According to EEA (2003) nitrogen pollution, particularly form agriculture has remained constant and there is no evidence of changes in nitrate levels in groundwater [4]. Organic matters are removed effectively in wastewater treatment plants (WWTP) as well as many organic trace pollutants. Pollution of rivers by heavy metals and some other heavily regulated chemicals is generally decreasing but data availability for many other pollutants is still too weak to make assessments and there is a lack of comparable data on the European scale. It can be assumed that many still unknown pollutants and especially polar metabolites are present in the aquatic environment at concentrations up to the µg/L-range. Investigations about the contamination of different water types are currently under way in many different European laboratories.

However, analytical methods exist, are validated and harmonized in almost each country of the EU, allowing both, a description of the analytical status according to sum and specific parameters.

Availability of analytical data of MPC and semi-arid areas

The evaluation of water quality or water treatment processes in the Mediterranean Partner Countries (MPC) is oftentimes solely based on the measurements of sum parameters like the chemical oxygen demand (COD) [mg O_2/L], the biological oxygen demand (BOD) [mg O_2/L], dissolved oxygen (DO) [mgO_2/L], the total dissolved solids (TDS) [mg/L], faecal coliforms (FC) [MPN/100mL], heavy metals, total suspended solids (TSS), phosphate, nitrite, nitrate, iron, oil & grease and ammonia [5]. The advantage of determining sum parameters besides being in general quite robust methods is that they can be determined with low cost analytical equipment which is also easy to operate. Determination of these parameters is not sufficient for that purpose since single anthropogenic pollutants are not identified nor quantified. The lack of certified laboratories in the respective countries and hence missing appropriate analytical methods, forces the dispatch of water samples to foreign institutions. This procedure implies both, errors caused by improper sample handling during storage and transport as well as increasing shipping costs. The existing analytical methods for the determination of anthropogenic pollutants like the priority substances, but also worldwide emerging compounds such as pharmaceuticals, pesticides and surfactants can be taken over from experienced institutes. Additionally, training programmes of the technical stuff can be offered by the partner institutions which are experienced in the field of education. Analytical methods being state-of-the-art nowadays are methods based on HPLC-MS/MS or GC/MS for qualification and quantification purposes.

Contrary to the above described information obtained from the “sum parameter analysis”, it can be easily seen that micropollutants, especially pharmaceuticals and pesticides seem to play, as everywhere else in the world, an important role in the MPC countries. It is strongly recommend using and elaborating these methods for wastewater, groundwater and drinking water analysis in the MPC countries in order to get a thorough database regarding occurrence, sources and potential risks being implied by that.

Occurrence and fate from selected pollutants analysed during selected monitoring programs conducted in the MPC

Monitoring programs are more or less routinely conducted in European countries in order to fulfil the criteria set in the WFD as well as detect relevant and so far non-regulated pollutants. GC-MS and LC-MS/MS methods are applied following SPE enrichment or, if applicable, direct analysis. Besides looking for marketed compounds, the search for degradation and transformation products is getting more and more important. All scoping studies have shown so far, that pesticides, human pharmaceutical residues, surfactants and industrial chemicals are present as contaminants in many European waters. It is suggested that in order to firmly establish the risk posed by emerging compounds in the aquatic environment, further data are required on the fate and effects of these compounds.

In **Spain**, for example, the presence of 21 emerging contaminants of various chemical groups (7 estrogens, 3 progestogens, 6 pharmaceuticals and personal care products (PPCPs), and 5 acidic pesticides) was investigated in the Llobregat river basin (NE Spain) [6]. Waters from the outlet of various sewage treatment plants (STP) and waterworks located along the river basin, as well as water samples from the river or its tributaries upstream and downstream of these plants were analysed in two pilot monitoring studies. Of the estrogens and progestogens analysed, only estrone-3-sulfate, estrone, estriol and progesterone were found to be present in the low nanogram per liter range in some of the samples investigated. Except for atenolol, all PPCPs studied (ibuprofen, diclofenac, clofibric acid, salicylic acid, and triclosan) could be identified at levels usually lower than 250 ng/L and up to 1200 ng/l (diclofenac). Of the various pesticides investigated (2,4-D, bentazone; MCPA, mecoprop and propanil) MCPA and 2,4-D were the most ubiquitous and abundant and bentazone the only one not detected. Individual concentrations were most often below 100 ng/L and never surpassed the EU limits.

During a further monitoring campaign conducted in the Ebro river delta, Spain, organophosphates, triazines, phenylureas, anilides, chloroacetanilides, acidic herbicides and thiocarbamates were analysed [7]. The study showed high levels, in the µg/L range, of bentazone, MCPA, propanil, molinate and atrazine, in basically all the samples investigated.

Available monitoring data from public monitoring are mostly water quality parameters based upon sum parameters. Conclusions regarding the validation of the presented data are difficult to make, since these are not available through peer-reviewed literature. Anyhow, as it can be seen from the monitoring data available from e.g. the agricultural drains or the industrial point discharges into the Nile, **Egypt** show, that the water quality is quite low. There is a lack of monitoring data from rivers and ground water itself, both regarding sum parameters and micropollutants.
Data from recent monitoring campaigns conducted in Egypt within the frame of the

Innovamed project will be presented during this lecture.

Concentrations of persistent organic pollutants in the Black Sea and Mediterranean Sea of **Turkey** will also be presented. Some pollutants, which have been banned in many European countries since years, can still be detected in this area at relevant concentrations. According to the results of the Survey of Sewage System Statistics of Municipalities exercised in 2004 by Turkish Institute of Statistics (TUIK); it was determined that 1421 of 1911 municipalities had furnished services of sewage systems. In the year 2004; 47 % of 2,77 billion m^3 of waste water was discharged into the rivers. Based on this figure, and the percentage of the type of treatment applied on this waste water, it is calculated that every year 738 million m3 untreated wastewater was discharged into rivers in Turkey (2004).

Compared to other studies conducted world wide, the obtained results for **Palestine** show very high concentrations for the pharmaceuticals diclofenac (mean = 54 µg/L; max. = 165 µg/L), ibuprofen (mean = 1869 µg/L; max. = 10125 µg/L) sulfamethoxazole (mean = 242 µg/L; max. = 1150 µg/L) and trimethoprime (mean = 61 µg/L; max. = 304 µg/L). An efficient removal of ibuprofen (> 90%) can be achieved when CAS is applied. The contribution of WWTPs to the pollution of surface water with organic pollutants has been demonstrated.

Additional data from recent Innovamed monitoring campaigns of water samples, which have been analysed upon selected micropollutants and investigated via a non-target-analysis conducted in **Tunesia** will also be presented during this lecture.

Conclusion
MPCs do not have the technologies so far to carry out analysis of single compounds, which is mainly related to equipment and installation costs, energy costs, man power, knowledge and maintenance. We strongly recommend investigating the input and further fate during waste water treatment in order to monitor the treatment efficiency, if waste water treatment is applied at all. And if not applied, indirect reuse of these micropollutants has to be investigated.

This leads to the following actual status regarding monitoring and analysis of water quality:

- There are given deficits in waste water treatment and monitoring, both industrial and municipal mainly due to the enormous financial costs needed
- If monitored, one can expect high concentrations of pollutants as shown for the samples obtained from Palestine

In general, sum parameters are determined. On the basis of these parameters a correct water quality evaluation cannot be made. The re-use of treated waste water is therefore a matter of concern. Since the contaminants are not identified, an adequate risk evaluation for the consumers is missing.

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NORMALIZATION OF TRACE METALS IN SEDIMENTS AS ANTHROPOGENIC POLLUTANTS AND DETERMINATION OF ENRICHMENT FACTORS AT WADI AL-QILT, WEST BANK, PALESTINE.

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Freshly deposited fourteen surface sediments from Al-Qilt catchment were sampled to determine the degree and distribution of trace metals pollution and enrichment. The concentrations of trace elements were measured by ICP-MS for the samples collected at different stations on June and December of 2008. Generally, the concentration of "Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb, Bi, U, B and Hg", the sediments reflected an anthropogenic inputs for 14 trace metals analyzed. Then anthropogenic trace metals were normalized to Fe, Al, LOI and TOC as reference elements to facilitate comparison for pollution sources between sampling sites along wadi Al-Qlit. Iron was found to be a good normalize for Co, Cr, Ni, B, Mn, Sr, Pb and Cd, but it is poor in correlation with for Cu, Zn, Ba, Ag as normalizer.

Results revealed that Aluminum was significant as element normalizer compared to Iron for Cu. On the other hand; Results for Total Organic Carbon (TOC) and Loss Of Ignition (LOI) normalization shoes that they can be used as alternative normalizer for trace metals with Iron mainly with LOI compared with TOC, since the results for LOI and TOC indicates that Zn r = 0.307 and 0.172, Ag r = 0.328 and 0.260 respectively which considered better correlation compared with Fe.

This study was to delineate the extent of heavy metal pollution in the wadi Al-Qilt sediments. Total metal contents from fourteen surface sediments were compared with continental crust baseline. Enrichment Factors (EF) were computed for each metal and for each site in order to assess the trace metals pollution and the degree of pollution at each site. Results revealed that the highest pollution intensity described as extremely severe were enriched with Cu, Zn, Ag, Cd, Hg and Bi. Therefore further study were recommended for sequential extractions to indicate the anthropogenic sources mainly for Cd, Zn, Cr, Pb, Hg, Ag, Bi and Cu, hence they are potentially more mobile than those inherited from geological parent material. Based on this indexes it is good to take the most in common between the EF and other related factors as source for pollution at the area of study for further contaminant transport.

SEWAGE EPIDEMIOLOGY: USING WASTEWATER TO ESTIMATE COCAINE CONSUMPTION AT NATIONAL LEVEL

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In the contemporary society, the knowledge of patterns and prevalences of illicit drug use is important to reduce the massive economical and sociological damage that is caused by their consumption. Until recently, only classical sociological and epidemiological studies based on interviews with consumers, population surveys and crime statistics at drug use prevalences are used to adress this problem. These studies are often not scientifically justified, because the study population is not representative for a general population and because the consumers themselves are included in the study, leading to subjectivity. Moreover, such studies are time-consuming and relatively expensive.

In 2001, Prof. Daughton introduced a new way of thinking in the field of epidemiology by hypothesising that the amount of used illicit drug can be estimated from the measurement of its urinary excreted metabolites in wastewater and by making a back-calculation from these concentrations to the amount of used illicit drug (Daughton 2001). The advantages of such approach would be: objectivity (being more like a “giant urine test” on a large population), lower costs compared with the classical approaches and rapidity in delivering results. Recently, Zuccato et al. (2005) have applied this idea on a local (“city”) scale in Italy and Switzerland for cocaine, and so was sewage epidemiology born! This new research field has been booming afterwards and several research groups have started to improve on the analytical and sampling methodologies, but conducting studies still at local/regional level (Huerta-Fontela et al. 2008; Kasprzyk-Hordern et al. 2008; Postigo et al. 2008; Zuccato et al. 2008a,b).

This approach was recently applied also toe a large, nation-wide scale campaign conducted during one year (summer 2007-summer 2008) and funded by the Federal Program on Drugs (FOD). A specific protocol was followed and 24-h composite influent wastewater samples were collected from 41 wastewater treatment plants (WWTPs) across Belgium. In the summer of 2007, each WWTP was sampled on a Wednesday (representative for a weekday) and a Sunday (representative for a weekend-day) to evaluate week-weekend variations. This sampling strategy was repeated in the winter of 2007-2008, each WWTP was thus 4 times sampled.

Samples were analysed for cocaine and its metabolites, benzoylecgonine and ecgonine methyl ester, with a fully validated method based on solid-phase extraction (SPE) and liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).

From the concentrations of the human metabolite of cocaine, benzoylecgonine, an amount of used cocaine for each WWTP region and for each sampling day was calculated. Figure 1 shows the followed path from the measured concentration benzoylecgonine to an amount of used cocaine.

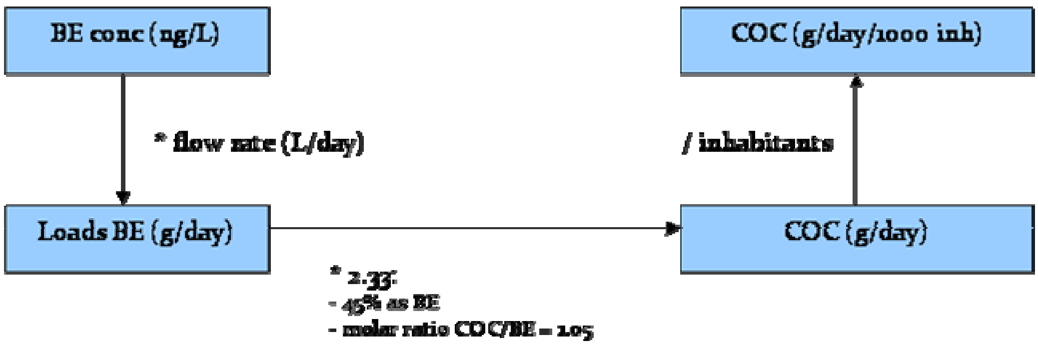

Figure 1. Pathway from concentration of benzoylecgonine (BE) in wastewater to an amount of used cocaine (COC).

The obtained results have been published in a series of papers (Gheorghe et al. 2008; van Nuijs et al. 2009a,b,c). The local results show higher cocaine use during the weekend and in WWTP regions with high urbanicity. No significant difference in cocaine consumption between the winter and summer samples was observed.

From the local results – all 41 WWTPs cover approximately 3 700 000 residents (35% of total Belgian population) – we estimated the yearly prevalence of cocaine use in Belgium. All local results were extrapolated to a complete year and summed. This was then further extrapolated from the amount of covered residents (3 700 000) to the total Belgian population (10 500 000). These calculations result in 1.88 tonnes of cocaine that are used yearly in Belgium.

Assuming that a cocaine dose is 100 mg and that an average cocaine user consumes 0.65 g/week (Cohen and Sas 1994), a yearly prevalence of 0.80% was calculated for the age class 15-64. This estimate fits in the European picture of cocaine use, which reports a range between 0.1% and 3% in the same age class and it is very close to the 0.90% prevalence estimation for Belgium (EMCDDA 2007).

Recently, an extensive sample collection was executed for the WWTP in Brussels with a design capacity of 1 100 000 residents. Also here, 24-h composite samples were collected on each day for 2 consecutive months. The samples were analysed for cocaine, benzoylecgonine and ecgonine methyl ester, but also for amphetamine, MDMA, methamphetamine, methadone and its metabolite (EDDP) and 6-monoacetylmorphine (the specific metabolite of heroine) using a newly developed method (van Nuijs et al., in press). We concluded that the amphetamine-like stimulants and cocaine show a clearly increasing use during the weekend, while we could not observe such trend for heroine and methadone consumption.

It is clear that sewage epidemiology has a great potential as a tool to monitor, synergistic to the classical approaches, illicit drug use at local and national level. In the future, efforts have to be made to fully optimise the approach.

Therefore collaborations with epidemiologists, sociologists, criminologists, and doctors, but also engineers have to be established. This will lead to studies that clarify uncertainties such as error on the flow rate, amount of served residents, the metabolism pattern of the illicit drugs, the stability in wastewater, drug doses, etc.

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SELF CLEANING POTENTIAL OF SURFACE WATERS ACCORDING TO SELECTED PHARMACEUTICALS - POSSIBILITIES AND LIMITS

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In the last decades the production and human consumption of pharmaceuticals has increased world wide. After human intake, more or less high percentage rates of the pharmaceuticals are excreted with urine or faeces to raw sewage unchanged and/or as metabolites. Passing the waste water channels either the sewage containing pharmaceuticals enter the surface water direct or even the processing of common waste water treatment plants can not avoid the emission of drugs into surface water because of the high stability like Diclofenac or oseltamivir carboxylate (OC) as the active metabolite of Tamiflu®. Modern high-tech waste water technologies like nano filtration or advanced oxidation processes are opportunities to minimize the entry of pharmaceuticals in surface waters, but common for all these technologies is, that they are expensive. Once arrived in the surface water the self cleaning potential triggered by biological and photochemical processes can be seen as main activities for the transformation and degradation of the pharmaceuticals.

Based on two selected pharmaceuticals Diclophenac and OC as the active metabolite of Tamiflu® the self cleaning potential with the limits will be discussed in detail.

Diclofenac as an example for photochemical degradation [1]:

In order to get first information about the light induced decomposition of diclofenac, 500 mL round-bottomed quartz glass flasks were exposed to natural irradiation in several experiments between July 2004 and November 2005. The used quartz glass flasks were filled with aqueous solutions of diclofenac in MilliQ water (22 mg/L to 50mg/L) and placed on the roof of the Helmholtz Centre for Environmental Research-UFZ in Magdeburg (11.39471°E, 52.07668°N). Any shading of daylight was avoided. The results of the laboratory exposition experiments show a strong dependence of diclofenac photolysis on irradiation. As an example, two decomposition curves for diclofenac are shown in Fig. 1.
The grey bars indicate the time between sunset and sunrise in November (light grey) and in March (dark grey) (www.wetterzentrale.de/sunrised.htm, 2006). At night (darkness) no significant degradation of diclofenac was observed. The absence of natural daylight leads to a strong inhibition of the diclofenac transformation. The half-life time was strongly dependent on the solar irradiation. The decrease of the diclofenac concentration during the first 6–7.5 h of daylight was much slower during rainy, cloudy days in autumn or winter (01.11.2005 and 02.02.2005) than on sunny days in spring or summer. It was shown that with increasing energy fluence the half-life time decreased, even if that did not appear to be inversely proportional. As a second factor according to the results of Andreozzi et al. (2003) [2] for diclofenac it can be stated that the lower latitude of Buser's [3] Swiss test region (47°N) influences the photolysis rate. Under similar conditions in fall the half-life time decreases approximately 30% in comparison to the half-life time at Magdeburg region (52°N).

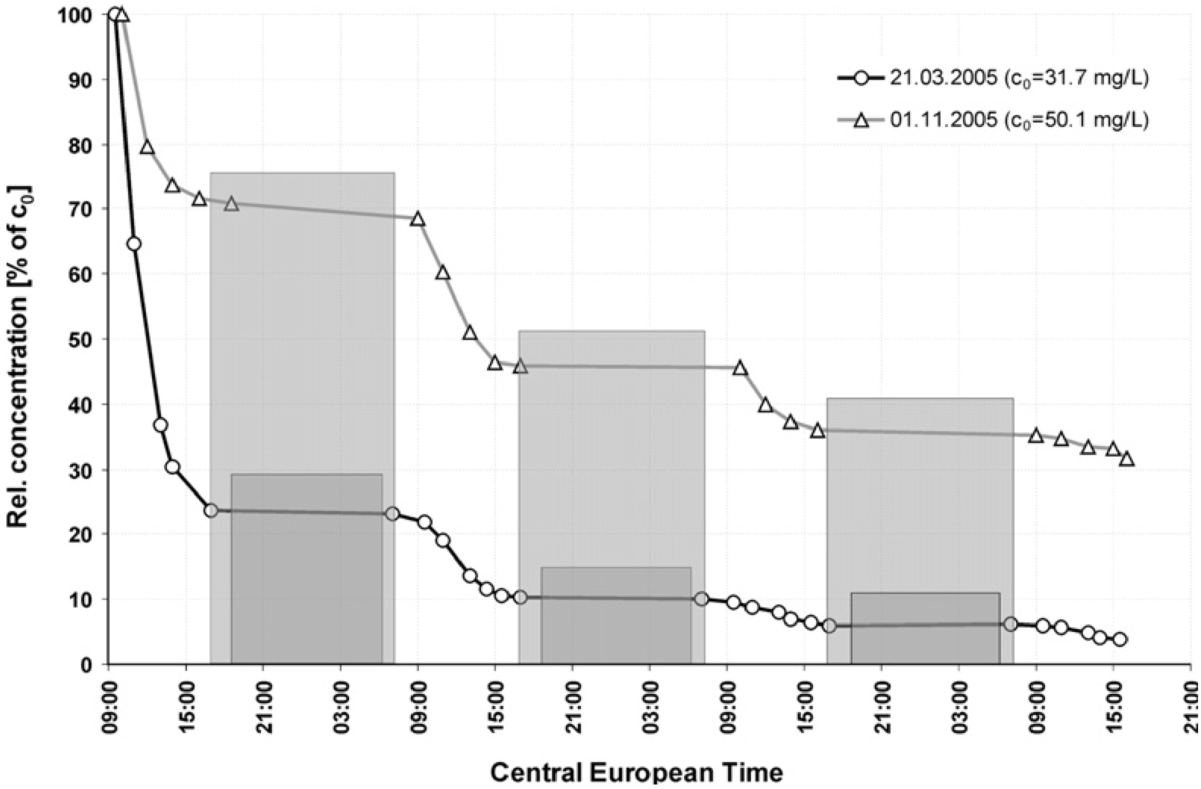

Fig. 1: Decomposition curves for Diclofenac

In order to prove the influence of natural light on the decrease of the diclofenac concentration in surface waters a field experiment at Lake Goitsche was performed in the summer of 2004. Surface water samples, filled in quartz glass flasks, were installed in different depths of Lake Goitsche (mining-lake near Bitterfeld; 12.40570°E: 51.61143°N). As it was expected the solar radiation decomposed the diclofenac completely in the flasks located near the surface of the water within 16 days. In a depth of 50 cm the solar radiation decomposed approx. 97% of the diclofenac within 2 weeks. In contrast to this, in the test flasks installed in a depth of one meter, only about 1/3 of the initial diclofenac was decomposed within two weeks (Fig. 2).

