



# 5<sup>th</sup> International Conference on Risk Assessment of PHarmaceuticals in Environment



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Centro Polifunzionale Paradiso-SALA 1  
Via G. Orlandi, 100

**Anacapri (NA)**

**24<sup>th</sup> - 25<sup>th</sup> June 2024**

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## Book of Abstracts



Divisione di Spettrometria di Massa





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# Agenda

24<sup>th</sup> June 2024

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8:15	<i>Registration</i>
	<b>Welcome and Introduction</b>
9:00	Giuliana Bianco - <i>President of Divisione di Spettrometria di Massa - SCI</i> Damia Barcelò - <i>University of Almeria, Spain</i> <b>Presentation of Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW)</b>
	<b>Session 1: Exposure assessment - Chairs: Marco Gaspari, Paola Verlicchi</b>
9:25	<b>PL01 - Nontarget screening approaches by HRMS and applications on the pharmaceuticals detection in environmental samples</b> Nikolaos S. Thomaidis - <i>National and Kapodistrian University of Athens, Greece</i>
10:15	<b>OR01 - Occurrence of pharmaceuticals in surface water sources and drinking water of the Romagna area (Italy).</b> Marilin Profita - <i>University of Bologna, Italy</i>
10:35	<b>OR02 - Presence of Pharmaceuticals and Other Emerging Contaminants in Biogenic Matrices Used in Agriculture as Fertilizer</b> Sara Castiglioni - <i>Istituto di Ricerche Farmacologiche Mario Negri, Italy</i>
10:55	<b>OR03 - Retrospective Data Mining for the Estimation of Public and Environmental Exposure to Household and Industrial Chemicals</b> Eva Hawkins - <i>University of Bath, United Kingdom</i>
11:15	<i>Poster Session &amp; Coffee Break</i>
	<b>Session 2: Wastewater-Based Epidemiology (monitoring) for Public Health - Ecological and Health Effects, Hazards and Risks - Chairs: Fulvio Magni, Sara Castiglioni</b>
12:15	<b>KN01 - Pharmaceuticals and emerging contaminants in the environment: estimating environmental and public health risks using water-based epidemiology</b> Barbara Kasprzyk-Hordern - <i>University of Bath, United Kingdom</i>
12:50	<b>OR04 - Untargeted nLC-MS/MS proteomic biomarkers characterization on population, health, environment and lifestyle status of three different neighbourhoods of Barcelona</b> Carmen Tesoro - <i>University of Basilicata, Italy</i>
13:10	<b>OR05 - Wastewater-based epidemiology as tool to monitor health and lifestyle of communities in near-real time</b> Nicola Ceolotto - <i>University of Bath, United Kingdom</i>
13:30	<b>OR06 - A first evaluation of presence of Polyfluoroalkyl Substances in stranded dolphins, sea turtles and sharks (Tuscany Coast)</b> Michele Mazzetti – <i>Agenzia Regionale per la Prevenzione e Protezione Ambientale della Toscana, Italy</i>
13:50	<i>Poster Session &amp; Buffet Lunch</i>

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**Session 3: Degradation and Innovative Remediation Technologies part I - Chairs: Sabino Bufo, Emanuela Gregori**

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<b>15:00</b>	<b>KN02 – The impact of using reclaimed waters for greenhouse crop irrigation: microplastics, pesticides and emerging contaminants</b> <i>Amadeo R. Fernández Alba - University of Almeria, Spain</i>
<b>15:35</b>	<b>OR07 - Using a flow mode tubular reactor under natural solar irradiation for antibiotics' removal from water</b> <i>Diana Lima - Health &amp; Technology Research Center, Polytechnic University of Coimbra, Portugal</i>
<b>15:55</b>	<b>OR08 - Biochar Derived from Forest Residues: A Sustainable Solution for Venlafaxine Removal, Promoting Waste Valorization and Water Reuse</b> <i>Oussama Baaloudj - University of Basilicata, Italy</i>
<b>16:15</b>	<b>OR09 - Sustainable photocatalysts for the treatment of antibiotic-polluted waters: A central composite design for optimizing the synergistic roles of TiO<sub>2</sub>, Carbon Quantum Dots, and Magnetic Nanoparticles</b> <i>Valentina Silva - University of Aveiro, Portugal</i>
<b>16:35</b>	<b>INSTRUMENTATION PILL: Innovative solutions to analyze trace pollutants in environmental samples</b> <i>Giuseppe Federico Labella - Bruker Italia Srl</i>
<b>16:45</b>	<i>Poster session &amp; Welcome Party</i>
<b>19:30</b>	<i>Dinner at restaurant "Da Gelsomina", Anacapri</i>

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## 25<sup>th</sup> June 2024

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**Session 4: Degradation and Innovative Remediation Technologies part II - Chairs: Filomena Lelario, Amadeo R. Fernandez Alba**

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<b>9:00</b>	<b>KN03 Recent advances in the degradation of pharmaceuticals residues in macroscale and microscale photoreactors</b> <i>Gianluca Li Puma - University of Palermo, Italy</i>
<b>9:35</b>	<b>OR10 - Photodegradation behaviour of antibiotics in environmental matrices under simulated solar radiation</b> <i>Carla Patrícia Silva - Health &amp; Technology Research Center, Polytechnic University of Coimbra, Portugal</i>
<b>9:50</b>	<b>OR11 - Enzyme-functionalized biochar for the enhanced removal of the anti-inflammatory pharmaceutical diclofenac from water</b> <i>Hugo F. Rocha - University of Aveiro, Portugal</i>
<b>10:10</b>	<b>OR12 - Innovative methods to remove phosphodiesterase 5 inhibitors from polluted water</b> <i>Angelica Rebecca Zizzamia - University of Basilicata, Italy</i>
<b>10:30</b>	<b>OR13 - Optimization of functionalized biomass-based materials for the removal of antibiotics from wastewater</b> <i>Vânia Calisto - University of Aveiro, Portugal</i>
<b>10:50</b>	<i>Poster session &amp; Coffee Break</i>

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**Session 5: Risk assessment - Chairs: Cecilia Bergamini, Fabiana Piscitelli**

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| <b>11:30</b> | <b>OR14 - Combating antimicrobial resistance through wastewater “fingerprinting”:<br/>Surveillance and environmental risk assessment of antimicrobial usage in Welsh hospitals<br/>and communities</b><br><i>Neil Byrnes - University of Bath, United Kingdom</i> |
| <b>11:50</b> | <b>OR15 - Overlooked Metabolic Pathways: The Impact of Phase II Metabolism of<br/>Pharmaceuticals on a One Health Assessment</b><br><i>Harry Elliss - University of Bath, United Kingdom</i>  |
| <b>12:10</b> | <b>OR16 - Tailoring Prioritization Strategies for Risk Assessment and Identification of<br/>Indicator Substances of Emerging Concern</b><br><i>Mira Celic - Catalan Institute for Water Research, Spain</i>   |
| <b>12:30</b> | <b>O17 - Pharmaceuticals in Water, a struggle that we can fight with mainly a single<br/>stationary phase</b><br><i>Emanuele Ceccon - Restek, Italy</i>   |
| <b>12:50</b> | <b>INSTRUMENTATION PILL: Exploring the Environmental Impact: Shimadzu's Analysis<br/>of Toxic Substances Adsorbed on Microplastics</b><br><i>Domingo Pastran - Shimadzu Italia</i>  |
| <b>13:00</b> | <i>Presentation of the next ICRAPHE conference in Aveiro from Vania Calisto</i>   |
| <b>13:20</b> | <i>Awards &amp; Closing Ceremony</i>  |
| <b>13:30</b> | <i>Buffet Lunch</i>   |
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# Scientific Program

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# *Plenary Lecture*

# Nontarget screening approaches by HRMS and applications on the pharmaceuticals detection in environmental samples

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**Keywords:** *untargeted HRMS workflows; chemometrics; fate and transformation*

Pharmaceuticals are the most extensively studied classes of emerging contaminants, since they are prevalent in the environmental samples, due to their incomplete metabolism in humans and animals, improper disposal practices, and inefficiencies in wastewater treatment systems. Their detection in various environmental matrices, such as surface water, seawater, wastewater, biota, and soils, underscores the urgent need for comprehensive research. Understanding the fate and behavior of pharmaceuticals in the environment is crucial for assessing their potential ecological and human health risks. Therefore, systematic studies are essential to elucidate their pathways, persistence, and effects, ultimately guiding effective management strategies to safeguard both environmental quality and public health.

To address these challenges cutting-edge high-resolution mass spectrometric (HRMS) methodologies have been developed, for the comprehensive chemical characterization of environmental samples. These methodologies encompass both targeted and untargeted workflows, along with advanced chemometric tools. Several sophisticated software tools have been developed to support nontarget screening (NTS). For instance, a Quantitative Structure–Retention Relationship (QSRR) prediction model has been established to predict the retention time of new compounds [1], while the development of Retention Time Indices (RTI) enables the harmonization of retention times across different laboratories and LC conditions globally [2]. Moreover, a new concept to facilitate identification of unknowns via the effect of pH on their elution pattern using Cocamide Diethanolamine Homologous Series (C(n)-DEA) has been introduced [3]. This work has enabled the first generation of RI bank under variant pHs of mobile phase for LC. Additionally, an optimized machine learning model has been devised to predict the most appropriate instrumental method (LC-HRMS, GC-HRMS, or both) for chemical analysis [4], thereby enhancing confidence in suspect and NTS identifications. Furthermore, novel semi-quantification methods have been developed to accurately estimate the concentration levels of newly identified chemicals, even in the absence of reference standards, by considering the ionization efficiency of these compounds [5,6]. Moreover, innovative trend analysis tools have revealed important patterns of pharmaceutical occurrence and fate in environmental samples [7,8]. Recently, a harmonized identification scoring system for LC-HRMS-based NTS has been proposed to the research community [9]. These advanced methodologies have been successfully implemented in numerous environmental monitoring studies worldwide, including investigations in the Danube River [10] and the Black Sea [11], as well as biota samples [12] and wastewater epidemiology studies [13,14].

