4th INTERNATIONAL CONFERENCE ON RISK ASSESSMENT OF PHARMACEUTICALS IN THE ENVIRONMENT

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BOOK OF ABSTRACTS

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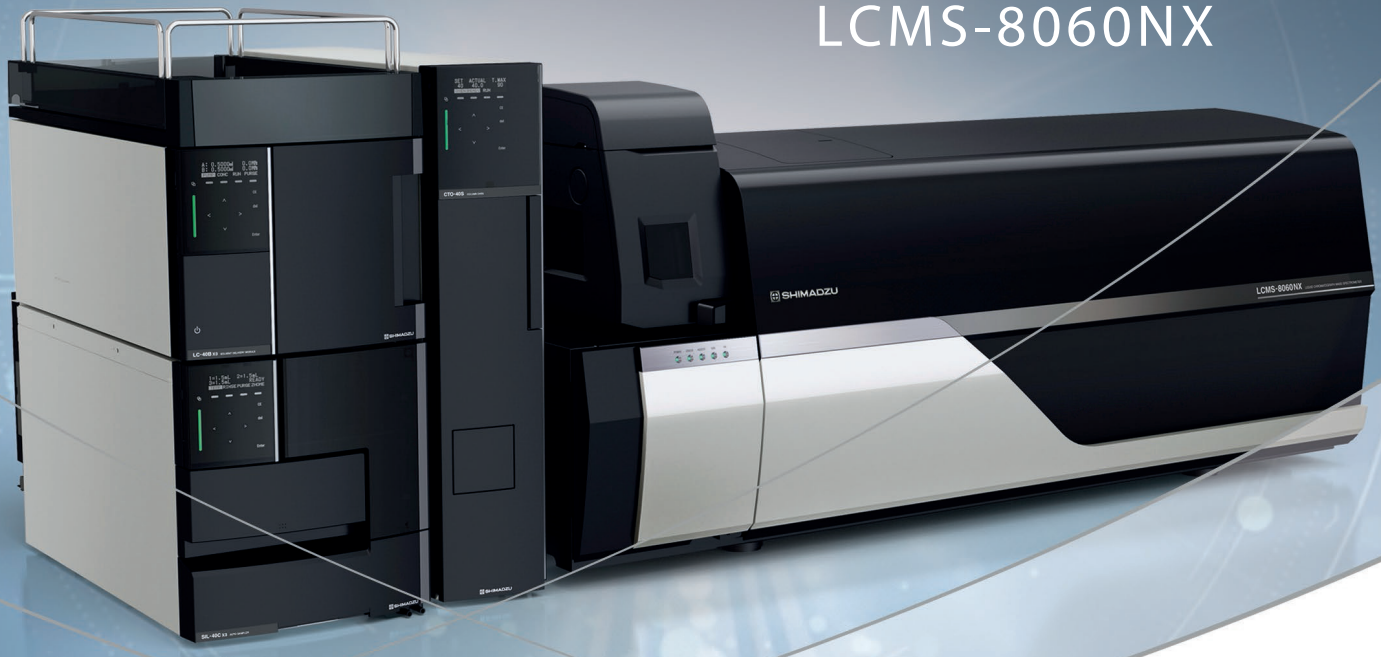

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Welcome

The **Fourth International conference on Risk Assessment of Pharmaceuticals in the Environment (ICRAPHE)** will take place in Barcelona, Spain, next October 9 and 10, 2023. This is a follow up of the First ICRAPHE international conference organized in Paris, September 8-9, 2016, the Second one in Barcelona, 28-29 November 2019 and the Third one (virtual) in Hangzhou, China, 14 October 2022.

The following themes have been selected:

- Environmental Monitoring including Non Target Analysis, Bioanalytical tools, Sensors and Bioinformatics of Pharma residues and Antibiotic Resistance Genes in the Water Cycle (session 1)
- Wastewater-Based Epidemiology for Public Health (session 2)
- Ecological and Health Effects, Hazards and Risks (session 3)
- Microplastics as vectors of Pharma Residues in the environment (session 4)
- Degradation and Innovative Remediation Technologies (session 5)

This conference aims to capture outstanding examples of active research in this field and to draw the attention to future research needs.

For those interested to submit a full manuscript, it is expected that a Virtual Special Issue will be planned in one of the Elsevier journals.

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LECTURES

Determination of pharmaceutical residues in influent and effluent wastewater samples from treatment plants by a three-phase solvent system LC-MS method

Giuliana Bianco, *Dipartimento di Scienze, Università degli Studi della Basilicata, Potenza, Italy*

Pharmaceutical compounds represent environmental pollutants occurring in different types of aqueous matrices [1]. The techniques used for their detection in complex samples are continuously developing and a significant increase in the number of methods reported in scientific literature has occurred [2]. Currently, the primary analytical obstacle in detecting these emerging pollutants is related to their chromatographic separation, particularly when compounds being studied share similar levels of polarity. We proposed a case study regarding the simultaneous separation of six pharmaceuticals with similar polarity, expressed as logarithm of the partition coefficient (logP), i.e. omeprazole, carbamazepine, clarithromycin and erythromycin as well as amoxicillin and metformin [3]. Since commonly employed solvent systems may not be suitable for effectively separating multi-class pharmaceuticals using reverse-phase chromatography, we introduced a novel RPLC-MS/MS method based on a non-traditional three-phase solvent system comprising acetonitrile, water, and water acidified with 0.1% formic acid. The optimized methodology was validated according to EURACHEM guidelines and applied for the determination of selected pharmaceuticals in influent and effluent wastewater samples, collected at the main wastewater treatment plant of Potenza (Italy). Good linearity and precision were achieved. For all the analytes a recovery from wastewater ranging between 0.70 and 1.18. was obtained, while LODs ranged from 0.0001 µg/L to 0.5114 µg/L. No significant matrix effect, evaluated by post extraction addition, was observed. The results confirmed that conventional wastewater treatment methods are inadequate for effectively removing pharmaceutical compounds present in municipal wastewater. The obtained data demonstrated satisfactory performance of the proposed method for its intended applications. Moreover, the proposed methos base on a three-phase solvent system holds the potential to be expanded to include additional pharmaceutical compounds depending on specific application requirements.

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Pharmaceutical Pollution: general problems, challenges and solutions

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To understand the impacts of pharmaceuticals in the environment it is essential to know the concentrations of these molecules in the environment. To gain an understanding of the occurrence and risks of pharmaceuticals across the World, the University of York recently co-ordinated the Global Pharmaceutical Monitoring project. In the project, concentrations of 61 pharmaceuticals were monitored at 1,052 locations in 104 countries. The monitoring results were then compared to 'safe' concentrations for ecosystems and antimicrobial resistance selection to establish the level of risk to ecological and human health.

Highest cumulative concentrations of the study pharmaceuticals were observed in sub-Saharan Africa, south Asia, and South America. The most contaminated sites were in low- to middle-income countries and were associated with areas with poor wastewater and waste management infrastructure and pharmaceutical manufacturing. The most frequently detected APIs were carbamazepine, metformin, and caffeine (a compound also arising from lifestyle use), which were detected at over half of the sites monitored.

Approximately 44% of the 1052 sites monitored had concentrations of at least one pharmaceutical above concentrations of ecotoxicological concern. At the most polluted sites, ecological effects are predicted from mixtures of pharmaceuticals on different trophic levels and on different endpoint types. Around 17% of locations had concentrations of at least one antimicrobial above concentrations considered safe for resistance selection.

This is the first truly global study to quantify the concentrations and risks of pharmaceuticals across the globe. Overall, the results show that API pollution is a global problem that is likely negatively affecting the health of the World's rivers and also human health. To meet the UN sustainable development goals we need to implement integrated approaches, involving green pharmacy, better regulation and waste and wastewater management and treatment methodologies to bring concentrations down to an acceptable level.

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Degradation of Pharmaceuticals by Advanced Technologies and new insights on the Degradation Pathways

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In recent years, there has been significant progress in the development of potable water reuse (direct or indirect) applications for treating wastewater to produce drinking water or to augment sources of drinking water supply. Such an approach provides an effective, sustainable, and reliable solution to countries, regions, urban cities, and communities facing increasing water scarcity and demand. Since the removal of potentially toxic emerging contaminants (ECs) by conventional technologies is limited, advanced oxidation processes (AOPs) can be promising treatment options to control the levels of ECs in the finished waters for potable reuse. The latest studies of AOPs for wastewater treatment mainly focus on the development of novel and effective technologies based on the generation of highly reactive species (i.e., •OH), selective radicals (SO4•−, reactive chlorine/nitrogen/phosphate species, carbonate radical, O2•−, etc.), and/or non-radical species (i.e., 1O2 and Fe at high valance). The non-selective radicals can be used to degrade almost all kinds of ECs, while they are easily affected by the co-existence of dissolve organic matter (DOM), inorganic ions, and other constituents in water. On the other hand, selective radicals have an affinity to contaminants with specific moieties, for example, carbonate radicals prefer contaminants with aniline and phenolic groups. Since non-radical species are highly selective to attack contaminants with certain properties, this provides opportunities for the development of selective catalysts used in heterogeneous catalytic-based AOPs. Based on the different properties of reactive species, the AOPs with a large amount of •OH can be used to partially degrade/transform DOM as well as trace contaminants of concern in wastewater before discharging to surface waters or water reservoirs. On the other hand, AOPs with selective radicals or non-radical species might be applied to transform contaminants of concern present at high concentrations to products of lower toxicity and enhance the biodegradability of wastewater, regardless the possible existence of high concentrations of DOM and salinity that inhibit the performance of •OH and SO4•−-based AOPs. As for potable water reuse, UV-based AOPs are usually used as the chemical barrier after reverse osmosis (RO) and decompose uncharged and small molecular weight contaminants that pass-through RO. Opportunities to improve the performance of AOPs exist and new discoveries at the intersection of materials science, environmental science, radical chemistry, and water treatment process engineering might provide solutions to develop lower cost sustainable water treatment and water reuse applications to augment available supply of drinking water. In this presentation we will discuss the application of AOPs in wastewater decontamination and potable water reuse and provide details on the kinetics and degradation mechanisms of organic contaminants of concern in water reuse and wastewater treatment applications.

Keywords: advanced oxidation, water reuse, potable, emerging contaminants, technologies

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Compound-Specific Isotope Analysis (CSIA) to trace sources and transformation of pharmaceuticals in the environment

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Pharmaceuticals are of great benefit to human and animal health but may become of potential concern when released into the environment as a result of patient use, improper disposal, or preventive veterinary medicine. Prominent examples are diclofenac, which has been linked to the mass eradication of vulture populations in India, and antibiotics which may support the emergence and spread of antibiotic resistance when present in wastewater, fertilizer, or agricultural soil. Dedicated efforts are therefore directed at monitoring concentrations of these chemicals in surface water, and at studying possible (bio)transformation pathways in relevant natural environments.
However, it is difficult to trace sources and transformation/degradation of pharmaceuticals in environmental settings, because these compounds are continuously released from multiple possible sources and simultaneously dissipate in the environment. If, in addition, degradation occurs, this process can, therefore, seldomly be identified separately in concentration trends over time. Here, compound-specific isotope analysis (CSIA) offers a complementary line of evidence. Stable isotopes are present within the molecular structure of pharmaceuticals, and the ratio in which these isotopes occur (e.g., 13C/12C, 15N/14N) can inform about different sources, and about further degradation of pharmaceuticals of concern.
Two approaches will be discussed to exploit the opportunity of using isotopes as reactive tracers within molecular structures. By introducing, on the one hand, 13C as isotopic label, dissipation and transformation of the pharmaceutical sulfamethoxazole - including analysis of transformation products - will be traced in an agricultural field experiment headed by the International Atomic Energy Agency (IAEA). On the other hand, prospects and limitations will be reviewed for analysis of isotope ratios (13C/12C, 15N/14N) at natural isotopic abundance within important pharmaceuticals like diclofenac and sulfamethoxazole. Prominent challenges are (i) the need to extract and purify these compounds at low environmental concentrations to obtain sufficient mass for CSIA and (ii) the ability to observe position-specific isotope effects by CSIA in larger molecules with multiple carbon atoms. Current efforts and potential solutions will be presented to overcome these current bottlenecks.

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Risk assessment of pharmaceuticals and microplastics in irrigated crops with reclaimed water in Almeria, south East of Spain

Amadeo Fernandez-Alba, *University of Almeria*; **M. Jesus Bueno**, *University of Almeria*; **M. Dolores Hernando,** *CISIC. EEZA. Almeria*

Reclaimed water contributes to mitigating water stress and represents a sustainable alternative for entrepreneurs and farmers in areas where there are large commercial interest, and which suffer from greater water scarcity. However, hundreds of scientific studies have documented the presence of organic contaminants of emerging concern (CECs), such as pharmaceuticals. In addition, new contaminants, plastic waste, are posing a new challenge to the scientific community. An assessment of the possible risks derived from the use of reclaimed wastewater for agricultural irrigation of protected greenhouse horticultural crops is relevant.

Three crops (cucumber, pepper and melon) were grown under agronomic conditions in a greenhouse. The plants were irrigated with treated water spiked with 70 chemicals, including antibiotics, anti-inflammatories, analgesics, anaesthetics, anxiolytics, and anticonvulsants at environmental concentrations (~ 1 µg/L). The average total concentration of contaminants detected in the soil samples ranged from 106 to 217 µg/kg d.w. Melon roots showed a higher number of contaminants than pepper and with mean total concentrations ranged from 196 to 635 µg/kg. Between 5 and 12 different contaminants were found in the harvested fruits, up to levels around 23 µg/kg in cucumber and pepper, and 13 µg/kg in melon. In general, cucumber fruit exhibited accumulation percentages of contaminants higher than the other fruits (pepper and melon) for most target analytes. The accumulation rates followed the order: root = stem (0.1-0.4%) < leaf (1-3%) < fruit (0.2-5%) < soil (13-28%). The experimental data obtained in this study were also used to assess the risk associated with the reuse of reclaimed water for crop irrigation as well to identify those contaminants. Carbamazepine and lidocaine showed the highest translocation rate through the xylem plant tissue and accumulation percentages in the leaves. Clonazepam and carbamazepine were the contaminants that showed the highest bioconcentration factor values (BCF) in vegetables. The total load of contaminants detected derived from the consumption of a mix of all vegetables were up to 8 orders of magnitude lower than the acceptable daily intake values (ADI) reported in the worse of the case, 380 ng/day for a conventional or 1145 ng/day for a vegetarian diet.

