SCARCE 2nd ANNUAL CONFERENCE

Integrated modelling and monitoring at different river basin scale

28-29 November 2011, Madrid, Spain

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Integrated modelling and monitoring at different river basin scale

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Book of abstracts of the SCARCE 2nd Annual Conference
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With contributions of all conference participants

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Water has been a major driver of socio-economic development in all civilizations. The increasing anthropogenic manipulation of the hydrological cycle, as well as the exacerbation of climate change forcing, result in relevant pressures that translate in even larger uncertainties in sensitive areas. In particular, the Mediterranean region is undergoing severe alterations in water availability because of a decrease in the number of precipitation days, and an increase in days with heavy rains. The imbalance between the available water resources during extended droughts and the increasing anthropogenic water demand results in major ecological and economical problems.

The SCARCE project is defined as a multipurpose project that aims to describe and predict the relevance of global change impacts on water availability, water quality and ecosystem services in Mediterranean river basins of the Iberian Peninsula, as well as their impacts on the human society and economy. The project assembles a multidisciplinary view through hydrology, geomorphology, chemistry, ecology, ecotoxicology, economy, engineering and modelling. The project also considers the active involvement of Water Authorities and other relevant agents as stakeholders.

The second SCARCE Conference aims to gather interested researchers and water managers at the cross-roads of using water resources and keeping its ecological quality and conservation. Particularly, specific topics of this conference would be:

- Monitoring programme design that includes long-term, concurrent hydrometeorological, water quality, morphology and biological monitoring of reference sites to improve evidence of causative links between climate variability and local ecological status.

- Analysis of interactions between surface and groundwater hydrology taking place at the mesoscale (dm to tens of m).

- Development of integrative simulation tools (process oriented models) to assess the effects of global changes in aquifers, streams and rivers.

- Development of system-oriented tools defined at the river network (water body scale), taking into account the integration of the water cycle into the water resources management at catchment scale.

- Assessment of the multiple effects of changes in the hydrological regime (duration, intensity, time, and frequency of floods and droughts) on both biodiversity and ecosystem processes.

- Methodological framework development to quantify global change effects in terms of environmental and human risks.
This SCARCE Conference is intended to be an informal venue that encourages an exchange of the latest information and ideas among scientists bearing pluridisciplinar approaches, in the deep belief that only through scientific debate it will be possible to produce good assessments and provide reliable predictions, later to be used and implemented by water managers.

We would like to thank to all participants, and especially those accepting our invitation to provide complementary views to those of SCARCE members. We appreciate the ETS de Ingenieros de Minas de la UPM for providing the excellent facilities of the Conference room.

Fco. Javier Elorza and Damià Barceló

Madrid, November 28th, 2011
Monday, 28th November 2011

9.00 - 9.30 Registration

9.30 - 9.50 Opening ceremony
Rosa de Vidania¹, Carlos Conde², Francisco Javier Elorza³ and Damià Barceló⁴,⁵,⁶
¹ General Director from the Instituto Geológico y Minero de España (IGME)
² Vice-rector of the Universidad Politécnica de Madrid (UPM)
³ Dept. Geological Engineering, Escuela Técnica Superior de Ingenieros de Minas, Universidad Politécnica de Madrid, Madrid, Spain
⁴ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
⁵ Catalan Institute for Water Research (ICRA), Girona, Spain
⁶ King Saud University, Riyadh, Saudi Arabia

Session I: Monitoring network programme

Chairperson: Mira Petrovic

9.50 - 10.20 The implementation of Chemical Monitoring in Surface Waters under the Water Framework Directive
Mario Carere
National Institute of Health, Department Environment, Italy

10.20 - 10.50 Monitoring water-polluting pesticides at the catchment scale in the Ebro, Llobregat, Jucar and Guadalquivir Rivers
Yolanda Picó, Ana Masia, Cristina Blasco and Pablo Vazquez
Food and Environmental Safety Research Group, Faculty of Pharmacy, University of Valencia, Burjassot, Spain

10.50 - 11.10 Automated analytical method for the determination of perfluorinated compounds in fish in Spanish rivers
Francisca Pérez¹, Marta Llorca¹, Marinella Farré¹ and Damià Barceló¹,²,³
¹ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
² Catalan Institute for Water Research (ICRA), Girona, Spain
³ King Saud University, Riyadh, Saudi Arabia

11.10 - 11.30 Poster session/Coffee break

Chairperson: Mario Carere

11.30 - 12.00 Levels and spatial distribution of emerging contaminants in the Iberian rivers
Mira Petrovic¹,², Marina Gorga³, Victoria Osório³, Sandra Perez² and Damià Barceló¹,³,⁴
¹ Catalan Institute for Water Research (ICRA), Girona, Spain
² Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain
³ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
⁴ King Saud University, Riyadh, Saudi Arabia
12.00 - 12.20  Integration of on-line and off-line methodologies for the assessment of river water quality
Ramon López-Roldán¹, Susana González¹, Sergi Pelayo², Benjamín Piña², Agustina de la Cal³, Raquel Céspedes³, Alfredo Diaz³, Maria Rosa Boleda³, Ricard Devesa³ and Jose Luis Cortina¹
¹ Water Technology Centre (CETaqua), Cornellà de Llobregat, Barcelona, Spain
² Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
³ Aguas de Barcelona, Barcelona, Spain

12.20 - 12.40  Presence of illicit drugs in different wastewater treatment plants in Mediterranean river basins of the Iberian Peninsula
Nicola Mastroianni¹, Miren López de Alda¹ and Damià Barceló¹,²,³
¹ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
² Catalan Institute for Water Research (ICRA), Girona, Spain
³ King Saud University, Riyadh, Saudi Arabia

12.40 - 14.00  Lunch

Session II: Analysis of interactions between surface and groundwater hydrology

Chairperson: Francisco Javier Elorza

14.00 - 14.30  Understanding the fate and behaviour of selected pharmaceuticals in soil-aquifer material prior to artificial recharge
Manuela Barbieri¹, Jesús Carrera¹, Carlos Ayora¹, Xavier Sanchez-Vila², Tobias Licha³, Karsten Nödler³, Victoria Osorio⁴, Sandra Pérez⁴, Marianne Köck-Schulmeyer⁴, Miren López de Alda⁴, Damià Barceló⁴,⁵,⁶, Joana Tobella Brunet⁷ and Marta Hernández García⁷
¹ GHS, Dept. of Geosciences, IDAEA-CSIC, Barcelona, Spain
² GHS, Dept. of Geotechnical Engineering and Geo-Sciences - Technical University of Catalonia, Barcelona, Spain
³ Hydrochemistry Group, Dept. of Applied Geology - Geoscience Centre of the University of Göttingen, Göttingen, Germany
⁴ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
⁵ Catalan Institute for Water Research (ICRA), Girona, Spain
⁶ King Saud University, Riyadh, Saudi Arabia
⁷ Water Technology Centre (CETaqua), Cornellà de Llobregat, Barcelona, Spain

14.30 - 15.00  Numerical solution of problems based on shallow water and St. Venant’s equations.
Arturo Hidalgo¹, Angel Balaguer-Beser² and Llanos Gascón²
¹ Escuela Técnica Superior de Ingenieros de Minas, Universidad Politécnica de Madrid, Madrid, Spain
² Universidad Politécnica de Valencia, Dep. Matemática Aplicada, Valencia, Spain
15.00 - 15.20  Modeling and mapping chemical reactions in complex subsurface natural systems
Daniel Fernàndez-Garcia, Xavier Sanchez-Vila, Felipe de Barros, Simonetta Rubol, Christopher Henri and Nicolás Iturra
GHS, Dept. Geotechnical Engineering and Geosciences, Universitat Politècnica de Catalunya, UPC-Barcelona Tech, Barcelona, Spain

15.20 - 15.40  The dynamics of groundwater resources in the El-Qaa irrigation district of Orontes Basin in Northern Bekaa Valley of Lebanon
Fadi Karam¹, Joseph Monical², Prasanta Kalita², Randa Massaad³, Ihab Jomaa³, Hassan Machlab⁴ and Schuyler Korban⁵
¹ Integrated Land and Water Management Program, International Center for Agricultural Research in the Dry Areas, The Middle East Water and Livelihood Initiative, Aleppo, Syria
² Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, United States
³ Department of Irrigation and Agrometeorology, Lebanese Agricultural Research Institute, Tal Amara, Lebanon
⁴ International Center for Agricultural Research in the Dry Areas - Lebanon, Beirut, Lebanon
⁵ Office of International Programs, University of Illinois at Urbana-Champaign, United States

15.40 - 16.00  Poster session/Coffee break

Session III: Assessment of the multiple effects of changes in the hydrological regime

Chairperson: Arturo Elosegi

16.00 - 16.30  The challenge of analysing climate change impacts on the hydrology of Mediterranean river basins - A perspective from the CLIMB project
Ralf Ludwig and the CLIMB consortium
Ludwig-Maximilians-Universität, München, Germany

16.30 - 16.50  Effects of metal pollution under high discharge conditions
Helena Guasch¹, Marta Ricart¹,², Berta Bonet¹, Natàlia Corcoll¹ and Awadesh Kumar¹
¹ Institute of aquatic ecology, University of Girona, Girona, Spain
² Catalan Institute for Water Research (ICRA), Girona, Spain

16.50 - 17.10  The use of wood sticks to assess stream ecosystem functioning: comparison with leaf breakdown rates
Maite Arroita, Ibon Aristi, Lorea Flores, Joserra Díez and Arturo Elosegi
Faculty of Science and Technology, University of the Basque Country, Bilbao, Spain
17.10 - 17.30  Toxicity testing and behavioral changes in two species exposure to several pharmaceutical compounds: the copepod *Tisbe battagliai* and the shrimp *Atyaephyra desmarestii*.
Elena Nieto¹, Pilar Drake¹, C. Trombini¹, Enrique González-Ortega, Miriam Hampel¹ and Julián Blasco¹
¹Instituto de Ciencias Marinas de Andalucía (ICMAN-CSIC), Puerto Real, Spain

17.30 - 17.50  Effects of global change on the functioning of Mediterranean rivers: breakdown of organic matter as an assessment tool
Ibon Arísti¹, Jose R. Díez², Aitor Larrañaga¹ and Arturo Elosegi¹
¹Faculty of Science and Technology, University of the Basque Country, Bilbao, Spain
²Faculty of Education, University of the Basque Country, Vitoria-Gasteiz, Spain

17.50 - 18.10  Vulnerability of hydrological services to climatic extremes in a Mediterranean river basin
Marta Terrado¹, Vicenç Acuña¹, Driss Ennaanay²,³, Heather Tallis² and Sergi Sabater¹,⁴
¹Catalan Institute for Water Research (ICRA), Girona, Spain
²The Natural Capital Project, Stanford University, California, USA
³Riverside Technology Inc., Fort Collins, Colorado, USA
⁴Institute of Aquatic Ecology, University of Girona, Girona, Spain

21:00  Joint Dinner

Tuesday, 29th November 2011

Session IV: Modelling developments

Chairperson: Ramon J. Batalla

9.00 - 9.30  Integrated Modelling and Monitoring of Pollutants in River Basins at European Scale
*Giovanni Bidoglio* and Faycal Bouraoui
*Joint Research Centre of the European Commission, Ispra, Italy*

9.30 - 10.00  Adaptation of the InVEST model to a Mediterranean catchment: global and spatial methods to investigate model sensitivity
Marta Terrado¹, Ana Passuello², Maria Schez-Canales³, Vicenç Acuña¹, Marta Schuhmacher², Alfredo López² and F. Javier Elorza³
¹Catalan Institute for Water Research (ICRA), Girona, Spain
²Environmental Engineering Laboratory, Departament d’Enginyeria Quimica, Universitat Rovira i Virgili, Tarragona, Spain
³Dept. Geological Engineering, Escuela Técnica Superior de Ingenieros de Minas, Universidad Politécnica de Madrid, Madrid, Spain
10.00 – 10.30 Application of scaling equations to deal with the spatial aggregation effect on watershed hydrological modelling
Miguel Barrios¹,² and Félix Francés¹
¹ Research Institute of Water and Environmental Engineering (IIAMA), Universidad Politécnica de Valencia, Valencia, Spain
² Faculty of Forest Engineering, Universidad del Tolima, Ibagué, Colombia

10.30 – 10.50 Flushing flows in the lower Ebro. Monitoring and modelling
Álvaro Tena¹,², L. Ksiazek³, Damià Vericat¹,²,⁴,⁵, Antonio Palau⁷,⁶ and Ramon J. Batalla¹,²,⁴,⁷
¹ Fluvial Dynamics Research Group
² Department of Environment and Soil Sciences, University of Lleida, Lleida, Spain
³ Department of Hydraulic Engineering and Geotechnics, University of Agriculture, Krakow, Poland
⁴ Forest Science Center of Catalonia, Solsona, Spain
⁵ Institute of Geography and Earth Sciences, Aberystwyth University, Ceredigion, UK
⁶ Endesa Generación SA, Lleida, Spain

10.50 – 11.10 Modeling nutrient loads and in-stream retention in basins under chronic human impact: lessons from the Llobregat River basin (NE Spain)
Rosana Aguilera¹, Rafael Marcé¹ and Sergi Sabater¹,²
¹ Catalan Institute for Water Research (ICRA), Girona, Spain
² Institute of Aquatic Ecology, University of Girona, Girona, Spain

11.10 – 11.30 Poster session/Coffee break
Chairperson: Giovani Bidoglio

11.30 – 12.10 Applying monitoring and modelling techniques to study sediment transport dynamics in a mesoscale catchment
José A. López-Tarazón¹,², Ramon J. Batalla¹,²,³,⁴, Damià Vericat¹,²,³,⁵ and Till Francke⁶
¹ Fluvial Dynamics Research Group
² Department of Environment and Soil Sciences, University of Lleida, Lleida, Spain
³ Forest Science Center of Catalonia, Solsona, Spain
⁴ Catalan Institute for Water Research (ICRA), Girona, Spain
⁵ Institute of Geography and Earth Sciences, Aberystwyth University, Ceredigion, UK
⁶ Institute of Earth and Environmental Sciences, University of Potsdam, Potsdam, Germany

12.10 – 12.40 Stochastic Modeling of a fuzzy index to determine the quality of water in the Cauca River
William Ocampo-Duque¹, Diana Carolina Osorio García¹, Christian Piamba Ceballos¹, Montse Mari² and Marta Schuhmacher²
¹ Facultad de Ingeniería, Pontificia Universidad Javeriana Cali, Colombia.
² Grupo de Análisis y Gestión Ambiental, Departament d’Enginyeria Quimica, Universidad Rovira i Virgili, Tarragona, Spain
12.40 - 13.00  An integrated modelling system for long term planning of water resources management and global change adaptation  
Laurent Pouget¹, Suzy Mc Ennis¹, Ernest Adrogué i Calveras¹, Pierre-Antoine Versini² and Daniel Sempere²  
¹ Water Technology Centre (CETaqua), Cornellà de Llobregat, Barcelona, Spain  
² Centre of Applied Research in Hydrometeorology (CRAHI), Barcelona, Spain

Session V: Methodological framework development to quantify global change effects

Chairperson: Antoni Ginebreda

13.00 - 13.30  The use of hydrologic modeling as a technical support for River Basin Management: The Case of the Confederation Hidrográfica del Júcar  
Javier Ferrer Polo  
Confederación Hidrográfica del Júcar, Valencia, Spain

13.30 - 15.00  Lunch

15.00 - 15.30  Forest fires in Spain in a context of global change: From the country, to the landscape and down to the ecosystem  
José Manuel Moreno  
Universidad de Castilla-La Mancha, Toledo, Spain

15.30 - 16.00  Title to be determined  
Justo Mora  
Confederación Hidrográfica del Tajo, Spain

16.00 - 16.30  Water Quality-Management model in the Jucár River Basin  
Javier Paredes, Joaquín Andreu, Abel Solera and Andrea Momblanch  
Institute of Water and Environmental Engineering. Technical University of Valencia, Valencia, Spain

16.30 - 16.50  Poster session/Coffee break

Chairperson: Damià Barceló

16.50 - 17.10  Global change impacts on water availability in three Mediterranean catchments of Catalonia (NE Spain)  
Diana Pascual¹, Eduard Pla¹ and Roger Milego²  
¹ Centre for Ecological Research and Forestry Applications (CREAF), Autonomous University of Barcelona, Bellaterra, Spain  
² European Topic Centre for Spatial Information and Analysis (ETC/SIA), Autonomous University of Barcelona, Bellaterra, Spain
Final programme

17.10 - 17.30  **Contribution of river basin ecosystem services to human well-being in Mediterranean Basins.**
**Graciela Ferrer¹, Miquel A. Gual², Sherman Farhad² and Francesc La Roca¹**
¹ University of Valencia, Department for Applied Economics, Valencia, Spain
² University Pablo de Olavide, Department for Economics, Quantitative Methods and Economic History, Seville, Spain

Final remarks and closure of the meeting

17.30 - 17.50  **Final remarks and closure of the meeting**
**Damià Barcelò¹,²,³**
¹ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
² Catalan Institute for Water Research (ICRA), Girona, Spain
³ King Saud University, Riyadh, Saudi Arabia

17.50  End of meeting

*In italics, invited presentations*
1. **Quantification of pharmaceuticals in soils and sediments of Pego-Oliva Marsh by LC-MS/MS.**
   Pablo Vazquez-Roig, Vicente Andreu, Juan Antonio Pascual, Cristina Blasco and Yolanda Picó
   1 Food and Environmental Safety Research Group, University of Valencia, Burjassot, Valencia, Spain
   2 Centro de Investigaciones sobre Desertificación-CIDE (CSIC, Univ. Valencia, Gen. Valenciana). Albal, València, Spain

2. **Fish community in wadeable stretches of the Guadalquivir River basin (southern Iberian Peninsula): a proposal of priority areas for its conservation**
   Carlos Fernández-Delgado, R. J. De Miguel, F. Aranda, R. Moreno-Valcárcel, C. Arribas, F. J. Oliva-Paterna and L. Gálvez-Bravo
   1 Departamento de Zoología, Universidad de Córdoba, Córdoba, Spain
   2 Departamento de Zoología y Antropología Física, Universidad de Murcia, Murcia, Spain
   3 Instituto de Investigación en Recursos Cinegéticos (IREC), Universidad de Castilla-La Mancha, Ciudad Real, Spain

3. **Antibiotic contamination and promotion of antibiotic resistance in aquatic microorganisms and fish in two Catalan reservoirs**
   Belinda Huerta, Elisabet Martí, Meritxell Gros, Sara Rodríguez-Mozaz, Jose Luis Balcázar, Damià Barceló and Rafael Marcé
   1 Catalan Institute for Water Research (ICRA), Girona, Spain
   2 Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
   3 King Saud University, Riyadh, Saudi Arabia

4. **Upwind fourth-order nonoscillatory schemes for nonhomogeneous hyperbolic conservation laws**
   Arturo Hidalgo, Angel Balaguer-Beser and Llanos Gascón
   1 Escuela Técnica Superior de Ingenieros de Minas, Universidad Politécnica de Madrid, Madrid, Spain
   2 Universidad Politécnica de Valencia, Departamento Matemática Aplicada, Valencia, Spain

5. **Simulating habitat restoration actions: a machine learning approach**
   Esther Julia Olaya Marín, Francisco Martínez-Capel, Juan Diego Alcaraz-Hernández and Rui Soares Costa
   Institut d’Investigació per a la Gestió Integrada de Zones Costaneres, Universitat Politècnica de València, Grau de Gandia, Spain

6. **Presence of UV filters in sediments and surface waters in the Guadalquivir river basin**
   Pablo Gago Ferrero, M. Silvia Díaz Cruz and Damià Barceló
   1 Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
   2 Institute of Environmental Assessment and Water Research, Barcelona, Spain
   3 Catalan Institute for Water Research (ICRA), Girona, Spain
   4 King Saud University, Riyadh, Saudi Arabia
7.- Nekton response to the freshwater inputs in a Temperate European Estuary with regulated riverine inflow  
Enrique González-Ortegón¹, Mª Dulce Subida¹, Alberto Arias¹, Francisco Baldó², Jose Antonio Cuesta¹, Carlos Fernández-Delgado³, César Vilas⁴ and Pilar Drake¹  
¹ Instituto de Ciencias Marinas de Andalucía (CSIC), Puerto Real, Spain  
² Instituto Español de Oceanografía, Cádiz, Spain  
³ Departamento Zoología, Universidad de Córdoba, Córdoba, Spain  
⁴ IFAPA Centro El Toruñoo, El Puerto de Santa María, Cádiz, Spain

8.- Development of a multi-compartmental physiologically based pharmacokinetic model for PFOS and PFOA in breast milk. Children exposure through breast milk  
Francesc Fàbrega¹,², Martí Nadal², Marta Schuhmacher¹,² and Josep L. Domingo²  
¹ Environmental Engineering Laboratory, Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Tarragona, Catalonia, Spain  
² Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Reus, Spain

9.- Relationship between metals bioavailability and speciation in river water depending on the stressors  
M.I. López¹, Neus Roig¹, Montse Mari¹, Martí Nadal², Marta Schuhmacher¹ and Josep L. Domingo²  
¹ Environmental Engineering Laboratory, Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Tarragona, Spain  
² Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Reus, Spain

10.- Hydrology and Water Quality Modeling under Data Scarcity for Low Flow River in Mediterranean Watershed  
Rubab Fatima Bangash, Ana Passuello and Marta Schuhmacher  
Environmental Engineering Laboratory, Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Tarragona, Spain

11.- Analysis of volatyl methylsiloxane in waters: comparison between MASE and headspace extraction methods  
Pablo Vazquez-Roig¹, Degao Wang², Tommy Bissicos², Yolanda Picó¹ and Mehran Alaeœ²  
¹ Food and Environmental Safety Research Group, University of Valencia, Burjassot, Spain  
² Water Science and Technology Directorate, Environment Canada, Burlington, Canada

12.- Freshwater inputs as forcing mechanisms on the lower trophic levels of the Guadalquivir estuary.  
Enrique González-Ortegón and Pilar Drake  
Instituto de Ciencias Marinas de Andalucía (ICMAN-CSIC) Puerto Real, Spain

13.- Functional bacterial diversity in the epipsammic biofilm at the Llobregat River  
Anna Freixa¹, Anna M. Romani¹, Lidia Ponsati² and Sergi Sabater¹,²  
¹ Institute of Aquatic Ecology, University of Girona, Girona, Spain  
² Catalan Institute for Water Research (ICRA), Girona, Spain
14.- Contamination of polar pesticides in sediments from Rivers of the Iberian Peninsula  
Ana Masia, Cristina Blasco, Pablo Vazquez and Yolanda Picó  
Food and Environmental Safety Research Group, Faculty of Pharmacy, University of Valencia, Burjassot, Spain

15.- Occurrence and partition of perfluorinated compounds in water and sediment from Xuquer River (Valencia, Spain)  
Matthias Onghena¹, Ana Masia¹, Marinella Farré², Yolanda Picó¹ and Damià Barceló²,³,⁴  
¹ Food and Environmental Safety Research Group, Faculty of Pharmacy, University of Valencia, Burjassot, Spain  
² Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain  
³ Catalan Institute for Water Research (ICRA), Girona, Spain  
⁴ King Saud University, Riyadh, Saudi Arabia

16.- Quantitative detection of trace perfluorinated compounds in environmental samples by Liquid Chromatography-Quadrupole-Time of Flight Mass Spectrometry  
Yolanda Picó¹, Matthias Onghena¹, Cristina Blasco¹, Marinella Farré² and Damià Barceló²,³,⁴  
¹ Food and Environmental Safety Research Group, Faculty of Pharmacy, University of Valencia, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain  
² Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain  
³ Catalan Institute for Water Research (ICRA), Girona, Spain  
⁴ King Saud University, Riyadh, Saudi Arabia

17.- Quinolone and fluoroquinolone residues in agricultural soils from Valencian Community (Spain)  
Vicente Andreu¹, Juan Antonio Pascual¹ and Yolanda Picó²  
¹ Centro de Investigaciones sobre Desertificación-CIDE (UV, Conselleria d’Agricultura, CSIC), Ctra. Naquera-Moncada, Valencia Spain  
² Food and Environmental Safety Research Group, Faculty of Pharmacy, University of Valencia, Burjassot, Spain

18.- Application of the Soil and Water Assessment Tool (SWAT) to model faecal indicator bacteria concentrations in the River Ouse catchment, UK  
Michael Dilley, Sarah Purnell, James Ebdon and Huw Taylor  
Environment and Public Health Research Unit, School of Environment and Technology, University of Brighton, Brighton, United Kingdom

19.- Seasonal monitoring of Pharmaceuticals on a sewage impacted section of a Mediterranean River (Llobregat River, NE Spain) and their relationship with hydrological conditions.  
Victoria Osorio⁵, Sandra Pérez¹, Asunción Navarro, Antoni Ginebreda¹ and Damià Barceló¹,²,³  
¹ Department of Environmental Chemistry, IDAEA-CSIC,Barcelona, Spain  
² Catalan Institute of Water Research (ICRA), Girona, Spain  
³ King Saud University, Riyadh, Saudi Arabia
20.- Ecological and micropollutants response of a Mediterranean river to hydrological natural variations: the Llobregat case study
Victoria Osorio¹, Lorenzo Proia², Marta Ricart¹, Sandra Pérez¹, Antoni Ginebreda¹, Sergi Sabater²,³ and Damià Barceló¹,²,⁴
¹ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
² Institute of Aquatic Ecology, University of Girona, Girona, Spain
³ Catalan Institute of Water Research (ICRA), Girona, Spain
⁴ King Saud University, Riyadh, Saudi Arabia

21.- Preliminary analysis of sediment fluxes at the Barasona Reservoir
José A. López-Tarazón¹,², Pilar López³, Damià Vericat¹,²,⁴,⁵ Isabel Muñoz³ and Ramon J. Batalla¹,²,⁴,⁵
¹ Fluvial Dynamics Research Group
² Departament de Medi Ambient i Ciències del Sòl (DMACS), Universitat de Lleida, Lleida, Spain
³ Departament d’Ecologia, Universitat de Barcelona, Barcelona, Spain
⁴ Centre Tecnològic Forestal de Catalunya, Solsona, Spain
⁵ Institute of Geography and Earth Sciences, Aberystwyth University, Ceredigion, UK
⁶ Catalan Institute for Water Research (ICRA), Girona, Spain

22.- An integrated sampling design to study the combined effects of regulation and Mediterraneity on fluvial dynamics
Gemma Lobera¹,², José A. López-Tarazón¹,², Álvaro Tena¹,², Ignacio Andrés³, Francisco Martinez-Capel⁴, Rafael Muñoz-Mas⁴, Francisco Vallés¹, Ibon Aristi⁵, José Ramón Diez⁶, Aruro Elosegui⁷, Lorea Flores⁵, Askoa Ibisate⁷, Damià Vericat¹,²,⁸,⁹ and Ramon J. Batalla¹,²,⁸,¹⁰
¹ Fluvial Dynamics Research Group
² Department of Environment and Soil Sciences, University of Lleida, Lleida, Spain
³ Institute of Water Engineering and Environment, Universidad Politécnica de Valencia, Spain
⁴ Research Institute for Integrated Management of Coastal Areas, Universidad Politécnica de Valencia, Spain
⁵ Department of Plant Biology and Ecology, University of the Basque Country, Bilbao, Spain
⁶ Didactics of the Mathematics and the Experimental Sciences, University of the Basque Country, Vitoria-Gasteiz, Spain
⁷ Department of Geography, Prehistory and Archaeology, University of the Basque Country, Vitoria-Gasteiz, Spain
⁸ Forest Science Center of Catalonia, Solsona, Spain
⁹ Institute of Geography and Earth Sciences, Aberystwyth University, Ceredigion, UK
¹⁰ Catalan Institute for Water Research (ICRA), Girona, Spain

23.- Multi-residue trace level determination of endocrine disruptors and related compounds in rivers of the Iberian Peninsula
Marina Gorga¹,², Mira Petrovic²,³ and Damià Barceló¹,²,⁴
¹ Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain
² Catalan Institute for Water Research (ICRA), Girona, Spain
³ Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain
⁴ King Saud University, Riyadh, Saudi Arabia
24.- Before and After Dams: Biofilm changes in Structure and Function.
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Oral presentations
The implementation of Chemical Monitoring in Surface Waters under the Water Framework Directive

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The recent European legislative developments in the field of chemical water policy oblige Member States to implement the chemical monitoring programmes for surface water-bodies. In particular, the Directive 2008/105/CE obliges Member States to achieve the good chemical status through the compliance with the environmental quality standard (EQS) included in the Directive for the substances of the European list of priority. The EQS have been developed mainly for water column, but also in biota for some bioaccumulative compounds as mercury, hexachlorobenzene and hexachlorobutadiene; furthermore the Directive gives possibility also to derive EQS for sediment in specific water-bodies. A European technical report, that gives recommendations on sediment and biota monitoring, has been published in 2010. The same Directive gives also obligations about trend monitoring in sediment or biota, elaboration of mixing zones and the definition of an inventory of sources, emissions and losses of the priority substances. The Directive 2009/90/CE, the so called QA/QC Directive, gives obligations about the minimum technical requirements for the chemical monitoring, in particular Member States shall ensure that all methods of analysis, including laboratory, field and on-line methods, used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025 standard or other equivalent standards accepted at international level. In this legislative context all the Member States need a support in order to implement the chemical monitoring programmes of surface water bodies. Furthermore is on-going the process of the review of the list of priority substances and also the methodology to define new priority substances for the future reviews is in discussion.

To this aim the Common Implementation Strategy (CIS) of the Water Framework Directive (WFD) has established in 2009 the expert group Chemical Monitoring and Emerging Pollutants (CMEP) that is a continuation of the past expert group called Chemical Monitoring Activity (CMA). This expert group, lead by JRC and Italy, is formed by representatives of all European members states, industrial and environmental stakeholders, experts from European projects and network (e.g. Norman), international conventions (OSPAR, MEDPOL); also Turkey, Switzerland and Norway participate to the activity. The aim of this expert group, that is a sub-group of the Working Group E “chemical aspects”, is mainly the elaboration of technical reports, recommendations and the exchange of experiences through the different member states in relation to the chemical monitoring programmes of the substances of the list of priority and other substances that are part of the ecological status, the so called “river basin specific pollutants”. CMEP has to pick-up the challenges arising from the revision of the list of priority substances as well as from the requirements stemming from Directive 2009/90/EC and in particular has to deal with aspects related to:

- Standardization and quality assurance issues stemming from the implementation of Commission Directive 2009/90/EC (QA/QC Directive); statistical methods to assessing compliance, methods to assess bioavailability for metals.
- Topics related to emerging pollutants, including analytical methods, hazard information, levels on the environment and use patterns.

CMEP has also the aim to make a review of the existing analytical methods for the present and future priority substances for all the matrices selected (that include also sediment and biota) with the scope to increase efficiency and to decrease costs of chemical monitoring; the QA/QC Directive obliges Member States to ensure that the minimum performance criteria for all methods of analysis applied are based on a limit of quantification equal or below a value of 30% of the relevant environmental quality standards. To
this aim, in the context of the activity, field trials specifically addressed to some priority substances have been organised by the Joint Research Center with the objective to harmonize at European level the sampling procedures and the analytical methods.

In particular the requirements that come from the QA/QC Directive 2009/90/EC need a continuous effort thus facilitating the organization of targeted laboratory intercomparisons, provision of suitable reference materials and other tools of quality control on the basis of the main standards. About emerging pollutants the aim is to collect information about levels and occurrences of emerging environmental pollutants (e.g. pharmaceuticals) which eventually can support the identification of new priority substances, information on performance of existing analytical methods for emerging pollutants and any other information deemed relevant for the activities of the WGE on this field.

A specific task of the CMEP activity is dedicated to the elaboration of a specific guidance on the use of alternative effect-based monitoring methods (e.g. biomarker, bioassays, TIE) needed for investigative monitoring and to better evaluate the link between chemical and ecological status and the effects of mixture of pollutants and emerging pollutants. This specific activity is necessary in order to integrate and rationalise the chemical monitoring programmes and has the aim also to better understand the real environmental quality of the aquatic ecosystems through the evaluation and detection of the effects of the pollutants on the aquatic organisms; in the aquatic environments there are often mix of pollutants or also unknown pollutants that cannot be detected with routinary chemical analysis; the effect based tools can detect for example estrogenic effects caused by endocrine disrupting chemicals or DNA alterations that can represent an early signal of pollution and can help to identify sources of pollution.

The CMEP has also the aim to address specific emerging risks that can modify also the design of chemical monitoring programmes such as water scarcity or flooding; in this context, also in previous CIS guidances there are recommendations for chemical monitoring linked to climate change issues taking into account the different geographical European areas: the correct design of chemical monitoring programmes is essential to understand and respond to climate change modifications. A long-term monitoring network of reference sites, for example, linked to meteorological data is the key to evaluate for example the effects of climate change on chemical quality of water-bodies; in particular will be necessary to select appropriate sites on the basis of the representativity of the whole river-basin; also contaminated areas where there are high level of sediment contamination due to historical pollution are particular vulnerable water-bodies that can be affected by climate changes for example through flooding or storm events, but also, in a long term perspective, by the erosion of coastal-areas due to sea-level rise that can remobilize the contaminants. It is very important to avoid abandoning monitoring stations which already have a long term consistent record, especially in the context of climate change. In particular will be necessary to evaluate the changes and modifications of physico-chemical parameters, as early warning signals, caused by climate changes such as temperature, dissolved oxygen, acidification, nutrient enrichment in the water-column and in sediment that can also modify the bioavailability of contaminants in water-bodies.

In conclusion, the implementation of chemical monitoring programmes to fulfil the obligations of the WFD represents a great effort for the Member States and the activity of CMEP, in this context, also through the exchange of experiences, can represent a key opportunity to facilitate the process and to answer to the different technical questions that progressively arise from the application of monitoring programmes, included climate change issues.

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References

Monitoring water-polluting pesticides at the catchment scale in the Ebro, Llobregat, Jucar and Guadalquivir Rivers

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Introduction

Agriculture related pollution, in the form of nutrients and pesticides, constitutes a major pressure to the quality of the river water and a threat for their ecological status. Thus, pesticide residue analysis in environmental samples has received increasing attention in the last few decades [1].

These studies often deal with samples with low analyte concentrations containing a large number of interfering compounds. Consequently, simple and highly sensitive analytical techniques are required to detect and quantify pollutants in water at trace levels. This usually includes an extraction step prior to the chromatographic determination [2-4].

This work presents the results of an extensive monitoring survey that was carried out in the Ebro, Llobregat, Jucar and Guadalquivir River using solid-phase extraction (SPE) with liquid chromatography tandem mass spectrometry (LC-MS/MS). The selection of the pesticides studied was based firstly on their presence in river as detected by the applied analytical and chromatographic techniques and secondly on their use in agricultural practices in Spain.