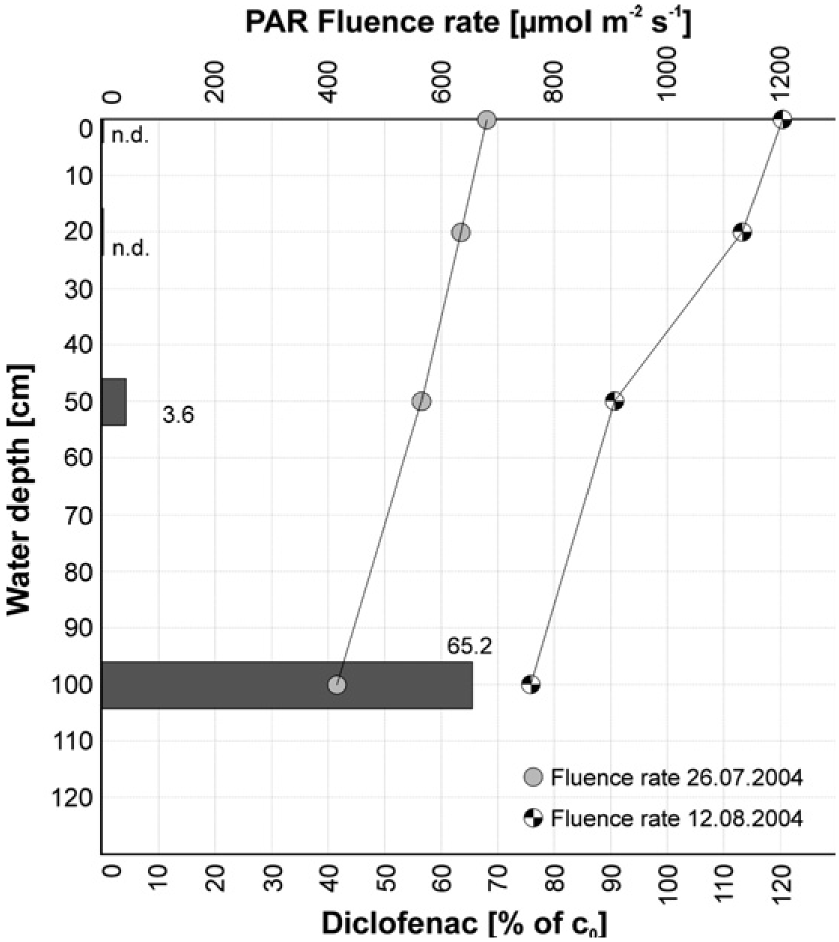

Fig. 2: Relative concentration of diclofenac after 16 days of natural daylight exposition in different depths of Lake Goitsche and fluence rates at the start and at the end of the experiment (n.d.: < limit of detection).

For that reason it can be concluded, that the intensity of the solar radiation as a function of the water depth in the surface water significantly affected the photochemical decomposition of diclofenac. Up to 50 cm depth sunlit shallow water zones and calmer waters or standing water bodies with shallow water areas e.g. groyne-fields and bayous, as well as the epilimnion of seasonal stratified lakes inhered an important rule in the degradation of the photo labile drug diclofenac.

Oseltamivir carboxylate (OC) as an example for biodegradation and indirect photolysis [4]:

To achieve detailed information about the stability of OC in different waters several sterile and non-sterile daylightexposition experiments were performed with pure water (i.e. deionised, analytical grade water generated with a Milli-Q Gradient water purification system) and surface water from the Elbe River with two different initial concentrations of OC. For comparison aliquots of the same aqueous solutions of OC were stored at +4 °C without any light exposition in a refrigerator. For all experiments half-life times (t1/2 est.) for OC were estimated using an exponential regression over the whole exposition time of each experiment. In experiment #1 for comparison the physical half-life time (t1/2 phys.) for diclofenac was calculated on the basis of the rate law for the first 3 h of daylight exposition assuming a first order kinetic.

The exposure experiments that have been performed can be interpreted as a simulation of shallow water zones of a standing water body without any turbulent flow during the warmer seasons. These conditions seem to be nearly optimal for a photolytic transformation of a special compound. Hence it must be assumed that the half-life time of OC in the aquatic environment, e.g. in rivers or in deeper lakes, may be even longer than the estimated half-life times presented. For concentrations of 50 μg l^{-1} OC (i.e. 36.8 μg l^{-1} pure OC) – almost the same as the predicted environmental concentrations in case of a pandemic outbreak of an avian influenza and the application of millions of Tamiflu® treatment courses – a half-life time t1/2 est. of about 18 days has been estimated for the degradation/decomposition of OC in natural river water. The disappearance of OC in the aquatic environment seems to be a result of a combination of a microorganism- induced biodegradation and indirect photolysis. Direct photolysis plays no or only a negligible role for the decomposition of OC. Due to its apparent persistence in river water we share the opinion of other researchers that ubiquitous use of Tamiflu® may result in selection pressures in the environment that may favour development of drug resistance. Otherwise OC does not seem to be as persistent as presumed so far. There are other pharmaceuticals – e.g. carbamazepine – that have considerably longer half-life times.

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WASTEWATER TREATMENT FACILITIES, AND LIFE CYCLE ANALYSIS A SUSTAINABILITY PERSPECTIVE

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Water industry has been one of the early established utility industries, with the objective of providing clean and safe potable water to communities. Wastewater treatment is the other side of the coin that complements that industry, ensuring the safe disposal of wastewater. With the growing demand for water becoming a crucial issues in a number of countries, the need for wastewater to augment water supply is a sound sustainable alternative. Wastewater industry is multi procedural operational units that involve diverse raw materials, chemicals, in addition to electricity consumption and others. The environmental impacts of wastewater is quite considerable. Most wastewater treatment systems require high level of energy to operate, especially advanced treatment systems such as membranes. Increased energy use may cause unforeseen problems for the site including increased energy costs, impacts on carbon generation. Sustainability of wastewater treatment facilities should meet a number of requirements, such as, minimal use of resources, minimal use of energy, stakeholders involvement, priority on recycling or reuse, considering all impacts, local and global alike. The role played by environmental management system to safeguard environmental integrity and human health has become imminent in establishing and running wastewater facilities. Environmental impact assessment EIA, risk assessment, RA, and life cycle analysis LCA are probably the most used environmental management systems in conjunction with wastewater stations. EIA is site – specific study that predicts possible impacts and put a management programme to avoid them if possible and mitigate those unavoidable ones. Risk assessment is used as a mean to quantify risks (quantitative risk assessment) or to determine their importance or priority in relative terms (qualitative risk assessment). Meanwhile, LCA is a holistic method that examines every stage of the life cycle, since the acquiring of the raw materials, through manufacture, distribution, use, possible re-use/recycling and then final disposal. For each stage, the inputs, in terms of raw materials and energy and outputs, in terms of emissions to air, water, soil, and solid waste, are calculated, and these are aggregated over the Life Cycle. The present study is an analytical study, delineating on the role played by each of these tools, with some special emphases on LCA and its application in wastewater treatment facilities.

CHALLENGES AND SOLUTIONS FOR WASTE AND WASTEWATER REUSE

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Abstract
The discharge of untreated wastewater seriously affects the quality of natural running waters and therefore presents a high risk for the population and can cause great ecological damage; both can be considered as economic loss. While the treatment of municipal wastewater in developed countries mainly contributed to public health and the extension of life expectancy, wastewater treatment is not very common in developing countries. The Middle East and North Africa is one of the most water scarce regions of the world – 5% of the world's population makes due with 1% of the planet's freshwater resources (UNEP, 2002)). The major causes of the increasing demand for water are rapid population growth, an increase in per capita consumption and agriculture, which is the main user of water in West Asia, accounting for nearly 82 per cent of the total water consumed compared to 10 per cent and 8 per cent for the domestic and industrial sectors, respectively. The water stress index in West Asia (expressed as a percentage of water used to available water resources) is more than 100 per cent in five of the seven countries in the Arabian Peninsula, and is critical in the remaining two. These countries have already exhausted their renewable water resources and are now exploiting non-renewable reserves (UNEP, 2002). To ease the situation, it is necessary to devote the efforts **from supply augmentation, to demand management and conservation**. Improvements in irrigation efficiency and wastewater reuse are another important conservation tool for non-potable uses. Future success in water reuse will depend on whether this can be done without adverse effects on human health and the environment.
The principal forces driving the increase in use of excreta and treated wastewater in agriculture are beside the increasing water scarcity and stress, and degradation of freshwater resources, the demand for food and fibre, a growing recognition of the resource value of excreta and their nutrients and also the Millennium Development Goals (MDGs) (UNDP, 2000), especially the goals for ensuring environmental sustainability and eliminating poverty and hunger.

In wastewater management one of the big challenges is the building of new toilets and the wastewater collection system. For those people with income levels so low that they can hardly provide enough food for themselves poverty prevents them investing in their sanitary conditions. Central sewage systems are in the first place intended for the transport and the treatment of human excreta. Water is required to transport the human faeces and urine from the toilet to the wastewater treatment plant, followed by disposal to a water body. Although one person produces about only 500 litre of urine and 50 kg faeces per year (Vinnerås and Jonsson, 2002), to flush them away at least 15,000 litres of drinking water are needed. In drought-prone countries like the Mediterranean countries, water saving systems would have an advantage.

As centralised systems consume a lot of water, are expensive and potentially unaffordable for

most rural areas, therefore a two way strategy should be considered. In urban areas, centralised systems should be preferred. In rural areas, **decentralise wastewater** systems including dry toilets and greywater treatment will provide advantages especially where water is scarce (Stracke, 2007). Urine usually does not contain high concentrations of pathogens but might contain eggs of the parasitic blood fluke *Schistosoma haematobium* or faecal cross-contaminations during collection could occur. The use of untreated faecal matter from on-site sanitation installations can pose significant health risks from the presence of worm eggs, which can survive for months or even years in the faecal matter and in the soil, but also from other pathogens. Nevertheless, for the remaining fractions of dry toilets or urine diverting toilets (urine and faeces – need to be kept separately) a safe storage and sanitising process of the separated urine and faeces, followed by a reuse of the sanitised excreta in agriculture, according to the guidelines of the World Health Organisation on reuse of human excreta (WHO, 2006) need to be implemented. The health-based targets may also relate to storage as an on-site treatment measure or further treatment off site after collection. Possibilities are shown in Tab. 1 for faeces from small-scale systems according to WHO (2006). The storage requires separation of fresh and stored materials.

Tab. 1: Recommendations for storage treatment of dry excreta and faecal sludge before use at the household and municipal levels[a] (WHO, 2006)

Treatment	Criteria	Comment
Storage; ambient temperature 2–20 °C	1.5–2 years	Will eliminate bacterial pathogens; regrowth of *E. coli* and *Salmonella* may need to be considered if rewetted; will reduce viruses and parasitic protozoa below risk levels. Some soil-borne ova may persist in low numbers.
Storage; ambient temperature >20–35 °C	>1 year	Substantial to total inactivation of viruses, bacteria and protozoa; inactivation of schistosome eggs (<1 month); inactivation of nematode (roundworm) eggs, e.g. hookworm (*Ancylostoma/Necator*) and whipworm (*Trichuris*); survival of a certain percentage (10–30%) of *Ascaris* eggs (≥4 months), whereas a more or less complete inactivation of *Ascaris* eggs will occur within 1 year.
Alkaline treatment	pH >9 during >6 months	If temperature >35 °C and moisture <25%, lower pH and/or wetter material will prolong the time for absolute elimination.

[a] No addition of new material.

In Tab. 2 different treatment options for faecal sludge are listed together with their removal efficiencies for the removal of helminths.

Tab. 2: Helminth removal in different treatment processes for faecal sludge (all references cited in WHO, 2006)

Treatment option or process	Helminth egg log reduction	Duration	Reference
Low-cost			
Faecal sludge settling ponds	3	4 months	Fernandez et al. (2004)
Faecal sludge reed drying beds (constructed wetlands)	1.5	12 months	Koottatep et al. (2004)
Drying beds for dewatering (pretreatment)	0.5	0.3–0.6 months	Heinss, Larmie & Strauss (1998)
Composting (windrow thermophilic)	1.5–2.0	3 months	Koné et al. (2004)
pH elevation >9	3	6 months	Chien et al. (2001)
Anaerobic (mesophilic)	0.5	0.5–1.0 month	Feachem et al. (1983); Gantzer et al. (2001)
High-cost			
pH elevation >12	3		Gantzer et al. (2001)
Thermophilic, in-vessel (aerobic/anaerobic)	3	1–5 days	Haug (1993); Eller, Norin & Stenström (1996)

The metal content of the excreta and greywater is usually low and will not impact plant uptake unless it reaches a threshold concentration in the soil and the metal is in a mobile phase as it occurs at pH values below 6.5 and/or with low organic matter content. In addition the plant roots act as an efficient barrier against uptake of non-essential metals. Excreta and greywater normally have also low contents of persistent organic compounds, although a high number as many as 900 different compounds can be detected (Eriksson el al., 2002). If excreta and greywater are treated prior to use in agriculture, the concentration of many of these compounds will be reduced by adsorption, volatilization and biodegradation in the treatment of later in the soil.

Reclaimed water, sometimes called recycled or new water, usually is wastewater collected in **centralized systems** and treated to remove solids and contaminants and as a major requirement remove pathogens. Recent studies support long standing concerns about possible public health effects of reclaimed water. It has been known for some time that treated wastewater effluent, or reclaimed water, contains pathogens that could be transferred to people through contact, including aerosols from sprinklers or by contaminated food. Particularly worrisome are high levels of parasites such as *Giardia* and *Cryptosporidium* which are not killed by chlorination. Treated wastewater is either used to recharge the aquifer or is directly applied in agriculture. In most cases the treated water is intended to be utilized for non-potable uses, such as irrigation or recreational water, but even there is controversy about possible health and environmental effects. In some locations, including Singapore, Windhoek and California's Orange County, it is used indirectly for landscape and agricultural irrigation, groundwater recharge and industry, but also for drinking water purposes after more advanced treatment.

The World Health Organization (WHO) published the third edition of its Guidelines for the Safe Use of Wastewater, Excreta and Greywater in Agriculture in 2006. These guidelines are intended to support the establishment of national standards and regulations. They are built on the assessment and management of health risks associated with wastewater use through the application of various health protection measures during all steps of wastewater use and until it reaches the consumer, because the consumer have a right to demand safe food. This code of good management practices is indented to ensure that, when wastewater is used in agriculture e.g. for irrigating crops, it is used safely and with minimal risks to health. Special focus is put on pathogen reduction, but WHO (2006) does not regulate in terms of water quality standards, but the new guidelines set health-based targets (to achieve 1 µDALY = Disability adjusted life years) and offer various combinations of risk management options for meeting them. Health based target can be reached when either all protection measures result in pathogens reduction 6-7 log units, or viral reduction of 6-7 log units; in addition helminthes eggs reduction need to achieve < 1egg/l or when the treatment of the wastewater treatment reaches the whole reduction demand. This approach distinguishes between restricted irrigation, and unrestricted irrigation, with wastewater-irrigated food, without the resulting infection and disease risks being unacceptably high (Fig. 1). In addition the guidelines explain how the health-based targets can be adapted to existing public health, socio-economic and environmental circumstances when setting national standards.

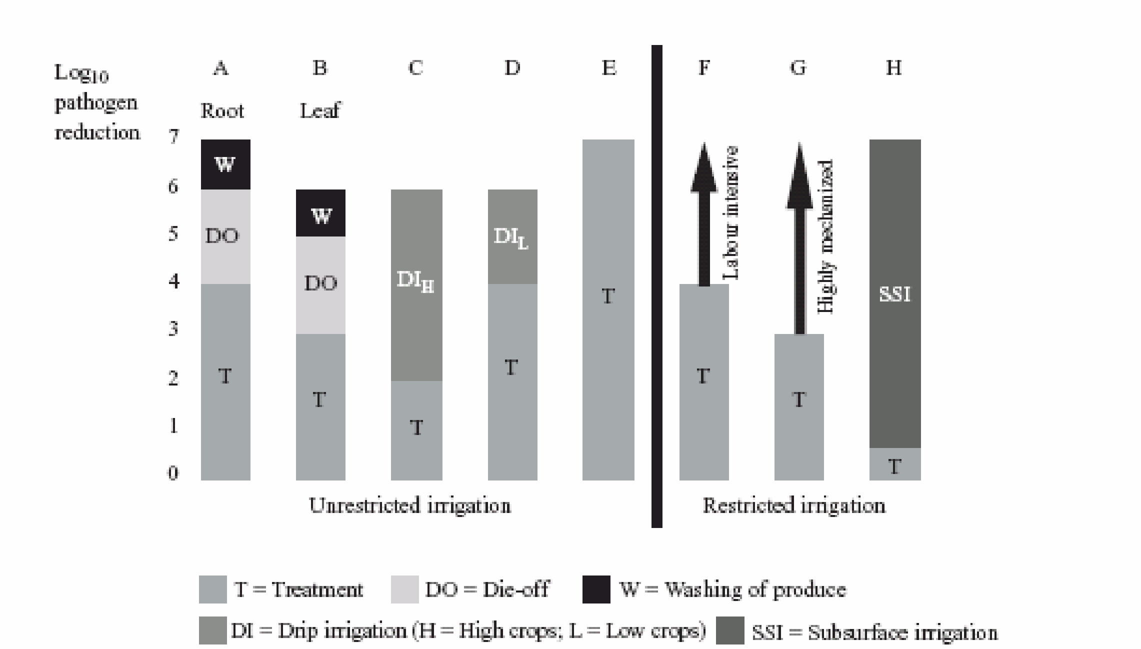

Fig. 1: Combination of different health protection measures to achieve the health based target of 10^{-6} DALY's per person per year

For treating the water to get sufficient quality for irrigation purpose or to become potable (or near-potable), a combination of different processes is necessary. These include physical, chemical and biological principles and disinfection measures, knowingly as primary, secondary and tertiary step. In the United States, reclaimed wastewater is generally treated to secondary level when used for irrigation, but there are questions about the adequacy of that treatment. Some leading scientists in the main water society, AWWA (American Water Works Association), have long believed that secondary treatment is insufficient to protect

people against pathogens, and recommend adding at least membrane filtration, reverse osmosis, ozonation, or other advanced treatments for irrigation water (Rose et al., 2004).
The WHO (2006) lists treatment processes and their efficiency in terms of pathogen reduction (Tab. 3).

Tab. 3: Log unit reduction or inactivation of excreted pathogens by selected wastewater treatment processes (all references cited in WHO, 2006)

Treatment process	Log unit pathogen removals[a]			
	Viruses	Bacteria	Protozoan (oo)cysts	Helminth eggs
Low-rate biological processes				
Waste stabilization ponds	1–4	1–6	1–4	1–3[b]
Wastewater storage and treatment reservoirs	1–4	1–6	1–4	1–3[b]
Constructed wetlands	1–2	0.5–3	0.5–2	1–3[b]
High-rate processes				
Primary treatment				
Primary sedimentation	0–1	0–1	0–1	0–<1[b]
Chemically enhanced primary treatment	1–2	1–2	1–2	1–3[b]
Anaerobic upflow sludge blanket reactors	0–1	0.5–1.5	0–1	0.5–1[b]
Secondary treatment				
Activated sludge + secondary sedimentation	0–2	1–2	0–1	1–<2[b]
Trickling filters + secondary sedimentation	0–2	1–2	0–1	1–2[c]
Aerated lagoon + settling pond	1–2	1–2	0–1	1–3[c]
Tertiary treatment				
Coagulation/flocculation	1–3	0–1	1–3	2[b]
High-rate granular or slow-rate sand filtration	1–3	0–3	0–3	1–3[b]
Dual-media filtration	1–3	0–1	1–3	2–3[b,d]
Membranes	2.5–>6	3.5–>6	>6	>3[b,d]
Disinfection				
Chlorination (free chlorine)	1–3	2–6	0–1.5	0–<1[b]
Ozonation	3–6	2–6	1–2	0–2[e]
Ultraviolet radiation	1–>3	2–>4	>3	0[e]

Sources: Feachem et al. (1983); Schwartzbrod et al. (1989); Sobsey (1989); El-Gohary et al. (1993); Rivera et al. (1995); Rose et al. (1996, 1997); Strauss (1996); Landa, Capella & Jiménez (1997); Clancy et al. (1998); National Research Council (1998); Yates & Gerba (1998); Karimi, Vickers & Harasick (1999); Lazarova et al. (2000); Jiménez et al. (2001); Jiménez & Chávez (2002); Jiménez (2003, 2005); von Sperling et al. (2003); Mara (2004); Rojas-Valencia et al. (2004); WHO (2004a); NRMMC & EPHCA (2005).

[a] The log unit reductions are $\log_{10}$ unit reductions defined as $\log_{10}$ (initial pathogen concentration/final pathogen concentration). Thus, a 1 log unit reduction = 90% reduction; a 2 log unit reduction = 99% reduction; a 3 log unit reduction = 99.9% reduction; and so on.

[b] Data from full-scale plants.

[c] Theoretical efficiency based on removal mechanisms.

[d] Data from tests with up to 2 log units initial content; removal may be greater than that reported.

[e] Data from laboratory tests.

Also more recent literature is in line with the removal rates given above. Cheng et al. (2009) investigated the fate of *Cryptosporidium parvum* and *C. hominis* oocysts and *Giardia duodenalis* cysts at four Irish municipal wastewater treatment plants and found that cysts are present throughout the wastewater processes and in end-products, and that 64% to over 97% of viable oocysts and cysts were eliminated in the final effluent. All sewage sludge samples were positive for *C. parvum* and *C. hominis*, and *G. duodenalis*, with maximum concentrations of 20 oocysts and eight cysts per gram in primary sludge indicating the need for further sludge sanitization treatments. Wen et al. (2009) investigated the removal of pathogenic microorganisms and their indicators in a laboratory scale biological treatment system that simulated the secondary treatment process of a wastewater treatment plant (WWTP). Four groups of microorganisms including bacteria, viruses (MS-2 bacteriophage), protozoa and helminths as well as the selected indicators (total coliforms, enterococci and particles <2.73 µm/L) were employed in the investigation. The results demonstrated that approximately 2-3 log10 removal of the microbial indicators was achieved in the treatment process. Ellouze et al. (2009) compared the removal efficiencies of pathogens such as salmonella (S), helminths ova (H), protozoan cysts (P), total coliforms (TC), faecal coliforms (FC) and faecal streptococci (FS), micro-toxicity and phyto-toxicity by three treatment processes: aerated lagoon (AL), activated sludge (AS) and anaerobic membrane bioreactor (MBR). The anaerobic MBR allowed an effective removal of 100% for all the microorganisms tested. The average removal of TC, FC, FS, S, H and P was 1.65 $\log_{10}$, 1.42 $\log_{10}$, 1.23 $\log_{10}$, 0.91 $\log_{10}$, 52.23% and 76.15% in AL system and 0.62-0.84 $\log_{10}$, 0.87-0.93 $\log_{10}$, 0.71-0.78 $\log_{10}$, 0.81-2.71 $\log_{10}$, 59-74.1% and 59.84-72.2% in AS processes, respectively. The anaerobic MBR showed also a high efficiency in removing toxicity. In other studies membranes – even microfiltration – indicated excellent removal rates for microbes and viruses.