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MODELLING AND CHEMOMETRIC TOOLS FOR THE EXPLOITATION OF MONITORING DATA: ORGANIC MICROPOLLUTANTS IN THREE MEDITERRANEAN RIVERS AS CASE STUDY

Antoni Ginebreda, *IDAEA-CSIC*; **Damià Barceló,** *IDAEA-CSIC ; ICRA*; **Romà Tauler,** *IDAEA-CSIC*

This work explores the exploitation of monitoring data of organic microcontaminants in rivers using different methodological tools. Our approach was tested in three Mediterranean rivers, i.e., Sava, Evrotas, and Adige, as a case study. These three rivers cover a broad range of characteristics in terms of basin area, discharge, land uses, or anthropogenic pressures. Samples were collected during two sampling campaigns conducted in 2014 and 2015 in three different matrices (water, sediments, and biota) as part of the GLOBAQUA project [1,2]. Monitoring encompassed more than 200 organic micropollutants, including relevant chemical groups (pharmaceuticals, personal care products, perfluorinated compounds, pesticides, pyrethroid insecticides, flame retardants, and persistent organic pollutants). The specific objectives sought in the study were: (a) the identification of the main pollutants occurring in the three rivers monitored, considering their partition behavior among the environmental compartments (water, sediments, and biota); (b) the spatial modelization of the pollutants using a data-based advection-reaction model [3,4]; (c) the identification and prioritization the river basin specific pollutants (RBSP) in terms of the potential ecotoxicological risk posed to the aquatic ecosystems, and (d) the identification of the more relevant pollutant mixtures at basin scale using advanced chemometric tools (MCR-ALS) [5].

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Analytical challenges in the determination of pharmaceutical compounds in microplastics

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Over the years, many research articles have been published in the scientific literature, providing valuable information regarding microplastics (MPs) presence in the environment and in biota. For a long time, the discussion has been centered on their behavior as environmental pollutants; however, there is another layer of complexity that must be considered, which is their ability to retain contaminants onto their surface. Through different mechanisms, many chemical pollutants can be preconcentrated in the polymer matrix and protected from degradation, prolonging their persistence in the environment. To understand the mechanisms involved, it must be acknowledged that these processes are influenced by multiple factors involving the nature of the MPs, their surrounding conditions, as well as the properties of the contaminant implicated. Apart from the previously commented issues, MPs in the environment suffer constant degradation through different mechanisms. This degradation overtime changes the surface of the MPs introducing modifications that can have important effects in sorption rates and capacities, as well as in the retention of more hydrophilic compounds.

Most of the analytical methodologies developed for the determination of contaminants from MPs are only capable of quantifying the analytes that the method “is able to extract”, since quantitative extraction is not so frequently achieved. Sometimes, internal standards are directly applied without even taken into consideration recovery values. Furthermore, the determination is carried out indistinctively from the type of MP selected. In this communication, the analytical challenges regarding the determination of contaminants, in particular, pharmaceutical compounds, in MPs will be reviewed. Our latest results in the field, concerning the determination of pharmaceutical compounds in marine MPs collected in Canary Islands beaches will also be presented and discussed.

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Population driven biochemical burden in a multi-city study: antibiotics, ARGs and implications for One Health actions

Barbara Kasprzyk-Hordern, *University of Bath*; **Natalie Sims**, *University of Bath*; **Kishore Jagadeesan,** *University of Bath;* **Felicity Elder,** *University of Bath*; ***Ruth Barden,*** *Wessex Water*

One Health is focused on a holistic understanding and management of public and environmental health. This talk will introduce Wastewater-Based Epidemiology (WBE) as an enabler of One Health actions in tackling key global challenges such as antibiotic use and antimicrobial resistance. Chemical mining of wastewater and the wider environment for antibiotics, antibiotic resistance genes and other groups of chemicals was undertaken in an intercity system including, in total, five cities/towns located in one river catchment (the Avon Catchment in the South-West UK covering an area of approximately 2000 km2 and a population of ~1.5 million which constitutes > 75% of the overall population in the catchment) using in-house mass spectrometry methods and polymerase chain reaction to understand spatiotemporal speciation of chemical and biological targets in the context of geographical as well as community-wide socioeconomic factors.
The five cities and towns tested have different characteristics including population size, industry presence and socioeconomic status. We applied WBE pipelines to:

(1) Understand spatiotemporal variabilities in chemical and biological target groups in the studied inter-city system.
(2) Provide better understanding of antibiotics and resistance genes associations in the context of 5-city spatial profiling and longitudinal (temporal) 13-month monitoring of one city.
(3) Provide better understanding of environmental and public health burden from key catchment users: from hospitals to citizens, to inform One Health actions aimed at reduction of antimicrobial resistance.

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New portable sensor technology for the detection of pharmaceutical residues in the aquatic environment

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The field of environmental monitoring has experienced a substantial progress but still the on-site control of contaminants is an elusive problem. In addition, the growing number of pollutant sources is accompanied by an increasing need of having efficient early warning systems. Environmental diagnostics are slow (from hours to days), labour-intensive and expensive. Environmental control is demanding novel analytical tools that could enable quick, accurate, reliable, and cost-effective results while operating on-site. Photonic biosensor devices can provide such sensitive, reliable, and selective analysis, while reducing test and turnaround times, decreasing and/or eliminating sample transport, and using low sample volume. Our main objective is to achieve ultrasensitive Point-of-care (POC) biosensor platforms accomplishing the requirements of disposability and portability for environmental analysis.

We have already demonstrated cutting-edge photonic biosensors that enable ultrasensitive analysis of analytes in a few minutes. By custom tailoring the biochemistry of the sensor biochips, our POC nanophotonic biosensor technology can perform direct detection of organic pollutants, pesticides or other contaminant residues within <15 min, with high sensitivity and selectivity. Moreover, we have developed an ultrasensitive methodology for the detection of genes associated with the multidrug-resistance found in Gram-negative bacteria as E. coli without using any PCR amplification step.

In a recently funded EU project (NIAGARA), we will develop multi-analyte biosensors for highly relevant and concerning water pollutants as BPA, H. pylori, imazalil and ibuprofen/paracetamol, with limits of quantification reaching the relevant values for human health. Our technology will be employed by non-expert personnel on-site and could have a strong impact in guiding quick decisions across various environmental scenarios.

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Options for a strategic approach to establish the pattern and risk of pharmaceuticals in the environment: the case study of Saudi Arabia

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Treated or untreated wastewater and sewage sludge from wastewater treatment plants (WWTPs) are the primary sources of pharmaceuticals released into the environment. This is particularly noteworthy due to the escalating utilization of wastewater to palliate water scarcity in arid countries. Studies have examined the uptake and translocation of different pharmaceuticals in plants. However, the majority of these studies have utilized unrealistic exposure concentrations or controlled laboratory conditions. The aim of this study is to make further progress and to better understand the distribution, fate and absorption of pharmaceuticals under environmental conditions in Saudi Arabia, which has actively pursued wastewater recycling to address its pronounced water scarcity. The extensive study of pharmaceuticals in the environment is hindered by matrix complexity, limited pharmaceutical quantities in samples, and a multitude of potential analytes to consider. Therefore, fist a strategic approach to identify and determine pharmaceuticals in the environment using liquid chromatography high resolution mass spectrometry (LC-HRMS) was developed. To this end, ThermoScientific™ Orbitrap Exploris™ 120 mass spectrometer and Thermo Scientific™ Vanquish™ UHPLC coupled with Thermo Scientific™ TracefinderTM and Compound Discoverer™ software to achieve data interpretation, structure elucidation and quantification were used. Various MS2 modes were investigated, including the combination of full m/z range followed by MS2 with 4 precursor isolation windows (data dependent analysis, DDA) that provided the best results. The MS2 was performed first against a mass list and in the case, that none of the included m/z appear selecting just the most intense ions to be fragmented helping to fill knowledge gaps and providing details on the pattern of pharmaceuticals present in different environmental contaminants. The second step was to apply the developed approach to trace the pattern of pharmaceuticals, metabolites and degradation products in water, soil and plant samples taken from different areas of Saudi Arabia. The detected concentrations of pharmaceuticals highlight the ubiquitous presence of these compounds in the environment, including plants, even at low levels. The findings from this study provide valuable insights that can be utilized to develop a more effective research framework and establish guidelines for the management of pharmaceuticals.

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Physicochemical Interactions of microplastics and pharmaceutical residues

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Pharmaceuticals were globally detected in drinking water/tap water, groundwater and surface water. More than 600 compounds were detected in 71 countries. Antibiotics followed by analgesics are the most frequently detected compounds.

Microplastics can be either primary or secondary. Primary are the ones produced for industrial purposes such as pellets or microspheres while secondary can be produced from the fragmentation of bigger plastics. Microplastics in the environment can suffer degradation, fragmentation, and ageing. As they have different densities according to different polymer types they can be distributed in the water column and deposited at the bottom. Plastics can aggregate, agglomerate, and can sorb other pollutants such as pharmaceuticals.
It is well known that bio and synthetic polymers interact with organic substances through various interactions. Recent reports and review papers have demonstrated similar interactions between plastics and microplastics with pharmaceuticals. Electrostatic, hydrogen bonding and hydrophobic interactions are considered the major interactions while π-π interaction, cationic bridging mechanism, van der Waals interaction, partition, and pore-filling mechanism are minor interactions.

Antibiotics, non-steroidal anti-inflammatory drugs, psychiatric drugs, or cardiovascular drugs are examples of pharmaceuticals that can sorb to microplastics surface. The adsorption of pharmaceuticals on microplastics will depend on different factors related to both the properties of microplastics and pharmaceuticals.

Environmental concentrations of antibiotics generally range from ng L−1 to μg L−1 but higher concentrations were used to assess the maximum adsorption capacity of microplastics.
The sorption capacity as a function of initial concentration was studied mostly with antibiotic compounds including sulphonamides, tetracyclines, and fluoroquinolones.

The simultaneous quantification of pharmaceuticals and microplastics in the same environmental matrices is rather scarce when compared to the number of studies regarding sorption.

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Sorption and risk assessment of pharmaceuticals sorbed to microplastics

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Microplastics have been recognized as an emerging environmental threat due to their persistence, ubiquity, and toxic potential. They have a large specific surface area, having the ability to sorb other contaminants that co-exist with them in the water column. Pharmaceuticals are extensively used worldwide, which led to their ubiquitous occurrence, co-existing with microplastics in the environment. Recent studies have shown the potential of microplastics to sorb hydrophilic contaminants, such as pharmaceuticals, acting as vectors or carriers of these contaminants. In this way, microplastics can affect the transport and environmental distribution of pharmaceuticals, as well as facilitate their contact with aquatic organisms. The partitioning between microplastics and pharmaceuticals can be influenced by microplastics properties, such as type of polymer, particle size, surface area, polarity, as well as by pharmaceuticals physical-chemical properties (e.g., pKa, log KOW). Environmental conditions such as aging/weathering processes, pH, salinity, dissolved organic matter, may also play a role on the sorption of pharmaceuticals to microplastics, due to the modifications induced in microplastics surface, which might change their physical-chemical properties.
Presently, the toxicological assessment of the combined effects of microplastics and sorbed pharmaceuticals is still poor understood. Once ingested, microplastics may influence the bioaccumulation and/or toxicity of pharmaceuticals in different ways: i) microplastics may desorb pharmaceuticals, increasing their bioavailability, which could promote their bioaccumulation and toxicity: ii) ingested microplastics may adsorb pharmaceuticals already accumulated in the aquatic organisms, acting as a sink of contaminants and decreasing their body burden; or iii) microplastics may not have impact on the bioaccumulation and/or toxicity of pharmaceuticals. However, studies under realistic environmental concentrations of microplastics and covering a wide range of plastic polymer types are still missing to better understand the interaction of microplastics and pharmaceuticals under real environmental conditions. The fate and toxicological effects of pharmaceuticals sorbed on microplastics on biota, including health risk for humans, are still poor understood and further studies are needed.

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Antibiotics in agriculture: risk assessment for the environment and human health

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The use of antibiotics in agriculture has been linked to potential risks for the environment and human health. Antibiotics are often used in animal husbandry to promote growth and prevent disease, leading to the emergence of antibiotic-resistant bacteria in animals, soil, and water. These bacteria can spread to humans through direct contact or consumption of contaminated food products. Food safety is one of the priorities according to sustainable development goals. In this area is very important to manage and control the biocontamination of ecosystems, especially agroecosystems by antibiotic-resistant bacteria. The soil microbiome plays an important role in the development and spread of antibiotic resistance in humans. Impact of enrofloxacin (1000mg*kg-1; 100mg*kg-1; 10mg*kg-1) on the functions and structure of soil microbiome and formation of soil resistome in agroecosystems with Lactuca sativa, Anethum graveolens, Thymus serpillum, Mentha piperita, Calendula officinalis was evaluated. Enrofloxacin belongs to the class of fluoroquinolone antibiotics that have been intensively used to treat bacterial infections in veterinary medicine. The highest phytotoxicity levels were observed at a concentration of 1000mg*kg-1, which had a negative impact on soil respiratory responses, reducing them significantly. Contamination by enrofloxacin affected the soil microbiome, the soil with high antibiotic concentrations had a low number of nitrogen-fixing microorganisms, which are crucial for the soil's fertility, and a high number of oligotrophic and spore-forming microbiota which indicates that the soil's microbial community is stressed and struggling to adapt to the contamination. The reduced activity of the microbial communities can have adverse effects on soil health and quality. Among isolated and tested bacteria, more than 33% were antibiotic-resistant. Multi-resistant were such pathogenic and conditionally pathogenic bacteria as Escherichia coli, Bacillus licheniformis, Serratia fonticola, Clostridium difficile, Enterococcus faecium, Acinetobacter baumannii, Pseudomonas aeruginosa, Hafnia alvei, Bacillus cereus, Bacillus megaterium, Enterococcus faecalis. Effective management of antibiotic-resistant bacteria in agriculture is crucial for protecting the ecosystem and human health. Therefore, it is important to implement measures to prevent the spread of antibiotic resistance, such as the responsible use of antibiotics and the implementation of appropriate waste disposal and treatment measures.