Experimental

The pesticides survey was conducted in 2010 between July, September and October depending on the catchment. Fig. 1 shows the location of the sampling points.

Figure 1: Sampling points along the course of the different Rivers.
Water samples were collected in 2.5 L amber glass bottles and immediately transported to the laboratory; where they were kept refrigerated at 4.5°C until their extraction.

The target analytes were acethochlor, alachlor, atrazine, desisopropylatrazine, desethylatrazine, azinphose-methyl, buprofezin, carbofuran, 3-hydroxycarbofuran, chlorfenvinphos, chlorpyriphos, diazinon, diuron, fenitrothion, fenthion, fenithion -sulfoxide, fenithion-sulfone, hexythiazox, imazalil, imidacloprid, isoproturon, malathion, methiocarb, prochloraz, pyriproxyfen, simazine, tolchlophos-methyl, molinate, omethoate, dimethoate, propazine, terbutilazine, propanil, diclofenthion, parathion-ethyl, parathion-ethyl, fenchlorphos, terbutryne, metolachlor, ethion, azinphos-ethyl, fenoxon, fenoxon-sulfoxide and fenoxon-sulfone.

Water samples (200 mL) were loaded in Oasis HLB cartridges at a flow rate of 1 ml min⁻¹. The cartridges were then dried under vacuum for ten minutes and analytes were eluted with 10 ml of the mixture dichloromethane-methanol (50:50, v/v). Extracts were evaporated to dryness and reconstituted with 1 ml of methanol.

The extract was analysed by LC-MS/MS in positive ionization (PI) mode using an Agilent 6100 with an electrospray ionisation (ESI) source. Separation was carried out on a Luna C18 column (150 × 2.0 mm, 3 µm) using a gradient elution profile and mobile phase consisting of 10 mM ammonium formate in methanol and H₂O. The two most intense precursor ion → product ion transitions were monitored to obtain unambiguous confirmation of the compound identity.

In general, recoveries ranging from 75% to 95%, with relative standard deviations better than 18% and low limits of detection and quantification (1 to 10 ng l⁻¹) were achieved for all selected pesticides.

**Results and discussion**

Of the 40 pesticides selected, 20 were detected in the river water samples, that is atrazine, atrazine-desethyl, buprofezin, carbofuran, chlorfenvinphos, chlorpyriphos, diazinon, fenoxon sulfoxide, hexythiazox, imazalil, malathion, methiocarb, prochloraz, pyriproxyfen, tolchlophos-methyl, molinate, dimethoate, dichlofenthion, parathion-ethyl, metholachlor, terbuthryl.

The most commonly encountered pesticides in river waters were chlorfenvinphos, diazinon, imazalil, atrazine, atrazine desethyl and tebutryn. Other pesticides such as is buprofezin, chlorpyriphos, fenoxon sulfoxide, hexythiazox, malathion, methiocarb, prochloraz, pyriproxyfen, tolchlophos-methyl, molinate, dimethoate, dichlofenthion, parathion-ethyl, metholachlor were also detected in some samples. The four river basins present different degree of contamination. The higher levels of pesticides were found in the Guadalquivir River.

The compounds were not distributed uniformly throughout the different sampling sites. Figure 2 shows the concentration of atrazine and its metabolites through the Jucar River. The maximum concentration levels for the atrazine were observed at “JUC7”. This point is located near the city of Alzira close to the outflows of the Alzira-Carcaixent waste water treatment plant (WWTP). Concentration values were 20 ng l⁻¹ for atrazine, 27 ng l⁻¹ for desisopropylatrazine and 30 ng l⁻¹ for desethylatrazine.
Pesticides enter surface water primarily as runoff from crops and are most prevalent in agricultural areas. Pesticides are also used on golf courses, forested areas, along roadsides, and in suburban and urban landscape areas. Because of this, they can also be found in the influents of WWTP. Several of these water treatment plants that spill their outflows to the rivers were also analysed.

Figure 3 shows the results of the Lleida WWTP that spills its outflows to the river Segre a tributary of the Ebro River. Twelve pesticides were detected in both in and out-flow—buprofezin, carbofuran, chlorfenvinphos, diazinon, diuron, imazalil, imidacloprid, isoproturon, prochloraz, pyriproxyfen, dimethoate and dichlofenthion at concentrations ranging from 1 to 2121 ng l⁻¹. The highest concentration is that of the imazalil (2121 ng l⁻¹), which is a fungicide mainly used in the post harvest treatment of apples, pears and oranges. It is also remarkable that concentrations in the in and out-flows are almost the same.

Figure 3. Pesticide levels detected in the in-flows and out-flows of the Lleida WWTP (Ebro River)
Conclusions

The pesticides most frequently detected in this study were chlorfenvinphos, diazinon, imazalil, atrazine, atrazine desethyl and tebutryn. Other pesticides up to 20 different ones also appeared in some samples. These results are not surprising as these sites have agricultural, industrial and human activities. This is the first pilot study undertaken in Spain that monitors 45 pesticides in river water belonging to four different catchments.

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References


Automated analytical method for the determination of perfluorinated compounds in fish in Spanish rivers.

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Perfluorinated compounds (PFCs) is the name given to a large group of chemicals with a fully fluorinated hydrophobic linear carbon chain attached to various hydrophilic heads. Their amphiphilic characteristic gives them the capability to reduce surface tension and repel water and oil. Another important characteristic property is their stability to various modes of degradation as well as acid and base reaction, oxidation and reduction and resistant to heat, given for the strong C-F bond. For these reason PFCs are used in many industrial and household products. (Monroy, Morrison et al. 2008)

In the present work, fish samples have been analyzed in order to evaluate the potential bioaccumulation and biomagnification of the perfluorinated contamination in Spanish rivers, and as an indicator of rivers pollution. Compounds found in higher concentration were PFOS (11 -107 ppb) and PFOA (26 -151 ppb) in agreement with other European studies (D’Hollander, De Voogt et al. 2010). In addition, is widely known that diet is a source of human exposure. Therefore, the work realized could be a way to evaluate one of the main sources of human exposure. (Haug, Thomsen et al. 2010)

A high-throughput method for measuring trace levels of 21 PFCs in fishes have been developed. The evolved method consists on an alkaline (Llorca, Farré et al. 2009) digestion and centrifugation followed by a fully automated on-line clean-up step utilizing the TurboFlow™ technology (Thermo Fisher Scientific, Franklin, MA) coupled to liquid chromatography-tandem mass spectrometry (LC-MS/MS). The new developed approach involves the use of two extraction columns in tandem: Cyclone and C₁₈ XL. The injection volume was 20 µl. The influent solvent consisted in water pH 3.4 formic acid at turbulent flow of 1.5 ml/min, 20 s. An extra clean-up step with water at 0.5 ml/min, 10 s, was included. The loop elution (250 µl) was performed with (water pH 3.4 formic acid : methanol (20:80)) and followed by (water at pH 3.4 formic acid: methanol (70:30)) at flow of 0.2 ml/min, 2 min. Separation was carried out in a LC-column Hypersil GOLD PFP (50 x 3) (Thermo Scientific) and an extracolumn was used after LC pumps in order to remove the contamination from the system (BDS Hypersil C₈ (50 x 3) from Thermo Scientific). The chromatographic separation was achieved using as mobile phase (A) aqueous ammonium acetate 20 mM, and (B) MeOH. The total run time for each injection was 16 min with a flow rate of 0.4 mL/min. Thermo Scientific TSQ Vantage mass spectrometer (Thermo Fisher Scientific, San Jose, CA), coupled to TLX-1, was used for analytical purposes, equipped with a Turbo Ion Spray source operated in the negative mode and working in single reaction monitoring.

References


Levels and spatial distribution of emerging contaminants in the Iberian rivers

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A wide range of man-made chemicals, designed for use in industry, agriculture and as consumer goods and chemicals unintentionally formed or produced as by-products of industrial processes or combustion, are potentially of environmental concern. Beside recognized pollutants, numerous new chemicals are synthesized each year and released into environment with unforeseen consequences. However, the term “emerging contaminants” does not necessarily correspond to “new substances”, i.e. newly introduced chemicals and their degradation products/metabolites or by-products, but refers also to compounds with previously unrecognized adverse effects on the ecosystems, including naturally occurring compounds. Their presence in environmental waters is directly related to their removal in wastewater treatment plants (WWTP) and the flow rate of the receiving waters. Iberian rivers are characterized by important fluctuations in the flow rates and heavy contamination pressures from extensive urban, industrial and agricultural activities. This translates in contamination levels in these rivers most often higher than in other larger European basins. Therefore, the study of their occurrence at river basin scale and distribution between water and solid phase is the prerequisite for proper risk assessment. Within the project SCARCE an extensive sampling of water, sediment and biota from four Iberian river basins has been undertaken. A total of 77 samples of water, 75 sediments, and 63 pools of fish were collected for chemical characterization. The levels of over 250 compounds belonging to different groups of priority (polycyclic aromatic hydrocarbons, organochlorine pesticides, and alkylphenols), and emerging contaminants (pharmaceuticals, drugs of abuse, personal care products, polar pesticides, perfluorinated compounds, endocrine disrupting compounds, halogenated flame retardants, and nanoparticles) have been determined using advanced analytical techniques based on gas chromatography- tandem mass spectrometry and liquid chromatography- tandem and hybrid mass spectrometry.

This work will focus on two groups of emerging contaminants: pharmaceutically active substances (PhACs) and endocrine disrupting compounds (EDCs) and some related compounds, including steroid hormones, alkylphenolic compounds, antiseptics, BPA, parabens, benzotriazoles and phosphate flame retardants. Their significance as trace environmental pollutants in waterways is due to several facts (i) continuous introduction via effluents from sewage treatment facilities and from septic tanks, (ii) some compounds such as pharmaceuticals and synthetic hormones they are developed with the intention of performing a biological effect, (iii) some have the same type of physico-chemical behavior as other harmful xenobiotics (persistence in order to avoid the substance to be inactive before having a curing effect, and lipophilicity in order to be able to pass membranes), (iv) some pharmaceutical substances and personal care products are used by man in rather large quantities (i.e. similar to those of many pesticides).

The results on the occurrence of PhACs and EDCs and related compounds in four Iberian rivers (Ebro, Llobregat, Jucar and Guadalquivir) are presented and their implications on the quality of water discussed. Discussion of the main findings also includes identification of main contamination sources, study of distribution of pharmaceuticals between water and solid (sediment) phase and calculation of estradiol equivalents (EEQ values) as a measure of estrogenicity of the samples. Figure 1 shows an example of levels of some EDCs detected in the water phase of the Ebro river basin.
Figure 1. Levels of nonylphenolic compounds (A), phosphate flame retardants (B) and benzotriazols (C) in the Ebro river basin.
Acknowledgements

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Integration of on-line and off-line methodologies for the assessment of river water quality

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Introduction

Nowadays legislation related to water quality is becoming more stringent both at the national and the international level. In the European context, the Water Framework Directive (2000/60/EU) (WFD) is an example of the new attitude adopted (risk-based) in terms of environmental impacts. The WFD involves both a good chemical and biological status of water bodies, but current methodologies do not allow knowing the status of water quality at acceptable operational costs. This highlights the need of alternative monitoring platforms that can be run, processed, interpreted and that provide information of changes in water quality on short notice (Dworak, 2005; Graveline, 2010).

A range of alternative tools are emerging and although they have not proved the same low level of uncertainty that is now taken for granted in classical analytical methods yet, they can provide more representative data, often at lower cost (Allan, 2006). We present here an integration and interpretation of several technologies as an integrated tool to detect changes in water quality. These include sensors, passive samplers, biological early warning systems, biomarkers, etc. It is important that further work is carried out to demonstrate the utility and reliability of these emerging tools in laboratory and field trials in comparison to classical methods. This will be necessary to provide a wide range of well characterised tools to enable them to select the most appropriate solution for each specific application.

Material and Methods

For that purpose, several technologies have been tested to evaluate their potential for river water assessment: a biological toxicity monitor using luminescent bacteria Vibrio Fisheri (TOXCONTROL) (Figure 1) and an online UV-VIS spectrophotometer (s::can spectro::lyser(TM)) (Figure 2) measuring TSS, COD, TOC, NO³. On-line technologies are complemented with other off-line equipments (advanced techniques at laboratory like zebrafish scales to determine the presence of dioxin-like compounds) and in-line techniques (passive sampling) to widen the range of parameters and pollutants monitored, creating and validating thus a monitoring platform adapted to local conditions.

Figure 1: Scheme of the biomonitor analyser
Experiments were performed in Llobregat River (Spain), the most important drinking water source for Barcelona and its surrounding area. Being one of the only water sources in the area the river water have been overexploited and effluents from more than 30 urban wastewater treatment plants (WWTP), industries and agriculture runoffs have been discharged into the river. For all those reasons real time control is crucial to control the water quality.

Results and Discussion

From the different methodologies tested the main results are summarized below. UV-VIS spectrophotometer probe measures the footprint of the whole spectra (from 200 to 750 nm). When comparing with laboratory measures the correlation was not satisfactory for some of the parameters, especially for nitrates (Figure 3). Therefore new correlations have been established between recorded spectra and values reported by the probe and the laboratory using statistics.

Concerning toxicity, in the Llobregat River, background levels using Vibrio Fisheri are comprised in a range of ±20% of light inhibition. When turbidity is high (due to weather conditions), we can see some positive toxicity due to the decrease of light arriving to the photomultipliers performing light detection in the equipment. In low turbidity episodes, toxicity values are negative because of the high content of nutrients in Llobregat water that makes metabolism of bacteria increase, and therefore, the emission of light. To further validate and to check dispersion of data and repeatability of Toxcontrol several samples were analysed in off line mode pumping the same sample several times, and the effective concentration (EC50) were calculated for 9 different compounds (including pharmaceuticals, pesticides and surfactants).
On the other hand, using offline methodologies, a protocol for the analysis of CYP1A mRNA levels in scales of zebrafish exposed to environmental and spiked samples was developed as a valid alternative method to detect dioxine-like contamination in water (Pelayo, 2011) (Figure 4). This test has the advantage that it does not imply animal killing (most fish recover without major problems) and that it only requires a 24-h exposure. When the method was tested with real samples from the Llobregat River (NE, Spain), clear temporal and spatial variations were observed, demonstrating its suitability for monitoring natural variations on water quality linked to both specific discharges or changes on the river flow.

Finally, passive sampling has been used as an advanced monitoring tool to corroborate the presence of contamination detected for the other monitoring tools tested. It has the main advantages of providing time weighted-averaged concentration (TWA) and better sensibility for a selection of compounds.

To conclude, the methods proposed exhibited clear temporal and spatial variations for the Llobregat water samples analysed in the same way for all the technologies evaluated, demonstrating its suitability for monitoring variations on water quality linked to both specific discharges and changes in the river flow. The combination of the UV-VIS spectrophotometer and the toxicity biomonitor with advanced laboratory technologies comprises a complete monitoring system with a high added value being capable of detecting the presence of contaminants at low concentrations and sudden changes in water quality. This combination allows the verification of alarm signals from one instrument with the signal of the other, reducing false alarm rates and simplifying sampling and sample preparation and reducing analysis costs.

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Presence of illicit drugs in different wastewater treatment plants in Mediterranean river basins of the Iberian Peninsula.

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In recent years an increasing number of works have demonstrated the presence of humans and veterinary pharmaceutical residues in the aquatic environment. Among them, illicit drugs are a new group of water contaminants with potent psychoactive properties and unknown effects to the aquatic environment.[1, 2] The main source of these substance to the environment is their production and consumption, while, unlike pharmaceuticals, direct deposition is less likely.

After consumption, different amount of the consumed drugs and its metabolization products are excreted via urine and faeces and they enter in the municipal sewage system, where, under the best case scenario they undergo physical-chemical and/or biological transformation. Depending on the removal efficiencies, they can persist through the wastewater treatment and be detected in the receiving water [3]

Relatively high concentrations of illicit drugs in water resources are related to the excretion of unalterated or transformed metabolites of the consumed drugs and to the high consumption rates reported for these substances.

Wastewater treatment is an important process to reduce the levels of these substances before their release into the aquatic environment. Dilution of treated wastewater, when discharged into natural water masses, helps to attenuate the potential negative effects that these substances may pose to the aquatic ecosystems, but, Mediterranean river basins may be more vulnerable to chemical pollution than other European catchments because they experience drought periods. Water scarcity is directly related to an increase of the surface water levels of polar micro pollutants present in discharged treated wastewater (e.g. pharmaceutical, illicit drugs and metabolites) which is often the main component of the river discharge in catchments with high industrial and urban pressure as it the case of the Mediterranean river basins of the Iberian Peninsula.

Another aspect important to consider is that often surface waters are used as raw source during drinking water production, thus contaminated surface water may affect the quality of the final tap water.

Another objective of the analysis of illicit drugs in wastewater is to obtain real-time profiles of illicit drug use as proposed by Daughton in 2001[4] and implemented for the first time by Zuccato and co-workers in 2005 [5]. This approach may provide more realistic estimations of drug consumption and it may be considered as a valid alternative to the statistical methods currently employed.

The present work reports the occurrence of 21 drugs of abuse and metabolites residues in influent and effluent sewage water from 15 wastewater treatment plants (WWTPs) located along various Mediterranean river basins of the Iberian Peninsula.

The compounds analysed were cocaine (COC) and its metabolites benzoylecgonine (BE) and cocaethylene (CE), the main psychoactive component of the cannabis plant, Δ9-tetrahydrocannabinol (THC), and four metabolic by-products, 11-nor-9-carboxy-Δ9-tetrahydrocannabinol (THC-COOH), 11-hydroxy-Δ9-tetrahydrocannabinol (OH-THC), cannabidiol and cannabiol, the opioids morphine (MOR), heroin (HER), and the heroin metabolic product 6-acetylmorphine (6ACM), the opioid-agonist methadone (METH), and its main excretion product 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP), the amphetamine-like compounds amphetamine (AM), methamphetamine (MA), 3,4-
methyleneoxymethamphetamine (MDMA or ecstasy), and ephedrine (EPH), the most potent known hallucinogenic substance, lysergic acid diethylamide (LSD), and one of its metabolites, 2-oxo-3-hydroxy-LSD (O-H-LSD), and the benzodiazepines alprazolam (ALP), lorazepam (LOR) and diazepam (DIAZ).

Data collected within this first sampling campaign have been used for the assessment of the presence of the selected compounds, the removal efficiency of the studied WWTPs and the back calculation of community drug consumption. The results presented in this work represent the first of the three monitoring planned in the Mediterranean basins.

Individual stock solutions were prepared by diluting each analyte with methanol (MeOH) at a concentration of 20µg/mL. Working standard solutions containing the mixture of the investigated target compounds were prepared at concentrations ranging between 0.1 ng/mL and 1000 ng/mL and they were used as spiking solutions for preparation of the aqueous calibration solutions and in the recovery studies. Individual stock solutions and working standard solutions were stored at -20°C in the dark. Deuterium labelled compounds were added to the calibration solutions, to samples and to blanks (LC-grade water) at a final concentration of 50 ng/L for the compounds ALP-d5, LOR-d4, DIAZ-d5, MOR-d9, THC-d3, THC-COOH-d3, OH-THC-d3, Cannabidiol-d3, COC-d3, BE-d8 and METH-d3 and 20ng/L for the compounds CE-d3, AM-d5, MA-d14, EPH-d3, MDMA-d3, EDDP-d3, HER-d9, 6ACM-d6 and LSD-d3. For the compounds 2-OXO-LSD and Cannabinol, the deuterium labelled compounds LSD-d3 and Cannabidiol-d3 were used as internal standard, respectively.

The analytical method applied is based on a modified on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry (on-line SPE-LC-ESI-MS/MS) method previously developed by our group for analysis of drugs of abuse in waste water [6].

Pre-concentration of the samples was performed using an automated on-line SPE sample processor Symbiosis Pico (Spark Holland, Emmen, The Netherlands). In this fully automated methodology, sample handling is limited to the filtration step, and the addition of the internal standard mixture. The system consists of two binary LC pumps, an autosampler, which holds two trays for up to 12 vials (10mL) each, an automated cartridge exchange (ACE) module, which holds two trays for up to 96 cartridges each one, and a high-pressure dispenser (HPD) module for handling of solvents and samples by way of a 2-mL high-pressure syringe. The ACE configuration, equipped with two clamps and two high-pressure valves, allows performing the elution of a cartridge and the pre-concentration of the following sample in a sequence, simultaneously. Sample pre-concentration is done with polymeric PLRP-s disposable cartridges (10 mm x 2 mm i.d.) from Spark Holland.

The Symbiosis Pico is connected in series with a 4000QTRAP hybrid quadrupole-linear ion trap (QqLIT) mass spectrometer equipped with a Turbo Ion Spray source (AB Sciex, Foster City, CA). Chromatographic separation was done by means of a reversed-phase Purospher Star RP-18 end-capped column (125 mm x 2.0 mm i.d., particle size 5 µm) preceded by a guard column (4 x 4 mm, 5 µm) of the same packing material, both from Merck (Darmstadt, Germany). The software that controls the Symbiosis Pico (Symbiosis Pico for Analyst, Spark Holland) was integrated within the MS software (Analyst 1.4., AB Sciex).

On-line SPE pre-concentration of all samples, aqueous standard solutions, and blanks was performed and automatically controlled by the Symbiosis Pico by loading an aliquot of 5 mL of the corresponding solutions at 1 mL/min through a PLRP-s cartridge previously conditioned with 1 mL of acetonitrile (ACN) and 1 mL of LC-grade water (flow rate 5 mL/min). After sample loading and prior to elution, the cartridges were washed with 1 mL of LC-grade water at a flow rate of 5 mL/min to complete transfer of the sample and remove some matrix interferences.

Upon completion of each SPE protocol, which takes place in the left clamp of the ACE unit of the Symbiosis Pico, the cartridge is moved to the right clamp, where the trapped analytes are eluted to the LC column with the chromatographic mobile phase (linear gradient ACN/ammonium formiate 20 mM (pH 3.8) aqueous solution, flow rate 0.3 mL/min). Meanwhile, a new cartridge is placed in the left clamp,
where pre-concentration of the next sample in a sequence is simultaneously performed. This kind of configuration allows short cycle times, which in our approach is 35 min.

The SRM transitions between the precursor ion and the two most abundant products ions for each target compound (only one SRM transition for the deuterated compounds) were registered in order to get enough identification points (n=4) to achieve analyte confirmation [7].

The methodology was validated in terms of linearity, accuracy, precision and sensitivity. Calibration curves obtained for each analyte were linear between 0.1 ng/L (or the limit of quantification if higher) and 1000 ng/L presented a linear behaviour, with correlation coefficients (r²) higher than 0.99 in all cases.

Collected samples were vacuum filtered through 1-µm glass fibers (GF-B) filter, followed by 0.45 µm nylon membrane filters (Whatman International Ltd., Maidstone, England) and stored at -20 ºC prior to analysis. Diluted influent water samples (influent water:HPLC grade water; 1:9, v/v) and effluent samples were spiked with a mixture of deuterium labelled compounds prior to extraction. For quality control, HPLC-grade water spiked with the internal standards was analysed every four real samples in order to check for possible carryover.

The quantified levels (median and concentration range) and the frequency of detection of the investigated drugs of abuse and metabolites in the sewage waters analysed, distinguishing between WWTP influent and effluent, are summed up in table 1.

| Compounds heroin, LSD and their respective metabolites, 6ACM and OH-LSD, were not detected in any of the samples analysed together with the compound THC and the respective metabolitesOH-THC, cannabidiol and cannabidiol. The compounds BE, COC, EPH, METH and the main metabolite of the last one, EDDP, were detected in the entire set of untreated wastewaters analysed, followed in order of detection frequency by MOR (87%) and MDMA (73%). These compounds were detected at maximum |

---

**Table 1. Frequency of detection, median and concentration range of the detected compounds.**

<table>
<thead>
<tr>
<th>Influent sewage water</th>
<th>Effluent sewage water</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE 100 631.0 107.0-1920.0</td>
<td>COC 100 178.0 13.0-667.0</td>
</tr>
<tr>
<td>CE 47 20.6 20.3-20.9</td>
<td>EPH 100 685.0 190.0-2260.0</td>
</tr>
<tr>
<td>MDMA 73 17.6 5.7-33.2</td>
<td>AM 40 297.0 67.2-768.0</td>
</tr>
<tr>
<td>MA 7 13.1 13.1</td>
<td>HER 87 113.0 57.9-238.0</td>
</tr>
<tr>
<td>MOR 87 113.0 57.9-238.0</td>
<td>6ACM - -</td>
</tr>
<tr>
<td>METH 100 33.4 18.5-106.0</td>
<td>EDDP 100 98.8 21.3-433.0</td>
</tr>
<tr>
<td>LSDD - -</td>
<td>OH-LSD 20 113.0 113.0</td>
</tr>
<tr>
<td>THC - -</td>
<td>THC-COOH 20 113.0 113.0</td>
</tr>
<tr>
<td>OH-THC - -</td>
<td>Cannabinol 20 96.8 96.8</td>
</tr>
<tr>
<td>Cannabidiol - -</td>
<td>DIA 20 - -</td>
</tr>
<tr>
<td>ALP 20 - -</td>
<td>LOR 40 156.0 129.0-184.0</td>
</tr>
</tbody>
</table>

**Note:** Compounds heroin, LSD and their respective metabolites, 6ACM and OH-LSD, were not detected in any of the samples analysed together with the compound THC and the respective metabolites OH-THC, cannabidiol and cannabidiol. The compounds BE, COC, EPH, METH and the main metabolite of the last one, EDDP, were detected in the entire set of untreated wastewaters analysed, followed in order of detection frequency by MOR (87%) and MDMA (73%). These compounds were detected at maximum.
concentrations of 1920 ng/L (BE), 667 ng/L (COC), 2260 ng/L (EPH), 106 ng/L (METH), 433 ng/L (EDDP), 238 ng/L (MOR) and 33 ng/L (MDMA) in influent wastewater. In effluent water, the compounds EPH, METH and EDDP were detected in 100% of the samples at maximum concentrations of 877 ng/L, 235 ng/L and 1260 ng/L, respectively.

As it might be expected metabolite transformation products were found at higher concentrations than the parent compound both at the inlet and outlet of the plants, with only two exceptions in STP10 (COC/BE) and STP1 (METH/EDDP). In influent water compounds COC, BE, EPH, AM and MOR were detected at concentrations higher by one or two orders of magnitude than in the effluent water indicating high removal rates during sewage water treatment. Other compounds showed higher frequency of detection in effluent water than in influent sewage water (MA, MDMA, THC-COOH, DIA, LOR and ALP) or higher concentrations as in the case of the compounds MA, METH, EDDP, THC-COOH and LOR. Figure 1 shows the cumulative levels (ng/L) of the drugs residues determined in the sewage waters collected at the inlet and outlet of the studied WWTPs.

a) influent sewage waters

b) effluent sewage water

Figure 1. Cumulative levels (ng/L) of the drugs residues determined in the sewage waters collected at the inlet and outlet of the studied WWTPs.
Cumulative levels indicate that the water treatment do not completely eliminates illicit drugs, as previously reported in the literature [8-12] Application of the sewage epidemiological approach to the concentration of drugs measured in influent wastewater also pointed out different geographical consumption patterns.

Acknowledgments

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References

Understanding the fate and behaviour of selected pharmaceuticals in soil-aquifer material prior to artificial recharge

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Soil-aquifer processes have demonstrated to work as a natural treatment for the attenuation or complete removal of numerous contaminants, and the predominant redox conditions have proven to be an important controlling factor. Nowadays, significant scientific effort is being devoted to verify if pharmaceuticals could also be efficiently removed from water. Nevertheless, knowledge on the behaviour of such semipersistent organic micropollutants in subsurface environments, their degradation pathways and the potential formation of transformation products is still limited.

Motivated by artificial recharge of groundwater practices we carried out a series of batch experiments involving aquifer material, selected drugs (initial individual concentration of 1μg/L and 1mg/L), and different anaerobic redox conditions. The fate and behaviour of three ubiquitous pharmaceuticals present in surface and wastewaters, namely, atenolol, diclofenac (DCF) and sulfamethoxazole (SMX) was investigated.

Different evolutions of atenolol could be observed depending on the experiment, i.e. mainly depending on the redox conditions dominating or being established in each system. Qualitatively it could be assessed that the faster atenolol biotic removal was observed in the sulfate-reducing experiment, under the most reducing condition up to that moment. Atenolol transformation product, atenololic acid, was detected in the 87 days long denitrifying test. The overall mass balance suggests that a small portion of atenolol molecules (14%) was sorbed during the experiment and that the rest removal (50%) could be attributed to biotransformation of atenolol into atenololic acid under nitrate reducing conditions.

During the denitrifying experiments, DCF and SMX concentrations consistently dropped in the middle of the tests, while nitrite was present. But they recovered towards the end, when nitrite had been fully reduced. This result suggests a complex effect of denitrifying conditions on aromatic amines. The transformation products nitro-diclofenac and 4-nitro-sulfamethoxazole were detected in the biotic experiments, developing almost opposite to that of their respective parent compounds. We conjecture that this temporal and reversible effect of denitrifying conditions on the studied aromatic amines could have a significant environmental impact, and could explain at least partially the wide range of removals in subsurface environments reported in literature for DCF and SMX, as well as some apparent discrepancies on SMX behaviour.

The results reported in the presentation show that soil aquifer treatment is an economic alternative to advanced treatments such as membrane bioreactors for the removal of emerging contaminants such as pharmaceuticals from surface and wastewaters.
Numerical solution of problems based on shallow water and St. Venant’s equations.

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Shallow water and St Venant’s equations are very useful models to simulate processes taking place in aquatic environment. In particular, the former are mainly used in dams, lakes or harbours, while the latter are widely used in fluvial hydraulics. An important reference regarding these problems and the numerical resolution is Toro (2000), especially those related to shallow water equations.

Among the numerical techniques available, finite volume methods are especially useful when solving problems related to computational fluid dynamics. This is the reason why we have chosen this technique for the problems considered in this work.

The general picture of the finite volume approach consists of discretizing the spatial domain in cells which are 1D intervals, 2D or 3D cells. After that, the equations which model the problem are integrated over each cell using integral averages. During this process, some sort of spatial reconstruction is needed, in order to compute intercell fluxes and values. Also time evolution is achieved by means of an ordinary differential equation solver.

The numerical technique applied in this work, to solve the proposed models, is a high order finite volume scheme, based on spatial 5\textsuperscript{th} order WENO reconstruction in space and 3\textsuperscript{rd} order Runge-Kutta TVD for time discretization, which give good results for this kind of problems.

The WENO reconstruction applied in this work follows the ideas put forward very recently in Dumbser et al (2008) and Hidalgo and Dumbser (2011) in which the linear weights are very large for the more centred stencils and very small for the more biased ones. Furthermore orthogonal Legendre basis functions are used in order to obtain an accurate polynomial reconstruction.

Numerical integration for the source term is carried out by means of two-point Gaussian quadrature rule. Some references regarding shallow water problems with bottom topography are Martinez-Gavara and Donat (2011) and LeVeque (1998).

As an example of the numerical solution for the shallow water model we solve a 1D problem in which we have a channel with a dam separating two constant states for water height and velocity. The initial values for both variables on the left and on the right side of the dam are given in Table 1.

\begin{table}[h]
\centering
\caption{Initial condition for dam break problem}
\begin{tabular}{|c|c|c|}
\hline
 & Left & Right \\
\hline
Height (m.) & 1 & 0.1 \\
Velocity (m/s) & 2.5 & 0 \\
\hline
\end{tabular}
\end{table}

The wall is supposed to be suddenly removed and therefore water is released from the initial situation. Results of water height and water velocity are given for an output time t=1s.
Figure 1: Dam break problem. Elevation over flat surface

Figure 2: Dam break problem: velocity
The behaviour of the numerical method used in this work has been assessed using references such as Toro (2000), Martínez-Gavara and Donat (2011) or LeVeque (1998), among many others, where the numerical solution has been obtained by means of different numerical methods to those used in this work.

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References

Modeling and mapping chemical reactions in complex subsurface natural systems

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The potential risk associated with polluted groundwater systems depends on the rate at which chemicals displace and interact through the aquifer or the overlying vadose zone. Major challenges associated with modeling flow and reactive transport in naturally heterogeneous porous media include the incorporation of the joint effect of physical, chemical and biological heterogeneity into multicomponent geochemical models and the quantification of its effects on the resulting spatially variable reaction rates. This is typically accomplished by means of reactive transport codes that can handle several species with different types of reactions. Codes based on Eulerian numerical methods (typically finite differences or finite elements) typically suffer from computational burden and numerical problems stemming from the required accurate description of heterogeneity in complex geochemical systems. This has prevented standard risk analysis to evaluate the likelihood that a toxic compounds reaches the nearby exposed population and ecosystems in the past, which is a key activity within WP 2 of SCARCE. Random walk particle tracking methodologies to simulate transport constitute an attractive alternative for their computational efficiency and absence of numerical dispersion. Yet, problems stemming from the reconstruction of concentrations from particle distributions have typically prevented its use in reactive transport problems. The numerical problem mainly arises from the need to first reconstruct the concentrations of species/components from a discrete number of particles, which is an error prone process, and then computing a spatial functional of the concentrations and/or its derivatives (either spatial or temporal). Errors are then propagated, so that common strategies to reconstruct this functional require an unfeasible amount of particles when dealing with nonlinear reactive transport problems. In this work, we provide with a methodology to directly reconstruct this functional based on kernel density estimators (KDE). Since the proposed KDE method avoids the propagation of the inherent fluctuations associated with the estimates of concentrations and their functionals, it renders particle tracking techniques the capability to be potentially coupled to any existing geochemical transport code. In this regard, it is shown that the coupling will be most efficient if the conceptual framework of De Simoni et al. [2005], which deconstructs the reactive problem into a conservative one plus speciation, is adopted to either calculate chemical species concentrations or their reaction rates.