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## *Keynote Presentations*

## **Pharmaceuticals and emerging contaminants in the environment: estimating environmental and public health risks using water-based epidemiology**

***Barbara Kasprzyk-Hordern<sup>1</sup>, Nicola Ceolotto<sup>1</sup>, Felicity Elder<sup>1</sup>, Beth Holton<sup>1</sup>, Kishore Jagadeesan<sup>1</sup>, Kathryn Proctor<sup>1</sup>, Natalie Sims<sup>1</sup>, Like Xu<sup>1</sup>***

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***Keywords:*** *Pharmaceuticals, Emerging contaminants, Wastewater-based epidemiology*

Water-based epidemiology (WBE) provides a holistic understanding of public and environmental health as it encompasses city's metabolism in a single framework: from lifestyle choices, through to community-wide health status, exposure to harmful chemicals and health outcomes. Several groups of environmental and public health indicators (BCIs) were investigated (water quality indicators, industrial chemicals, personal care products, pesticides, illicit drugs, lifestyle chemicals, prescription pharmaceuticals, as well as genetic targets, such as antibiotic resistance genes) across cities in England. Mining of wastewater for BCIs was undertaken to understand spatiotemporal variability of BCIs in the context of geographical, city function as well as community-wide socioeconomic and demographic factors. The methods used were LC/MS (liquid chromatography and mass spectrometry), and q/dPCR (quantitative or digital polymerase chain reaction).

Spatiotemporal variabilities in BCIs in the studied inter-city system were investigated to estimate public and environmental exposure to hazardous chemicals and resulting environmental risks. Associations between public exposure and health outcomes were explored using pharmaceutical BCIs as proxies for community's health.

## The Impact of Using Reclaimed Waters for Greenhouse Crop Irrigation: Microplastics, Pesticides and Emerging Contaminants

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**Keywords:** Reclaimed water, irrigation, contaminants, microplastic

Adopting reclaimed water stands out as a key alternative to address water scarcity and quality issues. This versatile option serves urban, industrial, environmental, and agricultural needs with a significantly lower environmental impact than water transfers, offering notable environmental, economic, and social benefits. As such, it's increasingly incorporated into global water management strategies, including in the United States, Singapore, and Israel. Globally, reclaimed water mainly supports agricultural irrigation (32%), landscape irrigation (20%), and industrial processes (19%).

In Europe, water reuse is vital in the European Innovation Partnership on Water's Strategic Implementation Plan, with about 1 billion cubic meters of wastewater reused annually, accounting for 2.4% of treated effluents and less than 0.5% of the EU's freshwater withdrawals. Spain and Italy lead in EU water reuse, contributing significantly to the strategy's success.

The current study examines a pilot project on the effects of using reclaimed water for irrigating crops in greenhouses located in southeastern Spain. It evaluates the presence of various contaminants commonly found in wastewater, including pesticides, pharmaceuticals, and microplastics, within the soil, leaves, and crops over an entire growing season. By analyzing the distribution of these contaminants, the study provides a crucial perspective on the potential impacts of regular use of reclaimed water for irrigation purposes. This investigation aims to shed light on the environmental and health implications of incorporating treated wastewater into agricultural practices, offering valuable insights for sustainable water management in agricultural settings.

## Recent advances in the degradation of pharmaceuticals residues in macroscale and microscale photoreactors

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**Keywords:** *Pharmaceutical, Photoreactor, Degradation*

Advanced oxidation processes (AOP), such as ozonation, photolysis, UV-H<sub>2</sub>O<sub>2</sub>, solar photo-Fenton, photocatalysis and photoelectrocatalysis have been demonstrated to be effective in the degradation of persistent pharmaceuticals residues in surface water, groundwater and wastewater. Radiation transport, fluid-dynamics and mass transport are all critical interlinked factors that govern the performance of chemical, photochemical and photoelectrochemical reactors. Through efficient reactor design, the radiation field in photoreactors can be optimized, the reactor fluid-dynamics can be matched to the radiation field to yield higher pharmaceuticals residues conversion, and the gas-liquid mass transfer in ozonation reactors can be intensified. In this presentation, the degradation of persistent pharmaceutical residues in water such as antidepressants, antibiotics, oestrogens, antiviral, antiretrovirals, antifungal and illicit drugs will be discussed in multi-scale photoreactors systems at both micro- and macro-scale such as multi-orifice oscillatory baffled column [1-2], fluoropolymer microcapillary array film photoreactors [3-5], pilot-scale solar fountain and compound parabolic collectors [6-8] and full-scale solar photo-Fenton raceway reactors [9]. The optimisation and intensification of pharmaceuticals removal in these and other AOP photoreactors will be examined.

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## *Oral Presentations*

# Occurrence of pharmaceuticals in surface water sources and drinking water of the Romagna area (Italy)

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Dept. of Biological, Geological and Environmental Science (BiGeA), University of Bologna

**Keywords:** *Pharmaceuticals, Drinking water, HPLC-MS/MS*

Pharmaceuticals have been designed to confer significant benefits for human and animal health. However, they are increasingly recognized as contaminants of emerging concern when their residues enter the aquatic environments, posing potential risks to both human health and ecosystems [1]. Despite occurring in the water cycle at low levels, conventional water treatment processes are not designed specifically to, nor do they fully, remove pharmaceuticals from water. Due to the growing concern about the risk to public and environmental health, some pharmaceuticals have been included in the EU monitoring programs, such as the Watch Lists, regarding surface and drinking water [2,3]. The present investigation focuses on the occurrence of pharmaceuticals and other contaminants of emerging concern (including perfluorinated compounds and endocrine-disrupting compounds) in three drinking water treatment plants (DWTPs), as a case study. These three DWTPs cover a broad range of characteristics in terms of basin area, water sources, and anthropogenic pressures in the Romagna area (Emilia-Romagna region, Italy). Sampling campaigns were conducted biannually during April- October over the period of 2015 to 2020, with the purpose of analyzing the worst scenario in the study area represented by higher temperatures and low rainfall. Specific and selective analytical methods were applied by combined liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) and bioanalytical tools [4,5]. The objectives of the study were: a) to assess the presence of the selected contaminants in the water sources feeding the DWTPs, b) to evaluate their levels in treated water intended for human consumption, and c) to evaluate the potential biological impact on drinking water. The results obtained revealed caffeine, and carbamazepine as the most frequently detected pharmaceutical residues, particularly in raw water sources (ng- $\mu$ g/L range). In addition to pharmaceuticals, a predominant occurrence of industrial chemicals such as nonylphenol, PFOA, and bisphenol A was also observed in both source and treated waters (ng/L range). Conversely, the occurrence of other pharmaceuticals (ibuprofen, atenolol, diclofenac, estradiol, and ethinylestradiol) was sporadic. No estrogenic or genotoxic activities were induced by the water assessed, except for one sample. These findings highlight the importance of continuous monitoring strategies to mitigate pharmaceutical contamination in water resources.

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## Presence of Pharmaceuticals and Other Emerging Contaminants in Biogenic Matrices Used in Agriculture as Fertilizer

Sara Castiglioni<sup>1</sup>, Marco Fossati<sup>1</sup>, Giulia Salmoiraghi<sup>1</sup>, Silvia Schiarea<sup>1</sup>, SLURP Team\*

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**Keywords:** *emerging contaminants, biogenic matrices, mass spectrometry*

Several organic residues, such as sewage sludge, compost, and manure, may be used in agriculture, as valuable resources of organic carbon, nitrogen, phosphorus and micronutrients. This practice represents an ideal solution in terms of waste management priorities and circular economy, but may have potential adverse effects due to the presence of several classes of emerging contaminants (ECs), such as pharmaceuticals, antibiotics, personal care products and perfluoroalkyl compounds. ECs can be transferred to soils and crops with potential risks for human health. The aim of this study was to investigate the presence of about 40 ECs in different substrates (sewage sludge, compost, digestate, pig and cow manures) and to assess whether their application in agriculture poses a threat to the terrestrial ecosystem and human health.

The selection of ECs was done following several specific criteria: (i) presence in wastewater and sludge; (ii) potential for adsorption in sludge based on properties such as solid-liquid partition coefficient ( $K_d$ ) and octanol-water partition coefficient ( $K_{ow}$ ); (iii) persistence in sludge; (iv) potential for developing toxicological effect to humans and the ecosystem. The analysis of ECs was performed by accelerated solvent extraction (ASE), solid-phase extraction (SPE) and liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) analysis. A method previously developed by our research group [1] was modified for the new panel of analytes, and validated according the current directives [2]. Recoveries were higher than 70% with variability generally lower than 15%. The limits of quantification were in the low ng/g range demonstrating the high sensitivity of the adopted method.

Several of the substances investigated were found in the samples investigated at concentrations up to  $\mu\text{g/g}$  dry weight. Results showed different profiles of contamination in the different substrates investigated, with prevalence of fluoroquinolones (ciprofloxacin and levofloxacin), antibiotics for human use, in sewage sludge and of veterinary antibiotics, such as lincomycin, oxytetracycline and sulphadimethoxine, and estrogens in manure. Sewage sludge had also high levels (0.1 -2.2  $\mu\text{g/g}$  dry weight) for antimycotics and disinfectants. Plasticizers were among the most abundant contaminants in all the matrices (up to 10  $\mu\text{g/g}$  dry weight) including the compost.

The discharge of ECs into agricultural lands through the application of biogenic matrices can create a stressful condition for the terrestrial ecosystems threatening its functioning. Moreover, the presence of antibiotics may also promote the spread of antibiotic resistance, a serious threat for human health. This study allowed improving information on ECs presence in sludge and manure and their potential discharge in the environment, with the overall goal to convert a potentially risky practice such as the application of biogenic matrices in agriculture into a safe process for circular economy.