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Wastewater-based epidemiology for monitoring chemical's patterns during the COVID-19 pandemic employing targeted and non-targeted approaches

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Wastewater-based Epidemiology (WBE) is a non-invasive, continuously developing scientific tool, with the potential for monitoring real-time data on illicit and licit drug consumption, chemical exposure and public health, providing geographical and temporal trends. WBE has been used widely over the last 20 years to reflect the effect of socioeconomic changes and public health crisis on population's mental and physical health. Over the last 3 years, it has gained global attention, for the prevention and control of the COVID-19 pandemic and has been included more systematically in the national surveillance strategies. SARS-CoV-2 genetic traces, parent drugs and their metabolites end up in Wastewater Treatment Plants (WWTPs) and their determination in influents provides data about COVID-19 prevalence and drugs consumption, supporting public health authorities with valuable data. Biomarkers of public health (parent compounds and their metabolites) were identified and quantified from 2010 until today in the WWTP of Attica (Greece), and the detected concentrations were back-calculated into normalized population loads and consumption. LC-MS/MS methodologies and High-Resolution Mass Spectrometry (HRMS) accompanied by novel data treatment tools were used to identify known and unknown compounds. In addition, SARS-CoV-2 levels have been monitored daily since 2020 by analyzing influents from the same WWTP, and correlated with chemicals' (e.g. pharmaceuticals, illicit drugs, antimicrobials, surfactants etc.) patterns.

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Reclaimed wastewater: Treatments and risk assessment

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Reclaimed water from municipal wastewater treatment plants represents a continuous source of water which could be intended for a direct reuse for irrigation needs at a much larger scale. The debate on the reclaimed water quality and its safety for this destination is ongoing; legislations and regulations are being developed and coming into force in many countries. An increasing attention is being paid to the presence of micropollutants, among them pharmaceutical compounds, and the evaluation of the effects and the environmental and health risks of their occurrence is within the scope of many researches and investigations worldwide, thus fostering and strengthening the collaborations among international research networks. The topic of this presentation is the environmental and human health risk assessment due to pharmaceuticals in the case of direct reuse reclaimed water in agriculture, focusing on the tools and frameworks available for the analysis and the main findings achieved in relevant studies.

The starting point is the secondary effluent of a municipal wastewater treatment plant. The talk analyses the (key) role of the (selection of the) polishing treatment in improving the final effluent quality not only in the mandatary respect of the legal requirements, but also from the pharmaceutical perspective, in the capacity of reducing their concentration and their potential adverse effects on the environment. In this context, different treatment trains are analysed and compared in terms of quality and environmental risk posed by the residues of pharmaceuticals. The attention is then posed to the fate of the pharmaceuticals on the soil and their main effects on the different crops with an overview of the main tools to evaluate the corresponding risks as well as the main findings achieved in some case studies worldwide. The presentation concludes with the main directions in which gaps are still evident and where research efforts should be addressed.

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Biotransformation products of pharmaceuticals compounds in a two-phase (acidogenic-methanogenic) anaerobic bioreactor

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Anaerobic digestion is a globally applied method for the treatment of different types of wastewaters. Its phase separation into acidogenic and methanogenic steps in series, has shown significant potential for maximizing energy recovery from the generated biogas and improving the removal of organic micropollutants such as pharmaceutical compounds. While many of these chemicals are effectively removed during the process, it is not well understood whether the residual metabolites maintain the active compounds of the original chemical structure of the drug. This work aimed to throughly investigate the biotransformation products (BTPs) of pharmaceuticals generated in an acidogenic-methanogenic anaerobic reactor. For that purpose, a low organic strength substrate (1 g-COD L-1) spiked with 10 µg L-1 of eight pharmaceuticals (sulfamethoxazole (SMX), ciprofloxacin, acetaminophen, naproxen, diclofenac, ibuprofen, metoprolol, and carbamazepine (CBZ)) was applied. Influent and effluent liquid samples of the bioreactor were processed by solid phase extraction, prior the analysis in an Acquity ultra-high performance liquid chromatographic system (UHPLC) coupled to a Q-Exactive Orbitrap mass analyser. Applying a suspect screening approach, it was possible to accurately detect > 25 BTPs. For example, in the case of SMX, two BTPs were detected including acetylation in acetylaniline, and another one showing cleavage of the isoxazole ring in the 4-aminothiophenol. Another example can be found in the CBZ, which presented hydroxylation in 2 BTPs - 2-hydroxy-CBZ and 10,11-dihydroxy-CBZ. From these tentatively identified BTPs, it was possible to elucidate probable biotransformation pathways during the different phases of anaerobic digestion. Some compounds were produced in the acidogenic step, being moderately or fully consumed in the methanogenic step (e.g., 4-aminothiophenol and acetylaniline), while others increased their concentration during methanogenesis (e.g., 2-hydroxy-CBZ and 10,11-dihydroxy-CBZ). This study shed light on the fate of key organic micropollutants during anaerobic digestion, which is essential for a better understanding of their biotransformation pathways. Additionally, promising results have been obtained from phase separation during acidogenesis and methanogenesis, indicating that it could enhance the removal of BTPs from pharmaceuticals compounds.

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ORAL COMMUNICATIONS

Advances on biomass-derived microporous carbons for efficient removal of pharmaceuticals from wastewater

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Wastewater treatment facilities are facing new challenges due to the increasing prevalence of pharmaceuticals, often resistant to conventional treatments. The improvement of wastewater treatment efficiencies for the removal of recalcitrant pharmaceuticals assumes a decisive role in the attenuation of this environmental threat. Microporous carbons and, in particular, activated carbons (AC) are massively applied in a large number of emergent environmental problems, including the removal of pharmaceuticals from water. Yet, currently available commercial options strongly rely on non-renewable fossil sources as AC precursors, raising concerns due to mid/long-term shortage of raw materials and process sustainability. Finding valid and reliable alternative precursors to produce AC with relevant adsorbent properties would trigger a significant increase in the greenness of these materials.
This communication presents recent advances on the use of carbon-rich residual biomass from industrial activities (paper and brewing industries) for the development of microporous carbons, with subsequent application in the adsorptive removal of pharmaceuticals from water. Residual biomass from the referred industries was subjected to thermal and chemical treatments of different complexity to obtain microporous carbons with distinct key features. In this sense, this research was focused on the development of powdered AC (prepared by pyrolysis combined with chemical activation) and functionalized AC (pyrolysis followed by chemical activation and grafting functionalization or magnetization). Along with conventional heating for the conversion of the biomass into a microporous carbon net, microwave-assisted pyrolysis was applied to increase the sustainability of the production routes, by optimizing low-energy processes and minimizing the use of reagents. Developed materials were fully characterized, addressing their chemical, physical and textural properties and their link with production conditions. The properties of the developed materials as adsorbents, foreseeing their application as advanced treatment for the removal of pharmaceuticals from water, were evaluated either in single or competitive conditions, considering pharmaceuticals from different therapeutic classes. The obtained results reinforce that biomass-derived microporous carbons are capable to attain similar or higher performances than commercial AC for this specific application.

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Assessing the burden of antibiotics and other pharmaceuticals in the water cycle from anthropogenic and animal farms sources

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Antibitotic resistance (AR) is a global health challenge and its spread at high rate may be due to antibiotic overuse, and misuse in clinical treatment, aquaculture and livestock. Antibiotics are ubiquitous contaminants in the environment and the main sources of contamination are human and veterinary use. Our research group is studying the occurrence and fate of antibiotics and other pharmaceuticals since more than two decades and had a historical dataset for Italy, which is one of the country with the highest consumption of antibiotics in Europe. The aim of this study was to assess the burden of antibiotics and other pharmaceuticals in surface water in an highly inhabited area in Italy and identify the main sources. The selection of active principles and metabolites (more than 40 compunds) was done according to the most used substances in human and veterinary medicine in the study area. Specific and selective analytical methods were developed using solid phase extraction and liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), and were validated according to current guidelines. The study included the basins of three main rivers in the North of Italy, the Po, Lambro and Oglio rivers, where mass balances of pharmaceuticals loads have been calculated by multiplying the concentrations by rivers flow rates. Pharmaceuticals and antibiotics loads were increasing along the river basins reflecting the increasing anthropogenic and animal farming impact. The mass loads of antibiotics were up to the kg/day range confirming the presence of potential selective pressure for AR in the environment. The most abundant classes of antibiotics were sulphonamides, macrolides, lincosamides and fluoroquinolones, and for other pharmaceuticals were anti-inflammatories and diuretics. Some areas had very high load of lincomycin probably related to local veterinary use. Seasonal differences were observed in surface water contamination of antibiotics reflecting the different pattern of use during the year. This study allowed to characterize the size of contamination by antibiotics and other pharmaceuticals and identify local sources of contamination. This information is particularly relevant for public authorities who have to plan legislation or mitigation interventions.

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Characterization and prioritization of organic micropollutants in wastewater from Catalonia Province, Spain

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The present study evaluated the occurrence of 140 organic micropollutants in raw and treated wastewater of three selected wastewater treatment plants from Catalonia Province (northeast of Spain). In total, fifty-four samples of effluent and influent wastewater samples were collected during three consecutive days over a period of three different seasons. Selected compounds belonged to the groups of endocrine disrupting compounds, antibiotics, pesticides, personal care products, and pharmaceuticals widely used in Spain. Antibiotics were the most frequently detected compounds, reaching the highest concentrations during winter season. Main contribution in effluents was from psychiatric drugs and analgesics. Approximately, 75% of compounds detected in influent wastewater were positively identified in effluent, revealing that these compounds are not completely removed by conventional treatments applied in WWTPs. Furthermore, total concentrations in effluent samples were up to 40 µg/L, showing a significant input of pollutants to water ecosystems from effluents. Thus, a prioritization strategy, based on the compound concentration, frequency of detection in effluent wastewater, WWTP removal efficiency, toxicity, and persistency in water environment, was applied to highlight the organic micropollutants of major ecological concern for the receiving surrounding environment. Finally, a priority chemicals list for further monitoring was developed, which should be include in current and future monitoring program of the receiving river water basins.

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Which are the antibiotic resistance strategies that soil bacteria adopt when irrigated with treated wastewater?

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In the context of scarce water resources, the use of treated wastewater (TWW) appears to be a fair and sustainable solution for irrigation of agro-ecosystems. Nevertheless, TWW is known to contain pathogens & pharmaceutical residues including antibiotics and resistant bacteria. To supervise and control this practice but also to assess whether or not TWW participates in the dissemination of antibiotic resistance and identify the resistance mechanisms adopted by bacteria, we have explored the response of the soil microbial communities when exposed to TWW spiked with increasing antibiotic concentrations.

The main questions we would like to answer are the followings: Which are the mechanisms and the dynamic of antibiotic resistance in soils? Which are the role of endogenous bacteria (in soil) vs exogenous bacteria (TWW) in antimicrobial resistance dissemination? Which are the fate of antibiotics in soils? Which bacteria are related to these different phenomena? How does the antibiotic concentration play a role on these events?

Lab scale microcosms, inoculated with an agricultural soil irrigated with TWW, have been set up and spiked with sulfamethoxazole at environmental concentrations and above (from 0.01 to 1 mg/kg-dry-soil). For 1.5 month, we have monitored key chemical compounds, quantified antibiotics and their transformation products (TPs), the copy number of genes involved in antibiotic degradation, resistance and nitrification/denitrification processes; and determined the bacterial abundance and diversity by qPCR and 16S rRNA sequencing.

LC-MS full-scan analysis showed a threshold at 0.5 mg/kg-dry-soil above which the degradation rate of sulfamethoxazole was more important. Different TPs could be detected: desamino & nitro derivatives associated with denitrification processes during the early stages (0-3 days), n-acetyl derivative detected at the highest concentration (1 mg/kg-dry-soil) (0-3 days) and hydroxy-derivative detected up to 28 days. Other TPs are still to be searched and discovered and the data processing using the non-targeted XCMS tool will certainly provide additional information.

The on-going multi-analyses will enable us to improve our understanding about the antibiotic resistance mechanisms that really take place in agro-ecosystems and to identify markers (bacterial, TPs or sulfamethoxazole threshold) to monitor in order to better manage the use of TWW.

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Removal of pharmaceuticals and personal care products from wastewater by soil-aquifer treatment: risk assessment related to drinking water production and agricultural use

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Available freshwater scarcity is driven by population growth, increased need for agricultural products, expansion of industrial activities, and especially climate change, which is becoming more evident day after day. Groundwater is the major source of potable water supply, about 75% in the EU, and is usually an important water source for agriculture. In this scenario, treated wastewater use for the replenishment of aquifers emerges as a suitable approach to increase water availability. However, it may lead to groundwater pollution because of the remaining contents of chemical and microbiological pollutants, such as the contaminants of emerging concern (CEC). Then, it is necessary to improve the natural capacity to degrade CECs in the soil-aquifer treatment (SAT) used as a procedure to recharge aquifers. To this end, we built a pilot SAT system including natural-based reactive barriers [1]. The pilot was fed with the secondary effluent of a Wastewater Treatment Plant, and the water obtained after SAT was applied to grow vegetables. Reclaimed water was monitored to evaluate the removal efficiency of selected CECs, namely pharmaceuticals and personal care products.
Two human health risk assessments were carried out to test the suitability of reclaimed water to produce i) drinking water and ii) irrigated crops intended to eat raw. For drinking water, risk quotients (RQs) were estimated and for the exposure through diet, estimated daily intake rates (EDI) were calculated.

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Mapping the chemical exposome of brain tumors: A pilot study

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Diffuse gliomas are a highly heterogeneous and aggressive brain tumours with poor prognosis and survival and few established risk factors. Environmental exposures are suspected in the pathogenesis of these tumours; however, results of existing studies are limited and inconsistent, particularly for exogenous organic chemicals, with no available characterization of the chemical exposome of these tumours. Also, better understanding of phenotypic differences in tumour types is needed in order to improve clinical decision making and provision of personalised treatment recommendations. In this proof of concept study we analysed 33 glioblastoma samples (Bellvitge Glioma Cohort (BGC), Spain, 2005-present), including 16 methylated and 17 non-methylated tumours combining HRMS-based wide-scope target and suspect strategies. Forty-six exogenous chemicals were identified in the tumour tissue samples (31 confirmed with standard) including a variety of industrial chemicals (e.g. plastic additives or perfluorinated compounds), personal care products and pharmaceuticals. Our findings provide novel evidence on the presence of these chemicals in brain tissue, highlighting the need for comprehensive evaluations of their potential effects in the tumour pathogenesis. Finally, after applying metabolomics methods we observed clear differences in the profiles of endogenous chemicals among the studied glioma subtypes, and identified possible biomarkers. These chemicals have potential to be determined in a non-invasive manner, either by LC-HRMS-based blood analysis or using complementary techniques (proton magnetic resonance (1H-MRS)). These are inspiring results since methylation is a strong independent predictor of survival as well as tumour response to chemotherapy for glioblastoma. Indeed, its non-invasive and presurgical determination would have a major impact on patient management. Our preliminary data is suggestive for the potential of nontargeted exposome methods to find new valuable biomarkers for diffuse gliomas diagnostic and prognostic stratification.