Introduction

Modeling reactive transport in naturally heterogeneous porous media is crucial for determining the likelihood that a toxic compounds reaches the nearby exposed population and ecosystems, which is a key activity within WP 2 of SCARCE. This is typically accomplished, for instance, by means of reactive transport codes that can handle several species with different types of reactions. The application of these codes is typically associated with computational burden and numerical problems stemming from the required accurate description of heterogeneity in complex geochemical systems. In this context, Random Walk Particle Tracking Methodologies (RWPT) constitute an attractive technique for their computational efficiency and absence of numerical dispersion [Salamon et al., 2006]. These methods simulate solute transport by tracking in time a large number of particles injected into the system, each one with a predefined associated mass. At any time step the particle moves due to the sum of two terms, one being deterministic (loosely associated to advective processes) and the other random (loosely associated to dispersive processes). For any given time, resident concentrations can be recovered by defining a grid and...
counting the mass per unit volume of the particles that are located within a given support volume. The concentration estimate of a given support is a random variable but eventually converges to the "true value" when the number of particles tends to infinity. Hence, the major problem associated with these techniques is that one needs to ultimately estimate solute concentrations and reaction rates based on few particles. This renders the problem of going from particles to concentrations to be just a reconstruction problem, where the spatial or temporal distribution of a given variable must be inferred from the observation of the spatial or temporal location of a relatively small subsample [Fernàndez-Garcia and Sanchez-Vila, 2011]. In this paper, we present a simple and automatic method based on Kernel Density Estimates (KDE) that can directly reconstruct the concentration gradients involved in transport quantities such as memory functions, mixing indexes and reaction rates, based on the estimation of marginal and conditional density functions of the concentration derivatives.

**Kernel Density Estimators**

Particle tracking techniques produce discrete distributions of particle attributes (mass) that have to be converted to a continuous distribution of concentrations. The mathematical representation of the concentration field from particle distributions depends on the type of observation. Particle clouds observed at given times to yield resident concentrations \( c \) (concentrations averaged over a support volume), which will be the focus of this article. By normalizing these concentrations we can define the following probability density functions,

\[
p(x) = \phi(x)c(x; t_0) / \int \phi(x)c(x; t_0)dx,
\]

where \( p(x) \) is the probability of finding a solute mass within the support volume \([x, x+dx]\) at a given time \( t \), and \( \phi(x) \) is the porosity. A natural estimate of \( p(x) \) is the relative frequency of mass, which basically consists in counting the particle mass falling into a given support. In the traditional approach to recover concentrations from particle mass distributions \( (m_p) \), this support is defined based on a given discretization of the domain in space so that \( p(x) \) is only evaluated at the centroid of the discretization elements,

\[
p(x_j) \approx 1/M_j \sum_p m_p I\{X_p \in B_j\} / \Delta V_j,
\]

where \( M_j \) is the total mass, \( B_j \) is respectively the support volume \( \Delta V_j \), and \( I\{.\} \) is an indicator function equal to 1 when \( X_p \) belongs to \( B_j \) and zero otherwise. In general, a small support combined with a finite number of particles leads to very noisy estimates, whereas an increase in the support tends to oversmooth (over or underestimate) the estimated concentration distribution. Thus, an optimum choice of the support size exists. In this context, kernel density estimators (KDE) provide a convenient mathematical framework to obtain this optimal support. The KDE approach starts by generalizing the previous estimators as

\[
p(x) \approx 1/M_j \sum_p m_p K_H(x - X_p), \quad K_H(s) = (2\pi H)^{-1/2} \exp\left(-s^2 H^{-1} s\right),
\]

where \( K_H \) is a kernel or weighting function dependent on the separation distance between the particle position and the point of estimation [e.g., Hardle, 1990]. The shape of the elementary Kernel functions, \( K_H \) and the choice of \( H \) determines the degree of smoothing of concentrations.

**Optimal Estimates of reaction rates**

Let us consider a precipitation problem involving the mixing of two different waters. Each water carries in solution two aqueous species, \( B_1 \) and \( B_2 \), in instantaneous local equilibrium with a solid mineral \( M_3 \).
The corresponding reaction is $B_1 + B_2 = M_3$. Assuming that the solution is diluted, then we can assume unit activity coefficients and the law of mass action implies that $K_{eq} = c_1 c_2$, where $K_{eq}$ is the equilibrium constant. In this particular transport problem, the mixing of any two waters in equilibrium with the mineral leads to oversaturation of the resulting mixture. Precipitation then takes place instantaneously in order to re-equilibrate the system. Assuming that both species sample the same advective process and both have the same dispersion coefficient, De Simoni et al. [2005] showed that the reaction rate can be expressed as a function of a conservative specie $u = c_1 - c_2$, so that

$$r(u) = f_{cm}(u) f_{mix}(u), \quad f_{cm}(u) = 2K_{eq}/[(u^2 + 4K_{eq})]^{3/2}, \quad f_{mix}(u) = \nabla^T u D \nabla u,$$

(4)

By using (1), the gradients of conservative concentrations can be written as a function of $p(x)$,

$$\nabla u(x; t) = M_i / \phi(x) (\nabla p(x) - p(x) \nabla \ln \phi(x)).$$

(5)

Here, the gradients of $p(x)$ are a function of space and therefore its estimation is difficult when the problem is not one-dimensional. Knowing that by the definition of the conditional density function, $p(x|y) = p(y|x)p(x) = p(x|y)p(y)$, where $p(x|y)$ and $p(y|x)$ are the conditional density functions, and $p(x)$ and $p(y)$ are the marginal density functions, and after some algebra, we found that

$$\left(\partial_x, p(x,y)\right)^2 = p(y|x) \frac{dp(x)}{dx} \frac{dp(x|y)}{dx} p(y), \quad \left(\partial_y, p(x,y)\right)^2 = p(x|y) \frac{dp(y)}{dy} \frac{dp(y|x)}{dy} p(x).$$

(6)

Thus, the problem of estimating the gradients of the resident concentrations is reduced to the evaluation of the derivatives of univariate density functions, which is a well known problem. The kernel density estimate of the derivative of a univariate probability density function is [Engel et al., 1994]

$$dp(x)/dx \approx 1/M_i \sum_p \hat{K}^{(1)}(x - X_p),$$

(7)

where $K^{(1)}$ is the derivative of its corresponding elementary kernel function. Using the mean integrated squared error criterion to evaluate the expected error of the estimator, and assuming that all particles carry the same mass, the optimal support associated with (8) is known from Engel et al. [1994].

**Computational Investigations**

In order to test the methodology, we compare the $f_{mix}$ estimates obtained with the proposed KDE method with an analytical solution. For this purpose, we consider a 2D homogeneous aquifer under steady-state uniform flow conditions. Solute transport is described by the traditional reactive advection-dispersion equation, without external forces. Initially, the two aqueous species $\{c_1, c_2\}$ are in local equilibrium with the solid mineral. The initial equilibrium is then affected by a point-like instantaneous injection of water, that is still in chemical equilibrium with the mineral but with a different chemical composition. In this situation, knowing that $u = c_1 - c_2$ is the conservative specie, the analytical solution of the mixing term is

$$f_{mix}(u) = \left(\frac{\Delta u_0}{4\pi \sqrt{D_L D_T}}\right)^2 \frac{\rho^2}{2t} \exp\left(-\frac{\rho^2}{2t}\right), \quad \rho(x,y,t) = \sqrt{\frac{(x-x_0 - vr)^2}{2D_L t} + \frac{(y-y_0)^2}{2D_T t}},$$

(8)

where $(x_0,y_0)$ is the point of injection, $\Delta u_0$ is the initial pulse of the $u$-concentration, $D_L$ and $D_T$ are the longitudinal and transverse dispersion coefficient, and $v$ is the groundwater velocity.

Figure 1 compares the analytical solution of $f_{mix}$ at time $t=60$ with their corresponding optimal estimates obtained using the proposed KDE method. The results are also contrasted against the traditional approach, which simply consists in counting particles within bins. In this approach, the gradients involved in $f_{mix}$ were computed using a finite difference spatial discretization of $u$ without any post-treatment. It is also compared to the coarse graining technique, where the size of the bins was manually changed to obtain the
most adequate smooth representation of $f_{mix}$. In overall, figures show that the proposed KDE method is capable to automate the reconstruction of concentrations and reactions rates from particle distributions, and further generate a more superior depiction of the reactions rates compared with the traditional solution.

A synthetic example of the effects of physical heterogeneity on reaction rates is presented in Figure 2. A water with a different chemical composition was then injected instantaneously in a rectangular area of 30 units width and 50 units height located orthogonal to the principal flow direction. At this particular time, transverse dispersion has still not induced complete mixing, and the shape of the plume of the conservative component $u$ is mostly distorted according to the velocity field. This produces sharp fronts and narrow mixing areas at the plume edges. Consistent with this picture, the proposed KDE method predicts chemical reactions to take place mostly at the plume boundaries.

**Conclusions**

The inherent fluctuations associated with the estimates of concentrations and their functionals (reaction rates) have typically prevented the use of particle tracking techniques to simulate complex reactive
problems. In this paper, we have shown that this appreciation stems from a naive understanding of the reconstruction of functionals of concentrations in the particle tracking literature. Based on kernel density functions, we have presented an efficient method for the reconstruction of the reactions rates of chemical species from particle distributions. Since the proposed KDE method avoids the propagation of the inherent fluctuations associated with the estimates of concentrations and their functionals, it renders particle tracking techniques the capability to be potentially coupled to any existing geochemical transport code. In this regard, we have shown that the coupling will be most efficient if the conceptual framework of De Simoni et al [2005], which deconstructs the reactive problem into a conservative one plus speciation, is adopted to either calculate chemical species concentrations or their reaction rates.

References


The dynamics of groundwater resources in the El-Qaa irrigation district of Orontes Basin in Northern Bekaa Valley of Lebanon

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Abstract

Close to 400 million m$^3$ of water are generated in the Lebanese part of the upper Orontes basin (Aquastat, 2008), mainly originating from the many springs that are supplied by infiltration of rainfall and snowmelt in the neighbouring mountain chains. Most of these springs, have long been used for agricultural activities and some irrigation canals date from the Roman Empire era.

Groundwater has been increasingly exploited along the basin and is now a critical problem in some parts, in particular in the region of El-Qaa, where the agricultural activities are more dominant with comparison to other parts of the basin. Surface water/groundwater interactions are therefore a crucial issue to understand the evolution of the basin hydrology. This allows a better quantification of the resource and its productivity. Policies for managing the groundwater resource have resulted in drawing up a management of the aquifer, mainly with respect to (i) balance the water drawn from the different available resources and to guard against the increases in salt content and (ii) preserve the quality of this resource by reducing the overlap with the aquifers near the surface.

This study will document current irrigation practices, surface water use, and groundwater use by farmers in the El-Qaa area and simulate surface water and groundwater hydrology. A conjunctive use water allocation model will be developed to evaluate both current agricultural production practices and feasible alternative scenarios under considerations of climate change and enhancing farmer and community livelihood. Measurements of relevant local hydrological parameters and well hydraulics data will be collected along with historical and ongoing meteorological data and estimates of relevant crop parameters from the literature. An appropriate integrated hydrologic-agronomic-economic model, such as that proposed by Cai et al. (2003), will then be selected, implemented, and calibrated for the upper Orontes region, or a similar dry Mediterranean region if sufficient data is not available for El-Qaa. The calibrated model will be used to evaluate future consequences of current and alternative agricultural production practices such as irrigation requirements, surface water use, groundwater depletion, salinity, and yields under appropriate scenarios of climate change and crop diversity.

Background

Lebanon has a Mediterranean climate, with abundant rainfall in the winters and dry summers. Rainfall is generally heavy on the coastal plains and limited inland. One third of Lebanon’s land is cultivable, and most of its production is rainfed. Despite the country’s relatively abundant water resources, water losses are estimated at 50%. Lebanon has lagged behind other countries in the region in water sector development due to poor management, weak institutional capacity and financial constraints.

Consumptive water use over about 55% of Lebanon agriculture is significantly dependent on groundwater. Use of groundwater exceeds surface water in both the cosatal strip and the inlands. Without groundwater, much of the nation’s agricultural activity would not be viable. The Bekaa Valley accounts by itself about 50% of the National agricultural activity, and is one of the country largest aquifer, namely
the Orontes basin in the northern and Litani in the southern parts of the Valley. Groundwater management is a significant and strategic issue. From traditional indigenous symbology to the digital products of today, hydrogeological mapping has been an important tool for groundwater managers and users in Lebanon.

The USAID-Water and Livelihoods’ Initiative seeks to increase income-generating opportunities while reversing the degradation of watersheds through sustainable water and land management strategies. The benchmark site of El-Qaa is situated in the Northern Bekaa Valley, the source of the Orontes River. The economy of the Bekaa Valley is predominately agricultural, and 20% of its approximately 100,000 inhabitants work in agriculture, with an additional 20% who are indirectly involved in the sector. The main crops include wheat, watermelon, apricot and almonds that are produced through irrigation and rainfed agriculture. Livestock production is predominantly limited to poultry and small ruminants. Agricultural production in the areas is, however, facing serious challenges as a result of dropping groundwater level, and the dramatically decreasing flow of the Orontes River in the dry season. Farmers need new and more efficient irrigation methods and improved extension systems at the sites. The irrigated area around and north of El-Qaa receives water from three different sources: the intermittent wadis from anti-Lebanon mountains, the 17 km long irrigation canal that brings water from the Laboueh spring, local tube-wells. But the greater and more reliable supply now comes from groundwater resources that are being overexploited.

Groundwater is in danger of losing its potential functions due to the deterioration of quantity and quality. While aiming at sustainability of the use, the vital functions of groundwater reservoirs are threatened by pollution and overexploitation (Karam and Karray, 2000). One very important problem of deterioration of groundwater quality is the increasing pollution from diffuse sources, like agricultural activities, groundwater nitrification and salinisation near the coastal areas and in many cases near in Northern Bekaa Valley. In many cases, it has been recognised that a rise in the groundwater table is one of the main causes of waterlogging and salinity increases near the top layer of the soil. As groundwater moves upward, salinity is increased by dissolving of salts in the soil (Tickell and Humphrys, 1985). The rising of the groundwater table arises from the effect of intensive actual irrigation combined with the disruption of the natural climate. In fact, intensive removal in the past of deep-rooted vegetation has reduced the natural drainage capacity of basins and destroyed the natural equilibrium between groundwater recharge and drainage. When the water table rises to a depth less than two meters below soil surface, salt concentrations are further increased by evaporation and damage to vegetation and soils is then likely.

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**Figure 1**: Precipitation rates (left) and topographical features (right) of the Orontes River Basin
The objectives of this study is to (i) strengthen the understanding of agrarian dynamics and groundwater use in the face of changing circumstances and (ii) provide a solid primary data sets to evidence the logics at work and the constraints faced by farmers. The major expected output of this research is the understanding of the current farming systems and groundwater use dynamics, in relation to changes in surface water supply and other factors such as energy price and water table depth in the El-Qaa irrigation district. Additionally, conjunctive use of surface water and groundwater will be simulated under various crop selection, land use, irrigation, and climate change scenarios to aid in future decision making.

References
Tickell S and Humphreys WG. Hydrogeological map of BENDIGO and part of DENILIQUIN (1:250,000 scale). Victorian Department of Industry Technology and Resources (1985).
The challenge of analysing climate change impacts on the hydrology of Mediterranean river basins - A perspective from the CLIMB project

Ralf Ludwig and the CLIMB consortium

Ludwig-Maximilians-Universitaet Muenchen, Department of Geography, Munich, Germany

According to future climate projections, Mediterranean countries are at high risk for an even pronounced susceptibility to changes in the hydrological budget and extremes. Threats include severe droughts and extreme flooding, salinization of coastal aquifers, degradation of fertile soils and desertification due to poor and unsustainable water management practices. These changes are expected to have strong impacts on the management of water and land resources as well as on key strategic sectors of regional economies, such as agriculture and tourism, and their macroeconomic implications. Such manifold developments bare a strong capacity to exacerbate tensions, and even intra- and inter-state conflict among the social, political, ecological and economic actors. Thus, effective adaptation and prevention measures need multidisciplinary preparation, analysis and action.

In its 4-year design, the presented project CLIMB (FP7-ENV-2009-1) analyzes ongoing and future climate induced changes in hydrological budgets and extremes across the Mediterranean and neighboring regions. This is undertaken in study sites located in Sardinia, Northern Italy, Southern France, Tunisia, Egypt and the Palestinian-administered area Gaza. The work plan is targeted to selected river or aquifer catchments, where the consortium will employ a combination of novel field monitoring and remote sensing concepts, data assimilation, integrated hydrologic (and biophysical) modeling and socioeconomic factor analyses to reduce existing uncertainties in climate change impact analysis. Advanced climate scenario analysis will be employed and available ensembles of regional climate model simulations will be audited and downscaled. This process will provide the drivers for an ensemble of hydro(-geo)logical models with different degrees of complexity in terms of process description and level of integration. The results of hydrological modeling and socio-economic factor analysis will enable the development of a GIS-based Vulnerability and Risk Assessment Tool. This tool will serve as a platform for the dissemination of project results, including communication with and planning for local and regional stakeholders. An important output of the research in the individual study sites will be the development of a set of recommendations for an improved monitoring and modeling strategy for climate change impact assessment.

CLIMB, started in early 2010, is part of a research cluster with the projects WASSERMed (= Water Availability and Security in Southern Europe and the Mediterranean, FP7-ENV) and CLICO (= Climate Change, Hydro-Conflicts and Human Resources, FP7-SSH). This cluster has been formed under a coordinated topic between the Environment and Social Science and Humanities Programs of EC’s FP7 to better assess the manifold consequences and uncertainties in climate impact on man-environment systems and water security in Southern Europe and neighboring regions. It comprises a critical mass of researchers from 44 partners (29 institutions from the EU, 5 institutions from S&T countries and 10 international institutions) to foster scientific synergy and policy outreach and to tackle the challenging research questions with regard to climate change impacts on water resources as a threat to security.

The presentation highlights the CLIMB approach and will focus on the major challenges in achieving its ambitious goals, among which the ‘no data’-issue in the case studies is most prominent. First findings, stemming from intense field campaigns and first model results will be discussed.
Effects of metal pollution under high discharge conditions

Helena Guasch¹, Marta Ricart¹,², Berta Bonet¹, Natàlia Corcoll¹ and Awadesh Kumar¹

¹ Institute of aquatic ecology, University of Girona, Girona, Spain
² Catalan Institute for Water Research, Girona, Spain

Water discharge, a key environmental factor strongly influenced by local and global changes, has also been considered a major factor influencing the fate and effects of pollution in fluvial ecosystems. Several studies indicate that low flow may increase metal exposure (due to low dilution), uptake (due to higher retention under low flow), toxicity and/or accumulation of metals (depending on the dose and time of exposure), but high flow may also increase metal exposure (due to sudden peak concentrations) when pollution comes from diffuse sources (Guasch et al. 2010). Similarly, Petrovich et al. (2011) concluded that dilution flow was not the unique factor governing the concentration levels of pharmaceuticals in the receiving water bodies. Sources of variability might be diverse and dilution (flow) might be just one among many others such as analytical error, compound environmental variability, sediment remobilization or seasonal use.

An extensive field sampling was designed to describe, under contrasting discharge condition, water pollution patterns in Mediterranean rivers and their impact on the aquatic biota. A set of results corresponding to the first sampling, representing a high-discharge episode, have been analyzed for this presentation. Water chemistry was focused on metal pollution and their impact based on biofilm responses, i.e. oxidative stress response measurements. Oxidative stress is a common form of stress likely to affect biofilms and to constrain their ability to respond to further stresses. Indeed antioxidant enzymes are expected to react quickly to avoid oxidative burst in cells and so to be early warning systems (Bonnineau et al. 2011).

In our multi-site field study, low metal concentration due to dilution was expected. On the other hand, peaks of metal pollution could also have occurred, but probably not recorded, after storm events due to runoff of metal polluted landfills. As a result, different levels of metal pollution were expected to occur at different temporal scales. Metal toxicity to fluvial biofilms can be very high if the community, developed under low metal exposure and low nutrient availability, is suddenly exposed to peak metal concentrations. This high sensitivity is attributed to the lack of adaptation to metal exposure and the lowered capacity of nutrients to counterbalance metal effects.

In agreement with our expectation, biofilm and water metal concentrations were in general low, and this was attributed to dilution (Figure 1). On the other hand, oxidative stress in biofilms increased with the CCU (Figure 1), indicating that metal loads were already affecting the benthic community and the type of response, a progressive increase in the activity of the antioxidant enzyme catalase, was probably caused by sudden increases of metal exposure. On the other hand, higher metal pollution and more persistent effects on biofilms are expected in the second sampling, corresponding to low-flow conditions. Our results highlight the pertinence of linking water pollution with stress measurements performed “in situ”, supporting further data analysis including a comprehensive study of water pollution and a larger range of water discharge conditions.
Oral presentations

SCARCE 2nd ANNUAL CONFERENCE
Integrated modelling and monitoring at different river basin scale
28-29 November 2011, Madrid, Spain

**Figure 1.** Water metal concentrations; calculated Cumulative Concentration Units; biofilm metal concentrations and plot of biofilm catalase activities vs CCU. Data include 19 sites located in the main course of the rivers LLobregat; Guadalquivir; Jucar and Ebre sampled during a high-flow episode in autumn 2010

**References**


**Acknowledgements**

This study was supported by the Spanish projects SCARCE (Consolider-Ingenio 2010, CSD2009-00065) and FLUVIALMULTISTRESS (CTM2009-14111-CO2-01)
The use of wood sticks to assess stream ecosystem functioning: comparison with leaf breakdown rates

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Faculty of Science and Technology, University of the Basque Country, Bilbao, Spain

There is an increasing interest in river functioning, as it drives important ecosystem services, threatened now by the global change (Constanza et al., 1997). Among the many methods used to assess river functioning, litter breakdown has been suggested as one of the most convenient for routine assessment, due to the fundamental role that allochthonous litter plays in forested streams and the effects of anthropogenic activities on its decomposition (Gessner & Chauvet, 2002). Nevertheless, picking leaves and assembling leaf bags is highly time consuming, what led to some scientists to use alternative materials, such as standard cotton strips (Tiegs et al., 2007) or wooden sticks (Young et al., 2008). The problem with these alternative materials is that there is little information on their performance under different conditions compared to that of typical leaf bags. In particular, wood breaks down much slower than most leaves (Tank et al., 2010), and its decay depends especially on the surface to volume ratio of wood pieces (Spänhoff & Meyer, 2004). Nevertheless, wood breakdown has been shown to respond to eutrophication in the same way as leaf breakdown (Diez et al., 2002), thus suggesting it might be a good surrogate for leaf breakdown.

The aim of this study is to check the performance of wooden sticks versus that of leaf bags, and to evaluate their suitability as functional indicators of stream functional status. Our hypotheses are that, a) wood breakdown will be slower than that of most leaf species, but that spatial variations in breakdown will be similar for both wood and leaves, and b) experiments of wood breakdown will be cheaper and less time-consuming that those of leaf breakdown.

For this purpose, we performed breakdown experiments with tongue depressors and with leaves of six common tree species at two contrasting large streams (width ca. 30 m) in Guipuscoa (the Basque Country, Spain). River Urumea in Ereñozu drains a basin of 218 km² with less than 800 inhabitants, mostly devoted to agricultural and forest activities. Therefore, water quality there is excellent and pressures on the river ecosystem limited to the effect of small hydropower plants. River Deba in Altzola, on the other hand, drains a basin of 464 km² with over 135 000 inhabitants and heavy steel and chemical industry. As the main water treatment plants on the basin are still under construction, the concentrations of nutrients and pollutants are high and the overall quality of water very poor.

Breakdown of tongue depressors (Populus nigra x canadiensis) was compared to that of leaves of black alder (Alnus glutinosa), poplar (Populus nigra), London plane (Platanus hispanica), common oak (Quercus robur), beech (Fagus sylvatica) and shining gum (Eucalyptus nitens). Tongue depressors were dried (70 °C, 72 h) and tied with fishing line to metal bars or roots in the stream channels (Figure 1). Freshly fallen leaves were air dried, enclosed in 5 mm mesh bags (5 g per bag) and tied like depressors. Regularly the material was retrieved (5 replicates per site), dried (70 °C, 72 h), weighed, ashed (500 °C, 5 h) and weighed again to obtain the ash free dry mass (AFDM). Breakdown rates were calculated following the negative exponential model. We also measured water physico-chemical characteristics following standard methods (APHA, 1992), and the initial content of the material used in both N and P (Perkin Elmer series II CHNS/O elemental analyzer and APHA, 1992, respectively). Finally, we calculated the cost of the experiments both in terms of time invested and of money, considering a price of 12 € per hour spent setting the experiments and making the field and laboratory work.
Stream water differed mainly in conductivity and nutrients: conductivity was ~9 times higher in the polluted stream and nitrites, ammonium and phosphates were respectively ~24, ~5 and ~3 times more concentrated (Table 1). Temperature, pH and nitrate concentration did not differ between streams.

All materials broke down significantly faster in the unpolluted (breakdown rate 0.012 - 0.0025 day⁻¹) than in the polluted stream (0.011 - 0.0011 day⁻¹, Figure 2). The species ranking remained constant: poplar > alder > eucalypt > plane > oak > beech > wood. Excluding poplar, this ranking had a strong correlation with initial N content of the material, being alder the richest species in N and wooden sticks the poorest in both nutrients (Figure 3).

Table 1. Mean ± SE of the physicochemical variables measured in both streams during the breakdown experiments.

<table>
<thead>
<tr>
<th></th>
<th>URUMEA</th>
<th>DEBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basin area (km²)</td>
<td>218</td>
<td>464</td>
</tr>
<tr>
<td>Population</td>
<td>778</td>
<td>135 000</td>
</tr>
<tr>
<td>Main pressure</td>
<td>Forestry</td>
<td>Industry</td>
</tr>
<tr>
<td>Q (m³/seg)</td>
<td>9.27 ± 0.63</td>
<td>10.68 ± 1.17</td>
</tr>
<tr>
<td>T (°C)</td>
<td>6.96 ± 0.29</td>
<td>6.44 ± 0.23</td>
</tr>
<tr>
<td>Cond (μS/cm)</td>
<td>69.46 ± 0.84</td>
<td>592.79 ± 8.28</td>
</tr>
<tr>
<td>O₂ (mg/l)</td>
<td>11.31 ± 0.07</td>
<td>12.31 ± 0.09</td>
</tr>
<tr>
<td>pH</td>
<td>7.38 ± 0.018</td>
<td>7.99 ± 0.24</td>
</tr>
<tr>
<td>[NO₃⁻] (mg/l)</td>
<td>2.41 ± 0.19</td>
<td>2.23 ± 0.28</td>
</tr>
<tr>
<td>[NO₂⁻] (μg/l)</td>
<td>1.65 ± 0.27</td>
<td>39.48 ± 6.46</td>
</tr>
<tr>
<td>[NH₄⁺] (μg/l)</td>
<td>25.35 ± 6.11</td>
<td>114.68 ± 15.07</td>
</tr>
<tr>
<td>[PO₄³⁻] (μg/l)</td>
<td>19.48 ± 2.52</td>
<td>54.44 ± 7.03</td>
</tr>
</tbody>
</table>
The experiments of breakdown with leaf bags were 10 times more time consuming and 4 times more expensive than those with tongue depressors (Table 2). Our experiment showed that wooden sticks perform similarly to leaf bags under different pollution levels, offering consistent results at a slower cost both in terms of time and money. Therefore, they hold potential for assessing river functioning and are a promising alternative tool for routine river health monitoring.

Table 2. Cost in terms of time and money required per breakdown experiment for leaf litter and tongue depressors

<table>
<thead>
<tr>
<th></th>
<th>TONGUE DEPRESSORS</th>
<th>LEAF LITTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf collection (h)</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Bag preparation (h)</td>
<td>1.5</td>
<td>18</td>
</tr>
<tr>
<td>Sample processing (h)</td>
<td>1.75</td>
<td>12</td>
</tr>
<tr>
<td>Price (€)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>Labour (12€/h)</td>
<td>39</td>
<td>480</td>
</tr>
</tbody>
</table>
Acknowledgements

This work has been supported by the Spanish Ministry of Science and Innovation through the project Consolider-Ingenio CSD2009-00065.

References


Toxicity testing and behavioral changes in two species exposure to several pharmaceutical compounds: the copepod *Tisbe battagliai* and the shrimp *Atyaephyra desmarestii*.

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Background and aims

The increase in the consumption of pharmaceuticals along with global change has increased the presence in recent years of emerging contaminants in the river ecosystems. Most of the drugs used in human or veterinary end up in surface waters of the rivers because many of the wastewater treatment plant (WWTP) are unable to eliminate them totally either in its compound form and its metabolites. These compounds are in very low concentrations in the aquatic environment, but their single and mixture toxicological effects in the short and long term on aquatic organisms are not well know. In order to improve the knowledge about the toxic effects of pharmaceuticals as single or mixture on aquatic biota we have exposed two model organisms, the harpacticoid copepod *Tisbe battagliai* (marine organism) and the crustacean decapod *Atyaephyra desmarestii* (freshwater organism) at different concentrations of individual and mixtures pharmaceutical compounds: Carbamazepine (anticolvulsant), Atenolol (β-blockers), Acetaminophen (Analgesic and antipyretic), Diclofenac (treat pain) and Ibuprofen (anti-inflammatory). In addition to mortality, the sublethal endpoints analyzed have been feeding, osmoregulatory and respiratory rates, which can give information about the chronic toxicity of these compounds.

Methods

Test for acute toxicity in the marine copepod *Tisbe battagliai* organisms were exposed <24h-old nauplii for 48h to increasing concentrations of single (nominal concentrations: 1 and 150 mg·L⁻¹) and mixtures of selected pharmaceuticals. The organism used in this study were obtained from cultures maintained at the Instituto de Ciencias Marinas de Andalucía (ICMAN-CSIC). The results from each single compound experiment were used to derive the LC50 and to assess environmental risk. Binary mixture experiments were conducted using the combinations of drugs tested at their 48h EC50 values. The other model organism used in the tests has been the crustacean decapod *A. desmarestii*. The freshwater shrimps were collected in the headwaters of the river Guadalete and maintained in aquaria at the ICMAN facilities. For acute toxicity testing organisms were exposed for 96 hours at concentrations in a range for individual compounds: (nominal concentrations: Carbamazepine 50-200 mg/L; Atenolol 200-1000 mg/L; Diclofenac 0.6-9.6 mg/L; Ibuprofen 1-35 mg/L). The dead specimens and the moults were removed daily. At the end of the experiment the survivors were frozen in liquid nitrogen at -80 °C for later analysis. Mortality data are treated with GLMstat software to estimate of mortality parameters (LCx). For chronic toxicity tests, the organisms were exposed to environmentally relevant concentrations (10-25µg/L). For ingestion test, the organisms were exposed individually (n=10 replicates) in glass container for 10 days and the status of the digestive tract was recorded each 30 minutes for 300 minutes. For testing osmoregulation, the organisms were exposed for 9 days. At the end, 10 µl of hemolymph was extracted for its analysis in the WESCOR 5520 vapor pressure osmometer to derive the dates of osmolality (mmol/kg). For testing the respiration rate (mg O₂/L), the organisms were exposed to the compounds at least for 7 days. The oxygen consumption of individual shrimps was measured using Strathkelvin 1302 polarographic electrodes connected to Strathkelvin 782 dual-channel oxygen meter. Respiration chamber were maintained at constant temperature (20±0.1°C). Significant differences (P < 0.05) of response variables were tested by...
Results

In the case of the copepod *T. battagliaii*, the concentrations for acute toxicity (EC50) for single and mixture compounds were very higher than environmental levels (Table 1). However, these results have been employed as a first approach for environmental risk assessment, as well as the detection of synergistic and antagonistic effects. For the crustacean decapod *A. desmarestii* similar behavior was reported with concentrations for acute toxicity very higher than environmental levels (Table 2). For chronic toxicity tests, no significant differences were found between controls and treatment for ingestion and osmoregulation test (Dunnett’s test *p*<0.05) as it is showed the Figure 1. The same behaviour was observed when the respiration rates were testing even under conditions of moderate hypoxia (3 mg O2 / L).

Table 1. Values of LC50 for *T. battagliai* exposed to four compounds and risk characterization in the surface waters with PNEC obtained by extrapolation with a factor 1000 from acute (96h) toxicity data.

<table>
<thead>
<tr>
<th>Substance</th>
<th>LC5 (mg/L)</th>
<th>LC10 (mg/L)</th>
<th>LC20 (mg/L)</th>
<th>LC50 (mg/L)</th>
<th>PEC (µg/L)</th>
<th>Reference</th>
<th>PEC/PNEC Risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaminophen</td>
<td>6,7</td>
<td>13,4</td>
<td>33,5</td>
<td>67,8</td>
<td>10</td>
<td>(Kolpin et al.,2002)</td>
<td>0,068 0,14 Low</td>
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<tr>
<td></td>
<td>n.D</td>
<td>(-13-28,4)</td>
<td>(15,0-44,8)</td>
<td>(58,2-77,8)</td>
<td></td>
<td></td>
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<tr>
<td>Carbamazepine</td>
<td>4,7</td>
<td>9,4</td>
<td>18,8</td>
<td>59</td>
<td>5</td>
<td>[5]</td>
<td>0,059 0,08 Low</td>
</tr>
<tr>
<td></td>
<td>n.D</td>
<td>n.D</td>
<td>(3,7-31,0)</td>
<td>(45,6-80)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>2,8</td>
<td>4,5</td>
<td>6,3</td>
<td>9,5</td>
<td>0,8</td>
<td>[5]</td>
<td>0,01 0,08 Low</td>
</tr>
<tr>
<td></td>
<td>(-0,4-4,7)</td>
<td>(2,0-6,1)</td>
<td>(4,4-7,8)</td>
<td>(8-11,3)</td>
<td></td>
<td></td>
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<tr>
<td>Ibuprofen</td>
<td>5,65</td>
<td>11,3</td>
<td>25,5</td>
<td>49,7</td>
<td>10</td>
<td>[5]</td>
<td>0,05 0,2 Low</td>
</tr>
<tr>
<td></td>
<td>n.D</td>
<td>(-10,9-24,7)</td>
<td>(8,4-36,7)</td>
<td>(38,8-59,8)</td>
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</table>

Table 2. Values of LC50 for *A. desmarestii* exposed to four compounds and risk characterization in the surface waters with PNEC obtained by extrapolation with a factor 1000 from acute (96h) toxicity data.