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# Retrospective Data Mining for the Estimation of Public and Environmental Exposure to Household and Industrial Chemicals

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**Keywords:** *retrospective, exposure, risk*

Household and Industrial chemicals (HICs) are used world-wide resulting in their ubiquitous presence in environmental matrices. Many of these compounds can be found in everyday products such as plastic food and drink containers, soap, and make-up as well as in pesticide products. As a result, HICs have been detected in wastewater. Detection of HICs in surface waters is largely due to the discharge of treated wastewater as well as agricultural run-off and industrial wastewater discharge [1,2]. This is of increasing concern as HICs have been linked to several adverse health effects including endocrine disruption, antimicrobial resistance, and neurotoxicity [3-5]. Estimating exposure to HICs by analysing parent compounds and human biomarkers in wastewater and river water is vital to monitor and assess public and environmental health.

A post-acquisition mass spectrometry data mining framework was developed for retrospective analysis of HICs in digitally frozen wastewater and river water samples from a multi-city Avon Catchment campaign (representing >75% of the whole catchment population [~1.5 million people] and covering a 2000 km<sup>2</sup> area). Digital samples were obtained using ultra-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry and stored as part of a mass spectral repository. The analytes selected included: 10 parent compounds (bisphenol A, 4 parabens and 5 antimicrobials) as well as metabolites (e.g., pyrethroid pesticide metabolites 3-phenoxybenzoic acid and DCCA). Confirmation was first undertaken with fragments and mass error, then with reference standards. Quantification of 14 analytes was achieved using an internal standard and calibration curve approach.

Results from the Avon Catchment campaign suggested that population size was the key driver of loads of the HICs studied with a few exceptions (e.g., bisphenol A and bisphenol A sulfate) which were driven by industrial contribution. For bisphenol A, inter-day variation indicative of occupational exposure was observed with higher daily loads on weekdays compared to weekends. Daily intakes were calculated for bisphenol A and pyrethroid pesticides using daily loads of their metabolites. When compared to tolerable daily intakes taken from literature, they suggested high risk from bisphenol A and low risk from pyrethroid pesticides. To evaluate environmental health, risk assessment was undertaken for 11 analytes using the risk quotient (RQ) method. Generally, RQ values obtained for river water were < 0.1 indicating low risk to environmental health. However, for triclosan and triclocarban (antimicrobial compounds), RQ values were > 1 across all matrices studied indicating high risk.

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## Untargeted nLC-MS/MS proteomic biomarkers characterization on population, health, environment and lifestyle status of three different neighbourhoods of Barcelona

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**Keywords:** *nLC-MS/MS, proteomic, sewage analysis*

Sewage Chemical-Information Mining (SCIM), whose wastewater-based epidemiology (WBE) plays an important role, is nowadays considered such a powerful approach to monitor health, environmental and lifestyle information of a specific community [1,2]. In this context, proteins have been proposed as potential biomarkers, which could complement the analytical information provided by currently available and often obsolete methods, e.g. Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD), both still used in order to estimate the percentage of inhabitants [3]. Anyway, proteomic dynamics in wastewater and the information hidden in these proteomic profiles are an open unexplored field of research yet [1]. A comprehensive untargeted protein characterization of wastewater, collected from 3 different economic status neighbourhoods sit in Barcelona (Catalonia, Spain), is proposed in this study. The soluble fraction of the aqueous samples was analyzed by using nano-Liquid Chromatography high-resolution tandem Mass Spectrometry (nLC-MS/MS) based on a shotgun proteomic approach: tryptic digests were injected into the chromatographic system coupled to an Orbitrap Exploris 480 High-Resolution Mass Spectrometer shotgun spectrometric analysis was performed in Data Dependent Acquisition (DDA) mode [4]. The tandem mass spectra were acquired in a positive electrospray ionisation (ESI) mode and in a Highest energy Collision Dissociation (HCD) mode, by setting the energy collision value at 28 eV. The MS/MS data were searched and matched in Protein Discoverer software, version 3.0 with the usual parameters for tryptic peptides and a 1% False-Discovery-Rate [5]. The complete proteomic fingerprint characterization, the identification between different organisms (human, animal or plant) and the semi-quantitative analysis of the main constituents are proposed here. The aim was to describe the proteic fingerprint observed and provide a possible correlation between the economic status of the three different neighbourhoods and the respective variability of eating, hygiene and health habits, by focusing on how different lifestyle habits can influence the management of aquatic purification plants and the environmental impact in general. The need for sustainable diets is then discussed by exploring the interactions between the food industry, nutrition, health and the environment, which are strongly interconnected [6].

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## Wastewater-based epidemiology as tool to monitor health and lifestyle of communities in near-real time

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In modern society, pharmaceuticals have an important role in managing various health conditions and improving overall individuals' wellbeing. Human activities and urban development contribute significantly to the release of pharmaceuticals into ecosystems and this discharge is related to human health and lifestyle habits[1–3]. Unlikely conventional methods reliant on surveys and prescription data, wastewater-based epidemiology (WBE) is an innovative approach for near-real time monitoring of population health and lifestyle. Human biomarkers (e.g., pain killers, illicit drugs, antidepressants, cardiovascular, and metabolites) are excreted by individuals into urban sewage system; as such, influent wastewater (IWW) can be considered as a cumulative sample representing entire community's health and lifestyle choices without the need to monitor everyone. Through the quantification of target compounds in IWW samples, it is possible to obtain information about pharmaceutical consumptions and lifestyle for a given wastewater catchment area[4]. In this study, a recent published WBE workflow [5] was applied to monitor trends in pharmaceutical usage during SARS-CoV-2 pandemic among communities in four catchments in Southwest of England, including pain killers, illicit drugs, cardiovascular, antidepressant drugs and personal care products (PCPs) and to assess health status, lifestyle and usage patterns across the pandemic. Two 24h-composite IWW samples per week were collected for two years across SARS-CoV-2 pandemic (Mar20-Mar22), processed using solid-phase-extraction and analysed using UPLC-ESI-QqQ. Daily loads (DLs) were calculated, considering concentrations and wastewater flows. Normalization of DLs using population served per catchment and human metabolism correction factors allowed estimation of per capita intake among different-sized communities. Furthermore, the environmental impact from PCPs usage was assessed in relation to PNEC and their application triggered during pandemic (e.g. sanitizing gel). Using this approach, it was possible to identify trends in pharmaceuticals consumption at different stages of the pandemic: pain killers' usage was aligned with SARS-CoV-2 cases, illicit drugs and physical activity related medications were aligned to lockdown restrictions and self-isolation. Cardiovascular drugs are used for chronic conditions, and in line with this they were unrelated to these SARS-CoV-2 indicators. PCPs showed higher environmental impact during lockdowns due to increasing awareness towards personal hygiene. This study showcased the application of WBE as innovative tool for monitoring health status of population. Indeed, WBE's near-real time monitoring of pharmaceuticals can prove fundamental in an identification of emerging health concerns due to the usage of pharmaceuticals data as proxy for a community's health and disease status. This will ultimately provide data-driven evidence to plan and assess effectiveness of interventions that can reduce environmental impact and resource wastage.

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## A first evaluation of presence of Polyfluoroalkyl Substances in stranded dolphins, sea turtles and sharks (Tuscany Coast)

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**Keywords:** PFAS, HRMS, Marine Animals

In this first study, we investigated the presence of PFAS in tissues of some specimen of striped dolphins (*Stenella coeruleoalba*), sea turtles (*Caretta caretta*) and different shark species (*Prionace glauca*, *Carcharhinus plumbeus* and *Isurus oxhyrinchus*) stranded or accidentally caught along Tuscany coast between 2020 and 2022.

Diverse PFAS were measured at high concentration in the tissues of dolphins (blood, brain, liver and muscle), whereas only PFOS was detected above detection limits in blood, liver and muscle samples of sea turtles and sharks. Liver tissue showed the highest PFAS levels, whereby PFOS was the dominant compound of the fingerprint. PFOS levels in dolphin liver ( $148 \pm 104$  ng/g ww; N = 23) were 10 fold higher than in the liver of the other marine species ( $1.12 \pm 1.09$  ng/g ww; N=9 and  $1.22$  ng/g ww; N=2 for sharks and sea turtles, respectively).

Suspect screening analysis allowed identifying 2 novel perfluorosulfonamides (FBSA(C4) and FHxSA(C6)) in all the analysed tissues of dolphin, as well as a series of n:3 fluorotelomer carboxylic acid (FTCA) in liver tissue only.

Lacking of accumulation pattern and elevated levels of PFCA in the liver suggested a high level of metabolism of PFCA precursor compounds. This hypothesis was supported by the presence in liver of high levels of n:3 FTCA - stable intermediates of the metabolism of perfluorotelomers. In contrast, the striped dolphin probably lacks, totally or partially, the ability of transforming perfluorosulfonamides to PFSA within the liver.

Our findings demonstrated that PFAA and perfluorosulfonamides accumulate in the marine cetacean species, whereas in sea turtles and sharks living in the same area accumulation does not occur. Metabolism in liver of fluorotelomer precursors seems to be the main source of PFCA in dolphins. Further studies should be necessary to disentangle if the main pathway of exposure to precursors is the breathing or the diet

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## Using a flow mode tubular reactor under natural solar irradiation for antibiotics' removal from water

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**Keywords:** *Antibiotics, Photocatalysis, Flow mode.*

Given that wastewater treatments are not designed for antibiotics' removal, and also due to their extensive use, these compounds are commonly found in the aquatic environment, which sets the risk for bacterial resistance. Thus, a growing effort in the development of efficient and sustainable treatments for their removal from contaminated effluents has been observed in the past few years. The use of photocatalysis is considered as a promising strategy for the sustainable solar-driven removal of antibiotics from aqueous effluents. For such purpose, in this work, photocatalysts were synthesized by the incorporation of 4 % (w/w) of carbon quantum dots (CQDs) into commercial (P25) titanium dioxide (TiO<sub>2</sub>) (TiO<sub>2</sub>/CQDs). Two types of CQDs, which were synthesized under hydrothermal treatment using: i) citric acid and urea (CQDs-CAU); or ii) citric acid only (CQDs-CA), were subsequently incorporated into P25 TiO<sub>2</sub>. The composites were evaluated for the solar-driven photocatalytic removal of sulfadiazine (SDZ) and oxolinic acid (OXA) from two different synthetic matrices - phosphate buffer solution (PBS, used to simulate fresh water) and synthetic sea salt solution (SSS, used to simulate brackish water). Initially, the evaluation of the photocatalyst dosage for each antibiotic and matrix was studied under batch conditions using a solar simulator. After selecting the appropriate photocatalysts dosage, they were tested in a tubular reactor operated under flow mode using natural solar radiation, to better assess the applicability in wastewater treatment plants. The use of 500 mg L<sup>-1</sup> of TiO<sub>2</sub>-CQDs-CA increased the SDZ pseudo-first order rate constant (*k*) 103 times, in PBS, while in SSS the increase was of 87 times using 1000 mg L<sup>-1</sup> of TiO<sub>2</sub>-CQDs-CAU. For OXA, the *k* increase was not as pronounced, being 8 and 6 times higher in PBS and in SSS, using 500 and 1000 mg L<sup>-1</sup> of TiO<sub>2</sub>-CQDs-CA, respectively. Obtained results showed that the produced TiO<sub>2</sub>/CQDs (4 % (w/w)) enhanced the photodegradation of both antibiotics, which confirmed their promising application in the treatment of contaminated effluents. Also, the employed solar-based flow mode tubular reactor was shown to be a sustainable and economical solution for water treatment systems.