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Combination of proteins, small-molecule and microbiological characterization for a holistic understanding of wastewater based epidemiological studies.

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A fraction of the of the chemicals used in consumer products, industries, agriculture and/or livestock areas are collected by sewerage systems and end up in wastewater treatment plants (WWTP). Therefore, an efficient chemical monitoring in WWTPs influents can provide constant and up-to-date information on chemical usage rates. This approach, called sewage epidemiology, have been widely applied to assess drug consumption, to evaluate exposure to contaminants, COVID-19 growth, Antibiotic Resistance Genes (ARGs) spread or animals and human proteins in WWTPs. The mail goal of the present work was to combine all these data to validate usefulness of multiclass WW-based epidemiology.
WWTP Influent samples were collected in 2022. 100 mL were treated for protein analysis, as described elsewhere [1], while other 150mL filtered with PTFE filters (0.2 µm) were treated as described elsewhere for small molecules [2], keeping the particulate in the filter for ARGs as described elsewhere [3]. HRMS instruments were used for both proteins and small molecule analysis, while qPCR were made for seven specific genes (intl1, qnrS1, tetM, mecA, blaTEM, blaCTX-M-32, blaOXA-5) which confers bacteria resistance against widely used antibiotics.
A suspect analysis of antibiotics, as well as human and farm animal specific proteins (retrieved from proteomics analysis) were determined. ARGs were also analysed, showing that wastewater bacterial communities are exposed to antibiotics and subsequently, generating ARGs despite clear correlations could not be established. However, a decrease in the levels of antibiotic does not immediately affect ARGs presence.
Influent wastewater was collected from WWTPs areas with clearly differentiated profiles in terms of economic sector of the population feeding it. Two of them serving primary sector towns, three serving areas heavily industrialized and one in the highly-populated area of Barcelona (mainly urban). Several correlations of different proteins with unknown small molecules were observed. Currently we are elucidating their identity to study potential links between them in the studied area, to explore the high potential of this strategy.

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Comprehensive profiling and semi-quantification of exogenous chemicals in human urine using HRMS-based strategies

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Chemicals are part of our daily lives, and we are exposed to numerous chemicals through multiple pathways. To obtain a holistic picture of such chemical exposome, human biomonitoring (HBM) is commonly applied. The classical approach is using target screening strategies (based on triple quadrupole instruments) of less than 100 compounds, but the latest advances in high-resolution mass spectrometry (HRMS) enables the use of wide-scope target, suspect and non-target strategies to obtain a wider characterization of the chemical exposome with closer limits of detection day by day. However, robust and simple sample treatment protocols accounting for a reliable analysis of a broad spectrum of the chemical realm are required. The main objective of this study was to validate a methodology to obtain an accurate and comprehensive profile of exogenous chemicals and its associated metabolites in urine samples using HRMS-based strategies. We have evaluated five extraction protocols for a wide range of chemical classes (including pharmaceuticals, plastic additives, personal care products or pesticides, among others) in terms of extraction recoveries, linearity, matrix effect, sensitivity, and reproducibility. Finally, the protocol which yielded best results was comprehensively validated and further applied in 10 real human urine samples, in a wide-scope target analysis (>2,000 chemicals). A total of 35 chemicals were identified and semi-quantified, including plastic additives, food- and tobacco-related chemicals, pharmaceuticals, or biocides, showing the good performance for the methodology. The need for a deconjugation step was dismissed as similar results were obtained when the protocol did not include this tedious and time-consuming process.

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The abundance of microplastics in a wastewater treatment plant in the Taiwan tourist area and the potential vector of UV filter

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Wastewater treatment plants (WWTPs) are crucial infrastructures for removing various pollutants from domestic and industrial wastewater. Among these pollutants, microplastics have gained increasing attention due to their persistence in the environment and potential adverse effects on ecosystems. However, research on microplastic contamination in WWTPs is still limited in Taiwan. This study aimed to investigate the presence and characteristics of microplastics in two tourist locations, one in the inland and one in the coastal area, during both summer and winter.

The selected tourist locations were equipped with simple treatment facilities that had limited capacity and were not specifically designed to address emerging contaminants, such as microplastics. To identify microplastics, samples were collected from the WWTP influent and effluent and analyzed based on size, shape and polymer type using a microscope and microFTIR spectroscopy.

The results revealed notable differences in microplastic abundance between the two wastewater treatment plants, influenced by seasonal variations and tourism activities. In the inland tourism area, only two types of polymers, rayon and polyethylene, were identified. On the contrary, the coastal area exhibited greater microplastic diversity, with five different types of polymers, including rayon, polypropylene, polyethylene, polyester, and others. The microplastic removal rates in WWTP ranged from 80% to 97%, indicating that these treatment facilities significantly impact the reduction of microplastic loads in wastewater. However, a substantial amount of microplastics, particularly in coastal tourism areas, raises concerns. This is attributed to the higher usage of UV filters and personal care products (PCPs by tourists), contributing to microplastic pollution.

Based on these findings, further research on emerging contaminants such as microplastics and PCPs is strongly recommended, particularly in tourism areas. Understanding the sources, fate, and impacts in these environments is crucial for developing effective mitigation strategies and protecting sensitive coastal ecosystems. By implementing targeted measures, such as advanced treatment technologies and public awareness campaigns, it is possible to reduce microplastic pollution and promote sustainable tourism practices in these vulnerable regions.

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Discovering new psychoactive substances and their transformation products in wastewaters via target, suspect and non target HRMS approaches

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The availability of New Psychoactive Substances (NPS) has posed a significant challenge over the last few years. In this context, the present study investigates the occurrence and contamination profile of NPS and their TPs in wastewaters over a period of two years in order to foresee any potential environmental risks they may pose to the aquatic environment. To do this, an integrated strategy was performed by combining the target, suspect screening-(SS) and non target approaches (NTA). Data analysis was performed by optimizing a SSA and NTA workflow. According to the results different categories of NPS including antipsychotics, antidepressants, benzodiazepines, opioids, dissociative anesthetics and psychoactives have been detected with a concentration ranged from <LOD to 732 ng L-1 . Overall, 15 out of 45 identified compounds were detected in at least half samples while the majority of them encompasses in the group of antidepressants with a concentration up to 352 ng L-1. Concerning the class of antidepressants and their transformation products (TPs); the highest detection frequency percentages were obtained for the TPs of venlafaxine. Namely, N,N-Didesmethyl venlafaxine, O-Desmethylvenlafaxine and Venlafaxine N-Oxide occurred in 94%, 78% and 56%, respectively. overall, suspect and non-target screening in wastewaters can be effectively used to determine the site which needs further in-depth investigation as well as establishment of future regulations and/or management strategies on chemicals of emerging concern.

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Pharmaceuticals in dolphins stranded in the Basque Country´s Coast

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The Stranding Network of the Basque Country has been collecting different tissues from stranded cetaceans in the Basque Coast since 2014, in collaboration with the Biscay Bay Environmental Biospecimen Bank (BBEBB) of the Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV/EHU).

One of the aims of the Basque Sustainable Pharmacy initiative is the promotion of research in the field of pharmaceuticals in the environment. Accordingly and as a pilot experience, analyzed tissue-concentrations of 99 pharmaceuticals from ten stranded dolphin tissue samples archived at BBEBB. Thus, we chose ten fresh cetacean individuals stranded along the Basque Country coast between 2016-2021: Three common dolphins (Delphinus delphis) and seven striped dolphins (Stenella coeruleoalba). Muscle, liver and blubber tissue samples of each individual were employed in this study for the cuantification of pharmaceutical by means of LC-MS qOrbitrap. All samples were collected in the first 12-15 hours after the death of the animal.

At least traces of one pharmaceutical were found in 7 out of 10 stranded dolphins. Two striped dolphins and one common dolphin showed no pharmaceuticals in their tissues. Only 3 pharmaceuticals out of 99 were found above their detection limits: orphenadrine, pizotifen and promethazine. One striped dolphin showed the presence of both orphenadrine and pizotifen in the liver, while other individual from the same species had pizotifen in the liver and promethazine in the blubber. No drugs were detected in muscle samples. Concentrations found were low, <1ng/g.

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Solid phase extraction using waste-based sorbents for the determination of pharmaceuticals in water matrices

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Pharmaceuticals, such as sulfamethoxazole (SMX) and carbamazepine (CBZ), have been detected in aquatic environment at ng/L and microg/L, respectively. Generally, due to low levels of contamination and complex water matrices, solid phase extraction (SPE) is mandatory previously to the quantification by high performance liquid chromatography (HPLC). SPE is more frequently used due to the vast diversity of sorbents available, however, its use in large environmental screenings brings a significant increase in the cost of the analytical process, generally associated to the cost of the sorbents. The development of alternative sorbents from wastes is especially attractive because the employment of conventional approaches in large environmental screenings significantly increases the cost of the analytical process. In this work, two biomass-based sorbents, derived from waste materials (spent brewery grains (SBG) and primary paper mill sludge (PPS)), were successfully produced through chemical activation and pyrolysis. The resulting materials were then used in SPE cartridges for the preconcentration of CBZ and SMX, followed by quantification using HPLC with UV or fluorescence detection, respectively. Optimization steps consisted of the evaluation of type and amount of sorbent used, eluent type, eluent volume, contact time and sample volume. Under optimized conditions, calibration curves were obtained for CBZ with standards ranging from 1 to 10 microg/L and for SMX, with standards ranging from 0.050 and 1 microg/L, with limits of detection of 0.69 microg/L for CBZ and 0.015 microg/L for SMX. Finally, matrix effects were evaluated in river water and wastewater, demonstrating good recovery in river water for both pharmaceuticals, although in wastewater a significantly decrease was observed, probably due to pH implications for SMX, and high DOC values for both SMX and CBZ. At the end, it was concluded that the developed method was accurate and repeatable, being suitable to be applied in the determination of SMX and CBZ in surface waters.

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Matrix Effects on the Removal of Pharmaceuticals from Wastewater through Filtration with Multi-Channel Mixed-Matrix Membranes

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Pharmaceuticals found in the environment and associated health and environmental risks have become a major issue over the last decades. Especially, the insufficient removal of micropollutants through wastewater treatment plants (WWTP) is considered to cause the accumulation of hazardous substances in the environment. Hence, the need for efficient and innovative technologies is high. Multi-channel mixed matrix membranes (MCMMM) are considered a promising combination of filtration and adsorption processes due to their geometry and surface activity. In this study, MCMMM with embedded activated carbon were applied to remove the pharmaceuticals carbamazepine (CBZ), diclofenac (DCF) and paracetamol (PAR) from different aqueous matrices. Removal rates of 47.9 %, 80.4 % and 84.4 % for DCF, CBZ and PAR could be achieved from spiked fresh water. WWTP effluent spiked with 15 mg/L of the pharmaceuticals showed a small increase in the removal efficiency for PAR and CBZ, and a decrease of 6.4 % for DCF. A decrease in membrane permeability of 18.1 % was observed during the filtration with WWTP effluent compared to fresh water causing longer retention times of the pollutants. Wastewater showed a slightly lower pH of 7.1 than fresh water with 8.0 and an increased chemical oxygen demand (COD) of 21.1 mg/L. Adsorption experiments with acidic and alkali pH resulted in a significantly higher removal rate for DCF in acidic medium. These findings are confirmed by filtration experiments at different pH showing an increase of the DCF removal from 25.2 % up to 66.2 % in acidic medium compared to alkali medium. CBZ and PAR showed the highest removal efficiency at a pH of 7. The change in the pH did not affect the permeability of the membranes. Based on the results, it can be stated that the matrix of the aqueous solution plays a crucial role in the removal efficiency of the pharmaceuticals. The effects of the pH has to be further investigated. Long-term experiments are suggested to study the interaction between dissolved organic matter and the pharmaceuticals. Overall, MCMMM are an auspicious technology for reducing the micropollutant contamination of the environment.

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Promoting educational activities at the University on Sustainable Pharmacy

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Developing learning activities prepared to respond to current and future challenges associated with the climate crisis is of major importance. The Sustainable Development Goals (SDG4) and even the European Commission are stimulating activities that may ensure quality education, including Universal primary and secondary education, on topics such as the impact of pharmaceuticals as emerging interest contaminants.
We have initiated at the Basque Sustainable Pharmacy program (Vitoria, Spain) a set of activities focused on defining and educating relevant aspects related to drug pollution and sustainable pharmacy. On the one, the first postgraduate course of drug pollution delivering contents on the problem of drug pollution and effects on the environment and on the potential solutions. On the other hand, a wide number of educational survey among students and professionals related to health about the current knowledge and attitude on this topic. In the present conference, I will update the most relevant highlights of both educational projects.

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Occurrence and risk assessment of pharmaceuticals and other Contaminants of Emerging Concern in surface water from a water reuse system

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Drought is a growing concern worldwide and has a significant impact on water availability, ecosystem health, agriculture, and socioeconomic well-being. In the midst of this problem, the reuse of regenerated water emerges as a solution to address water scarcity. The use of regenerated water for different purposes is subject to a legal regime that establishes permitted uses, basic quality criteria, and the treatments that must be received. For instance, for agricultural irrigation, the criteria and treatments applied depend on the crops irrigated and the type of irrigation. Nevertheless, water systems recharged with reused wastewater have shown the presence of some contaminants of emerging concern (CECs) due to their incomplete removal in wastewater treatment plants (WWTPs), which could represent a risk to the environment and human health. To investigate this issue in an agricultural area where the irrigation water is a mixture of surface water and regenerated water, the occurrence of 43 preselected CECs was monitored monthly over one year at different points of the network of irrigation channels and in two wells. The targeted contaminants had been identified in a previous study conducted in the area through a suspect screening approach and estimation of the potential risk for the aquatic environment. The target analysis of these prioritised compounds has been performed using liquid chromatography-tandem mass spectrometry with a hybrid quadrupole time-of-flight analyzer (LC-QToF-MS/MS) in positive ionization and an on-line solid-phase extraction (SPE) with a polymeric cartridge. Subsequently, an environmental risk assessment was conducted based on the Measured Environmental Concentration (MEC) and the Predicted Non-Effect Concentration (PNEC) in freshwater.
The results obtained showed slightly higher concentrations in colder than in warmer months, possibly due to distinct microbiological activity. The pharmaceuticals found at highest concentrations were O-desmethylvenlafaxine, 10,11-dihydro-10,11-dihydroxycarbamazepine and sitagliptin. However, those posing the highest environmental risk (RQ >10) were the antidepressive venlafaxine and its metabolite O-desmethyl venlafaxine, and the antibiotic ofloxacin. In addition to pharmaceuticals, a predominant occurrence of industrial chemicals (such as phthalates, phosphate plasticizers, fire retardants, and corrosion inhibitors) was also observed while pesticides such as diuron and carbendazim and drugs of abuse like MDMA presented a more residual occurrence.