<table>
<thead>
<tr>
<th>Substance</th>
<th>LC5 (mg/L)</th>
<th>LC10 (mg/L)</th>
<th>LC20 (mg/L)</th>
<th>LC50 (mg/L)</th>
<th>PEC (µg/L)</th>
<th>Reference</th>
<th>PEC/PNEC Risk</th>
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</thead>
<tbody>
<tr>
<td>Carbamazepine</td>
<td>36,6</td>
<td>49,7</td>
<td>63,9</td>
<td>88,2</td>
<td>5</td>
<td>[5]</td>
<td>0,088 0,06 Low</td>
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<tr>
<td></td>
<td>(2,9-54,8)</td>
<td>(22-65,4)</td>
<td>(42,3-77,4)</td>
<td>(74,2-100,6)</td>
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<tr>
<td>Diclofenac</td>
<td>0,1</td>
<td>1,9</td>
<td>3,9</td>
<td>7,3</td>
<td>0,8</td>
<td>[5]</td>
<td>0,007 0,11 Low</td>
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<tr>
<td></td>
<td>(-3,2-1,8)</td>
<td>(-0,5-3,3)</td>
<td>(2,3-5,0)</td>
<td>(6,2-9)</td>
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<tr>
<td>Ibuprofen</td>
<td>5,4</td>
<td>6,5</td>
<td>7,7</td>
<td>9,7</td>
<td>10</td>
<td>[5]</td>
<td>0,01 1,03 Medium</td>
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<tr>
<td></td>
<td>(0,3-7,1)</td>
<td>(2,6-7,9)</td>
<td>(5,0-8,9)</td>
<td>(8,4-11,3)</td>
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<tr>
<td>Atenolol</td>
<td>14,3</td>
<td>101,3</td>
<td>195,7</td>
<td>357,1</td>
<td>0,89</td>
<td>[5]</td>
<td>0,357 0,002 Low</td>
</tr>
<tr>
<td></td>
<td>(-151,6-110,8)</td>
<td>(-31,1-182,7)</td>
<td>(95,7-264,9)</td>
<td>(290,3-427,3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Discussions and conclusions

*T. battagliai* is a suitable candidate for the evaluation of the effects of pharmaceuticals compounds in estuarine ecosystems. Effect concentrations of single compounds and mixtures were significantly higher than environmentally relevant concentrations, showing several combinations additive effects. *A. desmarestii* is a species sensitive to oxygen changes in the environment because it has very little oxygen-regulatory capacity which makes it also a good reference for the assessment of the effects of pollutants. On the basis of the ratio between environmental concentrations and PNEC, the risk associated of the occurrence of these compounds in STPs effluents is “low risk” ranging from 0.01 to 0.1, whereas ibuprofen presents at “medium risk” from 0.1 to 1 [7].

Acknowledgement

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Reference


Effects of global change on the functioning of Mediterranean rivers: breakdown of organic matter as an assessment tool

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Human population has been rising steadily in the last centuries, hence the use of resources has increased with it, resulting in a global environmental change (Vitousek 1994; IPCC 2007; UNEP 2007), which is affecting every ecosystem on earth, especially those in highly populated areas (Millennium Ecosystem Assessment, 2005). Streams and rivers are among the most affected ecosystems (Dudgeon, 2010), especially those in areas with shortage of water (Vörösmarty et al., 2010), like the European Mediterranean region. Mediterranean rivers are subjected to multiple impacts: pollution, changes in discharge regime and channel morphology, modification of riparian areas, invasion of exotic species, etc. (Sabater, 2008; Ricart et al., 2010). These impacts are seldom additive and usually interact in complex ways.

As a result of global change, large effects are expected in river ecosystem functioning (Rockstrom, 2009), which is the base of many ecosystem services (Sweeney et al., 2005). Nevertheless, most of the information available on the response of river ecosystem functioning to the global environmental change derives from studies of limited spatial extent. Indeed, measuring ecosystem functioning simultaneously at multiple sites needs either large teams (e.g., Bernot et al., 2010) or large investments in monitoring stations (e.g., Izagirre et al., 2008). Litter breakdown is a potentially useful tool to monitor river ecosystem functioning (Gessner & Chauver, 2002) that can record the action of multiple drivers and stressors through an extended period of time. Among the unlimited number of substrates that can be incubated in the water to estimate breakdown Young et al. (2008) advocated for the use of sticks to standardize the procedure and reduce the variability of the measure.

In an attempt to determine the spatial variation of ecosystem functioning of Mediterranean rivers in the Iberian Peninsula, we performed stick breakdown experiments at 78 sites spread across the basins of rivers Llobregat, Ebro, Júcar and Guadalquivir (Figure 1), covering a range of environmental conditions as wide as possible, including variations in climate, in hydromorphology, in human activities, and in water pollution. Tongue depressors (15 x 1.8 x 0.2 cm) made of untreated Canadian poplar wood (Populus nigra x canadiensis, Moench) were individually tagged, weighed, arranged in bunches of 5, and 3 bunches tied in summer 2010 to metal bars, roots or rocks at each study reach. After 54 to 106 days of incubation, depressors were recovered, carried to laboratory, washed with tap water and brushed, dried (70 °C for 3 days), weighed and ashed (500 °C for 5 h) to estimate the remaining ash free dry mass (AFDM). Breakdown rates were calculated according to the negative exponential model. Data on channel form and hydraulics, on water chemistry, and on biological communities were either collected by the SCARCE project team, or by water agencies. Linear regressions, quantile regressions, non-metric multidimensional scaling (NMDS) and partial least square (PLS) regressions were used to relate the variations on breakdown rate with environmental variables.
The study sites spanned a large range of environmental variation (Table 1): altitude ranged from 1179 m.a.s.l to estuaries, channel width from 1.6 to 385 m, and discharge from 0.05 to 193 m³/s. The range displayed by water physico-chemical variables was considerable too; turbidity 30 Nephelometric Turbidity Units (NTU), suspended solids 98 mg/L, conductivity 3000 µS/cm, pH 2.5, temperature 15 ºC, dissolved oxygen 11 mg/L, ammonium 9 mg/L and phosphorus 3 mg/L. Ordination analysis with NMDS considering site characteristics revealed a high degree of overlapping among the four basins, with locations of every four basins spread along the two axes.

Table 1. Mean and range values of different physico-chemical and geomorphological characteristics at the study sites.

<table>
<thead>
<tr>
<th>Units</th>
<th>Average</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altitude</td>
<td>m.a.s.l.</td>
<td>371.77 0-1179</td>
</tr>
<tr>
<td>Width</td>
<td>m</td>
<td>36.43 1.6-384.8</td>
</tr>
<tr>
<td>Slope</td>
<td>m/m</td>
<td>0.05 1e-4 – 0.08</td>
</tr>
<tr>
<td>Discharge</td>
<td>m³/s</td>
<td>17.38 0.05-192.98</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>35.13 4.87-35.13</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>mg/L</td>
<td>35 2-100</td>
</tr>
<tr>
<td>Conductivity</td>
<td>µS/cm</td>
<td>1061.33 170-3194.4</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.93 6-8.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>ºC</td>
<td>19.87 10-26.83</td>
</tr>
<tr>
<td>Dissolved O₂</td>
<td>mg/L</td>
<td>7.54 3.16-14.47</td>
</tr>
<tr>
<td>NH₄</td>
<td>mg/L</td>
<td>0.5 0.024-9.05</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/L</td>
<td>0.32 0.015-3.475</td>
</tr>
</tbody>
</table>
Remaining mass after incubation ranged from 16 to 99%, and breakdown rates, as well as time expected to loss 50% of the initial mass ($T_{50}$), were very different too: 0.0003 to 0.017 (days$^{-1}$) and 41 to 2029 days, respectively (Table 2). We performed simple regressions between breakdown rates and environmental variables. Regressions were significant for temperature, conductivity, suspended solids, macroinvertebrate and diatom biological indexes, altitude, and land uses. Nevertheless, for most of these factors the relationship departed from lineal. Two of the most evident constraining relationships were found for altitude and phosphorus (Figure 2). In the case of altitude, breakdown rates were consistently low for high altitude sites, but their variance tended to increase towards lower reaches. In the case of phosphorus, breakdown rates increased with phosphorus concentration, reached a plateau around a concentration of 0.45 mg/L, and decreased again for higher values.

Table 2. Minimum and maximum of remaining mass (RM), decomposition rates (K) and time expected to loss 50% of the mass ($T_{50}$) at every basin.

<table>
<thead>
<tr>
<th>Basin</th>
<th>RM (%)</th>
<th>K (days$^{-1}$)</th>
<th>$T_{50}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebro</td>
<td>16.99-98.6</td>
<td>0.000342-0.01457</td>
<td>2028.5-47-6</td>
</tr>
<tr>
<td>Llobregat</td>
<td>24-98.38</td>
<td>0.000865-0.01647</td>
<td>801.23-42.07</td>
</tr>
<tr>
<td>Júcar</td>
<td>37.71-94</td>
<td>0.001049-0.00511</td>
<td>660.83-135.61</td>
</tr>
<tr>
<td>Guadalquivir</td>
<td>17-98.6</td>
<td>0.001045-0.01672</td>
<td>662.79-41.45</td>
</tr>
</tbody>
</table>

Figure 2. 90 % quantile regressions for altitude (a) and phosphorus (b) with breakdown rates.

It seems that the relationship found between breakdown rate and altitude derives from the effect of temperature. Nevertheless, because our temperature dataset is uneven, and includes sites with continuous records as well as sites with only one or two measurements during the study period, no clear relationship was found between breakdown rate and temperature. On the other hand, land-use changes (e.g., urbanization or agriculture) increase stressors and nutrients in river ecosystem (Allan, 2004) that affects their functioning (Meyer et al., 2005). Decomposition of organic matter can either be accelerated due to the increased nutrient availability (Imberger et al., 2010, Menéndez et al., 2011) or inhibited above certain nutrient levels (Lecerf et al., 2006), and our results seem to confirm this. An analysis or residuals after removing the effects of both altitude and phosphorus yielded no clear results, thus suggesting that multiple factors are affecting simultaneously breakdown of organic matter in Iberian rivers.

In conclusion, breakdown of organic matter shows large variability in functioning of Iberian river ecosystems. The maximum breakdown rates seem constrained by temperature and phosphorus, although in a non-linear way. Nevertheless, for any range of temperature and nutrient concentration, a large variability remains, thus reflecting the multiple stressors affecting ecosystem functioning.
Acknowledgements

This work has been supported by the Spanish Ministry of Science and Innovation through the project Consolider-Ingenio CSD2009-00065. The compilation of environmental data was possible thanks the Water Agencies of Ebro, Júcar, Guadalquivir and Catalonia. We are specially grateful to the people that assisted us in the field.

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Vulnerability of hydrological services to climatic extremes in a Mediterranean river basin

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Introduction

Landscapes differ in their capacity to provide ecosystem goods and services, which are the benefits humans obtain from nature (Daily 1997). Ecosystems have been considerably modified by human activities and stand to be further affected by climate change, especially in Mediterranean regions, where extreme climatic conditions are increasingly common (Hisdal et al. 2001). To help mitigating the impacts of global change, the vulnerability of hydrological ecosystem services to climatic extremes in a Mediterranean basin (Llobregat River basin, NE Spain) was assessed. InVEST (Tallis & Polasky 2011), a spatially-explicit modeling tool, was applied to evaluate the delivery of one provisioning (water) and two regulating services (water purification and erosion protection). Selected services are crucial in the Llobregat basin but also in many Mediterranean watersheds. The Llobregat basin constitutes an example of highly populated, exploited and consequently impacted area. The river is the main water supply for Barcelona and its metropolitan area (more than 3 million people). Climate in the basin is Mediterranean with a strong seasonal fluctuation in temperature and rainfall, mainly occurring in spring and autumn. There are three large reservoirs at the upper part of the basin: la Baells (115 hm\textsuperscript{3}), la Llosa del Cavall (80 hm\textsuperscript{3}), and Sant Ponç (24 hm\textsuperscript{3}).

Followed approach

With regard to the benefits and values of the selected services, the conceptual framework outlined by Haines-Young and Potschin (2010) was followed, describing the pathway from ecosystem structures and processes to human well-being (Figure 1). The assessed benefits of the water provisioning service were hydropower production and potential water available for drinking, which were valued according to the market price of energy and water for consumers. In the case of water purification, the assessed benefit was a higher water quality provided by ecosystems through the retention of nutrients, preventing levels in the water course to exceed the drinking water quality standards (WQS). Valuation was based on the avoided treatment cost of drinking water. For erosion protection, the assessed benefit was the avoided sedimentation in reservoirs, which is particularly problematic since it reduces reservoir capacity and affects the functioning of turbines. Valuation was based on the avoided cost of dredging sediment. Services were quantified under current average conditions, and subsequently compared to their provision under wet and dry periods (taking average conditions for the 5 rainiest and the 5 driest years of period 1970-2000).
Model calibration

Model fit for the three selected services was fairly good, especially for water provisioning and water purification. For erosion protection, the model underpredicted exported loads to La Baells reservoir and overpredicted exported loads at the outlet (Table 1).

Table 1. Observed values used for model calibration and predicted values for mean, dry and wet conditions. Data sources are Catari et al. (2009) (a), Lique et al. (2009) (b), and Ludwig et al. (2009) (c).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Observed</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Dry</td>
</tr>
<tr>
<td>Water provisioning (hm³ y⁻¹)</td>
<td>606</td>
<td>606</td>
</tr>
<tr>
<td>Exported TN (Mg y⁻¹)</td>
<td>6000</td>
<td>5998</td>
</tr>
<tr>
<td>Exported TP (Mg y⁻¹)</td>
<td>420</td>
<td>422</td>
</tr>
<tr>
<td>Exported sediment -1 (Gg y⁻¹)</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>Exported sediment -2 (Gg y⁻¹)</td>
<td>602 – 1418</td>
<td>1535</td>
</tr>
</tbody>
</table>

Analysis of the impact of climatic extremes in biophysical terms

The total annual water volume reaching the outlet of the watershed was 80% lower in dry conditions and 160% higher in wet conditions (Table 1). Higher values of water provisioning were found in areas of important water yield production and low demand, coinciding with high altitudes. These locations experienced the highest decrease (~75%) during dry periods. The center and south of the basin were the most resistant areas to drought and in some parts were estimated to exceed 800% increase in supply during wet years. Despite the differential change between uplands and lowlands, the former continued being the water source in both periods. Changes in nutrient export under wet and dry conditions were closely related to changes in water yield. Annual loads of total nitrogen (TN) and total phosphorus (TP) reaching the outlet were 10% lower in dry conditions and 6% higher in wet conditions (Table 1). In the case of climatic extremes in the Llobregat basin, dry years were characterized by less aggressive rains. Wet years, on the other hand, where characterized by more intense rains, increasing simultaneously erosion and retention. Total sediment delivery at the outlet was 53% reduced in dry conditions and 70% increased in wet conditions (Table 1). Erosion specially concentrated in areas close to the river channel, while retention did not follow the same pattern. Higher values surrounding the hydrological network were also obtained for nutrient export, meaning that sediment and nutrient would have fewer chances to be retained and probably end up in the river.
Analysis of the impact of climatic extremes in economic terms

A total value of 9.1 M€ y\(^{-1}\) was calculated for reservoir hydropower production in the Llobregat basin. Areas located at higher altitudes received larger economic values (>200€ ha\(^{-1}\) y\(^{-1}\)) (Figure 2a). Results reflected the double use of water generated within the territory upstream la Llosa del Cavall for energy production: first at La Llosa reservoir, and after at Sant Ponç reservoir. A zero economic value was assigned to those parts of the territory with no downstream reservoirs, even though some of them were delivering an important amount of water and small water power stations do occur. Potential water for drinking in the basin was valued in 979 M€ y\(^{-1}\). Higher monetary values were assigned to the northern part, and the same occurred to areas devoted to urban land use, where all the runoff was assumed to fulfill drinking purposes (Figure 2b). The water purification service was not given any value in the Llobregat basin in average climatic conditions. The established WQS was not exceeded by nutrient loads reaching the river neither for TN nor for TP, even in the case of a non-existent nutrient retention in the basin. This meant that reducing pollution was not a monetary issue there and that the avoided cost of removing nutrients thanks to retention in that case was zero. The erosion protection service was estimated to generate a total value of 9.7 M€ y\(^{-1}\). Analogous to the hydropower production, only the landscape upstream reservoirs received an economic value for erosion protection (Figure 2c).

The economic value of the water provisioning service for hydropower production decreased around 90% in dry conditions and slightly increased in wet conditions (Figure 3). For drinking water, the water provisioning service decreased nearly 100% in dry conditions and increase around 150% in wet conditions. Effects of climatic extremes were particularly relevant for the water purification service, receiving economic value exclusively in dry conditions (Figure 3), since only then was the WQS threshold for both TN and TP exceeded by the emission of nutrients. In dry conditions, this service was assessed to provide 146 M€ y\(^{-1}\). The economic value of the erosion protection service decreased around 60% in dry conditions, and increased around 70% in wet conditions (Figure 3).
Figure 3: Total Economic Value (TEV) of hydrological ecosystem services in the Llobregat basin under mean and extreme (dry and wet) climatic conditions.

Estimated hydrological ecosystem services in the Llobregat River basin generated a total economic value (TEV) of around 1000 M€ y⁻¹ in average conditions (Figure 3). Drinking water provisioning was the service providing the highest economic returns in absolute value, followed by erosion protection and water provisioning for hydropower production. The value of these services decreased to 154 M€ y⁻¹ (around 85%) in dry conditions, and increased to 2444 M€ y⁻¹ (around 145%) in wet conditions. Areas providing the highest TEV to the population were located at high altitudes, where the main water sources or ‘water towers’ were found.

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References


**Integrated Modelling and Monitoring of Pollutants in River Basins at European Scale**

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Joint Research Centre of the European Commission, Ispra, Italy

Contaminants spread across different environmental media through atmospheric deposition, leaching from soil to groundwater, accumulation in rivers and lakes, and discharge into the sea.

FATE is the ensemble name for the pool of activities related to the assessment of fate and impacts of pollutants in terrestrial and aquatic ecosystems carried out at the Institute for Environment and Sustainability (IES) of the Joint Research Centre (JRC). Understanding the fate and impact of pollutants on the terrestrial/aquatic interface is the core objective of FATE project. Main geographical focus of our assessment is continental Europe.

The adopted tiered approach links modelling and monitoring for a multiscale impact assessment in a risk-based framework. FATE addresses the fate and impacts of pollutants across a range of temporal and spatial scales depending on the policy question and making the best use of available data. The results are pollution risk and vulnerability maps, which are very useful to assess the impact of EU policies, raise public awareness and facilitate planning of management scenarios.

- At the scale of continental Europe the focus is on identifying “hot spots“, spatial trends and general pathways of pollutants.
- At the catchment/coastal zone scale the interest is more on the apportionment of mass inventories and aggregated in and out fluxes.
- At local scale the assessment of ecosystem exposure to potential pollutant risks is important for decision-makers in order to evaluate impacts of management strategies.

FATE supports the development and implementation of monitoring requirements in various key EU environmental policies (e.g. Water Framework Directive, Marine Strategy Framework Directive, Biowaste Directive, the Thematic Strategy for Soil) and international commitments (e.g. as stemming from the Stockholm Convention).

Environmental models are efficient tools to evaluate sources of pollution, propose sustainable alternative management practices to alleviate such pressure on water, soil and air, assess the impact on contaminant losses on ecosystems, and develop appropriate sampling strategies for monitoring the impact of implementation of best management practices. The implementation of the European environmental legislation raises new challenges for the research community and models have been identified as tools to fulfill the requirements stated in the policy framework. Several models have been developed within FATE covering a wide range of spatial and temporal scales and level of processes representation according to the scope of application.

**References**

Adaptation of the InVEST model to a Mediterranean catchment: global and spatial methods to investigate model sensitivity

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Objective

In this work, the Integrated Valuation of Ecosystem Services and Tradeoffs (InVEST) model will be adapted to a Mediterranean basin of the Iberian Peninsula. Then, global and spatial sensitivity analysis tools will be applied to the adapted version of the model to understand the model behaviour and its limitations.

The sensitivity analysis of the model, once InVEST has been applied to the Mediterranean basin, will be sequentially performed using two complementary sensitivity analyses methods. The application of sensitivity analysis to InVEST will allow identifying the most important variables of the model and will give trends regarding model’s application to Mediterranean river basins.

First, a global sensitivity analysis using the Morris method will assess the importance of each parameter, and then a spatial analysis using the One-At-a-Time (OAT) method will determine the distribution and spatial relevance of these parameters within the studied territory.

Model description

InVEST (Tallis & Polasky 2011) is a spatially explicit tool consisting of a suite of models that use land use and land cover patterns to estimate the levels and economic values of ecosystem services. The model runs in a gridded map at an annual average time step, and results can be reported in either biophysical or monetary terms, depending on the needs and the availability of information. In the present work, InVEST will be applied to assess three services: water provisioning, water purification and erosion protection.

The biophysical models in InVEST calculate the relative contribution of the different parts of the landscape to the provision of services. Thus, for the water provisioning service, the amount of water provisioned from each cell in the landscape (water yield) is calculated as the annual amount of rainfall that do not evapotranspire, determined by the cell vegetation characteristics (Canadell et al. 1996). Water demands for consumptive uses other than the evaluated are removed from the total yield before assessing the benefit.

The service water purification, which is the relative contribution of the different parts of the landscape to nutrient retention, is estimated in terms of total nitrogen and total phosphorus. Nutrient retention is calculated as the difference from the received (either from upstream cells or generated within the same cell) and exported nutrients. The amount of nutrients emitted from each cell is estimated from export coefficients, which correspond to annual averages of nutrient fluxes, whereas the retained amount of nutrients by each cell is a function of the retention coefficients associated to vegetation covers (Reckhow et al. 1980).

The service erosion protection, which is the relative contribution of the different parts of the landscape to sediment retention, is estimated considering the land use patterns that affect sedimentation in downstream reservoirs. The function sediment retention is calculated as the difference from received (from upstream
cells) and exported sediment. Eroded soil from each cell is estimated using the Universal Soil Loss Equation (USLE) (Wischmeier & Smith 1978), while the retained amount of sediment by each cell is a function of the retention coefficients associated to vegetation covers.

Our previous studies (Terrado et al. *In preparation*) showed the need of performing some changes in the model for it to be applicable to the Mediterranean basin. These changes regard the inclusion of in-stream processes, water extraction and return points, and the possibility of valuing water for uses other than the hydropower production. These improvements are key for the model application to the studied areas, since they strongly influence the dynamics of Mediterranean basins.

**Sensitivity Analysis Methods**

Once adapted (with the proposed changes) and applied to the Mediterranean basin of the Iberian Peninsula, the InVEST model will be analyzed by performing sequentially two different and complementary sensitivity analyses (S.A.).

a. **Global S.A.**

Among the various statistical techniques available for sensitivity analysis (Saltelli et al., 2005) we will use the method proposed by Morris (1991) and later modified by Campolongo et al. (2007), because it allows studying the sensitivity of a model against a large number of parameters at a relatively small computational cost. The Morris method defines the importance of each parameter that will determine later the degree of effort devoted to sampling. It has the advantage of covering the entire route of the variables involved in the model and also can analyze the impact of all of them together. Furthermore, the interpretation of results is relatively simple and provides a qualitative ranking of the most influential parameters on the simulated variables.

b. **Local S.A.**

After that, the spatial analysis OAT method will be applied to determine the spatial significance of these parameters within the studied area. The method consists in changing input factors One-At-a-Time to see the effect produced in the output (Chen et al., 2010). Through its application, the results may be easily compared and the effects of each input may be assessed. In addition, it is easy to implement and has a low computational cost.

The spatial sensitivity of several model inputs may be investigated, according to the results obtained in the previous phase. The OAT method will be applied to investigate the stability of the evaluation, based on the uncertainty of the inputs, and to visualise the spatial changes of evaluation results. The ranges are defined as a set of discrete percent changes, from the original input value, based on previous evaluations of the inputs uncertainty and/or expert knowledge. In this case, a single range may be applied to all the inputs or different ranges can be applied to each input, if required.

The applied methodology is useful not only to evaluate the stability of the model outputs for the current scenarios, but also to estimate its uncertainty in climate change scenarios predictions.

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Scarce Consolider-Ingenio 2010 Project

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Application of scaling equations to deal with the spatial aggregation effect on watershed hydrological modelling

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²Faculty of Forest Engineering, Universidad del Tolima, Ibagué, Colombia

Introduction

Spatial effects have been identified as a major issue in hydrological science since a few decades ago (Rodríguez-Iturbe and Gupta, 1983; Wood et al., 1986; Sivapalan and Kalma, 1995) and still constitutes an unresolved problem. Scale issues in distributed hydrological modelling are driven by the existence of particular dominant processes at different scales, the nonlinear behaviour of hydrological systems and the presence of spatio-temporal variability at different scales (Blöschl and Sivapalan, 1995; Wigmosta and Prasad, 2005; Tetzlaff et al., 2010). Understanding the role of these factors in watershed hydrology is fundamental to enhance the development of a multiscale theory. Therefore, it is highly relevant enrich the knowledge related to the scaling of hydrological processes, parameterization and linkages of parameters across scales.

The use of effective parameters is a common approach to take into account sub-grid effects and model misconceptualizations through model calibration based on series of historical data (Todini, 2011). However, effective parameters depends on storm size (Binley et al., 1989) and scale, and a good calibration is not a guarantee of a satisfactory model performance for a different scenario (Romanowicz and Beven, 2003; Francés et al., 2007). In this context, the transfer of information across scales is an interesting approach to diminish parameter’s dependence on scale and input. The importance of sub-grid variability has been addressed by some hydrology researchers (Sivapalan and Woods, 1995; Woolhiser et al., 1996; Merz and Bárdossy, 1998; Bronstert and Bárdossy, 1999; Liang and Xie, 2001), they have found that sub-grid variability is relevant for medium wetting conditions but the effect is marginal for saturated system states and for dry states in which the entire inflow volume is stored.

In this work we introduce the application of scaling equations to incorporate sub-grid variability of three hydrological parameters (static storage capacity, upper soil saturated hydraulic conductivity and deep soil saturated hydraulic conductivity) in watershed modelling using the TETIS distributed hydrological model. The developed scaling equations estimate non-stationary effective parameters at each time step as a function of input, system state and constant parameters related to the spatial heterogeneity of the hydrological parameters at sub-grid scale. The application of this modelling approach on a real watershed seeks to contrast the hydrological model performance using the scaling equations with its performance without such equations. Moreover, we analyse the decreasing of simulated discharge sensitivity to changes in spatial scale due to the use of scaling equations.

Case study

The study was carried out in Goodwin Creek experimental catchment, which is a sub-catchment of the Yazoo river basin in Mississipi. This catchment has been continuously monitored for more than thirty years and has a dense network of gauging stations to make an intensive number of spatio-temporal validations of model performance. Goodwin Creek drains an area of 21.6 km² with the outlet at latitude 34° 13’ 55’’ and longitude -89° 54’ 50’’. We used 16 rain-gaging stations to generate interpolated rain fields with a temporal resolution of 5 minutes, 6 stream-gaging stations and a digital elevation model with 30 m of spatial resolution (Figure 1).
Three spatial resolutions of the hydrological parameters were used to test the performance of the scaling equations for storm hydrograph prediction. R1 represents parameter maps with 900 m$^2$ of spatial resolution; R2 corresponds to a spatial resolution of 3.026 km$^2$, and R3 represents an average parameter value for the whole catchment (Table 1). Parameter estimation for R1 was conducted by Montoya (2008) through statistical adjustment among environmental variables and the hydrological parameters. Parameter maps with resolution R2 were computed by averaging R1 maps at a resolution of 1740 x 1740 m$^2$ and R3 parameter maps were calculated by averaging R1 maps for the whole catchment.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$H_u$, $k_s$ and $k_p$ maps with a resolution of 900 m$^2$, without scaling equations</td>
</tr>
<tr>
<td>R1+EE</td>
<td>$H_u$, $k_s$ and $k_p$ maps with a resolution of 900 m$^2$, with scaling equations</td>
</tr>
<tr>
<td>R2</td>
<td>$H_u$, $k_s$ and $k_p$ maps with a resolution of 3.026 km$^2$, without scaling equations</td>
</tr>
<tr>
<td>R2+EE</td>
<td>$H_u$, $k_s$ and $k_p$ maps with a resolution of 3.026 km$^2$, with scaling equations</td>
</tr>
<tr>
<td>R3</td>
<td>$H_u$, $k_s$ and $k_p$ aggregated maps for the whole catchment, without scaling equations</td>
</tr>
<tr>
<td>R3+EE</td>
<td>$H_u$, $k_s$ and $k_p$ aggregated maps for the whole catchment, with scaling equations</td>
</tr>
</tbody>
</table>

**Table 1. Spatial resolutions of hydrological parameters $H_u$, $k_s$ and $k_p$**

**Results**

We found good efficiency indices (Table 2) for the calibration event in the six model conditions (Table 1). R1, R1+EE, R2 y R2+EE have a similar distribution of mean catchment states, but R3 and R2+EE obtain a smaller simulated mean static storage. The calibrated corrector factors change through the different aggregation scales, even in cases involving the use of scaling equations. This is explained in the fact that parameter maps at the 30 m resolution have a degree of uncertainty related to the spatial heterogeneity estimation; the estimated heterogeneity is partially lost by aggregating them and the variability effect is optimized by the scaling equations’ parameters. In Goodwin Creek, the optimized parameters of the scaling equations correspond to coefficients of variation in the range of 1.5 to 2.5 for $H_u$, 3 to 4 for $k_s$ and 0.8 to 2 for $k_p$. This implies that scaling equations tend to represent high sub-grid heterogeneity in the studied hydrological parameters.

The spatial validation shows that the best performances are reached by R1+EE and R2+EE, the indices that display better performance are the time to pick error, RMSE and Nash-Sutcliffe index. Temporal validation does not show differences among R1, R1+EE, R2, R2+EE, R3 y R3+EE, this is attributed to a compensation of errors on channel propagation process. This observation agrees with results of Li et al.
(2011), in the sense that comparing simulations with different parameter resolutions at the outlet do not display differences among them. But, the differences are expected at sub-basins outlets.

According to the aforesaid, we found a better performance using the scaling equations in the spatio-temporal validation. The increase of performance is notable for the smallest sub-basins. Figure 2 shows that decreasing basin area the performance of R1+EE and R2+EE is better in contrast to the case of neglecting sub-grid variability via scaling equations (R1, R2, R3). The storm events ‘19/11/83’ and ‘27/08/82’ exhibit the largest differences. These storms has the smallest magnitude suggesting that sub-grid variability is more important for small storms, which is consistent with the find of Merz and Plate (1997).

Table 2. Efficiency indices in calibration for the six model conditions

<table>
<thead>
<tr>
<th>Index</th>
<th>R1</th>
<th>R1+EE</th>
<th>R2</th>
<th>R2+EE</th>
<th>R3</th>
<th>R3+EE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pick flow error (%)</td>
<td>2.22</td>
<td>-4.13</td>
<td>8.38</td>
<td>9.98</td>
<td>-2.87</td>
<td>-7.83</td>
</tr>
<tr>
<td>Time to pick error (%)</td>
<td>0.66</td>
<td>0.33</td>
<td>0.66</td>
<td>0.66</td>
<td>0.00</td>
<td>0.33</td>
</tr>
<tr>
<td>RMSE</td>
<td>2.68</td>
<td>3.40</td>
<td>3.71</td>
<td>3.66</td>
<td>2.87</td>
<td>6.42</td>
</tr>
<tr>
<td>Nash-Sutcliffe</td>
<td>0.98</td>
<td>0.98</td>
<td>0.97</td>
<td>0.97</td>
<td>0.98</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Figure 2. Nash-Sutcliffe efficiencies as a function of basin area for the six model conditions presented in Table 1
Conclusion
The implementation of scaling equations in TETIS and its application in Goodwin Creek catchment using three different levels of parameter aggregation has shown the importance of represent sub-grid variability for hydrological simulation. The use of scaling equations implies a better model performance in spatio-temporal validation, especially in the smallest sub-basins and for the smallest storms. Therefore, the effect of sub-grid variability is more important for small storm events than extreme storms of high return period. This paper illustrated the utility of non-stationary effective parameter concept to address the parameterization of sub-grid variability obtaining a better performance of R1+EE and R2+EE in comparison to the reference model (R1).

Acknowledgements
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Flushing flows in the lower Ebro. Monitoring and modelling
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Introduction

The lower Ebro experiences a series of geomorphic and ecological alterations caused by human induced impacts. Large areas in the basin have been subject to an increase in forest cover during the second half of the 20\textsuperscript{th} century; while at around 190 dams impound $\frac{2}{3}$ of the river’s annual runoff. As a consequence, water yield and, especially, flood and sediment transport regimes have been substantially altered (i.e. Batalla et al., 2004; Vericat and Batalla, 2006; Vericat et al., 2006; Tena et al., 2011), affecting not just channel morphology and sedimentology, but also river's ecosystem functioning. One of these effects is the accelerated growth of macrophytes, in river reaches downstream from dams. Since mid-1990s aquatic plants have colonised most of the riverchannel, this phenomena being described as the consequence of flow regulation, changes in nutrient supply, reduction in sediment load and river-bed stability. Within this context, flushing flows (i.e. controlled dam releases, hereafter FF) have been implemented (i.e. design, monitored, and modelled) in the lower Ebro River since 2003, with the objective of removing the excess of macrophytes and keeping sedimentary activity in the channel (Palau et al., 2004; Batalla et al., 2006, Batalla and Vericat, 2009).

Monitoring of Flushing Flows

Flushing flows are periodically used (i.e. twice a year) to entrain gravels, thus dislodging and removing macrophytes anchored in the bed. Here we present an integrated monitoring design to assess the effectiveness of flushing flows. Four categories are integrated in the design (Figure 1): a) macrophyte density, b) flow hydraulics, c) sediment transport, and d) bed mobility. Macrophyte densities were estimated in experimental sections before and after the FF by means of the backscatter of a sonar. A board-mounted ADCP was used to measure discharge and hydraulics in a monitoring section during the entire FF. Water samples were obtained in order to study suspended sediment transport dynamics. The ADCP was also used as an acoustic surrogate bedload monitoring technique aiming at study channel stability: bed velocity (bedload) and bed incision. Additionally, water slope was calculated using a reflectorless total station. This approach allows analyzing a) the effects of macrophytes on flow routing through a monitoring section, b) the competence and capacity of the FFs and c) the relation between bed mobility-incision and macrophyte removal. Owing to their specific design (i.e. based on physical criteria such as particle entrainment), FFs exhibit potential for riverbed scour and sediment mobilization higher than natural floods. Overall, suspended sediment concentration during FFs is more constant through time and doubles that of natural floods, although discharges are lower. Flashiness, measured as the rate of discharge increase per unit time, is an order of magnitude higher during FFs than during natural events. Consequently, FFs exhibit higher transport capacity than their natural counterparts FFs flows may remove up to 95% of macrophytes in river reaches close to the dam, but their effectiveness reduces with distance downstream. FF designs were performed with the objective of removing macrophytes with minimum geomorphic effects. Nevertheless, FFs may alter river morphology, most likely causing riverbed incision driven by the unbalanced condition between sediment supply and river's transport capacity lead by the impoundment. It is thus important to evaluate the potential geomorphic responses of the riverbed associated to a given FF design and, according to these, redesigning FFs regularly to maximize...
macrophyte removal but minimizing the adverse effects. Such potential geomorphic responses associated to a given design may be evaluated by means of hydraulic and sediment transport modelling.