The treatment for the **use of sewage sludge** in agriculture requires biological, chemical or heat-treatment, long term storage and any other appropriate process to reduce fermentability and health hazards associated with its use.
I terms of human and environmental health recently, there is increasing concern about:

- the spread of multi-drug resistant pathogens in the environment or about fragments from cell walls which are not alive and not affected by disinfectants. This intact genetic material can transfer both virulence and drug resistance to living micro-organisms in water or soil.
- organic chemicals, including endocrine disruptors in wastewater
- or pharmaceuticals.

In **future water management** should shift from a supply driven approach to water demand management as this is a way to get the most out from limited supplies by using water efficiently and promoting conservation as a response to scarcity instead of seeking new sources of supply from already overtaxed water resources. This also includes the use of treated wastewater where it is possible to offset the demand for fresh supplies. Reusing wastewater has a high potential of risk related to the presence of pathogens. Therefore wastewater streams need to be either treated properly to achieve 6 – 7 log reductions of viruses and 3 log reductions of helminths or appropriate combinations of application strategies. For water scarce rural areas separating wastewater into its black water and greywater components and the separate treatment according to the guidelines could be beneficial.

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WATER REUSE IN SPAIN: DATA OVERVIEW AND COSTS ESTIMATION OF SUITABLE TREATMENT TRAINS

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Abstract

Until now, there has not been a compilation of data concerning the reuse of treated effluent in Spain. Since January 2005 and at the request of the Ministry of Environment, the Centro de Estudios y Experimentación de Obras Públicas (CEDEX) has been preparing a Database with information regarding the reuse activities in every Autonomous Region. This information compiles the types and characteristics of regeneration treatments adopted for various uses and the places where regenerated water is being used. In addition, it includes tertiary treatment under construction and future projects as well, which have been gathered together from different sources such as River Basin District Plans or Autonomous Region Reuse Programs. This whole laborious job is composed of four main parts: Database design, fieldwork collection of data, checking and storage of data and to make easier the management of data, integration of this Database in Geographic Information System (GIS). This basic information is essential to develop the State Water Reuse Plan that is currently being written in Spain.

This presentation shows the main results of the Database and a proposal of regeneration treatments to meet legal requirements; especially Royal Decree 1620/2007 [1] which establishes the “legal regime for the reuse of treated municipal wastewater” where a general estimated cost of investment and operation are included. The majority of costs presented are based on real Spanish regeneration plants although there are prototype process in which costs have been calculated with additional references and using the knowledge of the authors and operators.

Roughly seventy percent of the total reuse water in Spain is dedicated to irrigation and the main treatment adopted to achieve the adequate quality for this use, according to current wastewater reuse regulation, consisting of a chemical coagulation and precipitation, granular filtration, and disinfection with ultraviolet (UV), chlorine or a combination of both. The investment cost is around €27-47 per m^3/day designed, depending on the required capacity and market conditions. Operations and maintenance (O&M); is approximately €0.06-0.09 per m^3 produced.

In addition, Database outcomes shows that nonpotable urban water requirements, industrial uses and overall environmental issues (wetland maintenance, seawater instruction and environmental flows), are increasing quickly.

This rise of regenerated water demand will serve the requirements established in European Directives as Water Framework Directive as well as satisfy a growing trend in activities with

environmental aims. However, the main purpose is the need to increase water availability in zones without enough fresh water.

1. Introduction

In Spain, three aspects have particularly enhanced the development of water reuse for ten years: a) the huge impulse given to wastewater treatment by Directive 91/271/EEC [2], which has led to the treatment of large volumes of treated effluents in areas of very high water demand; b) the development of regeneration technologies for purified effluents, which have produced reliable systems at affordable costs; and c) reuse regulation development.

The enforcement of Directive 91/271/EEC in Spain was carried out under the National Sanitation and Purification Plan (NSPP), which set up coordinated actions by the different Administrations (Central, Regional and Local). In 2007, the number of water treatment plants was 2,533 treating a volume of 3,370 Hm^3 per year (The Ministry of the Environment, 2007).

After the completion of the NSPP, the Ministry of the Environment, in collaboration with the Autonomous Communities, drew up the 2007-2015 National Plan for Water Quality, Sanitation and Purification (NPWQSP), the aim of which is to ensure compliance with Directive 91/271/EEC requirements that have not yet been met, and to implement actions stemming from the application of the Water Framework Directive. The maximum treated volume for reuse could reach 1,500 Hm^3 per year at the end of these plans.

Though the majority of reuse practices in Spain have agricultural purposes, an increasing toward reuse in environmental, recreational and urban uses has been detected recently. In addition, this volume of reclaimed water in other applications will be increase compared to irrigation water use due to Directives such as ACP (Agrarian Common Policy) which will suppose a reduction of the production and agricultural extension (Iglesias R, 2005) [3].

With respect to Spanish reuse regulations, Royal Decree 1620/2007 [1] is principle State water reuse regulation and it has represented an important advancement to standardize water reuse practices despite the large cost of implementation.

Royal Decree also contributes to the consolidation of water reuse inside the global water resources management. The regulations in Spain and Europe in general, are based on World Health Organization (WHO) and Programme for Pollution Monitoring and Research (MED POL) reuse guidelines [4-5] instead of American regulations [6-7], so health and environmental risk analysis are required to set up agreed upon of acceptable risk. Therefore, the Good Practices Manual (GPM) is being made by the Ministry of the Environmental in collaboration with the Ministry of Health to assess and manage possible risks depending on applications.

Water quality regulations on continental and maritime waters in Europe, such as the Water Framework Directive (WFD) [8] or Bathing Water Directive [9], together with the future need of more extensive treatments due to the presence of priority or emerging pollutants [10], creates an exceptional frame to reuse and an option to bear in mind. This regulation frame boosts Spanish Government to create a new scheme for reuse, taking into account current reuse practices in Spain which do not meet new water quality criteria. Consequently, the Ministry of the Environment asked CEDEX to gather the main information about water reuse through a comprehensive Reuse Database (RDB) in order to make a first approach in 2005. The final report about RDB contents was delivered to the requester in 2008.

This RDB is being used to draw up State Water Reuse Plan (SWR) that will provide adequate quantities and quality of reclaimed water in addition to an important budget to help users to fulfill legal requirements and set up new water reclamation plants together with storage and distribution infrastructures. With regard to the budget, this paper shows any general costs which are being used to implement the SWR as well.

Finally, reuse of treated effluents provides a regular supply to users and aids to assure the quality from sanitary point of view as well as environmentality. To tackle these issues, it will be necessary to carry out and to study adequate technologies, in depth, for different population segments, both for wastewater treatment and for the reclaimed water.

2. Development and contents of Spanish Reuse Database

The RDB contains not only a summary of water reuse systems, but also stores all available information through table connections shown in Figure 1. According to the terminology in Royal Decree 1620/2007 of 7 December which establishes the legal regime for the reuse of treated water, in accordance with article 2, the following definitions must be taken into account:

a. Water reuse: the use of water, before it is returned to the public water resource and public coastal resource area, for a new exclusive use, after having been put to the use for which it was diverted, having undergone the treatment process or processes established in the corresponding discharge authorisation and that are necessary for attaining the required quality according to the uses for which it is intended.
b. Treated water: wastewater that has undergone a treatment process after which it complies with the quality required by the applicable discharge regulation.
c. Reclaimed water: treated wastewater that has undergone an additional or complementary treatment process if required, following which the quality is appropriate for the use for which it is intended.
d. Water reclamation plant: the group of facilities in which treated wastewater undergoes additional treatment processes that may be necessary to ensure that the quality is appropriate for the use for which it is intended.
e. Storage and distribution infrastructures: the group of facilities used to store and distribute reclaimed water to the use point through a supply pipeline network or using public and privately-owned mobile tanks.
f. Water reuse system: the group of facilities, including the water reclamation plant, if there is one, and the infrastructures for the storage and distribution of reclaimed water to the user supply point, with the defined amount and quality according to the planned uses.
g. First user: physical or legal entity that holds the concession for the first use of the diverted water.
h. Reclaimed water user: physical, legal or public entity that uses reclaimed water for the anticipated use.
i. Treated water supply point: point at which the holder of the wastewater discharge authorisation supplies the treated water in the quality conditions stipulated in the discharge authorisation for its reclamation.

j. Reclaimed water supply point: point at which the holder of the water reuse concession or authorisation supplies the reclaimed water to a user, in line with the quality conditions according to its use as laid down in Royal Decree 1620/2007.
k. Reclaimed water use point: area or facility in which the reclaimed water supplied is used.
l. Self-monitoring: an analytical control programme for the correct operation of the reuse system, carried out by the water reuse concession or authorisation holder.

The first step was to develop a tab questionnaire, as shown in Figure 2, which provided the data that the Ministry of the Environment considered of interest to obtain a reliable overview of reuse in Spain. The information is structured in three sections:

A) General data of system reuse and concession or authorization requirements: This section is split into two distinct tiers: The first tier includes general data such as the date of completion of the questionnaire, who owns and manages the water reclamation plant, and which autonomous region, municipality, town and area the plants are located. The second tier includes other data relating to the permissions associated with the water reuse system, the reclaimed water volume and uses permitted and the location of application and consumption of water reuse.
B) Information concerning the wastewater treatment plants (WWTP). This section lists basic information about the treatment plants that supply water reuse as name, type of treatment, designed and treated volume and the treated effluent quality in four basic parameters; BOD_5, suspended solids, turbidity and electrical conductivity.
C) Data relating to the water reclamation plant: This section is developed in several parts. The first includes the installation code, location, state of water reclamation plant (is it operating, under construction or planned), the date of implementation, capacity, delivery point, and the number of days per year that the plant is in operation. The second is devoted to the treatment or processing of treated water to make it reusable. This includes all types of regeneration technologies that are installed or planned in the Spanish water reuse systems. The third part includes reclaimed water quality. The parameters which are established by Royal Decree 1620/2007 are intestinal nematodes, Escherichia coli, suspended solids, turbidity, BOD_5 and other parameters such as electrical conductivity are stored as well. The fourth stores investment and O&M costs.

All the above mentioned information were turned into data fields of the RDB, and can be stored by reclaimed water users. However, it is uncommon for users to have all information.
Following field creation, questioner development, and data capture was carried out during 2005-2006 in the regions of Murcia and Valencia and during 2006-2007 the rest of the Autonomous Communities.

The development of the pre-work tasks of the RDB was made as follows:
1. Presentation of RDB project to management users at different levels, basin departments, municipalities, and state and local entities responsible for checking or running water reuse systems.
2. Analysis of data of concessions and authorization from Basin departments and Autonomous entities are the main information supplier.
3. Planning visits. First contacts (managers or operators of the different water reclamation plants), getting the appropriate permissions and reviewing dates received in- site. Main applications are visited.

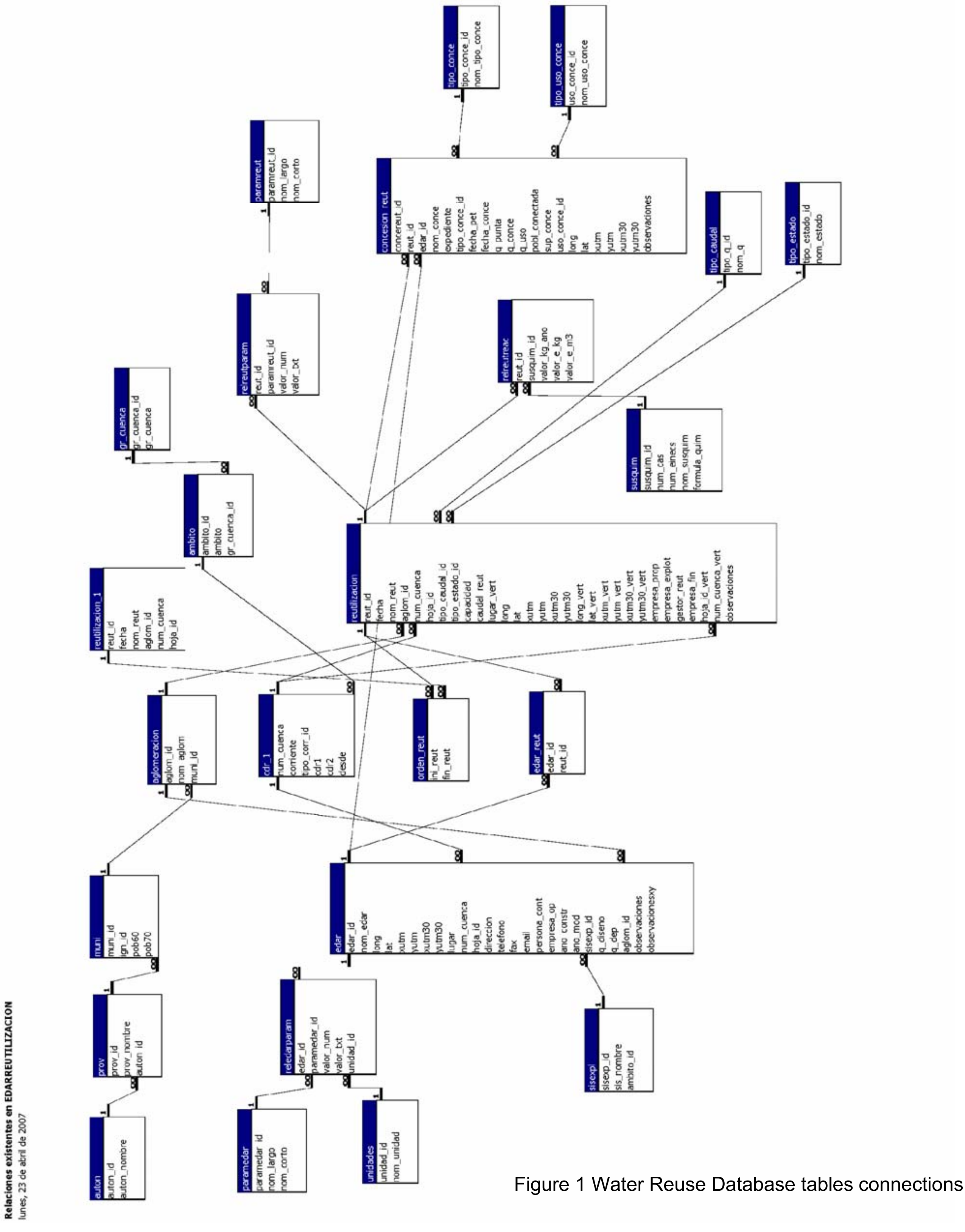


Figure 1 Water Reuse Database tables connections

The RDB was designed to allow the data integration from other Databases that belong to CEDEX or the Ministry of the Environmental, such as the WWTP Database.

The CEDEX IT department developed a GIS compatible with the geographic information available at the Center for Hydrographic Studies to view the different layers of information drawn from the database and available for reuse. Web applications have also been developed allowing access of the RDB for updating records.

"State of the reuse of treated effluent in Spain" is an internal report based on the RDB data and delivered by CEDEX to the Ministry of the Environmental last year. It gives an overview of the status of water reuse in Spain by Basin Departments and Autonomous Communities.

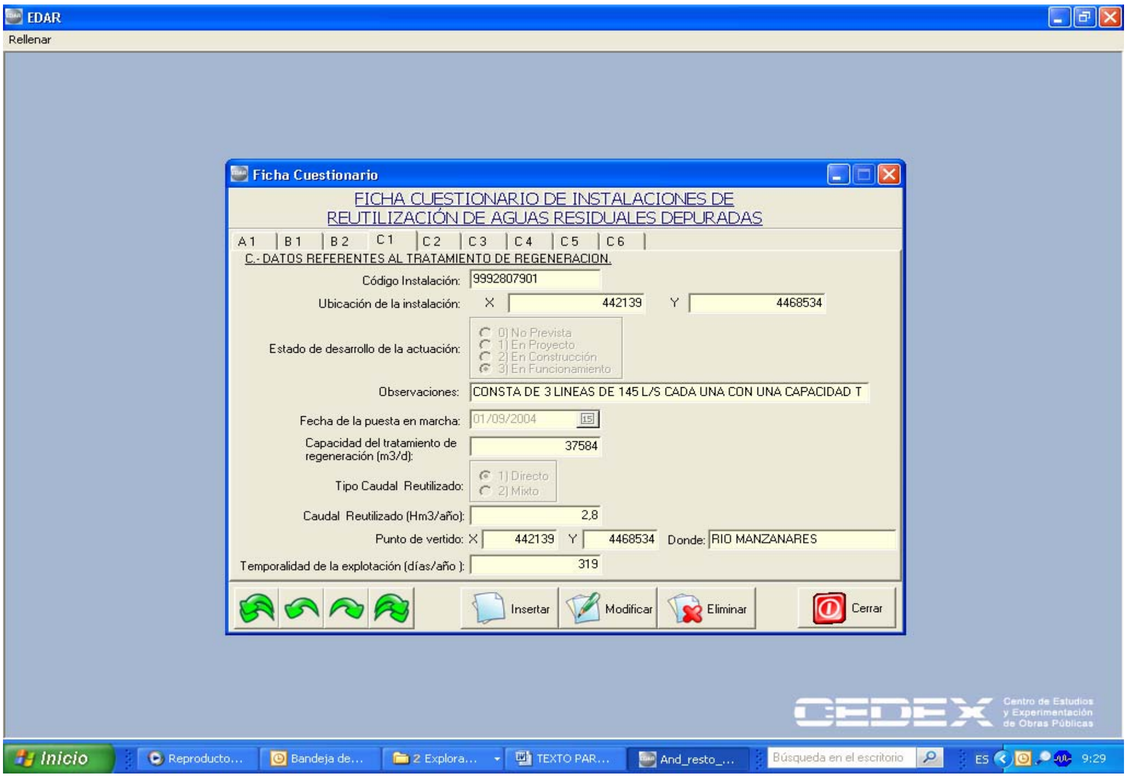


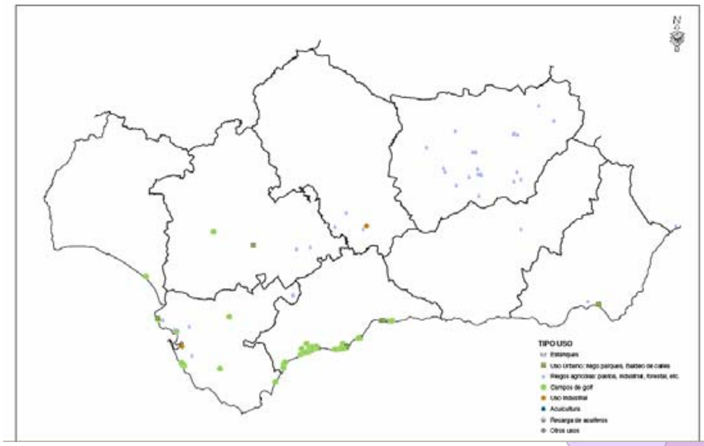
Figure 2 Tab-questionnaire used for data input to database

The design of the RDB had to be adapted while data collection was made to include different reuses practices. MS Access and Visual Basic for Applications (VBA) were used to store and check the collected information.

The GIS layers related to RDB currently available are: rivers, dams, basins, municipal, provincial and autonomous boundaries, geographic reference of WWTPs and water reclaimed plants.

GIS allows the user to obtain data in different formats (tables, graphs, etc.). The development program for GIS is ArcGIS (version 9.2).

Through a dialog box, and depending on the outcome you want to export, the application will present a number of options in ArcGIS maps, Figure 3, and tables in ASCII or dBASE.



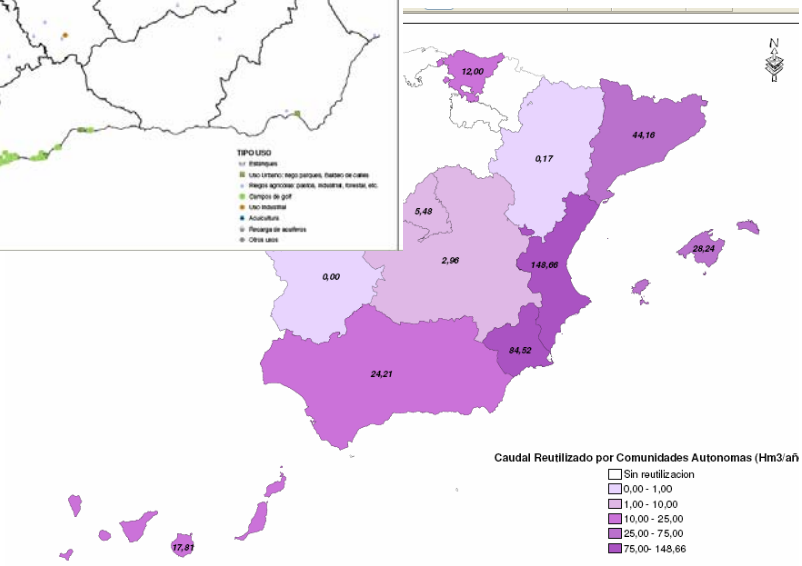
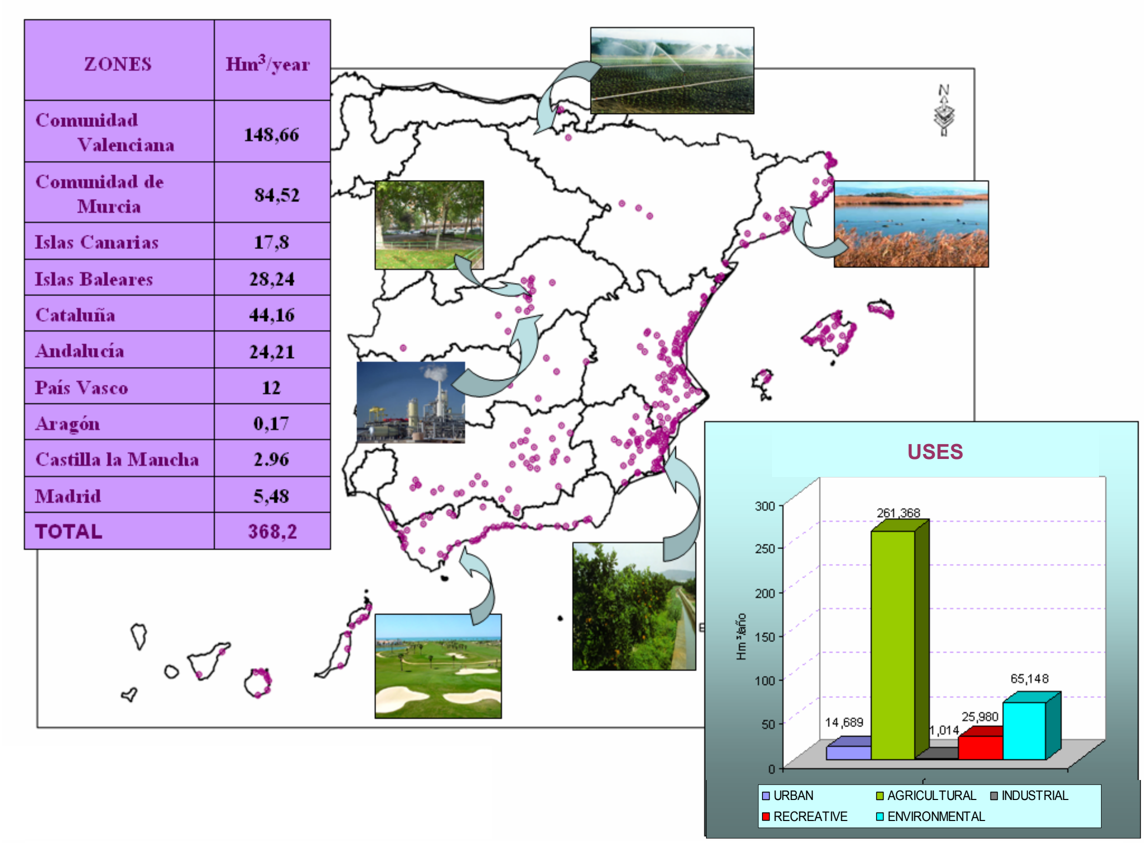


Figure 3 Views from ArcGIS maps

3. State of Water Reuse in Spain

According to the information from the RDB, gathered by the CEDEX for the Ministry of the Environment (RDB, 2005-2007), the number of existing reuse systems in Spain is 322 and the volume of reclaimed water is 368,2 Hm^3 per year, which is about 10,6% of the total treated wastewater volume. Although reused water only accounts for a small percentage of the total Spanish water demand, in some areas, like the Canary Islands, Valencia or Murcia, this percentage is quite high, meaning that water there has become a strategic non-conventional resource. The breakdown by zones, reuse system locations and uses percentages are shown in Figure 4 and Figure 5, it is observed agricultural irrigation is the most frequent use, although the percentage of environmental or urban use are increasing recently.

