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ABSTRACT BOOK

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CONTENTS

PLENARY LECTURE

KEYNOTE LECTURES

PLENARY LECTURE

THE GLOBAL PROBLEM OF PHARMACEUTICAL POLLUTION

Alistair B A Boxall, John Wilkinson, Emily Burns
Department of Environment and Geography, University of York

We will probably all use pharmaceuticals at some stage in our life. Following use, pharmaceuticals are excreted into the sewage system and can then pass through sewage treatment plants into surface waters. Pharmaceuticals can also be released during the manufacturing process or as a result of disposal of unused medicines. As pharmaceuticals are biologically active molecules, in recent years there has been increasing interest from scientists and the general public over the potential impacts of pharmaceuticals on aquatic organisms and on humans that consume drinking water containing pharmaceuticals. To understand the impacts of pharmaceuticals in the environment and the subsequent risks to human and animal populations, it is essential to understand the concentrations of these molecules in the environment. The levels of exposure and the types of pharmaceuticals will likely vary significantly in different regions of the World due to differences in pharmaceutical availability, wastewater treatment connectivity and infrastructure, regulation and disease pressure. However, there is a paucity of data for many regions of the world. For example, in a 2016 review, it was concluded that data are only available on pharmaceutical concentrations in around 70 countries. Even where data are available, these are often extremely limited covering a small number of compounds in a small number of samples. To address, this major knowledge gap, over the past two years the University of York have been co-ordinating the Global Pharmaceutical Monitoring project which involves 88 collaborators from around the world. In the study, river water samples have been collected from more than 1000 locations from more than 200 river systems in 102 countries. All samples have then been couriered to York where they have been analysed for 61 pharmaceuticals using sensitive, high throughput LC-MS-MS method. The study has therefore generated a unique data set to help us understand the scale of the problem of pharmaceutical pollution and to identify major sources of contamination in different regions. In this talk, the monitoring approach will be presented and the findings from the monitoring study will be described. The implications of the observations for ecological and human health will then be discussed.

Key words: monitoring, environmental risk, antibiotics

Correspondence to: Alistair.boxall@york.ac.uk; john.wilkinson@york.ac.uk

KEYNOTE LECTURES

GPCPE : NEW GLOBAL PANEL ON THE CHEMICAL POLLUTION OF THE ENVIRONMENT

*D. Barcelo [1], A. Boxall [2], W. Brack [3], H. Budzinski [4], A. Covaci [5], G. De Aragao Umbuzeiro [6], D. Fatta-Kassinos [7], K. Gin Yew-Hoong [8], M. Hammami [9], F. Hernandez [10], J. Hollender [11], F. Jaber [12], B. Kasprzyk-Hordern [13], S. Khan [14], B. Lalonde [15], P.A. Lara Martín [16], Y. Levi [17], ,*C. Metcalfe [18], C. Montagner [19], T. Msagati [20], V. Pham Hung [21], M. Reid [22], M. Reinhard [23], S. Snyder [24], F. Sodre [25], K. Thomas [26], M. Tripathi [27], D. Wunderlin [28], E. Zeng [29], E. Zuccato [30].*

[1]Catalan Institute for Water Research - Quart (Spain), [2]York University - York (United Kingdom), [3]Helmholtz Centre Environm. Res. - Leipzig (Germany), [4]Universite Bordeaux, CNRS - Talence (France), [5]University Antwerp, - Antwerpen (Belgium), [6]Faculty Tecnologia, Limeira - Limeira (Brazil), [7]University Cyprus, Nireas-International Water Research Center - Nicosia (Cyprus), [8]National University, Department of Civil and Environmental Engineering - Singapore (Singapore), [9]National Inst. Res. Phys.-chem. Analysis - Ariana (Tunisia), [10]Univ. Jaume I, Institute of Pesticides and Water - Castelló de la Plana (Spain), [11]EAWAG - Dubendorf (Switzerland), [12]Lebanese University - Beirut (Lebanon), [13]University of Bath Centre for Sustainable Chemical Technologies - Bath (United Kingdom), [14]Univ. New South Wales, School of Civil & Environmental Engineering - Sydney (Australia), [15]French Academy for Water - Nanterre (France), [16]University of Cadiz - Cádiz (Spain), [17]Universite Paris Sud, UMR CNRS, AgroParisTech - Chatenay-Malabry (France), [18]Trent University, Wat quality center - Peterborough (Canada), [19]Univ. Estadual de Campinas - Cmpinas (Brazil), [20]Univ. Johannesburg, Research Unit of Nanotechnology and Water Sustainability - Pretoria (South Africa), [21]VNU Univ. of Science - Hanoi (Vietnam), [22]Norwegian Inst. Water Research - Oslo (Norway), [23]Stanford University - Stanford (United States), [24]Nanyang Environm. Water Research Inst. - Singapore (Singapore), [25]University Brasilia - Brasilia (Brazil), [26]Univeristy of Queensland - Woolloongabba (Australia), [27]French academy for water - Nanterre (France), [28]University of Cordoba - Cordoba (Argentina), [29]Jinan University - Guangzhou (China), [30]Mario Negri Inst. Pharmacol. Res. - Milano (Italy)

Progress in analytical methods has made possible to detect and quantify a wide range of chemicals in the various compartments of the environment. Among are chemicals already known as pesticides, heavy metals, polycyclic hydrocarbons, dioxins... and also new "emerging" contaminants (plasticizers, flame retardants, perfluorinated, pharmaceuticals...). Numerous reports and publications describe levels of contaminations for all continents and all the compartments of the environment. These data were generated by research laboratories and under the impulse of national or international regulations such as European directives or national programs as in North America, Australia, Japan. Contaminant transfers occur between compartments but also between regions and continents. This global aspect requires integrative work. No quantitative risk analysis (environmental or health) can be done without knowing the exposures with great precision. To contribute to international assessment of environmental and health risks, to assist and guide management decisions, it is essential to collect and compile existing data. This is the goal set by our international researcher panel initiate by the "French Water Academy" and with financial support of the Michelin Corporate Foundation, since 2018 and entitled: Global Panel on the Chemical Pollution of the Environment - GPCPE.

The objective is to collect existing data of environmental chemical contamination to compile in order to publish, every 3 years, a report presenting the knowledge on the presence, in the environments (water, air, soil, biota), of chemical substances.
This panel, of collective scientific expertise, has been structured to be a guarantee of objectivity for the production of factual and rigorous data and cartography for the benefit of all through open international access. Experts are from academic world, specialists in analytical and environmental chemistry. This will allow to compare geographic zones and concentration levels and help to develop models. The panel propose to present this initiative to the ICRAPHE community, to detail the project, inform the community and call for participate and involve institutional and industrial partners to support their actions, guarantee their independence and allow the widest dissemination of the publications to the service of the entire chemistry community.

Correspondence to: yves.levi@u-psud.fr

MONITORING OF PHARMACEUTICAL RESIDUES IN THE ENVIRONMENT: FROM TARGET ANALYSIS, SUSPECT SCREENING TO NON-TARGET ANALYSIS. LIMITATIONS AND PITFALLS

Mira Petrovic[1,2], Merixell Gros[1,3], Mira Celic[1,3]

[1]Catalan Institute for Water Research (ICRA), Girona, Spain
[2]Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain
[3]University of Girona, Girona, Spain

Although many methodologies have been developed to detect pharmaceuticals in wastewater and various environmental matrices, the monitoring of different therapeutical classes of pharmaceuticals, inducing parent compounds, metabolites and their transformation product remains a challenge. Among methods applied is mass spectrometry (MS) with distinctive ability to identify small amounts of organic chemicals from increasingly complex mixtures providing therefore a large amount of information on contaminants of interest within.

This paper will discuss three main groups of workflows using liquid chromatography (LC) coupled to low and high resolution MS that broadly separate into targeted, suspect, and non-targeted screenings. Nowadays, non-targeted analysis drives the exploration of organic microcontaminants in engineered and natural systems gradually displacing the interest in targeted methods in the researcher community. Despite apparent maturity of methods and protocols for the monitoring of pharmaceuticals, the methodological challenges are still numerous. This paper discusses the potential pitfalls in the quantitative multiresidue target analysis of pharmaceuticals in environmental samples, and discuss some new approaches and trends.

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Keywords: monitoring pharmaceutical; target analysis; suspect screening, non-target analysis

Correspondence to: mpetrovic@icra.cat, mgros@icra.cat, mcelic@icra.cat

HIGH RESOLUTION MASS SPECTROMETRY AS A TOOL TO ELUCIDATE THE FATE AND BEHAVIOR OF EMERGING CONTAMINANTS, ESPECIALLY DRUGS AND METABOLITES, IN WASTE WATERS

H. Budzinski, C. Gardia-Parege, MH. Devier
University of Bordeaux, EPOC / LPTC – UMR 5805 CNRS, 33405 Talence cedex, France

In the context of global environmental changes and more precisely the anthropization of ecosystems, chemical contamination is still an important issue in terms of knowledge to better understand and ultimately regulate and reduce it. Indeed, the introduction of toxic substances of synthetic or natural origin is an alarming factor of degradation of the quality of the environment. Voluntary or involuntary dispersal of many substances (pesticides, hydrocarbons, metals, cosmetics, detergents, biocides, etc.) can lead to contamination of environmental compartments, even in remote areas. In the environment, the existence of toxic molecules, for the majority not yet identified, requires finding appropriate strategies to assess the health of the natural environment, chemical pollution having a very strong impact on the biodiversity of all environments.

In this context of widespread and proven chemical pollution, it is therefore necessary to improve the characterization of this pollution, to reduce it either at source or in the environment. Fine and sustainable monitoring of the evolution of the quality of the environment appears as one of the major scientific and political issues of the coming decades. Indeed, it is essential to have reliable and documented information on the temporal evolution of the levels of anthropogenic contaminants which will make possible to measure the effectiveness of the solutions undertaken in the targeted environments and to optimize their management.

In order to be able to document chemical contamination as comprehensively as possible and to link the presence of contaminants with the toxic impact on organisms, it is necessary to correctly diagnose the contamination pressure. Typically, the steps undertaken are based on targeted approaches to search for contaminants, selected on the basis of the results of priorization studies. This approach, provided we have the required modern ultra-trace methodologies, is powerful but insufficient because we can miss the actual compounds responsible for the observed effects. It is therefore important to develop non-targeted approaches aimed at identifying unknown or non-targeted contaminants (eg transformation products of parent molecules). Indeed, if gas chromatography coupled with tandem mass spectrometry (GC-MS / MS) and liquid chromatography coupled with tandem mass spectrometry (LC-MS / MS) are the reference techniques for the analysis of micro-pollutants in environmental samples, making it possible to reach increasingly weak detection limits (of the order of ng / L or even lower), and which have made it possible to highlight and monitor many families of chemical pollutants (pesticides, perfluorinated compounds, drugs and body care products, detergents, plasticizers, hormones, etc. from products used in everyday life, in industry and in agriculture), they involve a preliminary selection of the compounds to be searched. If this selection is imperfect or incomplete, it will not be able to target the “good” compounds and thus it will lead to erroneous conclusions about the quality of the environment and about the link presence / toxic effect. High resolution mass spectrometry (HRMS), allows a non-targeted approach without a “a priori” selection of analyzed compounds, contributes to change the way of characterizing chemical contamination and micropollutant presence in environmental samples. The chemical formula of unknown compounds can be obtained by measuring the exact mass of compounds with good accuracy. The fragmentation of the compounds then makes it possible to identify the most likely structure among those possible. The use of HRMS has already allowed progress in the characterization of metabolites and degradation products of organic compounds (photodegradation, biodegradation in water treatment ...). HRMS approaches can also be implemented in the development of Effects-Directed-Analysis (EDA). Indeed, the EDA approach is particularly suited to the characterization of complex environmental matrices that contain thousands of molecules, most of which are unknown. These unknown compounds difficult to characterize from a chemical point of view can be more easily and in a more sensitive way from a biological point of view. This approach can make it possible to link the presence and potential biological / toxic effect of the identified and quantified compounds. This presentation will illustrate the use of HRMS and EDA methodology for the analysis of pharmaceutical compounds in sewage treatment plant samples (raw and treated waters) focusing for a part on psychotropic drugs and on their transformation products.

Key words: psychotropic drugs, HRMS, sewage treatment plants

Correspondence to: helene.budzinski@u-bordeaux.fr, caroline.gardia-parege@u-bordeaux.fr, marie-helene.devier@u-bordeaux.fr

EFFECT BASED METHODS FOR THE DETECTION OF PHARMACEUTICAL CONTAMINATION IN THE CONTEXT OF THE WATER FRAMEWORK DIRECTIVE

*Mario Carere**
**Italian Institute of Health, Department Environment and Health*

The EU Water Framework Directive (WFD) is the legal framework for the protection of all water resources (surface and ground) at european level. The monitoring, assessment and classification schemes of the WFD for surface waters include mainly chemical and ecological parameters (biological quality elements) and should be updated to take into account of the scientific and innovation progress. In the context of the Working Group Chemicals of the Common Implementation Strategy of the WFD a technical activity, shared by several Member States, about the application of effect based methods (EBM) for the monitoring programmes of the waterbodies is currenly in place. Effect based methods are mainly bioassays (in vivo, in vitro) and biomarkers, but can include also other methods such as metagenomics and ecological tools; EBM are included in the WFD for the derivation of environmental quality standards, but they are not used for monitoring; they can be valuable for different applications: screening, early warning system, investigative monitoring, to detect effect of mixtures and to link chemical and ecological status of the WFD.

Pharmaceuticals are emerging contaminants for which monitoring data about their effects on the ecosystems and human health are needed. The recent European strategy for the pharmaceuticals in the environment includes the objectives at policy and research level and the effects and problems caused by pharmaceuticals mixtures are clearly mentioned.
In relation to pharmaceuticals effect based methods could have an important role also for the assessment and classification of surface waterbodies. In the context of the Common Implementation Strategy an EU WFD voluntary project has been realized in relation to the 3 steroidal estrogens E1, E2 and EE2 with the aim to evaluate the possible use of EBM for the detection of the effects of these substances that are included in the EU watch list, the results have demonstrated the applicability of these methods for the detection of pharmaceuticals. In conclusion the current review of the WFD and the recent European strategy for pharmaceuticals in the environment represent an opportunity for the inclusion of EBM in the european legislation.

Keywords: effect based, pharmaceuticals, water framework directive

Correspondence to: mario.carere@iss.it

VETERINARY ANTIBIOTICS IN THE SOILS OF CHINA: PROBLEMS AND MANAGEMENT REQUIREMENTS

Haibo Zhang, Jiaqing Wang*, Yufan Fei*, Yongming Luo**, Longhua Wu**, Yujuan Huang***

**Zhejiang A&F University*
***Nanjing Institute of Soil Science, Chinese Academy of Sciences*

The use of antibiotics in animal feeds has been regulated In China since 1989, however many antibiotics are used uncontrolled as feed additives. The average usage of veterinary antibiotics has reached approximately 6000 tons annually and most of this use occurs in the economically developed regions. The veterinary antibiotics may enter soils through land-application of manures in the farmland and further release into water by runoff or leaching, which has been concerned of worldwide. A total of 125 surface soils covering from east to west of China were sampled for the analysis of 17 antibiotics in order to identify antibiotics contamination in the soils caused by long-term manures application. The results indicate that the agricultural land has accumulated a statistically significantly higher antibiotics concentration than conventional open croplands. The maximum oxytetracycline concentration was 8400 μg kg-1, the highest level that has ever been reported for oxytertracycline in soils. The residual concentration is decided by both plant duration and manure type. Short-term (<5 years) planting shows the highest residues of tetracyclines and fluoroquinolones in the soils. Soil contamination of antibiotics has also contributed to the spread of antibiotic resistant genes (ARGs) in the environment, which might result to an even more serious risk to human health. A management policy was therefore proposed for the using of veterinary antibiotics in livestock and poultry breeding and the disposal of animal manures.

Correspondence to: hbzhang@zafu.edu.cn

A SYSTEMS MEDICINE APPROACH TO UNVEIL THE METABOLIC PLASTICITY UNDERLYING METASTATIC POTENTIAL AND DRUG RESISTANCE

Marta Cascante[1,3;]

Co-authors: Cristina Balcells[1,2], Igor marin de Mas[1,5], Esther Aguilar[1] , Erika Zodda[1], Pedro de Atauri[1,3], , Josep J. Centelles[1,3], Balázs Papp[5], Francesc Mas[2] , Timothy Thomson[3,4], Silvia Marin[1,3]

[1] Department of Biochemistry and Molecular Biomedicine, Faculty of Biology, Universitat de Barcelona, Barcelona, Spain, Institute of Biomedicine of University of Barcelona (IBUB), Barcelona, Spain
[2] Department of Material Sciences and Physical Chemistry and Research Institute of Theoretical and Computational Chemistry (IQTCUB), University of Barcelona, 08028 Barcelona, Spain.
[3] Centro de Investigación Biomédica en Red de Enfermedades Hepáticas y Digestivas CIBEREHD), Instituto de Salud Carlos III (ISCIII), 28029 Madrid, Spain.
[4] Department of Cell Biology, Barcelona Institute for Molecular Biology (IBMB), National Research Council (CSIC), Barcelona, Spain
[5] Synthetic and Systems Biology Unit, Institute of Biochemistry, Biological Research Center of the Hungarian Academy of Sciences, Szeged, Hungary

Tumors harbor combinations of heterogeneous neoplastic cells. In this complex ecosystem, all modalities of mutual cell interactions can take place within the context of environmental cues that exert selective pressures. In spite of the underlying heterogeneity, two broad operational categories of neoplastic cells, namely cancer stem cell (CSC) and non-CSC, are most relevant with regards to two key properties of evolving tumor cells: survival to stress and metastatic colonization. Using a dual model of two clonal subpopulations isolated from an established prostate cancer cell line (PC-3), we have applied a systems biology approach including experimental data integration into genome-scale metabolic models to unveil metabolic differences and potential vulnerabilities to be exploited as putative drug targets. The dual model consists of a CSC-subpopulation (PC-3M-high metastatic potential and low invasiveness) and a non-CSC-subpopulation (PC-3S-expressing EMT markers with high invasiveness and low metastatic potential). Results show that EMT and metastasis programes display different metabolic traits. The main differences observed have been at the level of differential use of glucose and glutamine to fuel TCA cycle, mitochondrial respiration, one-carbon metabolism, beta-oxidation and eicosanoids metabolism. We applied the same approach to identify the metabolic reprogramming associated to platinum resistance and we have also identified metabolic alterations emerging from platinum resistance to be used in combined drug therapies.