Figure 1. Monitoring and modelling of Flushing Flows in the Lower Ebro
Modelling

In our case, the particular role of a monitored FF in causing adverse geomorphic effects has been examined by means of the hydrodynamic model CCHE2D®. Model performance has been evaluated in terms of hydraulics and sediment transport by comparing observed with modelled values. Statistical indices show that, overall, simulations are in agreement with field observations. The FF initially modelled (i.e. May 2008, in which peak discharges of 1350 m³s⁻¹ and 1150 m³s⁻¹ were released from the Ribarroja Dam) shows that the flushing flow design implemented in the lower Ebro, theoretically, did not cause severe geomorphic impact; mean net topographic change across the entire reach has been estimated at around -1.2 mm. The use of this tool, in combination with pre and post-flood field surveys, entails another step in the evaluation of the effectiveness of artificial flows in mobilizing the active layer of the channel. Likewise, the model has provided for the first time visualization on the spatial patterns of erosion and deposition, allowing the identification of critical zones where degradation or aggradation processes may cause severe impacts. Results must be, however, treated with caution because of the complexity of nature and inherent model limitations; and the approach and results should be routinely evaluated and adjusted as river-channel evolves.

Remarks

Despite several constraints, FFs have significant potential to entrain and transport sediment and careful management of these releases may, therefore, play an important role in enhancing physical habitat in the river. The Ebro case study shows that artificial releases are not incompatible with HEP production, and may result in a positive trade-off due to minimizing clogging of water intakes. It remains, however, important to reassess their effectiveness regularly and monitor adverse geomorphic effects such as riverbed incision. These data are important to re-evaluate critical thresholds for bed entrainment, improving the design of FFs and, consequently, increasing their effectiveness (macrophyte removal) and decreasing associated geomorphic impacts (incision) in a sediment supply limited fluvial system. Flushing flows are an important instrument of river management, but one which must be employed as part of a spectrum of approaches to enhance physical habitat conditions.

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Oral presentations


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Modeling nutrient loads and in-stream retention in basins under chronic human impact: lessons from the Llobregat River basin (NE Spain)

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Water quality in Mediterranean watersheds is known to have been shaped by anthropogenic activities throughout history. Over the past few decades, particularly, one of the most common global concerns regarding water pollution has been the excessive load of nutrients that reaches the streams. Mediterranean streams and rivers are usually subjected to additional pressures such as damming, water extraction and urbanization, which, in turn, worsen the effect of pollutants on the already vulnerable water cycle.

The relative importance of the nutrient sources at the basin scale is better expressed in terms of in-stream processes, compared to merely analyzing the direct nutrient inputs from measurements and observations made in the field (Smith and Alexander, 2000). Streams and rivers transport nutrients from terrestrial sources and serve as hot spots for nutrient transformation, storage and removal. To date, nutrient in-stream processes have been mainly studied at the stream level, however, their functioning should be evaluated from the perspective of river networks. In fact, considering that a reach is part of a stream or river which, in turn, pertains to a network of streams within a catchment, it becomes evident that conditions found at the reach level are affected by those found at larger spatial scales (Allan et al., 1997).

Modeling tools become useful in determining the sources and the processes by which pollutants are transported at the basin scale (Grizzetti et al., 2005).

A hybrid process-based and statistical model (SPARROW, SPAtially Referenced Regression On Watershed attributes) was applied to the Llobregat River basin, a highly impacted watershed in NE Spain, in order to estimate the annual nitrate and phosphate loads that reach the drainage network. This study emphasized the description of the in-stream processes that affect nutrient transport and retention in impaired rivers. Most modeling exercises undertaken at the network level, including previous SPARROW applications, have focused on the effects of hydrological variability on nutrient retention. Nonetheless, when modeling in-stream processes, it is also important to consider those factors that are germane to biological uptake, instead of exclusively relying on hydrology-related variables such as channel depth and discharge. Nutrient Spiraling metrics attempt to combine both the hydrological and biological factors that are involved in nutrient removal. Among these, the uptake velocity is able to describe non-hydrologic-related properties of nutrient removal as it is, in effect, a biological measure that is mathematically independent of surface water hydrological characteristics (Wollheim et al., 2006).

The analysis of published data of nutrient spiraling metrics showed that the efficiency of process rates relative to available nutrient concentration eventually declines, following the behavior of the Efficiency Loss Model (EL). Within the EL concept, log-transformed uptake rates increase with log-transformed nutrient concentration, where the slope of the relationship is less than one (O’Brien et al., 2007). Therefore, the SPARROW in-stream decay specifications were modified to include a partial saturation effect in uptake efficiency (expressed as a power law) and better capture the processes related to biological nutrient removal. Using the aforementioned statistical-mechanistic modeling tool, we deliberately defined the in-stream processes in such a way that a wide range of responses were a priori possible, including first-order kinetics and EL dynamics. This heuristic exercise served to understand how nutrient retention develops across a watershed including impaired reaches up to the fourth order, as a first step in gathering knowledge on the effects of land use and climate variability on Mediterranean rivers.

Model parameters were determined by calibration against calculated loads, which were based on
measured nutrient concentrations in 23 water quality sites for each year between 2000 and 2006. Model calibration results provided a reasonable fit between measured and predicted loads of nitrates and phosphates. Slightly better results in model fit were obtained for nitrates, which is not surprising considering previous modelling efforts at the basin scale that have consistently shown inferior performance for phosphate. In both models, the stream decay coefficients were statistically significant, indicating the potential role of in-stream processing in limiting the nutrient export to downstream water bodies. However, overall, our results suggested that nutrient uptake capacity in the Llobregat River basin did not follow the EL dynamics previously observed in the analysis of bibliographical data, probably due to severe impacts of chronic pollution on the biological communities.

Nitrates ($R^2=0.86$)

Phosphates ($R^2=0.80$)

Figure 1: Predicted relative to observed nutrient flux (kg/yr) in 161 sites in the Llobregat River basin (natural logarithm applied to predicted and observed values)

Figure 2: Uptake velocity ($v_f$) response curves obtained from SPARROW parameter values in this study compared with literature values (black dots; linear regression represented by black dotted line)

Nitrate removal capacity slightly increased with the transition from a year characterized by wetter conditions (higher values for mean runoff and discharge) to a drier one. Contrasting with the case of nitrates, there was no major evidence of differences in phosphate removal capacity between humid and dry years. Also, compared to nitrates, overall phosphate in-stream retention appeared to be larger. Regarding the main nutrient sources in the basin, diffuse sources accounted for the most part of nitrates
exported from the sub-watersheds considered in the model. In the case of phosphates, loads associated to urban and industrial spills (point sources) were predominant over the diffuse pollution arriving from cultivated and natural land, and showed contrasted spatial heterogeneity.

Figure 3: Mean source contribution (%) to in-stream nutrient flux (nitrates, left; phosphates, right) in the Llobregat River basin under wet and dry hydrological conditions

Figure 4: Share of incremental diffuse and point sources contribution to annual in-stream PO₄ flux under dry conditions in sub-watersheds of the Llobregat River basin
Acknowledgements
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References


Applying monitoring and modelling techniques to study sediment transport dynamics in a mesoscale catchment

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Introduction

Research on sediment transport in catchments draining highly erodible materials (e.g., soft marls forming badlands) has become of interest because of the possibility of setting maximum thresholds and magnitudes of sediment transport and for allowing model calibration and validation in highly active geomorphic environments (e.g., López-Tarazón et al., 2009). Badlands are considered to be characteristic of arid regions, but they also occur in wetter climates (such as in the Mediterranean) that have high intensity storm events. Vegetation growth is no longer limited by water availability or slope but by the high erosion rates caused by freeze–thaw cycles on exposed north-facing slopes. Consequently, very high sediment loads can be delivered from the badlands.

This study aims to study sediment dynamics and calculate the sediment budget of the Isábena River, a 445-km² catchment which drains a very active area of badlands, for the period 2007-2009. For this purpose, we have applied a methodology to monitor suspended sediment transport and a modelling approach that allows the interpolation of intermittent measurements of suspended sediment concentrations. To construct the budget, we have estimated the sediment introduced into the system, the suspended sediment yield of all the subbasins, as well as that at the basin outlet, together with the amount of sediment that is stored in the main channel.

Study area and methodology

The Isábena is a mesoscale mountainous catchment located in NE Iberian Peninsula (Fig. 1A) that drains into the Ésera River. Both rivers are the main tributaries of the Cinca, in turn the second largest tributary of the Ebro (Fig. 1B). The Isábena basin is characterised by heterogeneous relief, vegetation, and soil characteristics. The climate is typical of Mediterranean mountainous areas, with mean annual precipitation of 767 mm. The central part of the catchment is mainly dominated by Eocene continental sediments, leading to the formation of badlands that have proven to be the major source of sediment within the catchment.

The study of the sediment dynamics and the determination of the sediment budget of the Isábena basin have been based in the quantification of the sediment that is introduced into the fluvial system (i.e., gross erosion from badland areas, input from tributaries), the sediment that moves out of the basin and the temporary storage of sediments in the main channel. Sediment input (i.e., gross erosion) was calculated from the sediment contribution of a typical badland formation by means of erosion pins, with their exposed height measured to estimate erosion rates. Erosion rates were estimated by extrapolating length readings and from topographical surveys of the targeted badland. On the other hand, the amount of fine sediment stored in the channel bed of the Isábena was determined using the method developed by Lambert and Walling (1988). The methodology consists in a metal cylinder that is carefully lowered into the water until it rests on the channel bed and then slowly rotated to create a seal with the gravels. Next, the channel bed is manually disturbed, in order to re-suspend the fine sediment and, thus, estimate the sediment storage. For more information about this technique and the calculation of the amount of sediment released from the bed and the later extrapolation to the whole catchment see López-Tarazón et al. (2011).
Suspended sediment transport has been monitored in the Isábena from 2005 to 2009 by means of direct and indirect techniques. Firstly, the Capella gauging station (i.e., EA047) was monitored in order to estimate the sediment load at the basin outlet (Fig. 1C). Continuous register of sediment transport has been obtained by a high range backscattering turbidimeter (measuring range up to 300 g l$^{-1}$, indirect technique) which has been calibrated by means of suspended sediment concentrations (SSC) obtained from water samples coming from manual and automatic samplings (direct technique; López-Tarazón et al., 2009; 2010). Secondly, suspended sediment was monitored at the subbasins by water stage samplers and manual samples collected during individual flood events and routinely during other periods. All samples were vacuum filtered or decanted when concentrations were above 2 g l$^{-1}$, oven-dried, and weighed to determine the suspended sediment concentration. Discharge was also monitored; at EA047 the Ebro Water Authorities provided a continuous register, while at the subcatchments capacitive water stage sensors/loggers were installed at suitable cross sections (Fig. 1C).

To estimate sediment yields a modelling approach had to be applied; the use of traditional flow duration curve methods was not possible due to the poor statistical relations between discharge and sediment concentration at all monitoring sections. Continuous sedigraphs were derived for all the subcatchments using random forest (RF) and quantile regression forest (QRF) models. QRF is a nonparametric multivariate regression technique based on RF regression tree ensembles. Both can efficiently handle non-linearities, do not depend on assumptions on the distribution of the data and are capable of capturing non-additive behaviour, which makes them a powerful tool for suspended sediment concentration modelling (Francke et al., 2008a,b). Despite QRF models allowing for the assessment of model uncertainty, RF models were used for sedigraph reconstruction because of their better performance. By applying the models, SSC data for each site were derived. Finally, suspended sediment loads were obtained by multiplying the SSC with the associated discharge value.

**Results and discussion**

A conservative approach is taken to estimate sediment mobilisation from badlands. Mean erosion value of the pin series is taken at 2.1 cm y$^{-1}$. From this figure, sediment contribution from all the badlands in the catchment (i.e., 4.75 km$^2$) reached the order of 260,000 t y$^{-1}$ during the 2-year study period. This value
would roughly mean an average erosion of 580 t km\(^{-2}\) y\(^{-1}\) for the whole catchment, enhancing the role of the badlands on the Isábena basin’s sediment load. In-channel storage’s magnitude and seasonal variability were assessed by López-Tarazón et al. (2011). They reported that, for a 1-year study period (2007-2008), cumulative annual storage in the channel bed of the lower Isábena was 679 t. Average values, extrapolated to the whole channel length, showed that the total storage would equate almost 10,000 t. In-channel storage was found variable in space and time and two interesting trends were pointed out: i) a clear tendency for the stored sediment to increase in the downstream direction, probably due to the increase in both the width of the channel and the likelihood of sediment deposition; and ii) a continuous year-round sediment accumulation mostly during low flow periods (which lack sufficient competence to entrain fines).

Modelled values represent a first approximation of the sediment transport patterns in the Isábena catchment. The sediment load in Villacarli was systematically much higher than in the other subcatchments, constituting the most important fraction of the load exported in Capella. Together with Villacarli, Lascauarre recorded the highest suspended sediment load (SSL). The SSL for the year 2007-2008 was 138,400 t in Villacarli and 53,200 t in Lascauarre; while Cabecera, Ceguera, and Carrasquero accounted for 25,000, 8815 and 444 t, respectively. Lascauarre lead the sediment yield for the year 2008-2009, with a total of 97,600 t; 65,500 t were estimated in Villacarli. Cabecera registered 47,950 t, and Ceguera and Carrasquero accounted for 29,400 and 3150 t, respectively. Figure 2 presents the spatial distribution of water and sediment contribution of each subcatchment to the whole basin.

Specific sediment yields (SSY) ranged over two orders of magnitude between subcatchments, varying from 72 t km\(^{-2}\) in Carrasquero, 250 t km\(^{-2}\) in Cabecera, 682 t km\(^{-2}\) in Ceguera, 1675 t km\(^{-2}\) in Lascauarre, and 2427 t km\(^{-2}\) in Villacarli. The notable difference in SSY between subcatchments underlines the predominant role of badlands as the primary sediment source, as well as the different hydrological response. Values from Villacarli and Lascauarre are in the range of those obtained in similar geomorphic landscapes (i.e., those with highly erodible areas), such as Vallcebre in the western Pyrenees (2800 t km\(^{-2}\) y\(^{-1}\); Regués et al., 2000), despite being more than 40 times larger in area. The SSY obtained for the entire
Isábena catchment was 527 t km$^{-2}$. This value plots above the 350 t km$^{-2}$ y$^{-1}$ for the entire Ésera catchment (1600 km$^2$) reported by Sanz-Montero et al. (1996) and ranks high in relation to data for 44 Mediterranean catchments given by de Vente et al. (2006).

Previous data were used to estimate the sediment budget of the Isábena basin for the period 2007-2009. This way, the 2-year sediment budget of the Isábena establishes a quantitative relation between sediment input and output and the temporary storage of sediment in the main channel. Sediment input, calculated as the contribution from a typical badland formation, would reach an average of 260,000 t y$^{-1}$; the storage in the active bed of the main channel, taken from López-Tarazón et al. (2011), can reach up to 5% of the total load transported at the catchment outlet, i.e., 12,000 t y$^{-1}$; finally, sediment output was estimated as the mean suspended sediment yield measured at the Capella gauging station (e.g., 235,000 t y$^{-1}$) for the study period. In absolute terms a balance is present between the sediment input (production from badlands) and the sediment output (yield at the basin outlet). Clearly, at the temporal scale of the study, the sediment output is the most important component of the budget. Finally, a long-term denudation rate can be estimated to be 0.2 m×10$^{-3}$ y$^{-1}$. Denudation rate in the badlands would attain 2 m×10$^{-3}$ y$^{-1}$. Basin denudation rate plots, for instance, remarkably higher in relation to studies by Dietrich and Dunne (1978) in a basin in Oregon (0.03 m×10$^{-3}$ y$^{-1}$) and by Batalla et al. (1995) in the Mediterranean basin of Arbúcies (0.02 m×10$^{-3}$ y$^{-1}$), both under low-intensity geomorphic conditions; in contrast, the current study suggests that the Isábena is controlled by high sediment production from the badlands and high connectivity between sources and the fluvial network, thus showing intense geomorphic and sediment transfer activity.

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References


Stochastic modeling of a fuzzy index to determine the quality of water in the Cauca River

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Introduction

Water pollution restricts its use for human consumption and for the development of a region's economy. This makes it necessary the use of tools to quantify and evaluate the quality of water bodies to give evidence to decision makers on the future of these bodies. To indicate the degree of contamination of water bodies, indexes can be used. Current methodologies for calculating quality indices do not take into account the variation of the parameters used in the assessment of water status, which have essentially stochastic behavior. Therefore, a thorough analysis should be performed using elements to quantify the uncertainty of variables using probability distributions instead of point values. This will ensure that quality levels are able to control the subjectivity and uncertainty present in these complex environmental problems. The application of fuzzy sets to the assessment of water quality has recently attracted the attention of several researchers (Giusti et al 2011, Lermontov et al 2009), including analysis of water quality by artificial intelligence coupled models (Ocampo Duke et al 2007). In order to design a water quality index able to cope with the problems described above, this study shows the design of an index based on a fuzzy inference system, as proposed recently by Ocampo-Duque et al (2006).

The aim of this work was to integrate a possibilistic model (Fuzzy) with a probabilistic model (Monte Carlo) to properly handle the uncertainty and variability in the calculation of a water quality index. The methodology was applied to the Cauca River, one of the most important rivers in Colombia.

Methodology

Case study

The Cauca River is one of the most important rivers in Colombia. The river spring is located in the department of Cauca at an altitude of 3215 m in the Colombian Massif, and flows into the Magdalena River. With a length of 1350 km is the second most important river in the country. For the development of this work we studied the stretch between the towns of Suarez - Cauca and La Virginia - Risaralda. During this stretch the river supplies water for human consumption and for agriculture and manufacturing. In Valle del Cauca the body responsible for managing the environment and renewable natural resources is the Regional Autonomous Corporation of the Valle del Cauca (CVC). This institution has ordered 19 fixed monitoring stations in the Cauca River Basin, which hosts the measurement of physical, chemical, microbiological and hydro parameters.

To develop the stochastic fuzzy quality index we analyzed data provided by the CVC during three years 2002, 2006 and 2009. Data from the 19 monitoring stations was used. Complete records from each one of them were taken for four periods each year. The data were grouped into three different parts along the Cauca River: Part I (Antes Suarez, Antes Rio Ovejas, Antes Rio Timba, Paso de la Balsa, Paso de la Bolsa, Puente Hormiguero), Part II (Antes Canal Navarro, Juanchito, Paso del Comercio, Puerto Isaacs, Paso de la Torre, Vijes, Yotoco, Mediacanoa) and Part III (Río Frío, Puente Guayabal, La Victoria, Anacaro, Puente La Virginia). Figure 1 shows the geographic location of the monitoring stations.
**Fuzzy Inference Systems**

Fuzzy inference systems (FIS) use heuristic rules to establish qualitative and quantitative relationships between variables. This method is based on verbal rules to manage the information. To do that, natural language is used, which is very convenient in the management and environmental modeling. This type of logic considers some input and output rules that can be parameterized to represent the expert knowledge. Figure 2 shows an input-output scheme for the problem of classification of water quality.

The FIS is based on three concepts that govern the essence of the theory of fuzzy logic, membership functions, logic operators and inference rules. A membership function is a curve that defines the membership of a variable to a fuzzy set, which acts as a qualifier. The fuzzy logic operators are mainly used intersection (AND) and union (OR). Finally, an inference rule has the form: "If x is A AND B THEN z is and is C" where A, B, and C are linguistic qualifiers defined by fuzzy sets in the universes of discourse X, Y, and Z, respectively. More details of the operation of the fuzzy inference systems can be found in (Ocampo-Duque et al 2006).
Monte Carlo Method and Non-Parametric Distributions
The Monte Carlo procedure used to simulate the stochastic behaviour. It was necessary to identify the probability distributions of the data sets of the input variables. Tests for goodness of fit were made, but some data sets did not fit to a parametric probability distributions. In those cases, non-parametric estimators were used. In the present study the non-parametric estimators used had kernel function with normal distribution.

Results and discussion
The water quality of the Cauca River was evaluated with the stochastic fuzzy quality index (FIS-Stochastic Index). The result was a histogram for each part of the river and for each year. Figure 3 shows box plots of water quality for the years 2002, 2006 and 2009. Figure 3 also shows the comparison of data of water quality for the three parts of the river. In the present study, the results of fuzzy-probabilistic method proposed were also compared with the results obtained with the WQI index developed by National Sanitation Foundation NSF. The WQI index received the same stochastic simulation method (WQI-Stochastic), as shown in Figure 4. Although the compared indexes had different methodologies, both indicated a deterioration of water quality downstream the industrial area and waste water discharges of Santiago de Cali. It also can be seen that the FIS-Stochastic index is more rigorous assessing the quality of water and also has a lower variability when it is compared with WQI-Stochastic.

![Figure 3: Box plots of FIS-Stochastic quality index in the different parts of the Cauca River](image)

The degree of membership of each membership function (MF) of the FIS was determined for the quartiles of each segment, as shown in Table 3. Quartile values were present mainly in the membership functions that represent the qualities "Bad" and "Regular". In Part I, for the three years of study, water quality belonged to the "bad" quality with membership value between 0.302 and 0.326. In the same table it can be observed that the quality of water increases its membership to "bad" quality for parts II and III and decreases its membership to "regular" quality downstream, in parts II and III.
Table 3. Results of the membership values in water quality for the three river parts during the three evaluated years

<table>
<thead>
<tr>
<th>Year</th>
<th>First Cuartil</th>
<th>Median</th>
<th>Third Cuartil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MF Bad</td>
<td>MF Regular</td>
<td>MF Good</td>
</tr>
<tr>
<td>2002</td>
<td>Part I</td>
<td>0.344</td>
<td>0.741</td>
</tr>
<tr>
<td></td>
<td>Part II</td>
<td>0.406</td>
<td>0.678</td>
</tr>
<tr>
<td></td>
<td>Part III</td>
<td>0.444</td>
<td>0.642</td>
</tr>
<tr>
<td>2006</td>
<td>Part I</td>
<td>0.336</td>
<td>0.750</td>
</tr>
<tr>
<td></td>
<td>Part II</td>
<td>0.431</td>
<td>0.654</td>
</tr>
<tr>
<td></td>
<td>Part III</td>
<td>0.449</td>
<td>0.628</td>
</tr>
<tr>
<td>2009</td>
<td>Part I</td>
<td>0.348</td>
<td>0.737</td>
</tr>
<tr>
<td></td>
<td>Part II</td>
<td>0.364</td>
<td>0.722</td>
</tr>
<tr>
<td></td>
<td>Part III</td>
<td>0.415</td>
<td>0.667</td>
</tr>
</tbody>
</table>

The deterioration of water quality downstream showed the same behavior in the three years analyzed. This is Part I> Part II> Part III. As expected, membership in the “good” set was minimal in all cases. The values agree qualitatively in the evaluation that was carried out with the WQI model. However, the fuzzy model was more robust because it deals with uncertainty and considers as variables the ranges in water quality, which is closer to the logical reasoning.

Acknowledgements

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References


An integrated modelling system for long term planning of water resources management and global change adaptation

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Introduction

In recent years, water resources management has been facing new challenges due to increasing changes and their associated uncertainties, such as changes in climate, water demand or land use. Around the world, sharing water resources among multiple users is becoming more complex especially in regions under water stress. In this context the Water Change project (Life+ funding) developed a methodology and a tool which can provide support to decision makers in assessing potential future impact of global change on water resources and provide guidance as to the effectiveness of the possible strategies of adaptation. In the context of this project, global change is defined as all the anthropogenic changes affecting directly or indirectly the quantity and quality of water, influencing the sustainable management of water resources.

Methodology

The general methodology proposed in this study to assess potential impacts of global change on water resources and evaluate adaptation strategies is based on the DPSIR framework: Drivers of change generate Pressure on the environment, modifying its State, therefore causing some Impacts that could finally stimulate a Response from the society. The different steps involved are identified on figure 1.

![Figure 1: DPSIR framework in the Water Change project](image)

Firstly the factors of global change are identified (climate change, land use practices and water demand variation). The possible evolution of the factors of global change lead to a range of future scenarios and the impacts on water quantity and water quality are assessed through the Decision Support System developed in this study (Water Change Modelling System - WCMS). Finally, adaptation measures are evaluated through the tool and a cost-benefit analysis is undergone to provide an overview of their effectiveness in terms of economic, social and environmental impact.

Modelling tool

When selecting the modelling approach, the following aspects have been considered for the WCMS: 1)
Decision Support System (DSS) for long-term planning of water resources, which helps in the decision making process of water management, 2) Integrated tool coupling various models of the water cycle, such as hydrological, water management, and water quality models to simulate transversal processes affecting water availability and water use, 3) Generic tool that can be customized by the users for each application. The components of the modelling system are displayed on figure 2:

Figure 2: Components of the Water Change Modelling System

Case study results

The methodology and tool developed in the project were applied to the Llobregat River Basin, Catalonia, Spain. This 5000 km² basin has a complex drainage system and supplies a large part of the drinking water to the metropolitan area of Barcelona. According to the IPCC, climate change in the Mediterranean basin is likely to lead to an increase in temperature and a decrease in precipitation (Nakicenovic 2000) which will diminish the water availability and enhance the seasonal variation. The water demand on the other hand is likely to increase, influenced by demographical trends, climate change and behavioural changes (ACA 2009). Thirdly, land use in the Llobregat Basin will be mostly characterised by an increase in forest area in the headwater zone which will decrease runoff (Gallart & Llorens 2003). The different scenarios of global change established for the Llobregat River Basin correspond to three time horizons: 2027, 2050 and 2100. A total of 60 scenarios were selected in order to represent the entire range of changes predicted. Scenarios were built based on hypothesis of change or derived from climate models by downscaling to the basin scale. The ranges of change are summarised in table 1, where data from different sources have been compiled (Gallart & Llorens 2003, IDESCAT 2011, IPCC 2000, ACA 2009):

<table>
<thead>
<tr>
<th>Factors</th>
<th>Water demand</th>
<th>Water availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Climate change</td>
<td>Demography</td>
<td>Behaviour</td>
</tr>
<tr>
<td>2027</td>
<td>From 0 to +1%</td>
<td>From +6% to +24%</td>
</tr>
<tr>
<td>2050</td>
<td>From 0 to +5%</td>
<td>From +7% to +42%</td>
</tr>
<tr>
<td>2100</td>
<td>From 5 to +12%</td>
<td>From +10% to +45%</td>
</tr>
</tbody>
</table>
The scenarios based on hypothesis were obtained by grouping together the factors of change and modifying the current water availability and water demand time series while the 30 scenarios based on climate models and downscaling methods predict the temperature and precipitation at the basin scale for the different time horizons.

Indicators are defined in order to compare the scenarios of global change in terms of impact. Among these indicators, maximum 1 year, 5 year and 10 year deficit have been calculated and the reliability and resilience of the system have been compared. Reliability is defined as follows (in%):

\[
\text{Monthly \ reliability} = 1 - \frac{\text{Number of monthly fails}}{\text{Total number of months in simulation}} \times 100
\]

\[
\text{Annual \ reliability} = 1 - \frac{\text{Number of annual fails}}{\text{Total number of years in simulation}} \times 100
\]

\[
\text{Volumetric \ reliability} = \frac{\text{Volume supplied}}{\text{Volume demanded}} \times 100
\]

The monthly and annual fail criteria were based on the IPH levels (Instrucción de Planificación Hidrológica) and a fail is obtained if the deficit for the period is higher than a given percentage of the demand over that period (5% for the monthly fail and 2% for the yearly fail).

Resilience is defined as the system’s capacity recovery. It indicates the probability that an unsatisfactory state of the system (fail situation as defined previously) will be followed by a satisfactory state. Some of the results are displayed on figure 3:

The base scenario (WD0WA0) is compared to 5 other scenarios: WD1WA1.1: low change scenario with 5% overall decrease in water availability, low seasonal variability and 10% increase in domestic water demand. WD2WA2.1 and WD2WA2.2 are scenarios of medium change with 20% increase in domestic water demand, 10% decrease in water availability and low and high seasonal variability respectively. WD3WA3.2 represents 40% increase in demand, 15% decrease in availability and high seasonal variation while WD4WA4.2 is the worst case scenario: 50% increase in demand and 20% decrease in water availability.

The most sensitive parameter between the base scenario (WD0WA0) and the worst case scenario (WD4WA4.2) is the annual reliability which drops from 89% to 18%, as opposed to the other two reliability parameters which decrease less abruptly from 95% to 45% for the monthly reliability and from 97% to 75% for the volumetric criteria. On the contrary the resilience of the system does not vary much with the scenarios and it changes by 6% (from 18% to 12% for both the annual and the monthly resilience). The aim of adaptation strategies is to ensure these criteria will remain at acceptable levels under future conditions. Different adaptation measures have been included in the model: construction of
desalination plant in different parts of the basin (DESAL_P and U), intensive use of ground water resources (GNDW_EXTR), link to another basin’s drainage system (TER_APO) and waste water reuse (WWTP_REUSE). Some of the simulation results are presented on figure 4 for three scenarios, where the indicators are similar to those of figure 3:

Results of the simulations show that the adaptation measures have a strong impact on monthly and annual reliability. For the worst case scenario the annual reliability improves from 18% up to 54% with the implementation of waste water reuse for example. The next step of the study relies on the grouping of adaptation measures in order to propose robust solutions to avoid deficit and optimise the costs. A cost benefit analysis is undergone to assess the costs of implementing sets of adaptation measures and the benefits obtained from the different possible combinations, compared to the costs of no intervention (figure 5).

Cost-benefit and cost-effectiveness analysis are two related (but different) types of analysis that are widely used to evaluate the desirability of different courses of action. Here, cost-effectiveness analysis is used to find out an optimal combination of interventions aimed at reducing the gap between supply and demand that is expected to occur in the future. Then a cost-benefit analysis is done to determine whether it is worth taking action and what is the amount of intervention that is the most desirable, comparing the costs and benefits of both intervening and not intervening (see Rietveld (2011) for a general approach to cost benefit analysis of climate change policies).
Conclusion

This study brings to the fore the potential impacts of global change on water resources and underlines the need to take this aspect in consideration for future water management strategies. Even though the uncertainty intrinsic to global change is a limit to the study, the tool aims to propose robust solutions for future water resources management. The development of this tool aims to ease decision making processes and decrease the risk of intense water stress more and more regions are facing. In this context, the tool and methodology developed can be used by River Basin Agencies and Water Utilities to make plans according to the framework of European Directives in terms of water quantity and water quality.

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The use of the hydrological modelling as technical support for the river basin authority: the case of the Júcar river basin authority

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The Júcar River Basin Authority (JRBA) is an organism with territory in four different Spanish autonomous regions and depends on the Ministry of Environment, Rural and Marine Affairs. It is main objective is the consecution of an integrated water resources management and planning, from an unitary point of view, at the river basin and river basin district level. Therefore the JRBA counts in its governmental, management and planning bodies with representatives of the regional governments, water users and stakeholders, being a meeting point for different perspectives and points of view.

Its main functions are: a) elaboration, follow-up and revision of the River Basin Management Plan (RBMP), b) administration and control of the public hydraulic domain and c) projects, construction and exploitation of hydraulic works. For this purpose it counts with three departments that depend directly on the Presidency, called respectively: Hydrological Planning Office, Water Commissariat and Technical Directorate.

The development of its functions requires an adequate characterisation of the corresponding hydrological systems and water resources, not only regarding quantitative and qualitative aspects but also regarding surface- and groundwater characteristics. This characterisation frequently uses numerical models with different features and objectives, but always from the practical point of view. In this sense, the experiences in using these models and the real availability of data is more important than the complexity of their formulation, with independence of the important collaborations carried out with universities and research centres, existing in the JRBA a large tradition of joint works with the Polytechnic University of Valencia (UPV) and the Centre for Hydrographical Studies (CEDEX).

The typology of the more frequently used numeric models is highly varied, but can be classified in function of the analysed process: a) flood hydrology and hydraulics, b) hydrological cycle at river district level, c) quality of surface water bodies at the district level, d) habitat in river stretches, e) water management systems at the river district level and f) various processes of detail in determined hydrological elements: river reach, aquifer, wetlands…

**Flood Hydrology and hydraulics.** The hydrologic modelling of floods for the design of infrastructures and the modelling of the development of floods in real time is usually tackled with event models but recently more sophisticated formulations are being introduced. With regard to the hydraulic modelling, the traditional steady and one-dimensional approach is varying progressively towards the use of transitory and bi-dimensional models due to their simplicity in the automatic generation of the riverbed geometry from LIDAR cartography and GIS support.

This type of models is mainly used in: a) flood management in real time in the Automatic Hydrologic Information System (AHIS), b) design of action plans and infrastructures among those are outstanding the Global Plan against flooding in the Ribera del Júcar and the Defence Plan in the Safor, and more recently in the area of Albacete and the regions of the Marinas, c) development of operation rules for dams in accordance with the Technical Regulation on Safety of Dams and Reservoirs (TRSDR), d) preparation of Emergency Plans for dams in accordance with the Basic Guideline of Civil Protection Planning for Flood Risk and e) flood hazard and flood risk maps, in compliance with Directive 2007/60/EC on the assessment and management of flood risk, including those additional cartographic elements defined in the National Flood Zone Mapping System (NFZMS).

**Hydrological cycle at river district level.** The characterisation of available water resources at the river district level is done with a monthly hydrological simulation of the rainfall-runoff process using the...
monthly quasi-distributed rainfall-runoff model in network segments integrated with water quality (PATRICAL). This model permits the simulation, both of the natural system when altered, and not only the surface components of the hydrological cycle, but also the different variables of the groundwater component: rain infiltration, lateral transfers between groundwater bodies, relation between rivers or the wetland and their connected groundwater bodies, and underground discharges to the sea. Moreover, this model permits the simulation of the development of the agricultural fertiliser surplus expressed as nitrate concentration, both in surface and groundwater resources.

This tool is being used in the preparation of the Hydrological River Basin Management Plan (RBMP) (in accordance to the Water Framework Directive (WFD) and in particular to: a) obtain monthly series of surface discharges in those stretches without flow control station, b) estimate the available and the renewable groundwater resources, after considering the environmental restrictions in groundwater bodies, c) analyse climate change effects for different scenarios with variations in rainfall and temperature and d) study the effects of the reduction measures for agricultural fertiliser doses on the nitrates concentration and estimation of the time horizon to reach the value that allows to ensure the good chemical status of groundwater bodies.

**Quality of surface water bodies at the district level.** An important part of the Programme of Measures to be included in the RBMP refers to the improvement the discharge quality in order to reach the good ecological status in surface water bodies. The design of this programme requires the effectiveness analysis of such measures and, given the complexity of these processes and the limited information available, it was decided to simulate only those physical-chemical parameters considered essential.