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## Biochar Derived from Forest Residues: A Sustainable Solution for Venlafaxine Removal, Promoting Waste Valorization and Water Reuse

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**Keywords:** *Venlafaxine, Adsorption, Biochar.*

Organic contaminants in water have surged due to industrial and agricultural expansion, leading to significant pollution and water scarcity [1,2]. Venlafaxine (VEN) stands out among these pollutants due to its harmful effects on human health and the environment [3,4]. Several methods like photo-Fenton and chlorine dioxide have been explored for VEN removal [3,4], and adsorption has proven highly effective. Intensive research efforts were undertaken to create effective adsorbents for eliminating VEN, such as vermiculite-derived adsorbents [5]; however, no study has yet focused on the removal of VEN using biochar, which has received significant scientific attention due to its significant properties, such as high surface area, availability, ease of preparation, and low cost. For this reason, this research investigates the adsorption efficiency of biochar for eliminating Venlafaxine as a pharmaceutical target. The adsorption parameters such as biochar mass, pH and VEN initial concentration have been evaluated and optimized. The biochar has shown an effective removal for VEN with an efficiency of 96% within only 45 min, which is high compared to other methods in the literature. Pollutant chemisorption on biochar surfaces was investigated using isotherms and kinetic models. After that, a regeneration investigation was conducted, and the results indicated a reusability of around 89% in the first cycle, which is acceptable. As the first study to focus on VEN removal using biochar, this communication aims to improve the quality of reclaimed wastewater for safe and sustainable reuse by using biochar as an adsorbent to eliminate hazardous organic compounds in water, promoting circular resource management practices and addressing environmental issues.

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# Sustainable photocatalysts for the treatment of antibiotic-polluted waters: A central composite design for optimizing the synergistic roles of TiO<sub>2</sub>, Carbon Quantum Dots, and Magnetic Nanoparticles

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**Keywords:** *Antibiotics, Photodegradation, Water remediation.*

Antibiotics are a must in the world health system to save the lives of millions of people. Yet, their presence in the environment is well documented and has been associated with increasing antimicrobial resistance. Wastewater treatment plants (WWTP) are not designed to efficiently remove these contaminants and, therefore, they constitute important sources of antibiotics for the aquatic environment. New solutions have been studied, including the application of solar-driven photocatalysis, an advanced oxidation process. This study aimed at the synthesis of a novel photocatalyst constituted by magnetic nanoparticles (MP), Carbon Quantum Dots (CQDs) and TiO<sub>2</sub> using a co-precipitation methodology. In order to optimize the synthesis of sustainable materials efficient in the photocatalytic removal of antibiotics from water, a Central Composite Design (CCD) was used. As a Response Surface Methodology (RSM), CCD is a statistical and mathematical tool that allows the description of interference by chemical, physical and engineering parameters/factors in a process by a regression equation. In this work, CQDs were synthesized applying a hydrothermal methodology using citric acid and urea (as dopant of N). Then, the photocatalysts were prepared by a co-precipitation technique with iron salts, TiO<sub>2</sub> (P25) and CQDs. For the optimization of the photocatalyst synthesis, the following factors were defined in the CCD: (i) Quantity of urea in CQDs; (ii) Proportion between Fe and Ti; (iii) Reaction time. Then, the photocatalytic removal of three different antibiotics from water, namely amoxicillin (AMX), sulfamethoxazole (SMX), and trimethoprim (TMP), using solar simulated radiation, together with results from vibrating sample magnetometry (VSM) were the selected CCD responses. The optimal synthesis procedure was determined using RSM and the so synthesized photocatalyst was tested for the removal of the target antibiotics. The practical application of the synthesized photocatalyst was assessed by evaluating the effects of photocatalyst dosage, pH and antibiotic concentration. Next in line is the application in real water matrices associated with reuse cycles to evaluate stability of the photocatalyst. Indeed, the magnetic recuperation of the synthesized photocatalyst and its subsequent reutilization are key features for its promising application as tertiary treatment in WWTP, allowing for a green solar driven removal of antibiotics.

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## Photodegradation behaviour of antibiotics in environmental matrices under simulated solar radiation

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**Keywords:** *Photolysis, antibiotics, solar radiation*

The presence of antibiotics in the aquatic environment contributes to the generation of antimicrobial resistance, which is one of the most important threats to global health and therefore matter of great concern. Photolysis is known to be a major degradation pathway for these pollutants, occurring as direct photolysis (the pollutant itself absorbs photons that induce transformations), and indirect photolysis (photosensitizers absorb solar radiation, reaching an excited state and generating reactive species effective on pollutant's degradation).

In this work, environmental factors affecting photodegradation (such as pH, dissolved organic matter (DOM), salinity) under simulated solar radiation were evaluated in order to have a better knowledge about the persistence of four antibiotics (sulfamethoxazole (SMX), oxolinic acid (OXA), sulfadiazine (SDZ), and amoxicillin (AMX)) in the aquatic environment. For this purpose, different synthetic matrices (phosphate buffer solution (PBS, pH 7.3-8.0), humic substances (humic acids, fulvic acids and XAD-4) and high salinity solutions) were used, as well as environmental aqueous matrices from fresh and brackish origin.

For SMX, a very fast photodegradation in PBS was attained, showing a half-life time ( $t_{1/2}$ ) of  $0.86 \pm 0.04$  h; however, in environmental matrices, the SMX photodegradation was much slower, with  $t_{1/2}$  between  $5.4 \pm 0.5$  h and  $5.9 \pm 0.4$  h. Same tendency was observed for OXA: photodegradation in environmental matrices ( $t_{1/2}$  between  $1.65 \pm 0.03$  h and  $4.03 \pm 0.04$  h) was slower than photodegradation in PBS ( $t_{1/2} = 0.99 \pm 0.04$  h). As for SDZ, photodegradation in environmental matrices ( $t_{1/2}$  between  $2.3 \pm 0.1$  h and  $2.32 \pm 0.05$  h) was found to be much faster than photodegradation in PBS ( $t_{1/2} = 6.76 \pm 0.07$  h). Finally, for AMX, photodegradation in environmental water ( $t_{1/2}$  between  $12.5 \pm 0.3$  h and  $3.8 \pm 0.3$  h) was, similarly to SDZ, faster than photodegradation in PBS ( $t_{1/2} = 21.0 \pm 0.6$  h). Observations may be related to the effect of the matrices' characteristics, previously evaluated. For instance, in what concerns DOM, it had an inhibitory effect on the photodegradation of SMX and OXA, whilst for SDZ and AMX, it represented a photosensitizing effect.

Overall, the characteristics of the matrices were found to be determinant factors in the photodegradation behaviour of the evaluated antibiotics in the aquatic environment.

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## Enzyme-functionalized biochar for the enhanced removal of the anti-inflammatory diclofenac from water

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**Keywords:** *Enzyme-mediated degradation; Waste-based biochar; Wastewater treatment*

Conventional wastewater treatment plants are not effective in removing pharmaceutical compounds, resulting in their accumulation in the aquatic environment. As a result, improving wastewater treatment is of vital importance to mitigate the entrance of these compounds into the environment. A large number of advanced wastewater treatments has been evaluated for this purpose, including adsorption and enzymatic degradation. While adsorption by carbon materials is quite effective, difficult regeneration/reutilization cycles are still a drawback of this methodology. In this context, functionalization of the adsorbent surface with enzymes can be an effective strategy to increase the lifetime of these materials. Therefore, this work aims to study the combination of adsorption and enzyme-mediated degradation of pharmaceuticals, with these biocatalysts are immobilized in biochar, as a plausible tertiary treatment for the removal of these microcontaminants from water. This approach intends to evaluate if the synergistic combination of adsorption with enzymatic transformation will lead to a higher removal of pharmaceuticals from water. Accordingly, a waste-based biochar obtained from spent-brewery grains (SBG) was produced by microwave pyrolysis of this industrial byproduct at 800 °C for 20 min. The obtained biochar was subsequently functionalized with commercial laccase, an oxidoreductase enzyme, by physical immobilization. The produced composites were evaluated in terms of immobilization percentage, enzyme activity, and enzymatic stability over time. The adsorption/degradation performance of the composite was tested for the removal of the anti-inflammatory pharmaceutical diclofenac (DCF) from aqueous matrices (with pharmaceutical concentration of 5 mg/L), at controlled pH (5 and 7) and temperature (40 °C) in batch conditions under stirring (350 rpm) for 24 h. The obtained results were compared to the removal efficiency of the non-functionalized biochar and the biochar functionalized with the inactive enzyme, to better understand the different contributions to the overall percentage of DCF removal.