The future of water reuse is essentially focused on the coastal areas of the Mediterranean and South-Atlantic Arc, and the Balearic and Canary Islands together with singular places inland, for instance Madrid and Vitoria-Gaztei. Such expectations are due to strong urban and tourist population growth and agricultural or industrial development, which entail a greater demand for water. Also to the difficulty in obtaining additional resources within an acceptable distance, in view of the depletion and deterioration of traditional supply sources, along with the progressive salination of aquifers and the frequent droughts that affect these areas severely.



ZONES	Hm^3/year
Comunidad Valenciana	148,66
Comunidad de Murcia	84,52
Islas Canarias	17,8
Islas Baleares	28,24
Cataluña	44,16
Andalucía	24,21
País Vasco	12
Aragón	0,17
Castilla la Mancha	2.96
Madrid	5,48
TOTAL	368,2

Figure 4 Locations and volume per year of water reuse broken down by regions and uses.

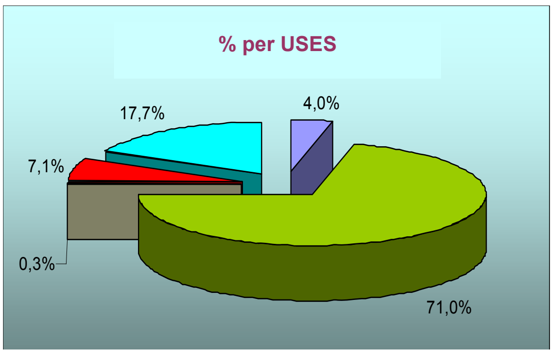


Figure 5 Percentages over total water reuse volume by uses.

Only 61% of the total volume reused in Spain has suitable reclaimed water treatment processes which could meet Royal Decree 1620/2007 requirements. The rest of the volume for water reuse has to be adapted to quality criteria in the coming years. At this moment, the least treated water reuse application is agricultural irrigation using effluent from secondary wastewater treatment plants and sometimes without treatment in specific rural zones. Each water reuse system will be unique because it has to be designed to meet local conditions. The technologies and systems are determined by many factors, including wastewater characteristics, users, and geography. (Asano, T., 2007) [11].

The volume of reclaimed water was 447.34 Hm^3 in 2008 according to the Ministry of Environmental based on data from Basin department's sources.

The different reclaimed water treatments in Spain are described in Table 1 where Technologies and process for removing salt are also included.

Of the 149 water reclamation plants operating in Spain in 2006, 12% of these plants have only a disinfection treatment, while the rest have minimum of a filtration treatment before disinfection treatment. However, the percentage of process made up of physical-chemical treatment via settling then sand filtration followed by disinfection, has growth recently. The process most wide spread in Spain consists of sand filtration then disinfection for control of biofilm in the distribution system. This alternative treatment processes is mostly used in agricultural applications.

Table 1 Summary of treatments to obtain reclaimed water in Spain. Number of water reclamation plants (ERAs) and the percentage of total lines broken down by treatment processes.

TREATMENT PROCESSES USED FOR RECLAIMED WATER					
WITHOUT DESALINATION	Nº	%	WITH DESALINATION	Nº	%
F + D	58	39,0	**F + EDR**	4	2,6
P/C + F + D	28	18,9	**P/C + F + EDR+ D**	2	1,4
F + M	8	6,0	**M + EDR**	1	0,7
P/C + F + M	1	0,7	**M +RO**	2	1,4
MBR	2	1,4	**MBR + RO**	1	0,7
NS	18	12,0	**F +M + RO**	4	2,6
D	18	12,0	**P/C + M + RO**	1	0,7
			P/C + F + M + RO	1	0,7
Total	**133**	**89,3**	**Total**	**16**	**10,7**

LEGEND: F = Filtration; P/C = Physical-chemical with settling; M: Filtration with Membranes; NS = Natural Systems; D = Disinfection; EDR= Electro-dialysis reversal; RO: Reverse Osmosis; MBR: Membrane Bioreactor.

Today, a physical-chemical treatment followed by sand filtration together with ultraviolet radiation or chlorination as disinfection treatments is the most regular water reuse train to meet any application in Spain, with the exception of direct aquifer injection where membranes treatments are included. Filtration is not sufficient pre-treatment to achieve suitable disinfection in some applications according to water reuse criteria or when treated wastewater has not constants features, so physic-chemical treatment is being to be used as safety measure. In addition, this treatment removes nutrients if it is necessary.

The technologies discussed above used for water reclamation in Spain achieve great removal of measurable constituents, but in response to dissolved solids, pathogenic organisms, or trace constituents, membrane processes are now being used to avoid possible environmental or health risks.

Systems with desalination processes represent 13% of the total water reclamation plants. They are located mainly in the Canary Islands. The treatment processes include filtration via ultrafiltration or microfiltration followed by reverse electro dialysis (EDR) or reverse osmosis membrane, and disinfection.

4. Spanish Treated Wastewater Reuse Regulations

At the national level, the reuse of treated wastewater is governed by a revised version of the Water Act (Royal Decree 1/2001 of July 20th) [12] and older regulations about wastewater treatments [13-14], and by the Royal Decree 1620/2007, of December 7th, which establishes the legal regime for the reuse of treated wastewater. In some regions and in two Water Basin Plans, a series of laws and regulations related to water reuse have been enacted.

The Water Act provides that “the Government shall establish the basic requisites for water reuse, indicating the required quality for purified water for different uses”. Likewise, it is established that water reuse will require an administrative concession, except when the application for reuse is made by the holder of the discharge permit which originated the treatment of that water, in which case only an administrative authorization will be required.

The Regulation on Public Water Domain (Royal Decree 849/1986of April 11th) [15] defines the requisites and steps for obtaining a concession for water reuse. The decision to issue such a concession, which is a binding decision, lies with the River Basin Authority, following the compulsory report made by the Health Authorities of the Autonomous Communities.

Royal Decree 1620/2007 of December 7th, which lays down the legal regime for the reuse of treated wastewater, establishes both the basic requisites for water reuse, and the necessary procedures to obtain the concessions and authorizations.

It has taken many years to implement the regulations on the basic requisites for water reuse. During this time, the requisites for water reuse have been established by the River Basin Authorities, in each concession, and this has led to differing criteria as regards the quality specifications for reclaimed water for each different use as well as a lack of equity regarding the obligations imposed on concession holders.

The Royal Decree 1620/2007 has been a considerable step forward in the regulation of water reuse, as it clarifies both the responsibilities of the Public Administrations and those of concession holders and end users, establishing permitted uses and quality criteria, the minimum frequency of sampling, the benchmark for analytical methods and the conformity criteria. It also specifies the procedures related to the concession, including an application form to obtain the concession or authorization for water reuse.

The quality criteria for reclaimed water are shown in Table 2, which differentiates 14 uses under five main headings: 1) Urban, 2) Agricultural Irrigation, 3) Industrial, 4) Recreational and 5) Environmental. The reuse of treated wastewater is forbidden for the following purposes: a) for human consumption, except in situations of declared disasters; b) for the specific uses of the food industry; c) for use in hospital installations; and other similar uses; d) for the breeding of filtering mollusks in aquaculture; e) for recreational use as swimming waters; f) for use in fountains and ornamental waters in public spaces or inside public buildings; g) for any other use that the Health Authorities may deem to be a hazard to human health. Use in refrigerating towers and evaporation condensers, is subject to very stringent requisites, and forbidden in urban areas and in places with public or commercial activities.

Table 2 Quality criteria for the reuse of treated effluent reuse. Maximum allowed values (Royal Decree 1620/2007, December 2007)

Wastewater reclamation Uses	**Maximum allowed values**				**Other Criteria**
	Intestinal nematode eggs	*Escherichia Coli* CFU/100 ml	Suspended Solids mg/L	Turbidity NTU	
1.- URBAN USES					
QUALITY 1.1 Residential: a) Private garden watering. b) Discharge of bathroom appliances	1 egg /10 L	0	10	2	*Legionella* spp. 100 CFU/L (in the case of aerosol hazards) *Other contaminants*(1)
QUALITY 1.2 Urban services: a) Watering of urban green areas (parks, sports grounds, etc.) b) Hosing down streets. c) Fire-fighting systems. d) Industrial car wash	1 egg / 10 L	200	20	10	
2.- AGRICULTURAL USES					
QUALITY 2.1. **a) Irrigation of fresh food crops for human consumption, through water application systems allowing for direct contact of regenerated water with edible parts.**	1 egg /10 L	100	20	10	*Legionella* spp. 1000 CFU/L (in the case of aerosol hazards) Presence/absence of pathogens *Other contaminants*(1)
QUALITY 2.2 a) Irrigation of crops for human consumption, through water application systems not avoiding direct contact of regenerated water with edible parts, but not for consumption as fresh food since there is subsequent industrial treatment. b) Irrigation of pastureland for milk or meat-producing animals. c) Aquaculture	1 eggs /10 L	1,000	35	No limit set	*Taenia saginata* and *Taenia solium* 1 egg / L (In irrigation of crops for consumption by meat producing animals) Presence/absence of pathogens *Other contaminants*(1)

QUALITY 2.3 a) Localised irrigation of ligneous crops impeding contact of regenerated water with food for human consumption. b) Irrigation of ornamental flowers, greenhouses and nurseries with no direct contact of regenerated water with crops. c) Irrigation of industrial crops, greenhouses, fodders stored in silos, cereals and oleaginous seeds.	1 egg /10 L	10,000	35	No limit set	*Legionella* spp. 100 CFU/L *Other contaminants*(1)
3.- INDUSTRIAL USES					
QUALITY 3.1 a) Process and cleaning water except in food industry. b) Other industrial uses	No limit set	10,000	35	15	*Legionella* spp. 100 CFU/L *Other contaminants*(1)
c) Process and cleaning water for use in food industry.	1 egg /10 L	1,000	35	15	*Legionella* spp. 100 CFU/L Presence/absence of pathogens *Other contaminants*(1)
QUALITY 3.2 a) Refrigeration towers and evaporation condensers	Absence	Absence	5	1	*Legionella* spp. Absence CFU/L Industrial use exclusively far from urban areas. Authorization is subject to the approval of the Health Authority responsible for the relevant control under RD 865/2003
4. - RECREATIONAL USES					
QUALITY 4.1 a) Irrigation of golf courses	1 egg /10 L	200	20	10	If irrigation water is applied directly onto the soil (drip, micro-spray) the QUALITY 2.3 criteria are applicable. *Legionella* spp. 100 CFU/L (in the case of aerosol hazards) *Other contaminants* (1)
QUALITY 4.2. a) Ponds, bodies of water and running water with no public access	No limit set	10,000	35	No limit set	Total phosphorus: 2 mg P/L (in stagnant water) *Other contaminants* (1)

5.- ENVIRONMENTAL USES

QUALITY 5.1. a) Recharge of aquifers by localised seepage through the soil	No limit set	1,000	35	No limit set	Total nitrogen: 10 mg N/L NO_3^-:: 25 mg NO_3^-/L
QUALITY 5.2. a) Recharge of aquifers by direct injection	1 egg /10 L	0	10	2	Art. 257 to 259 of Royal Decree 849/1986
QUALITY 5.3. a) Irrigation of forests, green zones and similar areas with no public access b) Forestry	No limit set	No limit set	35	No limit set	*Other contaminants* (1)
QUALITY 5.4. a) Other environmental uses (maintenance of wetlands, minimum flows and similar uses)	The minimum quality required is studied on a case by case basis				

NOTE (1):
The liberation into the environment of the Other Contaminants contained in the wastewater discharge authorisation must be limited (See Annexe II of Royal Decree 849/1986, of 11 April). In the case of hazardous substances (See Annexe IV of Royal Decree 849/1986, of 11 April, modified by Royal Decree 606/2003, of 23 May), compliance with the Environmental Quality Regulations must be ensured (See Article 245.5 of Royal Decree 849/1986, of 11 April, modified by Royal Decree 606/2003, of 23 May).

Minimum acceptable limits are established for each type of use under the following parameters: intestinal nematode eggs, Escherichia coli, suspended solids and turbidity. Furthermore, the following parameters have been added: a) Legionella spp. for use in industrial refrigerating systems or in case of hazards due to aerosols, pursuant to Royal Decree 865/2003, [16]; b) Taenia saginata and Taenia solium, in the case of irrigation of pastureland for milk or meat-producing animals; c) total phosphorus for environmental and recreational uses (pools, water bodies and running watercourses); d) total nitrogen in the case of groundwater recharge.

The implementation of these regulations, which impose rigorous quality requirements for reclaimed water, will make it necessary to adapt an important part of the current reuse systems [17-20]. The regulation itself sets a 2-year deadline for the current systems to comply with the requisites of the Royal Decree 1620/2007.

5. Technologies and Systems for Water Reclamation according to Royal Decree 1620/2007 Quality Standards. Treatment Trains and Costs broken down by Applications

The development of programs for planned reuse of wastewater has spurred The Ministry of Environment to study technology issues and important factors in the selections of treatment processes for water reuse [21].During 2008, Department of Wastewater Treatments, Reclamation and Reuse of CEDEX was working on the treatment trains efficiency to meet different applications criteria regulated by Royal Decree 1620/2007 as to estimate costs based on running water reclamation plants set up in Spain.

Therefore, the purpose of this chapter is to provide the selection of technologies for water reuse applications, described in Table 2, providing suitable treatment trains which are based on the experience of Spanish water reclamation plants. This also serves as an introduction to

first view to modify or upgrade existing water reclamation plants as well as how to design new ones according to RD 1620/2007 requirements.
To establish a typical treatment process flow diagram based on different uses and quality criteria, 14 applications listed on the RD 1620/2007 were divided into groups in terms of bacteriological requirements [22].

Table 3 shows 6 quality groups (A, B, C, D, E and F), taking into account the limits set out primarily with respect to Escherichia coli, and then other standards such as intestinal nematodes and Legionella spp.

Table 3 Quality groups according to the bacteriological limits established on the RD 1620/2007

APPLICATIONS		Quality	Escherichia Coli CFU/100 ml	Intestinal nematode eggs /10 L	Legionella spp. 100 CFU/L
Industrial 3.2 a)	Refrigeration towers and evaporation condensers.	A	Absence	Absence	Absence
Residential 1.1 a) y b)	Private garden watering. Discharge of bathroom appliances.		Absence	1	100
Direct Recharge 5.2 a)	Recharge of aquifers by direct injection.		Absence	1	No limit set
Urban services 1.2 a), b), c) y d)	Watering of urban green areas Hosing down streets. Fire-fighting systems. Industrial car wash.	B	100 -200	1	100
Irrigation crops 2.1 a)	Through water application systems allowing for direct contact of regenerated water with edible parts.				
Recreational 4.1 a)	Irrigation of golf courses.				
Agricultural uses 2.2 a), b) y c)	Irrigation of crops for human consumption not avoiding direct contact of regenerated water with edible parts. Irrigation of pastureland for milk or meat-producing animals. Aquaculture.	C	1.000	1	No limit set
Industrial 3.1 c)	Process and cleaning water for use in food industry.		1000	1	100
Indirect Recharge 5.1 a)	Recharge of aquifers by localised seepage through the soil.		1.000	No limit set	No limit set
Agricultural uses 2.3 a), b) y c)	Localised irrigation of ligneous crops impeding contact of regenerated water with food for human consumption. Irrigation of ornamental flowers, greenhouses and nurseries with no direct contact of regenerated water with crops. Irrigation of industrial crops, greenhouses, fodders stored in silos, cereals and oleaginous seeds.	D	10.000	1	100
Industrial 3.1 a) b)	Process and cleaning water except in food industry.				
Recreational 4.2 a)	Ponds, bodies of water and running water with no public access				
Environmental 5.3 a) y b)	Irrigation of forests, green zones and similar areas with no public access.	E	No limit set	No limit set	No limit set
Environmental 5.4 a)	Maintenance of wetlands, minimum flows and similar uses.	F	The minimum quality required is studied on a case by case basis		

In selecting appropriate treatment operations and processes for water reuse applications, the provision of multiple barriers is an important consideration when planning general water reuse systems. With the increased reuse treatment knowledge over the past 10 years in Spain, Department of Wastewater Treatments, Reclamation and Reuse of CEDEX has selected treatment trains to meet current regulations even though some of these treatment process flow diagrams are not set up in any water reclamation plant today.

Nitrogen or phosphorus limits have to be taken into account in some applications such as ponds and water circulating uses where PT <2 mg P/L is required or aquifer recharge use whose limits in nitrogen are NT < 10 mg N/L and NO_3 <25 mg/L. That means unit process in which these constituents are removed by chemical or biological reactions must be included.

Thus, proposals of treatment trains which achieve different quality groups are shown in Tables 4-5.The general categories of treatment trains discussed in this chapter, attempt to approach and summarize treatments. However, in depth analysis of the features should be done for each case. The majority of suggested treatment trains are in operating water reclaimed plants.

Table 4 Treatment processes flow diagram without desalination that can be met RD 1620/2007 requirements by quality groups

Quality	Type	Treatment train without desalination
A	1	Chemical precipitation[1], filtration with membranes[2] and Disinfection (residual chlorine may be needed in distribution system) Type 2 can achieve quality A about E. coli, Legionella spp and intestinal nematodes standards but it is difficult to achieve turbidity limit that sets in 1-2 NTU. Recharge of aquifers by direct injection is being used treatment train 5a [3]
B	2	Chemical precipitation, depth filtration and disinfection (ultraviolet radiation together with chlorination) ; residual chlorine may be needed in distribution system
C	3	Filtration and disinfection (tendency to use ultraviolet radiation followed by residual chlorine)
D		
E	4	Filtration [4]
F	-	It is studied on a case by case.

[1] Physical-chemical treatment with a lamella settling system. With regular concentrations of constituents in treated wastewater which are meeting RD 11/1995 requirements [13], this unit operation can be omitted.
[2] Cases studied have ultrafiltration.
[3] All treatment trains in Spain include RO to remove nutrients and trace constituents.
[4] With regular treated wastewater quality standards but it is recommended any surface or depth filtration for distribution system management.

Table 5 Treatment processes flow diagram with desalination that can be met RD 1620/2007 requirements by quality groups

Quality	Type	Treatment train with desalination
A-F	5a	Chemical precipitation[5] , Filtration, Filtration with membranes[6], RO desalination and residual chlorine.
B, C ,D, E	5b	Chemical precipitation[7], Filtration[8], EDR desalination and Disinfection (tendency to use ultraviolet radiation followed by residual chlorine)

6. Establishment and Operation Cost of Selected Treatment Trains

Table 6 shows the costs of treatment trains listed in Tables 4-5. The values were based on information from departments of water resources and operators of water reclamations plants. Costs have been calculated from tenders and current contracts. In operation and maintenance costs mainly staff and routine analysis are included. In addition, energy, chemicals, and spares are included as well, but VAT, amortization and all analytical established on RD 1620/2007 are not included in the following costs because most of the water reclamation plants are adapting to the new regulation.

Table 6 Costs of treatment train filtered through one implementation and one operation

Treatment train	Costs	
	Establishment	Operation
	€/($m^3_{designed}$/$_{day}$)	€/ ($m^3_{produced}$)
Type 1	164 - 351	0,14 - 0,20
Type 2[9]	27- 47	0,06 - 0,09
Type 3	9 - 22	0,04 - 0,07[10]
Type 4	5 - 11	0,04 - 0,07
Type 5.a	259 - 458	0,35 - 0,45[11]
Type 5.b	248 - 405	0,35 - 0,45[12]

[5] Physical-chemical treatment with a lamella settling system.
[6] Typical process flow diagrams incorporating membranes before RO as protective barrier.
[7] Physical-chemical treatment with a lamella settling system.
[8] Double depth filtration with continuous washing is being used.
[9] This treatment train is used for industrial applications 3.1a), b) and c) due to E. coli and Turbidity requirements.
[10] Disinfection means €0.005 per m^3 produced so this unit process is not seen in the displayed value.
[11] Cases where physical-chemical treatment operation can be left out, cost may be ranging from €0.30 to €0.40 per m^3 produced.
[12] Cases where physical-chemical treatment operation can be left out, cost may be ranging from €0.30 to €0.40 per m^3 produced.

Such broad displayed ranges are due to the different sizes of water reclamation plants, climatic and geographical conditions and inlet treated water features that have been assumed to make these estimated costs.