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Microbial community structure changes in three soil types soils exposed to non-steroidal anti-inflammatory drugs. A laboratory experiment

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Non-steroidal anti-inflammatory drugs (NSAIDs) may enter soils due to treated wastewater reuse for irrigation purposes or because of biosolids application as an alternative to synthetic chemicals. Three different type of soils (cambic chernozem, luvisoil, calcareous rendzinas) collected from Cluj-Napoca, Romania, were used for laboratory experiment with aim to assess inhabiting soil microbiota response to NSAIDs. In this study, we focused on the immediate, short- and long-term effects of ibuprofen, diclofenac, and mixture amendment on the microbiota of three different types of soils. Microbiota abundance and structural changes were determined by monitoring phospholipid fatty acids (PLFA) profiles by gas chromatography. Soil microbiota abundance differed in the three soil types, varying within 71 – 128, 49 – 63 and 58 – 75 nmol×g-1 d.w. soil for controls of cambic chernozem, luvisoil and calcareous rendzinas soils, respectively. Studies of NSAIDs proved different effects on soil microbial populations. Principal component analysis of microbial PLFA revealed the alteration of microbial biomarkers and the impact on microbial community abundance and structure due to NSAIDs stresses. The first two principal components accounted for 72 % and 20 % (cambic chernozem soils), 56 % and 32 % (luvisoils), and 68 % and 23 % (calcareous rendzinas soils), respectively. In the current study, some bacterial functional groups showed higher NSAIDs tolerance and grew better than other functional groups (e.g., some fungal communities). These results confirmed that fungi had more sensibility under pharmaceutical stress than bacteria, which led to microbial species replacement and diversity alteration.

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Antibiotics Degradation and Bacteria Inactivation in Water by Silver Nanoparticles

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Contamination of aquatic resources with antibiotics poses a threat to the environment and human health, leading to the enhancement of antimicrobial resistance (AMR), which is predicted to be the leading cause of death by 2050. Conventional water treatment systems are often ineffective in removing antibiotics and inactivating microorganisms[1]. Nanomaterials have shown efficiency as photocatalysts in the degradation of organic pollutants, due to their high surface area/volume ratio. Among these nanomaterials are silver nanoparticles (AgNPs), which are easy to prepare, low cost, and have shown good performance in photocatalysis. Furthermore, AgNPs have shown excellent antibacterial properties in the treatment of infections in biological media[2]. Thus, in this project, AgNPs were developed for the treatment of water contaminated with the antibiotic ciprofloxacin, under sunlight irradiation, and for the inactivation of bacteria in water. The AgNPs were prepared through the process of chemical reduction in water, with spherical and prismatic shapes. The results revealed that the prismatic AgNPs presented superior performance than the nanospheres, in the photodegradation of ciprofloxacin, and in the inactivation of bacterial strains of Escherichia coli and Staphylococcus aureus. Thus, AgNPs present the potential for the treatment of contaminated waters.

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Evaluation of Hydrogen as an Alternative Carrier Gas for GC-MS/MS Analysis of Pesticides

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Gas chromatography coupled with mass spectrometry (GC-MS) is a well-established method for analyzing volatile and thermostable organic compounds. Helium, an often-used carrier gas, faces supply challenges due to its non-renewable nature and increased costs. This has prompted interest in alternatives, including nitrogen and hydrogen (H2). This study aimed to assess the feasibility of H2 as a carrier gas in GC-MS/MS for analyzing a suite of 150 pesticides, in terms of sensitivity, efficiency, and safety. A comprehensive GC-MS/MS method was optimized to address the known challenges associated with H2. The performance metrics, including linearity, reproducibility, and matrix effects, were studied using various matrices. H2 has superior diffusion and reduced viscosity compared to helium and nitrogen, resulting in faster analyses with maintained or improved resolution. However, its flammable nature necessitates special precautions in the laboratory. Modern equipment, featuring internal leak detection and automatic shutdown, mitigates some safety concerns. Despite the benefits, H2 can react in the ion source, potentially affecting sensitivity. Preliminary findings suggest that, with appropriate optimization, H2 can serve as a viable, sustainable, and cost-effective carrier gas for GC-MS/MS in pesticide residue analysis.

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Target/non-target screening and risk assessment for a coming indirect potable water reuse: Three case studies in Catalonia

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Since the beginning of 2021, Catalonia has been immersed in a sustained situation of meteorological drought that has put significant pressure on its water resources.. Subsequently, the Catalan Water Agency (ACA) is searching for alternative water sources, aiming to increase the availability of pre-potable water in the Catalan River Basin District.

The scenarios under scrutiny include the exploitation of new riverbank filtration wells in a river impacted by wastewater and close to Barcelona Metropolitan Area (case study A), the implementation of indirect potable reuse schemes in central Catalonia (case study B), and the introduction of additional wastewater effluents in an already operational indirect potable reuse system (case study C).

During the last decades, ACA has routinely conducted comprehensive analyses of target contaminants in these points, which translates into a proper understanding of the occurrence of 281, 151 and 159 chemicals in sites A, B and C, respectively. However, in order to fully identify the potential risks and ensure their functionality as pre-potable resources, exhaustive additional screenings have been recently performed by liquid chromatography coupled to high resolution mass spectrometry. Briefly, we employed a combination of wide-scope target screening (in-house database of >700 chemicals with available chromatographic retention time) along with suspect screening (including >10,000 chemicals from the NORMAN database). Additionally, we applied non-target prioritization based on negative mass defect (an indicator of the presence of halogenated chemicals) to broaden the scope of potential toxic chemicals in the method.

Several additional, non-regulated, pollutants were identified at trace concentrations with (at least) level 2 confidence, including pharmaceuticals, antibiotics, plastic additives, biocides, oligomers, UV filters, synthetic musks, and other miscellaneous anthropogenic contaminants. These compounds were detected in water before its planned potabilization, and their risk has been assessed with human health-based thresholds (collected from drinking water regulations, WHO recommendations, and water reuse guidelines; or derived from acceptable daily intakes, minimum therapeutic dose values and chronic toxicity studies).

The present study will provide useful information to choose the optimal treatment train for upcoming purification plants, thus obtaining high-quality potable water that meets the strictest drinking water regulations, protecting the consumers' health and their confidence.

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The effects of micropollutants mixtures on marine and brackish microorganisms

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The occurrence of emerging contaminants poses a potential threat to the aquatic ecosystems. At present, risk and hazard assessments primarily rely on the evaluation of the impacts of individual chemicals. Nevertheless, ecosystems are subjected to the influence of pollutant mixtures. The interactions among these pollutants, coupled with their continuous presence in the aquatic environment, could increase the overall risk to organisms and lead to unanticipated consequences.

Pharmaceutical residues, including antibiotics, have been detected in the marine environment, including coastal and estuarine waters. The marine and estuarine environment can act as a sink for some pharmaceutical residues. They can also accumulate and persist in these environments, leading to potential negative impact on marine ecosystems. Ionic liquids (ILs) are a type of organic salt that has garnered attention due to their promising potential for applications in various industrial areas. However, their distinctive physicochemical properties and resistance to biodegradation have raised concerns regarding their impact on the environment. As a result, ILs are now recognized as a potential threat to aquatic ecosystems.

The objective of this presentation is to offer an outline of the difficulties and hazards linked to the existence of micropollutant mixtures, which includes the impacts of mixtures of representative antibiotic oxytetracycline OXTC and ionic liquid 1-dodecyl-3-methylimidazolium bromide IM1-12Br. The obtained results involve studying the long-term effects of mixtures of two target compounds on various microorganisms present in brackish coastal waters and the open Baltic Sea basin. The microorganisms investigated include the green algae Chlorella vulgaris, the cyanobacteria Microcystis aeruginosa, and the diatom Phaeodactylum tricornutum. Moreover, the study examined the effects on Aliivibrio fischeri, a luminescent marine bacterium. The growth, photosynthesis process, and pigment ratios of all microorganisms under investigation were found to be affected. The application of concentration addition (CA) and independent action (IA) mathematical models, followed by the Model Deviation Ratio (MDR) evaluation, enabled the identification of primarily synergistic interactions within the examined mixtures. The findings of this study contribute to a better understanding of the impact of pharmaceuticals and other micropollutants mixtures on aquatic organisms.

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TiO2/Carbon dots nanocomposites: Solar driven photocatalysts for the removal of antibiotics from aquaculture effluents

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Aquaculture exploitation has grown to satisfy the world's demand for fish and other seafood. However, aquaculture is associated with the consumption of antibiotics, such as sulfadiazine (SDZ), sulfamethoxazole (SMX) and trimethoprim (TMP). Consequently, and given that aquaculture wastewater treatments are not actually designed for the removal of antibiotics, they are ubiquitous in aquaculture effluents, which sets the risk of bacterial resistance. To face the need for an efficient and sustainable treatment to remove these antibiotics from the referred effluents, photodegradation under natural irradiation may be a sustainable alternative if a proper efficiency is achieved. For such purpose, in this work, novel photocatalysts were synthesized by the incorporation of carbon quantum dots (CQDs) into commercial (P25) titanium dioxide (TiO2). Two types of CQDs were synthesized under hydrothermal treatment by using citric acid and urea (CQDs-CAU) and citric acid only (CQDs-CA). Through a facile hydrothermal-calcination method, nanocomposites were produced by incorporating different percentages ((4%, 5%, 6% and 8%) (w/w)) of each type of CQDs into TiO2. Afterwards, they were evaluated for the solar driven photodegradation removal of SDZ, SMX and TMP from two different synthetic matrices, used to simulate fresh and brackish water. It was found that 4% (w/w) of CQDs-CAU and CQDs-CA incorporated into TiO2 (TiO2/CQDs-CAU 4% (w/w) and TiO2/CQDs-CA 4%(w/w), respectively) were the most efficient photocatalysts. After the corresponding selection and dosage optimization for each antibiotic and matrix, kinetic results demonstrated that the produced materials allowed for remarkable reductions of SDZ, SMX and TMP half-life times (between 19 and 68 times). Therefore, the application of these photocatalysts in the advanced treatment of aquaculture effluents is promising, allowing for a green solar driven removal of antibiotics.

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Paper-based microfluidic device for rapid and on-site wastewater surveillance

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Pathogen detection in wastewater is critical for early warning of pandemic, contributing to public health surveillance. We have demonstrated the application of paper-based microfluidic devices for veterinary diagnosis in India and malaria testing in Uganda, Africa. The severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) causes respiratory illness and gastrointestinal infections, with viral material being excreted in feces (and surviving within sewage for several days). Here, we propose a low-cost and user-friendly paper-based microfluidic device incorporating reverse transcription loop-mediated isothermal amplification (RT-LAMP) for the detection of SARS-CoV-2 and influenza. Qualitative results were displayed by a UV torch, observed with naked eyes or recorded using a mobile phone camera. The paper-based platform could complete the concentration, extraction, amplification and detection of viruses in wastewater within 1.5 hours, with a detection limit as low as 10 copies μL-1. The device was used for on-site detection of SARS-CoV-2 in wastewater samples from four quarantined hotels at London Heathrow Airport, showing results comparable to those obtained using reverse transcription quantitative polymerase chain reaction (RT-qPCR) assays. The N gene presented the highest detection rate in wastewater samples, followed by the S and ORF1ab genes. ORF1ab gene shows less sensitivity than N, and S genes due to shorter sequence which is likely be degraded in the wastewater system. Our platform enables rapid detection of viruses without the need to send wastewater samples to centralized laboratories. Compared to gold-standard PCR assay, our platform provides similar or higher specificity and sensitivity for pathogen detection at a much cheaper and faster way, providing a high-resolution data set for highly responsive measurement during the pandemic. It has a clear potential that the platform can be used as a public health early warning tool for various applications in community settings and shows great potential for rapid and on-site wastewater surveillance at community settings in both developing and developed countries.

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POSTERS

ASSESSING MICROPLASTIC PRESENCE AND OCCURRENCE OF RELATED BISPHENOLS IN BEE PRODUCTS

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Nowadays, there is a great concern about the relationship between diet and its effects on physiological and pathological processes. Indeed, the consumption of organic foods has increased considerably in recent years, and especially, those foods from the beehive like honey and bee pollen due to both its beneficial effects on health and its nutritional properties. However, the global problem of plastic contamination exposes pollinators as bees to multiple sources of pollution from different sectors, including microplastics (MPs). MPs are defined as plastic particles ranging in size from 5 mm to 1 µm, which are highly persistent and ubiquitous, and may be transmitted through the trophic chain resulting in retention of environmental contaminants and release of additives causing toxic effects. Bisphenols are plastic components as they are used as additives in plastics manufacturing. Moreover, some bisphenols are classified as an Endocrine Disrupting Chemical (EDC) because they can act as xenoestrogens having adverse effects on human health and other living organism. All these contaminants can be also found in beehives and their related food products. Consequently, it is required to establish analytical methods to control their presence in bee related foods in order to avoid potential health risks for consumers and pollinators.

Therefore, the main objective of this study is to evaluate the presence MP particles and hormone-disrupting compounds, bisphenols, in honey and bee pollen by developing adequate analytical methods. For the analysis of MPs, a sample treatment has been developed that consisted of an oxidative digestion followed by a characterization of the particles by means of microscopic and spectroscopic techniques. Meanwhile, EDCs analysis was performed by using liquid chromatography coupled to tandem mass spectrometry. Several stationary phases were tested when optimizing the method, as well as different sample treatments with the aim of obtaining the best recoveries and minimum matrix effects for both bee foods. Finally, the proposed method for determining EDCs was successfully validated and applied to quantify the target EDCs in different honey and bee pollen samples, and in which the presence of MPs was also evaluated.

