WASTEWATER REUSE IN MEDITERRANEAN SEMI-ARID AREAS: THE IMPACT OF DISCHARGES OF TERTIARY TREATED SEWAGE ON THE LOAD OF POLAR ORGANIC POLLUTANTS
The Llobregat River case study

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Contents

1. Introduction
   • Global change in the Mediterranean Area
2. Catalonia (NE Spain): Hydrological Scenario
3. Case study: El Prat (Barcelona) WWTP
   • Overview
   • Emerging contaminants
   • Mass balances
4. Conclusions
1. Introduction: Global change in the Mediterranean Area

*Global Change in the Mediterranean Area*

a) CLIMATE CHANGE

**Temperature**  
**Precipitation**

Predicted relative changes in Temperature and Precipitation in the Mediterranean Area (A1B scenario).

(Source: Christensen et al., 2007)
Mediterranean rivers

Mediterranean rivers are subjected to sequential seasonal events showing high flow regime variation (dry and wet seasons), and extreme events like sudden floods and severe droughts.

Climate change will increase their occurrence!

Global Change in the Mediterranean Area

b) LAND USE CHANGE

Ex.: Reforestation:

- Evapotranspiration
- Runoff
Global Change in the Mediterranean Area

c) SOCIO-ECONOMIC CHANGE

Ex: Population growth and concentration in the BCN and coastal area

Scenarios of population evolution. Red line: the most probable scenario pointing to ca. 9,000,000 inhabitants on the 2025 (8.5 + 0.4).
Expected growth expressed on percentage for the different municipalities of Catalonia.

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Hydrological scenario: River Flow decrease

River Ebro Year Flow in Tortosa
average decrease in 60 years: 538 m³/s to 270 m³/s

Source: MIMAM, 2000
Global Change in the Mediterranean Area

MEDITERRANEAN FORESEEN SCENARIO UNDER GLOBAL CHANGE

Water Scarcity
Aquatic Ecosystem impairment
Loss of water resources (quality and quantity)
Effect on ecosystem Services

“Global Change”

2. Catalonia (NE Spain): Hydrological Scenario
The Catalan River Basin District

Catalonia is a representative region of the northwestern Mediterranean area.

- **Internal** Basins
  - 16,628 km² (52% of the territory)

- Interregional Basins (Ebro)
  - 15,268 km² (48% of the territory)

Catalonia: hydrological scenario

**DISTRIBUTION OF POPULATION, RESOURCES AND WATER USES IN CATALONIA**

- **Ebro Basin**
  - 15,268 km² (48% of the territory)
  - 92% Population
  - Present Water demands: 1827 hm³/year

- **Internal** Basins
  - 16,628 km² (52% of the territory)
  - 92% Population
  - Present Water demands: 1138 hm³/year

**Water uses distribution 2006**

- Agriculture: 92%
- Urban: 52%
Hydrological scenario: Increase of drought periods

- Catalonia (NE Spain) basins, a typical representative of Mediterranean region, is frequently suffering from water scarcity
- Water demands are close to available water resources, which are expected to decrease in the medium and long term

Reserves al sistema Ter - Llobregat

Evolution of water reserves on the reservoirs of the Ter – Llobregat system, showing drought periods (■)

The 2008 drought episode: extraordinary measures

- Sau, Ter River 18%
- La Baells, Ter River 23%
- Llosa del Cavall, Carender River 15%
- February, 2008

Llega el agua

El primer buque cargado con 20,000 toneladas de agua llegó a Barcelona ayal de Tarragona

“La Vanguardia” 13th May, 2008
Catalonia is suffering what has been qualified as

“Structural Water Shortage”

Estimated Water Deficit in the Catalan Internal Basins (projection 2025):

300 Hm$^3$/year

NEW WATER RESOURCES ARE NEEDED!

Planned Management Measures (2025):

<table>
<thead>
<tr>
<th>NEW RESOURCES</th>
<th>Hm$^3$/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desalination</td>
<td>190 (80)</td>
</tr>
<tr>
<td>Reuse</td>
<td>101 (51)</td>
</tr>
<tr>
<td>Groundwater Recharge &amp; Recovery</td>
<td>43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INFRASTRUCTURE IMPROVEMENT</th>
<th>Hm$^3$/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improvement of water treatment, regulation and systems</td>
<td>55</td>
</tr>
</tbody>
</table>

TOTAL INCREASE (by 2025) 389 Hm$^3$/year

Source: Catalan Water Agency (ACA), 2009

Current and planned reuse of water in Catalonia

- Reclaimed water can not be directly reused for drinking, but are suitable for urban uses (irrigation streets, gardens and other urban services), for agricultural use, for environmental uses (ecological flow maintenance, supply of wetlands) and, with appropriate treatment, to recharge aquifers and some industrial uses.