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## Innovative methods to remove phosphodiesterase 5 inhibitors from polluted water

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**Keywords:** *Erectile dysfunction, environment, advanced oxidation processes*

The Fourth International Consultation on Sexual Medicine defined Erectile dysfunction (ED) as "the constant or recurrent inability to achieve and maintain a penile erection sufficient for sexual satisfaction" [1]. One of the solutions to ED is the use of phosphodiesterase 5 (PDE5) inhibitors. Among them, sildenafil and tadalafil are two of the most commonly used [2]. In recent years, PDE5 inhibitors have received particular attention from the scientific community due to the high number of sales and the consequent presence in the environment, particularly in wastewater [3]. According to a study carried out in 2023, sales of sildenafil are incredibly high, even among young people aged 20-30 years, who perceive sildenafil and similar drugs as substances for fun purposes rather than under medical prescription to treat an actual pathology [4]. As a result, leaching of these pharmaceuticals into the aquatic environment is expected [5]. Besides, these molecules, so-called "emerging contaminants", escape conventional activated sludge treatments and spread into the environment. For this reason, the aim of this work is the identification of additional technologies that can completely remove these recalcitrant compounds. Advanced oxidation processes (AOPs) and adsorption on natural materials represent an alternative and promising treatment of wastewater containing recalcitrant organic compounds. The results obtained showed that AOPs combined with adsorption on natural materials are efficient processes for the removal of PDE5 inhibitors and their transformation products from aqueous bodies.

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## Optimization of functionalized biomass-based materials for the removal of antibiotics from wastewater

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**Keywords:** *Multivariable optimization; adsorption; activated carbon*

Adsorption by activated carbon (AC) has proven to be an effective process for the removal of recalcitrant pharmaceuticals, namely antibiotics, from water. High specific surface area ( $S_{\text{BET}}$ ) and controllable surface functionalization are some of the most relevant properties of AC in this context. However, some drawbacks still hinder the large-scale application of AC, including the non-renewable nature of most of the precursors of commercially available AC. The use of agro-industrial biomass wastes as AC precursors can help to overcome such disadvantages by extracting maximum value from underutilized carbon sources, which are frequently discarded without being properly valorized. To ensure that these alternative raw materials lead to adsorbents with high adsorption performance, it is crucial to optimize their conversion into AC and test the effectiveness of the obtained AC in wastewater matrices and under competitive conditions to understand their potentialities.

In this work, the microwave-assisted conversion of spent brewery grains, one of the major solid wastes of the brewing industry, into AC for application in the removal of antibiotics from wastewater was evaluated. A multivariate analysis was carried out to optimize the production of AC and minimize the use of activating agents and production time. For this purpose, a fractional factorial design was applied to study the effect of three production variables, i.e., activating agent:precursor ratio, pyrolysis temperature, and residence time, at 3 levels, as well as of a fourth variable, i.e., nature of the activating agent, at 2 levels. Product yield,  $S_{\text{BET}}$ , total organic carbon, and the removal of three antibiotics (sulfamethoxazole; trimethoprim, and ciprofloxacin) in batch adsorption systems were selected as responses for statistical analysis, which allowed finding the optimal production conditions. The AC produced under the optimum conditions (with  $\text{K}_2\text{CO}_3$  at an activating agent:precursor ratio of 1:2, obtained at 800 °C for 20 min) was then used for adsorption kinetic and equilibrium studies on the removal of the three target antibiotics in ultrapure water, buffered ultrapure water (pH 8), and effluent from a wastewater treatment plant. The effects of pH (between 4 and 10) and competitive conditions on adsorption were also evaluated [1]. Finally, to enhance the performance of the optimized AC, different surface functionalization strategies with nitrogen, sulfur, and oxygen groups were explored [2]. Elemental analysis and X-ray photoelectron spectroscopy were carried out to support the success of the functionalization and the produced materials were evaluated under the same conditions tested for the non-functionalized AC. Oxygen functionalization was the most successful method to enhance the performance of the biomass waste-derived AC produced here, with a Langmuir maximum adsorption capacity up to 58% higher than that of the non-functionalized one. The results obtained demonstrate that spent brewery grains are an adequate AC precursor for the efficient removal of antibiotics from wastewater.

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## Combating antimicrobial resistance through wastewater “fingerprinting”: Surveillance and environmental risk assessment of antimicrobial usage in Welsh hospitals and communities

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**Keywords:** antimicrobial resistance, environmental risk assessment, public health

Antimicrobial resistance (AMR) has been identified by the World Health Organization among the top 10 greatest threats to global health [1]. Consumption of antibiotics results in antibiotic residues and their metabolites entering wastewater, where their continued presence, even at low concentrations, has been shown to exert a selective pressure on bacteria leading to increased antibacterial resistance [2]. Further, hospital wastewater can contain significantly higher concentrations of antibiotics [3] posing ecotoxicological risks [4]. The aim of this research is to investigate the spread of AMR via wastewater by comparing antimicrobial residue prevalence data with AMR data (i.e., prevalence of antibiotic resistant genes). For antimicrobial residue surveillance, over 275 wastewater samples were collected from 15 sites (influent from 8 community wastewater treatment plants and effluent from 7 hospitals) across Wales during two 3-month sampling campaigns—a summer campaign (May–July 2023) sampling 5 consecutive days per week each month, and a winter sampling campaign (Dec. 2023–Feb. 2024) sampling 3 consecutive days per week each month from selected sites. Using a validated UPLC–MS/MS method, over 120 antimicrobials and metabolites were quantified from numerous classes including: quinolones, beta-lactams, macrolides, sulfonamides, tetracyclines, antifungals, and antivirals. This comprehensive assessment presents a spatial evaluation of antimicrobial usage across Wales, and identifies seasonal trends. Surveillance data from a smaller selection of antimicrobials during the summer sampling campaign will be presented with a focus on the ecotoxicological risks. Interim results support the hypothesis that hospital wastewater is an area of concern as antimicrobial concentrations are significantly higher than community wastewater across numerous antimicrobial classes. During this time period, three hospitals had sulfamethoxazole concentrations which were more than double the predicted no-effect concentration for antibiotic resistance selection (PNEC-RS), and over 50-fold higher than the predicted no-effect concentration for ecotoxicity (PNEC-Eco) [5]. For clarithromycin, the overwhelming majority of community sites and all hospital sites exceeded the PNEC-RS, with one hospital having concentrations exceeding the PNEC-Eco by >1500-fold on numerous days [5]. These results confirm the importance of hospitals as hotspots of AMR.

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## Overlooked Metabolic Pathways: The Impact of Phase II Metabolism of Pharmaceuticals on a One Health Assessment

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**Keywords:** *Environmental Risk Assessment, Mass Spectrometry, Phase II Metabolism*

Wastewater Treatment Plants (WWTPs) act as a primary interface between humans and the environment, sharing an “immediate, intimate and inseparable” connection[1]. As a result, One Health frameworks are adopted to simultaneously understand human health and the impact of humans on the environment. Human health is often estimated via wastewater-based epidemiology (WBE), where concentrations of pharmaceuticals in influent wastewater can be back-calculated to estimate their consumption at the community level, which can be used as a proxy for public health. During pharmaceutical consumption, a compound undergoes a chemical change, typically increasing hydrophilicity and, in turn, facilitating excretion. Pharmaceutical residues enter the environment via wastewater effluent after treatment, or sewer overflows. During excretion, 40-75% of all clinical drugs undergo phase II metabolism via glucuronidation[2]; this commonality requires further investigation to establish frameworks enabling the accurate back-calculation of pharmaceutical consumption and further understanding of its impact on the aquatic environment. Wastewater treatment processes of phase II metabolites can be limited due to the required deconjugation, leading to poor removal efficiency and high concentrations entering the water system; this is evident during observed direct-disposal events[3]. This study assesses the impact of phase II metabolism in influent wastewater to highlight the uncertainties of WBE calculations and model this impact to the wider environment. In the case of sewer overflows, phase II conjugates can release hotspots of the parent molecule downstream (via deconjugation), leading to microenvironments containing high pharmaceutical concentrations, causing potential acute ecotoxicological effects. Enzymatic deconjugation via  $\beta$ -Glucuronidase uncovers the degree of phase II metabolism. A comprehensive LC-MS/MS framework for over 250 compounds was deployed to analyse this time-dependent sample set, with a comprehensive understanding provided for 30 pharmaceuticals and lifestyle chemicals. The extent of phase II metabolism varied from 22%  $\pm$  4% and 59%  $\pm$  8% to 93%  $\pm$  2% for carbamazepine, morphine and nicotine, respectively. This is not limited to parent compounds as large degrees of phase II metabolism were also observed in the excretion of phase I metabolites, such as O-desmethyl naproxen, where a 132%  $\pm$  17% increase in concentration occurred following deconjugation. A complete understanding of influent wastewater allows for accurate prediction of the potential risk to the aquatic environment in both normal and wet-weather scenarios where combined-sewer overflows are common.