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Key words: Systems Biology, Cancer, Drug resistance

Correspondence to: martacascante@ub.edu

OCCURRENCE, BIOCONCENTRATION, METABOLOMICS AND BEHAVIOURAL EFFECTS OF PHARMACEUTICALS IN FRESHWATER INVERTEBRATES

Leon Barron,*[a] *Thomas Miller*,[a] *Keng Tiong Ng*,[a] *James MacRae*,[b] *Nicolas Bury*,[a,c,d] *Stewart Owen*[d]

[a]*Analytical & Environmental Sciences Division, Faculty of Life Sciences and Medicine, King's College London, 150 Stamford Street, London, SE1 9NH, UK*
[b]*Metabolomics Laboratory, The Francis Crick Institute, 1 Midland Road, London, NW1 1AT, UK*
[c]*Faculty of Science, Health and Technology, University of Suffolk, James Hehir Building, University Avenue, Ipswich, Suffolk, IP3 0FS, UK*
[d]*Division of Diabetes and Nutritional Sciences, Faculty of Life Sciences and Medicine, King's College London, Franklin Wilkins Building, 150 Stamford Street, London, SE1 9NH, UK*
[e]*AstraZeneca, Global Environment, Alderley Park, Macclesfield, Cheshire SK10 4TF, UK*

Pharmaceuticals, personal care products, illicit drugs, pesticides and a suite of industrial chemicals are now considered to be contaminants of emerging concern (CECs) in the aquatic environment. To assess risk, exposure concentrations in water are often linked to observed effects, mainly due to the analytical challenge of measuring low internalised CEC concentrations in complex biological samples, especially in small invertebrate specimens. However, the development of more sensitive and selective methods based on liquid chromatography-mass spectrometry (LC-MS) has recently enabled their measurement in biota. Here the focus will be on pharmaceuticals and illicit drugs in Gammarus pulex, a freshwater benthic amphipod that is an important indicator of river health. Specifically the presentation will overview recent advances made in our laboratory regarding (a) the occurrence and bioconcentration factor (BCF) measurement of pharmaceuticals and illicit drugs both in water and internalised within biota; (b) integration of machine learning-based tools for prediction of BCF for CECs; (c) untargeted metabolomics of invertebrates at environmentally relevant concentrations; and (d) lethal and sub-lethal effect-based studies. The extraction and quantitative measurement of 67 CECs in G. pulex was complex and based on pulverised liquid extraction, two-stage solid phase extraction and LC-MS/MS. Preliminary experiments involving MS imaging of gammarids following exposure to diazepam are also presented. For prediction of BCF, a quantitative structure-activity relationship-based neural network was generated and tested using data for both fish and gammarids with some success. This approach along with other BCF prediction tools were then used with measured concentrations in the wild to assess any potential for effects of those compounds identified. For endogenous metabolite profiling, gammarids were exposed in the laboratory to a selection of drug compounds at environmentally relevant concentrations (200 and 2000 ng L^{-1}) over 7-days. Extracts were analysed using an optimised hydrophilic interaction liquid chromatography-high resolution mass spectrometry-based method and data was pre-processed using optimised peak-picking parameters through XCMS in R. Visualisation of the samples by PCA showed no obvious clustering in treatment groups, however, there were significant changes in 20 metabolic features that are presented for two psychoactive drug compounds, haloperidol (antipsychotic) and cocaine (stimulant). Finally, LC50 and an initial experiment measuring gammarid movement over the same exposure and any effects are discussed in detail.

Correspondence to: Leon.barron@kcl.ac.uk

LOW-COST ADSORBENT FOR ENVIRONMENTAL REMEDIATION OF PHARMA RESIDUES- HOW RESILIENT IS THE APPROACH?

Ajit K Sarmah, Febelyn Reguyal, Farzaenh Feizi*

Department of Civil & Environmental Engineering, The Faculty of Engineering, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

Numerous studies have revealed that common and cost-effective available treatment options (e.g. flocculation, filtration, activated sludge, chlorination) are not effective in the removal of various pharmaceutical drugs from water. This creates a dilemma for the wastewater industry as most technologies able to remove various pharma residues employing advanced oxidation, reverse osmosis and membrane filtration, can be prohibitively expensive. The use of ozone or ultraviolet light for disinfection is costly, while the process of chemical disinfection of using chlorine could often result in the production of disinfection by-products which are carcinogenic. Given the available treatment technologies are costly; removal of pharma residues by low cost sorbents seems to be an ideal solution due to their potential versatility and efficiency. Low-cost adsorbents refer to materials with little or no value, wastes or derived from wastes, and require minimal processing used to adsorb various contaminants. These adsorbents may be directly used in the sorption process or undergo cost-effective processes prior to their applications. Waste-derived adsorbents are materials that require chemical or thermal treatment to be produced and the additional cost of production is assumed to be compensated by its high sorption capacity. However, until now, there has been no reported industrial scale application of low-cost adsorbent which may be due to lack of desirable characteristics of good adsorbent or the optimisation issues for parameters such as contact time, sorbent to solute ratio, flow rate as well as due to uncertain economic benefits from its application and more importantly the resiliency of the low-cost adsorbent system.

The production system of biochar based adsorbent should be designed to be able to adapt to various raw materials (wood, sludge, poultry litter etc.); flexible towards different processing technologies (auger, ablative, fluidised bed, circulating bed, vortex reactors) and the end product should be versatile enough to cater for diverse market demands. The design and marketing of biochar based adsorbent system may be subdued due to the immense inter–connectivity in the present world which takes time to accept a new product. This connectivity includes and is not limited to singular product, firms, economy, services, logistics etc. As a result of this dense network of entities, which has immense impact on each other, it becomes imperative to consider the safety; processing; energy; efficiency; environmental effect and recyclability in a biochar based adsorbent system. Therefore the biochar based adsorbent system should be imparted with characteristics that would make it flexible as well as sturdy.

In this work, findings of recent studies using biochar (biomass-derived carbonaceous material) as a low-cost adsorbent for adsorptive removal of selected organic contaminants will be presented with a resilience perspective of biochar mediated contaminant remediation in water and the challenges associated with scaling-up the technology.

Key Words: Green adsorbent, biochar, adsorptive removal, scaling-up, resiliency

Correspondence to: a.sarmah@auckland.ac.nz

PHARMA RESIDUES AND MICROPLASTICS IN SAUDI ARABIAN LAKES AND POOLS IRRIGATED WITH WASTEWATERS. BIOACUMULATION AND PLANT UPTAKE

Yolanda Picó[1], Rodrigo Alvarez-Ruiz[1], Ahmed H. Alfarhan[2], Mohamed A. El-Sheikh[2], Hamad O. Alshahrani[2], Damià Barceló[2,3]

[1]Environmental and Food Safety Research Group (SAMA-UV), Desertification Research Centre CIDE (CSIC-UV-GV), Moncada-Naquera Road Km 4.5, 46113 Moncada, Spain
[2]Department of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[3]Water and Soil Quality Research Group, Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain

Humid areas and specially wetlands increasing depend on the recycling of industrial effluents and other type of wastewater (e.g. domestic wastewater, agricultural runoff, etc.), previously treated or not to palliate the good quality surface water scarcity [1,2]. Our study aimed at assessing the occurrence of pharmaceutical and personal care products (PPCPs) and pesticides in different environmental compartments and microplastics in water of a characteristic lagoon wetland in Saudi Arabia to establish the transport, accumulation and fate of these pollutants in a water-stressed area under high anthropogenic pressure [3].

Water samples were extracted by solid-phase extraction (SPE) whereas soil, sediments and vegetables were extracted by solid-liquid extraction (SLE) followed by a SPE clean-up. Determination was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS).
In water, diazinon (up to 1016 ng L^{-1}), caffeine (up to 20663 ng L^{-1}), diclofenac (up to 1390 ng L^{-1}) and paracetamol (up to 3069 ng L^{-1}) were at the highest concentrations. The substances with the highest frequency of detection were carbendazim, atorvastatin, caffeine, etoricoxib, lorazepam, metformin, ofloxacin, paracetamol, salicylic acid and tramadol. Considerably less pesticides and PPCPs at concentrations ranging from 0.01 to 126 ng g^{-1} dry weight (d.w.) were detected in the other matrices (sediment >> soil > plants). The concentration of microplastics in water ranged from 0.7 to 7.8 items /L in the Al-Asfar lake and from 1.1 to 9.0 items L^{-1} in the Al-Hubail lake. Risk assessment [using hazards quotients (HQ)] was used to highlight pesticides and PPCPs of major ecological concern that should be closely monitored to avoid adverse effects. Furthermore, the potential bioaccumulation and plant uptake was also tested on the surrounding crops that are irrigated with wastewater. Mostly pesticides, coming from the direct treatment (including chlorpyrifos and diazinon at high concentrations) were found. Several pharmaceuticals and PCPs (such as bisphenol A or paracetamol) were also found in vegetables but at very low concentrations (<10 µg kg^{-1}).

Further studies are needed to obtain a better estimate of the range of chemical contaminants that can be present in crop and wild flora under different condition as well as the public health risk that may arise not only of the presence of contaminants and residues but also of the exposure to mixtures of substances or their metabolites, which could produce different toxic effects.
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Correspondence to: Yolanda.Pico@uv.es

PHARMACEUTICALS IN THE ENVIRONMENT – A PRODUCT DEVELOPMENT AND MANUFACTURING PERSPECTIVE

Torkel Gren, PhD, Science & Technology Officer, Recipharm AB, Stockholm

The development and manufacture of pharmaceutical products contributes to improved health across the world. However, there are certain negative impacts, such as the effects caused by drug substances being emitted to the environment. Traditionally, potential environmental effects have not been considered during the development of pharmaceutical products. However, today we recognise the importance of considering environmental aspects together with the therapeutic effect, safety and other characteristics when producing a new medicine. Due to the complex nature of R&D, solving the problems caused by drug substances in the environment will be a slow process. To this end, the industry will need to identify new approaches. This presentation will discuss how development and manufacture can contribute to reduced emissions and environmental impact.

Correspondence to: torkel.gren@recipharm.com

ORAL PRESENTATIONS

COMBINED SAMPLING AND RETENTION MECHANISMS IN LC-HRMS SCREENING OF PHARMACEUTICALS AND OTHER EMERGING POLLUTANTS IN WATER

Verónica Castro, Rosario Rodil*, Rafael Cela*, José Benito Quintana**

**IIAA-Institute for Food Analysis and Research (Univesidade Santiago de Compostela)*

One of the great challenges in Analytical Chemistry is the development of sampling and analytical tools enabling the deployment of comprehensive strategies to measure the impact of chemical pollutants in the different environmental compartments. The improvements in high resolution mass spectrometry (HRMS) instrumentation and data analysis software in the last decades popularized screening as a non-targeted approach for water quality assessment. Further, passive sampling, such as polar organic compounds integrative samplers (POCIS) may complement spot sampling strategies in order to characterize water pollution [1]. Finally, another major challenge is the retention of organic chemicals in liquid chromatography (LC), where hydrophilic interaction chromatography (HILIC), mixed-mode liquid chromatography (MMLC) and supercritical fluid chromatography (SFC) can provide a complementary selectivity in the analysis of polar analytes, as compared to reversed-phase liquid chromatography (RPLC) [2-3].

The main objective of this study was to compare two sampling strategies (POCIS Vs. spot sampling) and four retention mechanisms (RPLC, HILIC, MMLC and SFC) in LC-HRMS screening of water organic pollutants. To this end, a suspect screening approach, using iterative data-dependent MS/MS driven by a library of ca. 3200 chemicals (pharmaceuticals, pesticides and other emerging pollutants) was employed.

The results show that POCIS can afford a larger number of positive identification as compared to spot sampling. On the other hand the best suited retention mechanisms, in terms of identified analytes are: SFC, followed by RPLC, MMLC and HILIC. Still, the best combination (POCIS + SFC) would only allow the identification of 67% of the analytes. Thus, we propose a combination of spot and passive sampling and RPLC and SFC in order to maximize the number of analytes detected. This strategy was applied to different surface water samples from Galicia (NW Spain) were several chemicals were identified.

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Correspondence to: veronica.castro@usc.es

LC-HRMS/MS DETECTION OF TRANSFORMATION PRODUCTS AND METABOLITES OF PHARMACEUTICAL COMPOUNDS IN ARTIFICIAL RIVER CHANNEL EXPOSED TO WASTEWATER TREATMENT PLANT EFFLUENT

Antoni Ginebreda, Laia Sabater-Liesa*, Nicola Montemurro*, Sandra Pérez*, Damià Barceló**

**IDAEA CSIC*

Wastewater effluents represent the primary source of anthropogenic chemicals such as pharmaceuticals into the environment. In recent years, a few methodologies based on liquid chromatography coupled to tandem mass spectrometry (LC-HRMS/MS) have been developed for the target analysis of different classes of drugs in wastewater samples. Moreover, a useful tool of LC-HR-MS/MS is the suspect screening of unknown compounds when the standards are not available in complex samples.

In this study, the effects of natural reduction of organic contaminants occurring in river was investigated using ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry (UHPLC-QqTOF-MS). Artificial streams were exposed to water from wastewater treatment plant Quart (Girona, Spain) under controlled conditions of light and water flow during 34 days. Wastewater was renewed twice per week, and the samples were collected from the artificial streams before/after water replacement. Samples were filtered and extracted passing through Oasis HLB SPE columns, eluted, evaporated and reconstituted in 1000 µL of the initial mobile phase conditions (acetonitrile/water – 3:97). Quadrupole time-of-flight MS system SCIEX X500R QTOF was used to identify organic compounds. Data acquisition was performed in MS/MSAll with SWATH acquisition. Confident identification and quantitation were achieved through a MS/MS library match against a HR-MS/MS spectral library, including the more relevant compounds. In our study, we detected and quantified several pharmaceutical parent compounds, metabolites, and their transformation products (TPs). For the first time, some TPs are identified in environmental samples. Results are also discussed in the context of biofilm's development in the artificial river channels.

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Correspondence to: agmqam@idaea.csic.es

ANALYSIS OF PPCP IN WATER SAMPLES USING LCMSMS

*Jianru Stahl-Zeng**

**SCIEX, Germany*

Pharmaceuticals and Personal Care Products (PPCPs) represent an ongoing relevant contaminant class in the environment and water samples which have been impacted by human activity. The ability to reliably and sensitively detect and quantify these diverse anthropogenic species in water and other systems is critical in the ongoing evolution of regulatory standards and frameworks around the world.

The SCIEX Triple Quad and High Resolution TOF LC-MS/MS System are presented as both quantitative (QQQ) and qualitative (QTRAP, TOF) platforms with exceptional performance in speed, polarity switching, linear dynamic range, and ease of use data handling with SCIEX OS-Q Software.

This Presentation describes the use of the SCIEX Triple Quad LC-MS/MS system to establish an optimized method for the quantitative analysis of anthropogenic contaminants in environmental water samples. The method combines both the positive and negative polarity electrospray ionization modes into one comprehensive screening method, that scans across a vast range of analytes without any sacrifice or compromise to data quality and integrity. Exceptional sensitivity and linear dynamic range provide the basis for a robust quantitative methodology for this large panel of chemically diverse species.

This Presentation will also describe non-targeted analysis by using SCIEX high resolution instrument in combination with SWATH workflow.

Efficiency in data processing with SCIEX OS-Q Software is increased with the ability to employ streamlining features such as: Automatic Outlier Removal, confirmatory traffic light system for rapid scoring and review of data, and AutoPeak intelligent peak integration.

Correspondence to: Jianru.Stahl-Zeng@sciex.com

VETERINARY PHARMACEUTICAL CONTAMINATION IN MIXED LAND USE WATERSHEDS: FROM AGRICULTURAL HEADWATER TO WATER MONITORING WATERSHED.

Jaffrezic Anne, Jardé Emilie**, Marengue Eric***, Le Bot Barbara*****

**UMR SAS, AGROCAMPUS OUEST, INRA, 35000 Rennes, France.*
***Univ Rennes, CNRS, Géosciences Rennes, UMR6118, 35000 Rennes, France.*
****LABOCEA, Ploufragan, France.*
*****Univ Rennes, Inserm, EHESP, Irset-UMR_S 1085, F-35000 Rennes, France.*

Occurrence of pharmaceuticals in superficial waters threatens human health and ecosystem functions. The main stake is the development of antibiotic resistance as selection of resistant bacteria can occur at sub-inhibitory concentration of antibiotics similar to those found in aquatic ecosystems. Most studies on pharmaceutical quantification occurred in large scale watershed. Identifying the sources and pathways of pharmaceuticals in watersheds is difficult because i) most veterinary pharmaceuticals are used in human medicine as well and ii) septic or sewer wastewater treatment plants (WWTP) can release pharmaceuticals into surface water, even in agricultural headwater watersheds. This study aims at analyzing the spatiotemporal variability of animal specific, mixed used and human specific pharmaceuticals in nested agricultural headwaters with intensive livestock production and a WWTP, the outlet being the Water Framework Directive monitoring station. Grab sampling were performed during one hydrological year in headwater watersheds and at three dates over 7 nested watersheds from 1.9 to 84.1 km². Twenty pharmaceuticals were analyzed. Animal-specific pharmaceuticals were detected at all sampling dates upstream and downstream from the WWTP and at concentrations higher than those of human-specific pharmaceuticals. The predominance of animal-specific and mixed-use pharmaceuticals vs. human-specific pharmaceuticals observed at these sampling points was confirmed at the other sampling points. Animal-specific pharmaceuticals were detected mainly during runoff events and periods of manure spreading. Mixed-use and human-specific pharmaceuticals predominated in the largest watersheds when runoff decreased. Concentration recorded at the main outlet could be reduced by acting at the major upstream watershed contributing to the pollution. Mitigation actions should be focused on headwater watershed (4.3 km²). Monitoring of water quality is necessarily at large scale (between 50 and 100 km²) to elaborate water quality indicators for European water policies. However, it should be completed by additional grab sampling in headwater watersheds encompassing one hydrological year to assess seasonal variability and to better rank mitigation strategies.

Correspondence to: emilie.jarde@univ-rennes1.fr

VETERINARY PHARMACEUTICAL RESIDUES IN WATER RESOURCES AND TAP WATER IN AN INTENSIVE HUSBANDRY AREA IN FRANCE

Le Bot Barbara, Charuaud Lise*, Jardé Emilie**, Jaffrezic Anne***, Liotaud Marine**, Goyat Quentin*, Mercier Fabien**

**Univ Rennes, Inserm, EHESP, Irset (Institut de recherche en santé, environnement et travail) - UMR_S 1085, Rennes, France*
***Univ Rennes, CNRS, Géosciences Rennes - UMR6118, F-35000 Rennes, France*
****UMR Soil Agro and hydrosystem Spatialisation (SAS), Agrocampus Ouest, INRA Rennes, France*

Context: In intensive livestock areas, veterinary pharmaceutical residues (VPRs) are released into the environment either directly with (1) urine and feces of animals in pastures or (2) during aquaculture activities, or indirectly during the spreading of contaminated manure and slurry. The continuous released of veterinary pharmaceuticals may represent a diffuse and pseudo-persistent pollution in the environment. Furthermore, VPRs may reach drinking water treatment plants, because treatment processes are not designed to remove these contaminants. In France, Brittany is an intensive husbandry area and 75% of tap water is produced from surface waters, which are very vulnerable to contamination. VPRs have been detected in natural waters at concentrations ranging from ng/L to µg/L, thanks to advances in analytical methods.

Objectives: The project aims to assess the occurrence of VPRs in water resources and corresponding tap water in an area with a strong agricultural pressure.

Methods: In Brittany, 25 catchments used for tap water production were selected in intensive husbandry watersheds. Sampling strategy's purpose was designed to reflect variations in veterinary practices, manure/slurry spreading times and water regime (low water or high water). A list of 38 VPRs was analyzed by solid phase extraction, followed by a liquid chromatography separation coupled with tandem mass spectrometry detection.

Results: In water resources, at least one VPR were quantified in 32% of the samples and 17 VPRs were quantified, including antibiotics, antiparasitic drugs and anti-inflammatory drugs. Concentration levels ranged between 5 ng/L and 2946 ng/L. VPRs were quantified in 20% of the tap water samples. Twelve VPRs were quantified, including ten compounds exclusively used in veterinary medicine and two mixed-use compounds. Concentration levels are inferior to 40 ng/L for all compounds, with the exception of the antibiotic florfenicol which was quantified at 159 ng/L and 211 ng/L.

Conclusion: VPRs have been quantified both in water resources and tap water in Brittany. Thus, the population may be exposed chronically via tap water to those contaminants. To our knowledge, this study is the most complete dataset of contamination by VPRs in France over a long period and at the scale of a region.

Correspondence to: barbara.lebot@ehesp.fr

EVALUATION OF THE IMPACT OF NSAIDS AND DIET REGIME IN FRESHWATER INVERTEBRATES THROUGH TARGET AND NON-TARGET METABOLOMICS

Sara Rodriguez-Mozaz, Albert Serra-Compte*, Damià Barceló*, Sergi Sabater*, Julio C. Lopez-Doval**

**Catalan Institute for Water Research (ICRA)*

Freshwater organisms can be exposed to different stress conditions in the Mediterranean zone, such as changes in food quality (mainly due to seasonality) and chemical pollution (e.g. pharmaceuticals). Non-steroidal anti-inflammatory drugs (NSAIDs) in particular, are known to interfere in the conversion of arachidonic acid (ARA) to prostaglandins in vertebrates. The objective of this work was to assess the effects of a mixture of four NSAIDs (diclofenac, naproxen, ibuprofen and ketoprofen) on freshwater invertebrates (Hydropshyche sp.) under different nutritional conditions through the diet (with and without ARA).