<table>
<thead>
<tr>
<th>Year 2008</th>
<th>Year 2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of reused water</td>
<td>Volume of reused water</td>
</tr>
<tr>
<td>51 hm$^3$</td>
<td>153 hm$^3$ (*)</td>
</tr>
</tbody>
</table>

Distribution of uses

(*) Net recovered resources 101 hm$^3$
Objective:
To investigate the impact of discharges of tertiary treated sewage on the load of polar emerging pollutants in a typical Mediterranean River (Llobregat) during a drought period (2007-2008).
**Llobregat River (Catalonia, NE Spain)-A profile**

- 156 km long, covering a catchment area of ~5,000 km²
- River flow suffers from extreme and sudden fluctuations, strongly influenced by the seasonal rainfall (1 m³/s -100 m³/s)
- Heavy contamination pressures from extensive urban (55+ WWTPs), industrial and agricultural activities
- Effluents may represent a high percentage of the total flow of the river, especially in drought periods
- Conc. of organic pollutants increase downstream the river, together with WWTPs discharges and population density

**WWTP + WRS (Water Reclamation Station):**
(El Prat, Barcelona, Spain)

- **2008:**
  - 266,500 m³/day of wastewater (97.5 hm³/y) [Design: 420,000 m³/day]
  - 1,141,538 eq. inhabitants

- Primary treatment
- Basic treatment
- Max flow = 320,000 m³/day
- Filtration and disinfection steps
- Advanced treatment (Reverse Osmosis)
  - Flow = 15,000 m³/day (can be 15,000 m³/day)

- Secondary treatment
  - 65.8 hm³/y, of the effluents discharged into the Mediterranean Sea through an emissary 3.2 km long.

- Tertiary treatment
  - to reuse 31.7 hm³/y
Tertiary treatment in WRS (El Prat)

Basic treatment
- Physico-chemical
- Microfiltration 10 microns
- UV disinfection + Chlorine

Advanced treatment with osmosis
- Ultrafiltration
- Reverse Osmosis

Water reuse in the Llobregat river:
Expected Regenerated Water Demands (~ 50 hm³/year)
- Flow maintenance in the Llobregat river
- Recharge ponds for the aquifer in the Llobregat delta
- Agricultural irrigation
- Wetlands irrigation in the Llobregat delta
- Industrial
- Hydraulic barrier against saline intrusion
- Green areas
Sampling Points

Sampling at lower section of the Llobregat River (NE Spain), in the surroundings of the town of Barcelona during the fall of 2008, as a consequence of the severe drought that took place during 2007-2008 in the area.

a) Point 1: river upstream
b) Point 2: intake of an important drinking water treatment plant supplying water to Barcelona
c) Point 3: treated water from the WWTP tertiary treatment of El Prat de Llobregat

Compound list and analytical methods

Compound selection:
(i) continuous introduction into the environment, either by diffuse or point sources via effluents from sewage treatment facilities
(ii) they are inherently biologically active
(iii) some of them are used by man in rather large quantities

<table>
<thead>
<tr>
<th>Family</th>
<th>Extraction</th>
<th>Analysis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>SPE</td>
<td>LC-UV/ESI-MS/MS</td>
<td>Gros et al. (2008)</td>
</tr>
<tr>
<td>Illicit Drugs</td>
<td>on-line SPE</td>
<td>LC-UV/ESI-MS/MS</td>
<td>Postigo et al. (2008)</td>
</tr>
<tr>
<td>Pesticides</td>
<td>on-line SPE</td>
<td>LC-UV/ESI-MS/MS</td>
<td>Kangari et al. (2005)</td>
</tr>
<tr>
<td>Estrogens</td>
<td>on-line SPE</td>
<td>LC-UV/ESI-MS/MS</td>
<td>Rodriguez-Mazon et al. (2004a)</td>
</tr>
<tr>
<td>Alkyl phenols and other ethoxylates</td>
<td>SPE</td>
<td>LC-UV/ESI-MS/MS</td>
<td>Gonzalez et al. (2004)</td>
</tr>
</tbody>
</table>