In treatment train selection, important factors and issues that must be considered include process flexibility, operating and maintenance requirements as well as chemical supplies and personnel. To propose the following six types of treatment broken down by health standards, the priority selected factor was to make sure the quality criteria required on RD1620/2007[1]. Some of these processes may necessitate special operational skills, thus requiring training of the existing staff or adding new personnel.

Summary of suitable treatment trains for which estimated cost has been calculated:
Type 1: Physical-chemical treatment with a lamella settling system, depth filtration, ultrafiltration, and disinfection.
Type 2: Physical-chemical treatment with a lamella settling system, depth filtration, and disinfection.
Type 3: Filtration, and disinfection.
Type 4: Depth filtration.
Type 5a: Physical-chemical treatment with a lamella settling system, depth filtration, ultrafiltration, reverse osmosis, and residual chlorine.
Type 5b: Physical-chemical treatment with a lamella settling system, double depth filtrations, electrodialysis, and disinfection.

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TREATED WASTEWATER REUSE FOR SUSTAINABLE WATER RESOURCES MANAGEMENT IN MEDITERRANEAN COUNTRIES

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Themes object of this paper concern Treated wastewater reuse for sustainable water resources management in Mediterranean countries region where the problem of water scarcity is continuously aggravating: while the renewable water resources decrease, the demand for potable water is increasing due to population growth and increasing economic activities. One of the most important future options for a sustainable management of water resources in the Mediterranean is the reuse of treated wastewater. Wastewater reuse management is one of the challenges that all Mediterranean countries will have to deal with in the coming decades. Therefore, these countries need water strategies that have to take into account alternative measures to cope with this situation. Wastewater reuse is one of the essential options for Mediterranean countries for the development of their national water policies and strategies.

In order to reduce the environmental and health impacts of wastewater reuse, several Mediterranean countries have adopted several standards and guidelines that differ from each other even at the regional level. Practice of wastewater reuse mainly depends on a country's economy, infrastructural status covering wastewater treatment capacity and capability, educational level, climate, water supply, balance between water requirement and demand, intensity of agricultural activities, population, social habits like cultural and religious prejudice, and many other factors.

In the region the current trend is related to the intensification of wastewater reuse: it can be used two or three times before being rejected into the natural environment. The treatment and the re-use of wastewater resources are the key components of the water management regarding their economic and ecological advantages. Indeed wastewater recycling is twice less expensive than the desalination of sea water. In spite of the reduction of the cost of this technology, the difference between these two solutions is still maintained because of simultaneous progress of recycling. From an environmental point of view, the benefits of this solution are also important:
- Recycling provides water resources saving at upstream level,
- It improves the reduction of waste at downstream level,
- It provides energy saving for pumping and transport of water,
- Finally, the reuse of wastewater's organic matter, in fact carbon, can provide energy that is necessary to treatment.

The innovative approach is actually not a question any more of extracting waste to obtain reusable water, but of extracting reusable water for then using the value elements contained in "waste". Therefore treated wastewater became a resource. Water extracted initially could be used at various applications, such as the irrigated agricultural, landscape irrigation or the production of drinking water, according to terms of references indicated by the end users.
The extraction of the value elements mainly relates to carbon, nitrogen, phosphorus and

sulfur. The value of these elements lies mainly in the biopolymers and energy production, being used in particular for plastic manufacture, using carbon. The nitrogen or phosphorus could also be used like fertilizers. As for reusable water, the extraction of these various elements will have to follow terms of references fixed by the end users.

This paper will give a critical overview of the new approach and practices in the reuse of treated wastewater in the Mediterranean and the implication on water resources management.

ACTIONS TOWARDS SUSTAINABLE AND SAFELY USE OF TREATED WASTEWATER IN AGRICULTURE: MOROCCO EXPERIENCES

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Since the sixties, Morocco has largely contributed to the mobilization of its hydraulic capacities in order to face the demographic increase and sustain its social and economic development. Nonetheless, and in addition to the continuation of the efforts directed to mobilization, and the control of the demand, the limited hydraulic potential requires the resort to unconventional resources (Wastewaters and brackish waters).

Due to the pronounced water deficit, the use of treated wastewater in irrigation is necessity for a better water resources economy. During the last three decades, the yearly volume of wastewaters has almost tripled. It has raised from 48 in 1960 to 600 million m^3 in 2008. It is expected that this volume may reach about 900 millions of m3 in 2020 (CSEC, 1994). These wastewaters lead to the degradation of surface and underground water resources and dangerous consequences on the potable water supply for many regions of the country.

At present, about 600 million m^3 of raw wastewaters are discharged in the natural receiving medium. Around 60% are discharged in the littoral coast; the remaining quantity is divided between draining-off and surface waters. In comparison with the conventional waters, the volume of wastewaters will never surpass 5% of the total water resources in Morocco around 2020. In addition, this volume cannot be totally mobilized

In spite of the existence of numerous processing plants, the quantity of wastewaters processed in Morocco is still weak. There are no wastewaters treatment plants in any of the large cities of Morocco at the exception of Agadir and Marrakech, while some plants have been built in medium size cities (ex. Nador, Benslimane, Boujaâd, Settat, Tiznit), in small urban centres. However, 60% of activated sludge treatment plants are out of order, due to the expensive cost of electricity, the absence of equipment maintenance and the lack of coordination between different contributors in the management of these plants.

Since early nineties, many multidisciplinary projects concerning the treatment and reuse of wastewater in irrigation have been launched in Morocco. The aim was to answer the major agronomic, health, and environmental concerns. The results of these researches have made the local communities and the regional agriculture services benefit from reliable data necessary to conceive and to size the treatment plants of wastewaters adapted to the local contexts and to disseminate the best practices for reusing treated wastewaters in agriculture.
There are four projects in Morocco considering the reuse of wastewater in conceiving the STEP: Ouarzazate (lagoon) Ben sergao (infiltration-Percolation), Benslimane (aerated lagoon) and Drarga (recycling infiltration-percolation)

The results of these works showed that the reuse of processed wastewaters can contribute to water saving, to improving agricultural products through the nutritional contribution of wastewaters and to protecting the health of the consumer and the environment.

In fact, the main objectives of these projects were to:

- Study the effects of using treated wastewaters on land, cultivations, and irrigation systems;
- Define the health criteria required for the use of treated wastewaters.
- Identify the most appropriate techniques for maximum exploitation rising treated wastewaters and the residual sludge.
- Study the efficiency of the wastewater treatment system per basin
- Follow the effects of reuse process on the environment and especially on the quality of underground waters.
- Reinforce national capacities in reusing treated wastewaters for agricultural purposes
- Exploit the results in extending the use of treated wastewaters at the national and regional level.
- Produce dimension standards for future plants
- Calculate the direct or indirect costs that come within a financial and economic analysis.

The financing of the projects concerning the construction of a processing plant constitutes the main handicap facing the realization of these projects. The majority of the projects of wastewater processing are financed by communes through state credits. Other plants have been built by way of experiment, within the framework of partnership gathering water distribution control services of the municipality. The financial contribution of International Organizations also helps in the construction of small plants in some cities and some small communes of Morocco
There are social reserves related to the use the treated waste water, (which is often perceived as unclean). This is paradoxical when one considers the quantities of waste water re-used in its raw state. Waste water goes through a processing station where influx of raw waste water is clearly visible. The origin of used water is thus known. There is therefore natural hesitation to consume fruit and vegetables irrigated with used water. In the region of Agadir, farmers whose products are exported to foreign markets are very reticent to use treated waste water in order not to compromises their markets.

In spite of the progress that has been achieved in the last decade on technical, institutional, financial and legislative levels as regards the development of the process "sewage network-Treatment-Re-use", obstacles still hinder the deployment of the re-use of treated waste water. In the current state of affairs, no project integrating the three components has been realized. This paradoxical situation is due to several constraints including Institutional Financial and legal issues

STRATEGIES FOR SUSTAINABLE REUSE IN MOROCCO
Morocco government have developed a national plan with the aim to reduce 90% of the wastewater pollution by the year 2030 and reserved a budget of 5 billion dollars to achieve this goal. In order to achieve safe and successful wastewater reuse schemes for irrigation purposes, WHO health guidelines were integrated with the national water quality guidelines for irrigation purposes. Accordingly there are common multi strategies ultimately combined the optimisation of crop production and protecting the human heath. These are related to wastewater treatment level, restriction of the crop to be grown, irrigation techniques and scheduling, as well as to control of soil salt accumulation, ground water nitrogen pollution.

Unfortunately, in many areas of the countries that are already using or start using treated wastewater as an additional water source, the monitoring and evaluation programme aspects are not well developed, loose and irregular. This is mainly due to the weak institutions, the shortage of trained personnel capable of carrying the job, lack of monitoring equipment and the relatively high cost required for monitoring processes.

Concluding remarks and recommendations

Domestic treated wastewater is one tool to address the water insecurity facing many regions in the south of Morocco. In coming years, in most areas of the countries particularly the southern part, valuable fresh water will have to be preserved solely for drinking, very high value industrial purposes, and for high value fresh vegetables crops consumed raw. Where feasible, most fruit and forage crops, city landscape, and golf courses will have to be grown increasingly, and eventually solely, with treated wastewater. The economic, social and environmental benefits of such an approach are clear. To help the gradual and coherent introduction of such a policy, which protects the environment and public health, governments shall have to adapt an Integrated Water Management approach, facilitate public participation, disseminate existing knowledge, and generate new knowledge, and monitor and enforce standards.

Awareness and information efforts targeted at farming communities, improved specialized extension services and assistance in marketing crops grown under safe planned reuse schemes are useful steps in improving reuse.

To ensure the sustainability of the system, a cost recovery analysis should not be neglected. The low income of most farmers, it is not realistic to expect farmers to pay any portion of the treatment cost, but tariffs should cover the cost of transferring and distribution of the reclaimed water

On the technology side, small-scale decentralized sanitation technology, such as lagoons, sand filters, constructed wetland, and even septic tanks combined with small-bore sewers, offer great potential in small rural areas. As far as irrigation technologies are concerned, bubbler irrigation may be considered the preferred method of application particularly for tree crops. It provides some water savings, and also provides some degree of protection against clogging and contamination exposure.

WATER RECLAMATION AND REUSE IN COSTA BRAVA (1989-2009): LESSONS LEARNED AND PRACTICAL CONTRIBUTIONS

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OVERVIEW OF WASTEWATER MANAGEMENT PRACTICES IN MEDITERRANEAN COUNTRIES

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Abstract

Mediterranean countries are known to be among the most water stressed regions in the world. Water resources in the region are limited and unevenly distributed over space and time. In addition to environmental and development issues, specifically in water resources management and development and pollution control, there is a need for the improvement of water supply and the efficient use of wastewater in this region. This will allow advancement for social, economic and possibly political stability in the region.

Due to fundamental differences in the approach with respect to reuse guidelines and regulation, serious difficulties are faced in creating unified policies for the Mediterranean countries. Egypt, Jordan, Tunisia, Palestine, Morocco, and Syria form a group of countries in great need for extensive reuse practices. In these countries, strict reuse standards, such as the ones proposed by EPA and/or California, cannot be easily achieved. The WHO guidelines, which are less strict may be more appropriate for these countries. The situation is different in countries, including Greece and Cyprus, where there is a higher stage of development. There countries will tend to adopt stricter standards and guidelines than the ones proposed by the WHO. The essential difference in the criteria from one Mediterranean country to the next is partly due to the different approaches undertaken by each country. Thus, in preparing guidelines for municipal water reuse for the Mediterranean Region, some principles must be considered for the variance in different countries. If unified Mediterranean guidelines are to be adopted, it is expected that they be minimum requirements which should provide the most basic water reuse regulations, so that they may be adopted in every country of the region.

Keywords: Wastewater Management, Mediterranean, Guidelines.

Introduction

In the Mediterranean region, water resources are limited and unevenly distributed over space and time. There are similar environmental and development issues, specifically in water resources management and development and pollution control, throughout the region. The improvement of water supply and the efficient use of wastewater in the Mediterranean countries will allow advancement for social, economic and political stability in the region, considering that the Mediterranean countries are among the regions of highest water stress in the world.

According to the Blue Plan (Margeta and Vallée, 2000), renewable water resources are very unequally shared across the Mediterranean basin with around 72% located in the North (Spain, France and Monaco, Italy, Malta, Bosnia-Herzegovina, Croatia, Slovenia, R.F. of

Yugoslavia, Albania, and Greece), 23% in the East (Turkey, Cyprus, Syria, Lebanon, Israel, Palestinian Territories of Gaza and the West Bank, and Jordan), and 5% in the South (Egypt, Libya, Tunisia, Algeria, and Morocco). Available water resources are becoming increasingly scarce, are threatened by over-exploitation, and are becoming increasingly vulnerable to different pollution sources.

Problems of water scarcity will increase because of population growth, rise in standard of living, and urbanization, in which these factors will lead to both an increase in water consumption and pollution of water resources. Most Mediterranean countries rely mainly on agriculture, tourism, industry and other economic activities for their economic and social development. Irrigated agriculture, which is in strong competition with other sectors, will face increasing problems of water quantity and quality considering increasingly limited conventional water resources and growing future requirements and a decrease in the volume of fresh water available for agriculture. Therefore, policy makers are feeling the need to develop additional water resources as well as to preserve the existing ones. Reclaiming and recycling water is becoming an important component of the national resources policy since it is designed to encourage integrated and efficient management and use of water resources.

This research was carried out under the INNOVA-MED Coordination Action, which is an integrated group of 8 EC funded projects dealing with wastewater treatment and water management. This paper is a summary of the research findings which deals with different aspects of wastewater management and water resources management through assessing the technical, financial, socio-economic, institutional, and regulatory influences on integrated wastewater management and provides an identification of weakness in current systems and further research needed.

Overview of Wastewater Management Practices in Mediterranean Countries

The provision of appropriate means of water supply and sanitation has long been considered a basic human right. Water supplied through piped networks is intermittent in many countries of the Eastern Mediterranean region, such as Jordan, Yemen, Lebanon and Syria. In some cases, people have to wait for several days or weeks for their turn, so they use private vendors to fulfill their water needs. The high percentage of unaccounted-for-water is another serious problem facing piped water supply systems in most countries. This has been estimated to range from 30% to 40% in countries like Morroco and Lebanon.

Sanitation services have been given less priority than water supply in many countries since the provision of water is considered more urgent. This has led to a serious deterioration of water and land resources and as a result effluent discharge standards were developed and are gradually being adopted. Proper wastewater management is now being increasingly required in the Mediterranean countries to ensure a sustainable environment through protecting public health, maintaining aquatic ecosystems, and improving and protecting water resources. Considering that freshwater resource availability in the Mediterranean region is low, this makes water scarcity a significant challenge currently facing the Region. Therefore, the reuse of wastewater is now being considered a resource rather than a waste.

The perception of wastewater management in most countries has generally shifted from its conventional objectives of health and environmental protection, to be considered as a valuable resource where treated effluents are utilized to increase national water resources.

For example in Jordan, there are plans to upgrade overloaded wastewater treatment plants and to build new ones to expand wastewater management provisions, particularly in rural areas. It is expected that by the year 2010, the quantity of treated wastewater will be about 220 million m^3 per year (CEHA, 2005). Effluents from most wastewater treatment plants in Jordan have been utilized for irrigation purposes. This has been necessary in order to increase the scarce water resources of the country.

Weaknesses in Current Wastewater Management Practices

Overall sewerage coverage is modest in most countries of the Region due to the high costs involved. In general, governments in the developing countries of the Mediterranean basin have not been encouraged to promote sanitation projects because it is presumed that huge investments are required. This is mainly due to the fact that most planners, engineers and decision-makers consider conventional sanitary sewers as the best way to collect wastewater. This has therefore slowed the development of sanitation services. This is especially apparent in urban areas where population increase and density are normally higher than in the rural ones.

In Morocco, at present about 90% of the rural areas are served with some type of the onsite systems, mainly cesspools, and the remaining 10% are served with septic tanks. Lack of piped water supplies, local habits and poverty have all been cited as major obstacles hindering the provision of improved sanitation facilities for the rural populations. In Egypt, onsite units are used by 36 million people (about 60% of the total population). A small number of this population utilizes septic tanks with unlined bottoms, while the majority relies on seepage pits (CEHA, 2005).

Overview of wastewater reuse in Mediterranean countries

Wastewater has been used in the Mediterranean basin as a source of irrigation for centuries. In addition to providing a low cost water source, the use of treated wastewater for irrigation in agriculture combines three advantages: (1) the fertilizing properties of the wastewater eliminates part of the demand for synthetic fertilizers and contributes to decrease levels of nutrients in receiving waters and land; (2) wastewater reuse increases the available agricultural water; and (3) it may eliminate the need for expensive tertiary treatment.

In most of the countries in the Mediterranean region, wastewater is being reused at different extents within planned or unplanned systems. In many cases, raw or insufficiently treated wastewater is applied. In other cases, wastewater treatment plants are often not functioning or overloaded and thus discharge effluents not suitable for reuse applications. This leads to the existence of health risks and environment impacts and to the occurrence of water-related diseases.

Irrigation with raw wastewater has been practiced in many countries of the Mediterranean, including sites of the West Bank, Palestine, where crops and vegetables like parsley, mint, peppers, eggplants, squash, cauliflower, radishes and olive trees are being irrigated with untreated wastewater without any official health control or consideration to possible health or environmental implications. Measures are being taken in Palestine to reduce these practices and to increase awareness on the potential use of reclaimed wastewater instead. Health and agricultural officials see great potential for reuse in agriculture and landscape irrigation, groundwater recharge, aquaculture and in industry, such as stone cutting (EMWater, 2005).

Only a few Mediterranean countries have incorporated water reuse in their water resources planning and have official policies calling for water reuse, these include Cyprus, Israel, Jordan, Egypt, and Tunisia. Jordan is recognized as one of the pioneer countries in the region that utilize their wastewater efficiently. Out of 79.5 million m^3 that was treated at 17 WWTPs in year 1999, about 67 million m^3 was indirectly used for irrigation in different parts of the country. About 52 million m^3 was indirectly used for unrestricted irrigation in the Jordan Valley after blending with freshwater in wadis (Abumadi, 2005). Due to the topography and the concentration of the urban population above the Jordan Valley escarpment, the majority of treated wastewater is discharged into various watercourses and flows downstream to the Jordan Valley, where treated or poorly treated effluents mix with the fresh surface water and is used for unrestricted irrigation.

The volume of treated wastewater compared to the irrigation water resources is about 7% in Tunisia, 8% in Jordan, 24% in Israel, and 32% in Kuwait. Approximately 10% of the treated effluent is being reused in Kuwait, 20-30% in Tunisia, 85% in Jordan, and 92% in Israel (Angelakis, 2002). General applications of wastewater reuse in Turkey are irrigation, process water, and recreational areas formation. Reclaimed wastewater in some areas is being designed to be used to irrigate parks, for washing cars and fire fighting (EMWater 2004). In the nearest future, wastewater reuse will be one of the most important environmental issues in Turkey. As an initial step towards effluent use in irrigation, the existing WWTPs must either efficiently operate their disinfection units and/or add such facilities to their treatment systems (I. Arslan-Alaton et al., 2007).

The need to increase water resources in finding alternative sources, as well as economic and environmental issues, are the main driving forces for water reuse development in the Mediterranean region. Recycled domestic water in Cyprus is presently used for the watering of football fields, parks, hotel gardens, etc. and for the irrigation of permanent crops in particular. Recently in Egypt, the Ministry of Agriculture and Land Reclamation has started an agricultural reform program that includes effluent reuse for woodland forests (CEHA. 2005).

With proper management, the reuse of recycled wastewater can reduce pollution of water resources and sensitive receiving bodies. It may also contribute to desertification control and desert recycling. Saline water intrusion may be controlled in coastal aquifers through groundwater recharge operations. Other social and economic benefits may result from such schemes such as employment and products for export markets. Yet it is of great importance that the development of reuse prevents negative effects on environment and public health since wastewater content in mineral and organic trace substances and pathogens represents a risk for human health. Therefore, adequate treatment is an essential pre-requisite which must be provided for the intended reuse.

Wastewater Recycling and Reuse guidelines in the Mediterranean Region

In the Mediterranean region, wastewater reuse schemes are primarily considered for agricultural and landscape irrigation (as such in Jordan, Palestine, Israel, Turkey, among other Mediterranean countries) and groundwater recharge. Industrial reuse is rarely practiced, although it is gaining importance and is beginning to appear as a feasible fresh water alternative to some industries.

In order to reduce the environmental and health impacts of wastewater reuse, some Mediterranean countries have adopted several standards and guidelines that differ from each other even at the regional level. Practice of wastewater reuse mainly depends on a country's economy, infrastructural status covering wastewater treatment capacity and capability, educational level, climate, water supply, balance between water requirement and demand, intensity of agricultural activities, population, social habits like cultural and religious prejudice, and many other factors. While most of the developed countries have established low risk guidelines or standards based on a high technology/high-cost approach, many developing countries have adopted an approach based on WHO guidelines that refer to low-cost technologies and focus on health risks. However, the current situation in some developing countries is the direct uses of untreated wastewaters for irrigation without taking into account the stated guidelines and standards, and associated risks (Idil, A et al., 2007).

Generally, wastewater reuse standards in countries of the Mediterranean Region are either adopted from WHO standards or other international standards without adapting them to suit local conditions (CEHA, 2006). Available standards are summarized for Egypt, Jordan, Lebanon, Palestine, Greece, Turkey, Tunisia, Cyprus, Spain, and Morroco. No official specific standards are recognized for wastewater reuse in Egypt, Lebanon, or Palestine yet there are generally accepted wastewater reuse guidelines.

Egypt: In Egypt, so far there are no adopted guidelines or codes of practice to regulate reuse activities and there are no programs to monitor the quality of reclaimed wastewater, before or after reuse, for possible health risks on farm laborers and end users of products (CEHA, 2005). There is no coherent irrigation reuse policy to manage the utilization of treated wastewater, however, the Ministry of Agriculture and Land Reclamation recently started an agricultural reform program that includes effluent reuse for woodland forests. There are many decrees in Egypt concerning the quality of wastewater effluent. These include the national regulation, Decree No. (44) /2000, which provides quality standards for liquid wastes yet no specific standards exist for wastewater reuse.

Jordan: Jordan has asserted a goal of 100 percent reuse of reclaimed water resources, thereby effectively integrating reclaimed water resources in the national water development strategy (Pedersen, T. et al., 2006). The Jordanian policy is to ensure that wastewater is managed as a valuable resource rather than as a waste. To help maximize the use of reclaimed water, a Water Reuse and Environment Unit has been established within the Water Authority of Jordan, with the responsibility of monitoring and regulating reuse activities. In addition, a National Water Reuse Coordination Committee has been established to provide a forum for discussing reuse issues among key stakeholders. All new wastewater treatment projects are required to include feasibility for effluent reuse.