A complete water quality model, named GESCAL, developed by UPV and integrated in a more complex management interface has been initially used, but a more simplified model is the final selection for this purpose. The analysis tool used is the GeoImPress model, developed in the JRBA and currently used by many Spanish river basin organisations. In the case of the JRBA, the determining parameters have proved to be BOD₅ and total phosphorus (P), allowing this model, using GIS tools, a simulation of the accumulation, decay and dilution of the two mentioned parameters and the effectiveness analysis of the water treatment measures on the water quality in the water bodies of the river district.

**Habitat in river reaches.** The estimation of environmental requirements in rivers, transitional waters, lakes and wetlands is included in the contents of the RBMP with the aim of their contribution to achieve the good ecological status of water bodies. In the case of the JRBA it is important to estimate the adequate minimum flow regime in river reaches and the adopted procedure has been the combined use of hydrological and biological methods. Among the latter an important use of the RHYHABSIM model for habitat simulation has been carried out, obtaining as result, for the selected target species, the variation of the potential useful habitat (PUH) - with respect to the flow. The Water Planning Instruction (WPI), which aims to provide common technical criteria in the complex hydrological planning process, provides a range of desirables PUH (included in the range 30-80% of the maximum PUH) which allows consequently to ensure the corresponding range of minimum flows in the analysed stretch.

The application in this modelling has required an important work of pre-selection of the target fish species and estimation of their preference curves with respect to the hydrological regime in each growth stage (juvenile and adult).

**Water management systems at the river district level or operating system.** The analysis of the satisfaction degree of individual demands is one of the traditional contents of hydrological planning in Spain, and is therefore an important content to be included in the RBMP. The methodology for such analysis is the simulation of the water resources management systems by the SIMGES model, developed by the UPV and with an general use and interesting experiences in the spanish River Basin Authorities, and that includes the following elements: a) surface and groundwater resources, b) demand units, c) environmental flows, d) regulation reservoirs, e) major transportation lines and f) operating rules.
The use of this model has allowed, among others, to address the following problems: a) management of the last drought 2005/08, simulating the satisfaction of demands by simulating different scenarios of water supply and contribution, b) establishment of operational standards for systems whose exploitation has been contrasted with the simulation of historical contribution series, c) analysis of the feasibility of implementing environmental flows, simulating the effects on the guarantee for corresponding demands and d) estimation of the allocation and reserves of water resources which can be made to different users.

Various processes of detail in determined hydrological elements. There are several recent examples for the use of more specific models amongst which we can mention the following:

- Simulation of chlorophyll concentration in the Albufera Lake in Valencia, by the bi-dimensional model SOBEK, analysing the strategies of inputs and wastewater treatment that resolve the actual eutrophication problem.

- Simulation of the groundwater flow in the aquifer of the Mancha Oriental, using the MODFLOW model, analysing in detail the relation river-aquifer and the various possible scenarios for sustainable exploitation from the point of view of sustainability of groundwater levels and groundwater discharges into the associated surface waterbody of the Júcar river.
Forest fires in Spain in a context of global change: From the country, to the landscape and down to the ecosystem

José Manuel Moreno
Universidad de Castilla-La Mancha, Toledo, Spain

Every year over 0.5 M Ha are burned by wildfires in the EU, a significant number of them in Spain. Fire is dominant in our landscapes nowadays. I will present some general figures about fire occurrence in Spain, and discuss the factors that control them, in particular weather and climate. I will use this relationships to make projections of future fire risk under various scenarios of climate change. Later, I will present landscape-level information to assess how fires alter landscapes and can further affect future fires. Thereafter, I will consider the relationship between vegetation and fire and how climate interacts with plant responses to fire by, for instance, modifying the germinative response in reaction to changes in temperature or rainfall. The ultimate goal of my presentation is to link information from the larger, regional level, to the landscape level and below (vegetation, plant) on the relationships between fire and vegetation that can be of interest to SCARCE researchers.
Water Quality-Management model in the Jucár River Basin

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Integral management of water resources systems is a necessary technique for achieving the requirements established by the European Water Framework Directive (WFD). Traditionally, water quality modelling has focused on modelling individual water bodies. However, water quality management problems must be analyzed at the basin scale. Water quality modelling at a basin scale presents the advantage of incorporating in a dynamic way the relationships between the different elements and water bodies. Currently, there are few tools to deal with water modelling of water quality and management at the basin scale. This work presents the development of a water quantity model and a water quality model for a very complex water resources system: the Júcar River Basin (Spain). The basin is characterized by a high degree of use of the water and by many water problems related to point and diffuse pollution, on top of a complex water quantity management of the basin. To deal with this problem, SIMGES (water allocation) and GESCAL (water quality) basin scale models have been used. Both are part of the Decision Support System AQUATOOL, one of the main instruments used in Spain in order to analyze water quantity and quality aspects of water resources systems for the compliance with WFD, as shown for the case of study.

Júcar River basin is a very complex case, where diffuse and point pollution coincide with water quantity management problems. The linked water quantity and water quality models in this study are being used by Júcar Basin Authority to test different measures in the water basin plan. Despite the difficulty of building a model at basin scale, this kind of models have a great potential in its use as decision support systems.

The main pollution source is a group of urban waste water loads in the lower part of the river. One goal of the study was to estimate the effect of the new wastewater Treatment Plant on the water quality of the river. Using GESCAL, it has been estimated that dissolved oxygen will improve in several points of the lower part. At the critical point of the river, dissolved oxygen concentration could change from 3.5 mg/l to 7.6 mg/l on average. The model also quantified the average reductions in suspended solids (from 28 to 9 mg/l) and ammonium (from 1.81 to 0.12 mg/l).

The second aspect studied, was a comparison of the system in the current, medium and long term scenarios, as defined by the Júcar River Basin Plan (CHJ 1998). These situations differ due to changes in future demands in the system, which affect flows in the river, reservoir storages, irrigation returns, etc.; and, consequently, it also affects water quality. The medium term scenario considers modernization of traditional irrigated areas (substitution of canals by pipes, and changing the irrigation procedures from furrow to drip irrigation), a water transfer to a neighbour basin, and the increase of some demands. The simulation of this scenario reflects maintenance of current water quality concentrations in the river. However, for the long term, with a significant increase of several demands, results show a decrease in water quality in the overall system in critical situations. Moreover, the model has allowed estimating that, in the reservoirs, the phosphorous contents will increase, and so will the trophic state, if water demands increase substantially.

Finally, for all the scenarios previously defined, environmental, incremental, and dilution flows were estimated for each alternative. These additional flows were estimated under the water quality criteria for aquatic life considering dissolved oxygen as the critical constituent. Results show that the effect of these environmental flows on the reliability of the supplies to demands is very low. In the case of the traditional users, this loss of reliability is less than 2%. For all the alternatives, it was estimated that 1.9 m³/s of flow increment is enough to achieve good water quality standards for aquatic life. In the critical summer months (i.e., July, August, and September) this quantity must be increased, depending on the scenario.
GESCAL module expands the AQUATOOL DSS modelling framework to achieve linking water quantity and quality modelling at basin scale. This module allows modelling of temperature, arbitrary constituents, dissolved oxygen and eutrophication processes. The main advantages of GESCAL are the variety of constituents that can be modelled, the integration with the water management module, its modular structure, and the integration of all the elements of a basin and their interdependences. Its integration in the AQUATOOL DSS environment provides easiness of use and of result display and analysis. Currently, this module is also being used by the Duero and Tajo river Basin Agencies in order to develop their Basin Plans for the WFD implementation.

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Global change impacts on water availability in three Mediterranean catchments of Catalonia (NE Spain)

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The Mediterranean Basin is one of the world’s most susceptible areas to suffer the impacts of global change because Mediterranean ecosystems have a complexity of interactions among multiple drivers: atmospheric and climatic change, land use change and natural resources consumption (Lavorel et al. 1998). In this region, water is the main limiting factor in terrestrial ecosystems. Water scarcity and the expected increase of extreme events (droughts, wildfires) caused by climate warming (EEA 2008) threaten both water resources and ecosystems functioning. This work assesses the main global change impacts in three medium-sized catchments in Catalonia (NE Spain) regarding to water availability: Fluvià, Tordera and Siurana. The main aim is to develop adaptive measures to cope with the expected climatic and social changes. The Soil and Water Assessment Tool (SWAT) was used to simulate the hydrologic response to global changes. Downscaled projections of ECHAM5 GCM under two IPCC emission scenarios (A2, B1) were used. In comparison with baseline conditions (1984-2008), climate projections predicted a 12% (B1) to 28% (A2) reduction in precipitation, and a 2.2ºC (B1) to 3.6ºC (A2) increment of mean annual temperature at the end of the XXI Century (2076-2100). Land use scenarios were developed for each catchment using the tool Land Use Change Modeller (LUCM) for the 2030 horizon based on different socioeconomic assumptions: a Trending Scenario (T) which projects the trends of the last decades in land use and water demand, and a Sustainable Scenario (S) which incorporates adaptive criteria in land use planning. In general, T and S scenarios for Fluvià and Tordera catchments showed small differences among them in future land cover areas and water demand. Contrary, Siurana catchment showed a contrasted difference depending on the full development of the projected irrigation plan. Results highlight the strong impact of global change in regional water resources and reflect the importance of incorporating theses analysis into adaptive management in the Mediterranean region.

Study area

The study area was chosen to represent Mediterranean heterogeneity at a local level, selecting three pilot catchments representative of littoral conditions: Fluvià, Tordera and Siurana. These three catchments represent a climatic gradient across the Catalanian coast, besides diversity on land use, pressures and environmental conditions. All three are non regulated watersheds, except for three small reservoirs on Siurana. All three are mainly forested basins which have presented similar trends in land use changes during the last decades, where the forest area has slightly increased, agriculture land has dropped and urban surface has growth. The analysis of the historic climate has shown a temperature increase during the last decades, which is consistent with global registered trends along the Mediterranean area (1.25ºC throughout the period 1951-2000). The main rise was observed on maxim temperature. A non significant decrease on annual precipitation was observed, but reductions were significant on some specific months (July and March), while there was a significant increase in January.

Data and methods

The Soil and Water Assessment Tool (SWAT) was used to simulate the hydrologic response to global changes. Model calibration was based on measured stream flow values along the watersheds with short periods, usually two or three years, depending on the quality data of the gauging station. Calibration was carried out at a daily time step to target three main objectives: (1) simulated curves similar to measured
ones, (2) mean flow values and total contributions similar between simulated and measured data, and (3) good statistics of Nash and Sutcliffe efficiency coefficient (NSE) and RMSE-observations standard deviation ratio (RSR). Calibration results showed a good adjust in the graphical comparison between simulated and measured data, although in all three basins simulations overestimated maxim flood peaks. In Fluvia and Tordera, simulations overestimated mean and total stream flow values. NSE and RSR statistics showed a satisfactory adjust. Validation results overestimated mean discharge values, although in a lower percentage. Statistics showed a satisfactory adjust except in the Tordera basin. At a monthly time step for the period (1984-2008), the calibrated model showed a good performed ratio and general overestimation between 10 and 15% (figure 1 and table 1).

### Table 1. Mean monthly discharge values from both simulated and measured data and adjust statistics.

<table>
<thead>
<tr>
<th></th>
<th>Simulated mean daily discharge (m³/s)</th>
<th>Observed mean daily discharge (m³/s)</th>
<th>NSE</th>
<th>RSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluvià (Garrigàs)</td>
<td>8.5</td>
<td>7.3</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Tordera (Can Serra)</td>
<td>3.9</td>
<td>3.5</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Siurana (Cornudella)</td>
<td>0.3</td>
<td>0.2</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The future climate data were provided by the SMC (Catalan Meteorological Service), which have generated downscaled projections of ECHAM5 GCM under two IPCC emission scenarios (A2, B1) for the period 2001-2100 and for the reference period 1971-2000 (Calbó et al. 2010). Climate projections estimated a precipitation reduction between 12% (scenario B1) to 28.3% (A2) and a mean annual temperature increment between 2.2 ºC (B1) to 3.6 ºC (A2) by the end of the XXI Century (2076-2100) (table 2). An analysis on trends in precipitation spatial distribution through the XXI Century showed major precipitation reductions on Fluvia and Tordera headwaters (between 30 to 53 mm per decade) whereas the lowest reductions are expected on the Siurana mouth.

### Table 2. Mean precipitation reduction percentage and temperature degrees incremented values per time slices per scenario.

<table>
<thead>
<tr>
<th></th>
<th>Mean annual precipitation</th>
<th>Mean annual temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluvià B1</td>
<td>-3.0 %</td>
<td>-14.8 %</td>
</tr>
<tr>
<td>Tordera B1</td>
<td>-2.4 %</td>
<td>-12.2 %</td>
</tr>
<tr>
<td>Siurana B1</td>
<td>-2.8 %</td>
<td>-15.3 %</td>
</tr>
<tr>
<td>Fluvià A2</td>
<td>-9.6 %</td>
<td>-28.3 %</td>
</tr>
<tr>
<td>Tordera A2</td>
<td>-9.3 %</td>
<td>-24.4 %</td>
</tr>
<tr>
<td>Siurana A2</td>
<td>-7.6 %</td>
<td>-24.0 %</td>
</tr>
</tbody>
</table>
Additionally, a land cover scenario modelling was carried out for the three basins. On the basis of two mentioned socioeconomic forecasts, a trending one (T) and a more sustainable one (S), and past land cover, two 2030 scenarios were calculated for each basin, by means of the Land Change Modeller (LCM) tools, running on Idrisi Taiga software. The set of tools provided by LCM allowed to analyse the nature and extent of landcover change, plus hard and soft prediction maps. This soft prediction maps vulnerability to change for a selected set of transitions and provides a comprehensive assessment of change potential. From these results, two land cover maps for 2030 were produced by each basin, which were introduced under the SWAT modelling as one of the required basic layers.

Results

Results were analyzed separately for climate change and for global change (considering both climatic and socioeconomic scenarios).

SWAT simulations with climate projections showed a generalized stream flow and real evapotranspiration reduction. Results were analyzed in two time slices: short term (2006-2030) and long term (2076-2100). Mean values for these periods were compared with the results for the reference period (1984-2008). Results were evaluated in two points per basin: in the basin headwaters and in the river mouth. Table 3 shows the percentage of stream flow reduction per climate scenario (B1, A2) at the two points. The highest reductions were observed in the A2 scenario (33 to 39% of reduction). The highest climate change effect was observed in the Fluvià headwater, with 48% of stream flow reduction.

Table 3. Predicted stream flow reduction per climate scenario, period and headwater/river mouth compared to the reference period (1984-2008).

<table>
<thead>
<tr>
<th></th>
<th>Short term (2006-2030)</th>
<th>Long term (2076-2100)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Headwater</td>
<td>River mouth</td>
</tr>
<tr>
<td>B1</td>
<td>Fluvià</td>
<td>-14 %</td>
</tr>
<tr>
<td></td>
<td>Tordera</td>
<td>-9 %</td>
</tr>
<tr>
<td></td>
<td>Siurana</td>
<td>+4 %</td>
</tr>
<tr>
<td>A2</td>
<td>Fluvià</td>
<td>-20 %</td>
</tr>
<tr>
<td></td>
<td>Tordera</td>
<td>-13 %</td>
</tr>
<tr>
<td></td>
<td>Siurana</td>
<td>-16 %</td>
</tr>
</tbody>
</table>

Season distribution of stream flow reduction was different depending on the time slice. At the short term, large reductions were predicted in spring and summer in the scenario B1, whereas in the scenario A2 the most affected seasons were winter and spring. At the long term, autumn and summer will be the most affected seasons concerning runoff reduction in the two scenarios, while slight increments will be expected in winter.

Potential and real evapotranspiration (PET and ET_{r}) were estimated by Penman-Monteith equation incorporated in SWAT. Results showed a PET-increment by the end of the XXI Century due to the expected temperature increment. A 14% to 25% real evapotranspiration reduction was predicted because of the expected precipitation reduction (Table 4).

Table 4. Predicted potential and real evapotranspiration variation (%) per scenario, period and basin compared to reference period (1984-2008).

<table>
<thead>
<tr>
<th></th>
<th>Potential evapotranspiration</th>
<th>Real evapotranspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Fluvià</td>
<td>+3%</td>
</tr>
<tr>
<td></td>
<td>Tordera</td>
<td>+3%</td>
</tr>
<tr>
<td></td>
<td>Siurana</td>
<td>+3%</td>
</tr>
<tr>
<td>A2</td>
<td>Fluvià</td>
<td>+3%</td>
</tr>
<tr>
<td></td>
<td>Tordera</td>
<td>+2%</td>
</tr>
<tr>
<td></td>
<td>Siurana</td>
<td>+3%</td>
</tr>
</tbody>
</table>
SWAT simulations with global projections showed a generalized stream flow and real evapotranspiration reduction. Results were analyzed only at short term (2006-2030), since the socioeconomic scenarios were developed for 2030. Results showed that land use change could affect the trends forced by climate drivers. In Siurana catchment this phenomenon was significative comparing with the other studied areas because the region will be affected by the potential development of the projected Catalanian Irrigation Plan. In this case, the short term reductions in stream flow could be more severe (4-5% of additional decrease when applying the Irrigation Plan).

Discussion and conclusions

Results were focused on two main hydrological variables that are relevant indicators of water dynamics: stream flow and evapotranspiration. Under climatic scenarios, SWAT predicted a 24% to 48%-reduction of stream flow, approximately a 10% more severe in the A2 scenario than in the B1 at the end of the XXI Century. Along a latitudinal gradient, most drastic reductions at the end of the century were found in the wet headwaters of the northern watersheds (Fluvia and Tordera) while reductions were less severe in the southern one (Siurana). Autumn and summer were the most affected seasons. A 15% to 27%-reduction of real evapotranspiration was predicted for 2076-2100 due to less water availability and soil drought. A strong alteration on water dynamics is expected during the XXI Century. A significant stream flow decrease will affect aquifer the recharge and stream-aquifer relationship. These trends have different environmental and socioeconomic consequences. In an ecological sense, expected stream flow reduction would imply longer periods in which stream flow will be smaller than the ecological one, affecting stream environment quality conservation. Riparian ecosystems would be deeply affected in some parts of the watersheds. At the same time, decreases in soil water availability and changes in intranual variability could impact on woodland development and suitability of some forest species. Water availability decrease and seasonality changes could affect seriously water supply for agricultural and urban uses. During the last decade, different water use restrictions have been applied several times in Catalonia due to lack of water availability. The interaction of these processes with land use changes is another focus in the ACCUA project, but they are out of the scope of this paper. Surprisingly, this analysis reveals a greater vulnerability of wet watersheds in northern Catalonia, which would be deeply affected by climate change despite its bigger buffer capacity. Globally, the ecosystems present in the wet watersheds are more sensitive to changes in environmental conditions. Contrariwise, ecosystems actually located in southern watersheds would be better used to drier conditions. Further studies should be carried out to corroborate these results. This work confirms SWAT as a useful tool to develop spatial analysis of climate change impacts on Mediterranean watersheds and to draw trends, considering all methodological limitations, about the main territorial vulnerabilities on water availability. Results highlight the strong impact of climate change on regional water resources and reflect the importance of incorporating these analyses into adaptive management in the Mediterranean region.

Acknowledgements

This work is part of ACCUA project (www.creaf.uab.cat/accua) coordinated by CREAF with different research partners (UPC, IRTA, ETC-SIA and UB). Valuable contributions were made by the Catalan Water Agency (ACA). Regional climatic projections were provided by the Catalan Meteorological Service (SMC). ACCUA has been founded by CatalunyaCaixa.

References


Contribution of river basin ecosystem services to human well-being in Mediterranean Basins.

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² University Pablo de Olavide, Department for Economics, Quantitative Methods and Economic History, Seville, Spain

Introduction

Human valuation of resources and services provided by ecosystems has varied significantly throughout history. The perception of human benefits gained from natural resources and services, the time horizon and the individual/collective character of human goals and interests are conditioning factors in the value assignment process. Moreover, the possibilities of appropriation and exclusive use of ecosystem services, the perceived relative abundance of one ecosystem service, or the lack of knowledge about the relevance of ecosystem services and functional interactions (Naredo 1987, Fisher et al. 2009) determine the relationship between ecosystems and societies.

The development of human civilization has been based on its ability to identify relevant ecological processes and structures for the provision of ecosystem goods and services considered “valuable” and to intervene on them for enhance such ecosystem goods and services. This has been possible through the ever-increasing exploitation capabilities of innovation-based technologies. As ecosystems structures and processes are complex, nested, overlapped, adaptive and running at different time and spatial scales (Gunderson et al. 1995, Allen and Holling 2010, Kay et al. 1999, Gual and Norgaard 2010, Walker et al. 2004), the intensified use or conservation of a subset of ecosystem goods or services can give rise to unforeseen and/or undesirable side-effects due to interactions with more basic ecosystem functions (Holling 1996, Kay et al. 1999, Chu et al. 2003, Wilson 2002). This, in turn, could affect the provision of “valuable” ecosystem services to humans, now or in the future (Chu et al. 2003). In managing ecosystem services, trade-offs with Nature’s provision of other ecosystem services are made. Even time trade-offs for one ecosystem service could take place if ecosystem resilience is lost (Holling 1996, Holling and Gunderson 2002). Sustainable management of social-ecological systems requires taking into account these trade-offs and cautiously managing them having in mind their inherent uncertainty (Faber et al. 1996, Walters 1986, Funtowicz and Ravezt, 1993, Mayumi and Giampietro 2001) as well as their socio-economic, institutional and ecological context (Fisher et al. 2009, Ostrom et al. 2007).

Research protocol

In the framework of the SCARCE project our research attempts to evaluate the contribution of water ecosystem services to human well-being in Mediterranean river basins as well as getting useful insights for sustainable management decision-making in a framework of global change. Having in mind the contextual feature of ecosystem services, a case study approach has been adopted. The first criterion considered in the case selection process was the distribution among the four great basins chosen for the SCARCE project: Llobregat, Ebro, Júcar (or Xúquer) and Guadalquivir. In second place, different criteria of size, complexity and completeness were introduced.

Following the size criteria we have determined small and medium cases, discarding whole basins for the difficulty/impossibility to study them with enough rigour and getting policy relevant results. Contextualised smaller cases allow for a deep analysis of some relevant micro-processes, which otherwise would be neglected, but that could become key factors in an up-scaling exercise.

However, given the relevance of taking into account a full set of interrelations which are present in a
basin and can not be included in a very partial case-study, we have selected intermediate cases were complete sub-basins become the goal of our study.

Table 1. Summary of criteria considered and selected case studies

<table>
<thead>
<tr>
<th>Case Criterion</th>
<th>Anoia (Llobregat)</th>
<th>Noguera de Tor (Ebro)</th>
<th>Arga (Ebro)</th>
<th>Baix Xúquer (Júcar)</th>
<th>Isla Mayor (Guadalquivir)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Medium</td>
<td>Small</td>
<td>Medium</td>
<td>Doesn’t apply</td>
<td>Small</td>
</tr>
<tr>
<td>Complexity</td>
<td>High</td>
<td>Reduced</td>
<td>High</td>
<td>High</td>
<td>Reduced</td>
</tr>
<tr>
<td>Completeness</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>One/all services</td>
<td>All</td>
<td>All</td>
<td>All</td>
<td>One</td>
<td>All</td>
</tr>
</tbody>
</table>

The final outcome is that we have two comparable (medium sized) full basin cases—Anoia and Arga—, two small cases—Noguera de Tor and Isla Mayor—and one single-service case—Baix Xúquer.

The Baix Xúquer case study has been selected because it allows studying the relevance and complexity associated to the provision of flooding protection river basin services in a Mediterranean large coastal flood-plain.

The analysis carried out in each case-study has been based on a socio-economic appraisal linked to water ecosystem services. To do so, a water ecosystem services’ checklist has been elaborated taking as reference precedent research on ecosystem services (MEA, 2005; Brink, Berghöfer et al., 2009; Ranganathan et al. 2008).

In order to characterise each water ecosystem service identified in the case studies, a template has been developed to register:

- a description of the ecosystem service in its context;
- the ecosystem functions of which it depends and with which it interacts (feedbacks);
- the relevant institutional framework;
- useful descriptive status indicators;
- drivers and directions of change (feedbacks) in the provision of the ecosystem service; and,
- multiple metrics valuation estimates.

First results

Initial findings about relevant water ecosystem services after a first approach to the socio-economic and biophysical situation for each location are summarised in Table 2.

Table 2. Summary of initial research findings about water ecosystem services in case studies.

<table>
<thead>
<tr>
<th>Ecosystem service</th>
<th>Anoia (Llobregat)</th>
<th>Noguera de Tor (Ebro)</th>
<th>Arga (Ebro)</th>
<th>Isla Mayor (Guadalquivir)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Livestock farming</td>
<td>Market-oriented and self-consumption Farm supply</td>
<td>Market-oriented and self-consumption Green water</td>
<td>Market-oriented and self-consumption Green water and farm supply</td>
<td>In the past, Market-oriented and self-consumption</td>
</tr>
<tr>
<td>Ecosystem service</td>
<td>Anoia (Llobregat)</td>
<td>Noguera de Tor (Ebro)</td>
<td>Arga (Ebro)</td>
<td>Isla Mayor (Guadalquivir)</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>----------------------</td>
<td>-------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Fisheries</td>
<td>Not detected</td>
<td>Market-oriented Fish farm, sport fishing</td>
<td>Market-oriented Fish farm, sport fishing</td>
<td>Market-oriented and self-consumption Traditional Fishing</td>
</tr>
<tr>
<td>Drinking and domestic uses</td>
<td>Affected (water import) Groundwater wells and surface water uptakes; drinking water supply network</td>
<td>Detected Groundwater wells; drinking water supply network; self-consumption</td>
<td>Detected Groundwater wells and surface water uptakes; drinking water supply network</td>
<td>Detected Surface water uptakes; drinking water through main city supply network</td>
</tr>
<tr>
<td>Water for industrial crops</td>
<td>Not detected</td>
<td>Not detected</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
<tr>
<td>Climate regulation</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td>Hydrological regimes</td>
<td>Affected Threatened by Water for Drinking and domestic uses &amp; Water for other economic activities</td>
<td>Affected Threatened by Water for energy</td>
<td>Affected Threatened by Water for energy, Drinking and domestic uses &amp; Water for crops</td>
<td>Affected Threatened by Water for energy, Water for crops &amp; Water for transport</td>
</tr>
<tr>
<td>Self-depuration</td>
<td>Exhausted by Water for other economic activities</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td>Soil &amp; sediment dynamics</td>
<td>Local dis-service Erosion &amp; sediment transport</td>
<td>Local dis-service Erosion &amp; sediment transport</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td>Extreme climatic events protection</td>
<td>Affected Regarding floods: Loss of river forest, modification of river channel, loss of floodplain</td>
<td>Affected Regarding floods: Loss of river forest, modification of river channel, loss of floodplain</td>
<td>Affected Regarding floods: Loss of river forest, modification of river channel, loss of floodplain</td>
<td>Affected Regarding floods: Loss of river forest, modification of river channel, loss of floodplain</td>
</tr>
<tr>
<td>Maintenance of ecosystems integrity</td>
<td>Affected Species diversity/population Threatened by Water for Drinking and domestic uses &amp; Water for other economic activities</td>
<td>Detected Species diversity/population Threatened by Water for Energy &amp; Water for other economic activities</td>
<td>Detected Species diversity/population Threatened by Water for Drinking and domestic uses, Water for Energy &amp; Water for other economic activities</td>
<td>Detected Species diversity/population Threatened by Water for energy, Water for crops &amp; Water for transport</td>
</tr>
<tr>
<td>Maintenance of genetic heritage</td>
<td>Affected Loss of endemic species / Invasive species</td>
<td>Detected Collection of medicinal plants</td>
<td>Affected Loss of endemic species / Invasive species</td>
<td>Affected Loss of endemic species / Invasive species</td>
</tr>
</tbody>
</table>
### Ecosystem service

<table>
<thead>
<tr>
<th>Ecosystem service</th>
<th>Anoia (Llobregat)</th>
<th>Noguera de Tor (Ebro)</th>
<th>Arga (Ebro)</th>
<th>Isla Mayor (Guadalquivir)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aesthetics</strong></td>
<td>Affected</td>
<td>Detected</td>
<td>Affected</td>
<td>Detected</td>
</tr>
<tr>
<td></td>
<td>Loss of river forests / Urbanization / Infrastructures / Loss of water quality and biodiversity (+) Historical heritage (+) Landscape</td>
<td>Landscape Historical heritage</td>
<td>Loss of river forests / Urbanization / Infrastructures (+) Historical heritage (+) Landscape</td>
<td>Detected Landscape Historical heritage</td>
</tr>
<tr>
<td><strong>Recreational</strong></td>
<td>Affected service</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td></td>
<td>Loss of water quality</td>
<td>Nature leisure, swimming, camping, sky</td>
<td>Sport fishing, nature leisure, swimming</td>
<td>Bird watching, navigation, hunting</td>
</tr>
<tr>
<td><strong>Spiritual and inspirational</strong></td>
<td>Affected</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td></td>
<td>Loss of positive qualities</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Psychological benefit</strong></td>
<td>Affected</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td></td>
<td>Loss of positive qualities</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Educational &amp; scientific</strong></td>
<td>Affected</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
</tr>
<tr>
<td></td>
<td>Loss of positive qualities</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: elaborated from La Roca et al. (2011).

In the case-study of Baix Xúquer, the only ecosystem service investigated is that of flooding protection. This ecosystem service is affected by river channelling, modification of the river channel, loss of river forests and occupation of river floodplain (urban and industrial facilities, citric crops and linear infrastructures perpendicular to the flood water direction) and loss of drainage capacity. An aspect particularly interesting of this case is the current elaboration of a risks prevention plan for flooding and an evaluation of alternatives and measures for recovery this function in the river basin.

### Present research problems and further research

Beyond the issue of monetization of ecosystem services, a basic problem is the definition of a baseline scenario as a reference to evaluate how an ecosystem in good status contributes to human well-being through the provision of ecosystem services. In the current situation, several ecosystem services susceptible of being valuated in money terms are severely affecting ecological functions from which the long-run provision of such services or other ones depends on. Furthermore, the assessment of the contribution to human well-being of aquatic ecosystem services like climate regulation presents difficulties derived from the uncertainty and complexity of interrelations among ecosystem services and functions. Also, the issue of ignorance is present in cases like that of maintenance of genetic heritage, where the contribution to human well-being has to do with currently not-known future use possibilities or unforeseen new ecological interactions. In this sense, the Millennium Ecosystem Assessment (MEA 2005) acknowledges its limitations and later initiatives like that of the TEEB project (Brink et al., 2009) have got limited results. A further analytical difficulty in the Ecosystem Services framework is the treatment of intangible assets, like inspirational and psychological benefits, which imply a great dose of subjectivity, and where it is not easy to differentiate the water component contribution from the global eco-social picture. In these cases, further collective research is needed in order to reach a similar level of understanding already reached for other more bio-physical or tangible services.

The immediate next steps in our research are: (a) the identification of indicators (physical, social and/or economic) in order to measure ecosystem services and trade-offs among them; (b) contrasting the research team’s appraisal of ecosystem services with local actors and the identification of relevant criteria and metrics for valuing ecosystem services. A further phase in our research will be the use of deliberative scenarios for shedding light on the social appraisal of local water ecosystem services under uncertainty conditions and for getting relevant policy recommendations accordingly.

### References


Poster sessions
Quantification of pharmaceuticals in soils and sediments of Pego-Oliva Marsh by LC-MS/MS.

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The UNEP-World Conservation Monitoring Centre has estimated that wetlands cover approximately 570 M hectares – roughly 6% of the Earth’s land surface. They are among the richest ecosystems in the world. In the Mediterranean, they support high concentrations of birds, mammals, reptiles, amphibians, fish and invertebrate species, many of which are endemic to the region. Furthermore, they are fundamental in the maintenance of the water cycle, purifying and recycling it, at the same time that capture and retain it from the rain. They also act controlling floods and flows, recharging aquifers, etc. In the Valencian Community, the Pego-Oliva Marsh is one of the most important mediterranean coastal wetland. But despite of its richness, it has to cope with an intense human pressure [1].

Pharmaceuticals come from human excretions, waste eluents of manufacturing processes and animal farms mainly. They can reach environment because the large quantities of production and consumption. This fact together with some of them have a not high degradation into wastewater treatment processes makes than some of them were disseminating in water environments.

A previously method developed in our laboratory [2] was put into practice to monitor the occurrence of a representative set of pharmaceuticals in the Pego-Oliva marsh.

In 11th June 2009 a total of 31 samples of soil (at two different depths) and sediment were collected, corresponding to different sampling points previously designed. Briefly, samples were concentrated by PLE using water at 90°C as solvent. Then, aqueous extract was pass through an Oasis HLB cartridge and extracted with methanol as solvent. Quantification was carried out by LC-MS/MS with an ESI interface working in both positive and negative mode. Except for ibuprofen, two transitions were utilized for each compound to obtain an unequivocal confirmation.

Acetaminophen (paracetamol) and carbamazepine were the pharmaceuticals more frequently found in sediment samples, in concentrations between detection limit and 15 ng/g for acetaminophen and from 0.51 to 1.7 ng/g for carbamazepine. In soils, acetaminophen and ofloxacin were commonly detected in concentrations until maximum of 3.5 ng/g and 3.7 ng/g respectively. Ibuprofen, diclofenac, clofibric acid and oxytetracycline were not detected in any sample. This results demonstrates the incidence of these pollutants in the protected area of Pego-Oliva marsh.

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References


Fish community in wadeable stretches of the Guadalquivir River basin (southern Iberian Peninsula): a proposal of priority conservation areas

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Their geographic location, between Europe and Africa and between the Atlantic Ocean and the Mediterranean Sea, implies that Andalusian rivers have a high biological interest, which increases with the isolation effects of the Iberian Peninsula mediated by the Pyrenees and the Atlantic Mediterranean saline bar. Thus Andalusian rivers are poor in species but rich in endemisms. Unfortunately the semi-arid character of the region, along with a long presence of human habitation, put these rivers under high degradation pressure. In this project we tried to analyze the conservation status of the Guadalquivir river basin, the largest river in the southern half of the Iberian Peninsula by focusing on the fish community.