The experiments were carried out in triplicate under controlled conditions in mesocosms during 16 days. Macroinvertebrates were exposed to four different conditions i) control: where organisms were fed with food containing ARA; ii) organisms fed with food containing ARA and exposed to a mixture NSAIDs in water (c.a. 20 µg/L in total); iii) organisms fed with food that does not contain ARA and iv) organisms fed with food without ARA and exposed to the mixture of NSAIDs. A target metabolomics approach was first applied to characterize changes in selected endogenous compounds from the cascade converting ARA to prostaglandins. Non-targeted metabolomics was further applied to reveal other potential impacts in the organisms. The bioconcentration of NSAIDs in the macroinvertebrates at the end of the experiment was also evaluated.

Concentrations of ARA, prostaglandin H2, prostaglandin D1 and prostaglandin E1 were higher in organisms fed with food enriched with ARA than those exposed to food without ARA. The exposure to NSAIDs did not alter significantly the levels of ARA and prostaglandins. However, non-target metabolomics revealed alterations in invertebrate`s metabolome due to type of diet, an also to the presence of NSAIDs. In addition, most of NSAIDs bioconcentrated in macroinvertebrates. The highest concentration found at the end of the experiment in organisms exposed to NSAIDs was 220 ng/g for ibuprofen followed by 122 ng/g for naproxen and 81 ng/g for diclofenac. Ketoprofen was not detected in any of the biota extracts. Future studies would help to confirm which compound plays the most critical role in the organism metabolism.

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Correspondence to: srodriguez@icra.cat

ANTIBIOTICS IN THE EU WATCH LIST PROGRAM AND CHALLENGES TO IMPROVE THE RISK ASSESSMENT

Teresa Lettieri, Isabella Sanseverino*, Anna Navarro Cuenca*, Robert Loos*, Dimitar Marinov*, Magdalena Niegowska**, Livia Gomez Cortes*, Dorota Napierska***, Helle Skejo**

**European Commission Joint Research Centre (EU JRC)*
***University of Sassari*
****HCWH*

The Watch List (WL) program, under the Water Frame Directive (WFD), is a mechanism for obtaining high-quality Union-wide monitoring data on the concentrations of potentially polluting substances in the aquatic environment to support the future selection of priority substances. The WL substances include pharmaceuticals (hormones and antibiotics), insecticides and other compounds. Among antibiotics, there classes are monitored under the WL program, the macrolides, beta-lactam and fluoroquinolone.

In the last years, antibiotics in water raised a high concern since they can act as constant pressure for the selection, transfer and spread of the antimicrobial resistance (AMR). Indeed, they are introduced into the water through different sources together with resistant bacteria, facilitating, in this way the selection of bacteria capable to survive by acquiring the antibiotic resistance genes (ARG). The challenge for the antibiotics' risk assessment, behind the toxic effect, would be to take into account their contribution to the AMR .

The presentation will show preliminary results on the characterization of the natural background of the AMR in aquatic pristine environment and on the assessment of the minimal antibiotics' concentration that might induce resistance in the microcosm studies. The water samples were collected from an alpine river (Italy), a pristine site, showing that the bacteria were resistant to ampicillin, amoxicillin, kanamycin, and erythromycin in July and October and only to erythromycin and kanamycin in September. The microcosms were exposed to low concentrations (up to 100ng/L) of three antibiotics: erythromycin, amoxicillin, and tetracycline over a period of eleven-thirteen days and the resistance was observed already at very low antibiotic concentration.

Correspondence to: Anna.NAVARRO-CUENCA@ec.europa.eu

LIFE CYCLE ASSESSMENT AT FRENCH SCALE ON HUMAN HEALTH AND AQUATIC ENVIRONMENT OF MICROPOLLUTANTS RELEASED BY WASTEWATER TREATMENT PLANTS

Quentin Aemig, Arnaud Hélias*, Dominique Patureau**

**INRA - LBE*

Wastewaters from industrial and domestic origins contain a huge diversity of organic and metallic micropollutants which concentrations range from ng to µg.L-1. In wastewater treatment plants (WWTP), they are more or less removed from the water (Clara et al. 2005; Martin Ruel et al. 2012; Michael et al. 2013; Besha et al. 2017) by different mechanisms such as sorption, volatilization, abiotic or biotic transformations (Rogers 1996).

Despite this partial removal, clarified water still contain part of the organic and metallic micropollutants present in wastewaters. Those micropollutants are then rejected to the environment through WWTP effluents and can impact aquatic environment and Human health.
To estimate those impacts, this study initiated by Synteau (French National Union of Water Treatment Professionals) is composed of the following steps:

- First, substances present in WWTP effluents were inventoried. Around 300 substances were identified using the European legislation (Water Framework Directive) and French national data survey that give the concentrations of a huge diversity of micropollutants in WWTP effluents. Among identified substances, around one third corresponds to pharmaceuticals compounds. Pesticides, metals and well known substances such as alkylphenols, polycyclic aromatic hydrocarbons, etc. were also identified.
- Second, the concentrations were collected from other different sources: French report linked to the Water Framework Directive application, PhD thesis, scientific articles from international and national journals and water treatment professionals' data. A mean national French concentration for each substance was calculated to estimate annual flow emitted to the environment at the French scale.
- Potential impacts associated were calculated with a Life Cycle Assessment (LCA) approach. Flows were multiplied by characterization factors coming from USEtox 2.1 ®, a reference model in LCA (Hauschild et al. 2008; Rosenbaum et al. 2008, 2011; Henderson et al. 2011). Potential impacts on Human health were estimated in DALY (Disability Adjusted Life Year) which corresponds to the number of years lost by illness, handicap, cancer or death. Potential impacts on aquatic environment were estimated in number of species potentially disappeared due to the release of micropollutants in the aquatic environment.

Concerning organic micropollutants, concentrations range from 0.1 ng/L to 10 µg/L which correspond respectively to 0.5 kg/year and 50 tons/year flows. Pharmaceutical compounds have high flows whereas hormones and hydrophobic compounds such polycyclic aromatic hydrocarbons (PAH) have the lowest flows. Some pesticides and some PAH have the highest contribution to the impact on Human health. Some pesticides, some hormones and some halogenated compounds have the highest contribution to the impact on aquatic environment.

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Correspondence to: quentin.aemig@inra.fr

EVALUATION OF THE ECOTOXICOLOGICAL IMPACT OF WATERING VEGETABLES WITH WASTE WATER CONTAMINATED WITH PESTICIDES AND PHARMACEUTICAL RESIDUES

Fabrice MARTIN-LAURENT, Sara Gallego-Blanco*, Jérémie Beguet*, Nadine Rouard*, Marion Devers*, Sandra Perez**, Serge Chiron***, Damia Barcelo***

**INRA*
***CSIC*
****IRD*

Climate change leads to repeated and severe drought events in all the Mediterranean area which threaten agricultural production. Within this context, the European Commission recently proposed a text defining the minimum required to propose a regulation on the reuse of waste water to irrigate agricultural crop production. One of the major problems of waste water reuse in agriculture is the contamination of arable soils with a range of chemicals such as pesticides and pharmaceuticals (including antibiotics) found as contaminants in waste waters. These chemicals can have an ecotoxicological impact on in soil living organisms and on supported ecosystem functions. They can also be transferred to the crop and contaminate the food chain.

Within this context, the European project AWARE coordinated by Pr Barcelo aims to evaluate the environmental risks of waste water reuse to irrigate vegetables crops. This presentation will present the results obtained so far to test 'the worst case scenario' in an experiment conducted under controlled conditions in order to evaluate the fate and the ecotoxicological impact of a mixture of 14 micropollutants (including pesticides and pharmaceuticals) spiked to waste water. Two culture cycles of lettuces were carried out on an arable soil watered daily either with clean water or with waste water spiked with 10 or 100 ppb of a mixture of 14 micropollutants (6 treatments, 5 replicates, n=30 per culture cycle). At the end of each culture cycle of 42 days, several measurements have been done: growth and yield of mycorhization of lettuces; fate of the micropollutants in the soil and in the lettuces (root/shoot); abundance, composition and diversity of fungal and bacterial communities by qPCR and next-generation sequencing of amplicons, respectively; activity of functional microbial guilds supporting N cycle and biodegradation of antibiotics (sulfonamides). A synthesis of all these results will be presented with the aim to assess the risks of waste water reuse under the 'worst case scenario'.

Correspondence to: fabrice.martin@inra.fr

REMOVING PHARMACEUTICALS BY A SURFACE WATER TREATMENT PROCESS TO PRODUCE DRINKING WATER

Eric Chauveheid, Sabine Scholdis**

**VIVAQUA*

Pharmaceutical compounds have been shown to be widespread in surface water due to their discharge from wastewater. Some studies have shown the presence of few pharmaceuticals in drinking water produced from surface water by traditional water treatment processes. VIVAQUA, a Belgian drinking water company, is producing about 150.000 m3/day of drinking water from surface water treated by a conventional drinking water process combining ozone and activated carbon steps. This multi-barrier industrial process optimized for the efficient removal of pathogens and micropollutants (such as pesticides) has been evaluated for its removal efficiency towards pharmaceutical compounds. Among the most significant pharmaceuticals found in this river, levetiracetam appeared as the most reluctant compound to the surface water treatment process. The combination of an ozone pre-treatment step (pre-ozonation), acting as an advanced oxidation process, with granular activated carbon filtration removed completely all monitored compounds, including levetiracetam. Irbesartan was also incompletely degraded by ozone pre-treatment, but completely removed immediately after the following granular activated carbon filtration. All other compounds were readily degraded after the initial ozone pre-treatment step, confirming the efficiency of ozone based advanced oxidation process for removing efficiently pharmaceuticals when producing drinking water from surface water. This study shows that a conventional optimized surface water treatment can produce drinking water devoid of many pharmaceuticals, contrary to previous studies.

Correspondence to: eric.chauveheid@vivaqua.be

DETECTION OF PHARMACEUTICALS AND THEIR PHOTOTRANSFORMATION PRODUCTS IN SURFACE WATERS

Enelton Fagnani, Nicola Montemurro*, Sandra Pérez**

**IDAEA-CSIC*

Pharmaceutical active compounds (PhACs) are ubiquitous contaminants that enters into the aquatic environment from domestic and industrial discharges. Wastewater treatment plants (WWTPs) are unable to sufficiently eliminate most of these substances, which achieve the water bodies and may result in ecotoxicity and endocrine disruption for humans. Once in the environment, these contaminants of emerging concern (CECs) should be degraded by abiotic processes such as photolysis, resulting in transformation products (TPs) with particular features regarding mobility and toxicity.

Classical target analysis, which uses certified standards for the confirmation of identity and quantification of analytes, normally is not applicable for TPs analysis because commercial standards are frequently not available. Comparison with databases is either complicated because each source of data acquires the analytical information by different ways, and again there is not an identical pattern to compare, besides the costs for accessing. In addition, the low concentration (ppt or less) in aquatic environment is an analytical challenge to be surpassed.

To overcome these issues, some techniques can be employed in the development of a complete methodology: solid-phase extraction (SPE) is used for cleaning up and preconcentrating the analytes form the samples; reversed phase ultra-performance liquid chromatography (RP-UPLC) is an excellent option to efficiently separate analytes in aqueous matrices; high resolution mass spectrometry (HRMS) is able to identify mass-to-charge ratio (m/z) of the analytes with high accuracy and yields the MS/MS spectra (tandem mass spectrometry) that is characteristic for each pattern molecule in the experimental conditions applied. All these tools are fundamental to implement a suspect screening protocol, which consists, in this case, in creating a particular database with MS and MS/MS spectra of TPs identified in laboratory experiments, and search for these same compounds in surface water samples. The use of isotope-labeled internal standards (ILIS) is important to validate the procedures of extraction and quantification.

In the present study, it is used a homemade extraction cartridge composed by the mixture of 4 different sorbents (generic, anionic exchanger, cationic exchanger, and one for more polar compounds) to ensure the retention of compounds with different polarities. A quadrupole time-of-flight high resolution spectrometer (Q-TOF) is used to acquire the data by two different modes, information-dependent acquisition (IDA) and sequential window acquisition of all theoretical fragment-ion spectra (SWATH) that is a kind of data-independent acquisition (DIA). Elucidation of the TPs structures will be performed based on the MS/MS spectra and specialized software

Correspondence to: efgqam@cid.csic.es

DEGRADATION OF PHARMACEUTICAL RESIDUES BY OZONATION AND OZONE-ACTIVATED PEROXYMONOSULFATE PROCESS: A COMPARISON IN EFFICIENCY AND RADICAL CONTRIBUTION

Emma Deniere, Stijn Van Hulle**, Herman Van Langenhove*, Kristof Demeestere**

**Ghent University - Research group EnVOC - department Green Chemistry & Technology*
***Ghent University - Research group LIWET - department Green Chemistry & Technology*

To increase water quality and re-use, advanced oxidation processes (AOPs) are of key importance to degrade emerging organic micropollutants. A large number of studies have proven the efficiency of ozone-based AOPs in synthetic (clean) water and in secondary effluent from wastewater treatment plants. These studies show, however, that the performance of AOPs reduces if the matrix becomes more complex. Rapid scavenging of both ozone and hydroxyl radicals by bulk organic matter reduces the amount of radicals that remain available for micropollutant removal. Recently, AOPs based on the generation of sulfate radicals have gained attention. These radicals are characterized by a higher selectivity, exemplified by lower reaction rate constants with organic matter than hydroxyl radicals while maintaining high reactivity towards a large set of micropollutants. Sulfate radicals can be generated by the activation of peroxymonosulfate (PMS). This can be done through reaction with ozone, but the process and its mechanisms have only been investigated to a very limited extent.

Therefore, in this work a comparative study has been performed of ozonation generating hydroxyl radicals versus an ozone-activated peroxymonosulfate process (O3/PMS) producing both sulfate and hydroxyl radicals. The efficiency of both processes has been studies for the degradation of eight micropollutants, mostly pharmaceuticals, selected based on their environmental relevance and their different reactivity with ozone. Insights have been gained on the fundamentals and performance of the new O3/PMS process showing – in synthetic clean water – better efficiency (up to 6 times higher) than ozonation, particularly for compounds with low ozone reaction rate constants (kO3 < 250 M-1s-1) and at neutral to alkaline pH conditions. For compounds with high ozone reaction rate constants (kO3 > 1000 M-1s-1) no significant difference between the O3 and O3/PMS process is noticed, because of their fast direct reactions with ozone. According to multiple scavenging experiments, sulfate radicals contribute by more than 50% to the removal of ozone-recalcitrant pharmaceuticals. Addition of relatively small amounts of PMS already shows a significant improvement of the ozonation process, given the fact that decreasing the molar ratio PMS:O3 by a factor of 10 (from 1:1 to 1:10) only lowers the removal of pharmaceuticals by 30 – 50%. Moreover, a more efficient use of PMS is observed at lower PMS doses. In conclusion, our work shows that sulfate radicals play an important role during the O3/PMS process and that this novel technique is promising for the improvement of AOPs aiming at the removal of organic micropollutants in secondary effluent.

Correspondence to: emma.deniere@ugent.be

AMENDED VEGETATION FILTERS TO REMOVE PHARMACEUTICALS FROM WASTEWATER

Blanca Huidobro, Virtudes Martínes Hernández*, Raffaella Meffe*, María Isabel López Heras*, Raul Pradana*, Jorge Antonio Hernández Martín*, Ana de Santiago Martín*, Gloria Teijón*, Covadonga Alonso Alonso*, Leonor Nozal**, Irene de Bustamante****

**IMDEA Water*
***Institute of Applied Chemistry and Biotechnology (CQAB), University of Alcalá*
****University of Alcalá, Department of Geology, Geography and Environment Science*

In Spain, almost 3 million people live in municipalities with less than 2,000 inhabitants. The technical and economic limitations of small and scattered populations impede the effective implementation of conventional wastewater treatments. Non-conventional treatments such as nature-based wastewater purification systems have been reported as feasible solutions for these communities, which have limited access to sewage networks. Vegetation Filters (VFs), a type of land application system, are non-conventional systems where wastewater and/or treated water is applied for the irrigation of a forestry plantation. The attenuation of contaminants occurs as a result of the mutual action of soil, microorganisms and plants that involve natural treatment mechanisms. This non-conventional wastewater treatment has been proved to be quite effective for common wastewater-originated contaminants (e.g. nutrients) whereas little is known about their capacity of attenuating contaminants of emerging concern such as pharmaceuticals.

A VF has the advantage of being a simple and low cost technology than can be further improved by amending the soil with materials that can be obtained from the VF itself. A readily-labile source of carbon used as a soil amendment is supposed to ameliorate the removal of contaminants by stimulating microbial activity. Whereas when soil is amended with a sorbent, mainly sorption processes are fostered. To assess if soil amendments with these properties can provide a better treatment efficiency of the pilot scale VF installed at the IMDEA Water facilities, biochar as a sorbent and woodchips as readily-labile source of carbon have been tested at laboratory scale through infiltration experiments.

These experiments were run using a stock solution of synthetic wastewater (SWW) mimicking the real composition of the wastewater used to irrigate the pilot scale VF. SWW was spiked with a mix of 9 pharmaceuticals (acetaminophen, amoxicillin, atenololic acid, 4-AAA, ketoprofen, clarithromycin, naproxen, estrone (E1) and ibuprofen) at 1,000 µg/L. To investigate the attenuation of pharmaceuticals during vadose zone infiltration, three unsaturated infiltration experiments were performed. In the first two assays natural soil from the pilot scale VF was amended with 3% w/w of woodchips and biochar separately. Whereas in the third assay used as a reference, only the natural soil was considered. SWW was applied following the irrigation schedule of the pilot scale VF. Oxygen concentrations and water contents were monitored along the flow path.

Results demonstrate that soil amended with biochar presents the highest pharmaceutical removal capacity from wastewater. Such a result can be explained by the higher sorption capacity of biochar to retain compounds compared to woodchips. Also, the increase of the soil surface when adding biochar may improve the development of a larger biofilm fostering biodegradation. The soil amended with woodchips do not improve the attenuation occurring in the soil itself and, in some cases, the lixiviation of pharmaceuticals is higher when this amendment is present. The degree of reversible sorption is compound dependent but, in general, hydrophilic pharmaceuticals are better desorbed. Retention times can also have an impact and its influence will be assessed.

Correspondence to: blanca.huidobro@imdea.org

CHIRAL ANALYSIS: AN INNOVATIVE TOOL TO INVESTIGATE THE FATE OF PPCPS IN SOIL IRRIGATED WITH TREATED DOMESTIC WASTEWATER

Monica Brienza, Rayana Manasfi*, Serge Chiron**

**UMR HydroSciences 5569*

This work aims to investigate the fate of pharmaceutical and personal care products (PPCPs) in soil irrigated by secondary treated domestic wastewater. In field study, others processes other than microbial degradations may contribute to the observed dissipation of PPCPs. These include uptake by plants, leaching to deeper soil layers and photodegradation processes. In this context, chiral analysis was investigated as an appropriate tool to discriminate between biodegradation and others abiotic degradation processes. Metoprolol, climbazole and fipronil were selected as probe compounds to investigate the enantiomeric enrichment - biodegradation dependency because they are marketed as racemic mixtures and are very often detected in wastewater treatment plant effluents. Chiral analytical methods were first developed using LC-HRMS with limits of detection down to ng/g of soil. These methods were then applied to investigate enantiomeric enrichment in microcosm and field biodegradation experiments. All targeted exhibited strong enantioselective biodegradation in lab-scale soil slurries experiments under dark conditions. Enantioselective degradation was found to be very specific to biodegradation processes. When the enantiomeric enrichment fraction was plotted against the compound residual fraction, the linear fit to the Rayleigh equation was obtained with r2 above 0.98 as quality control parameter, opening the possibility of predicting the biodegradation rates against time. Surprisingly, in field experiments, the degradation of targeted compounds was not found to be enantioselective excluding biodegradation as a major dissipation route. Photodegradation processes were relevant due to the detection of specific TPs related to these transformation routes. After irrigation, a considerable portion of compounds were transported away from the soil surface but they were probably transported back to the soil surface, where they were exposed again to sunlight irradiation due to an upward water movement. Photodegradation needs to be considered when deriving rates for biodegradation from field studies. The influence of leaching and plant uptake will be further evaluated on the basis of the chiral analysis of soil samples from deeper soil layers and in plant root and leaf.