Lebanon: In Lebanon, as in many developing countries, nuisance, health conditions, and public pressure brought about an increasing demand for more effective means of wastewater management, particularly in large metropolitan areas along the Mediterranean Sea (El-Fadel, M. et al., 2000). Years of civil unrest accompanied with major demographic changes, unplanned development, and inadequate institutional support have hindered Lebanon from developing environmental management and control procedures to comply with its commitments, thus, there are no formal wastewater reuse schemes implemented. Ministry of

Environment 1996 Standards for urban wastewater minimum levels for treated domestic wastewater, yet no specific standards exist for wastewater reuse.

Palestine: Due to water scarcity, the reuse of reclaimed wastewater has been taking an increasing interest throughout Palestine. The reuse of reclaimed wastewater in Palestine is a major priority, as confirmed by the Palestinian Water Policy recently adopted by the Palestinian Water Authority and the Ministry of Agriculture. In 2002 the PWA issued the Water Law Number (3/2002). This law aims to develop and manage the water resources, increasing their capacity, improving their quality and preserving and protecting them from pollution and depletion. No specific standards exist for wastewater reuse. According to By Law No. 2 (1996), PWA is responsible for wastewater treatment and reuse. Preparation of policies and strategies for management of wastewater, industrial wastewater, legal and administration are under way.

Greece: In Greece, the problem of water shortage is less acute, compared to other countries such as Palestine and Jordan, and rather local (e.g. mainly in the islands and along the east coast). Several research and pilot projects dealing with wastewater recycling and reuse are currently under way in Greece, in addition to a few small projects on wastewater recycling and reuse which are in practice. Yet no guidelines or criteria for wastewater recycling and reuse have been yet adopted beyond those for discharge (No. E1b/221/65 Health Arrangement Action). The evaluation of the existing situation in Greece, concerning among others reuse priorities, available treatment plants and effluent characteristics, has led to the formulation of recommendations for developing future guidelines or regulations appropriate to Greek conditions (Andreadakis et al., 2001).

Turkey: Reuse of wastewater in agriculture is officially not a recent practice in Turkey. As in many other countries in the Mediterranean, indirect (unplanned) irrigational reuse has been applied for many years. The majority of the treated wastewater in Turkey is discharged into seas (62%) making it very difficult for these wastewaters to be reused since most WWTPs that practice sea disposal have only preliminary treatment (İ. İmamoğlu, 2006). The technical regulations and constraints for irrigational wastewater reuse, issued in 1991 by the Ministry of Environment, officially legitimized water reuse. According to the “Water Pollution Control Regulations”, treated wastewater can be used in irrigation. The Turkish Water Pollution Control Regulations provide effluent quality criteria for irrigation, which are generally adopted from the WHO guidelines. In addition to the regulations there are other criteria included, regarding the classification of the waters to be used for irrigation (Angelakis, 2002).

Tunisia: Wastewater reuse in agriculture has been practiced for several decades in Tunisia, on a seasonal basis, and now it is an integral part of the national water resources strategy. Wastewater is being reused for irrigation of fodder crops (alfalfa, sorghum), cereals, fruit trees (citrus, olives, peaches, pears, apples, grenades, and vineyards), tobacco, cereals, golf courses, green belts and roadsides (Abumadi, 2005). It is important to note that in Tunisia, the farmers pay for the treated wastewater they use to irrigate their fields (Angelakis, 2002). In addition to the reuse of treated wastewater for irrigation, it is currently reused for such other purposes as recharge of the aquifers and the protection of biodiversity in wetlands, as in the wetland of Korba, for instance (INNOVA, 2009). A gradual approach to expanding reuse since the mid 1960s has been adopted in Tunisia (Akissa, 2002). The water reuse policy was launched at the beginning of the 1980s. The main applications of water reuse are agricultural irrigation, and landscape irrigation. Wastewater reuse in agriculture is regulated by the 1975 Water Code (law No. 75-16 of 31 March 1975), by the 1989 Decree No. 89-1047 (28 July 1989), by the Tunisian standard for the use of treated wastewater in agriculture (NT 106- 003 of 18 May 1989), by the list of crops than can be irrigated with treated wastewater (Decision of the Minister of Agriculture of 21 June 1994) and by the list of requirements for agricultural wastewater reuse projects (Decision of 28 September 1995). They prohibit the irrigation of vegetables that might be consumed raw (Angelakis, 2002).

Cyprus: The basic sources on water supply in Cyprus are water dams and ground water. Recently, as a result of the water shortage in Cyprus, two new sources of water supply are being developed rapidly, namely, desalination and the wastewater reuse (Papaiacovou, 2001). The provisional criteria related to the use of treated wastewater effluent for irrigation purposes in Cyprus, which are in the form of guidelines and Code of Practice for Wastewater Reuse and Sludge Application, are extremely strict guidelines. They are stricter than the WHO guidelines and take the specific conditions of Cyprus into account. These criteria are followed by a code of practice to ensure the best possible application of the effluent for irrigation (Angelakis, 2002).

Spain: In Spain ten years ago, the Government issued one Law and one Decree where wastewater reuse was indicated as a possibility, and a minimal statement appeared, indicating the need for an administrative concession and a compulsory report of the Health Authorities. An indication was made that further legal developments would be needed. While there is no national legislation in Spain, at least three autonomous regions (Andalucia, Catalunia and Baleares) have either legal prescriptions or recommendations concerning wastewater recycling and reuse. The reuse of treated wastewater is already a reality in several Spanish regions for four main applications: golf course irrigation, agricultural irrigation, groundwater recharge (in particular to stop saltwater intrusion in coastal aquifers) and river flow augmentation.

Morocco: To date, there are no regulatory standards for treated wastewater reuse in Morocco but reference is usually made to the WHO recommendations. There is however a requirement in the 1995 Water Law which affirms the need for reused effluents to comply with the national norm. The irrigation of market garden crops with raw wastewaters is forbidden in Morocco, but this ban is not respected (INNOVA, 2009). This makes the consumer of agricultural products and the farmer face risks of bacteria or parasite disease, thus the 1989 World Health Organization's microbiological guidelines for agricultural reuse were adopted.

Further Research Required

Generally, wastewater reuse standards in countries of the Region are either adopted from WHO standards or other international standards without adapting them to suit local conditions. It is essential that such adopted guidelines be adapted to prevailing local conditions. Local studies are necessary as they may result in the formulation of guidelines and thus augment the quantities of reclaimed water without compromising and to protect public health. Such studies are essential to ensure effective and safe implementation of wastewater reuse guidelines, as this will increase confidence in reclaimed water as a valuable resource.

The highest priority in the wastewater management sector in the Mediterranean countries which are facing problems can be given to the setting up an effective wastewater management system, which will include: maximization of collection of wastewater; upgrading the existing wastewater collection systems; rehabilitation or upgrading of existing wastewater treatment plants or the construction of new plants; establishment of proper standards for influent and effluent wastewater quality; education of farmers (Fatta et al., 2004). To assure the public and protect the public health, there is a need to update the scientific basis of the regulations to ensure that the chemical and pathogen criteria are supported by current scientific data and risk assessment methods and to validate the effectiveness of recycled water management practices (Angelakis, 2002). Additional scientific work is needed to reduce persistent uncertainty about the potential impacts on human health and the environment from exposure to reclaimed water.

Wastewater Reuse Policies and/or Guidelines for Mediterranean Countries

The management of wastewater in the Mediterranean varies from country to country. Any available criteria and their enforcement also differ widely. Some countries have very little or poorly running wastewater treatment facilities and direct reuse of raw wastewater is occurring. This is resulting in serious health hazards and environmental problems. Other countries have a national reuse policy which is being implemented.

Wastewater treatment and reuse criteria differ from one country to another and even within one country. In countries such as Morocco, Jordan, Egypt, Tunisia, Cyprus, Greece and Spain, several major projects are already in operation or under planning, where the main reuse projects in the region are related to agricultural and landscape irrigation, and groundwater recharge. Industrial reuse is very rarely practiced.

Due to fundamental differences in the approach with respect to reuse guidelines and regulation, serious difficulties are faced in creating unified policies for the Mediterranean countries. Egypt, Jordan, Tunisia, Palestine, Morocco, and Syria form a group of countries in great need for extensive reuse practices. In these countries, strict reuse standards, such as the ones proposed by EPA and/or California, cannot be easily achieved due to their prevailing technological, institutional and, most importantly, economical constraints. The WHO guidelines, which are less strict with the intention to encourage treatment of wastewater prior to crop irrigation, particularly in developing countries, may be more appropriate for these countries until there is an ability to produce higher quality reclaimed water.

The situation is different in countries, including Greece and Cyprus, where there is a higher stage of development. These countries enjoy greater available funds, existing infrastructure and more advanced legislation regarding environmental pollution control. There countries will tend to adopt stricter standards and guidelines than the ones proposed by the WHO. Therefore, the essential difference in the criteria from one Mediterranean country to the next is partly due to the different approaches undertaken by each country, where some opt for minimizing any risk and have adopted strict effluent reuse criteria, while others generally act to prevent negative effects and thus adopt a set of water quality criteria based on the less strict WHO guidelines. This has led to substantial differences in the criteria adopted by Mediterranean countries.

In preparing guidelines for municipal water reuse for the Mediterranean Region, some principles must be considered for the variance in different countries. Wastewater quality policies or guidelines should reflect the variances in climate, water flow and wastewater characteristics. They should take into consideration the local conditions of the country, e.g. socio-cultural and environmental factors. They must also be feasible and enforceable.

If unified Mediterranean guidelines are to be adopted, it is expected that they be minimum requirements which should provide the most basic water reuse regulations, so that they may be adopted in every country of the region. For the less developed countries, this will allow them to comply and for the wealthy countries, then they have the choice to opt for higher protection if desired. Due to the high variance in development of wastewater treatment in several countries, all of them cannot be expected to comply with the guidelines in a specified time frame yet these countries must be encouraged to give a commitment to reach the guidelines within a time frame, depending on its current equipment and financial capacities.

Conclusions

In the Mediterranean basin, wastewater has been used as a source of irrigation for centuries. In addition to providing a low cost water source, the use of treated wastewater for irrigation in agriculture provides three advantages: First, using the fertilizing properties of the water eliminates part of the demand for synthetic fertilizers and contributes to decrease levels of nutrient in receiving waters (such as rivers, sea, ocean, lakes). Second, the practice increases the available agricultural water. Third, wastewater reuse may eliminate the need for expensive tertiary treatment. However, wastewater is often associated with environmental and health risks. As a consequence, its acceptability to replace other water resources for irrigation is highly dependent on whether the health risks and environmental impacts entailed are acceptable.

In the Mediterranean countries, there is a need for a holistic approach with respect to water resources management, and this imposes the need for wastewater reclamation and reuse criteria. Some countries in the Mediterranean, such as Cyprus, Tunisia, and Turkey, have established national regulation or guidelines, and regional guidelines exist in Spain. Other countries such as Egypt, Greece, Lebanon, and Morocco, are considering guidelines and/or regulations concerning wastewater recycling and reuse. Establishing unified Mediterranean guidelines for municipal water reuse is a challenge because of the lack of comprehensive international guidelines, and of an agreement on the scientific approach that should be adopted to issue such guidelines. Thus, it is expected that providing minimum requirements, which should provide the most basic water reuse regulations, in every country of this region will encourage compliance by all countries and will reduce the threat of water scarcity.

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CONSTRAINTS TO WASTEWATER TREATMENT AND REUSE OF WASTEWATER AND SLUDGE IN MEDITERRANEAN PARTNER COUNTRIES

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The scarcity of water and the need for protecting the environment and natural resources are the main factors leading countries in the Mediterranean region to introduce the reuse of treated wastewater as additional water resource in their national plans of water resource management. In Mediterranean Partner Countries, treatment and reuse of wastewater are already applied to a certain extent, while sludge is being reused to a more limited extent.

Based on a review of existing literature and project experience of INNOVAMED partners, the presentation identifies and discusses factors, which act as constraints to the broader application of treatment and reuse practices and technologies in Mediterranean Partner Countries (MPC). The presentation mainly concentrates on the reuse of wastewater for the purpose of irrigation which is the most common reuse activity in MPC countries.

The key types of constraints identified are the following:

- *Financial constraints* (related e.g. to high costs of treatment systems and sewerage networks, high operational costs especially for electricity, low prices of freshwater compared to reclaimed wastewater, low user willingness to pay for reclaimed wastewater).
- *Health impacts and environmental safety* especially linked to soil structure deterioration, increased salinity and excess of nitrogen.
- *Standards and regulations*, which are in some cases too strict to be achievable and enforceable and, in other cases, not adequate to deal with certain existing reuse practices.
- *Monitoring and evaluation* in both treatment and reuse systems, often related to lack of qualified personnel, lack of monitoring equipment or high cost required for monitoring processes.
- *Technical constraints*, including, for instance, insufficient infrastructure for collecting and treating wastewater, inappropriate set up of existing infrastructure (not designed for reuse purposes), improper functioning of existing infrastructure.
- *Institutional set-up* (especially poor coordination at relevant intra- and inter-sectoral levels) and lack of appropriate *personnel capacity*
- Lack of *political commitment* and of national policies/strategies to support treatment and reuse of wastewater.
- *Public acceptance and awareness*, related to low involvement and limited awareness of both farmers and consumers of crops grown with reclaimed wastewater (and/or sludge).

Table 1. Key types of constraints to treatment technologies of wastewater (WW), reuse of WW and reuse of sludge

Type of constraint	WW treatment	WW reuse	Sludge reuse
Financial constraints (e.g. funding, cost-recovery issues, crop marketing)	√	√	√
Health impacts & environmental safety		√	√
Presence and enforcement of standards & regulations	√	√	√
Monitoring and evaluation of technology/scheme	√	√	√
Technical constraints	√	√	√
Institutional set-up & personnel capacity	√	√	
Policy & political constraints	√	√	
Public acceptance & awareness		√	√

Some good practice examples are given on how certain countries such as Tunisia, Jordan and Egypt are dealing with certain constraints in practice. For instance, in the cases selected, positive steps have been made on gaining political support for wastewater treatment and reuse in the context of national water resource strategies, on raising awareness and user involvement, standard development as well as development of affordable technical treatment solutions for rural areas.

Considering that the Mediterranean population becomes increasingly urban, it becomes more important to ensure that wastewater receives proper treatment and is reused to permit additional uses. The current Mediterranean water deficits could be in part alleviated by the adoption of safe wastewater reuse programs, therefore, further action and research is needed to address the factors currently limiting the application of these technologies in Mediterranean Partner Countries.

In this context, the last part of the presentation puts forward a set of recommendations on priority actions and research needed, to overcome key constraints to treatment and reuse of wastewater and sludge in MPC. Priority recommendations concentrate on the aspects of financing and costs, political commitment for treatment and reuse and ways of mitigating risks on public health and the environment (including standard development and monitoring). Some additional recommendations are made on the improvement of technical infrastructure for treatment and reuse, raising awareness and user acceptance as well as improvement in the institutional coordination and personnel capacity.

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THE ROLE OF pH ON SULFAMETHOXAZOLE REMOVAL BY WALNUT SHELLS

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The discharge of pharmaceutical and personal care products (PPCPs) into environment has become a matter of concern in recent years[1,2]. This group of substances comprises a large class of chemical compounds that can arise from human usage and excretions, veterinary applications and also industrial and agricultural practices. Among this wide variety of pharmaceutical compounds, antibiotics assume special significance due their extensive use, but also due to their ability to alter microbial community structure facilitating the development of antibiotic-resistant human pathogens[3].

Adsorption is, nowadays, a well-established technique to remove pollutants being activated carbon the main adsorbent for the purification of water with low pollutant concentration. Nevertheless the poor economic feasibility, limited applicability and effectiveness, and a short lifetime, often due to low and expensive regeneration capacities are the major drawbacks associated to this technology. In this sense agricultural by-products have been receiving attention as raw materials for water pollution control due to their low cost and availability[4]. However the performance of the adsorbent will also play an important role on the economic feasibility of the overall adsorption process and should not be disregarded. In this way, the main objective of the present work was to study the effect of solution pH in the sulfamethoxazole removal from solution, by walnut shells. Sulfamethoxazole is one of the most commonly used sulphonamide antibiotics and has been frequently detected in the environment[2]. This antimicrobial possesses two ionizable functional groups considered relevant to the environmental pH range: the anilinic amine and the amide moieties. The cationic species dominates at low pH values; the neutral form is the principal species a pH values between $pK_{a,1}$ and $pK_{a,2}$, and the anionic species is the main form at higher pH values. On the other hand the pH of the solution will also have an effect on the surface charge of the adsorbent. Sorption experiments, to investigate the pH-dependent adsorption, were conducted between pH 2 and 8. Textural and surface chemistry characterization of the adsorbent was also considered, in this work, and its influence in adsorption performance is discussed. Sulfamethoxazole adsorption to walnut shell exhibited pronounced pH dependence consistent with sorbate speciation and walnut shell properties.

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REGENERATION OF PAPER MILL WASTEWATER WITH FENTON AND PHOTO-FENTON PROCESSES

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Traditionally, paper mills involve significant environmental problems related to the use and management of water within the process, due to the fact that they consume large amounts of water as well as a variety of chemical compounds, which generate highly contaminated sewages. To accomplish the current local legislations, the sector confronts the challenge of effective wastewater remediation. Additionally, water reuse should be considered within their water management strategy to overcome irrational fresh water intake and saving costs.

Conventional treatment technologies can hardly achieve such a sustainable double objective, and therefore advanced practices are required. In this direction, *Advanced Oxidation Processes (AOPs)*, which are based on the generation of highly reactive hydroxyl radicals ($^{\bullet}OH$), are emerging alternatives for the efficient destruction of recalcitrant products in water. Among them, the Fenton and photo-Fenton type reactions attain the highest reaction yields with the lowest treatment cost.

In this study, data and discussions concerning the application of Fenton type processes as a tertiary stage in the treatment of real paper mill wastewaters are reported. The AOP is performed as a post-treatment of conventional physicochemical treatment practices to achieve suitable water qualities for internal reuse.

The effect of some parameters like Fenton reagent dosage, irradiation and temperature is investigated through the Total Organic Carbon (TOC) evolution as a key parameter. The resultant physicochemical water characterization confirms the suitability of the AOP performed with this aim. 70% TOC reduction is obtained at 25 ºC under artificial light irradiation and optimal reagent doses. Special attention may be paid to the possibility of performing the experiments under solar irradiation, in order to achieve an economical and environmentally friendly system.

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FENTON AND BIOLOGICAL-FENTON COUPLED PROCESSES FOR TEXTILE WASTEWATER TREATMENT AND REUSE

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Textile mills are major consumers of water and one of the largest sectors causing intense water pollution. Generated wastewaters collect different effluents with variable volume and chemicals. Consequently, an important challenge of textile industry will be the water reuse in order to overcome irrational fresh water consumption.

Different chemical and microbiological parameters need to be controlled in order to assess water for reuse (*Real Decreto 1620/2007*). Among these parameters, we can find Suspended Solids, Turbidity, *Legionella* and *Escherichia Coli*. In addition, the iron concentration is also an important parameter in Textile Industry.

Conventional methods such as biological, physical and chemical processes are common practices, but they result quite inefficient in front of most textile sewages. Alternatively, *Advanced Oxidation Processes* (AOPs) appear as emerging technologies for the efficient destruction of recalcitrant products in water. Among them, the use of Fenton's process achieves the highest reaction yields with the lowest cost treatment.

In this study, data and discussions concerning the treatment of a real textile wastewater by using the Fenton reagent alone and as a post-treatment of an aerobic *Sequential Batch Reactor (SBR)* are reported. Both strategies focus on achieving suitable water qualities for internal reuse.

The effect of Fenton reagent dosage (H_2O_2/Fe(II)), temperature, as well as the evolution TOC, COD, aromatic compounds (UV_{254}) and nitrogen is investigated through both approaches. Special attention has been paid to the microbiological characterization of the resultant water and the operational costs associated to these treatments. Results confirm the suitability of the treatments, since the obtained COD and TOC reductions -under optimal conditions- are higher than 70 and 64%, respectively. Moreover, *Legionella* is not present at the end of the treatment and *Escherichia coli* parameter accomplished *Real Decreto 1620/2007* levels. On the other hand, highest remediation yields are obtained when applying Fenton process as a biological polishing step, while reducing the economical and environmental burdens of the stand-alone process.

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ADVANCED OXIDATION PROCESSES WITH ZEOLITES TO REMOVE GASOLINE COMPOUNDS FROM WATER

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In recent years, increasing attention has been paid on heterogeneous Fenton-like systems for removal of organic compounds from water [1]. Zeolites possess unique sorption properties with respect to smaller organic molecules which make them interesting candidates as adsorbents and catalyst carriers in water treatment processes. Adsorption affinity and capacity with respect to a certain compound depend on the hydrophobicity of adsorbate and zeolite and the congruence of molecule and pore sizes. These sorption properties can be utilized in the case of Fe-zeolite catalysts for favored enrichment of the target organic contaminants in the vicinity of the catalytic centers. This work reports experimental results of the use of Fe-zeolites for the removal of organic compounds from water in batch and column studies in order to assess the practical applicability of these materials in water treatment. Two types of iron containing zeolites, Fe-Beta and Fe-ZSM5 were used as catalysts for wet peroxide oxidation of organic compounds such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), benzene, toluene, and o-xylene at pH = 7. Steric hindrance effects were less important in Fe-Beta than in Fe-ZSM5 (Fig. 1). The fuel oxygenates showed good removal efficiency with Fe-Beta. Laboratory scale column experiments including the use of contaminated groundwater were conducted in order to test the stability of the Fe-Zeolites catalyst under flow-through conditions.