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Pharmaceutical residues in crop irrigation water: a potential threat to groundwater

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Unplanned reuse of surface water impacted by wastewater treatment plant (WWTP) effluents for crop irrigation can easily spread pharmaceutical residues in the environment. The aim of this study is to investigate the presence of pharmaceutical residues and transformation products (TPs) in irrigation water and their spread to groundwater. The agricultural scenario selected for the study is the Vega Baja of the Jarama River, whose water is strongly impacted by the effluents of the main WWTPs of the Community of Madrid (Spain). After the hydrogeological study of the area, we selected two locations where two piezometers for sampling the groundwater of the Jarama alluvial aquifer were drilled. Piezometric levels were also monitored using additional wells in the area. A subsurface discharge zone where runoff, drainage, and irrigation water are mixed was identified. From June to September 2022 (during the maize irrigation campaign), biweekly samples of the irrigation water, discharge zone, and groundwater were collected. Outside the irrigation season, groundwater samples were taken once a month to cover one hydrological year. Through a first screening of the irrigation water, 284 substances were tentatively identified of which 29% were pharmaceutical residues (82) and 10% TPs (27). A prioritization study was applied to select those with the highest persistence, mobility and toxicity. Subsequently, the 21 selected pharmaceutical residues and TPs were analyzed in the 80 collected samples (irrigation water, discharge zone, and groundwater). Analyses were performed by using liquid chromatography coupled with mass spectrometry (LC-MS/MS). In general, concentration levels in the irrigation water are in the order of ng/L and only 4 pharmaceuticals reach values of µg/L: the antihypertensive valsartan, the antidiabetic sitagliptin, the main venlafaxine TP (o-desmethylvenlafaxine), and the antifungal fluconazole. In the discharge zone, the same pharmaceuticals are observed but with lower concentrations. However, only 9 target contaminants are found in groundwater suggesting that natural attenuation processes are taking place. Fluconazol, carbamazepine, and sulfamethoxazole are detected with the highest concentrations, supporting evidence about their persistence. Indeed, these substances currently generate concern for the integrity of water resources and associated ecosystems.

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MONITORING MICROPLASTICS IN WASTEWATERS UTILIZING MICROSCOPIC AND ANALYTICAL PYROLYSIS TECHNIQUES

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Microplastics (MPs) have been spotted in various substrates around the world. To throw light on the distribution profiles and for delivering a starting point for risk assessments, inclusive data on MP concentrations and polymer compositions are required. The present study investigated the presence of MPs found in effluents of two wastewater treatment plants (WWTPs) located in Thessaloniki (Greece) and Guangzhou (China). The evaluation was conducted employing a stereomicroscope and a Pyrolysis−Gas Chromatography/Mass Spectrometry (Py−GC/MS) instrumentation, as to evaluate the temporal input of MPs into the receiving water bodies. Concerning the applied protocol, a systematic sampling was carried out in a yearly basis. After collection, the samples were concentrated into smaller volume after sieving through metal sieves of different mesh sizes. Concentrated samples were further filtered through fiberglass filters and an oxidation digestion step was applied to remove the organic matter. Then, the obtained filters were dried and a mapping process with a stereomicroscope was conducted as to categorize the suspected MPs according to their shape, size, and colour. In a next step the analysis with the aid of Py–GC/MS identified and quantified several types of the most common using plastics. Fibers were found to be the dominant shape of MPs for both studied WWTPs, with the majority of them being <1.5 mm in size for the WWTP of Thessaloniki and <0.125 mm for the samples of Guangzhou's WWTP, while polyolefines held the first place among the detected polymer types for both WWTPs. Since MPs presence presented a temporal tendency during the studied period, the findings underline the necessity for the assessment of background parameters in upcoming MPs monitoring studies in both countries, Greece and China.

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Estimation of anxiolytic and antidepressant drugs consumption in low-medium-high income neighborhoods by wastewater analysis

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The increasing consumption of drugs, both illicit and legal, is generating great concern worldwide, due to its negative consequences for health, safety, social welfare and economy. Monitoring psychoactive pharmaceuticals drugs within communities of varying socioeconomic status is crucial for comprehending drug consumption patterns, identifying high-risk areas, and formulating targeted prevention and intervention strategies. Wastewater-based epidemiology (WBE) has become an increasingly accepted and widespread tool, that is useful for establishing spatial and temporal patterns in drugs consumption in a fast, cost effective and objective way. This study aims to understand anxiolytic and antidepressant drug consumption patterns in neighborhoods (NGBs) with different socioeconomic statuses. NGB-L represents low-socioeconomic status (18,042 inhabitants; 53 restaurants & pubs), NGB-M the medium-socioeconomic status (8,914 inhabitants; 89 restaurants & pubs), and NGB-H the high-socioeconomic status (5,090 inhabitants; 25 restaurants & pubs). Three by-pass sewer monitoring stations were deployed in a large Spanish city equipped with a flow-meter, a pump, and a fridge to compose 24-h continuous flow-based composite samples and keep them at 4ºC until collection. Four intensive sampling campaigns were executed (March 2021, June 2021, November 2021, March 2022); in each campaign, samples were collected daily over 1 week (in total 84 (3x7x4) samples). The results showed that anxiolytics and antidepressants are prescribed differently in the NGBs: e.g. Citalopram, Venlafaxine, and Lorazepam are more present in NGB-H and Diazepam more in NGB-L.

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Fate of pharmaceuticals after applications of human urine-based fertilisers in long-term field experiments

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Current agriculture is heavily dependent on the use of fertilisers derived from fossil resources. On the other hand, most of the nutrients in food are excreted in urine, mostly collected and mixed with wastewaters, whose management allows little recycling of these nutrients and leads to numerous environmental impacts. The direct use of human urine in agriculture would enhance the recycling of their nutrients and develop a more circular management of crop fertilization as a cheaper and more sustainable source of nutrients than fossil-based fertilisers. However, it may indirectly contribute to the dissemination of pharmaceuticals in the environment.

The objective of this work was to determine the concentrations of pharmaceuticals in human urine-based fertilisers and in the receiving soils after one or several applications in France and in Denmark where the long-term effects of repeated use of different alternative fertilisers including human urine were studied since 2003 in the CRUCIAL field experiment.
Fifty-nine molecules, including active compounds or metabolites of antibiotics (28), anti-inflamatories (9), neuroleptics (5) were analysed by online SPE-UHPLC-MS-MS in urine-based fertilisers (stored urines, fermented urines, Aurin®, Granurin®) and in soils after one spreading (France) and 18 spreading (Denmark). Caffein was also analysed as an anthropic marker.

Up to 11 and 20 molecules were found in stored urines, respectively. The concentrations ranged between 1 µg/L (e.g. carbamazepine, diclofenac) and 11 mg/L (acetaminophen) and for some compounds were similar to published data. The concentrations varied depending on the year and the origin of urine. In treated urine, only 4 to 8 compounds were at generally lower concentrations than in stored urine, as already shown. Salicylic acid, caffein and some anti-inflammatories were in all types of urine-based fertilisers. One month after one spreading, 2 to 3 compounds were at very low concentrations in soil. In the CRUCIAL experiment, only two compounds were quantified between 0.1 and 3 µg/kg DW in soils fertilised during 18 years, i.e <6% of the total spread amount.

Even though pharmaceutical concentrations in some urine-based fertilisers could be high, they were low in soils even after decades of urine fertilisation, indicating dissipation of the molecules in soil.

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Wastewater-based epidemiology and water quality monitoring using omics techniques.

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A comprehensive characterization of proteins, pesticides and pharmaceuticals in the influent and effluent waters of several WWTPs has provided new potential markers for industrial and living activities (1,2). These compounds can also give a more thorough evaluation of WWTP treatment. This is routinely evaluated through bulk parameters such as chemical and biochemical oxygen demand. However, with a plethora of dynamic and changing conditions linked to water practices, the diagnosis of water quality based on this data is far from optimal. Monitoring proteins and pharmaceuticals will generate complementary and unique data that will help understanding population characteristics and evaluate wastewater treatments. We studied the protein and small molecule composition in the influent and effluent waters of different WWTP in Catalonia which serve communities of different population and industrial profile. Water samples (24-h composites) were filtered and the soluble part was submitted to the different studies. Proteins were concentrated in a SDS-PAGE gel, digested with trypsin and analyzed by HR-LC-MS/MS and database search (1). Small molecules were obtained through different solid phase extraction methods targeting more than 140 micropollutants, including pesticides, pharmaceuticals and antibiotics. Extracts were analyzed by LC-QqQ (2). We have identified hundreds of proteins from different species including human, livestock and bacteria. Most proteins originated from main sources: excreta (urine and feces) from humans, and blood and other residues from livestock. Species-specific protein forms allowed obtaining separate profiles for species such as rat, mouse, cattle, pigs, and poultry. The integration of the protein and small molecule data (pharmaceuticals) reveals relations between the origin of the proteins and some drugs. For example, the amount of proteins derived from livestock correlates with higher levels of veterinary antibiotics. This data will be very valuable to implement new control methodologies in the WWTPs and to investigate the effect of wastewater discharge in environmental buffers but also to identify contaminants that have been so far overlooked but are persistent or formed at a significant concentration.

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NON-TARGET SCREENING FOR THE COMPREHENSIVE MONITORING OF ORGANIC CONTAMINANTS IN LARGE RIVERS AND SMALL STREAMS IMPACTED BY AGRICULTURAL ACTIVITIES IN JAEN

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Surface waters are continuously exposed to organic contaminants (OCs) and their transformation products (TPs), which may be more mobile, toxic, and persistent than parent compounds. In rural areas, where agriculture is the main economic activity, pesticides are one of the main sources of contamination. Likewise, wastewater treatment plants of small populations have poorly upgraded secondary or tertiary wastewater treatments to completely remove OCs at trace levels, so pharmaceuticals or personal care products may be dumped into surface waters. In recent years, the scientific community has mainly addressed the monitoring of environmental contamination by applying analytical techniques based on liquid chromatography coupled with high-resolution tandem mass spectrometry (LC-HRMS/MS). Moreover, the development of novel non-target screening (NTS) approaches based on LC-HRMS has expanded the scope of analysis beyond target compounds, allowing the discovery and monitoring of unknown contaminants and their qualitative and semi-quantitative details.

In this work, an NTS strategy using LC-HRMS and MS-DIAL as open-source software was applied to investigate the occurrence of OCs and their TPs in large rivers and small streams of the province of Jaén, located in the southeast of Spain, where olive oil production is the main economic activity. Software pre-processing settings were carefully optimized using 20 target compounds. MassBank of North America (MoNA) was used as a spectral library database for compound annotation. This strategy was successfully applied to retrospectively analyze 37 water samples collected from 12 sampling points over 2 years of monitoring. A total of 37 OCs, comprising pesticides, pharmaceuticals, and TPs were tentatively identified with high confidence, proving the applicability of the developed NTS strategy for monitoring contaminants out of the scope of analysis.

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Exploring the Role of Endocrine-Disrupting Chemicals (EDCs) in Frontal Fibrosing Alopecia (FFA): A Preliminary Study

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Frontal fibrosing alopecia (FFA) is currently the leading cause of scarring alopecia, exhibiting a rising prevalence primarily among postmenopausal women. While its pathogenesis is still unclear, hormonal and genetic components seem to be involved. It has been suggested that environmental factors, including exposure to endocrine-disrupting chemicals (EDCs), could be involved in its development. In this proof-of-concept study, we aim at evaluating whether exposure to a wide range of EDCs can be linked with the development of FFA. To achieve this, we recruited 10 FFA patients and 10 age-matched controls, collecting blood, urine, and hair samples for analysis.

The extraction process was carried out following previously in-house developed methods. Briefly, hair samples were cleansed of surface contaminants with DCM and MeOH, ground with bead beating, and EDCs were extracted using MeOH. Urine samples underwent centrifugation to remove solids, and Captiva cartridges were employed for endogenous chemical filtration. Serum samples were deproteinized with ACN. The analysis was performed using liquid chromatography coupled to high-resolution mass spectrometry (LC-QTOF). Among the 48 EDCs analyzed, 35 were detected, with the highest number of compounds found in hair samples (63%), followed by urine (42%) and serum (27%). Eight compounds were detected in all three matrices, primarily parabens (ethylparaben, propylparaben and isobutylparaben) and flame retardants (TEP and TCEP). The concentration range in hair was notably higher than in the other two matrices, ranging from nondetectable (ND) to 88.12 µg/L, 26.47 µg/L, and 3134.38 µg/kg for serum, urine, and hair, respectively. To assess differences between groups, the Mann-Whitney U test was performed due to the non-normal distribution of the data. Although statistically significant differences ($p<0.05$) were only observed for mono(2-ethyl-5-oxohexyl phthalate) and TPhP in urine samples, there was a noticeable trend towards higher concentrations in FFA cases compared to controls across all studied EDC families ($p \approx 0.15$), likely influenced by the small sample size. In short, different concentration levels were found in each matrix, being the largest differences between case vs. control participants in hair and urine samples. Hair exhibited the highest concentrations, being the matrix that collect more information on long-term exposure. However, further research is needed to fully understand the potential associations between EDCs and FFA.

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Are slaughterhouse effluents safe for water reuse?

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The food industry constitutes one of the major water consumers in Europe, with a 12% of the total water used in the industrial sector. Among the food industry, the meat processing sector is one of the biggest water users, with an estimated average water consumption in Spanish slaughterhouses between 500-1000 and 250-500 litres per animal in the cattle and swine production, respectively. Slaughterhouse effluents are characterized by a high organic matter and nutrient content, with high loads of veterinary pharmaceuticals, antibiotic resistance genes (ARGs) and microbial pathogens. Accordingly, most slaughterhouses usually have their own wastewater treatment, with an outlet connected to the municipal sewer to further treat these waters in the urban wastewater treatment systems.