Correspondence to: m.brienza81@gmail.com

PHOTOBIOREACTORS BASED ON MICROALGAE-BACTERIA AND PURPLE PHOTOTROPHIC BACTERIA CONSORTIA: A PROMISING ECO-TECHNOLOGY TO REDUCE THE LOAD OF VETERINARY DRUGS FROM PIGGERY WASTEWATER

Pedro Antonio García-Encina, Rebeca López-Serna*, Dimas García**, Silvia Bolado*, Juan José Jiménez***, Foon Yin Lai****, Oksana Golovko****, Pablo Gago-Ferrero*****, Lutz Ahrens****, Karin Wiberg****, Raúl Muñoz**

**Institute of Sustainable Processes (ISP), Dr. Mergelina, s/n, 47011, Valladolid, Spain*
***Centro para la Investigación en Recursos Acuáticos de Nicaragua, CIRA/ UNAN-Managua, Apdo. Postal 4598, Nicaragua*
****Department of Analytical Chemistry, Faculty of Sciences, University of Valladolid, Campus Miguel Delibes, Paseo de Belén 7, 47011 Valladolid, Spain*
*****Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), Uppsala, SE-750 07, Sweden*
******Catalan Institute for Water Research (ICRA), H2O Building, Scientific and Technological Park of the University of Girona, 101-E-17003 Girona, Spain*

Traditional swine manure treatments are not fully effective in the removal of veterinary drugs. Moreover, they are costly and entail a significant carbon footprint in many cases. Innovative biological approaches based on phototrophic microorganisms have recently emerged as promising alternatives to overcome those limitations. This work evaluated the removal of 19 veterinary drugs (i.e., 16 antibiotics, 1 analgesic, 1 anti-parasitic and 1 hormone) from piggery wastewater (PWW) in two open photobioreactors (PBR) operated with a consortium of microalgae-bacteria (AB-PBR) and purple photosynthetic bacteria (PPB-PBR). Multiple hydraulic retention times (HRT), in particular 11, 8 and 4 days, were tested during stage I, II and III, respectively. Ten out of 19 target compounds were detected with inlet drug concentrations ranging from 'non-detected' (n.d.) to almost 23,000 ng L-1 for the antibiotic oxytetracycline. Moreover, three of the antibiotics (i.e., enrofloxacin, sulfadiazine and oxytetracycline) were found at concentrations above the analytical linearity range in some or all of the samples under study. AB-PBR supported higher removal efficiencies (REs) than PPB-PBR, except for danofloxacin. Overall, REs progressively decreased when decreasing the HRT. The highest REs (>90%) were observed for doxycycline (95±3%) and oxytetracycline (93±3%) in AB-PBR during stage I. The other drugs, except sulfadimidine that was the most recalcitrant, showed REs above 70% during stage I in the same photobioreactor. In contrast, no removal was observed for danofloxacin in AB-PBR during stage III, sulfadimidine in PPB-PBR during stage III or marbofloxacin in PPB-PBR during the entire experiment.

Correspondence to: rebeca.lopezserna@iq.uva.es

INFLUENCE OF DICLOFENAC ON THE DIURNAL EXPRESSION PATTERN OF STRESS GENES IN LACTUCA SATIVA

Yvonne Bigott, Soumitra Paul Chowdhury**, Sandra Pérez***, Peter Schröder**

**Helmholtz Zentrum München GmbH, Research Unit for Comparative Microbiome Analysis, Ingolstädter Landstraße 1, 85764 Neuherberg, Germany*
***Helmholtz Zentrum München GmbH, Institute of Network Biology, Ingolstädter Landstraße 1, 85764 Neuherberg, Germany*
****IDAEA-CSIC, Water and Soil Quality Research Group, Department of Environmental Chemistry, c/ Jordi Girona, 18-26, 08034 Barcelona, Spain*

The use of reclaimed wastewater for agricultural irrigation practices is an important alternative water source especially in arid and semiarid regions. Besides this considerable benefit, reclaimed wastewater can pose potential risks by pharmaceuticals and their metabolites disposed to the sewage system. Those wastewater-derived contaminants are taken up by edible plants and can therefore enter the human food chain. Thus, this study focusses on the potential uptake of pharmaceuticals into lettuce and gives insights into the possible changes in the plant caused by xenobiotics. Lettuce was grown in a hydroponic system under controlled conditions in a phytochamber and treated with Diclofenac (20 µg/L) in an environmentally relevant concentration. Analytical results in addition to transcriptional analysis and enzyme activity measurements are assembled to investigate the deposition of the pharmaceuticals as environmental contaminants in the crop as well as to examine the detoxification mechanisms for these xenobiotics in lettuce. First results of RT-qPCR and enzyme activity measurements suggest an influence on the circadian rhythm of the expression pattern of different plant stress genes triggered by Diclofenac. Transcript levels of oxidative stress-, glutathione S-transferase- but also pathogenesis related-genes therefore were affected. Further scrutinizing for plant metabolites and general plant stress responses are required to evaluate the significance of the reaction for food quality. The results are critically discussed in view of agricultural practice and the safety of food derived from fields irrigated with reclaimed waters.

Correspondence to: yvonne.bigott@helmholtz-muenchen.de

FATE AND UPTAKE OF PHARMACEUTICALS AND THEIR METABOLITES IN THE SOIL/ EARTHWORM/LETTUCE SYSTEM IRRIGATED WITH TREATED WASTEWATER

Sandra Perez, Damià Barceló*, Rayana Manasfi**, Serge Chiron**, Nicola Montemurro**

**Department of Environmental Chemistry, IDAEA-CSIC*
***UMR HydroSciences 5569, HSM, Montpellier University*

Europe is one of the world's largest and most productive supplier of food in which agriculture is the economic sector with the highest water consumption. Therefore, there is an Increasing risk of water scarcity and drought which calls for the use of treated wastewater as an alternative source of water supply. This practice preserves freshwater resources and contributes to nutrient recycling. For centuries wastewater was improperly used in agriculture showing potential risk for the environmental and public health. Today there are concerns remaining about the safety of irrigation with treated wastewater from conventional wastewater treatments plants because it contains various contaminants among them pharmaceuticals and their metabolites. Soil irrigated with treated wastewater will therefore be exposed to these xenobiotics. Besides, soil fauna such as earthworms is sensitive to environmental pollutants contributing direct or indirectly to their degradation. Therefore, in real crops, pharmaceuticals and their metabolites can be retained in the soil, metabolized in earthworms, directly taken up by crops or translocated from soil to plant tissues above the ground.

With the increasing use of wastewater for irrigation, and thus the potential uptake and translocation of pharmaceuticals and their metabolites in crops, concerns about food safety are growing. Unfortunately, as of today information on their behavior in the soil-earthworm-lettuce system is scarce, this is in part due to the lack of simple yet robust methodologies for the analysis of pharmaceuticals and their metabolites in complex matrices such as soil, earthworm and plant tissue.

A promising extraction and clean-up method is the simple and versatile QuEChERS ("quick, easy, cheap, effective, rugged, and safe") methodology which was first reported in 2003 by Anastassiades and coworkers [1]. QuEChERS has been traditionally applied to analyze pesticides in many food matrices (i.e., fruits, vegetables and cereals) but it is now increasingly accepted in food, environmental and clinical applications. Therefore, it is considered an interesting alternative for the extraction of pharmaceuticals and their metabolites from soil, lettuce and earthworms [2, 3], because traditional methods are time-consuming and require large volumes of solvents.

Regarding the detection and quantification of chemically diverse group of pharmaceuticals and their metabolites, high resolution (HR) mass spectrometers such as Orbitrap-mass spectrometry (MS) based instruments and time-of-flight (TOF-MS) systems, are now the most powerful tool for multi-residue determination. LC-HRMS provides robust analysis with high selectivity and sensitivity in even the most complex environmental matrices. Indeed, HR hybrid mass systems, such as TOF spectrometers and quadrupole (quadrupole-TOF or QTOF), have the ability to perform quantitative multi-target analysis detections increasing selectivity with MRMHR or SWATH (Sciex technology).
The aim of our work was to develop extraction methods using QuEChERS and HR-MS based approaches for the determination of the fate of 40 relevant wastewater-derived pollutants, mainly pharmaceuticals and their metabolites in lettuce-soil-earthworm system.

The combination of QuEChERS and LC-HRMS (QToF-MS X550R) worked satisfactory for the determination of pharmaceuticals and their metabolites in the soil-earthworm-lettuce system Neutral pharmaceuticals and metabolites were detected in leaves while acidic compounds were not taken up. Lipophilicity and speciation affected the uptake of pharmaceuticals by plants. However, some basic drugs were detected in higher concentrations in leaves than in soil, probably because they underwent degradation in soil.

The concentration of pharmaceuticals decreased in general when soil contain earthworms, further work will be performed to determine the presence of pharmaceuticals in earthworms.

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Correspondence to: spsqam@idaea.csic.es

FATE OF PHARMACEUTICALS IN SOIL-CROP SYSTEMS IN A MEDITERRANEAN SUBURBAN AGRICULTURAL AREA

Raffaella Meffe, Ana de Santiago Martín*, Gloria Teijón*, Virtudes Martínez Hernández*, Covadonga Alonso Alonso*, María Isabel López Heras*, Leonor Nozal**, Irene de Bustamante****

**IMDEA Water Institute*
***Institute of Applied Chemistry and Biotechnology (CQAB), University of Alcalá*
****University of Alcalá, Department of Geology, Geography and Environment Science*

The unintentional use of water whose wastewater effluents account for a substantial fraction of a river discharge is defined as unplanned water reuse. The health risk associated with the unplanned water reuse in agricultural activities is mainly linked to the introduction of undesirable compounds into the food chain. Results from several studies point out the necessity of providing data on contaminant uptake by crop plants under actual farming conditions. The project FatePharM aims to assess if pharmaceuticals contained in the surface water used for crop irrigation are uptake by the plants or natural attenuation processes prevents the contaminant propagation. For this purpose, we selected a study site that constitutes an excellent scenario to carry out such a research. Indeed, it is an extensive agricultural land (~75 km2) downstream the city of Madrid (Spain) where a flood-based farming is used to cultivate mainly corn crops. The surface water for irrigation belongs to two rivers, that prior to be retained by a dam, flow throughout the urban settlements. During the irrigation period, sampling campaigns were conducted to collect the irrigation water, soils and corn fruit. Beside physicochemical analyses, all samples were analyzed for the detection of a group of 50 pharmaceuticals (analgesics, anti-inflammatories, antibiotics, cardiovascular, bronchodilators, lipid regulators, antidiabetics, antiulcer, hormones, psychiatric drugs and life style compounds) and several transformation products (TPs). The selection has been based on different criteria such as the EU Watch lists, data about national consumption and previous screenings at the watershed level. Several analytical methods based on liquid chromatography coupled to mass spectrometry were developed and validated for the detection of pharmaceuticals and TPs in the three environmental matrices (water, soil and corn fruit).

Results demonstrate the ubiquitous presence of several pharmaceuticals. Some compounds are being transformed, as shown by the appearance of their more persistent TPs whose effects in the environment are still largely unknown. The pharmaceuticals that appear with concentrations higher than 1000 ng L-1 are those that act over the nervous and cardiovascular systems. With the exception of the estrone (E1), hormones were never detected, whereas macrolide antibiotics (erythromycin, clarithromycin and azithromycin), amoxicillin and ciprofloxacin included in the EU Watch list occurs in the irrigation water with concentrations lower than 100 ng L-1. The anti-inflammatory diclofenac, excluded in the more recent EU Watch list, shows higher average concentrations. The pattern of pharmaceutical content in the agricultural soils does not match that of pharmaceutical concentration in the irrigation water indicating that low levels in the water can hide higher contents in the soil. Such a result highlights the importance of tackling the issue of the contaminant transfer to other environmental compartments. Concerning the plant uptake, the pharmaceuticals quantified in the corn fruit are acetaminophen, carbamazepine, ibuprofen and nicotine, but an extended group (e.g. metformin, caffeine, gemfibrozil) were detected with concentrations lower than the methodological detection limits. Due to the described results, the potential dietary uptake of pharmaceuticals by humans was predicted to be low.

Correspondence to: raffaella.meffe@imdea.org

THE WHOLE IS GREATER THAN THE SUM OF ITS PARTS – PERFORMANCE OF PHRAGMITES AND ITS ENDOPHYTES IN PHYTOREMEDIATION OF CARBAMAZEPINE

Peter Schröder, Andres Sauvetre**, Yvonne Bigott*, David Mamdouh Kamel**

**Helmholtz Zentrum Muenchen, German Center for Environmental Health*
***University of Montpellier*

Among alternative methods of waste water treatment, phytoremediation with high biomass plants like reed, cattail, Cyperus or even tree species has led to convincing results. Phytoremediation, as a green technology with low energy and maintenance requirements, can excellently contribute to treatment of effluents with low contamination level. Attempts to improve the efficiency and speed of phytoremediation have been made, using plants with higher hydraulic conductivity, higher biomass, or even with gene manipulation. For a long time, the largest difference between standard water treatment and phytoremediation seemed to be the presence and activity of microbes. Whereas conventional WWTPs highly rely on microbial processes, plants were thought to utilize their own detoxification system.

Recent studies have shown that holobiontic approaches are needed to completely understand processes during phytoremediation. Plants, their rhizospheric bacteria, attached biofilms and plant inhabiting endophytes seem to represent a metabolic continuum that interacts during the remediation process, sometimes at higher efficiency than microbial systems alone. We studied the role of microbes in the remediation of carbamazepine (CBZ), using Phragmites australis, the common reed, as pilot species, and a horseradish hairy root culture (Amoracia rusticana, HR) as an axenic model. HRs are a well suited model to study interactions between endophytic bacteria and plants and allowed us to described CBZ metabolism in the plant holobiont, discerning between the plant (10,11-diol and GSH pathways) and the bacterial part (2,3-diol and acridine pathways).
We demonstrate that microbial degradation of CBZ may be restricted, whereas cooperation between plants and microbes leads to more than one pathway for activation and detoxification of the compound. Integrating metabolic studies reveals that only the cooperation of microbes and plants promotes satisfying detoxification of the parent compound. Proteomic analyses revealed an essential role of the endophytic bacteria R. radiobacter and D. nitroreducens in plant health by enhancing their antioxidative defense systems as well as enzymes involved in CBZ detoxification. In recent experiments, P. australis (and its endophytes) removed 90% of the initial [CBZ] after 9 days without symptoms of stress.

Correspondence to: peter.schroeder@helmholtz-muenchen.de

EXPOSURE AND ACCUMULATION OF DIFFERENT CONTAMINANTS OF EMERGING CONCERN IN RADISH CROPS GROWN UNDER CONTROLLED CONDITIONS

Nicola Montemurro, Rayana Manasfi**, Albert Guerrero*, Serge Chiron**, Damià Barcelò*, Sandra Perez**

**Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA), Spanish Council for Scientific Research (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain*
***UMR HydroSciences 5569, HSM, Montpellier University, 15 Avenue Ch. Flahault, 34093 Montpellier cedex 5, France.*

The constant search for good quality water for agriculture has meant that water resources are under pressure in many regions, representing the main limiting factor for social welfare and economic development of many countries.

Treated wastewater represents a valid alternative to the consumption of good quality water for the irrigation of agricultural crops. However, this practice could contribute to the spread of some organic contaminants in the soil and in the environment. In fact, the presence of contaminants of emerging concern (CECs) is notoriously reported in effluents of wastewater treatment plants (WWTPs), since conventional treatment are not specifically designed for their removal. Their impact is of particular relevance for the disposal and re-use of wastewater in agriculture due to the use and accumulation of CECs in food crops and the consequent spread in the food chain and ecosystems.

The present work aimed to evaluate the effects of exposure and the bioaccumulation of 30 relevant CECs (mainly pharmaceuticals) in radish leaves and roots as well as in soil. Radish plants were grown in pots in a controlled environment and irrigated during the entire growing period (25 days from germination) with spiked tap water containing the target compounds at low and high concentrations (10 and 100 ng mL-1, respectively). The high spiking level was used to facilitate the detection and quantitation of the target compounds and their metabolites in all tissues. Control plants were irrigated only with tap water.

Pharmaceutically active compounds were extracted from crop tissues and soil samples by 3 different modified QuEChERS-based methods whereas the detection was performed using the new SCIEX X500R QTOF-MS, a compact hybrid quadrupole time-of-flight mass spectrometer combining advantages of TOF and QqQ systems with accurate mass. In this study, we investigated the use of MRMHR and MS/MSAll with SWATH® acquisition performed in parallel for the targeted analysis (using reference standards) and non-target screening on a routine basis.

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Correspondence to: nmoqam@cid.csic.es

PHARMACEUTICAL PLANT UPTAKE AND SOIL ACCUMULATION IN CROPS IRRIGATED WITH TREATED WASTEWATER: A FIELD STUDY

Manasfi Rayana,**, Brienza Monica*, Montemurro Nicola**, Perez Sandra**, Chiron Serge**

**UMR HydroSciences 5569, HSM, Montpellier University, 15 Avenue Ch. Flahault, 34093 Montpellier cedex 5, France*
***Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-24, Barcelona (Spain)*

The use of treated wastewater is one of the most relevant alternative for renewable water in many countries. The use of wastewater in agriculture represents a source of nutrients and organic matter to the soils. However, there is concern about the accumulation of organic contaminants in the soil and the uptake in crop plants.

This study was developed to assess environmental and health risks associated with irrigation of lettuce crops with treated domestic wastewater. The test was performed under real crop cultivation conditions where experimental data is currently lacking. This work will contribute to the update of the Regulation of the European Parliament and of the Council on minimum requirements for water reuse (COM/2018/337 final - 2018/0169 (COD)) where the annex II also specifies precise requirements concerning pesticides and pharmaceuticals for water quality and monitoring that are additional to disinfection. For this purpose, lettuce (Lactuca Sativa var. Batavia) and leek (variety Maxim) crops were grown in a greenhouse using drip irrigation and four different water sources (i.e., groundwater, raw wastewater, treated wastewater, spiked wastewater at a 10 µg/L). Fourteen pharmaceutical active compounds (including Diclofenac, Sulfamethoxazole, Carbamazepine, Valsartan, Irbersartan, Ciprofloxacin, Citalopram, Metoprolol, Clarithromycin, Acesulfame K, Sucralose, Benzotriazole, Hydrochlorothiazide, Climbazole) were chosen due to their wide presence in wastewater. Five crop campaigns were carried out between April 2018 and July 2019 with three months stop during the winter season. Soil and leaf samples were analyzed for the presence of the selected pharmaceutical using QuEChERS ("quick, easy, cheap, effective, rugged, and safe") extraction methodology and high resolution mass spectrometry. These 2 years' field experiments have allowed us to collect enough samples in an attempt to draw conclusions on the risks related with crop irrigation with treated domestic wastewater.

Preliminary results revealed the presence of targeted analytes in crop tissues and soil samples irrigated with spiked wastewater at high concentration. Neutral compounds (e.g.., carbamazepine) together with very hydrophilic compounds (e.g., sucralose and acesulfame) showed higher accumulation in leaves than the others compounds. First results have shown that lettuce crops are unable to take up most of target compounds when irrigated at environmental concentration using treated wastewater. However, bioaccumulation in leaves could be correlated with the increase concentration in irrigation water, the need of water and season's temperature.