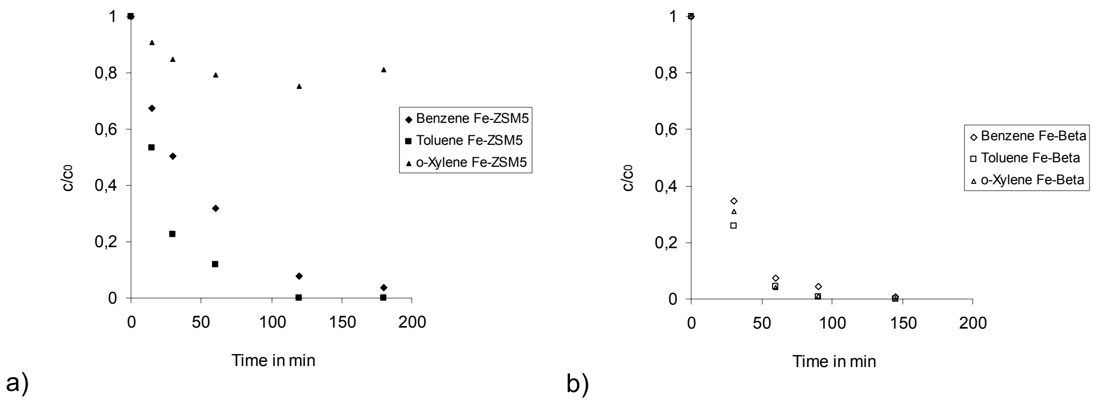

Figure 1. Degradation of aromatic compounds in batch experiments with (a) Fe-ZSM5 ($C_{compound,\ 0}$ = 100 mg/L, $C_{zeolite}$ = 5 g/L, C_{H2O2} = 7.5 g/L) and (b) Fe-Beta ($C_{compound,\ 0}$ = 20 mg/L, $C_{zeolite}$ = 25 g/L, C_{H2O2} = 7.5 g/L).

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MERCURY REMOVAL UNDER CONTINUOUS FLOW CONDITIONS

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Mercury(II) removal from wastewaters is one of the mayor environmental problems, due to its high toxicity, negative effects in human health and transmission through the food chain. Biosorption can be an economical and effective alternative to conventional techniques to reduce mercury levels in wastewaters using “low cost materials” as biosorbents. This kind of materials are easily obtained substrates or waste by-products from another industry and require little treatments for being use in sorption studies[1,2]. This work deals on mercury elimination from synthetic solutions through biosorption process using different biomaterials.

Four different materials were tested, brown alga *Sargassum muticum*, beach cast seaweed, bracken fern (*Pteridium aquilinum*) and exhausted coffee grounds. The kinetics of mercury elimination from solution was studied for these materials and also the isotherms were determined. The best results were obtained for the brown alga *S. muticum*, showing that this is a promising material to achieve high levels of elimination of this toxic heavy metal[3]. Although bracken fern kinetics and isotherm are not so favorable as in *S. muticum*, its abundance and ease to process allows preparation of large quantities of this material, which is an interesting fact in order to apply this biomass at industrial scale. Consequently this material was chosen to carry out continuous flow studies in columns. Competition with other heavy metals was also analysed in the column studies. Results obtained indicate that mercury is eliminated from solution but only approximately a 25% is eluted after 20 hours. SEM (Scanning Electron Microscopy) microphotographs and EDS (Energy Dispersive X-ray Spectroscopy) analysis of the column filling material after the continuous flow study shows that and important fraction of mercury is reduced on the surface of fern to oxidation states I and 0 after the sorption process.

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PHYSICOCHEMICAL ASPECTS ON THE REDUCTION OF Cr (VI) LEVELS IN SOLUTION USING BRACKEN FERN BIOMASS

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Chemical contamination of water from wide range of toxic derivates, in particular heavy metal, is a serious environmental problem owing to their potential human toxicity. Increased quantities of chromium compounds have been used by man and introduced into the environment as a consequence of its wide use in modern industries, mainly in electroplating and tanning factories. The effluents from these industries contain chromium on its most common oxidation states on aqueous phase, Cr (VI) and Cr (III).
These two Cr forms exhibit very different toxicity; while Cr (III) is an essential nutrient, Cr (VI) is highly active, very dangerous due to its carcinogenic and mutagenic properties [1]

Several treatment technologies have been developed to remove chromium from water and wastewater. Chemical precipitation has traditionally been the most used method. The disadvantage of precipitation is the production of sludge, which constitutes a solid waste, a disposal problem. Ion exchange is considered a better alternative. However, it is not economically appealing because of high operational cost. Biosorption constitutes an eco-friendly and cost effective alternative to these methods [2,3]

There are a great amount of papers devoted to the biosorption of chromate anions by different kinds or organic materials. Several authors have demonstrated that the interaction of Cr (VI) anions with organic matter is mainly a redox process. That is, the elimination of Cr (VI) pollution by biomass is due to the reduction of Cr (VI) anions to Cr (III) cations and not a simple adsorption process on the surface of the biomass. Moreover, X-ray photoelectron spectroscopy studies demonstrate that the oxidation state of chromium bound to the biomaterials is mostly or totally in trivalent form [4]. Hence, the elimination of Cr (VI) pollution by biomass is due to the adsorption-coupled reduction of Cr (VI) and not a simple adsorption process on the biomass surface.

This study presents equilibrium and kinetic data on Cr (VI) remediation by use of bracken fern (*Pteridium aquilinum*). Parameters affecting Cr (VI) remove like pH, initial metal concentration and contact time were studied. Results obtained show that fern constitutes a good choice for chromium removal.

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PHOTOCATALYTIC OXIDATION OF 17α-ETHINYLESTRADIOL UNDER SIMULATED SOLAR LIGHT IN AQUEOUS TiO_2 SUSPENSIONS

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The oxidative degradation of a 17α-ethinylestradiol (***EE2***), a synthetic estrogen used in the oral contraceptive pill, was investigated by means of simulated solar light driven photocatalysis in the presence of TiO_2 in aqueous suspensions. Two commercially available pure un-doped TiO_2 catalysts, namely Degussa P25 and Hombikat UV100, as well as four carbon-doped TiO_2 catalysts, namely Kronos vlp7000, Kronos vlp7001, Kronos vlp7100 and Kronos vlp7101 were screened for their photocatalytic efficiency to decompose EE2 in aqueous solutions under simulated solar light. As can be seen in Figure 1, Degussa P25 was more active than the other TiO_2 samples, even than those catalysts that absorb light in the visible region of the electromagnetic spectrum, such as carbon-doped TiO_2.

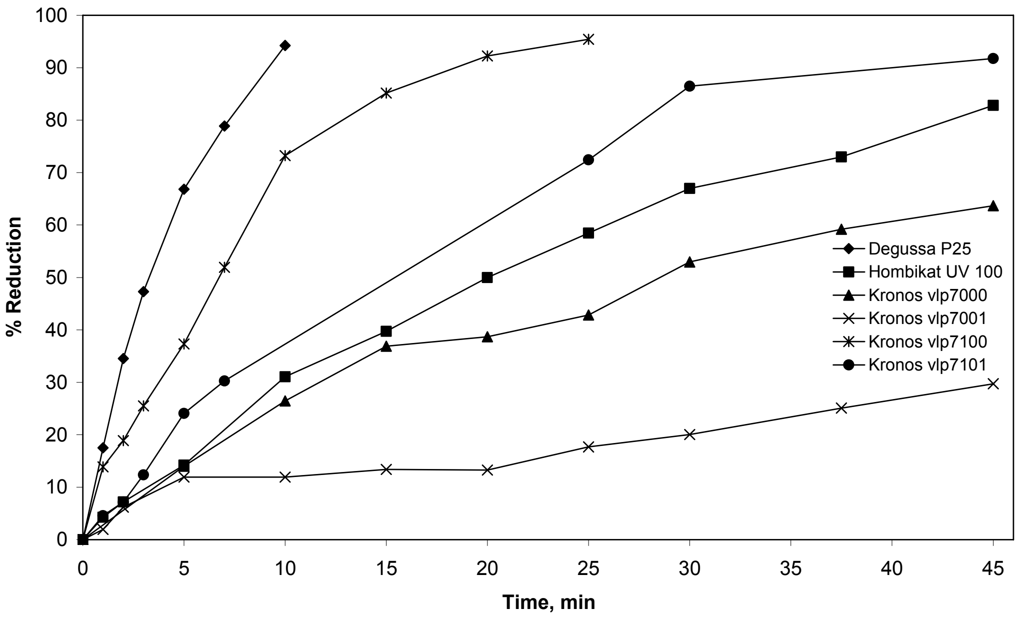

Figure 1. Screening of various TiO_2 catalysts for EE2 photocatalytic degradation at 300 μg/L initial concentration and 50 mg/L catalyst loading.

Several factors that affect the photocatalytic oxidation of EE2 were investigated, such as TiO_2 and EE2 concentration, effect of air sparging and water matrix.

REMOVAL OF EMERGING POLLUTANTS IN CONVENTIONAL TERTIARY TREATMENT SYSTEMS AND REED BEDS.

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The widespread occurrence of emerging pollutants in the aquatic environment is a recognized problem of unknown consequences[1]. One of the sources of emerging pollutants in aquatic environments is the effluent from wastewater treatment plants (WWTP), since it is known that emerging pollutants are not completely removed during treatment.[2]. It is well known that the use of different tertiary treatment systems and more specially the advanced ones (e.g. ozonitzation and MBR) enables the removal of these substances [3]. Nevertheless the use of reed beds as tertiary treatment systems for that propose is not well known, being this topic of high interest. Constructed wetlands are land-based wastewater treatment systems that consist of shallow ponds or trenches that contain floating or emergent, rooted wetland vegetation[4]. The main advantages of CWs are the low cost and the landscape integration, but they have the disadvantage of a high surface area requirement. Firsts published results on CWs used a tertiary treatments systems manifested similar removal efficiency on emerging pollutants than some advanced treatment systems[5].

The aim of this work was to evaluate the removal efficiency of 28 emerging pollutants in two conventional tertiary treatment systems and one constructed wetland. The target emerging pollutants belonged to the group of the pharmaceuticals, personal care products, disinfectants, fire retardants and plasticizers. The conventional tertiary treatment systems are situated in the municipalities of Blanes and Tossa de Mar (north-east of Catalonian). Both treatments consist in a flocculation tanks and lamella clarifiers followed by pulsed-bed filters and a UV reactor. Constructed wetlands are feed with the Empuriabrava WWTP effluent and consist in a two parallel ponds followed by two serial surface flow constructed wetlands (SFCWs). The hydraulic residence time was set to 4 days. Weekly campaigns (n=5) in July 2009 were carried out in three treatments systems. The samples were analysed for emerging pollutants as described elsewhere[5]

Emerging pollutants were detected in tertiary influents at concentrations ranging from high ng/L to low µg/L levels. The results show that SFCWs are in general more efficient (80% in average) on the removal efficiency of emerging pollutants than conventional tertiary treatment systems are (40% in average). Hence, the feasibility of using CWs rather than high-cost technologies to remove emerging pollutants from wastewaters is opened to discussion.

ACKNOWLEDGEMENTS
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TRANSPORT AND TRANSFORMATION OF PHARMACEUTICALS, ESTROGENS, AND OTHER ANTHROPOGENIC WASTE INDICATORS THROUGH WASTEWATER-TREATMENT PROCESSES

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The importance of point-source discharges of treated wastewater as sources of estrogens, pharmaceuticals, and other anthropogenic waste indicators (AWIs) has been demonstrated repeatedly in recent studies. However, the processes controlling the transformation or removal of these compounds from wastewater influent to discharged effluent and land applied biosolids are only beginning to be understood.

In this study, liquid and solid waste samples were collected at major treatment stages through four large municipal wastewater-treatment plants (WWTPs) that use different treatment technologies (mesophilic anaerobic digestion, mesophilic aerobic digestion, thermophilic anaerobic digestion, and lime stabilization) that are representative of WWTPs across the United States. Concentrations of pharmaceuticals, estrogens, and other AWIs in these samples were determined to evaluate the efficiency of each treatment stage for removal and transfer between liquid and solid phases during treatment and to determine mass balances of individual compounds within the treatment train in these specific WWTPs.

Preliminary results suggest that most pharmaceutical, estrogen, and AWI concentrations in liquid-phase samples decrease substantially after activated sludge treatment, frequently by 90 percent or more. Concentrations of triclosan and the fragrances galaxolide and tonalide were high in primary unthickened sludge, decreased substantially in secondary thickened sludge, and increased through subsequent treatment processes such that the highest concentrations were present in the final digested sludge. However, concentrations of several pharmaceuticals, including diphenhydramine, miconazole, and carbamazepine, were highest in primary unthickened sludge, decreased substantially (by 50 percent or more) in secondary unthickened sludge, and remained relatively constant in subsequent sludge-treatment steps. Development of solid and liquid mass balances is underway to determine total contaminant loads in liquid and solid waste streams, which is critical to evaluating the relative importance of phase transfer and remineralization in the environmental fate of targeted AWIs.

MULTI-WALLED CARBON NANOTUBES FOR ELECTROCHEMICAL SENSING OFTHE ANTIBIOTIC CIPROFLOXACIN IN WASTEWATER

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There are about 1 billion people in the world, mostly in developing countries, whom have no access to potable water and a further 2.6 billion people lack access to adequate sanitation[1]. In addition to the well-documented economic, social, and environmental impacts of poor water supply and sanitation, the health and welfare of people, especially of vulnerable groups such as children, the elderly and poor, are closely connected to the availability of adequate, safe and affordable water supplies.

Recently, the attention of many researchers working in the environmental field has been focused on the presence in the environment (and more specifically in waters) of pharmaceuticals as a new class of pollutants. Speculation and public concern have increased considerably over the past several years as improved analytical techniques and limits of detection have confirmed the presence of pharmaceuticals in the environment. One of the primary tasks has been the detection, determination, and fate studies of pharmaceuticals in different compartments of the environment, particularly in water ecosystems. However, the most important problem with monitoring is the lack of appropriate analytical procedures for the quantitative determination of residues of active pharmaceutical components and their metabolites.

Currently, much attention has been focused on developing nanomaterials, which are used for signal amplification in electrochemical sensors. Nanomaterials are usually used to take advantage of a larger surface area on which biomolecules can be immobilized [2]. Various types of nanomaterials are used in electrochemical sensors. Carbon nanotubes (CNTs) are one of the most exciting materials because of their unique electronic, chemical, and mechanical properties, particulary multiwalled carbon nanotubes (MWCNT).
In this communication the development and application of a new sensor based on MWCNTs-modified electrodes for the determination of the antibiotic ciprofloxacin in wastewater will be presented. The results suggest that this new electrochemical sensor will represent a very promising analytical method for the quantification of antibiotics owing to its high degree of selectivity and sensitivity.

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CLEAN-UP STRATEGIES IN THE DETERMINATION OF SEVERAL THERAPEUTIC CLASSES OF PHARMACEUTICALS IN WASTEWATER SAMPLES BY LC-MS/MS AND THEIR IMPACT ON RECEIVING SURFACE WATERS

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The growing use of pharmaceuticals and their resulting ubiquitous distribution in the aquatic environment has recently awakened great concern worldwide. Ecotoxicological information on this issue is scarce, but worry over hazards associated with long-term risks for non-target organisms, and indirectly on human health, is emerging.[1,2,3] Among other sources, wastewater treatment plants (WWTPs) are known as one of the main contributors to this aquatic pollution, since some pharmaceuticals are incompletely removed in the treatment process.[4,5,6] This work aimed to develop and validate a quantitative LC-(ESI)-MS/MS method for the simultaneous determination of 24 pharmaceuticals of diverse chemical nature, among the most consumed in Portugal, in wastewater samples.

Several clean-up strategies exploiting the physical and chemical properties of the analytes vs interferences, alongside with the use of an internal standard, were assayed in order to minimise the influence of matrix components in the ionisation efficiency of the target analytes. The main challenge was to find the best combination of adsorbent/elution solvent or technique which would remove selectively the interferences, without affecting the analytes. Adsorbents such as silica gel, florisil and graphitised carbon black (GCB) (normal phase), as well as SAX and WAX (NH_2 -) (ion exchange) and MAX (mixed-anion exchange) were assayed. Selective wash of the SPE extracts with increasing percentages of MeOH in water and filtration with narrow pore glass fibre filters were also attempted.

Concerning the selective wash approach of the cartridge, a 10% MeOH content didn't improve the extract cleanliness and some compounds were even lost. Regarding the physical filtration, our experiments on a filtered spiked sample allow us to conclude that this process is not capable of preventing ionisation suppression effects, leading to low recoveries and loss of some compounds. The clean-up using LC-Si cartridges (Supelclean), after testing several elution solvents, was characterised by dirty extracts and by low efficiency, later on confirmed by low recoveries and absence of several compounds. LC-Florisil (Supelclean) and GCB (Restek) cartridges gave apparently clean extracts. However, none of the solvents (n-hexane, dichloromethane, $CHCl_3$, ether, ethyl acetate, ACN, acetone, THF, isopropanol, MeOH) pure, mixed or acidified was able to elute a considerable amount of the compounds. Acidified MeOH even led to the formation of a white precipitate by reacting with the adsorbents. When comparing SAX with NH_2 cartridges (Supelco), both allowed the recovery of all compounds, but a previous acidification of the sample to pH~2 with HCl is mandatory. Nevertheless, the latter were consistently better in terms of recoveries. Note that the clean-up was applied to the integral sample, subsequently enriched on JTBaker H_2Ophilic cartridges. Finally, Oasis MAX cartridges provided better recovery rates for the majority of the compounds, even when compared to NH_2 cartridges. The recoveries (%) with MAX cartridges for paracetamol (41), ciprofloxacin (100), indapamide (77), paroxetine (100), bromazepam (68), fluoxetine (100), alprazolam (72), nimesulide (60), bezafibrate (92) and gembrosil (98) were significantly higher (n=3, average RSD=9%) than with NH_2 cartridges. This analytical method comprising both enrichment and clean-up with MAX adsorbent was applied to gather preliminary results on the influents and effluents of 2 WWTPs located in Gaia (Porto, Portugal), that discharge their effluents into Douro river. Some sampling spots in this river were also analysed.

Keywords: *pharmaceuticals; wastewater; clean-up; MAX cartridges; LC-MS/MS*

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PHOTO-ASSISTED TREATMENT OF MICROCONTAMINANTS IN SEWAGE WASTEWATER FOR WATER REUSE

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Atrazine (ATZ) has been used as pesticide in agriculture for years and its considerable use has caused consequences on environment. Besides, it is often found in drinking water and in effluents of municipal sewage treatment system [1-2]. Several oxidation methods to remove microcontaminants have been, so far, considered. Nevertheless, only a few applications involving the degradation of micropollutants in effluents of municipal sewage treatment system can be found on literature. In this work, a secondary effluent from the Gavà municipal wastewater treatment plant was polluted with ATZ. Pesticide degradation was investigated under UV (254nm) and UV-H_2O_2. The experiments showed that UV irradiation and UV-H_2O_2 treatment were able to remove the total content of ATZ from the wastewater after 60 and 45 minutes, respectively (Fig. 1). On the other hand, after 120 minutes of treatment, the methods achieved COD removals up to 20 %. Preliminary studies indicated that disinfection was achieved on the first minutes of UV and UV-H_2O_2 treatments. In addition, those treatments allow the reduction of physicochemical parameters as turbidity and SST under the limit values to water golf courses defined by Spanish legislation of wastewater reuse (*REAL DECRETO 1620/2007)*. In conclusion, this study showed the capacity of UV and UV-H_2O_2 to degrade the studied micropollutant present in wastewater samples as well as the disinfection and reduction of their physicochemical water parameters.

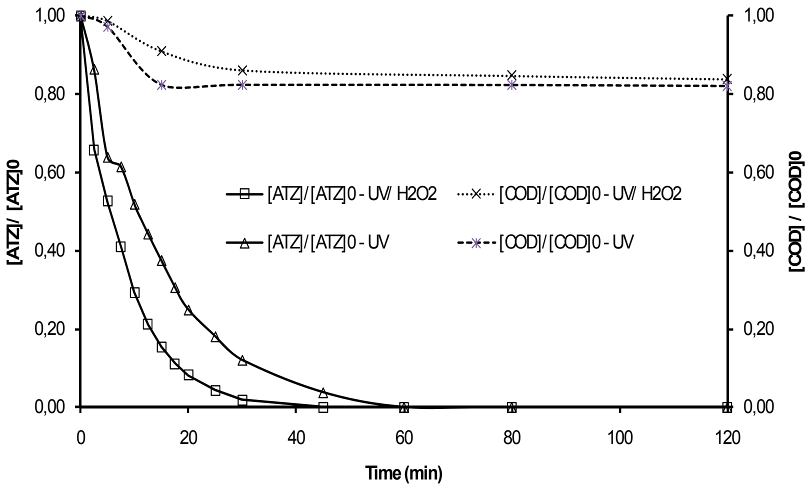

Fig. 1: Monitoring of degradation of ATZ and material organics by UV and UV-H_2O_2 process. Conditions: $[H_2O_2]_o$= 50 ppm and $[ATZ]_o$= 20 ppm

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Acknowledgements

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NEW RECEIVING WATER BODY FOR A LARGE WASTEWATER TREATMENT PLANT IN A SENSITIVE AREA IN NORTHERN ITALY: REFITTING WITH NATURAL SYSTEMS AND WATER REUSE

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The change of the receiving water body for the effluent of a large wastewater treatment plant (WWTP) is not an usual choice and it must necessarily think over receiving water quality conditions and autodepurative capacity, with respect to different and expected hydro-climatic regimes, predicted effluent pollutant loads (in quantitative and qualitative terms), as well as the use of the receiving water body. As to reduce and mitigate environmental impacts, it can be convenient not only to change the discharge point of a WWTP final effluent, towards a site whose environmental characteristics can favour *natural* dilution, autodepurative processes and pollutants degradation on their way to the final discharge point, but also to improve effluent quality by plant refitting and by adopting adequate polishing treatments. In addition, it can be convenient reusing reclaimed wastewaters characterized by a really high quality for irrigation, gardening, industrial uses...This paper deals with a study referring to a large WWTP (200.000 equivalent inhabitants) situated in a *sensitive* area in the River Po Delta (town of Ferrara) in which the change of the receiving water body for the final effluent has to guarantee the preservation of a *delicate* environment. The effluent high quality is achieved by means of *natural* systems (constructed wetlands + lagoons) and it has to satisfy water demands for different uses (industries, agriculture, ecological…), which are more and more increasing even in those areas, like Northern Italy, where theoretically there is abundant good surface water, in reality more and more scarce, especially during Summertime.

The town of Ferrara is placed in an *area* declared at risk of environmental crises, as a prolonged drought period can reduce fresh water availability for the different uses and due to recurrent eutrophication of the river (Po) and the Northern Adriatic Sea, the final receiving body of the Po River. For this reasons different interventions aimed at guaranteeing the preservation of this *delicate* environment are under study and intervention are declared urgent.