1037 sites were sampled from January 2006 to December 2009 throughout the river network. The data collected included 165 environmental variables (habitat, shelter, climate, geomorphology, hydrology and human disturbances) and fish quantification. Fish were sampled throughout the year except during the dry season (July-September/October) by electrofishing in wadeable sections of rivers, 100-300 m in length, depending on river width (wading upstream with one or two anodes using 240 V pulsed direct current). 13 native species were found in the study area: Anguilla anguilla, Luciobarbus sclateri, Anaecypris hispanica, Squalius alburnoides, Squalius pyrenaicus, Iberochondrostoma lemmingii, Iberochondrostoma oretanum, Pseudochondrostoma willkommi, Cobitis paludica, Salmo trutta, Liza ramada, Mugil cephalus and Aphanius baeticus. In addition, 12 exotic species were also caught: Alburnus alburnus, Cyprinus carpio, Carassius gibelio, Gobio lozanoi, Tinca tinca, Phoxinus phoxinus, Micropterus salmoides, Lepomis gibbosus, Gambusia holbrooki, Oncorhynchus mykiss, Esox lucius and Ameiurus melas. No fish were observed in 556 of the sampling sites visited; 178 were abnormally dry; another 168 were so polluted that no fish could live there and 210 had good water quality, but with abnormal fish absence. Three main mechanisms were identified to explain these findings: habitat destruction (e.g. river channelization), habitat degradation (e.g. pollution) and habitat fragmentation (e.g. damming).

Using the presence-absence of endangered species (UICN criteria); number of native species and predictive models based on logistic-regression analysis, we selected the best areas for conservation of native freshwater fishes in the Guadalquivir River basin. A total of 47 priority areas were suggested: A, reaches with presence of endangered species and B, reaches with the best native fish community according to their distribution, density and endemicity. We added a third category (C; presence of three or more native species) for the Guadalquivir left bank, since its low fish numbers made it impossible to estimate the other categories in this area.

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Antibiotic contamination and promotion of antibiotic resistance in aquatic microorganisms and fish in two Catalan reservoirs

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Pharmaceutical contaminants have attracted increasing attention because of the continuous release from run-off and wastewater treatment plants and their potential threat to the environment, even at very low concentrations and persistence rates. Among these compounds, antibiotics may pose a risk to the ecosystems since they are designed to have a biochemical effect in the microorganisms, and thus have a significant impact in the processes controlled by native microbial communities. One of the greatest concerns about the presence of antibiotics in the environment is the escalation of antibiotic resistance and its possible impact in public health.

In this line, the objective of this study was to determine the levels of antibiotics in different environmental compartments (water and sediments) in the upstream section of two Catalan reservoirs (La Llosa del Cavall & Foix), the first one chosen for its pristine condition, while the last one has considerable levels of pollution.

Samples (water, sediments and fish) were collected in May 2011. For chemical analysis water samples were pre-concentrated and purified using solid phase extraction (SPE) technique, while solid samples were extracted applying pressurized liquid extraction (PLE) and purified with SPE. Analysis of the extracts was performed in a UPLC system coupled to an AB SCIEX QTRAP 5500 mass spectrometer to determine antibiotic concentrations. This method included more than 50 compounds belonging to 8 antibiotic families. This data was correlated with the levels of microbial resistance genes measured by qPCR in the microbial communities of water, sediment and fish intestine.

The general chemical characterization showed a clear difference between the reservoirs in terms of eutrophication and chemical pollution, with exceptional high values in Foix. Foix samples showed the higher antibiotic content in water and in sediment, as it was expected according to the pollution gradient of the target reservoirs. Load was particularly high for macrolides family, which is consistent with data related to antibiotic consumption last years. Remarkably, antibiotic concentration found was coherent with the quantity of qnrS gene copies (index of antibiotic resistance for the quinolone family). Copies of qnrS genes were detected in Foix Reservoir at much higher levels than in La Llosa, the reservoir less affected by anthropogenic contamination. The combination of chemical and biological data provided a broader perspective to assess the impact of antibiotics released into the environment and their potential effect as promoters of antibiotic resistance.

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Upwind fourth-order nonoscillatory schemes for nonhomogeneous hyperbolic conservation laws

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In a previous work, Gascón and Corberán (2001) describe a strategy which provides a suitable technique to extend well-known second-order non-oscillatory schemes for the homogeneous case to nonhomogeneous conservation laws, guaranteeing the balance of the flux and source terms at steady states of a natural way. The technique is based on the transformation of the nonhomogeneous problem to homogeneous form though the definition of a new flux formed by the physical flux and the primitive of the source term. Additionally, this transformation allows us to include correctly the source terms as a divergence term providing the balance between flux and source terms of a natural way.

Balaguer and Conde (2005) describe a fourth-order non-oscillatory scheme for solving hyperbolic conservation laws, which is based on a new reconstruction procedure that may be applied to upwind and central schemes. This reconstruction employs a fourth-order accurate approximation of point values of the solution at the two extrema and at the mid-point of each cell which are modified in order to enforce monotonicity and shape preserving properties. It guarantees that the resulting numerical scheme satisfies the properties that generate its nonoscillatory behavior.

In this paper, we present a revision of the procedure described in Gascón and Corberán (2001) in order to adapt it to obtain an extension of the numerical schemes developed in Balaguer and Conde (2005) for nonhomogeneous hyperbolic conservation laws. The integrals respecting the two variables, space and time, are evaluated by means of a two-point Gauss quadrature. The values of the solution at half-time steps are calculated using a Taylor expansion with a fourth-order error, using the local Cauchy–Kowalewski procedure to approximate the time derivatives of the solution as a function of the derivatives with respect to \(x\).

Some problems with known analytical solution are solved to verify the order of the schemes presented here and to compare their behavior with the schemes developed in Gascón et al. (2003).

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References

Simulating habitat restoration actions: a machine learning approach

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The European Water Framework Directive (WFD) considers inland fish as an important biotic element to assess the ecological status of rivers (EC, 2000). In fact, native fish species richness is considered an indicator of aquatic ecosystems health and has become a key element in managing the quality of rivers (Lek et al., 2005; He et al., 2010). In this context, a predictive model of native fish richness is a management tool that can be used to assess the potential effect of habitat restoration actions on species richness and may help to accomplish the requirements of the WFD. This study used a multilayer perceptron neural network (hereafter ANN) to predict the richness of native fish in the Júcar, Cabriel and Turia river basins (East Spain). Model development was supported by the use of k-fold cross-validation method and Levenberg-Marquardt learning algorithm. The importance of the ANN’s input variables was determined using the partial derivatives (PAD) method. The results indicated that the ANN successfully predicted the fish richness in the study area, because the correlation coefficients between observed and predicted values both in training and validation were significant ($r = 0.90, P < 0.05$ and $r = 0.81, P < 0.05$, respectively). The most significant variables that described the native fish species richness were: IBMWP, percentage of riffles (in the river segment) and mean annual flow rate. The ANN model was used to simulate the effect of two restoration actions; the first was the increase of the percentage of riffle in two segments downstream of the Alarcón reservoir (Júcar river). The second one was the removal of three obsolete weirs in the same river. From simulations, we obtained an increment of fish richness together with increase of river length without barriers and the percentage of riffles. This study shows that ANNs are a powerful tool to support decision-making in the management and restoration of rivers.

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References


Presence of UV filters in sediments and surface waters in the Guadalquivir river basin

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UV filters are widely present in personal-hygiene products and they are included in emerging contaminants from so-called personal care products (PCPs). These compounds may enter the aquatic environment directly (when released from the skin during swimming and bathing) or indirectly via wastewater treatment plants. The removal of these compounds during wastewater-treatment processes is not as effective as it should be. These compounds are continuously released to the environment and they may act as pseudo-persistent compounds. As a result, aquatic organisms are exposed over their entire life cycle. Several of these compounds are known to display estrogenic activity [1-3] and their wide occurrence may be of environmental concern. Conclusive data about their impact on the ecosystems are still scarce.

In this scenario, precise data regarding their presence is urgently required. In order to fill this gap, the presence of 11 UV filters in surface waters and sediments of the Guadalquivir river basin was evaluated. A total of 25 river water samples and 25 sediments were processed by means of solid phase extraction (SPE) and pressurized liquid extraction (PLE) for waters and sediments, respectively, and further analyzed by liquid chromatography-tandem mass spectrometry (HPLC-MS/MS).

Due to the remarkable lipophilic character of most of these compounds, their occurrence in sediments is larger than water. Concentrations up to 30 ng g⁻¹ of Octocrylene were detected in sediments. In surface waters, 5 to 11 studied compounds were detected. In water samples, 4-methylbenzilidene camphor was found to be the most ubiquitous compound (present in 56% of samples) with concentrations above 170 ng L⁻¹. These values are in agreement with previous studies in other European river basins [4] and constitute the first data on UV filters occurrence in Guadalquivir river.

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References

Nekton response to the freshwater inputs in a Temperate European Estuary with regulated riverine inflow

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Although interannual variability in river discharges to the Guadalquivir estuary has been extremely high since the construction of the dam of Alcalá del Río (110 km from the river mouth) in 1930, a significant decreasing trend in dam’s discharges has been observed in the last 80 years (Spearman ρ = -0.49, P < 0.01). From May 1997 to November 2009 the nekton of this estuary was sampled monthly along the last 30 km of the main river course. Prey availability (mysid density), environmental water conditions (temperature, salinity and turbidity) and freshwater inputs (local rainfall and dam’s discharges) were simultaneously recorded.

During this 12-year study, mean local rainfall and dam’s discharges were representative of the hydrological condition of the estuary during the last 30 years. Regarding rainfall, an alternation of wet, standard and dry years occurred without significant long-term changes (Spearman ρ = 0.01, P > 0.05). River discharge, in turn, showed a considerable interannual variability and a significantly decreasing long-term trend (Spearman ρ = -0.26, P < 0.01). Freshwater inputs have an immediate effect on estuarine salinity and turbidity, and consequently on prey availability (mysids). A total of 123 fish and crustacean decapods were collected, but only 48 of them (adding 99.7 % of total abundance) were regularly present in the estuary: 33 marine migrants, 13 estuarine species and 2 diadromous species. As previously observed in other temperate estuaries, well-defined temporal changes in species composition and abundance yielded clear seasonal patterns in the nektonic community of the Guadalquivir estuary (ANOSIM test statistic = 0.63, P < 0.01). Maximal and minimal average dissimilarities occurred between six-month lagged samples and one/twelve-month lagged samples, respectively. However, considerable short-term (intermonthly) changes were occasionally observed relating to freshwater inputs, mainly in winter/autumn of wet years. Thus, some significant interannual differences in the nektonic community were also observed (ANOSIM tests, P < 0.05) within each season, with marine migrants tending to be more abundant in dry years. However, changes in the studied nektonic community did not show long-term (12 year) trends.

In conclusion, natural and human-controlled freshwater inputs currently play a significant role in determining the physicochemical conditions and the biota within the Guadalquivir estuary. However, although freshwater input seemed to transitorily affect the estuarine nekton, either directly (flushing out) or indirectly (through changes in salinity, turbidity and prey availability), the assemblage showed a strong resilience: following freshwater inputs, a quick reestablishment of the estuarine nekton was observed together with the reestablishment of the environmental conditions within the estuary.

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Development of a multi-compartmental physiologically based pharmacokinetic model for PFOS and PFOA in breast milk. Children exposure through breast milk

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Classically, human health risk assessment only considers the exposure dose to evaluate the potential hazard of different pollutants. However, in the human body there are several processes that can change the toxicity of the chemicals. In order to evaluate the human health risk for the population, Physiologically Based Pharmacokinetic models (PBPK) are being developed in recent years. These tools can estimate the distribution of chemicals on the different tissues and organs, along the time. PBPK models are mathematical representations of the human body where the organs are considered as compartments, and they can be resolved computationally as a set of equations. The goal of the present study was to create a PBPK model to assess the baby exposure PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid), and evaluate the health risk of this exposure. These two perfluorinated compounds (PFCs) have been chosen due to their long persistence in the human body (4-6 years), and important concern among the scientific community and the health authorities. In fact, PFOS was listed under the Stockholm Convention in May 2009 as a persistent organic pollutant (POP), while PFOA is a serious candidate to enter that list. In addition to the accumulation of PFOS/PFOA in breast milk, PFCs are cause of concern since they may be present in several other tissues of the human body. Plasma and liver compartments are considered as the main accumulation tissues. The model developed here evaluates the PFC concentration along the time in several target organs during the gestation and the breastfeeding period (Verner et al. 2009). PFCs are well intestinal absorbed, poor eliminated and not metabolized (Loccisano et al. 2011). Therefore, 3 ways of elimination were considered: partum, lactation and urine. The same compartments were considered in both adult women and children. The conceptual PBPK model considers other organs of possible concern like kidney or brain. The PBPK model here presented was validated by comparing theoretical values with experimental data of perfluorinated chemical in blood serum and breast milk collected in Catalonia, Spain (Kärrman et al. 2010). For toxicity, the tissue residue approach (TRA) was used. The TRA is the use of tissue concentrations as the dose metric for characterizing toxicant potency. Finally, a normalized local sensitivity analysis was performed on the model to examine the influence of each model parameter on the model output. Sensitivity coefficients were calculated for the predicted plasma area under the curve (AUC; total concentration) with the original parameters and for those resulting from a low change in each parameter value.

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References

Relationship between metals bioavailability and speciation in river water depending on the stressors

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It is well known that the toxicity associated to heavy metals is not directly caused by the total amount of metal, but only by its bioavailable form, being this closely linked with the fraction of free metal. The main objective of this study was to assess metals bioavailability in Francolí River waters and to correlate it with the influence of the several stressors (concentrations of other ionic species, amount of organic matter, etc) to which Francoli basin is submitted.

For this purpose, the concentration of potentially toxic metals was analysed in freshwater, filtered water samples and in passive samples DGT taken along the Francolí River. DGTs have been used in recent studies to estimate the bioavailable fraction of metals (Buzier et al. 2006). In addition, other important parameters that have a great influence on metal speciation and bioavailability such as DOC, pH, hardness of water, etc. were also determined. On the other hand, the MINEQL+ software, a chemical equilibrium modelling system, was used to check the consistency of experimental data. The evaluation of metal concentrations with competitive factors, such as water hardness or dissolved organic matter, mostly explained the amount of free ion metals responsible for bioaccumulation in DGT. The maximum dynamic concentrations for metals were determined by means of two methodologies (Balistrieri and Blank; Unsworth et al 2006). The results of Unsworth model showed a better correlation between predicted and measured bioavailable fractions.

In conclusion, the integration of modeling (chemical software) and monitoring (passive methods) seems to be crucial to understand the hazard of metals in aquatic compartments and thus to establish the real river ecological status.

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References


Hydrology and Water Quality Modeling under Data Scarcity for Low Flow River in Mediterranean Watershed

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Global change impacts on water availability, water quality and ecosystem services in Mediterranean river basins of the Iberian Peninsula, as well as their impacts on the human society and economy makes it a key issue on the EU agenda. It is likely that the first impacts of climate change will be felt in the Mediterranean water resource system through increased frequency of water shortages and decline in water quality. Even relatively well-endowed countries, such as Spain, Greece and Italy, could suffer ever-more frequent regional water shortages due to the twin problems of climate change and rising demand.

Economics is very important for controlling the management of land and water resources, not just in a micro and macro sense, but also the costs of change for scientists and other organisations to adopt new ways of working and the need to advance payments for ecosystem services (Macleod and Haygarth, 2010). Simulation with hydrological model provides insight into the nature and structure of connections between water resources and socio-economic and environmental change. That will be the simulated effects of a new water stress definition that incorporates both water quality and water quantity effects into the measurement of water scarcity.

The challenge of managing catchment systems in temperate regions under environmental change is complex and requires greater levels of integration between academic scientists, policy makers and operational staff to enable more holistic approaches to understanding and managing land and water resources (Macleod et al., 2007). The general aim of this study is to provide a better overall understanding of the effects of climate change, water scarcity and results of loss of quality in low flow rivers by developing hydrological model. A small river of Catalonia (Northeastern Spain), River Francoli with a low flow (~2 m$^3$/s) is selected for catchment assessment and development of hydrological model. Several techniques are used to cope with the data scarcity and make all the input data available by comparison of history records. It is insight that in the future models and tools will be developed on basis of this hydrological study to support decision-making, describing and quantifying the bio-physical and socio-economic components of the watersheds, and defining how they interact to provide goods and services using DSS models like Bayesian Networks (Bns), a decision analysis framework, based on Bayesian probability theory, which allows the integration of scientific and experiential knowledge, and the uncertainty associated with this knowledge (Castelletti and Soncini-Sessa, 2007). Individual future objectives will cover the analysis of river basins with respect to characteristics of the water bodies, impact assessments for human activities and economic analysis to achieve good water status for all waters to comply with European water framework directive for River Basin Management Plan.

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References
Analysis of volatile methylsiloxane in waters: comparison between MASE and headspace extraction methods

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Volatile methylsiloxanes (VMS) are chemical compounds with a backbone of alternating silicon and oxygen atoms, each silicon atom bearing one or several methyl groups. They were introduced commercially in the 1940s and have a significant impact as specialty materials for consumer and industrial products. It has resulted in widespread distribution in the environment.

Some siloxanes are bioaccumulative, while others are toxic to sensitive aquatic organisms. In addition occurrence of VMS in the biogas of digested sludge can damage gas engines used in energy production from the biogas [1].

Only few GC-MS methods deal with the analysis of this compounds in waters [2] and analysing of them in a single run is problematic: L2 the most volatiles VMS coelute with the solvent, keeping the filament on during the elution of solvent front will reduce the filament lifetime. In addition, if injector is configured to eliminate the solvent, there will be significant losses of volatile compounds, resulting in drop in method sensitivity. To achieve a good response in the detector of all VMS analyzed, a solventless method has been proposed. Headspace was utilized successful for the extraction of nine linear and cyclic siloxanes (D3, D4, D5, D6, L2, L3, L4, L5 and M4Q) and their subsequent analysis by GC-LVI-MS. Recoveries were good for all compounds. Quantification was based on isotope dilution technique using ¹³C labeled analogs of D4, D5 and D6. In this study, selectivity, linearity, precision, limits of detection (LOD) and quantification (LOQ) were determined. The results of the validation procedure confirmed that the method is suitable for screening these compounds in the wastewater.

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**References**


Freshwater inputs as forcing mechanisms on the lower trophic levels of the Guadalquivir estuary.

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The effects of freshwater inputs of the Guadalquivir estuary seem to respond to a combination of several (physical, physiological and trophic) forcing mechanisms. Natural and human-controlled freshwater inputs currently play a significant role in determining the physicochemical conditions and the biological production within the estuary. Nutrient, SPM and allochthonous photosynthetic pigment importation linked to freshwater inputs (rainfall/riverine) was observed, as well as changes in the mysid populations which were directly or indirectly (via physicochemical water conditions) related to freshwater management. Despite the high nutrient concentrations (mainly nitrogen hypernutrification due to cropland runoff), the high turbidity suggests that there is light-limited primary production (physical forcing) in the estuary, at least in the oligohaline region, and that the autochthonous primary production is constrained to the most seaward and less turbid reaches. The effects of freshwater inputs on mysids varied depending on their specific salinity tolerances and trophic features. The populations of marine mysids *Mesopodopsis slabberi* and *Rhopalophthalmus tartessicus* only showed high densities at salinities above physiological thresholds (physiological forcing), while the more euryhaline and detritivorous *Neomysis integer* mainly showed high densities in less saline but more turbid waters (higher SPM, trophic forcing). In contrast, under physiologically suitable conditions for mysids, the availability of preferred preys (*M. slabberi* density for *N. integer* and *R. tartessicus*; Chl a for *M. slabberi*) affected the densities of the dominant mysid species (trophic forcing). Moreover, low *M. slabberi* densities were observed under conditions of high inorganic matter probably due to particle impact injuries on this small mysid (physical forcing) and/or diminished food quality (trophic forcing). This led to an increased detritivory/herbivory ratio and a consequent transitory alteration of the estuarine food web.

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Functional bacterial diversity in the epipsammic biofilm at the Llobregat River

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River benthic microorganisms are highly responsible for decomposition, use and uptake of flowing water solutes. Their decomposing activity is mainly determined by their enzymatic capabilities which might be reduced in low diverse communities at highly polluted sites. At the same time, floods and droughts modulate the pollution effects in Mediterranean rivers. The effect of a pollution gradient on the heterotrophic functional bacterial diversity in the epipsammic biofilm was analysed along the Llobregat River (NE Spain). This river is a major drinking water source and is subjected to Mediterranean climate. The bacterial density, functional diversity and richness, community respiration (ETS) and content of extracellular polymeric substances (EPS) were analysed in five sites along the main axis. In parallel, we tested the potential application of the Biolog EcoPlates™ for analysing the heterotrophic functional diversity and compared the results between frozen (-80°C with nitrogen liquid) and unfrozen sediment samples using this technique.

Significant differences in community respiration and polysaccharide content were observed downstream, linked to an increase of pollutants, total carbon and nutrients content. After Biolog EcoPaltes analysis we observed different significant results during incubation time. Although after 24 hours of incubation a significant decrease in functional diversity was observed downstream, but after 144 hours, a significant decrease in the metabolic capacity and potential functional diversity was measured in the two middle points in the river. This result was probably affected by a high flow event, which homogenized the epipsammic biofilm community along the river and diluted pollutant concentrations. However this technique allows us to observe that after frozen samples some metabolic activities of the community had been lost probably due to bacterial dead or inactivation. Therefore we conclude the use of this technique appears to be useful to define microbial functional response patterns in fresh environmental samples.

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Contamination of polar pesticides in sediments from Rivers of the Iberian Peninsula

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River sediments are distinctive in providing historical contamination patterns and are appropriate monitoring tools to evaluate pollution episodes. In addition, river sediments reflect the quality of surface water. Since sediments contain multiple classes of pesticides, it is important to use multiresidue methods capable of determining as large number of them as possible. Most of the work carried out up to now is focus on the determination of organochlorine pesticides. On the contrary, there are few data on the presence of currently used pesticides in such important matrix [1,2]. The aim of this work has been to develop a sensitive multi-residue method for the simultaneous target analysis of 41 pesticides in sediments. The proposed method has been applied to study the levels of pesticides in sediments from several Iberian river basins (Ebro, Jucar, Llobregat and Guadalquivir).

Sediment samples were taken with a Van Veen dedge and stored in aluminium platters. Once at the laboratory, samples were dried up and sifted through a 2 mm Φ sieve. They were kept into small bottles at -20 ºC. The 41 selected pesticides belong to different chemical classes: triazine and acetamide herbicides, organophosphates, ureas and several fungicides and acaricides. QuEchERS method was used to extract pesticides from sediment samples. The procedure is based on extraction of 5 g of sample with 7.5 ml water and 10 ml acetonitrile followed by a salting-out step with 6 g MgSO4, 1.5 g NaCl, 1.5 g sodium citrate dihydrate and 0.75 g di-sodium hydrogen citrate sesquihydrate. The clean-up step of the samples was carried out with 50 mg primary secondary amine, 150 mg MgSO4 and 50 mg C18 before filtration of the sample through 0.45 µm. The resulted extract was then analyzed by liquid chromatography-mass spectrometry (LC-MS/MS) in positive ionization with an electrospray ionisation (ESI) source. Separation was carried out on a Luna C18 column (150 × 2.0 mm, 3 µm) using a gradient elution profile and mobile phase consisting of 10 mM ammonium formate in methanol and in water. The two most intense precursor ion → product ion transitions were monitored to obtain unambiguous confirmation of the compound identity.

In general, recoveries ranging from 75% to 95%, with relative standard deviations better than 18% were obtained; and low limits of detection and quantification (0.03 to 0.05 ng g⁻¹) were achieved for all selected pesticides. In the sediment samples under study, only seven currently used pesticides were detected in the river basins -chlorpyriphos, diazinon, hexythiazox, imazalil, malathion, prochloraz and terbutryn. As an example, in the Ebro River terbutryn is present at concentrations ranging from 10 to 50 ng g⁻¹ dry weight (d.w.), chlorpyrifos in concentrations from 2 to 24 ng g⁻¹, diazinon in concentrations from 1 to 35 ng g⁻¹, malation in only one sample at 5 ng g⁻¹ and prochloraz also in one sample at 18 ng g⁻¹. Although these pesticides have a relatively short half-life in sediments (days–months) they have been found in several river catchments all around the world [1].

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References


Occurrence and partition of perfluorinated compounds in water and sediment from Xuquer River (Valencia, Spain)

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Over the last decades, perfluorinated compounds (PFCs), including perfluorosulfonates (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), have been widely produced and used as surfactants, lubricants, paints, polishes, fire-retardants and water repellents for leather, paper, and textiles. Due to the large amount of usage, PFCs are omnipresent in environmental matrices, even in remote areas (Llorca et al. 2011). The presence of these chemicals in the environment is of great concern due to their bioaccumulation and adverse effects to biota and humans. Most PFCs exhibit high solubility in water and moderate sorption to solids. Because of their amphoteric character, their partition behavior between water and sediment may be different from the non-ionic hydrophobic chemicals. As compared to surface water, the study of PFCs in sediment is very sparse. The goal of current study was to determine the distributions of PFCs in water and sediment in the Xuquer River Basin. The composition profile of PFCs in water and sediment was compared. Partition coefficients Kd and log Koc were calculated to investigate the partition behavior of these PFCs between water and sediment. Water and sediment samples were collected from Xuquer River in October of 2010. Eight sites were distributed along the Xuquer River and seven were its main tributaries Cabriel and Magro. At each site, water was collected at least 5 m off riverbank and sediment with a Van Veen dradge. The partition coefficients of PFCs between sediment and surface water were estimated using the concentration of PFCs in the sediment and in the overlaying water at the same sampling sites. The partition coefficient Kd was calculated using the following equation:

\[
K_d = \frac{C_s}{C_w}
\]

where Cs and Cw are the PFC concentrations in sediment (ng g⁻¹ dw) and in water (ng L⁻¹).

\[
K_{oc} = K_d \times 100/f_{oc}
\]

where Koc is the organic carbon normalized partition coefficient and foc is the percentage of organic carbon in sediment.

The results present in current study demonstrate that PFCs are widely present in the surface water and sediment of Xuquer River. In the water samples, PFOA and PFOS were the most detected PFCs. PFOS and PFOA are significantly lower than those reported in the main wetland of River L’Albufera in a previous study (Picó et al. 2011). The contributions of PFOS and long chain PFCAs in sediments were much higher than in water samples. This fact is explained by their preferential partition to sediment. The sediment–water partition coefficients (log Koc) of PFHxS, PFOS and PFOA are significantly lower than those of typical hydrophobic organic chemicals such as PAHs, HCHs and DDTs. As compared to these chemicals, PFCs are prone to stay in water column.

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References


Quantitative detection of trace perfluorinated compounds in environmental samples by Liquid Chromatography-Quadrupole-Time of Flight Mass Spectrometry

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The family of PFCs includes as most remarkable congeners perfluoroalkyl sulfonates (such as perfluorooctyl sulfonate (PFOS), perfluorobutyl sulfonate (PFBS), and perfluorohexyl sulfonate (PFHxS)), perfluoroalkyl carboxylic acids (such as PFOA and other short-chain or long-chain perfluoroalkyl acids), and sulfonamide derivatives (perfluorooctane sulfonamide (PFOSA)) (Pico et al. 2011).

High-performance liquid chromatography (HPLC) with triple quadrupole mass spectrometry in electrospray negative mode is the most extensively applied method for the analysis of PFCs in various environmental and biological matrices, because triple quadrupole mass spectrometry has high precision, wide linear range and high sensitivity for PFOS and PFOA determination in complicated matrices. QTOF-MS technique is considered to be one attractive alternative for the unequivocal identification of unknown compounds using full-spectrum scan. However, it is seldom applied to quantitative analysis because of its relatively narrow linear range for most of the compounds. Recent developed instrument have overcome this drawback achieving linear ranges up to three orders of magnitude and an improved sensitivity (Pico et al. 2011).

In present study, quantitative detection of 18 PFCs [13 perfluoroalkyl carboxylic acids (C4-C18), 4 perfluoralkylsulfonates (C4-C10) and PFOSA] by LC-QqTOF-MS (MS) is reported for the first time. The method (conventional SPE and UPLC-QqTOF-MS) was developed and applied for PFCs quantification in environmental water.

A total of 18 PFCs were measured to identify their occurrences. SPE with Oasis WAX cartridges was used to extract the PFCs from the water samples. PFCs were determined using a UPLC Agilent Technology 1260 infinity combined with a QqTOF ABSciex Triple TOFTM 5600. Separation was achieved on a Poroshell 120 EC-C18 analytical column (30x50 mm, 2.7 µm) using methanol-water, both with ammonium formate (10 mM), in a gradient that start with 70 % of methanol linearly increases to 95 % in 12 min and maintained for 5 min.

Using this method, recoveries ranged from 65 to 99 % and RSDs from 10 to 20 %. The limits of quantification achieved were lower than 1 ng/L and the linearity covered four orders of magnitude. This method was applied to different water samples from Ebro, Llobregat, Jucar and Guadalquivir rivers. Several PFCs including PFOS, PFOA and PFHxS were identified and confirmed at trace levels.

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References

Quinolone and fluoroquinolone residues in agricultural soils from Valencian Community (Spain)

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Fluoroquinolones (FQ) represent a major group of synthetic antibiotics, which have been widespread use during the last 15 years in human and in veterinary medicine for the treatment of bacterial diseases. Their use leads to an entry of these compounds into the environment through the excretion of unmetabolised quinolones and the disposal of unused drugs (Andreu et al. 2007). Quinolones are rather persistent with half-lives of 151 days. They interfere with bacterial DNA metabolism by inhibiting two enzymes, topoisomerase II and IV. These enzymes introduce negative super helical twists into the DNA strands. Inhibition of these reactions prevents DNA replication, repair, recombination and transposition (Pico & Andreu, 2007).

For instance, in soil, most of the quinolones come from sludge soil amendments and irrigation with waste-water. The amount of quinolones in soils is of importance because of their effects on soil organisms and plants. As a result of their widespread presence, quinolones are generally introduced in monitoring programs for emerging pollutants in waters. On the contrary their determination in soils is still scarce and there is a need of analytical methods developed for it (Petrovic & Barcelo, 2007; Vazquez-Roig et al. 2010).

In this study, PLE and ultrasonic extraction were compared for the extraction of eight quinolones in soil, followed by liquid chromatography coupled to triple quadrupole (LC–QqQ-MS/MS) determination. Both extraction procedures combined with the chromatographic method was used to determine quinolones at trace levels in soil samples taken from different agricultural areas of the eastern of Spain. Pressurized liquid extraction (PLE) and ultrasonic extraction methods were optimized. Parameters such as type of solvent, extraction time, extraction temperature and number of extractions were optimized. There were no significant differences among the two extraction methods although better extraction efficiencies were obtained when PLE was used, minimizing extraction time and solvent consumption. Both procedures were validated, obtaining limits of detection (LODs) ranging from 0.02 to 0.75 ng g⁻¹ and limits of quantification (LOQs) ranging from 0.07 to 2.50 ng g⁻¹ for the selected quinolones. Recoveries were in the range of 59–110%, except for enrofloxacin, which was the most volatile quinolone. Finally, the method was applied to real soil samples from Southeast of Spain. Quinolone concentrations were low, and enrofloxacin, ciprofloxacin and ofloxacin were the most frequently detected analytes in the samples.

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References
Application of the Soil and Water Assessment Tool (SWAT) to model faecal indicator bacteria concentrations in the River Ouse catchment, UK

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Aquatic Management of Catchments for Health & Environment (AquaManche) is a European cross-border initiative that aims to deliver practical tools to improve prediction, mitigation and management of river, estuarine and coastal waters in the France (Channel) - England region. As part of the AquaManche project the flow regime of the River Ouse (East Sussex, UK) was simulated using the Soil and Water Assessment Tool (SWAT) within the ArcGIS interface. Data requirements included a digital elevation model, a land use layer, and soil and climatic data, which were integrated to create sub-catchments defined by the sampling locations of the AquaManche project. Three years of modelled data were calibrated using SUFI-2 uncertainty analysis routine and then a subsequent period of independent data was used to validate the model. Following calibration and validation water quality parameters indicating faecal contaminants were introduced to the model using the bacteria transport routine within the SWAT interface. The model produced daily time-steps of flow and microbial content for the River Ouse. The results of the model indicate a significant relationship between simulated and monitored concentrations of faecal indicator organisms (FIO) within the River Ouse. The results illustrate the potential for SWAT modelling, to help predict likely FIO concentrations in river catchments under different conditions, informing future mitigation and management decisions, with a focus on supporting the development of the European Union (EU) Water Framework Directive (WFD).

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Seasonal monitoring of Pharmaceuticals on a sewage impacted section of a Mediterranean River (Llobregat River, NE Spain) and their relationship with hydrological conditions.

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Mediterranean rivers are characterized by a high flow variability, which is strongly influenced by the seasonal rainfall. When water scarcity periods occur, water flow and dilution capacity of the river is reduced, increasing the potential environmental risk of pollutants. On the other hand, floods contribute to remobilization of pollutants from sediments. Contamination levels in Mediterranean rivers are frequently higher than in other European river basins, including pollution by pharmaceutical residues. Around 3,000 different pharmaceuticals (PhACs) of different therapeutic classes are used in human medicine in the European Union (EU). Regarding Spain, it was the ninth largest world market in 2010, whereas, it took the fifth position in Europe’s top pharmaceuticals market. The main route of PhACs into the aquatic environment is the excretion by humans and the direct disposal through domestic wastewater. Despite its previous treatment in WWTPs, depending on the treatment efficiency and chemical properties of the compound are able to reach surface and ground waters. PhACs are widespread pollutants in the aquatic environment. A wide range of human PhACs are present in effluents from sewage treatment plants that continuously enter freshwater systems. More than 150 PhACs have been identified in surface, ground and even drinking waters. Levels of PhACs detected in WWTP effluents are in the range of μg/L, whereas in river and groundwater are much lower, generally in the ng/L range. Nevertheless, little attention has been paid to the transport behavior of emerging contaminants in surface waters once they are discharged from WWTP into a river. In this context, this work aimed to trace presence of PhACs in sewage impacted surface waters and to study levels and fate of these pharmaceutical compounds under different hydrological conditions of a typical Mediterranean River (Llobregat, NE Spain). For that purpose, a selected list of the most frequently studied PhACs, belonging to different therapeutic families, were monitored in fresh surface water from Llobregat River and levels of PhACs were related with two characteristic hydrological parameters, namely flow and dissolved organic carbon (DOC). Water samples were collected during storm-flow events and river base-flow periods, from October 2009 to July 2010. Sampling was carried out twice a week over periods of five weeks at two main sampling sites downstream a dominant WWTP. Aiming to gain further insight about different hydrological events, three additional sampling points were added, one upstream a dominant WWTP and two located at the main tributaries of the Llobregat River. Sampling sites were selected in order to study pollution gradient. Levels of PhACs were determined in surface waters using a multiresidue analytical method based on LC-MS/MS after solid-phase extraction. Flow and DOC data of the sampling sites were obtained from the public website of the Water Authority that records measures of the catalan watershed every five minutes and aggregated at daily intervals.