In spiked experiments, neutral compounds (carbamazepine and climbazole) and anionic hydrophilic compounds are preferentially uptaken by plants. While in non-spiked experiments, bioaccumulation was observed for few compounds. More than half of the target compounds were detected in plant tissue. Carbamazepine were taken up by crops irrigated with all type of wastewater. The detected concentration was 660 µg/g > 7.2 µg/g >3.6µg/g (dry weight) in lettuce irrigated by spiked, raw and treated wastewater, respectively. Sucralose was detected in leaves irrigated using spiked wastewater whereas their concentration in others samples was below the limit of quantification (LOQ).

Correspondence to: rayana.manasfi@hotmail.com

POSTER PRESENTATIONS

MONITORING OF PHARMACEUTICALS AND TRANSFORMATION PRODUCTS IN THE RIVER LIS

Manuela Correia, Paula Paíga*, Luísa Correia-Sá*, Joana Vieira**, Sandra Jorge**, Cristina Delerue-Matos****

**REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto*
**Águas do Centro Litoral, SA, Grupo Águas de Portugal
****REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto*

In the last few decades much attention has been given to the monitoring of pharmaceutical compounds and their transformation products in the aquatic environment. Due to their massive use, pharmaceuticals are continuously discharged from households and animal production facilities and, even if the effluents are treated in wastewater treatment plants (WWTPs), complete removal is only attained for a part of these substances. Hence, concentrations in the range of ng/L and mg/L can be found in treated effluents and consequently in the rivers where these effluents are discharged posing a risk to aquatic ecosystems.

The purpose of this study is to present the results of two monitoring campaigns that took place in February 2018 and May 2019, comprising surface water samples from five different locations along the River Lis (Leiria, Portugal) and 24-h composite samples of the influents and effluents of two WWTPs discharging to the river. A set of 83 pharmaceutical compounds belonging to different therapeutic classes were analysed by solid-phase extraction (SPE) and ultra-high performance liquid chromatography coupled with triple quadrupole mass spectrometry (UHPLC-MS/MS).
When considering all types of samples, a total of 48 compounds were detected mainly from the classes of psychiatrics, antibiotics and non-steroidal anti-inflammatory drugs (NSAIDs). As regards influent samples, 37 pharmaceuticals were detected at least in one of the samples, of which 28 with 100% detection frequency. Carbamazepine, caffeine, diclofenac, hydroxyibuprofen, acetaminophen, carboxyibuprofen, ibuprofen, salicylic acid, azithromycin, and clarithromycin were detected in concentrations in the microg/L range. In effluent samples, 38 compounds were detected and similarly the concentrations of carbamazepine, azithromycin, caffeine, diclofenac, and hydroxyibuprofen were in the microg/L range. Azithromycin and caffeine were the two compounds detected with the highest concentrations both in influent and effluent samples.

A total of 27 pharmaceuticals were detected in the surface water samples. The number of compounds detected was lower upstream and higher downstream the WWTPs. Venlafaxine, caffeine, hydroxyibuprofen, ibuprofen, and salicylic acid showed 100% detection frequency. Carboxyibuprofen and hydroxyibuprofen were detected in the microg/L range.

These new results will be compared with two previous studies regarding monitoring campaigns that took place in 2013 – 2017. Trends in pharmaceutical occurrence, removal efficiencies, mass loadings, and environmental risk will be discussed.

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Correspondence to: mmb@isep.ipp.pt

BIOMARKER RESPONSES IN LUMBRICUS TERRESTRIS EXPOSED TO MODEL DRUGS

Montserrat Solé, Daniel Romano**, Nicola Montemurro***, Sandra Pérez****

**ICM-CSIC*
***CSIC*
****IDAEA-CSIC*

The earthworm Lumbricus terrestris, is a common anecic key species in natural soils used also as bioindicator in soil pollution assessment. Specimens of L. terrestris were exposed in Petri dishes to filter paper embedded with 1 mg/mL to different model compounds for 48 h. The chemicals were: Lamotrigine, Cocaine, Fipronil (as RegentÒ800WG) and the organophosphorus pesticide bis-4-nitrophenyl phosphate (BNPP). At the end of this period, earthworms were immediately frozen in liquid N2 and their tissues, homogenized by cryogrinding, targeted to determine chemical exposure and metabolite formation as well as to biomarker determinations. The biomarkers analyzed were the activities of the enzymes Acetylcholinesterase (AChE), Glutathione-S-transferase (GST) and Carboxylesterase (CES) using different substrates. The results obtained revealed differences in enzymatic activity among substrates, being CE activities with the substrates 4-nitrophenyl butyrate (4-NPB) and 1-naphthyl butyrate (1-NB) the most responsive to cocaine and BNPP. These results for BNPP, corroborate data obtained after in vitro exposure. This study highlights the utility of long chain butyrate esters in CE measures in invertebrate and the agreement between in vivo and in vitro responses in L. terrestris. Chemical analysis and metabolite formation should confirm the extent of the exposure and other range of concentrations should be used to assess any dose-response effects.

Correspondence to: msole@icm.csic.es

PHARMACUTICALS IN THE ENVIRONMENT – PREDICTING ENVIRONMENTAL FATE, AND ENVIRONMENTAL AND FOOD SAFETY

Trine Eggen, Augustine Arukwe**, Eldbjørg S. Heimstad***, Vladimir Nikiforov***, Ingebrigt Sylte****, Stefan Trapp*****, Christian Vogelsang******

**Norwegian Institute for Bioeconomy (NIBIO), Ås, Norway*
***Norwegian University of Science & Technology (NTNU) Dep. of Biology, Trondheim, Norway*
****Norwegian Institute for Air Research, (NILU), Tromsø, Norway*
*****UiT The Arctic University of Norway, Dep. of Medical Biology, Faculty of Health Sciences, Tromsø, Norway*
******Denmark Technical University (DTU) Dep. Environmental Engineering, Denmark*
*******Norwegian Institute for Water Research (NIVA)*

Pharmaceutical residues in the environment (e.g. wastewater sewage sludge, surface water, drinking water, manure), their fate and adverse effects to non-target organisms has gained much attention, particularly exposure and effects towards aquatic organisms due to high loading in waste water effluents (1-3). Even though a great number of pharmaceuticals are not necessarily persistent by definition, they are characterized as pseudo-persistent since the discharge into the environment is constant.

The majority of pharmaceuticals is water soluble, and many are not completely removed by conventional treatment systems (4). Positively charged pharmaceuticals are attractive to negatively charged organic matter, however, their transfer to sewage sludge has been overlooked/ underestimated in previous risk assessment related to application of sewage sludge to soil for food cultivation due to assumed low transfer of water soluble organic compounds to sludge (5). For instance, the dicationic – and highly water soluble - metformin has been found in 8 mg/kg dry weight in sludge (Færøyene) and 750 ng/L in recipient water (3).

Recently, accumulation of the anti-diabetic pharmaceutical metformin in oily rape seeds (Brassica napus and Brassica rapa) was reported, 15-70 times higher than in cereals (6). The hypothesis that metformin, a small molecule with structural similarity to natural plant compounds e.g. guanidine and arginine, is "mistaken" as natural plant organic-N compound and translocated via transporters into seeds was put forward (6,7). The mechanisms for metformin uptake into plant cells are not known. However, from comparison with other eukaryotes, organic cation transporters (OCTs) can be considered as putative candidates for being important in uptake and accumulation of metformin. In mammals, metformin is actively transported into cells by OCT1, OCT2 and OCT3 (8), and in Arabidopsis, OCTs are expressed in roots, leaves, flowers and young siliques (9). The effects of metformin on the expression of important enzymes involved in steroidogenesis (cyp11A and 3b hydroxysteroid dehydrogenase:3b-hsd) and the cholesterol transporter steroidodogenic acute regulatory (StAR) protein, and CYP17 activity in mammalian system has been reported (10). Recently, it was demonstrated that exposure of fish to environmentally relevant concentrations produced endocrine disrupting effects (11).

Many pharmaceuticals function by interfering with human/animal target proteins (receptors, transporters, ion-channels and enzymes). When taken up by non-target organisms, pharmaceutical may interfere with proteins structurally related to the human/animal drug targets and result in a harmful outcome.

There is a huge knowledge gap regarding pharmaceuticals and their fate in different treatment processes (e.g. waste water treatment plants, anaerobic digestion processes, composting) and environment, and their exposure and effects on non-target organisms. What knowledge do we need to better predict their fate and risk? How much can we predict with use of physicochemical properties? Which limitations and challenges have existing models and approaches? Can structure-similar pharmaceuticals be taken up actively by non-target organisms – and if so – will this results in a higher risk of adverse effects?

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Correspondence to: trine.eggen@nibio.no

ACCUMULATION OF PHARMACEUTICALS RESIDUES IN FISH TISSUES FROM POLLUTED RIVERS

Juan Manuel Peña-Herrera, Nicola Montemurro*, Damia Barceló*, Sandra Pérez**

**Water and Soil Quality Research Group, Dep. of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain*

Pharmaceuticals (PhACs) have been measured in municipal wastewater effluents and in receiving waters for a long time. However, the number of PhACs analyzed to date is far smaller than the number of PhACs already detected in waters because. these substances are more polar and assumed to be less bioaccumulative and/or there are few analytical methods that allowed their rapid and sensitive determination in complex biological matrices such as fish matrices.
In the present work, we have developed an analytical method for extraction of PhACs from biota samples based on ultrasound extraction, including d-SPE clean-up with zirconium salts. A method validation has been carried out (recovery, precision, linearity, matrix effects, limit of detection and limit of quantification). Analytical detection and quantification has been carried out using a QToF-MS system supported by the SWATH (Sequential Windowed Acquisition of All THeoretical MS) technology, based on a data-independent acquisition (DIA) MS strategy. This technology has been applied to collect all MS2, where every detectable ion from the sample is fragmented. The MS/MS SWATH spectra has been used to confirm target and suspected compounds, matching SWATH data against pre-assembled MS/MS spectral libraries.

We analyzed 32 samples of nine different species of homogenized fish from four european rivers. We determined positive findings of bezafibrate, caffeine, carbamazepine, clarithromycin, diltiazem, furazolidone, ketoprofen, sulfapyridine, trimethoprim, and verapamil in the range from BLQ to 70 ng of pharmaceutical/g of fish. Additionally, using a suspect screening list of more than 250 PhACs, we detected positive findings of benzoylecgonine, cocaine, nicotine, and ofloxacine.

Using the validated method, we analyzed also different tissues corresponding to four different fish species collected from the Llobregat river (Spain) for study of the distribution of PhACs in fish tissues: skin, gills, blood, muscle, liver, kidney, brain, bile, hearth, and pancreas. Relevant results about the distribution of PhACs in fish tissues will be presented.

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Correspondence to: juan.pena@idaea.csic.es

PHARMACEUTICALS IN ALGERIAN WASTEWATER SLUDGE: THE CASE OF THE WASTEWATER TREATMENT PLANT IN GUELMA'S CITY

Benouareth Djamel Eddine, Khallef Messaouda*, Bounar Choayb*, Montemurro Nicola**, Pérez Sandra**, Barceló Damià***

**Biology department, Faculty of life and natural sciences and earth and universe sciences, university 8 May 1945 BP 401 Guelma 24000; Algeria.*
***Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*

Water scarcity is a growing concern for countries surrounding the Mediterranean Sea characterized by predominantly arid soils with few nutrients. The reuse of wastewater as well as sewage sludge represent an important strategy to reduce the demand for fresh water and the consumption of chemical fertilizers. However, pharmaceutical products and other organic compounds that are not completely removed during conventional treatments could potentially affect the environment and human health. A modified QuEChERS ("quick, easy, cheap, effective, rugged, and safe") extraction methodology was employed to analyzed the presence of the selected pharmaceuticals in the wastewater sludge samples at three different maturation stages (liquid sludge after treatment, semi-solid sludge from the drying beds and stored solid sludge). The samples were collected at the activated sludge wastewater treatment plant (WWTP) from the city of Guelma located at 36"28"50.3"N and 7"26"20.3"E which collects sewage of different origin (hospital, industrial, and domestic) in quantities corresponding to 200,000 equivalent people (EP).

The analytical determination was performed by means of the new quadrupole time-of-flight MS system SCIEX X500R QTOF. High resolution data were acquired using SWATH acquisition technology for a confident identification and quantitation. Hence, 28 out 37 target compounds were successfully identified and quantified. The detected pharmaceuticals belong mainly to the following classes: 11 substances for psychiatric medications, 3 analgesics and anti-inflammatory, 3 antihypertensives, 2 products processing, 2 β-blockers, 2 antibiotics, 1 corticosteroid, 1 lipid regulators, 1 stimulant, 1 histamine antagonist and 1 other compound. Dexamethasone a corticosteroid was the most abundant compound of pharmaceutical compounds in different sludge states, triclocarban is the most abundant antibiotic mainly in liquid and semi-solid sludge, Valsartan is the most abundant antihypertensive in its class products found in the wastewater sludge at its various states as well. As an analgesic and anti-inflammatory diclofenac is the most abundant in liquid and semi-solid sludge followed by acetaminophen but absent in solid sludge while the anti-inflammatory ketoprofen is present in solid sludge in more important quantities than liquid and semi-solid sludge. In addition, 1,2,3-Benzotriazole, which is a commonly used product as an anti-corrosive additive in industrial cooling liquids as well as in hydraulic fluids and dishwasher detergents, has been the most abundant compound in liquid sludge from the treatment plant station.

Correspondence to: benouareth_dje@yahoo.fr

MUTAGENIC AND GENOTOXIC EFFECTS OF GUELMA'S URBAN WASTEWATER, ALGERIA

Benouareth Djamel Eddine, Tabet Mouna*, Abda Ahlem*, Khellaf Messaouda**

**Biology department, Faculty of life and natural sciences and earth and universe sciences, university 8 May 1945 BP 401 Guelma 24000; Algeria.*

Assessment of water pollution and its effect upon river biotic communities and human health is indispensable to develop control and management strategies.

In this study, the mutagenicity and genotoxicity of urban wastewater of the city of Guelma in Algeria were examined between April 2012 and April 2013. For this, two biological tests, namely Ames and chromosomal aberrations (CA) test in Allium cepa root tips were employed on the samples collected from five different sampling stages (S1–S5). In Ames test, two strains of Salmonella typhimurium TA98 and TA100 with or without metabolic activation (S9-mix) were used. All water samples were found to be mutagenic to S. typhimurium TA98 with or without S9-mix. A significant decrease in mitotic index (MI) was observed with a decrease in the percentage of cells in the prophase and an increase in the telophase. Main aberrations observed were anaphase bridges, disturbed anaphase-telophase cells, vagrants and stickiness in anaphase-telophase cells. All treatments of wastewater in April 2012, at S5 in July 2012, at S1 and S5 in November 2012, at S5 in February 2013, and at S1 in April 2013 induced CA when compared to the negative control. Some physicochemical parameters and heavy metals (Cd, Pb, and Cu) were also recorded in the samples examined.

Correspondence to: benouareth_dje@yahoo.fr

PERSPECTIVE BIOCATALYSTS FOR NEUTRALIZATION AND DETOXIFICATION OF PHARMACEUTICAL POLLUTANTS

Elena Tyumina, Grigorii Bazhutin*, Aleksandr Selyaninov**, Elena Vikhareva***, Irina Ivshina**

**Perm Federal Research Center of the Ural Branch of the Russian Academy of Sciences; Perm State University, Perm, Russia*
***Perm National Research Polytechnic University, Perm, Russia*
****Perm State Pharmaceutical Academy, Perm, Russia*

The kinetics and mechanisms of metabolization of pharmaceutical pollutants using actinobacteria from the Regional Specialized Collection of Alkanotrophic Microorganisms (acronym IEGM, WDCM # 768, www.iegmcol.ru) were studied by the examples of drotaverine (isoquinoline derivative), diclofenac (phenylacetic acid derivative), and paracetamol (p-aminophenol derivative). Changes in the morphometric parameters and properties of the cell surface of actinobacteria exposed to pharmaceutical pollutants were investigated using a combined atomic force and confocal laser scanning microscope; physiology of key bio-oxidizers was studied by high-resolution respirometry; functional genes involved in biodegradation of these ecotoxicants were studied by a comparative bioinformatic analysis of the whole genomes of Rhodococococcus erythropolis IEGM 767, R. ruber IEGM 231; the pathways of biodegradation of the pharmaceutical pollutants were elucidated and new metabolites with pronounced bioactivity were discovered; and biocatalysts with high functional stability characterized by repeated (up to 5 consecutive cycles) use and storage for 6–8 months were developed. The developed biocatalysts are promising for use in pharmaceutical wastewater treatment, as well as for the disposal of pharmaceutical waste.

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Correspondence to: tyumina@psu.ru

LOW-COST BIOPURIFICATION TECHNOLOGY AS ALTERNATIVE FOR TETRACYCLINE-CONTAMINATED WATER TREATMENT

Marcela Levio, Gabriela Briceño*, Barbara Leiva*, Andres Huenchupan*, Francisco Mejias*, Sebastian Lopez*, Maria Cristina Diez**

**University of La Frontera*

There is a worldwide growing concern regarding the presence of antibiotic residues in different environmental compartments, including soils, water and air, which can affect negatively to humans, animals, and environment. Tetracycline (TC) is one of the most widely used antibiotics in veterinary and human medicine and the presence in the environment it is growing. Therefore, considering the complexity of this molecule, new and efficient alternatives to removal TC are necessary. In this work, removal of TC from an aquous solution using a biopurification system packed with an organic biomixture composed by soil, peat and wheat straw in volumetric proportion of 1:1:2. was studied. Batch experiments were carried out on biomixture at natural pH (6.0) and TC initial concentration of 100 µmol·L-1. Adsorption curves fit well to the Freundlich (R2 = 0.99) and Langmuir (R2 = 0.90) equation. For Freundlich model, Kf was of 21,285 Ln· µmol1−n·kg-1 and n was 1. For Langmuir model, KL was of 0,2 L µmol-1 and qm of 25,000 µmol kg−1. Besides, the adsorption capacity (qa) were ranged from 101 to 22,285 µmol kg−1. TC retention on biomixture was high, with adsorption values between 98.6% and 99.8% and desorption values lower than 15%. The results indicate that properties of the organic biomixture and their components as soil (37% sand, 34% silt, 28% clay, 7% organic carbon, pH 5.4), commercial peat (36% organic carbon), and wheat straw (34% organic carbon) increase the effective cation exchange capacity, and affecting TC adsorption and desorption. Therefore, this organic biomixture can be used in a biopurification system as an efficient alternative for TC removal from contaminated wastewater.

Correspondence to: marcela.levio@ufrontera.cl

PHYTOTOXICITY OF SEWAGE SLUDGES AND TETRACYCLINE EXTRACT IN GERMINATION OF *LOLIUM PERENNE, TRIFOLIUM SP. AND TITRICUM AESTIVUM*

Maria Cristina Diez, Marcela Levio*, Gladys Vidal**, Gabriela Briceño**

**University of La Frontera*
***University of Concepción*

The sewage sludge has been used as soil amendment by promoting physical and chemical processes in soils. However, they can contain a high percentage of pharmaceuticals, between them tetracycline (TC) which are poorly degraded even in biological wastewater treatment plants and, therefore, accumulated in sewage sludge (reported between 0.09 to 16.79 mg kg-1). The bioassays of phytotoxicity (germination, root elongation and enzymatic activities) are commonly used to evaluate the toxic effect of substances in plants. Some enzymes (amylase and protease) are synthesized during seed germination to mobilize stored food until of making photosynthesis. Then, contaminants can cause inhibition of amylase activity suppressing the mobilization of soluble carbohydrates essential for growth and development of plants. Germination should be above 80% to consider that no negative effects on seedlings.

We evaluated the phytotoxicity effect on Lolium perenne, Trifolium sp. and Titricum aestivum seeds germination of three sewage sludges added to two soils (Andisol, serie Pucon and Ultisol, serie Araucano) at doses of 30 to 120 Mg ha-1. Furthermore, seeds germination and, alpha-amylase activity and reducing sugars were evaluated during 8 days in the soils contaminated with TC extract at doses of 0.05 to 2 mg kg-1.