The WWTP of Ferrara is located in the first outskirts of the town, within the Urban park, a 1000 hectare area extending from the town to the right side of Po River (fig. 1). The park is used partially for recreation (sports centre, golf courses, bycicle paths) and mainly for agriculture. It treats urban (28 000 $m^3\ d^{-1}$) and industrial (28 000 m^3d^{-1}) wastewaters into two separate and identical lines, including conventional pre-treatment, primary sedimentation, biological treatment, secondary sedimentation and final disinfection (by adding NaClO). In 2001 the urban line has been upgraded with the construction of a nitrification-denitrification tank in order to reduce the nitrogen compounds content in the final effluent and to preserve the final water body from eutrophication risks.

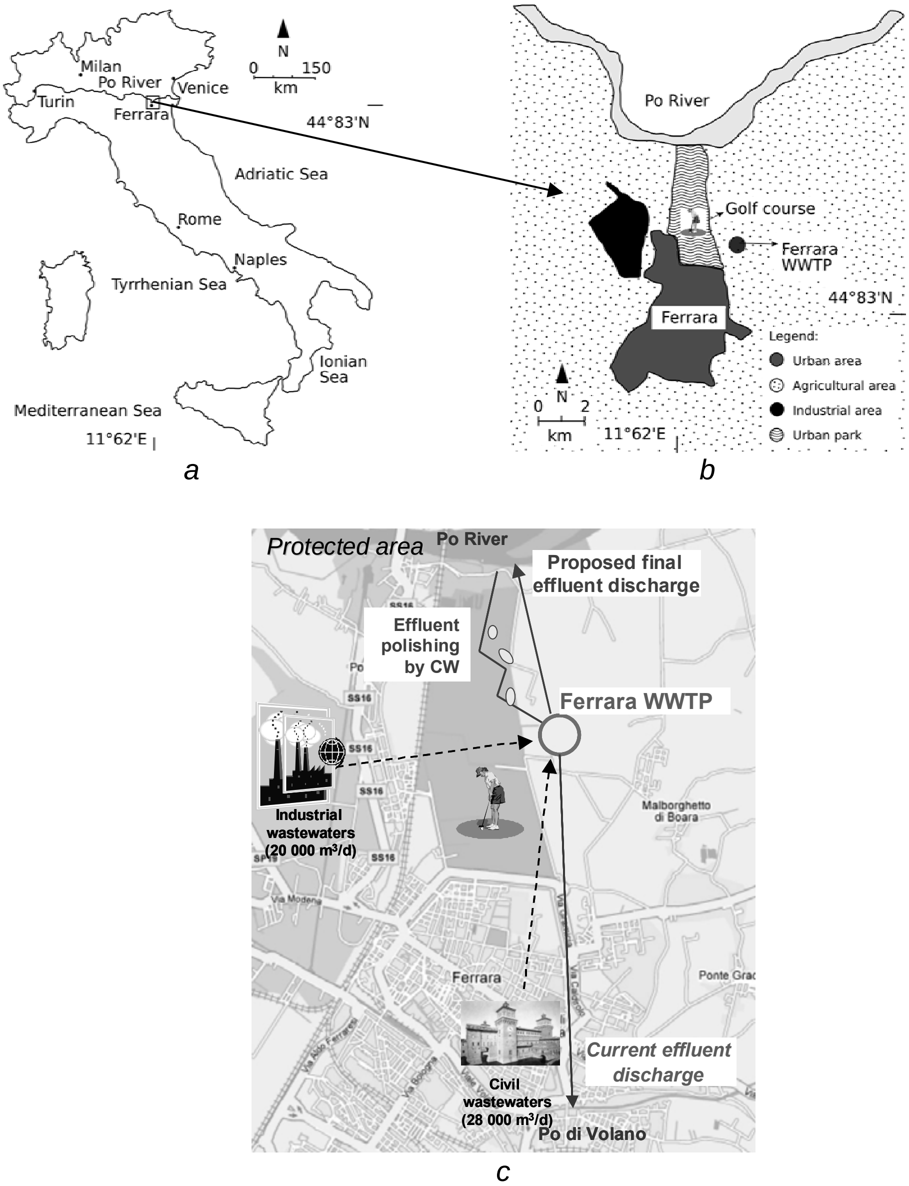

Fig. 1 The area under study (a, b) and scheme of the proposed intervention (c).

According to the recently approved local planning Act, this is an area of high environmental interest that could be further exploited for recreational activities. Moreover, the quality of the WWTP final effluent could be improved by *natural* systems (including subsurface flow systems and lagoons) for reuse purposes. Currently the whole local huge water demand for agricultural and recreational activities is satisfied by the water withdrawn from the local surface water network. The possibility to reuse reclaimed wastewater would significantly reduce the seasonal request of water from natural resources and at the same time the water volume discharged from the WWTP into the local surface water bodies, including its pollutants load.

In order to support and help policy makers in comparing different scenario in the polishing treatment of the secondary effluent of Ferrara WWTP a water quality index has been defined and used for comparisons among the different treatment sequences investigated including natural systems (horizontal subsurface flow and lagoons) as well as conventional treatments (rapid filtration).

The present study illustrates and discusses the results of deepened environmental investigations: (i) a prediction of the main pollutants loads reduction and their environmental impact in the two receiving water bodies (the current Po di Volano and the proposed Po River); (ii) the feasibility of a discharge in a protected area and the main design parameters for polishing treatment of a secondary effluent by natural systems (constructed wetlands and lagoons). A new index, Polishing Wastewater Index. PWWI is defined and proposed in order to quickly compare achieved water quality levels by means of different polishing treatments.
Finally, the main outlines of the project are presented and discussed, including construction and operation costs.

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UV-A AND SOLAR DRIVEN CATALYTIC REMOVAL OF OFLOXACIN PRESENT IN SEWAGE INTENDED FOR REUSE

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Currently in Cyprus, like in many other countries worldwide, there is an increasingly growing momentum towards the reuse of wastewater for irrigation and groundwater replenishment, while at the same time the concern with respect to the presence of xenobiotic compounds including pharmaceutical residues in the treated wastewater effluents follows also an increasing trend. Since the treated effluents are used for irrigation purposes, negative environmental impacts may occur over long periods of application, where chemicals like drugs, can persist and bio-concentrate through partitioning to soil and possibly plants. For this reason, the occurrence and removal efficiency of 29 pharmaceutical compounds at the three largest urban wastewater treatment plants in Cyprus, which apply activated sludge treatment, was studied recently. The presence of a number of drugs was confirmed and for some of them, high concentrations were obtained for the final effluents (e.g. ofloxacin, diclofenac, carbamazepine, metoprolol). The existing conventional treatment processes biological (secondary step) and sand-filtration + chlorination (tertiary step) applied are not capable to remove various classes of organic xenobiotic compounds. Therefore, the purpose of this study was to apply advanced oxidation to remove ofloxacin, as an example, from aqueous solutions and actual sewage. In this context, heterogeneous photocatalysis using TiO_2 as photocatalyst and photo-Fenton have been applied for the degradation and mineralization of ofloxacin (10 mg/L) spiked in pure water and in actual urban wastewater. The experiments were carried out using a UV-A lamp (9W) and also a solar simulator (Newport, Xenon 1kW). The operating conditions studied include the catalyst loading, the initial substrate concentration, the solution pH, the initial Fenton reagents concentration, the initial $[Fe(II)]/[H_2O_2]$ ratio and the water matrix on the kinetics of the drug conversion. The changes in the ofloxacin substrate concentration (i.e. parent compound + potential byproducts that absorb at the same characteristic wavelength) were monitored using a UV-Vis Spectrophotometer (Jasco V-350). To determine the extent of mineralization, TOC was measured by a Shimadzu TOC analyzer.

The higher substrate conversion (100%) was achieved by the photo-Fenton method in comparison to TiO_2 photocatalysis (36%). Furthermore, it was found that small amounts of iron in the photo-Fenton process were capable to achieve satisfactory reaction rates for the ofloxacin and TOC removal (40%). The proposed poster presentation will include the kinetics of the conversion and mineralization and the effect of the various parameters studied on the rate of the conversion/mineralization.

ALTERNATIVE BIOLOGICAL TREATMENT FOR DEGRADING MICROPOLLUTANTS IN WATER USING LIGNINOLITIC FUNGI

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In the last years, the presence of emerging micropollutants such as pharmaceuticals and personal care products (PPCP), endocrine disruptors chemicals (EDC) such as hormones, and brominated compounds in the environment has received much attention [1]. After their consumption, some of these compounds can be transformed partially in the body and thus excreted as a mixture of metabolites primarily into the sewage systems. Once in the sewage treatment plants (STP), these micropollutants are barely reduced and pass throughout the STP to the receiving waters as unchanged parent compound or transformed to a more hydrophilic form. Their sorption to suspended solids and subsequent disposal with sludge is also another route by which they can be released to the environment.
To date, most of the research interests in emerging contaminants were focused on the occurrence and behaviour of them in the environment and in STP's. However, it seems that bacteria in these facilities are not able to degrade some of these compounds.
The present work asses the feasibility of emerging micropollutants remediation of waste waters by white-rot fungi (WRF). WRF are a cosmopolitan group of microoganisms with a high capability to degrade a wide range of xenobiotics and recalcitrant pollutants due to the complexity of their enzymatic systems, able to act on diverse substrates through the attack of extracellular and intracellular enzymes. The fungus *Trametes versicolor* was able to degrade completely 10 mg/L of Ibuprofen after 7 days of incubation. Clofibric acid and carbamazepine were 91% and 58% degraded respectively under the same conditions [2]. Non detectable levels were achieved for ketoprofen in 24 hours, whereas at low concentration of 50 µg/L it was almost completely removed (95%). Naproxen (10 mg/L) was also degraded (>99%) after 6 hours, and 95% removed at low concentration (55 µg/L). Decabromodiphenyl ether was 68% degraded after 7 days. A bioreactor with *T. versicolor* pellets was continuously operated at a HRT of 120 h treating 17β-estradiol (18.8 mg/L) and 17α- ethynylestradiol (7.3 mg/L). These compounds were almost completely removed [3].
These results demonstrate the great interest of fungi as a bioremediation agent for the treatment of micropollutants in waters.

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PRESENCE OF DICLOFENAC AND ITS HUMAN METABOLITES IN WWTP AND EVALUATION OF THEIR TOXICITY

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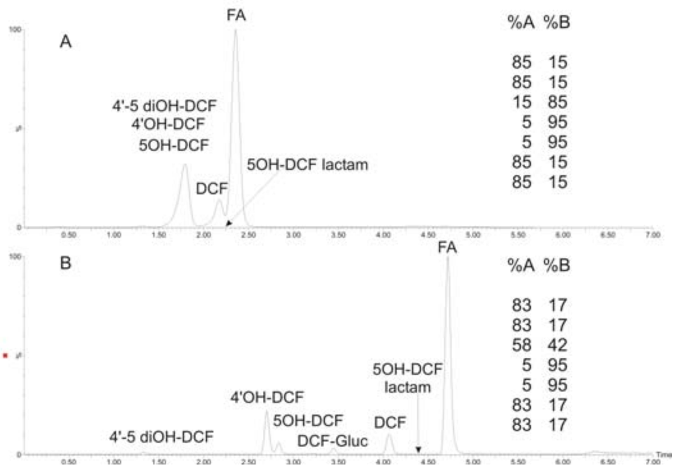
Many pharmaceuticals along with their metabolites have been detected in different environmental matrixes like surface and wastewaters, sewage sludge, landfill sites, soils, ground water and even in drinking water. Among the aqueous samples, several studies have reported the presence of pharmaceuticals and their metabolites with concentrations ranged from ng/L to μg/L. These levels of concentration detected, are supposed to be directly related with the high consumption in the population.
Diclofenac (DCF), a non-steroidal anti-inflammatory drug (NSAID), is mainly metabolized to its hydroxilated metabolites or methoxylated derivatives and further conjugated and in a minor extent to a reactive acyl glucuronide metabolite, namely diclofenac-1-O-acyl glucuronide. Excretion of the main metabolite 4′-hydroxy diclofenac and its conjugates in human urine correspond to 16 %. About 10-20 % of the oral dose is excreted as unaltered DCF and its acylglucuronide. Other minor oxidative metabolites excreted by humans are the 5-hydroxy, 4',5-dihydroxy, 3-hydroxy and 3′-hydroxy-4′-methoxy derivatives of DCF either as such or conjugated with glucuronic acid. Once DCF and its metabolites are excreted they reach the wastewater treatment plants (WWTP). Several studies have reported the presence of DCF in untreated sewage at low υg/L level, associated with high consumption rates. DCF presents low removal efficiencies during conventional activated sludge treatment in WWTPs and therefore has been frequently detected in monitoring surveys on sewage-impacted surface waters. However, little attention has been paid to environmental field data of its metabolites**.** This work presents the first determination of several human metabolites of DCF including their glucuronides in wastewater samples from different WWTP using new developed extraction and detection methods relying on SPE and LC-MS/MS (ultra performance liquid chromatography coupled to triple quadrupole mass spectrometer, equipped with a Z-spray ESI interface (ACQUITY-TQD) Oasis HLB (200 mg, 6 mL) and Strong cation Exchange Oasis MCX (150 mg, 6 mL)). Only DCF and its human metabolites 5-hydroxyDCF an its lactam were detected in the extracts of the new developed extraction method for effluent and influent wastewater samples from WWTP Rubí. Regarding the range of concentration quantified for DCF and its metabolites, both in influent and effluent wastewawater samples, the concentration of DCF was higher than the concentracion of its human metabolites.

Figure1. Chromatograms registered by UPLC/(-)-ESI-QqToF-MS in MRM mode for the development of the separation method of DCF and its human metabolites. (A) first gradient tested (B) final gradient used for the analysis.



Moreover, in the present work, the individual toxicity of DCF metabolites was evaluated according to standard procedures using as test species the microcrustaceum Daphnia magna, a chlorophite algue Selenastrum capricornutum and the marine bacteria Vibrio fischeri. The metabolites responses will be presented in contrast to result for the parent compound.

Acknowledgments

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LINKING EFFLUENT DISCHARGES, RIVER FLOW AND MEASURED ENVIRONMENTAL CONCENTRATIONS OF EMERGING CONTAMINANTS IN THE LOW LLOBREGAT RIVER (NE SPAIN)

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Presence of emerging contaminants in environmental waters is directly related to their removal in wastewater treatment plants (WWTP) and the flow rate of the receiving river waters. Moreover, Mediterranean rivers are characterized by (i) important fluctuations in the flow rates and (ii) heavy pollution pressures resulting from extensive urban, industrial and agricultural activities. This translates into contamination levels in these rivers often higher than in other larger European basins.

The present work provides an overview of the occurrence of five groups of emerging organic contaminants, namely, pharmaceutically active substances (PhACs), illicit drugs, polar pesticides, estrogens and alkyphenol ethoxylates, in WWTP tertiary treatment effluents and the receiving surface waters, using as illustrative case example the data gathered in the experiences of water reuse carried out in the low part of the Llobregat River (NE Spain), in the surroundings of the town of Barcelona during the summer and fall of 2008, by the responsible Water Authority (Catalan Water Agency) as a consequence of the severe drought that took place along the years 2007-2008 in the area.

The issue of water reuse and its effect on surface waters is discussed on quantitative terms using load mass balances. Predicted and found concentrations of the contaminants are compared, and the influence of flow dilution factors is studied.

REMOVAL OF ANTHELMINTIC DRUGS AND THEIR PHOTODEGRADATION PRODUCTS BY NF/RO – LABORATORY SCALE STUDY

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The fate and effects of the most of known pharmaceuticals as they are exposed to the environment is yet not known. After certain pathways and possible reactions in human and animal body, variety of unchanged active pharmaceutical compounds and their metabolites are excreted through urine or faeces. Entering the environment, pharmaceuticals and their metabolites are exposed to the sunlight that can cause degradation of such compounds and even increase in toxicity. Therefore the great efforts and hopes are laid in the advanced water and wastewater treatment technologies to be implemented on the point where contamination occures.

In this study anthelmintic drugs were investigated. This drugs used in veterinary practice to threat infections with parasitic worms, applied in great quantities, have the potential to appear in surface waters. The photochemical behaviour of the four anthelmintics, albendazole, praziquantel, levamisole, and febantel in water was investigated followed by laboratory scale removal through RO/NF membranes. In this study a NF/RO laboratory scale up for wastewater treatment using membrane technology was applied and membranes' removal potential for anthelmintic drugs and their photodegradation products was investigated.
Samples were exposed to UV light of 254 nm. Even though the UV light of 254 nm could not pervade on the Earth surface, irradiations were performed at the above mentioned wavelengths to determine as much photodegradation products as possible. Water solutions of anthelmintics before and after irradiation were passed through six different types of RO/NF membranes. The results (HPLC chromatograms of water samples) show efficient removal of active pharmaceutical compounds and the majority of photodegradation products (>99%) by two RO membranes (LFC-1 and XLE) and by the tight nanofiltration NF90 membrane. Other nanofiltration membrane elements tested incompletely remove investigated active compounds and their degradation products.

Key words: anthelmintic drugs, photodegradation products, RO/NF membrane treatment

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CHARACTERIZATION OF PRODUCED WATER FROM COALBED METHANE PRODUCTION WITH EMPHASIS ON ORGANIC CONSTITUENTS RELEVANT FOR TREATMENT

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Interest in energy independence has led to the utilization of coalbed methane (CBM) natural gas, an unconventional gas source with large reserves worldwide. Environmental impacts of CBM development are associated with the disposal of substantial amounts of co-produced, highly saline water that accompanies CBM production. Beneficial use of CBM co-produced water is presently limited by the lack of knowledge of co-produced water quality and variations related to geographic location. This information is crucial to optimize treatment processes for beneficial use. This poster focuses upon determining spatial variation of produced water quality in CBM producing basins, characterizing organic matter present in produced water for insight into treatment system development, and predicting water quality spatially within a basin based on hydrologic flow and geochemical data analysis. Overall, inorganic constituents in produced water appear to be influenced most heavily by groundwater flow paths and organic constituents appear to be influenced by the coal forming process and microbial activity.

MULTI-RESIDUE METHOD FOR TRACE LEVEL DETERMINATION OF PHARMACEUTICALS IN SOLID SAMPLES USING PRESSURIZED LIQUID EXTRACTION FOLLOWED BY LIQUID CHROMATOGRAPHY/QUADRUPOLE-LINEAR ION TRAP MASS SPECTROMETRY

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The presence of low levels of pharmaceutically active compounds (PhACs) in the environment is presently an issue of concern due to possible adverse biological effects on the ecosystem. One of the significant points of collection and subsequent release of PhACs into the environment are wastewater treatment plants. The studies of effluent waters and river sediment show that wastewater treatment achieves only partial removal of these organic pollutants. The important question is if these compounds degradate or just sorb to the sludge produced during the wastewater treatment. Occurrence and distribution of PhACs in sewage sludge demands detailed investigations, especially because the digested sludge is disposed to landfills or used as agricultural fertilizer.

This study was performed in an effort to develop and validate a simple and sensitive method for simultaneous analysis of 43 pharmaceutical compounds in sewage sludge and sediment samples. The target compounds belong to different therapeutic groups of pharmaceuticals. The target compounds were extracted using Pressurized Liquid Extraction (PLE) and then purified and pre-concentrated by Solid Phase Extraction (SPE) using a hydrophilic-lipophilic balanced polymer. PLE extraction was performed on temperature of 100ºC, with methanol/water mixture (1/2, v/v) as extraction solvent. The quantitative analysis was performed by liquid chromatography tandem mass spectrometry using a Hybrid Triple Quadrupole Linear Ion Trap mass spectrometer (LC-QqLIT-MS). Data acquisition was carried out in Selected Reaction Monitoring (SRM) mode, monitoring two SRM transitions to ensure an accurate identification of target compounds in the samples. Additional identification and confirmation of target compounds were performed using the Information Dependent Acquisition (IDA) function. The method was validated through the estimation of the linearity, sensitivity, repeatability, reproducibility and matrix effects. The internal standard approach was used for quantification because it efficiently corrected matrix effects. Despite the strong matrix interferences, the recoveries were generally higher of 50% in both matrixes and the detection and quantification limits were very low. Beside the very good sensitivity provided by LC-QqLIT-MS, an important characteristic of the method is that all the target compounds can be simultaneously extracted, treated and analysed. Hence, it can be used for routine analysis of pharmaceuticals providing large amount of data. The method was applied for the analysis of pharmaceuticals in river sediment and wastewater sludge from three treatment plants with different treatment properties (i.e. capacity, secondary treatment, quality of influent waters). The analysis showed a widespread occurrence of PhACs in the sludge matrices.

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DETERMINATION OF MULTI-CLASS PHARMACEUTICALS IN WASTE WATER BY FULLY AUTOMATED ON-LINE SPE-LC-MS/MS

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A fully automated multicomponent method for the determination of more than 70 pharmaceuticals in waste water has been developed.

This method consist of online SPE-LC-ESI-(QqLIT) MS/MS. The online SPE and the LC separation are carried out by Symbiosis™ Pico System (Spark Holland, Emmen, The Netherlands). This is connected in series with a 4000QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer equipped with a Turbo Ion Spray source, where MS/MS is accomplished. A filtration by a 0.45 µm pore size is the only previous task that must be realized.

The main advantages of this method are:

- good sensitivity (limits of quantification down to below ng/L level);
- full automation and therefore minimum sample manipulation;
- elevated number of pharmaceuticals analyzed simultaneously (more than 70 compounds);
- high throughput (full analysis of all compounds for each sample in 30 + 37 minutes);
- application in complex matrixes like waste water (equivalent surrogate for every compound is used to correct the losses in the SPE and the matrix effect), and
- small sample volume needed (2.5 mL per sample).

All of the pharmaceuticals analyzed were selected because of their widespread use so they are likely to be found in sewage. Several therapeutic groups are included, such as analgesics and antiinflammatories, β-blokers, lipid regulators, antibiotics, diuretics, psychiatric drugs, antidiabetics, antihipertensives, etc.

The method developed shows significant improvements in comparison to currently available methods:

- throughput (several fold less time needed for each sample analysis);
- sensitivity (lower LODs and LOQs for most of compounds comparing);
- confidence (almost no human sample manipulation);
- sample transportation, storage and management (2.5 mL versus hundreds or even thousands of mL), and
- applicability (appropriate method for complex samples).

All this features are essential to satisfy the current interest about human contribution to water contamination as well as to support the search of ways of minimizing that impact.

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