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## Tailoring Prioritization Strategies for Risk Assessment and Identification of Indicator Substances of Emerging Concern

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**Keywords:** *Compounds of Emerging Concern; Ultra-performance liquid chromatography (UPLC); Risk Assessment.*

Contaminants of Emerging Concern (CECs), known for their adverse effects on aquatic organisms and potential risks to the environment and human health, are not currently integrated into legislation or national routine monitoring programs. However, given their widespread occurrence and significant impact, future legislation may mandate their inclusion. With the abundance of CECs, it's crucial to selectively include a limited subset in monitoring programs tailored to specific study areas, focusing on those of major environmental concern. While many studies have employed prioritization criteria, the majority rely on risk-based approaches. Yet, there's a need to broaden these criteria to encompass relevant compounds. Hence, this study aims to customize prioritization strategies for selecting indicator substances of wastewater contamination deserving monitoring across various environments, including urban, agricultural, and industrial areas. Initially, a comprehensive assessment was conducted to identify a vast number of CECs in influent and effluent samples from three wastewater treatment plants (WWTPs) across three different seasons. A total of 140 monitored compounds were analyzed using multiresidue methods, revealing 91 compounds in influent wastewater and 87 in effluent, with concentrations ranging from ng/L to µg/L in a total of 54 samples. Despite treatment, significant levels of CECs persisted in effluent samples, highlighting the necessity for improved wastewater management strategies. However, the urban industrial area exhibited a higher number of detected contaminants (79) compared to the agricultural area (67) and the suburban area (39). Priority CECs in each area were further selected by applying a novel multifactorial methodology, considering different criteria such as persistence, mobility, toxicity, bioaccumulation, occurrence, frequency of detection, and removal. After applying our multi-criteria prioritization, among the 87 detected compounds in all effluents, 26 exceeded the established threshold in the study, comprising 15 pharmaceuticals, 10 antibiotics, and 1 pesticide. Notably, 4 compounds were identified as most relevant in suburban areas, 13 compounds in agricultural urban areas, and 24 compounds in industrial-urban areas. Finally, only 3 out of the 26 indicator chemicals were consistently present across all three zones, highlighting their priority status: the anti-inflammatory diclofenac (DCF), psychiatric drug lorazepam (LZP), and diuretic hydrochlorothiazide (HCTZ). Our findings contribute to a better understanding of CEC occurrence and behavior in wastewater systems, stressing the importance of comprehensive monitoring and prioritization of indicator chemicals to safeguard environmental and human health. This proposed prioritization strategy for CECs, based on their exposure levels and adverse biological effects, provides valuable insights for risk assessment and management in wastewater treatment practices specific to various areas.

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## **Pharmaceutical in water a struggle that we can fight with mainly a single stationary phase**

*Emanuele Ceccon*

Restek S.r.L.

**Keywords:** *Pharmaceuticals. Enviro, byphenil*

One of the most important release of pharmaceutical into the enviro is caused by human consumption and usage, this lead to have a first final destination for this substancies the water, the same water that we do use to clean ourself or to drink.

Which are the major pharmaceutical families involved in this struggle?

Which impact do they have for us?

Is there a solution that could definitely address The vast majority of our analytical needs when it come to analyze our samples by LC MSMS?

Why this solution work and how?

This presentation as in Restek style aim to approach in the most technical direction that even if pharmaceuticals in water are a huge world, actually do exist a broad and simple solution to try to solve it

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## *Poster Presentations*

## Effects of environmental metformin and its main metabolite guanylurea on the marine mussel *Mytilus galloprovincialis*, at adult and early life stages

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**Keywords:** Pharmaceuticals, marine mollusks, biomarkers

Metformin (MET) is by far the most prescribed glucose-lowering oral medicine worldwide. It is estimated that >150 million people each year take this drug, and its consumption is expected to increase assuming the current epidemic of diabetes mellitus [1]. MET acts on the regulation of glucose levels by activating adenosine monophosphate kinase, thus impacting cellular energy balance; additionally, its therapeutic effects are believed to derive from an insulin-sensitizing action. Due to such widespread use and the fact that it is excreted by the kidney primarily unchanged, MET is one of the most commonly found drugs in aquatic environments [2] where it has the potential to exert biological effects on aquatic organisms [3]. Considering their occurrence in the environment, MET and its main transformation product, guanylurea (GUA), have been included in 2022 in the fourth version of the European surface water watch list [4] under the Water Framework Directive. Surprisingly, the limit of quantification that have been set for MET (156 µg/L) is much higher than the concentration of MET found in Europe surface waters, with an average value of about 1 µg/L [5]. The goal of this study has been to evaluate the effects of the exposure of the non-target species *Mytilus galloprovincialis* to environmentally relevant concentrations of MET and GUA. Adult mussels were exposed to 0.5, 5, and 10 ng/L MET and GUA for three days and biomarker responses were assessed in digestive gland. Mussels exposed to the highest tested concentration (10 ng/L) of MET and GUA showed a significant decrease in lysosome membrane stability and increase of lysosome/cytosol ratio; MET also significantly increased neutral lipid and lipofuscin contents in the gland. Since drugs, even at low concentrations, can adversely affect organisms particularly in the early stages of development, we extended our study on early life stages. Eight concentrations of each drug (0.5-500 ng/L range) were tested on gamete fertilization and larval development at 48 h post fertilization, and no significant effects were found. Specific mechanisms of action of MET and GUA in marine mollusks are not known, yet. Thus, further studies are needed to find their cellular/molecular targets and to understand the risk they represent for non-target organisms. It is noteworthy, that alteration of digestive gland parameters has been observed in adult mussels after the exposure to 10 ng/L MET or GUA, confirming that mussels are affected already at concentrations much lower than those suggested as LOQ by the UE Watch list, thus supporting the request to lower this limit [6].

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## PFAS presence in Antarctic drinking waters

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**Keywords:** Per- and polyfluoroalkyl substances, Antarctic, drinking waters.

Per- and polyfluoroalkyl substances (PFAS), are highly persistent substances, known as the “forever chemicals”. According to scientific results (EFSA 2020), health consequences caused by PFOA and PFOS can be hepatotoxicity, growth disturbance, neurobehavioral toxicity, immunotoxicity, reproductive toxicity, pulmonary and renal toxicity, and hormonal effects (thyroid gland involvement in the case of PFOS). Drinking water is at the moment being evaluated as one of the main exposure routes of PFAS for humans, and can be particularly relevant in isolated locations where poor potabilizing systems are implemented or long storing periods for drinking water are required.

Thus, this work aims to analyze 6 samples of drinking water from Argentinian Antarctic bases: the Belgrano Base (Vashel Bay, main tank and secondary tank), Orkney Base (Laurie Island of South Orkney Islands, supply well water), and Petrel base (Dundee Island, water from the supply tank and tap water of the main house), all of them on the Antarctic Peninsula. This is the first study to analyze the presence of PFAS in water for human use in Antarctica.

The analysis was done using high-throughput cutting-edge methodologies based on HRMS combining ionization sources such as heated electrospray (HESI) and atmospheric pressure chemical ionization (APCI) to sort out the complexity on the analysis of PFAS by extending the analyte coverage of the LC-HRMS methodologies. Briefly, a validated protocol using solid phase extraction HLB cartridges was applied to extract not only the acknowledged and regulated ionic PFAS, but a wide variety of compounds, including 42 targeted substances from different families. Among the targeted compounds there were also brand new emerging PFAS such as ADONA or HFPO-DA (GenX). The analysis was performed on a Thermo Scientific Dionex UltiMate 3000 UHPLC coupled to a Thermo Scientific Q Exactive Focus quadrupole-Orbitrap mass spectrometer using independent runs a HESI and an APCI ionization sources (Thermo-Fisher Scientific, CA, USA).

Preliminary results show that 14 individual PFASs have been detected in the drinking water from the 3 Argentinian bases, including PFOA, PFBA, PFBS and FOSA. PFOS was detected under the quantification levels. The highest individual concentrations were always below 5 ng/L, for short chain acids such as PFBA, PFBS and PFHxPA. The highest total concentrations were found at Orcadas base (9.39 ng/L) followed by both tanks from the Belgrano base (8.23 and 8.65 ng/L). The preliminary results indicate “safe” levels of PFAS according to EU Drinking Water Directive (2020), as the sum of 20 PFAS were far below 100 ng L<sup>-1</sup> or a limit of 0.5 µg/l for individual PFASs. Other organizations such as the US EPA limit the permissible content of PFOA and PFOS to 4 parts per trillion in drinking water, three additional PFAS chemicals are limited to 10 parts per trillion, which indeed are in the same range in some of the samples.

For the non-target screening including novel ionization modes such as APCI, is being conducted using the Compound Discoverer 3.3.2.31 (Thermo-Fisher Scientific) software to treat the data with a PFAS specifically designed workflow. The different filters used included the Kendrick Mass Defect (KMD). This analysis aims to detect the max number of fluorinated substances, not only the regulated ones (to match with the requirements of the legislation) but also to discover other PFAS in drinking water at Antarctic bases. A system of surveillance and control of the presence of these substances in Antarctic bases should be implemented to protect researchers and itinerant population as well as reduce their environmental presence.

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## Degradation of estrogenic hormones using UV-Visible Spectroscopy

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**Keywords:** Estrogens; Degradation; UV-Visible

Estrone, 17 $\beta$ -estradiol and estriol are natural female sex hormones produced by humans, mammals, and other vertebrates. Ethynilestradiol is a synthetic estrogen that has therapeutic uses, like oral contraception.

The estrogens monitorization in the environment has been coming to win great interest, especially due the fact of frequent detection in Waste Waters Treatment Plants, waters for human consumption, rivers, lakes, etc., at concentrations in the order of  $\mu\text{g/L}$  and  $\text{ng/L}$ . The presence of these compounds in water can cause several adverse effects in the physiology of human being or other present organisms in the waters, as the fish.

The present work aims to study the degradation of estrona, 17 $\beta$ -estradiol, 17 $\alpha$ -estradiol and estriol on some conditions like direct solar radiation and the effect of temperature at 4°, 20° and 30°C, stored at darkness.

Individual solutions of the four estrogens were prepared in aqueous solution with sodium borate and cholic acid, at concentration of 0,1g/L and with a final pH of 9,2.

The individual degradation determinations were analysed by UV-Visible Spectroscopy, after 7, 14, 21, 28, 35, 63, 91 and 126 days, in the above referred conditions, at a wavelength of 281nm. The spectrum shows the variation of absorbance of each estrogen, expressed as percentage, as a function of time.

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## Degradation of estrogenic hormones using Capillary Electrophoresis

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**Keywords:** Estrogens; Degradation; Capillary Electrophoresis

Estrone, 17 $\beta$ -estradiol and estriol are natural female sex hormones produced by humans, mammals, and other vertebrates. Ethynilestradiol is a synthetic estrogen that has therapeutic uses, like oral contraception.

The estrogens monitorization in the environment has been coming to win great interest, especially due the fact of frequent detection in Waste Waters Treatment Plants, waters for human consumption, rivers, lakes, etc., at concentrations in the order of  $\mu\text{g/L}$  and  $\text{ng/L}$ . The presence of these compounds in water can cause several adverse effects in the physiology of human being or other present organisms in the waters, as the fish.