The sewage sludges (A, B and C) had TC concentration of 1.23, 3.12 and 4.46 mg kg-1, respectively. The soils had acidic pH, and the addition of sludge improved their quality, increasing pH (to neutral), organic matter, available N, P and K, between others) as sludge concentration increased from 30 to 120 Mg ha-1. However, the application of sludge greater than 60 Mg ha-1showed phytotoxicity in L. perenne and Trifolium sp. but not in T. aestivum, where there was only phytotoxicity in Araucano soil in doses greater than 90 Mg ha-1. Respect to the soils contaminated with TC extract at doses of 0.05 to 2 mg kg-1, phytotoxicity on L. perenne seeds was at TC concentration above of 0.1 mg kg-1, while for the seeds of Trifolium sp. and T. aestivum the phytotoxic effect was in TC concentration greater than 0.5 and 1.0, respectively. Alpha-amylase activity and reducing sugars were strongly affected during L. perenne and Trifolium sp. germination by the increasing TC doses, while these activities were no affected during T. aestivum germination and, no significant differences were found between Araucano and Pucon soils. In conclusion, the TC content did not affect T. aestivum germination; contrarily, TC content showed phytotoxicity during germination of L. perenne and Trifolium sp.

Correspondence to: cristina.diez@ufrontera.cl

DEVELOPMENTAL AND REPRODUCTIVE RESPONSES OF TWO BIO-INDICATOR FRESHWATER SPECIES TO PHARMACEUTICAL DRUG EXPOSURE: SETTING THE STAGE FOR EVALUATING AQUATIC MICRO-POLLUTANT ENVIRONMENTAL IMPACT.

Florence GERET, Alice Saunier*, Elsa Bonnafe*, Morgane Lebreton*, Jean-Michel Malgouyres*, Laurence Salomé***

**Institut National Universitaire Champollion*
***University of Toulouse*

Face with population growth and climate change, the reduction of our accessible water resources and their quality is a considerable challenge. Despite undeniable progress over recent decades, a large number of micro-pollutants (including drugs) are ubiquitous in water at concentrations below mg/L and may constitute a risk for water quality and aquatic environments. There are overwhelming evidences that aquatic environment is continuously the discharge of wastewater effluents where pharmaceuticals are increasingly found due to the non-specific methods of degradation at sewage treatment plant level. In this context, it is of prime interest to evaluate the eco-toxicological impact of drugs on the aquatic ecosystems. For this purpose, we analysed the presence of various drugs within representative waters of both treatment effluents of psychiatric hospital (Montpon-Menestrol, Dordogne, France) and urban wastewaters (Albi, Tarn, France). Two points were sampled per site, at the direct station exit and in the receiving waterway rejection. Based on the quantification of these four natural wastewaters, an anti-epileptic drug (carbamazepine) and two other major pharmaceuticals were chosen. Toxic effects of each drug and their synergic effects in association with carbamazepine were tested at three different concentrations on two non-models species commonly found in French rivers: the flatworm Schmidtea polychroa and the freshwater gastropod Radix balthica. Toxicological impacts of these pharmaceuticals have been performed on exposed adult flatworms (fertility and fecundity) and embryos offspring snails (malformation and delayed hatching). Previous studies conducted in the lab on the psychotropic drug carbamazepine have already highlighted a developmental delay in R. balthica (> 8 days). Contrastingly, while the cocoon production by planarian (fecundity) significantly decreased, the number of juveniles per cocoons (fertility) remained stable. This present work will help further investigations and provide a better understanding to the toxic effect of pharmaceuticals on aquatic environment.

Correspondence to: florence.geret@univ-jfc.fr

EFFECTS OF AN ANXIOLYTIC DRUG ON EMBRYOGENESIS, GROWTH AND LOCOMOTION OF A NON-MODEL FRESHWATER GASTROPOD

Florence GERET, Morgane Lebreton*, Elsa Bonnafe*, Jean-Michel Malgouyres**

**Institut National Universitaire Champollion*

French psychotropic drugs consumption is one of the most important in Europe. These molecules are a significant part of emerging contaminants in aquatic ecosystems. Indeed, derived from both hospital and domestic effluents, some psychotropic drugs are barely eliminated by wastewater treatment plants and can be found at significant concentrations in freshwater. Among these contaminants, the oxazepam, which belongs to the benzodiazepine family molecule, acts as an inhibitor of the central nervous system by interacting with the GABA receptors. Despite its prevalence in the freshwater, the toxicity of oxazepam on aquatic organisms remains little investigated. The aim of our study is to assess the toxicity of oxazepam at environmental concentrations on the European freshwater gastropod, Radix balthica. Therefore we have conducted our toxicity assessment on the first stages of development of R. balthica and on the juveniles stage, which are known to be the most sensitive stage at the environmental contamination. The embryo rotation rate has been measured during the trochophore stage (3 days post fertilization), the heart rate has been observed at the hippo stage (6 dpf) and at the post hatching stage (8-15 dpf), developmental abnormalities, developmental delay and hatching rate have been investigated. Furthermore, juveniles (two months old) have been exposed to oxazepam during 4 weeks and the shell growth and the locomotion have been monitored. This preliminary study tends to show that embryonic rotations decreased with oxazepam exposure while embryos exposed to the highest dose hatch earlier than the control. Finally, juveniles exposed to environmental concentration of oxazepam showed a shell which grown faster and a displacement speed quicker than the control. These results remain to be linked with transcriptomic level.

Correspondence to: florence.geret@univ-jfc.fr

CONCENTRATIONS AND RISK ASSESSMENT OF SELECTED ANTIBIOTICS RESIDUES IN MARINE SEDIMENTS FROM THE SOUTHERN BALTIC SEA.

Grzegorz Siedlewicz, Lilianna Sharma*, Marta Borecka**, Anna Białk-Bielińska**, Piotr Stepnowski**, Ksenia Pazdro**

**Institute of Oceanology of the Polish Academy of Sciences*
***University of Gdańsk, Faculty of Chemistry*

In recent years, environmental scientists have paid increased attention to the occurrence, fate, transport and effects on organisms of pharmaceutical residues. Among these chemicals, special attention should be paid to antibiotics because of their bioactive properties. The study contributed to filling a knowledge gap about levels of antibiotic residues in Baltic Sea sediments and characterising their ecological risk. Concentrations of 14 antibiotic compounds from sulphonamides, tetracyclines and quinolones groups were measured in sediment samples collected in 2011-2013 from the southern Baltic Sea (Polish coastal zone). Antibiotics were determined at concentration levels of a few to hundreds of ng·g-1 d.w. The most frequently detected compounds were sulfamethoxazole, trimethoprim, oxytetracycline in sediments and sulfamethoxazole and trimethoprim in near-bottom waters. The occurrence of the identified antibiotics was characterised by high spatial and temporal variability, which can be attributed to their use in the surrounding region and environmental behaviours. The highest concentrations were measured in the Szczecin Lagoon and the Gulf of Gdańsk. Risk assessment analyses revealed a potentially high risk of sulfamethoxazole, trimethoprim and tetracyclines in sediments. The highest risk quotient values were assessed for sulfamethoxazole and oxytetracycline in Gulf of Gdańsk and Pomeranian Bay. Both chemical and risk assessment analyses show that the coastal area of the southern Baltic Sea is highly exposed to antibiotic residues.

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Correspondence to: gsiedlewicz@iopan.pl

TRANSFORMATION PRODUCTS OF VETERINARY DRUGS IN SWINE MANURE DURING PHOTOBIOTREATMENTS BASED ON PHOTOTROPHIC MICROORGANISMS

Pedro Antonio García-Encina, Rebeca López Serna*, Dimas García*, Juan José Jiménez*, Frank Menger**, Foon Yin Lai**, Oksana Golovko**, Pablo Gago-Ferrero***, Lutz Ahrens**, Karin Wiberg**, Raúl Muñoz**

**Institute of Sustainable Processes (ISP)*
***Swedish University of Agricultural Sciences (SLU)*
****Catalan Institute for Water Research (ICRA)*

This work identified transformation products (TPs) from 16 antibiotics, 1 anti-parasitic, 1 analgesic and 1 hormone, present in spiked real piggery wastewater (PWW) before and after two different treatments in two open photobioreactors operated continuously with a consortium of microalgae-bacteria and purple photosynthetic bacteria. For this purpose, suspect and non-target strategies based on liquid chromatography quadrupole-time-of-flight mass spectrometry (LC-QTOF-MS) were used. The application of quantitative structure-retention relationship (QSRR) prediction models, in addition to a comprehensive evaluation of the obtained MS/MS spectra, provided valuable information to support the identifications. The confirmation of the TPs was carried out with the corresponding reference standards, when these were commercially available. Alternatively, probable structures of the TPs based on diagnostic evidence were proposed. To the best of our knowledge, some of the identified TPs have never been reported before. A transformation pathway for their biotransformation has been proposed. The presence of the identified TPs was assessed in real PWW samples through retrospective analysis. Ultimately, the potential ecotoxicological risk posed by these nineteen veterinary drugs and their TPs was evaluated by means of risk quotients.

Correspondence to: rebeca.lopezserna@iq.uva.es

CONTROL OF CONTAMINANTS OF EMERGING CONCERN (CECS) FROM MUNICIPAL WASTEWATER VIA ELECTRICALLY ENHANCED MEMBRANE BIOREACTOR

Prof. Shadi Wajih Hasan, Laura Borea**, Tiziano Zarra**, Vincenzo Belgiorno**, Vincenzo Naddeo***

**Khalifa University of Science and Technology*
***University of Salerno*

Contaminants of emerging concern (CECs), including pharmaceuticals and personal care products (PPCPs), are increasingly being detected at low levels in environmental water. Wastewater treatment plants (WWTPs) are considered one of the main hotspot of CECs in the environment. There is a huge concern that these compounds may have an impact on the ecosystems and human health. Particularly the discharge of pharmaceutical pollutants such as antibiotics, or hormones (e.g. estradiol) into the environment can pose huge risks. For example, it may cause further biological effects and potential health issues. These include hormonal or endocrine disruption in animals (e.g. fish and marine life), and creating antibiotic resistance in environmental or animal bacteria/fungi when treated effluents from WWTPs are being discharged into the marine environment and/or used for irrigation of the natural environment, food, animal fodder, etc. Recently, the removal of emerging contaminants has been receiving a global attention through which innovative solutions are being proposed. In this study, an innovative wastewater treatment system combining electrochemical processes with membrane bioreactor (MBR) (known as eMBR thereafter) was designed, operated and tested for the removal of emerging contaminants from municipal wastewater. A 13 L continuous flow lab-scale eMBR system was used. Mixed liquor suspended solids (MLSS) sludge was brought from the WWTP in Salerno (Italy) and acclimatized for over a month. Electrodes made of aluminum and stainless steel were used as anode and cathode, respectively. They were connected to a low DC voltage power supply and were 6 cm spaced apart. The reactor operated in four intervals through which the first interval mimicked the performance of a conventional MBR, whereas the performance of the eMBR system from the second to the fourth intervals was investigated. Different current density ranging between 0.3 and 1.15 mA/cm2 was applied in the eMBR system. Hydraulic retention time (HRT) of 19 h was used while sludge retention time (SRT) was kept long. Air diffusers were installed in the reactor to 1) provide sufficient dissolved oxygen necessary for microbial growth, 2) enhance mixing throughout the reactor, and 3) scour the membrane. A ZeeWeed-1 (ZW-1) submerged hollow fiber ultrafiltration (UF) module (SUEZ WTS Italy S.r.l.), having a pore size of 0.04 µm and an effective surface area of 0.047 m2, was used. The eMBR system was continuously fed with synthetic wastewater having amoxicillin (AMX), diclofenac (DCF) and carbamazepine (CBZ) purchased from Sigma-Aldrich. AMX, DCF and CBZ concentrations were analyzed using 4000Q Trap LC–MS/MS System (Applied Biosystems, Foster City, USA). Results showed that the eMBR system has a great potential for the degradation of pharmaceutical pollutants reporting 76.5±9.5%, 79.1±8.5%, and 77.2±8.3% of AMX, DCF, and CBZ; respectively.

Correspondence to: shadi.hasan@ku.ac.ae

EFFECTS OF ANTIBIOTICS ON GROWTH AND PHOTOSYSTEM II PERFORMANCE IN MARINE MICROORGANISMS.

Lilianna Sharma, Grzegorz Siedlewicz*, Adam Żak**, Alicja Kosakowska*, Ksenia Pazdro**

**Institute of Oceanology, Polish Academy of Sciences*
***University of Gdańsk*

The study aimed to evaluate the influence of a wide range of oxytetracycline and sulfamethoxazole concentrations, with particular attention to the low levels of the antibiotics, on cyanobacteria Microcystis aeruginosa and Nodularia spumigena, diatom Phaeodactylum tricornutum and the model green algae Chlorella vulgaris by conducting prolonged toxicity tests for 10 days. Standard measurements (cell number, optical density, chlorophyll a concentration) were combined with OJIP fluorescence transitions measurements. The obtained results go beyond previous reports showing that oxytetracycline present at concentration levels lower than those applied in ecotoxicity tests and described in the literature adversely affects tested microorganisms. It was found to decrease photosystem II efficiency and disrupt the photosynthesis process. A careful analysis of OJIP measurements results allowed a better understanding of the mode of action of both oxytetracycline and sulfamethoxazole concerning non-target photoautotrophic organisms like cyanobacteria and microalgae. In conclusion, it would appear that the use of standard chronic toxicity tests (72h) does not allow to accurately and reliably assess the chronic impact of bioactive compounds including drugs and their metabolites in water organisms.

Correspondence to: lsharma@iopan.pl

IDENTIFICATION AND CHARACTERIZATION OF METHOTREXATE PHOTODEGRADATION PRODUCTS

Anaïs Espinosa, Sylvie Nélieu*, Pierre Benoit*, Raphaël Labruère**, Edwige Kouadio**

**INRA*
***ICMMO*

Antineoplastic agents are of particular environmental concern due to their highly potent mechanism of action (cytotoxicity, genotoxicity, mutagenicity and teratogenicity). They are detected in surface waters at range of ng.L-1, some of them could be detected even in drinking water. Methotrexate (MTX) is an antineoplastic folate analog and one of the most widely prescribed for cancer as well as psoriasis or rheumatoid arthritis. MTX is mostly excreted unchanged and its main metabolite, the 7-hydroxymethotrexate, is on priority list for environmental risk assessment due to its persistence and toxicity. However, less information is available on other transformation products (TPs) potentially formed in the environment. Our study aims at identifying these other TPs in order to determine their occurrence, fate and potential impact in environment.

In the presented study, we compare the kinetics and transformation pathways during MTX photodegradation under two different conditions, one representative of environmental conditions encountered in surface water (300-450 nm lamps, pyrex reactor) and another one at 254 nm (quartz reactor) representative of drinking water treatment. The MTX photodegradation and TPs evolution were monitored by HPLC-UV. These studies complemented by identification using UHPLC-ESI-MS/MS (positive and negative modes) led to characterize a number of photoproducts formed at 300-450 and/or 254 nm and hypothesize the transformation pathways.

Correspondence to: anais.espinosa@inra.fr

ANTIBIOTIC RESIDUES AND ANTIBIORESISTANCE IN THE ENVIRONMENT: IS THERE A LINK IN THE CONTEXT OF FRENCH CATTLE FARMING?

Sylvie Nelieu, Marjolaine Bourdat-Deschamps*, Anais Espinosa*, Armelle Crouzet**, Nathalie Bernet*, Valentin Serre*, Sylvie Nazaret***

**INRA*
***CNRS*

The dissemination in the environment of antibiotic residues, antibiotic-resistant bacteria and/or antibiotic resistance genes and mobile genetic elements is nowadays of major concern. The combined presence of these chemical and biological contaminants in the environment has been demonstrated in a context of cattle breeding in some countries where antibiotics are used in a massive way (eg China, United States, Brazil) but never documented in contexts where the treatments are significantly lower, as in France.

The objective of this study was to search a possible link, in a context where antibiotic usage was low, between: (i) the antibiotic residues in agricultural soils subjected to organic waste products (OWP) inputs of bovine origin and (ii) the prevalence dynamics of phenotypes and antibiotic resistance genes within bacterial communities.

We targeted several experimental sites and farms with different history of OWP (manure and slurry) fertilizer amendments, both in terms of frequency and abundance of amendments but also pre-treatments undergone by the amendments (eg composting). The soil and OWP samples were collected just before and one month after spreading. Chemical analyses were performed by ultrasonic-assisted extraction, QuEChERS purification and online solid-phase extraction coupled to ultra-high performance liquid chromatography with tandem mass spectrometry. Antibioresistance was determined by relative and absolute quantitative PCR (eg qPCR and digital droplet PCR) performed on bacterial DNA extracts from soils and OWP.

Very few antibiotics were present, both in the soils and in the OWPs themselves. Although detectable or even quantifiable levels of antibiotics belonging to the families of fluoroquinolones, tetracyclines, sulfonamides and / or macrolides were regularly present in the OWP, it was exceptional that these compounds were evidenced in the soil one month after application. Despite low levels of antibiotic residues, sulfonamide and tetracycline resistance genes and integrons have been consistently observed. Their presence in soils likely resulted from a history rather than a one-time application. But their frequency and level remained well below what was observed in situations of massive use of antibiotics: French agricultural practices for recycling of cattle waste seem sustainable in terms of antimicrobial resistance.

Correspondence to: sylvie.nelieu@inra.fr

ANTIBIOTICS AND ANTIBIOTIC RESISTANCE GENES IN NATURAL SPRINGS AS TRACERS OF AGRICULTURAL CONTAMINATION

Meritxell Gros, Josep Mas-Pla**, Alexandre Sànchez-Melció*, Mira Celic*, Anna Menció**, José Luis Balcázar*, Carles Borrego***, Mira Petrovic*,****

**Catalan Institute for Water Research (ICRA), University of Girona (UdG)*
***GAiA Research Group-Geocamb. University of Girona (UdG)*
**** Catalan Institution for Research and Advanced Studies (ICREA)*

In agricultural areas, chemical and microbiological groundwater quality might be seriously compromised by the excessive use of livestock waste as organic fertilizer. The quantity of certain antimicrobials used in animal husbandry can be several-fold greater than the amounts used in human medicine. Thus, livestock waste can be an important reservoir of antibiotic residues and bacteria carrying antibiotic resistance genes (ARGs). Natural springs stand as undisturbed locations where flow paths outcrop and, consequently, they can provide information about the transport of these emerging contaminants, according to the nearby land use. Natural springs are therefore surrogate sampling points that characterize the pollution levels that will otherwise reach the water table and the whole groundwater system.

In this study, eleven natural springs, which represent four distinct hydrogeological settings, were sampled in three distinct campaigns. Sampling sites were selected based on their nitrate concentrations, which were attributed to livestock waste fertilization. Spring water was collected and analysed for hydro-chemical, isotopic, and antibiotic concentrations. ARGs conferring resistance to the detected antibiotic classes were also monitored as a response of the groundwater microbiome to antibiotics and to measure their persistence effects on groundwater quality.

All sampled natural springs presented agricultural influence as pointed out by nitrate concentrations usually larger than 100 mg L-1. Identified antibiotics were tetracycline, doxycycline, chlortetracycline, oxytetracycline, sulfamethoxazole and sulfamethazine, at concentrations ranging from ng L-1 to low µg L-1, while other analysed antibiotics (up to 25) remained non-detected. For ARGs, sul1, tetW and intI1, a proxy for anthropogenic pollution, were detected in most of the samples. Nevertheless, gene concentrations never exceeded 10E4 gene copies/L. Seasonal sampling pointed out a large variability of occurrences and concentrations of antibiotics. This variability is thus interpreted based on the local hydrogeological dynamic and sets some clues about the fate of this pharmaceutical residues towards deeper zones of the aquifer system. Moreover, our results reveal the difficulties to assess spring water quality for public uses, as well as the implementation of efficient monitoring strategies. [Funded by project H2020-MSCA-IF RESOURCE (grant agreement ID: 750104) and PACE-IMPACT, FEDER-MCIU-AEI/CGL2017-87216-C4-4-R].