In this study, we carried out the chemical and microbiological characterization of slaughterhouse wastewater effluents within the framework of the project REAQUA, funded by the Catalan Department of Climate Action, Food and Rural agenda (DACC) and within the Cooperació per a la Innovació program (2020-2022). The main goal of the project is to demonstrate the feasibility of reusing the treated slaughterhouse effluents by using innovative treatments at pilot scale (e.g. membrane technologies and advanced oxidation processes), to use the produced water in external activities to the production process. Treated effluent wastewaters were collected for four weeks, in the period from October 2022 to January 2023, in four major slaughterhouses in north-eastern Catalonia, an area with intensive livestock production, and analyzed for veterinary pharmaceuticals and ARGs concentrations. Identified compounds included antibiotics of major use in veterinary medicine, such as tiamulin, sulfamethoxazole, sulfamethazine, tilmicosin, lincomycin, oxytetracycline, enrofloxacin and marbofloxacin, the anti-helmintic flubendazole and the analgesic flunixin, at concentrations ranging from 10 to 1330 ng L-1. For ARGs, sul1 (resistance to sulfonamides) and tetW (resistance to tetracyclines) were the most prevalent, together with intl1 gene, with concentrations ranging from 105 to 108 gene copies/mL. The other genes, ermB (resistance to macrolides), qnrS (resistance to fluoroquinolones) and mcr1 (resistance to colistin) were less represented. These results suggest that the implementation of advanced treatment technologies is recommended to ensure safe water reuse in the meat sector

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Determining of a broad range of organic chemicals in seminal plasma through an innovative LC-HRMS-based methodology suitable for target and non-target analysis

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In recent years, there has been a growing concern about the impact of emerging pollutants on reproductive health and semen quality in healthy men. Most studies have focused on investigating the association between human semen quality and exposure to organic contaminants in blood or urine samples. However, there is a notable lack of effective methodologies for detecting a wide range of organic chemicals in semen. To address this gap, we have developed and validated a robust LC-HRMS methodology for semen analysis. This methodology is capable of determining over 2,000 chemicals in seminal plasma and is compatible with suspect and non-target strategies, making it valuable for studies on male fertility. To demonstrate the potential of this methodology in characterizing the chemical exposome in seminal plasma, we analyzed exogenous organic chemicals and associated metabolites, such as plastic additives, PFAS, flame retardants, surfactants, and insecticides, in ten samples obtained from the LED-FERTYL general population cohort based in Catalonia, Spain. Notably, prevalent plastic additives such as phthalic acid esters and bisphenols were identified, indicating potential health risks. Additionally, we uncovered previously understudied chemicals like the tyre additive 2-mercaptobenzothiazole and specific organophosphate flame retardants. The purpose includes to illustrate how the methodology could be of significant value in assessing large cohorts and advancing the study of the association between exposure to contaminants and male fertility impairments.

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Investigation of pharmaceuticals and personal care products in small water bodies using polar organic chemical integrative samplers (POCIS) and non-target screening

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Pharmaceuticals and personal care products (PPCPs) are a class of organic pollutants that pose a growing concern in the context of circular economy strategies due to their potential adverse impacts on both biota and human health. This study focuses on the occurrence of PPCPs and pesticides in three small water bodies located in Norway. To assess the presence of these contaminants over an extended period, polar organic chemical integrative samplers (POCIS) were employed as sampling devices.

Over the course of one year, water samples were collected at three-week intervals and subsequently analyzed using non-target screening on Orbitrap LC-MS. Confirmation of identified compounds was achieved through the utilization of reference standards. The aim of this study was to comprehensively investigate the distribution and concentration levels of PPCPs and pesticides in the selected water bodies, shedding light on their potential impact on the surrounding ecosystem and human health.

The results of this study will contribute to a better understanding of the prevalence and persistence of PPCPs and pesticides in aquatic environments. Additionally, the utilization of POCIS in combination with advanced analytical techniques offers a valuable approach for comprehensive and time-resolved monitoring of these contaminants. The findings underscore the importance of implementing effective strategies to mitigate the release and accumulation of PPCPs and pesticides in water bodies, thereby promoting sustainable practices within the circular economy framework.

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Regenerated water as a potential source of organic contaminants and microplastics in irrigated crops

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Proposing the utilization of reclaimed water for crop irrigation supposed as a viable alternative, addressing the water scarcity prevalent in the coastal areas of Mediterranean countries. However, water quality is clearly the main threat to the future of this practice. To now, several scientific publications have evaluated the detection and identification of organic contaminants of emerging concern (CECs) such as pharmaceuticals, personal care products (PPCPs), and microplastics (MPs) in wastewater treatment plants (WWTPs) influents and effluents. However, reclaimed water for crop irrigation have been poorly evaluated yet, especially in terms of MPs load. Prolonged exposure to advanced treatment processes leads to the progressive decomposition of plastic into countless smaller plastic particles called MPs as well as the degradation of the organic contaminants themselves into other transformation products. Thus, due to their increasing presence in the environment and their potential negative effects on ecosystems and human health, the quality of reclaimed water is posing a new challenge to the scientific community.

MPs were visualized under the stereomicroscope to identify the number and classify plastic particles according to their shape, size, and color, and after they were confirmed by μFTIR. In summary, one of the three macrolide antibiotics included in the Commission Implementing Decision (EU) 2018/840 (clarithromycin) and two of the pesticides (diuron and terbutryn) included in the list of priority substances covered by the Water Framework Directive (Directive 2013/39/EU) were detected in the irrigation water samples and irrigated soil samples. However, none of them were detected in the vegetables permanently irrigated with that water. Carbamazepine and caffeine were the only compounds detected across the entire water-soil-plant continuum. This finding emphasizes the great potential of this contaminants to translocate through the plant. The results obtained in this work support the reuse of water for agricultural irrigation since the concentration levels of the CECs detected in all the commercial produce analysed were very low compared to their therapeutic doses. Reclaimed water constitutes a source of MPs, and its presence should be evaluated in future studies.

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LC-MS/MS screening of 325 PPCP Contaminants in Tap and Surface Water

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There is growing concern over the exposure of humans to their chemical waste, flushed down everyday in the conventional wastewater network: pesticides, household chemicals, pharmaceuticals and personal care products (PPCP). Many countries worldwide are regularly monitoring and assessing over a hundred PPCP from wastewater. Specific and highly sensitive detection is required. LC-MS/MS is widely used, however it can hardly be exhaustive due to the wide variability of target chemical properties. Each method is developed as a compromise for a restricted list of compounds only. With a Nexera X2 UHPLC coupled to LCMS-8060 high sensitivity triple quadrupole mass spectrometer Shimadzu has developed a single automated system, switching between several methods, for total water analysis.

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Direct Determination of Trace Hormones in Drinking Water by Large Volume Injection at Sub ng/L Levels

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Endocrine disrupting compounds enter the aquatic environment primarily through the discharge of treated and raw sewage and are detrimental to aquatic organisms even at subnanogram per litre levels. In the majority of North American and European cities wastewater treatment plant effluent is indirectly re-used, through discharge into rivers which are also a source of drinking water. Consequently, there is the possibility that trace amounts may enter into drinking water even after special treatment processes. Several hormones are routinely monitored by the US EPA in drinking water as part of the Unregulated Contaminant Monitoring program (UCMR3). In this study, the LCMS-8050 triple quadrupole mass spectrometer was used for the highly selective and sensitive detection of hormones in water to meet the requirements of UCMR3. This direct high volume injection method of analysis avoids the disadvantages associated with extracting samples using SPE as is commonly performed. Ammonium fluoride as an aqueous mobile phase additive was found to significantly improve response for all studied hormones in comparison to ammonium hydroxide. The excellent sensitivity of the final method provided detection limits ranging from 0.005 ng/L (testosterone) to 0.330 ng/L (17-α-ethynylestradiol).

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Aquasearch: a new software for fast proteomic characterization and classification of wastewater samples analyzed using MALDI-TOF

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The study of wastewater is a valuable source of information about the environment, health and industrial activities of the inhabitants of an area. Although the study of wastewater has traditionally focused on small molecules such as pharmaceuticals or illegal drugs, recent studies have been published reporting the valuable information that can be obtained from large molecules in wastewater, introducing proteomics as an emerging field in environmental monitoring.

In the studies mentioned above, Liquid Chromatography coupled with High-Resolution Mass Spectrometry (LC-HRMS) instrument was used to identify the proteins in wastewater using a shotgun proteomics approach. Although the entire process reports comprehensive and accurate results, it is expensive and time-consuming. Therefore, Matrix-Assisted Laser Desorption/Ionization coupled with Time of Flight (MALDI-TOF) is proposed as a high-throughput instrumental approach for faster and more cost-effective sample characterization. In this work, we present Aquasearch, a newly developed software in Python for the characterization and classification of samples in a multisampling analysis. Aquasearch primarily performs two tasks: 1) signal filtering from wastewater proteomics samples analyzed by MALDI-TOF and identification of peptides belonging to livestock and human biomarkers using an in-house database and 2) using the identification results to classify the samples based on their proteomic profile in a non-supervised analysis. To facilitate the use of Aquasearch, including the parameter selection and result visualization, the program can be run through a graphic user interface (GUI).

To test the program, 4 wastewater samples collected from 4 WWTPs in Catalonia, Spain (Besòs, Girona, Vic and Figueres), were analyzed by MALDI-TOF. The Aquasearch analysis of the corresponding protein profiles showed the dominance of human biomarkers in Besòs and Girona, while pig and chicken biomarkers were the major components in Vic and Figueres. Finally, these proteomic profiles clustered the samples in the non-supervised multisampling analysis based on their origin.

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MONITORING ANTIBIOTICS IN OLIVE GROVES SOILS BY ULTRASOUND-ASSISTED EXTRACTION COMBINED WITH SOLID-PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY - TANDEM MASS SPECTROMETRY

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Antibiotics are substances used primarily to combat bacterial infections in living organisms. The annual consumption of antibiotics worldwide is nearly 100,000 tons1. Within the European Union, the annual consumption of antibiotics for animal production is estimated at 5,219.6 tonnes2. Their presence in manure and fertilizers directly impacts the environment and its inhabitants. Antibiotics fixate in soils through diverse mechanisms, given their nonvolatile nature and high polarity. Their existence in soils is closely tied to their presence in manure. Applying manure treatments like anaerobic digestion can reduce antibiotic content, thus lessening their environmental impact.

The first aspect to consider is that soil is filled with microorganisms, such as bacteria, which interact with antibiotics. They will be transformed in a certain way by the living organisms in it, while some antibiotics can be mineralized and degraded, the overall rate of such processes remains low. The main interaction between soils and antibiotics are solid-phase sorption and desorption mechanisms, depending heavily on the physicochemical properties of the antibiotics themselves3.

Sample treatment is vital for successfully extracting and isolating antibiotics from soils and manure. The main challenge relies on dealing with matrix effects. The goal is to minimize these effects while maintaining high extraction efficiencies. A methodology combining solid-liquid extraction ultrasound-assisted extraction followed by solid-phase extraction and detection by ultrahigh-performance liquid chromatography-tandem mass spectrometry has been developed to address this. The identified antibiotic families include quinolones, tetracyclines, β-lactams, ionophores, diaminopyrimidines, macrolides, sulphonamides, cephalosporins, and amphenicols. The method's validation showed favourable analytical properties with acceptable recovery, good linearity, and precision (relative standard deviations below 18%) for successfully determining analytes in various olive grove soils at µg/kg level.

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Assessing the human exposure during pregnancy: wide-scope target analysis (>600 chemicals) in serum from a Barcelona Cohort

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The human exposure to organic chemicals has become a topic of major concern in the last years. The project AirNB, which includes the Barcelona Life Study Cohort (BiSC) cohort, focuses on evaluating prenatal exposure to environmental contaminants and assessing their potential effects in offspring health lifelong. Prenatal exposure is, in fact, critical in early life stages, such as first trimester of pregnancy, as it can cause severe problems in the newborn during his/her entire life. In this work, we have conducted a wide scope target screening of >600 chemicals potentially hazardous in 300 serum samples from pregnant women at 12th week of pregnancy, to unravel the chemical exposome of xenobiotics.

Samples were thawed at room temperature, deproteinized with acetonitrile, centrifuged and spiked with isotopically labelled internal standards. Procedural blanks (n = 30) were also processed. Then, the supernatant was analyzed using a LC-HRMS instrument (Q-Exactive, Thermo Scientific). All samples were injected in Data Dependent (DDA) and Independent (DIA) acquisition modes, in both positive and negative electrospray ionization mode. TraceFinder 5.2 software (Thermo Scientific) was used to conduct the data analysis including the fragments confirmation. The detected compounds were quantified with two different approaches, some of them through matrix-matched calibration curves and for the remaining compounds using an in-development semi-quantification tool specifically developed by us for biological matrices.

A total of 126 exogenous chemicals were detected at least in one sample, while 11 did have a frequency of detection higher than 50%. Different families of pollutants including phthalates, tire additives, pharmaceuticals, pesticides, PFAS, parabens, among others, were detected in the analyzed samples. An extended suspect screening will be performed (including >10.000 extra chemicals) as well as nontarget screening, to comprehensively define the chemical exposome in the cohort. These results will be the basis to perform further epidemiological and metabolomics studies to investigate the link between potential adverse health effects of the presence of the found chemicals.

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STRATEGY OF ANALYSIS OF PHARMACEUTICALS IN RECLAIMED WATER USING TARGET AND NON-TARGET METHODOLOGY WITH LIQUID CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION MASS SPECTROMETRY

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The main source of pharmaceuticals in rivers is the discharge of treated effluents from wastewater treatment plants (WWTP). The Llobregat river has more than 30 urban WWTP along their river basin and is characterized by important fluctuations in the flow rates and heavy pollution levels, and it will likely increase in the future due to climate change. In 2019, a special reuse trial was carried out in the lower Llobregat river, discharging into its reclaimed water from the effluent of the largest WWTP, to increase water availability (1). Nowadays, in a drought context, reclaimed water has been discharging upstream the most important drinking water treatment plant (DWTP) in Sant Joan Despí, which supplies drinking water to the Barcelona Metropolitan Area, to maintain flow in the river. To evaluate the presence of pharmaceuticals in water samples, a group of 18 pharmaceuticals were selected in base of the results obtained in the previous trial and recent scientific publications.

Quantitative target analysis with liquid chromatography coupled to high resolution mass spectrometry (Target LC-MS/MS) was applied to the reclaimed waters from the WWTP and to raw and treated water from the DWTP. A total of 16 contaminants were detected in the reclaimed and raw water samples. Only iomeprol was finally detected in all drinking water samples, between 0,28 and 0,91 µg/L.

In addition, a non-target suspect screening methodology (non-target LC-HRMS) was developed and applied in drinking water samples to ensure that no drug or metabolite survives treatment in the DWTP. Only one pharmaceutical product (Amantadine), which was not on the target analysis list, tested positive in all samples and was later confirmed by an analytical standard. We subsequently added it to the target group of pharmaceutical products to monitor in the future.