The present work aims to study the degradation of estrona, 17 $\beta$ -estradiol, 17 $\alpha$ -estradiol and estriol on some conditions like direct solar radiation and the effect of temperature at 4°, 20° and 30°C, stored at darkness.

Individual solutions of the four estrogens were prepared in aqueous solution with sodium borate and cholic acid, at concentration of 0,1g/L and with a final pH of 9,2.

The degradation of the four mixed estrogens was determined using Capillary Electrophoresis, with a diode array detector and cholic acid, sodium salt plus sodium borate as a background buffer. The results showed no significant degradation rates on samples subjected to different temperatures. However, the results from Capillary Electrophoresis analysis showed that, under direct solar radiation, after 126 days, the degradation rate varied between 75% and 100%.

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## Wastewater Based Epidemiology: Exposure to chemicals via household contaminants.

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**Keywords:** *Public Health, Wastewater-Based Epidemiology, Biomarker*

Every day we are exposed to a vast array of chemicals, whether that being intentionally, via the use of pharmaceuticals, or unintentionally, for example via polluted air, food, or occupational exposure. The monitoring of potentially hazardous chemicals is important in households due to the extended and repeated periods of time the public may spend within their homes, chronic exposure therefore may be a concern to public health. Potential chemicals of concern via households include mycotoxins and polyaromatic hydrocarbons both contained within foods or in contaminated air.<sup>1-3</sup> Wastewater-based epidemiology (WBE) can be utilised to calculate public exposure of these chemicals by quantifying the human metabolic products contained in wastewater through the use of high resolution mass spectrometry.<sup>4</sup> Chemicals used in the household, such as household pet medications, can cause environmental damage if exposed to river systems and therefore should be monitored. Targeted and non-targeted data-mining workflows have been applied to mass spectral repositories to determine potential chemicals of concern for both the public and the environment. Wastewater from five communities in south-west England (2015, 2023) were tested for biomarkers indicating human exposure to mycotoxins (e.g., deoxynivalenol, T-2 toxin, zearalenone), polyaromatic hydrocarbons (e.g., benzo[a]pyrene), and veterinary medications (e.g., imidacloprid, fipronil) - three classes of chemicals where exposure can cause negative health outcomes. WBE workflows were applied to calculate community wide intake, while river water samples collected from the same region were analysed to evaluate environmental exposure.

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## Evaluation of pharmaceuticals in water after the flood occurred in 2023 in Emilia-Romagna: a focus on Ravenna area

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**Keywords:** *pharmaceuticals; LC-MS/MS; Emilia-Romagna flood*

Many classes of pharmaceuticals have been detected in the aquatic environments worldwide over the last few decades, owing to increasing concern for the ecosystem and human health [1]. It is difficult to declare a safety level for each compound, thus most of them are still considered contaminants of emerging concern and generally not included in environmental regulations or drinking water standards. Several pharmaceuticals however have recently been added into the watch list of substances monitored by European countries in the field of water policies [2][3].

Extreme weather events are increasingly frequent also in territories where historically there was no need for prevention and protection, leading to the re-evaluation of emergency measures but also of environmental interventions. The flood event of May 2023 in Emilia-Romagna has been dramatic for people and infrastructure. Moreover, the environmental damage has been huge as the wastewater collection systems were compromised and there was an overload of the artificial drainage channels which rapidly poured anomalous quantities of water into the sea. The aim of our study was to investigate the occurrence of pharmaceuticals in fresh, coastal and drinking water after the flood in the Ravenna area, adopting an integrated chemical and biological approach. Chemical analysis, carried out via liquid-chromatography coupled to tandem mass spectrometry LC-MS/MS, were applied to evaluate the presence in the waters of 4 anti-inflammatory drugs (ibuprofen, diclofenac, naproxen, ketoprofen), 2 diuretics and 3 estrogens (17 $\beta$ -estradiol E2, estrone E1 and 17 $\alpha$ -ethynyl estradiol EE2); biological analysis were applied to evaluate the estrogenic potential of inland water samples.

Three sampling campaigns were conducted right after the flood, after one month and after four months. Water samples were collected from two main rivers involved in the flood, four artificial drainage channels also afflicted and the corresponding outlets to the sea for a total of forty-three samples. Further eight samples from the Ravenna drinking water treatment plants were also analysed to evaluate whether the altered quality of the incoming water could have compromised the purification process.

Water sampled from the Lamone river in May and June showed a slight estrogenic activity, while cellular cytotoxicity was found in the Reno river in October; water sample of the Cerba canal in June induced a weakly estrogenic activity too.

The results provide a detailed scenario of the water systems in the area for what regards pharmaceutical contamination. However, the lack of historical data does not allow to strictly correlate the effect of the flood to the data collected, although monitoring actions should be enhanced, especially for the drainage channels.

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## Quantification of nanoplastic uptake and distribution in the root, stem and leaves of the edible herb *Lepidum sativum*

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**Keywords:** *Nanoplastic uptake, Bioaccumulation, Translocation, Quantification, Food safety*

This study confirms the uptake, translocation and bioaccumulation of 100 nm polystyrene nanoplastics in the root, stem and leaves of the plant *Lepidum sativum* at exposure concentrations ranging from environmentally realistic 10 µg/L up to a high of 100 mg/L. Accumulation in plant tissues was characterised by aggregation in the intercellular spaces and heterogeneous distribution. Nanoplastic presence was confirmed in the root tips, root surface and stele, lateral roots, root hairs, stem vascular bundles, leaf veins and mesophyll, as well as leaf epidermis including stomatal sites. Quantification results show that majority of the particles were retained in the root and accumulation in stem and leaves was only 13 to 18 % of the median value in roots. There was a reduction of  $38.89 \pm 9.62$  % in the germination rate, 55 % in plant fresh weight, as well as in root weight (> 80 %), root length (> 60 %), shoot weight (51 to 78 %) and number of lateral roots (> 28 %) at exposure concentrations at and above 50 mg/L. However, lower, environmentally probable exposure concentrations did not affect the plant health significantly. Our results highlight the urgent need for further exploration of this issue from the point of view of food safety and security.

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## Assessment of Microplastic Release from Reclaimed Water to Agricultural Soil

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**Keywords:** *Microplastics; Agricultural soil; Reclaimed water*

Proposing reclaimed water for agricultural irrigation presents a pragmatic remedy for addressing water scarcity in coastal regions of Mediterranean nations. However, prolonged exposure to advanced treatment processes leads to the gradual breakdown of plastic materials, generating numerous smaller plastic particles known as microplastics (MPs). These particles accumulate in significant quantities within agricultural soils irrigated with reclaimed water, potentially endangering terrestrial ecosystems. Despite the extensive use of plastics in agriculture, there remains limited understanding regarding the presence of MPs in the agro-environment. Persistent plastic pollution could further diminish agricultural output, yet the precise impact on terrestrial ecosystems, particularly agri-food systems, remains largely unexplored. Consequently, this study aims to ascertain the presence and/or accumulation of MPs in agricultural soils irrigated with reclaimed water, specifically in protected crops (greenhouses), and to identify the chemical composition of the extracted MPs.

A total of 10 different types of synthetic polymers were identified. The polymers detected by  $\mu$ FTIR analysis were PE, PET, PNR, PA, PAN, PVA, PS, PO, PP and PTFE. In the reclaimed water, blue was the dominant colour in all shapes of MPs found, while in the agricultural soil samples it was black. In general, most of the fibres showed a size between 100 and 1000  $\mu$ m, while for fragments it was between 100 and 250  $\mu$ m. The work supports the reuse of water for agricultural irrigation. Nevertheless, the results highlight the importance of carrying out a long-term controls on agricultural soil that is irrigated for a long period with reclaimed water to avoid high accumulation rates of these contaminants.

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## Colorimetric and visual detection of ciprofloxacin using silver nanoparticles

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**Keywords:** *Optical sensor; Antibiotics; metallic nanomaterials.*

Ciprofloxacin (CIP) is a broad-spectrum antibiotic from the fluoroquinolones family, which has been widely used for treating multiple infections. The improper disposable or incomplete metabolism of this antibiotic, together with inefficient removal by wastewater treatment systems, has contributed to its presence in water ecosystems. CIP has been found in water resources with a concentration of around 2.5 ng/L, while in hospital wastewater could go up to 41 mg/L [1]. CIP molecule is stable and is difficult to biodegrade in aquatic environments, thus, it is important to develop simple and practical methods for its on-site detection [2,3]. Silver nanoparticles (AgNPs) have been used to develop colorimetric sensors for antibiotics [3]. Recently, one work used AgNPs coated with polyethyleneimine as sensors for CIP, having its detection based on the AgNPs coloration loss [2]. In this work, AgNPs were prepared in water and used to visually detect CIP in water. The AgNPs were prepared by the chemical reduction method, achieving nanostructures with an absorption maximum of around 390 nm and a yellow coloration. Upon addition of CIP, the intensity of the band at 390 nm decreases and a new band at higher wavelengths appears, which can be explained by the AgNPs agglomeration in the presence of the analyte [3]. Using these AgNPs, it was also possible to visually detect the presence of the CIP, since the solution colour changed from yellow to orange, and then to pink (Figure 1). CIP can be detected in concentrations higher than 0.1 and 0.5 mg/L by Uv-Vis spectroscopy and visual detection, respectively. Further studies regarding the optimal AgNPs dosage and pH are being carried out. Nevertheless, these results indicate that AgNPs could be an easy, practical, and sensitive method to detect visually CIP in aquatic environments.