Correspondence to: mgros@icra.cat

RISK ASSESSMENT BASED PRIORITIZATION OF PHARMACEUTICALS OF MAJOR CONCERN IN THE EBRO DELTA (SPAIN)

Mira Čelić*, *Meritxell Gros**, *Paola Verlicchi***, *Mira Petrović**,***

**Catalan Institute for Water Research (ICRA), University of Girona (UdG)*
***Department of Engineering, Univesity of Ferrara*
****Catalan Institution for Research and Advanced Studies (ICREA)*

This study presents a preliminary risk assessment characterization, in different environmental compartments (waters and sediments), of data collected on the occurrence of pharmaceutical residues in the vulnerable area of the Ebro Delta region (Catalonia, Spain). The survey was carried out using data from three sampling campaigns and including 27 different sampling points, such as: reaches of the Ebro River located upstream and downstream the main wastewater treatment plants (WWTPs), surrounding channels, estuaries, and the associated receiving seawater. In all samples collected, which include water and sediment, 81 commonly used and prescribed pharmaceuticals (PhACs), belonging to 18 therapeutic classes, were determined. The risk assessment for waste, fresh and marine water and sediment was performed by calculating risk quotients (RQs) for each individual pharmaceutical, at each site. For water samples, measured maximum environmental concentration (MEC) were used while for sediment samples, the concentrations detected were converted to the equivalent pore water. These concentrations were divided by the lowest predicted no effect concentration (PNEC) available. PNEC values used were those achieved from the NORMAN Ecotoxicology Database, comprising lowest PNECs for 39 992 substances which were either predicted by QSAR or obtained experimentally and it included toxicity towards to three standard test organisms, namely Daphnia magna, Selenastrum capricornutum and Pimephales promelas. Based on the calculated RQ values, 8 out of the 11 pharmaceuticals highlighted with high risk in effluent wastewater posed high risk (RQ>l) to the organisms living in freshwater and marine ecosystems as well. These compounds include the antibiotics azithromycin, ofloxacin and ciprofloxacin, the analgesic/ant-inflammatory diclofenac and the psychiatric drugs carbamazepine, venlafaxine, lorazepam and trazodone. For sediments, only four pharmaceuticals, namely azithromycin, hydrochlorothiazide, phenazone and carbamazepine were found to induce high risk in sampling sites located downstream WWTPs and in the surrounding channels. These analyses revealed that WWTPs are an important source of PhACs contamination in the Ebro Delta region and that the levels of some PhACs remaining in fresh and coastal waters may induce potential environmental risks to aquatic ecosystems.

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Correspondence to: mcelic@icra.cat

A COMPARATIVE ANALYSIS OF WATER MANAGEMENT IN GERMANY, SWITZERLAND AND SWEDEN REGARDING PHARMACEUTICAL POLLUTION

Marie Marchand-Pilard, Jean-François Loret*, Xavier Litrico*, Romain Journel**, Béatrice Parance****

**SUEZ*
***SANOFI*
****Université Paris 8 Vincennes-Saint-Denis*

The adverse effects of pharmaceuticals on aquatic environment are well established. Although scientific reports agree that adverse health impacts to humans are unlikely when considered directly, questions arise as to their combined effects with other chemicals (cocktail effect) and the consequences of long term exposure to low doses. In Western countries, these substances are found mainly in domestic wastewater and end up in the environment because waste water treatment plants (WWTPs) were not conceived to remove them. There is currently no legal framework in the European Union (EU) that compels States to reduce pharmaceutical substances in water and aquatic environment.

Objective and Methods

This study sought to identify and compare the technical and financial approaches taken by Germany, Sweden and Switzerland, and the political and legal instruments implemented to reduce pharmaceutical pollution in waters. This comparison will be used to identify possible future trends in the EU legislation related with the limitation of pharmaceuticals in the water environment. The study was organised in four stages. The first one aimed to identify the political organisation of each State. The second stage focused on water management legal framework. The third sought to identify national issues and response for water management, focusing on pharmaceutical pollution. The last stage aimed to draw a common pattern from those three stages to emphasise the incentives and triggers that led to such decisions. The documents analysed for this study include governments' reports and communications; laws and regulations; scientific, legal, environmental and economic journals; and official websites.

Results and Conclusion

As a result, several national incentives have been identified, depending on history, values, tradition, policy and organisation of the country. As for technical solutions, actions to reduce pharmaceuticals in water are twofold: (1) Preventive actions, that aim to encourage e.g. the development of greener pharmaceuticals manufactured according to greener processes, (2) End-of-pipe actions, consisting on removing pharmaceuticals from wastewater before the release of WWTPs' effluents into natural environment. To achieve the most effective elimination of pharmaceuticals, it seems paramount to combine prevention and end-of-pipe actions. Finally, operating costs and funding of infrastructures are one of the major issues discussed. Switzerland has opted for additional financing through a national tax based on the polluter-pays principle. In Germany, the use of extended producer responsibility (EPR) as complementary funding is under discussion. It is indeed considered that the pharmaceutical industry is just as responsible as patients for drug pollution in water and must therefore pay a tax. Used this way, EPR could contribute to the funding of advanced treatments in WWTPs and to the encouragement of pharmaceutical companies to move towards greener manufacturing processes and active ingredients.

As a conclusion, although there is no legislation requiring the elimination of pharmaceutical substances in water, more constraining EU policies are expected in a near future on this matter. Furthermore, the EU"s regulatory framework is only a minimum legal basis, but leaves to the States the possibility to adopt stricter measures. The absence of EU regulations is therefore not an excuse to limit efforts to upgrade WWTPs. According to the precautionary principle, the doubt surrounding the adverse effect of pharmaceutical on human health and the observed effects on the aquatic wildlife should trigger governments" actions. Thus, Germany and Sweden seem to be moving towards a more demanding legal framework for pharmaceutical substances in water, both to establish themselves as leaders in this sector and to anticipate regulatory changes. This overall context might suggest future pressures on the EU legislator.

Correspondence to: marie.marchandpilard@suez.com

RISK ASSESSMENT AND ENVIRONMENTAL HAZARD OF EMERGING POLLUTANTS DETECTED IN THE ANTARCTIC PENINSULA

Yolanda Valcárcel Rivera, Adrián Olalla López*, Luis Moreno Merino***

**Rey Juan Carlos University*
***Instituto Geológico y Minero de España (IGME)*

Although Antarctica is under protection and human activity is reserved exclusively for scientific research, and with numerous restrictions on tourism, the increase in presence is causing a significant impact on terrestrial and aquatic ecosystems, especially marine ones. It is estimated that in 2016, 4490 scientists or support staff, carried out work on Antarctic bases or research vessels and left their mark (Antarctic Population 2019). In 2017-2018 the number of tourists who landed in Antarctica amounted to a total of 42,576, it is estimated that for the 2018-2019 financial year they received the arrival of up to 45,864 tourists (IAATO, 2018). Proof of this excessive presence is the recent detection of contaminants linked to human presence, in places that should be considered virgins. The latest publications of the authors have demonstrated the presence of drugs, plasticizers, drugs of abuse, disruptors, perfluorinated, pyrethroids, sunscreen and stimulants such as caffeine.

This work aims to determine the environmental risk and hazard from the concentrations detected, for this the 51 substances that were found above the detection limit will be analyzed.

The risk and hazard characterization was calculated for all sampling points using the hazard quotient (HQ) and the Persistence, Bioaccumulation, and Toxicity Index (PBT). The results show that acetaminophen, diclofenac, ibuprofen analgesics, and anti-inflammatories have HQ values well above 10 (high risk) at the concentrations detected in several sampling points, including streams, wastewater and glacier. The antibiotic clarithromycin was detected at all sampling points where some adverse effects could be expected on aquatic life. Within sex hormones, the metabolite of estradiol estriol (E3) has been similarly characterized as "moderate" risk in wastewater. At the same sampling point, nonylphenol diethoxylate was detected, which is in Category 1 within the group of possible endocrine disruptors, presented a high risk to the concentrations obtained. Pyrethroids insecticides have a very high aquatic toxicity, presenting a moderate or high risk in each of the samples in which they were detected. Finally, long-chained perfluorinated agents, whose toxicity is higher, had an HQ value well above 10 at the point of discharge of wastewater. These results allow us to establish a first list of possible emerging pollutants that should be monitored, creating a list similar to the existing "Watch List" for emerging pollutants in Europe (Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013, as regards priority substances in the field of water policy).

From this first observation list, it would be considered to advance and expand these results with ecotoxicological tests, to assess the toxicity of the compounds obtained.

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Correspondence to: adrian.olalla@urjc.es

OCCURRENCE OF ESTROGENIC COMPOUNDS AND PHARMACEUTICALS IN FRENCH SURFACE WATER: A WATCH LIST SURVEY

LARDY-FONTAN Sophie, Bristeau Sébastien**, Le Diouron Véronique*, Fallot Carine*, Staub Pierre-François***, Togola Anne***

**LNE*
***BRGM*
****AFB*

According to WFD and Directive 2013/39/EU [1], the monitoring programs should generate high-quality data on the concentrations of priority substances and other pollutants in the aquatic environment. Decision EU 2015/495 specifies a "Watch List" of substances pursuant to the WFD that must be monitored across Europe. The Watch List (WL) is a mechanism for obtaining high-quality Union-wide monitoring data for potential water pollutants for which only insufficient monitoring data (or data of insufficient quality) are available. Its final goal is to determine the risk they pose at EU level and to decide if EQS should be set for them.

At French level, this monitoring was implemented on 26 sampling stations of the national surveillance network. Four monitoring campaigns, between the beginning of 2016 and the end of 2017 were performed. This presentation presents the results obtained during these two years of monitoring. The results are discussed in terms of occurrence, concentrations levels and spatial distribution. They are compared with other existing national data, but also with European data acquired during the same exercise. Thus, regional and national specificities are discussed. Limitations of actual risk assessment approach (R=MEC/PNEC) will be discussed.

Correspondence to: sophie.lardy-fontan@lne.fr

INTERNATIONAL COMPARISON FOR THE IDENTIFICATION OF PHARMACEUTICAL, PESTICIDES AND ILLICIT DRUG COMPOUNDS IN WATER USING HIGH RESOLUTION CHEMICAL ANALYSIS AND MACHINE LEARNING

Helena Rapp Wright, Fiona Regan*, Blánaid White*, Leon Barron***

**DCU*
***KCL*

Over the last decade, contaminants of emerging concern (CECs) have been shown to occur in surface waters at ng/L to µg/L concentrations and their risks in the environment require further knowledge. The consumption of such compounds is growing and therefore reliable analytical methods for identification of new compounds and their determination need to be constantly re-developed. Two countries of the European Union were selected in order to do a comparison between them using river waters as we were focused on what persists in the environment post treatment. Water samples in the River Thames, UK, and in the River Liffey, Ireland, were collected daily over one week in February 2019 from the central London tideway catchment and central Dublin in order to prioritise these contaminants. Herein, a more flexible methodology combining liquid chromatography-high resolution mass spectrometry (LC-HRMS) and machine learning-based data analysis is presented. They were subjected to analyte enrichment with solid-phase extraction before analysis with LC-HRMS. A previously developed LC-HRMS method for >190 CECs was used to generate an artificial neural network-based retention time prediction tool [1]. Predicted retention time accuracies of <3 min were achieved generally for gradient separations over 27.5 min on a reversed-phase C18 analytical column. Overall, the use of chemical analysis and machine learning in this way could enable more rapid shortlisting of CEC candidates for prioritised monitoring. Ultimately, such approaches may also inform more efficient ecotoxicity testing strategies for potentially toxic compounds in the aquatic environment.

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Correspondence to: helena.rappwright2@mail.dcu.ie

STRATEGIES TO CONTROL THE DISSEMINATION OF ANTIBIOTIC RESISTANCE IN THE ENVIRONMENT: A SYSTEMATIC REVIEW

Sylvie NELIEU, Anais GOULAS*, Drifa BELHADI**, Pierre BENOIT*, Sophie COURTOIS***, Christophe DAGOT****, David MAKOWSKI*, Sylvie NAZARET*****, Dominique PATUREAU*, Fabienne PETIT*****, Cedric LAOUENAN*****

**INRA*
***AP-HP*
****SUEZ*
*****INSERM*
******CNRS*

The massive use of antibiotics in human and veterinary medicine led to the worrying spread of antibiotic resistance (ATBR). Antibiotic residues, antibiotic-resistant bacteria (ARB), their genes (ARG) and mobile genetic elements (MGE) are introduced in aquatic and terrestrial environments by the rejection of wastewaters and organic wastes,. Dynamics of ARG/MGE in these environmental reservoirs contribute to the dissemination of ATBR. The French Ministry of Ecological and Inclusive Transition commissioned a systematic review of literature to identify effective solutions for controlling the ATBR dissemination. According to One-Health approach and protocol [1], three sub-questions were addressed in this review to assess the effectiveness of: 1) antibiotic use restriction, 2) treatments of wastewaters and organic wastes and 3) in situ environmental management, to reduce the contamination of natural environments. Articles were analyzed through evidence map, qualitative and quantitative syntheses.

After screening of 17,798 articles from eight publication databases, 931 articles were included in the evidence map. While knowledge gaps were obtained for sub-questions 1 and 3, studies on full-scale wastewater treatment plants (WWTPs) were critically appraised (324 studies, sub-question 2). A lower confidence level was attributed to 64% studies due to poor sampling strategy resulting in performance and detection biases. Results of high confidence studies were qualitatively analyzed; WWTPs can be efficient to remove ARB, ARG and MGE from wastewater, depending on markers, origin of influent, WWTP size and process. Furthermore, a meta-analysis was carried out to determine effects of organic waste treatments on ATBR (126 studies, sub-question 2). Composting (27 studies) significantly reduces the relative abundance of ARG/MGE with 84% removal (95% confidence interval [63%; 93%]) while anaerobic digestion is less efficient due to more heterogeneity. The systematic review results allow to: i) identify knowledge gaps for research (e.g., ATBR indicators) and ii) develop recommendations for stakeholders and policy makers.

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Correspondence to: sylvie.nelieu@inra.fr

CAN CILIATE BE USED AS MODEL ORGANISMS TO REPRESENT AQUATIC SYSTEM? A CASE STUDY OF CAFFEINE

Jéssica Andrade Vilas-Boas, Gabrielle Quadra*, Marcus Senra**, Pedro Souza*, Aline Ribeiro*, Jorge Nascimento*, Roberto Dias**

**Universidade Federal de Juiz de Fora*
***Universidade Federal de Itajubá*

The presence of caffeine in aquatic ecosystems may work as a warning to the presence of other organic pollutants in the environment, such as illicit and licit drugs and personal care products. Caffeine is found in the environment in the order of mg L-1 and, possibly, this concentration is not enough to cause acute effects. However, caffeine is continuously disposed in the environment, refilling its concentrations and, then, chronic effects are expected to occur. Ciliates are considered an important component of the aquatic ecosystems and they can be used in freshwater biomonitoring due to their efficient capacity to respond to different levels of impacts. For this reason, ciliates are considered good biological models and potential candidates as test organisms in ecotoxicological studies. This study aimed to evaluate the responses of Paramecium caudatum to caffeineP. caudatum was obtained initially from an urban stream and cultivated using Cerophyl culture medium. All tests were performed with the necessary criteria. Only individuals from populations at logarithmic growth phase (stock culture = 48 h) were used for tests. The acute toxicity test was carried using six concentrations: 50 mg L-1, 100 mg L-1, 200 mg L-1, 400 mg L-1, 800 mg L-1 and 1,600 mg L-1 (300 µl per concentration). Negative controls with mineral water were performed in parallel. The endpoint evaluated was mortality after 24 h of exposure. After 24 h of caffeine exposure, the LC10 was 190 mg L-1 ranging from 150 to 240 mg L-1 and, the LC50 was 710 mg L-1 ranging from 600 to 810 mg L-1. The caffeine affect P. caudatum after acute exposure. However, the LC50 (710 mg L-1) exceeded the compound solubility in water (200 mg L-1). Although P. caudatum did not show high sensitivity to caffeine, a representative number of studies have already demonstrated the potential of ciliates as bioindicators to assess water quality. Moreover, previous studies found potential environmental risks of caffeine in aquatic ecosystems as well as ecotoxicological effects in mixtures. Therefore, understanding the long-term effects of caffeine isolated and in mixtures is crucial for risk assessment since it is a widespread contaminant.

Correspondence to: jessica_biol@outlook.com

EDC-WFD: A PROJECT TO DELIVER RELIABLE MEASUREMENTS OF ESTROGENS FOR BETTER MONITORING SURVEY AND RISKS ASSESSMENTS

LARDY-FONTAN Sophie [(1)], Piechotta Christian [(2)], Heath Ester [(3)], Perkola Noora [(4)], Balzamo Stefania [(5)], Cotman Magda [(6)], Gokcen Taner [(7)], Gardia-Parège Caroline [(8)], Budzinski Hélène [(8)], Lalère Béatrice [(1)]

1) LNE
2) BAM
3) JSI
4) SYKE
5) ISPRA
6) NIC
7)TUBITAK
8) EPOC

Monitoring programs should generate high-quality data on the concentrations of substances and other pollutants in the aquatic environment to enable reliable risk assessment. Furthermore, the need for comparability over space and time is critical for analysis of trends and evaluation of restoration of natural environment. Additionally, research work and exercises at the European level have highlighted that reliable measurements of estrogenic substances at the PNEC level are still challenging to achieve.

The project EDC-WFD "Metrology for monitoring endocrine disrupting compounds under the EU Water Framework Directive" aims to develop traceable analytical methods for determining endocrine disrupting compounds and their effects, with a specific focus on three estrogens of the first watch list (17-beta-estradiol (17βE2), 17-alpha-ethinylestradiol (EE2), and estrone (E1)). Estrogens 17-alpha-estradiol (17aE2) and estriol (E3) will be included to demonstrate the reliability of the developed methods - Mass Spectrometry based method and effect-based methods (EBM) - and to support the requirements of Directive 2013/39/EC, Directive 2009/90/EC and Commission Implementation Decision (EU) 2018/840, hence improving the comparability and compatibility of measurement results within Europe. During the EDC-WFD project four EBM will be deeply investigated in order to improve their rationale use and their support in water quality assessment. This contribution will present the objectives and methods applied within the EDC-WFD project.

Correspondence to: sophie.lardy-fontan@lne.fr

LIFE CYCLE ASSESSMENT OF PHARMACEUTICALS IN IRISH SURFACE WATERS

DYLAN O"FLYNN, Blánaid White*, Jenny Lawler*, Fiona Regan**

**Dublin City University*

At each stage of the pharmaceutical lifecycle, there is a significant risk of environmental exposure. For this reason, it is imperative to implement both source directed and end of pipe control measures to mitigate any potential hazards to the environment or humans. The ever-increasing use and availability of pharmaceuticals in the last decade have led to the contamination of surface water ecosystems from ng/L to µg/L concentrations. The environmental fate and toxicological implications of many pharmaceuticals and their residues remain generally unknown. Additionally, the stability and biological activity of these "micro-pollutants" can lead to chronic environmental exposure, with ensuing behavioural and health-related effects. Eight pharmaceuticals have been incorporated into the updated surface water "Watch List" (Decision (EU) 2018/840), indicating that insufficient data exists to assess their potential impact. These 8 pharmaceuticals, in addition to pharmaceuticals commonly found in European surface waters which have a low removal efficiency in conventional activated sludge type wastewater treatment plants (trimethoprim, sulfamethoxazole, carbamazepine, gemfibrozil and diclofenac) are investigated in this project. By performing a life cycle assessment of these 13 pharmaceuticals, an holistic view of how the pharmaceuticals are manufactured, prescribed, used and disposed can be achieved. This project aims to create a comprehensive prioritisation framework and a risk-based assessment by calculating the risk quotient for each of the chosen pharmaceuticals. Additionally, findings from this project will give some insight into the occurrence, movement and impact that pharmaceuticals may have on Irish surface water catchments. Outcomes from this research will aim to improve education surrounding appropriate use, disposal and waste management of pharmaceutical products.