Carbamazepine

Metolachlor

Naproxen

Cocaine
Occurrence of Emerging Contaminants

RESULTS: Levels of emerging contaminants in water.

a) Pharmaceuticals

b) Pesticides

c) Illicit drugs and metabolites

d) Estrogens

e) Alkylphenols & ethoxylates derivatives

Mass balance model

Load (point i, compound j) = \( Q_i \cdot c_{ij} \)  

\( Q_{\text{load river downstream(#2)}} = Q_{\text{load river upstream(#1)}} + Q_{\text{effl. discharged(#3)}} \)

No additional sources

\( Q_2 \cdot c_{2j} = Q_1 \cdot c_{1j} + Q_3 \cdot c_{3j} \)

\( Q_2 = Q_1 + Q_3 \)

Flow variation

<table>
<thead>
<tr>
<th>Flow variation</th>
<th>16/10/2008</th>
<th>21/10/2008</th>
<th>22/10/2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet</td>
<td>0.85</td>
<td>1.13</td>
<td>1.5</td>
</tr>
<tr>
<td>WWTP: influent</td>
<td>0.99</td>
<td>0.99</td>
<td>1.0</td>
</tr>
</tbody>
</table>

No additional sources

\( C_{ij}(\text{calc}) = \frac{Q_1 \cdot c_{1j} + Q_3 \cdot c_{3j}}{Q_2} \)
**Loads (mass-flows) balances (1)**

**Experimental vs. Calculated concentrations**

\[ \text{Load (point } i, \text{ compound } j) = Q_i \cdot c_{ij} \quad \text{dimension: } M \cdot T^{-1} \]

Load (mass flow) per family of pollutants

<table>
<thead>
<tr>
<th>Family</th>
<th>Load (mg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>15471</td>
</tr>
<tr>
<td>Estrogens</td>
<td>92</td>
</tr>
<tr>
<td>Pesticides</td>
<td>2279</td>
</tr>
<tr>
<td>Illicit Drugs</td>
<td>1149</td>
</tr>
<tr>
<td>Alkyl Phenols</td>
<td>7820</td>
</tr>
</tbody>
</table>

**PHARMACEUTICALS > ALKYL PHENOLS > PESTICIDES > DRUGS >> ESTROGENS**

**Loads (mass-flows) balances (2)**

**River vs. Effluent relative contributions**

\[ \text{Load river downstream(\#2)} = \text{Load river upstream(\#1)} + \text{Load effl. discharged(\#3)} \]

\[ \text{Load (point } i, \text{ compound } j) = Q_j \cdot c_{ij} \]

Upon aggregation of the loads at family level:
- Both river upstream and effluent discharged contribute to pharmaceuticals, drugs and pesticides
- Estrogens originate from the WWTP tertiary effluent
- In contrast, the presence of alkyl phenols derivatives (Figure 3e) can be associated to the upstream river (ca. 80%).
**Conclusions (1)**

- Detection of a broad spectrum of organic pollutants corroborates the heavy impact on water quality by urban, industrial and agricultural activities in the Llobregat catchment area.

- As expected, in general terms, effluent waters usually show higher concentrations of pollutants than the river.

- Loads (mass-flows) provide a more realistic way to compare in bulk the weight contribution of the different pollutant families studied in quantitative terms:

  The following order per families holds:

  **PHARMACEUTICALS > ALKYL PHENOLS > PESTICIDES > DRUGS >> ESTROGENS**
Conclusions (2)

• From the loads calculated in the Llobregat river, and recalling the high diversity of compounds examined, it follows that no general rules can be easily established at compound level, each one requiring an individual study.

• Upon aggregation of loads at family level, and comparing the upstream river and effluent respective contributions, it can be concluded that:
  – **PARMACEUTICALS, DRUGS** and **PESTICIDES**: both the river upstream basin and the tertiary effluent have comparable load contributions
  – **ESTROGENS**: even though at low concentration levels, are almost exclusively associated to the tertiary effluent (urban origin)
  – **ALKYL PHENOLS**: is mostly associated to river upstream (industrial origin)

Thank you for your attention

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