**Figure 1.** AgNPs dispersions in the presence of different concentrations of CIP, ranging from 0 to 1.7 mg/L.

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## Exploring enzymatic biotransformation of pharmaceutical drugs for water treatment

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**Keywords:** *green catalysts, organic micropollutants, biotransformation*

Enzymes are green catalysts that have been used for the transformation of organic micropollutants in water treatments, emerging as an eco-friendly approach compared with the conventional methods used for this purpose [1]. Enzymatic processes have high reaction kinetics, and work under mild reaction conditions (e.g., pH, temperature), with the expense of less water, energy, and chemicals. In addition, as enzymes are not consumed during the treatment, they can be recycled. The main class of enzymes applied for water treatment are oxidoreductases, which catalyze the transfer of electrons from an electron donor (reductant) to an electron acceptor (oxidant) molecule. Among them, Laccase and Peroxidase, with important roles in the metabolism of organisms from which they are extracted (e.g., fungi, plants, bacteria) have been applied for the removal of phenolic and non-phenolic compounds, including pharmaceutical drugs, pesticides, dyes, and personal care products. This work intends to explore the capacity of commercially available Laccase (Lac, from fungi) and Peroxidase (HRP, from horseradish) to biotransform pharmaceutical drugs belonging to different classes commonly present in water bodies (3 antidepressants, 1 antibiotic, 1 non-steroidal anti-inflammatory drug). For this, for each enzyme, a solution of a defined concentration was prepared by dissolving the enzyme in a pharmaceutical solution of concentration 5 mg/L. The tests were conducted at a fixed pH (5 and 7, for Lac and HRP, respectively), temperature (40 °C), contact time (24 h), stirring (350 rpm), and variable enzyme concentration (0.1 and 0.01 mg/mL), and substrate concentration (hydrogen peroxide 0.1, 0.5 and 2 mM, only for HRP). After 24 h of incubation, the samples were filtered and analyzed by HPLC. Overall, the results showed that the biotransformation of contaminants was compound-specific, with the non-steroidal anti-inflammatory drug diclofenac and the antibiotic amoxicillin presenting concentrations below the lowest limit of quantification of the method. Comparing the two enzymes it was also possible to observe that Lac was more efficient than HRP since at a lower concentration (0.01 mg/mL) biotransformed the totality of the contaminant present, using only the dissolved oxygen present in the solution as the electron acceptor. In terms of enzymatic activity, Lac and HRP maintained their activity during the period of incubation, showing to be stable for future applications with similar conditions. These results reinforce the use of enzymes as green catalysts for water treatment, highlighting their role in sustainable environmental management practices.

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## PFAS distribution in drinking water, surface and groundwater in Basilicata region in 2023

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ARPAB

**Keywords:** PFAs, Basilicata, drinking, surface and ground water

Per- and polyfluoroalkyl substances (PFAS) are a suite of anthropogenic organic compounds, most of which contain alkyl chains with carbon atoms bonded to fluorine atoms [1–3]. A number of sources of PFAS can be found in everyday life, such as firefighting agents, medical devices, and industrial applications that can include photo-imaging, photoresist, waterproofing, and anti-reflective coatings, as well as carpet, textile, and leathertreatments [4–6]. Over the past decade, there have been increased detections of PFAS compounds in natural waters [7]

According to IARC PFOA is carcinogenic to humans (Group 1); PFOS is possibly carcinogenic to humans (Group 2B) [8].

Basilicata, a southern Italy's region, is rich of surface water resources and, in a lesser way, of ground water resources, these are mainly used for drinking and irrigation purposes, and a significative quantity of resource is transferred in other regions, like Apulia.

Basilicata region is characterized by a wide and complex hydrographical network; some of the main water bodies, such as the Bradano, the Basento, the Cavone, Agri and Sinni rivers flow into the Ionic sea, and dams and weirs as the Pertusill, Montecotugno and Camastra, drinking water is produced from these dams.

The Water Framework Directive (WFD) fixed the list of priority substances that Member States must monitor in surface waters and Environmental Quality Standards must be met to achieve good surface water chemical status within 22 December 2027; The EU annual average environmental quality standard (AA-EQS) for PFOS in surface freshwater is set at a very low criterion of 0,00065 µg/l, for PFOA is 0.1 µg/l (Dlgs 172/2015, implementation of Directive 2008/105/EC). Currently, Threshold Values are foreseen for groundwater only for six polyfluoroalkyl substances, PFOS, PFBS, PFPeA, PFHxA, PFOA, (DM 6/7/2016, implementation of Directive 2014/80/UE).

Drinking water standards developed by EU member states are 0.1 to 0.5 µg/l for sum and total PFAs (Dlgs 18/2023, implementation of Directive UE 2020/2184). However, the legislation on PFAs is constantly evolving: Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) endorses the *relative potency* approach for PFAS and suggests using a quality standard for surfacewater and groundwater of 4.4 ng L<sup>-1</sup> for PFOA equivalents: *Relative Potency Factors* (RPFs) are used for weighted sum of PFAS24 calculating [9].

During 2023 ARPAB analysed 23 Perfluoroalkyl substances in 16 samples of drinking water, 92 samples of groundwater, 70 samples of surface water. This work highlights the environmental quality standard (AA-EQS) for PFOS and PFOA equivalents.

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## **Determination of heavy metals carried out by applying the ICP-MS technique in surface waters intended for drinking water production and in drinking water - ARPA Basilicata controls**

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ARPAB

**Keywords:** Heavy Metal, drinking water, inductively coupled plasma mass spectrometry (ICP-MS)

The results reported in this work concern the determination of some chemical elements, present in surface and drinking water. Al, Sb, As, B, Cd, Cr, Fe, Mn, Hg, Ni, Pb, Cu, Se, V were determined through technique inductively coupled plasma mass spectrometry (ICP-MS)[1].

The monitoring was carried out by Environmental Protection Agency of Basilicata(ARPAB, from 2021 to 2023, on a drinking water basin called Camastra, (located in Potenza district). The monitoring involved the determination of the analytes on the waters of the basin after purification process, too.

The determined analytes are naturally present in environment or may result from anthropogenic activities.

They occur naturally in rocks in the form of insoluble compounds such as oxides, sulphides, etc. [2].

Anthropogenic activities such as the production of chemical products, oil refining, metalworking, plating, tannery activities, plastic production determine the release of these elements into nature in their toxic form.

The water could be enriched by Iron and Aluminium too, which are used as coagulants in the clarification phases during the purification process.

Heavy metals are pollutants which, although present in very low concentrations, can cause a wide range of negative effects on the environment and humans; Nickel, Cadmium and Lead can be toxic and carcinogenic for humans. Their presence in the environment can cause bioaccumulation in both animal and plant tissues.

In order to safeguard public health, the Legislator has imposed limits for these elements whether in surface water to be purified [3](Legislative Decree 152 /06 Part III All.2 tab.1A ) or in drinking water [4] (Legislative Decree 18/2023); the greater the toxicity of the element, the lower the limit value of the permitted concentration. The limits of the most toxic analytes for drinking water are reported (as an example)below: 1 µg/l for Mercury, 0.1 µg/l for Cadmium, 0.5 µg/l for Antimony, 1 µg/l for Arsenic, 1 µg/l for Chromium, 200 µg/l for Aluminum and Iron.

The results of quantification of dissolved elements by ICP-MS reported in this work, made it possible to evaluate the exposure of the population present in the study area.

We report the average and maximum values of the concentrations of those elements which were found to be higher than the analytical quantification limit.

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## Distribution of pharmaceuticals in coastal water of the Iberian Peninsula

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**Keywords:** *pharmaceuticals, seawater, ecopharmacovigilance*

Among all marine ecosystems, coastal areas are especially vulnerable to human impacts due, among other factors, to a larger population residing near these areas, and related human activities. This increase in human presence is accompanied by an increase in anthropogenic pollution.

Drugs are included in the so-called emerging contaminants group. These substances are released from the advanced purification systems or come from other type of sources reaching our beaches. They are currently not regulated, although some are included as substances to be monitored in the 4th Watch List under the Water Framework Directive, such as some antibiotics and antidepressants (venlafaxine and its metabolite).

In this study, 16 beaches were selected along the Portuguese coast, mainly in the area of Lisbon and the Algarve and 30 in the Spanish area, 18 in the Cádiz-Málaga area and 12 on beaches in Murcia (Mar Menor). The beaches selected in both countries covered a wide range of occupation, from areas close to natural spaces with protection figures to urban beaches in densely populated and highly touristic areas, or pristine beaches. In total, 61 water samples were collected from the different sampling areas during the spring and/or summer of 2021.

The objective of the study was to provide a descriptive analysis of the presence of drugs and metabolites in the coastal waters of the Iberian Peninsula. For this, 37 drugs (including metabolites) belonging to the main therapeutic groups consumed by the population were analyzed: anti-infectives, sex hormones, cardiovascular and digestive systems, analgesics, anti-inflammatories and antipyretics, nervous and respiratory systems.

Within the three scenarios analyzed, Lisbon-Algarve was the area in which the greatest number of compounds and in the highest concentrations were detected, while the Mar Menor area was where the lowest concentrations were detected. The beach with the highest total concentrations was Arcos beach (Lisbon), 2072ng/L, being the beach where the largest number of compounds reached their maximum concentrations. In relation to the substances analyzed, acetaminophen was the substance detected in the highest concentration, in Mar Menor and Cádiz, being 37.5 ng/L and 203 ng/L, respectively, while on the coast of Lisbon the highest concentration recorded was for diclofenac (1616 ng/L) in Arcos beach, followed by acetaminophen (100 ng/L).

We conclude that the monitored concentration levels are relatively low. None of the drugs included in the 4th Watch List have been found in particularly notable quantities. Arcos beach, the beach closest to the Tagus River mouth, in Lisbon, has been the sample point where the highest total concentration was found. Although these substances do not pose a risk to public health, they have proven to be good indicators of anthropogenic contamination.

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## *Instrumentation Pills*

## **Instrumentation Pills List**

### **Innovative solutions to analyze trace pollutants in environmental samples**

*Giuseppe Federico Labella* - Bruker Italia Srl

### **Exploring the Environmental Impact: Shimadzu's Analysis of Toxic Substances Adsorbed on Microplastics**

*Domingo Pastran* - Shimadzu Italia





# 5<sup>th</sup> International Conference on Risk Assessment of PHarmaceuticals in Environment



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