Sixty-two of the 70 compounds targeted were present in at least one of the samples analysed. Seven of them presented maximum concentrations higher than 500 ng/L, being analgesics and antiinflammatories the most ubiquitous and highest concentrated therapeutic group along the river section studied, which were determined in the range of 700-1700 ng/L. Far from expected natural attenuation of pollutants (Fono et al. 2006), target compounds were detected following an increasing gradient together with number of WWTPs distributed along the river section studied. Positive and negative correlations between the concentrations of the target analytes and hydrological variables like river flow and DOC were observed pointing out the relevance of different hydrological phenomena like dilution effects or sediment re-suspension. Sensitivity calculations showed that the majority of compounds were more sensitive to DOC variations than to flow, suggesting the importance of response of PhACs to organic matter.
Ecological and micropollutants response of a Mediterranean river to hydrological natural variations: the Llobregat case study

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Pharmaceuticals (PhACs) have been detected in the aquatic environment and their presence have been grown a scientific concern. Several studies have reported the presence of these compounds in surface waters 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, industrial application as well as low removal efficiencies for these compounds during their treatment in WWTPs. However, little attention has been paid to environmental behaviour of emerging contaminants once they are discharged from WWTP into rivers as primary receptors, which can vary depending on their chemical proprieties and several environmental factors such as pH, light, or dissolved oxygen. Moreover, since PhACs are intrinsically bioactive compounds with a continuous input into surface waters, knowledge about the effects on biological communities, and therefore on aquatic ecosystems, resulting from long-term low-dose exposure to PhACs is almost lacking and is a matter of current active research.

Mediterranean rivers are intrinsically characterized by hydrological irregularity with a high flow variability, which is strongly influenced by seasonal rainfall. Furthermore, the occurrence of extreme hydrological events (floods and droughts) is expected to increase under the foreseen (IPCC) scenarios of climate change.

River biofilms are complex microbial benthic communities composed by autotrophic and heterotrophic organisms embedded in extracellular polymeric matrix. As interface, they interact and respond rapidly to changes of environmental conditions therefore they are able to act as warning systems after disturbances. Moreover they play a fundamental role in the trophic web and in the geochemical cycles within aquatic ecosystems. For this reasons they have been considered a good model to study the effects of pollutants on freshwater ecosystem and have been recognized within the WFD as a necessary target.

The study was carried out along a sewage impacted section of the Llobregat River (NE Spain), which is a prototypical example of a Mediterranean river, following a pollution gradient. The research aimed to investigate the effects of PhACs detected in the river waters on structural and functional responses of river biofilms. To this aim, a translocation of biofilms experiment was performed, from less to more polluted sites of the river Llobregat. Based on the hypothesis of bioactive compounds affecting biofilms response to translocation, responses of communities to pollutants concentrations and other environmental factors were linked by combining multivariate analysis approaches. As well as that, the results observed were related with changing hydrological conditions of the Llobregat River in terms of flow variability.

For that purpose, concentration of pharmaceuticals in surface water samples were determined in surface water samples collected at two sampling points downstream a dominant WWTP along a 36 km course of the river, located in Abrera (ABR) and Sant Joan Despí (SJD). Sampling was performed during two periods of six weeks (March-April 2010 and June-July 2010) covering a moment of low flow stability (first sampling campaign) followed by a rainfall with a consequent flood (during second sampling campaign).

Levels of PhACs were detected in the range of ng/L to μg/L, being analgesics and antiinflammatories the most ubiquitous and highest concentrated therapeutic group along the river section studied, which were
determined in the range of 700-1700 ng/L. Dilution and re-mobilization effects of PhACs were observed as a consequence of the peak flow event which occurred during the second sampling campaign. Biofilm development and responses were different in the two sampling sites depending on the campaign. In general more variability between sites and more pronounced responses to translocation were observed during the second campaign performed. For instance, differences between biofilm grown in SJD and ABR were more important in the second campaign. In both sampling periods biofilm bacterial mortality increased downstream while other descriptors like peptidase activity or chlorophyll $a$ density, only showed differences in the second one. Response of biofilms to translocation was quite different in the two experiments performed, showing more variability of responses in the second campaign. Differences observed in levels of pharmaceuticals in both campaigns and response of biofilms to these emerging pollutants based on changing river flow, reinforces the hypothesis of the importance of flow variations in the ecological and chemical status of Mediterranean Rivers.
Preliminary analysis of sediment fluxes at the Barasona Reservoir

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The Barasona Reservoir (i.e., responsible of the irrigation of more than 70,000 ha in Aragon and Catalunya) experiences acute siltation problems threatening its long-term impoundment capacity. Sediment load mainly come from Eocene marls located in the middle part of its draining basin (i.e., Ésera and Isábena rivers). Reservoir siltation puts on risk cyclically water resources and, therefore it requires special attention from the Ebro Water Authorities. Within this context a pilot study is being carried out within SCARCE with the aim of studying the transfer of sediments and its chemical characteristics through the Barasona Reservoir to accomplish two main objectives: i) establishing the basic chemical characteristics of the fine sediment that is deposited in the reservoir and flows out through the dam and, ii) studying the retention of C, N and P associated to fine particle sedimentation. A fingerprinting approach based on geochemical determinations (i.e., major elements) of the samples will also be applied, to trace sediment contribution from rivers and the movement of the sediment through the reservoir. An integrated sediment monitoring strategy allows controlling sediment input to the reservoir, by means of sampling at the outlet of the Rivers Ésera and Isábena, and the output from the reservoir itself. Sampling at the monitoring stations will be done using an ISCO 3700 automatic sampler which will be set up with the objective of obtaining water samples during flood events. These samples will be completed with manual samples taken (weekly or fortnightly) directly from the river during field visits. Therefore, by the combination of manual and automatic samples, the whole range of discharge conditions (baseflows, medium flows, high flows and flood events) will be analyzed. Finally, samples will be combined by discharge classes to obtain integrated averaged samples at each sampling point at a given flow strength. In addition, samples are collected spatially distributed across the reservoir during different seasons. Reservoir sampling was designed based on a bathymetrical survey done during reservoir maximum water level conditions to define the optimum location for 12 sampling points. Sediments samples were taken with a Lenz-type dredge with a 400 cm² area. Besides that, a second sampling campaign will be done during reservoir minimum water level. In this campaign, samples will be taken at different locations on dry surfaces. Chemical characteristics of such dry samples will be compared with those taken before at full conditions to study the effects of the dry/wet periods on sediment characteristics. Finally, three different physiochemical analyses are being carried out: i) grain size distribution, ii) C and N determination at all samples; iii) major elements determination at selected samples. Grain size distribution will be determined with a Beckman-Couter LS 230 particle analyzer in two aliquots: one aliquot will be analyzed directly after dispersion with pyrophosphate and ultrasound, and the other will be treated for organic matter elimination by adding H₂O₂. Total C, and N will be determined through dry material using an elemental CN auto-analyzer. Also organic C will be determined after acid treatment of bulk sample and further analysis for total carbon. Major elements (Al, Fe, Si, K, Ca, Mg, Ti, Mn, P) will be determined through X-ray fluorescence (XRF) after fusion at 1100°C with Lithium tetraborate.
An integrated sampling design to study the combined effects of regulation and Mediterraneity on fluvial dynamics

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Mediterranean climate is characterized by irregular and markedly seasonal and torrential rainfalls. This way, Mediterranean river-basins' hydrology can be distinguished by showing low discharges or even long dry periods during low-rainfall seasons and flashy events during wet seasons. Global change may exacerbate this temporal variability by reducing the days with precipitation but increasing thunderstorms. At the same time, Mediterranean rivers present long-lasting anthropic alterations in their basins and river-banks. Such alterations affect river's dynamism, modifying its physical characteristics and related ecological functioning. Dams are one of the main responsible of these alterations by changing hydrological regime (flow and floods magnitude and frequency), sediment transfer and basic erosion and deposition processes in the channel, and the associated morphology and bed sedimentary structure. Overall alterations reduce the quality of the fluvial ecosystem. The main objective of the work is to study fluvial dynamics in regulated rivers as a function of their mediterranean degree. To achieve this aim, SCARCE Consolider WP3 structured the research in two different working scales: 1) A general characterization of different hydraulic, sedimentary and vegetation parameters at 78 selected sites covering four representative watersheds in the Iberian Peninsula: Llobregat, Ebro, Júcar and Guadalquivir. After fieldwork carried out during 2010 and 2011 in collaboration with WP5, acquired data are been processed to determine different variables on channel form (i.e., local slope, bankfull levels) and on grain size distribution (i.e., sorting, armouring). Besides, researchers are currently collecting and analyzing historical hydraulic data (i.e., mean annual flow, return periods), climatic data (i.e., precipitation, temperature) and data on catchment characteristics (i.e., land uses, drainage area); 2) An intensive monitoring campaign in 2 different sub-basins of the Ebro: the Ésera (i.e., low Mediterraneity, Barasona Reservoir) and the Siurana rivers (i.e., high Mediterraneity, Siurana Reservoir). In addition, two sections in the River Xúquer are also being evaluated for monitoring. Two sections are being set up in each river, upstream and downstream the dams. Work is carried out to determine: a) bed stability (i.e., river-channel changes, particles movement); b) sedimentary dynamics (i.e., surface and subsurface grain size distribution; proportion, distribution and characteristics of fine sediments); and c) hydrology (i.e., flood-events magnitude and frequency). To evaluate the methodology developed to achieve the previously-mentioned objectives, fluvial dynamics have started to be studied, as a pilot case, in the Perarrúa monitoring section (Figure 1) in the River Ésiva, upstream the Barasona Reservoir. This section is formed by a central gravel-bar and the different morphologic unities around it. Morphological and hydraulic characterization is based on topographical surveys combining different technologies, as differential GPS, robotic total station and ADCP River surveyor M9. A Digital Elevation Model is also produced for hydraulic modelling. Surface grain size distribution, measured by using the lineal transects method, has been carried out in the bar and in the hydromorphologic unities; D\textsubscript{50} in the unities ranged...
between 63 and 150 mm, while in the bar was 72 mm. Subsurface grain size distribution was measured in the bar by means of the volumetric method, resulting in a $D_{50}$ of 51 mm. By comparing aerial photographs taken before and after flood events, changes in morphological units and their characteristics will be detected and further analyzed. To carry this out, and to determine descriptively grain size variables, an aerial photograph of the reach is taken using a digital camera attached to a 1 m$^3$ helium balloon. Bed stability and mobility is been studied by locating 1 m$^2$ painted areas, waiting for these to be active under different flood scenarios. Finally, suspended sediment transport is measured continuously by a high-range backscatter turbidimeter.

Figure 1: Aerial photograph of the Perarrúa monitoring section taken by a digital camera attached to a 1 m$^3$ helium balloon together with the surface and subsurface grain size distribution of the sampled bar and plates of the 1 m$^2$ painted areas located to study bed mobility. The black square shows a zoom of one of the plates that have composed the mosaic.
Multi-residue trace level determination of endocrine disruptors and related compounds in rivers of the Iberian Peninsula

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The Mediterranean basin is one of the most vulnerable regions of the world to the global change due their climatic conditions characterized by summer drought and their characteristic topographical regions\textsuperscript{1}. Moreover, the high activity close to the Mediterranean rivers, either by the industry or agricultural, intensive use of the water resources, and the high population density in these zones, are the principals arguments to evaluate the water quality of these rivers.

The organic pollutants such as endocrine disruptors are a group of substance that interfere with the endocrine system and disrupt the physiological function of hormones. Some of these contaminants are found in a high variety of products commonly used in the daily life (detergents, in personal care products such as cosmetics, pharmaceuticals and in different industrial formulations\textsuperscript{2}). For all of this, is important to evaluate the occurrence of these compounds in river and waste water.

The objective of this work was the determination of endocrine disruptors and related compounds belonging to different groups of chemical substances (10 steroids, natural and synthetic, in free and conjugated form, 8 surfactants and their metabolites, 4 antiseptics, 2 antibacterials, 3 flame retardants, 2 anticorrosives, BPA and caffeine) in four representative watersheds in Spain: Llobregat, Ebro, Júcar, and Guadalquivir.

The growing number of samples analyzed in laboratories that carry out monitoring studies requires employment of high-throughput and fully automated analytical techniques. In this study, a multiresidue analytical method for the analysis of water samples was applied, using the Thermo Scientific Equan LC-MS system, an automated online preconcentration method. MS analysis was carried out on a Thermo Scientific TSQ Vantage triple quadrupole mass spectrometer with an ESI source. Two different selected reaction monitoring (SRM) transitions were monitored per compound.

The results show widespread occurrence of target compounds, although the level of concentrations of different compounds detected varied considerably depending on the sampling point. For example, phosphate flame retardants were found in all the samples at concentrations up to 500 ng/L. Steroid estradiol was detected in the 90% of the samples in the pg/L or low ng/L range. Estrone and estriol were found in about 50% and 10% of samples respectively, while ethinylestradiol was detected in only three samples.

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References

Before and After Dams: Biofilm changes in Structure and Function.

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Over 1000 reservoirs have been built in Spanish large rivers. The Ebro catchment is one of the most regulated by large dams in the Iberian Peninsula. Large dams not only alter hydrology and river connectivity, but also the physical, chemical and biological characteristics change downstream the impoundment.

Epilithic biofilms are subject to these conditions and their structure and function could be modified with regard to the communities upstream the reservoir. The hypothesis was that epilithic biofilms upstream of the dam would present higher variability in structure and function than downstream, subjected to natural disturbances and higher availability of habitats.

In order to test the effects of dams on epilithic biofilms two different systems of the Ebro basin were selected. The first one is formed by the Ara-Cinca River, one of the major’s tributaries of the Ebro and regulated by El Grado Reservoir. The second one is the Siurana River (regulated by the Siurana reservoir). While the former has a Pyrenean character, the Siurana is submitted to a Mediterranean regime. Five transects across each reach were defined in both the control site (before the dam) and the impact site (after the dam). Four replicates in each transect allowed to obtain a reliable representation of the habitat variability. Samples for chlorophyll-a, the community composition of epilithic biofilms and extracellular enzymatic activities (β-glucosidase, phosphatase and leucine peptidase), were used for determining the biofilm structure and function. Photosynthetic capacity and photosynthetic efficiency were also measured.

Results show an increase of chlorophyll-a after the dams in the two systems. Phosphatase activity and the associated variability were higher in control that in impact reaches. In contrast, glucosidase activity of the Ara-Cinca system was higher after the dam reach that in the control reach. Leucine peptidase activity did not present significant differences between control and impact sites. Biofilms of Siurana river had a higher photosynthetic capacity and efficiency downstream of the dam that communities upstream, but in Ara-Cinca system this variation is not perceived.

![Fig. 1 Enzymatic activities (phosphatase and β-glucosidase) in Ara control reach.](image1.png)

![Fig. 2. Enzymatic activities (phosphatase and β-glucosidase) in Cinca impact reach.](image2.png)
Halogenated flame retardants in sediment and biota from the Iberian river basins.

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a type of flame retardants which have been widely used as additives in different materials, such as building materials, textiles, electronic equipment, plastic polymers, etc. Many of them are considered toxic, persistent and bioaccumulative. Most used commercial mixtures are the Penta- and Octa-BDE mixtures, while the most used PBDE is the Deca-BDE or BDE209. Since both commercial mixtures and Deca-BDE were banned, new brominated flame retardants, such as DecaBDEthane, Hexabromobenzene (HBB) and Pentabromoethylbenzene (PBE), have been used as substitutes and are considered emerging brominated flame retardants. Other emerging halogenated flame retardants are Dechlorane plus (DP) and its related compounds. DP is a chlorinated flame retardant used as a substitute of Mirex, which was banned to be used as a flame retardant on the 70s. Commercially, Dechlorane plus exists as a mixture of two isomers, syn- and anti-, with a ratio about 1:2 respectively. This commercial mixture is used for cable coatings, computer and television materials, etc. It was not found in the environment until 2006 and since then it has been found in different matrices such as eggs, dust and air.

Samples were collected in four Iberian river basins: Ebro, Llobregat, Júcar and Guadalquivir. Sample extraction was done using selective pressured liquid extraction (SPLE) in the case of sediments, while fish samples from different species were extracted using PLE and then purified with acid and solid phase extraction (SPE). Instrumental analysis was carried out by Gas Chromatography-Mass spectrometry working in Negative Ion Chemical Ionization (NICI) mode in the case of PBDEs and other emerging brominated flame retardants, and by Gas Chromatography-Tandem Mass spectrometry, also working in NICI, for Dechlorane plus and related compounds.

Traditional PBDEs and new flame retardants such as DBDPE, HBB, PBE, Dechlorane plus and related compounds (Dechlorane 602, Dechlorane 603, Dechlorane 604, Dechlorane plus mono aduct and Mirex) have been monitored. There are few studies of Dechlorane plus at these zones, since most of the studies are done in Canada and China, where DP is produced. Actually, these are the first reported results on a Spanish aquatic food web. Syn- and anti- ratio was evaluated in order to study the bioaccumulation behaviour of the two isomers.

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References


Obtaining demographic projections with zero migratory balance. 
Nonparametric graduation: wavelets.

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Demographic projections are designed to estimate future values of growth rates, number of individuals of a population according to the assumption about mortality, fertility and migration. This is a topic widely studied in demographic field and widely used in the practice. This work proposes the use of a nonparametric technique which has been used successfully in a variety of fields of knowledge: the wavelet technique.

The techniques used to do estimations are usually separate between parametric and nonparametric, and between fit, graduation and interpolation. This paper proposes nonparametric graduation with wavelet, which has been introduced for the first time (that I know) in the demographic and actuarial field [Baeza-Morillas, 2011], and has been used successfully in other fields of knowledge. On the introductory character of the work assumes a model with net migration, birth rates and death rates constant over time. The variability is assumed inherent in each age.

To do this to end, we assume a theoretical model with empirical parameters and use this to obtain a great number of the ‘synthetics experiences’ with the goal to graduate it. Then, we compare each of the reconstructions with the values of the model to measure the goodness of the technique.
Using Tandem mass spectrometry for the detection of Iodinated Contrast Media’s (ICM’s) Transformation Products (TPs) in the Environment

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Iodinated X-ray contrast media (ICM) are used for diagnostic imaging of soft tissues based on X-ray radiography. High content of iodine enables them to highlight specific parts of the body and enhance their contrast. ICM are among the most widely used intravenous drugs with the worldwide consumption of about $3.5 \times 10^6$ kg per year [1]. They are metabolically stable in the human body and are rapidly eliminated via urine or faeces. Most of these radiographic contrast media are derivatives of 2,4,6-triiodobenzoic acid that possess polar carboxylic and hydroxyl moieties in their side chains. The potentially adverse environmental impact of ICM has been considered since it was discovered that these compounds contribute substantially to organically bound halogens adsorbable on activated carbon (AOX) in hospital wastewater. Up to 90 % of the AOX values could be traced back to the presence of ICM [2] thus the importance of identifying the TP of ICM for their photoproducts could show equal or similar behaviour in the environment.

Method for identification and quantification of ICM has been developed and afterwards used to as a tool for identification of ICM TPs. Photodegradation of ICM (eg. iomeprol) was performed under controlled laboratory conditions simulating environmental settings in surface water. In order to simulate sunlight-induced photodegradation of Iomeprol, test solutions of ICM were prepared in an artificial freshwater and irradiated in a Suntest apparatus (Heraeus, Germany) equipped with a xenon lamp. Chemical structures of the photoproducts were identified using high resolution mass spectrometry (ESI-QqToF-MS). Once the photoproducts were identified, QLIT-MS was used for the detection and quantification of Iomeprol in the environment along with its Transformation products (TPs)

![Iomeprol](image)

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References

Occurrence of persistent organic pollutants in Iberian River Basins

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Iberian rivers are subjected to high pressures for satisfying population and economies requirements affecting the quantity and quality of water resources. In addition, the Iberian Peninsula climate is characterized generally by long periods of drought which becomes in a conditioning factor for the water availability. Furthermore, Iberian rivers cross through important economic areas, which means high loads of contaminants coming from agriculture (run-off waters and directly from pesticides application), industry and urban sources (mainly from wastewater treatment plants).

During last years exists a great awareness of the need for establishing control programs to ensure the chemical quality of water environments. Besides, the European Community is focussing its efforts on assure the water quality and availability. One of the most promising measures currently in force is the Water Framework Directive (WFD). Monitoring programs suppose a great strategy to evaluate the chemical quality of aquatic environments. In the framework of SCARCE CONSOLIDER project (2010-CSD2009-00065), four Iberian rivers are being deeply studied (Ebro, Guadalquivir, Jucar and Llobregat) in order to assess the water quality on the basis of ecosystem health.

Persistent organic pollutants (POPs) are able to remain in the environment during years since they show low degradation rates (months or years). Their environmental effects are well known and some POPs present toxic, carcinogenic and endocrine disruption effects. Although these compounds were forbidden decades ago, even at the present they are found in river basins. For this project has been selected a large number of POPs, both agricultural (cyclodienes, hexachlorocyclohexane, diphenyl aliphatics and trichlorobenzenes), industrial and urban origin (polyaromatic hydrocarbons, hexachlorobenzene and polychlorinated byphenyls). As POPs are hydrophobic compounds sediment matrix was selected for assessing the POPs occurrence.

A GC-MS multiresidue method was applied for the determination of 53 POPs in 74 sediment samples from the aforementioned four Iberian rivers. After the samples preparation, the first step was to perform a pressurized liquid extraction (PLE) by using ASE 350 (Dionex Corp., Sunnyvale, USA) for the extraction, clean-up, and concentration of analytes. For correcting possible analytes losses during the sample treatment 12 isotopically labelled compounds were used as surrogates.

The GC analyses were carried out on Trace 2000 (Thermo Electron, San Jose, CA, USA) gas chromatograph equipped with a fused silica capillary column (HP-5MS, 30m × 0.25-mm id, 0.25-µm film thickness) (J&W Scientific, Folsom, USA). Carrier gas was helium at constant flow rate of 1.2 mL/min. For the chromatographic separation an oven temperature program was applied. Analytes detection was performed with a TRACE MS (Thermo Finnigan, Manchester) mass spectrometer operating under electron ionization mode and selected ion monitoring acquisition.

Concentrations obtained in sediment matrix throughout the four studied river basins manifest a widespread contamination by PAHs (more pronounced in large cities with important industrial or urban activity). Although most of chlorinated compounds are banned for years, some sampling points reveal also the occurrence of both pesticides (DDT and derivatives) and industrial compounds (PCBs or hexachlorobenzene).
Connectivity analysis between overland flow generation and erosion under Mediterranean semiarid conditions (Portacoeli experimental micro-basin, Valencia, Spain)

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Overland flow generation within the same basin is dependent on different factors that facilitate sectors connectivity and flow concentration. Dominant factors (climatic, topographic, ecologic, etc.) may not be the same according to the area size and hence their interaction is dependent on scale (drainage area size) and dimensions (rainfall intensity and duration).

Hydrological connectivity is also behind of the subsequent process of erosion, which is understood as a major threat in Mediterranean semiarid ecosystems due to vegetation scarcity. Surface water connection will determine the existence of erosion production, transport and accumulation inside and outside the basin. If hydrological connectivity may produce also erosion connectivity, soil depletion and loss of soil capacity to sustain plants will be undesirable consequences producing the final degradation of soils and increasing the risk of desertification.

In this work a methodology to study overland flow generation and sediment (erosion) yield has been developed in the Portacoeli experimental micro-basin nested in the greater Barranc de Carraixet watershed in the proximity of the city of Valencia, Spain. Hydrological connectivity and response to rainfall events has been analysed at three scales: (1) The greater Barranc de Carraixet watershed, (2) the micro-basin (both instrumented with automatic flow records) and (3) seven experimental plots, four under controlled conditions with different vegetation cover and three under natural conditions. Erosion response related to rainfall events and overland flow was studied in all experimental plots. The analysis has been applied to a one year records of rainfall, overland flow and sediment data, from April 2008 to March 2009.

Results show that scale is a key element to establish flows concentration and hence connectivity. There is an exponential relationship between the size of the draining area and flow production, regardless of the type of cover. Nonetheless, at plot scale the type of vegetation cover has influence on overland flow production where open spaces with bare soil spaces may be crucial to organized water connections through some slope sectors. Other factor as topography and lithology (e.g. areas of rock outcrops) may result relevant to micro-basin scale where slope sectors connectivity has to be overcome. To greater scale, major landscape or land cover units together with anthropogenic and meteorological characteristics have to be considered to produce concentrated flow. In fact no record has been registered at the watershed (Barranc de Carraixet) scales during more than ten years.

At plot scale erosion has been scarcely produced. Of the total 26 rainfall events recorded very few were identified as erosive, and in all cases with very small amounts mainly obtained under natural conditions. Such results suggest that erosion connectivity, when exists, may be produced at slope scale and further incorporated to concentrated flow at the micro-basin scale. The absence of flow registers to the watershed scale suggests that the small proportion of sediments conveyed at micro-basin scale may not abandon such scale unit being redistributed internally without further connections.

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Variation in heavy metal muscle concentrations related to species and size of Llobregat River fish

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The Llobregat is a Mediterranean river characterized by its irregular regime. Its watercourse is subjected to many different impact sources, e.g. water abstraction, habitat banalization, as well as urban, agricultural and industrial pollution. Organisms living in Llobregat River are exposed to a wide range of pollutants found both in river water and sediments. Since fish occupy the highest trophic levels in aquatic ecosystems, they are strongly affected by lower levels and bioaccumulate toxic elements and compounds, showing biomagnification in some cases. The importance of fish communities for the balance within aquatic ecosystems, as well as their economic value, has lead to their increasing use as bioindicators in inland waters. The objective of this ongoing study is to assess the concentrations of a vast range of heavy metal elements in sediment, water, algae, fish tissues and gut content. Here we show preliminary data on the fish muscle, with regard to fish species and size.

Muscle samples from several species (Alburnus alburnus, Barbus graellsi, Gobio lozanoi and Lepomis gibbosus) were analyzed through atomic absorption spectrophotometry. All the analyzed elements are commonly found in altered aquatic environments. Cd, Hg, Pb can be toxic at very low concentrations. Al, Mn, Fe, Co, Ni, Cu, Zn, As are essential elements when in traces, fundamental for many organisms’ metabolism but toxic at higher levels.

The average burden of Cd, Hg, Pb found in each fish species was below the limits imposed by UE for human consumption (Commission Regulation -EC- N. 1881/2006). Results of linear regression analysis showed a significant negative relationship between fish size and concentration of Al and Pb in G. lozanoi, which was the most abundant species. The most likely cause is that young fish have higher metabolism than adults, processing more trophic resources and accumulating the metals contained in it. The highest concentrations of metals, especially Hg and As, were found in L. gibbosus. These two elements show uncorrelated behavior: Hg is known to be assimilated with food, mainly in the methylated form, and biomagnified, whereas As burden is normally associated to aqueous concentration and is influenced by different biological processes (e.g. algal uptake and biotransformation) and the trophic status (phosphate concentration) of the aquatic system. Water, sediment, algae and fish gut content analysis will be necessary to clarify the origin of each element found in fish muscle and their behavior through the trophic web.

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References


Changes in consumption rates and reproduction of invertebrates in Ebro, Júcar and Llobregat rivers

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In the last years, the development of new bioassays with caged, single species or communities has allowed determining pollutant effects in situ. Some advantages of in situ bioassays are greater relevance to the natural situation, especially with respect to the contamination scenario; and higher ability to detect effects in caged individuals or communities more rapidly (hours to days) than resulting changes in community structure (months to years). In order to study the effects of pollution on invertebrate functional features, two simultaneous in situ field experiments have been done in three of the Scarce studied basins. In the main course of the rivers between 4 and 5 sites were selected along a pollution gradient to expose animals to river natural conditions. Additional water and sediment samples were collected for chemical analysis.

One of the experiments tested changes in algae consumption rates of caged *Daphnia magna* organisms during 24 h. The second experiment studied the reproduction behaviour of the freshwater snail *Physella acuta* during 8 days. Both *D. magna* individuals in groups of ten and *P. acuta* in groups of eight were transplanted in specially designed cylindrical cages to allow water to pass throughout. *P. acuta* cages had also food to overcome nutritional differences across sites. From five to six cages were placed in each site. Measured responses included mortality and post exposure algae consumption rates in transplanted *Daphnia* individuals and mortality, number of clutches, total number of eggs and egg development in the snail.

No mortality occurred in *D. magna* but algae consumption rates decreased significantly in 6 out of 12 studies sites relative to laboratory controls. Inhibition rates varied from 40% in Castellbell (Llobregat) and Antella (Júcar), 50-60 % in Sant Joan Despi (Llobregat), Bocal-Tudela (Ebro) to 75% in Cuenca (Júcar). Low mortality was also observed for snails but higher variability (depending on site and river) was observed for reproduction endpoints. Future work will involve the determination of up to 10 molecular markers in transplanted *D. magna* individuals, the analyses of changes in macroinvertebrate assemblages and of a broad number of contaminants and physico-chemical factors in water and sediment. This will allow to link molecular, behavioural and reproduction responses of caged organisms with those of the invertebrate community and to identify potential contaminants affecting those responses.

These assays will detect lethal and sub-lethal responses that are biologically linked with key ecological processes and constitute a useful tool since it already consider single and community level effects.
Analysis of PDE-V and analogues in WWTP of Spain by LC-MS/MS

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The presence of pharmaceuticals in waters has been continuously reported in recent years. Phosphodiesterase type V (PDE-V) inhibitors are used for effective treatment of erectile dysfunction (ED). Sildenafil (Viagra®), tadalafil (Cialis®), and vardenafil (Levitra®) are the three drugs approved by the European Medicines Agency (EMEA). The presence of these drugs in waste water treatment plants (WWTP) has been reported in recent years [1]. After consumption, these drugs are metabolized, normally sildenafil and vardenafil undergo N-dealkylation. In addition, these drugs require prescription and some synthetic analogues of sildenafil are used to adulterate herbal medicines and cosmetic products that are available through Internet websites markets. These untested products suppose a risk for human health.

Besides this potential health threat, concern has been raised due to their detection in WWTP and the subsequent risk on the aquatic organisms resulting from effluent discharges. In the mean of this context, our research was focused in developing a method to analyze PDE-V inhibitors: sildenafil, vardenafil and tadalafil, two main metabolites (demethylsildenafil and desethylvardenafil) and also some analogues such as, hydrohomosildenafil, homosildenafil, thiosildenafil and norneosildenafil.

The analysis of PDE-V was carried out by automatized solid phase extraction (SPE) followed by liquid chromatography – mass spectrometry analysis (LC-MS/MS). The validation of the method showed satisfactory parameters like sensitivity (limits of detection below 2 ng/L), accuracy (absolute recoveries above 65%) and repeatability (relative standard deviations below 15%). The most abundant compounds were sildenafil and demethylsildenafil in influent water (wastewater).

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References

Complex stressors in Mediterranean river ecosystems in the Iberian Peninsula: effects on biofilm communities.

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We examined the presence of metal pollution in the Llobregat, Ebro, Júcar and Guadalquivir basins (Spain) and their effects on benthic biofilm communities. The Llobregat river is one of Barcelona’s major water resources. It has been polluted by industrial, agricultural and urban wastewaters. The Ebro river is the most important river in Spain, with the highest discharge volume. It has been largely regulated by dams and channels. The regulation, irrigation and industrial activities around the main cities have deteriorated soil and water quality, where pollution is relevant. The Jucar river is located in a semiarid zone with an intensive water use that has lead to an overregulation of the system. Moreover, urban, industrial and agricultural pressure increases downstream, where water quality decreases. The Guadalquivir river receives many inputs, from both natural and anthropogenic origin, that cause deterioration of water quality. The lower part is also impacted by reservoirs and dams and its regime is rather artificial.

Five sites were selected in each river, where we analysed the occurrence of metals (Mn, Fe, Co, Ni, Cu, Zn, As and Pb) as well as their bioaccumulation in biofilm communities. Biofilm samples were taken to measure several metrics related to both the algal and bacterial components of the community.

Water metal content (Table 1) showed an upstream-downstream gradient in all the river systems, being the Guadalquivir and Llobregat rivers the most polluted, followed by Ebro and Júcar. Metal bioaccumulation (Table 1) followed the same pattern.

Multivariate analyses revealed that both physical and chemical parameters and metal pollution were influencing the biofilm community. The total variance explained was 80%. In terms of physical and chemical variables, soluble reactive phosphorus and conductivity had a significant effect on the biofilm responses, explaining a 9.2% of the variance. Metals alone accounted for 22.7% of the explained variation, with the bioaccumulation of copper and the presence of arsenic in water being the two statistically significant variables. Shared variance represented 48.1%.

Soluble reactive phosphate and conductivity described a downstream gradient of eutrophication for all the rivers (Fig. 1). Downstream sites were also characterised by high algal and bacterial biomass, as well as high values of photosynthetic efficiency (Fig. 1). Metal pollution described a gradient in which the sites with high content of metals had lower algal biomass and photosynthetic efficiencies but high detoxification capacity (increase of catalase antioxidant enzyme activity).

Multivariate analyses showed certain effects in both structural and functional aspects of the biofilm community, but the sensitivity of each metric to particular stressors must be assessed before we can assign causality. Complemented with laboratory experiments, this approach could be successfully incorporated into environmental risk assessments to better summarise biotic integrity and improve the ecological management of fuvial systems.

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Detection of priority and emerging contaminants in the Henares River Basin by stir bar sorptive extraction (SBSE) and dynamic headspace (DHS) followed by comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry (GCxGC-TOF-MS)

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Waste generation due to the expansion of industrial activity, agriculture and the human activities have a serious negative impact on the water resource base. Rivers not far from residential, industrial and agricultural areas are dirty and contaminated. This problem cannot be ignored, since together with changes in climatic conditions can have large scale adverse impacts over the quality of waters.

There is a need to conduct a more complete and accurate assessment of the chemical quality of the water. For this task multi-residue methods, which cover different kinds of organic pollutants as well as their major transformation products are demanded. GCxGC-TOF-MS allows simultaneous determination of hundreds of pollutants at low levels in a single analysis. In addition, in recent years the trend to simplify the analytical procedures have led to the development of new extraction techniques, in which the clean-up and concentration steps are removed. SBSE and DHS are examples of such techniques. Besides, these extraction techniques are simple, inexpensive and solvent-free.

In this study new analytical methods based on stir bar sorptive extraction (SBSE) and dynamic head space (DHS) followed by comprehensive two-dimensional gas chromatography (GCxGC-TOF-MS) have been developed for the automatic searching and evaluation of volatile organic compounds (VOCs) and non-polar or semi-polar contaminants in river waters. The methods were very useful for the analysis of target compounds and screening of non-target compounds.

The results of this study show SBSE/DHS-GCxGC-TOF-MS as powerful tools for identifying and quantifying priority and emerging contaminants in waters. Besides, to obtain analytical information of target analytes, with these techniques have been possible to screening for unknowns.
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