This study englobes the strategy of analysis of known selected pharmaceuticals (target list), which act as indicators of contamination, and analysis of suspect substances (non-target) in water during winter, spring and summer of 2023.

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Hydrological effects of droughts on the occurrence of pharmaceuticals and endocrine disrupting compounds in groundwater

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Groundwater, a crucial resource during severe drought periods, is mainly affected by pollution caused by agriculture and wastewater treatment plant (WWTP) discharges. This study evaluated the presence of pharmaceuticals (PhACs), their transformation products (TPs) and metabolites, and endocrine disrupting compounds (EDCs) along the Onyar River basin (NE Catalonia) in two sampling campaigns: first, an exploratory survey in June-July 2021 including the analysis of 45 PhACs in 14 groundwater samples, and a second one in March 2023, following an extremely dry period, on 12 groundwater and 10 stream water samples for the determination of 45 PhACs, 9 TPs and metabolites, and 32 EDCs. Their occurrence is explored under two distinct hydrological conditions to understand whether hydrological factors suppose an actual risk for groundwater quality given the reactive transport nature of these contaminants in the subsurface.

During the first campaign, six PhACs were detected in groundwater (acetaminophen, carbamazepine, hydrochlorothiazide, ibuprofen, sulfamethoxazole and venlafaxine) at 0.6 to 57 ng/L. In the second survey, the same PhACs were found at concentrations from 0.5 to 20ng/L, with the addition of sulfamethazine and sulfapyridine, while ibuprofen was not detected. In river samples, a similar chemical profile was observed, including 8 PhACs such as trimethoprim, clindamycin, sulfamethoxazole, sulfapyridine, flubendazole, carbamazepine, citalopram, and venlafaxine, at concentrations from 5.9 to 81.8 ng/L. TPs and metabolites, such as carbamazepine-10,11-epoxy and carbamazepine-2-hydroxy were found in river samples, while metoprolol acid was present in river and groundwater. Several EDCs were present in both matrices as well, including tolyltriazole, benzotriazole-1H, bisphenol A, caffeine, methylparabens, TCEP, TBEP, TCPP and estrone at concentrations from 0.3 to 142.2 ng/L.

These results highlight the impact of hydrological factors. Induced stream water recharge, caused by groundwater withdrawal, is more intensive during drought periods, enhancing the transport of contaminants introduced from the WWTP inputs to stream discharge in the subsurface. Conversely, in wet periods (June-July 2021), the hydrological setup reverses and pollutants introduced by stream recharge, do not reach wells located far away from the drainage network. Such results indicate a temporal variability of ECs concentration in groundwater governed by the hydrological conditions during the sampling campaign.

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Pharmaceuticals and other pollutants in sediment cores from the lake of L'Albufera Natural Park (Valencia, Spain)

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Sediments of lakes and other shallow waters have been considered in different studies as excellent archives for defining long-term variations of pollutants in the environment. For this reason, records derived from the chemical analysis of sediment cores could be useful to trace the history of pollutant emissions in a selected area. This study is aimed to assess the vertical variation of pharmaceuticals and other organic and inorganic contaminants (OICs) in sediment cores of two different sites from the lake of L´Albufera Natural Park (Valencia, Spain), to obtain information regarding the historical variation of their accumulation in sediments. A sediment core sampler was used to extract the cores from the lake and then were cut into 8 segments of the same thickness using a stainless-steel cutter. The compounds were extracted by different extraction methods, and pharmaceuticals were detected by an Orbitrap Exploris 120 mass spectrometer (Thermo Scientific), while metals by an ICP-MS ICAP6500 DUO (Thermo Scientific). Contaminants were determined both using wide target screening against a positive list of compounds, and non-target screening applying ddMS2 of the 4 more intense ions in each cycle as well as all ions fragmentation. Bisphenol A, butyl paraben, ethyl paraben, methyl paraben, propyl paraben, salicylic acid and codeine were detected in the sediment in contact with water and in the inner layers. Generally, the higher heavy metal concentrations appear in the more recent sediments (depth < 20 cm), reflecting the increased agricultural and industrial activities in the area during the 20th century. This study showed that organic contaminants were lixiviated in different amounts through sediments, and their occurrence cannot be directly related with the age of the sediments. However, these sediments can also be used to examine pollution mechanisms, which are significant for predicting future pollution tendencies, and assessing potential environmental risks in important areas as L'Albufera Natural Park.

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AOP Removal of Benzodiazepines from Contaminated Water: the Case of Diazepam

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The domestic and industrial use of water generates a high quantity of sewage and residual wastewater after sewage treatments, which direct disposal into natural channels considerably impacts the environment. Together with the need to recuperate water for new uses, wastewater purification is practically essential to achieve the desired quality. The release of pharmaceuticals and personal care products into the environment has intensified remarkably due to their extensive global use and the dramatic increase in the world population over the past half-century.

Benzodiazepines have received recent consideration. A most known member of the benzodiazepines is diazepam used to relieve anxiety, muscle spasms, and seizures and control agitation in both adults and children. It is anticonvulsant, anxiolytic, sedative and muscle relaxant.

The human metabolism of benzodiazepines is only partial, with the consequent release of significant amounts of various degradation products into the aquatic environment. These substances can further transform during sewage treatment, and by-products can cause considerable concern for their potential toxicity.

Building on those considerations and considering that previous studies have demonstrated the inefficiency of the conventional water and wastewater treatment processes, the need to eliminate those residual compounds from a different kind of water appears evident.

As reverse osmosis is very expensive, and brine production is inevitable (10% of the total volume of treated water), we experimented with AOPs. TiO2, used as a catalyst, owns two essential properties: high photocatalytic activity and low cost. Photodegradation of diazepam was much faster under light irradiation + TiO2 (half-life = 6 hours) than under the sole light treatment in solar simulator equipment (half-life = 34 hours). Considering that the photocatalytic process starts after the biological treatment of the wastewater containing a minimal quantity of contaminants, the removal of this pharmaceutical compound was quite complete, and the degradation products were below the legal limit. Transformation products were identified by LC-MS methods. Selected factor levels cover a range of values of practical interest. The results of this study suggest that the proposed approach could represent a valuable strategy for in-situ and ex-situ remediation of diazepam in wastewater.

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Metabolomics analysis in plasma of Anguilla anguilla species exposed to a mixture of pharmaceuticals.

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Pharmaceuticals can have a negative impact on aquatic ecosystems. To assess the impact of these compounds on fish and determine whether altered molecules in plasma could serve as biomarkers for fish in future monitoring, a bioaccumulation study was conducted in Anguilla anguilla. The plasma metabolome of both the control group and the group exposed to pharmaceuticals was analyzed. Untargeted metabolomics analysis with Orbitrap Exploris 120™ mass spectrometry (Thermo Scientific™) was performed on plasma samples of Anguilla anguilla species exposed for 30 days to some pharmaceuticals often used in massive livestock farming and fishing, also found in wastewater discharge. The European eel has been shown to be a reliable bioindicator for assessing the ecological quality of aquatic ecosystems. This is attributed to their physiological and behavioral characteristics, which render them vulnerable and highly responsive to the presence of pharmaceuticals. Metabolomics studies revealed several metabolites and pathways that were detected after 7th day of exposure in plasma samples using Compound Discoverer v3.2. (Thermo Scientific™) and MetaboAnalyst 5.0 software. The data were subjected to a variety of statistical techniques. A total of 31 differentially expressed metabolites were identified in different time of exposure (7th, 28th and 30th day), among which 25 occurred in the positive ion mode and 9 in negative ion mode, respectively. Specially, the last days of exposure (28th and 30th), several pathways involving amino acids metabolism (L-phenylalanine, L-tyrosine, L-isoleucine, L-methionine, L-proline, etc.), glycerophospholipid metabolite (1-Stearoylglycerol) indicating a possible oxidative damage, steroid hormone (cortisol), fatty acids (hexadecanoic, octadecanoic, linoleate, stearic, palmitic, oleic, pentadecanoic, arachidic, decanoic acids, etc.) increased their levels significantly. Furthermore, the developed approach serves as a significant tool for toxicity assessment, as they offer a deeper comprehension of the physiological function and underlying mechanisms responsible for the observed responses.

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Health risk related to the chronic ingestion of greywater irrigated crops from decentralized water reuse application

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The presented study intends to help bridge the knowledge gap identified in the European water reuse regulation (2020/741), about the potential human health risk related to agricultural irrigation in water reuse applications. It specifically concerns the accumulation of pharmaceuticals and endocrine disrupting compounds in the edible part of crops irrigated with light greywater.

To minimize environmental influences, lettuce planters were planted in a hydroponic system built under controlled environmental conditions with inert expanded clay substrate. The experimental plants were fed with a light greywater from hotel rooms sinks and showers. Serving as a control, additional plants were grown in commercial hydroponic nutrient solution. A final set of plants were grown in the greywater amended with the same nutrients used to prepare the commercial nutrient solution. Each water was renewed twice per week and the plants were harvested after 4 weeks of experiment.
The effect of using greywater instead of freshwater on the plant growth was assessed using traditional plant growth parameters e.g., “relative growth rate”. The presence of several pharmaceuticals and endocrine disrupting compounds was searched by UPLC-QqLIT in water as well as their accumulation in the plant material (leaves and roots) after freeze drying, extraction, and clean-up. All samples are currently being quantified. A human health risk assessment using both the lowest daily therapeutic dose as well as the threshold of toxicological concern approach will follow, to assess the risk of chronically ingesting the produced crops throughout a human’s life.

Plant growth: Greywater does support plant growth. However, by itself it does not provide enough nutrients to achieve comparable plant growth to commercial nutrient solution. Nevertheless, greywater amended with nutrients produces bigger and morphologically stronger leaves than the commercial solution prepared with deionized water.
Uptake & human health risk assessment: The occurrence and degradation of pharmaceuticals in the water samples, as well as their accumulation in the plant material, divided into edible and non-edible parts are currently being quantified. Preliminary results of the human health risk assessment for the ingestion of analysed compounds in the lettuces will be presented in the poster.

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Enantio-specific Fate of Chiral Pesticide Pydiflumetofen in Wheat (Triticum aestivum L.)

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Pydiflumetofen (PYD), the newest chiral fungicide, recently has found enantioselectivity in plant degradation and bioactivity. The enantioselective fate of PYD in crops is still poorly characterized. More importantly, its mechanism of enantioselectivity also remains unclear. Thus, the present study aims to systematically investigate the uptake, translocation, and biotransformation of PYD in wheat via a hydroponic experiment. Attempts were then made to explore the mechanism of uptake. Furthermore, the metabolites of PYD in wheat were detected by LC-Q-TOF-MS. The molecular interactions between PYD enantiomers and TaLTP1.1 and CYP71C6v1 were clarified by homology modeling combined with molecular docking. The results demonstrated that the residue concentration of R-PYD in wheat was higher than that of S-PYD, because of its higher uptake rate (k1=0.0421 h-1) and lower elimination rate (k2=0.0459 h-1). A total of 9 metabolites including hydroxylated, demethylated, demethoxylated, dechlorinated, hydrolyzed, and glycosylated-conjugated products were detected in wheat roots and shoots. Both root adsorption and inhibition experiments confirmed that the uptake pathway of PYD was a symplastic pathway, dominated by the aquaporin and anion channels. Meanwhile, no enantioselective differences in the root uptake process. Enantioselective driving roles of plant biomacromolecules (TaLTP1.1 and CYP71C6v1) in bioaccumulation and biotransformation have been explored by combining homology modeling and molecular docking method. R-PYD presented better binding with TaLTP 1.1 with a lower grid score (-6.79 kcal/mol), whereas lower interaction with the metabolic enzyme (CYP71C6v1) compared with the S enantiomer. These results preliminarily illustrated the enantioselective fate of PYD in wheat and emphasized the role of plant biomacromolecules in enantioselective bioaccumulation and biotransformation. This study provides both experimental and theoretical evidence for the uptake, accumulation, and biotransformation of chiral pesticides in plants from the enantioselective perspective.

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Novel data handling strategies for the analysis of dissolved organic matter in wastewater using high resolution mass spectrometry

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There is a growing interest in understanding the dissolved organic matter (DOM) composition in wastewater effluents. To this aim, a promising strategy is the use non-targeted analysis with high-resolution mass spectrometry, in conjunction with novel data processing methods to handle the significant amount of information generated.

Advancements in analytical instrumentation are enabling the discovery of a higher number of micropollutants in water than previously reported. However, processing the large amounts of data can be a daunting process. Moreover, is not yet clear how representative are these newly discovered compounds in wastewater, and how significant are they in water treatment processes. To address these questions, new statistical data treatments are being employed aiming to offer a more relevant, summarized, and clearer understanding of the types of micropollutants found in wastewater samples.

This study introduces the idea of using innovative data processing methods. The main objectives are: (1) to enhance our understanding of the structure, composition, and behavior of DOM in wastewater treatment processes; and (2) to derive more valuable and representative outcomes from the extensive analysis of micropollutants in wastewater samples using compositional data treatments.

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COMPARISON OF ADVANCED OXIDATION PROCESSES FOR THE DEGRADATION OF SILDENAFIL IN WATER

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The erectile dysfunction drug sildenafil, commonly known as Viagra, has attracted much attention in recent years due to its widespread legal and illegal use worldwide and the increasing use of the drug by young people for recreational rather than medical purposes. This trend can be dangerous because it poses significant risks to human health and the environment. The human body does not fully utilize the drug doses, and an unknown amount, metabolized or not, is excreted in urine and feces. Consequently, municipal sewers transfer these substances, once evacuated, and many other pharmaceuticals to wastewater treatment plants. They are only partially degraded there and often accumulate or photo-transform in the receiving waters. Therefore, It is essential to investigate the residues of these drugs in the environment to eliminate them.

Sildenafil seems very stable in water under different environmental conditions. Hence, research should also study alternative removal methods that limit the formation of derivatives. Our research evaluates the efficacy of various sildenafil removal treatments, including advanced oxidation processes (AOPs).

Here, we report on the solar phototransformation of sildenafil in distilled water and synthetic wastewater (SWW) in the presence of three different oxidants, peroxymonosulphate (PMS), peroxidisulphate (PS) and hydrogen peroxide (H2O2), with particular emphasis on potentially toxic phototransformation products. LC-ESI-MS and MSn performed the identification of sildenafil and its photoproducts. The results showed that AOPs are important processes for removing this drug and its transformation products from aquatic environments. These processes are environmentally friendly, low cost, and low energy consumption and therefore have potential applicability as a treatment in conventional wastewater treatment systems.

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