Correspondence to: dylan.oflynn5@mail.dcu.ie

OPTIMIZATION OF A WORKFLOW FOR ENVIRONMENTAL SCREENING BY GAS CHROMATOGRAPHY-QUADRUPOLE-TIME OF FLIGHT ACCURATE MASS SPECTROMETRY

Verónica Castro, Rosario Rodil*, Rafael Cela*, José Benito Quintana**

**Universidade de Santiago de Compostela*

Due to complexity of environmental matrices and the increasing number of putative (emerging) pollutants that could be present in such samples, it is necessary to have powerful screening approaches capable of detecting trace level components and extract specific signals of complex chromatograms. These screening methods can be used as a first step in prioritizing the compounds that could later on be determined at a quantitative level. In this context, liquid chromatography-high resolution mass spectrometry (LC-HRMS) has become the most prominent technique in environmental screening analysis. However, LC-HRMS has a limited applicability for less polar compounds or those with poor ionization efficiency by electrospray. Hence, gas chromatography-HRMS (GC-HRMS) is an interesting alternative which could complement LC-HRMS, having as a further advantage its higher separation power and being less prone to matrix effects. Also, there are already many electron impact (EI) databases, though mostly based on low resolution MS and being non-specific in some cases.

Screening in GC-HRMS is typically performed by deconvolution. In the case of the GC-HRMS system developed by Agilent (a quadrupole-time of flight, QTOF) a specific software has been developed to deconvolute HRMS data, namely Unknown Analysis. The goal of this work was the optimization of several parameters in order to achieve the best compromise between false positives and false negatives.

To this end, an accurate mass library of 28 model compounds was created. Then, five replicates of mussel extracts were spiked with a mixture of these 28 compounds at two concentration levels (500 ng mL-1 and 50 ng mL-1) and injected in the GC-EI-QTOF. Compound identification was carried out with the Agilent MassHunter Unknowns Analysis B.10.00 using the SureMass algorithm and matching against the above mentioned library of 28 compounds. Different method parameters affecting data processing (pure weight factor and accurate mass tolerance) were tested in order to obtain the greater and reliable number of compounds identified. Results were evaluated using multivariate statistics analysis.

Once the method was optimized, an accurate mass library, which over 300 chemicals of derivatized and non-derivatized compounds was generated. A preliminary application to real samples will also be presented.

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Correspondence to: veronica.castro@usc.es

METAL DETERMINATION (ZN, CU, CD AND PB) AND INTEGRATION OF OXIDATIVE STRESS BIOMARKERS IN FISH AND BIVALVE SPECIES FROM NORTH-WESTERN COAST OF SPAIN

Salomé Martínez-Morcillo, Marcos Pérez-López*, Yolanda Valcárcel**, Francisco Soler*, Maria del Prado Míguez-Santiyán**

**Unit of Toxicology, Veterinary Faculty, University of Extremadura, Caceres, Spain*
***Research and Teaching Group in Environmental Toxicology and Risk Assessment (TAyER). Rey Juan Carlos University 28933, Móstoles (Madrid), Spain*

Non-polar hazardous contaminants (toxic, persistent and bioaccumulative) such as heavy metals are an environmental and public health risk and therefore included in monitoring programs. The aims of this study were determine in animal tissue the levels of: I) two essential metals, zinc (Zn) and copper (Cu) and two toxic metals, cadmium (Cd) and lead (Pb) and, II) a set of biomarkers applied on biomonitoring: glutathione S-transferase (GST); catalase (CAT), glutathione peroxidase (GPx); glutathione reductase (GR) activities; reduced glutathione (GSH), oxidized glutathione (GSSG) and malondialdehyde (MDA). The study was carried out on three fish species (horse-mackerel Trachurus trachurus, blue whiting Merluccius merluccius and pout Trisopterus luscus), and two bivalve species (mussels Mytilus edulis and pod razor Ensis siliqua), captured in Galician Rias from North-Western Spain. The concentration pattern of the different metals analyzed in all species, in decreasing order, was Zn> Cu> Pb> Cd. The highest concentrations of Cd and Pb appeared in bivalve tissues being a magnitude greater than on all other fish species. The integrated biomarker responses (IBRs), as an indicator of environment stress has been calculated. The IBR values for each species were: T. trachurus=14.08; T. luscus=17.37; M. merluccius=18.51; M. edulis=18.52 and E. siliqua=22.97. IBR values tended to increase in bivalve species, especially on pod razor E. siliqua. In both bivalve species we observed stimulated antioxidant enzyme responses (CAT, GPx, GR) and oxidative damage (MDA) higher than in fishes. The principal components analysis (PCA) was assessed to determinate the relation between biomarkers and metal concentrations. In this model, the first of the two PCs (PC1) explained 57.7% of the variance and 22.73% was explained by the second (PC2). The PC1 can perform a relatively good separation between bivalve and fish species. Samples of E. siliqua were related with high level of Cd and Zn that seem to be related to GSSG biomarker while M. edulis also was well linked with Pb associated with GSH levels. Cu was related with antioxidant GR and GPx and with T. trachurus. The results of this study provide support the need of further to assess the risk posed by metals in coastal and marine systems. Our work also supports the usefulness of biomonitoring programs, using biomarkers, in the assessment of possible ecological and human health risk or in decision-making related to seafood farming in marine ecosystems.

Correspondence to: salome.martinez-morcillo@hotmail.com

MOBILITY OF A PHARMACEUTICAL COCKTAIL IN SOIL POROUS MEDIA – ROLE OF THE COLLOIDAL TRANSPORT

Marjolaine Bourdat-Deschamps, Kossa Tatiana Montouo**, Pierre Benoit*, Jérôme Labille****

**INRA*
***CNRS*
****CNRS-CEREGE*

Pharmaceutical products excreted by treated animals or humans are transferred to manure or wastewater, respectively. In wastewater treatment plants, pharmaceuticals can be degraded and/or removed from water through adsorption to sludge. Recycling of the organic waste products-OWP (sludge, compost, slurry, manure...) in agriculture is largely encouraged nowadays for their fertilising properties, but it may indirectly contribute to the dissemination of pharmaceuticals in the environment (soils, surface and ground waters). In soil, both organic and mineral-bearing phases can contribute to the transport of pharmaceuticals.

The objective was to evaluate the affinity for soil microstructures (colloids) to three pharmaceuticals, ofloxacin, ibuprofen and carbamazepine.

Experimental approach based on simplified and synthetic systems were used to better focus on the physical-chemical interactions between contaminants and soil constituents. Flow-through experiments were performed using 40 cm length and 2.75 cm internal diameter columns filled with sand or a sand/soil (95-5) mixture saturated with a percolating solution carrying the contaminant cocktail. Two concentrations of CaCl2 in the percolating solution were tested in order to stabilise soil aggregation (CaCl2 concentration: 10-2 M) or to mobilise suspended colloids (CaCl2 concentration: 10-3 M).

At the column outlet, using a fraction collector, pharmaceutical breakthrough was measured using online SPE-UHPLC-MS-MS and colloids mobilisation was measured using light scattering. Column experiments were carried out in duplicate and as a function of the soil composition and the solution chemistry.

In the sand filled column used as a reference free of soil, ofloxacin was surprisingly only little mobile, probably due to strong interactions with silica, whereas carbamazepine and ibuprofen were highly mobile at 55-60%. In sand-soil filled columns with CaCl2 (10-3 M), ofloxacin was steel not transported but ibuprofen and carbamazepine were more mobile (80-95%) than in sand only, probably due to the interactions between these pharmaceuticals and the colloids mobilised from the soil within the percolating solution. The fraction of pharmaceutical transported by colloids vs. the fraction free in solution was estimated using filtration at 0.2 µm, which revealed 27 vs. 73% respectively. In CaCl2 (10-2 M), instead of a stabilised soil aggregation, the injection of pharmaceutical surprisingly caused a greater dispersion of soil colloids. This led to colloidal vectorisation of 36% of the percolating molecules.

These results evidence the significant role played by micrometric particulate matter constituting soil in the mobility of pharmaceuticals in the environment. These colloids may cause either retention or vectorisation of the pharmaceuticals through the soil porous media, as a function of the physical-chemical conditions that determine dispersion conditions.

Correspondence to: marjolaine.deschamps@inra.fr

GEOREFERENCED MODELLING AS COMPLEMENTARY APPROACH TO ENVIRONMENTAL MONITORING

Volker Lämmchen, Gunnar Niebaum*, Joerg Klasmeier*, Frederik Hilling**, Richard Schlicker***

**University of Osnabrueck*
***Geoplex GmbH*

Water is a basic element of life on earth and of fundamental importance for all life forms. Despite its limitations, freshwater is used in almost all areas of life. The Water Framework Directive (WFD) created a legal framework that imposed the protection of common water resources on European states. The aim of the directive is to achieve good ecological and chemical status in European waters. For this, the member states are obliged, among other things, to monitor water quality. Water quality is defined by the occurrence of certain substances listed on a watch list within the WFD. For this reason, knowledge about emissions, transport and fate of pollutants in waters is of special interest. This is why there are good reasons for a permanent monitoring of all water bodies. At the same time, however, it seems understandable that such permanent monitoring is difficult to implement. Simulation models can be used to estimate predicted environmental concentrations (PEC) based on chemical and physical properties and consumption data. The Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER) constitutes a model tool for exposure and risk assessment of chemicals in surface waters that calculates spatially resolved substance concentrations in a whole catchment under the assumption of steady state. GREAT-ER has already been successfully applied in a number of studies. The objective of this study is to show that the model results can be easily used for evaluation of risk management options for pharmaceuticals in surface water.

The study area contains the catchment of the river Vecht, a medium sized river (50m³/s) located in the Dutch-German border region and covers an area of around 6000 km² and with around 1,500,000 inhabitants. To represent the status quo of contaminations in the whole Vecht watershed, probabilistic simulations with 10,000 runs were performed. The results are shown as a color-coded map of the whole catchment.

Although comprehensive monitoring is often the first choice, it is evident that this approach is limited by time and money. The georeferenced simulation model GREAT-ER closes the gap by delivering basin-wide concentration estimations for different scenarios. Selected results will be made publically available on a Web GIS platform, the so-called WIS (Watershed Information System) that has been developed within the EU-Interreg project MEDUWA. It constitutes a map-based platform on which basic information and simulation results for selected reference compounds in the Vecht catchment are presented. The interactive maps offer stakeholders and interested citizens the possibility to inform themselves about aqueous concentrations of pharmaceuticals in the area. Thus, the system effectively contributes to the field of science communication. By comparison of predicted concentrations with target values, possible risks for different endpoints can be identified. The information system combines, manages and properly visualizes data from several sources, which are collected by different partners, including background information, monitoring data and potential risks.

Pharmaceutical concentrations in the catchment area can be assessed based on GREAT-ER simulations even without cost-intensive on-site measurements. The user can additionally evaluate the effect of different hydrological flow conditions (low water runoff, mean annual runoff, different runoff percentiles as well as hydrological parameter shifts of selected climate scenarios) on the concentration of reference substances. Various emission reduction measures can be defined by the built-in scenario creator. These include, for example, equipment of sewage treatment plants with tertiary/quaternary treatment (ozonation, activated charcoal) or newly developed techniques such as nanofiltration and treatment with plasma-activated water. The simulation results can be compared with the status quo (simulations and monitoring data) for an a priori evaluation of the effectiveness of the measures.

Correspondence to: volaemmchen@uos.de

OCCURRENCE OF PHARMACEUTICALS AND LEVEL OF BIOMARKER IN SEAFOOD SPECIES FROM THE NORTH-WESTERN COAST OF SPAIN

Salomé Martínez-Morcillo, José Luis Rodríguez-Gil**, Javier Fernández-Rubio***, Sara Rodríguez-Mozaz****, Maria del Prado Míguez-Santiyán*, Damià Barceló, Yolanda Valcárce****

**Unit of Toxicology, Veterinary Faculty, University of Extremadura, Caceres, Spain*
***Department of Biology, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada*
****Research and Teaching Group in Environmental Toxicology and Risk Assessment (TAyER). Rey Juan Carlos University 28933, Móstoles (Madrid), Spain*
*****Catalan Institute for Water Research (ICRA), H2O Building, Scientific and Technological Park of the University of Girona, Emili Grahit 101, 17003 Girona, Spain*

The aims of this study were to study the occurrence in biota of 27 drugs of the main therapeutic groups (cardiovascular, psychiatric, analgesic and antibiotics) and to check if those could explain biomarkers responses of seafood species collected in marine and coastal environment. Tissues of representative seafood species of bivalves, cephalopods, arthropods, and fish of high economic importance and consumption rates in North-Western Spain were used. The selected sampling sites were located along the coastline of the Rías Baixas area which includes three different rías, namely, Ría de Muros e Noia, Ría de Arousa, and Ría de Pontevedra.

Four of 27 pharmaceutical compounds analyzed were detected in the tissue collected samples. Three belonging to psychotropic drugs (citalopram, venlafaxine and alprazolam) and one to the antibiotic (ronidazole). The benzodiazepine citalopram was detected in the tissues of common octopus (14.10±4.15 ng/g dry weight) and pod-razor (9.38±0.15 ng/g dry weight). The anxiolytic venlafaxine was detected in the tissues of common cockle (2.91±3.47 ng/g dry weight). The veterinary antiparasitic ronidazole was found in pod razor (2.26±0.51 ng/g dry weight). The psychoactive compound alprazolam was also measured in common octopus (0.31±0.33 ng/g dry weight). The location with the greatest concentrations and variety of drugs in seafood was Muros-Noia. Hazard quotients were calculated to assess the hazard posed by the consumption of the sampled seafoods. Octopus and pod razor tissues containing citalopram and alprazolam exceeded our chosen hazard limits for toddlers who are high consumers of seafood.

A battery of biomarkers of effects was applied to samples of the study species with the aim of characterizing their basal levels and evaluating their suitability as a tool in the monitoring chronic exposure to environmental contaminants such as those analyzed in this study. According to the measured biomarkers, pod razor and cockles have the potential to be good bioindicator species. Cockles could be good bioindicators for enzymatic biomarkers involved in neurotransmitter effects (acetylcholinesterase activity), detoxification (glutathione S transferase activity) and oxidative damage (malondialdehyde production). In addition, razor-shell could be an excellent bioindicators using biomarkers of oxidative stress such as antioxidant glutathione peroxidase activity. Therefore, it would be important to use more than one bioindicator species, depending on the responses that are evaluated. The biomonitoring of the effects on wild populations to evaluate contaminants exposure, can be more ecologically relevant than performing laboratory tests.

Correspondence to: salome.martinez-morcillo@hotmail.com

METHOD FOR ROUTINE MONITORING PHARMACEUTICAL METABOLITES IN ENVIRONMENTAL AQUEOUS SAMPLES

Irene Aparicio, José Luis Malvar*, Juan Luis Santos*, Julia Martín*, Esteban Alonso**

**Department of Analytical Chemistry, Escuela Politécnica Superior, Universidad de Sevilla*

Pharmaceuticals are anthropogenic pollutants of high concern that are continuously being released into the aquatic media mainly through wastewater discharges from wastewater treatment plants. They have been detected not only in wastewater and surface water but also in tap water [1]. Pharmaceuticals can be released to wastewater as parent compounds and/or as free or conjugated metabolites and, then, they can be transformed into degradation products in wastewater treatment plants and in the aquatic environment whereas their metabolites can be transformed into their parent compounds. Nevertheless, to the date, most of the studies have considered just the parent compounds, not their metabolites in spite that they can be present at higher concentrations, be more toxic and can be transformed into the parent compound [2]. One of the main drawbacks for routinely monitoring pharmaceutical metabolites is the lack of affordable, easy-to-perform and reliable analytical methods for their determination.

In this work, an analytical method has been developed and validated for the simultaneous extraction and determination of the main metabolites of the diclofenac, ibuprofen, sulfamethoxazole, carbamazepine and caffeine in wastewater and tap water samples [2]. Sample extraction was based on solid-phase extraction with OASIS HLB cartridges that is an extraction technique widely used in routine laboratories. Analytical determination was carried out by liquid chromatography-tandem mass spectrometry with electrospray ionization. The method was validated for its application to wastewater and tap water. Average accuracy was in the range from 68 to 119%, in wastewater, and from 86 to 110%, in tap water. Precision, expressed as relative standard deviation, was lower than 17% for all the compounds. Method quantification limits were in the range from 1.0 to 33 ng L−1 in wastewater and from 0.5 to 28 ng L−1 in tap water. The method was applied to wastewater and tap water samples. None of the target compounds was detected in tap water whereas all of them were detected in wastewater. Metabolites were at similar or even up to 4.5 to 24 times higher (some metabolites of ibuprofen and carbamazepine) than those of the parent compounds.

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Correspondence to: iaparicio@us.es

SELECTIVE PRESSURIZED LIQUID EXTRACTION METHOD FOR MONITORING METABOLITES OF PHARMACEUTICALS IN SLUDGE AND SOIL

Irene Aparicio, José Luis Malvar*, Juan Luis Santos*, Julia Martín*, Esteban Alonso**

**Department of Analytical Chemistry, Escuela Politécnica Superior, Universidad de Sevilla.*

In the last years, there is an increasing concern about the occurrence and fate of the so-called emerging pollutants in sludge and soils, and even in crops, affected by sludge amendments or by irrigation with reclaimed wastewater what is a common practice in arid and semiarid regions [1]. Among them, special attention has been focused on pharmaceuticals that can be released to wastewater as parent compounds and as metabolites. They can enter into the food chain through vegetables cultivated in soils amended with treated sewage sludge [1] or irrigated with reclaimed wastewater. Nevertheless, to the date, there is scarce information about the presence of metabolites of pharmaceutical compounds in sludge and soils in spite that they can be present at higher concentrations, be more toxic and can be transformed into the parent compound [2].
In this work, an analytical method has been developed and validated for the first-time simultaneous determination of caffeine, carbamazepine, diclofenac, ibuprofen and sulfamethoxazole and their main metabolites in soil, composted sludge and digested sludge. Box-Behnken experimental design was applied for method optimisation due to the high number of experimental variables to optimize and the different physical-chemical properties of the target compounds. The method involves simultaneous sample extraction and clean-up by selective pressurized liquid extraction and analytical determination in a single run by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Good linearity, accuracy (mainly from 80 to 112%) and precision (<11%) was obtained. Method quantification limits were in the range from 0.12 to 9.2 ng g-1 dry matter. The application of the method to soil, composted sludge and digested sludge revealed that metabolites of carbamazepine, diclofenac and ibuprofen were at similar or higher concentrations than their parent compounds in digested sludge. In compost samples, only were detected the metabolites of carbamazepine.

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Correspondence to: iaparicio@us.es

ENVIRONMENTAL RISK ASSESSMENT FOR MEDICINAL PRODUCT: PERSPECTIVE AND CHALLENGES

JOURNEL Blandine, GONY Sylviane*, BELTRAN Estelle**

**CEHTRA SAS*

An environmental risk assessment (ERA) must be performed on the active pharmaceutical ingredient (API) for the market authorisation of human medicines. The current scientific guideline (under revision) published by the European Medicine Agency (EMA) lists the minimum data requirements for the assessment of PBT/vPvB properties and environmental risks, and defines how to conduct a regulatory compliant ERA. Fate of substances in the environment is driven by numerous factors: among them are the physical and chemical properties of the substance, which impact on how substance behaviour is modelled in the different abiotic compartments (soil, water, sediment, air), to predict exposure levels for risk assessments. API are often difficult substances to study (very low water solubility, very high adsorption…) and scientific reasoning is necessary to apply EMA guideline.

A comparison of requirements and modelling within other regulations (REACh, biocides, plant protection products…) will allow to underline similarities and differences in the approaches for environmental risk assessments. Experience gained with other regulations regularly helps avoiding pitfalls related to dealing with difficult substances such as API.

Difficulties that had previously arisen with environmental risk assessment of difficult substances other than API, including pesticides, biocides and other chemicals, will be discussed. The contribution of this knowledge to API assessment in the framework of EMA regulatory requirements could benefit to API dossiers, solving some of the most problematic issues, including technical challenge to conduct the required OECD tests, need to tailor the experimental design of studies, or selection of parameters for modelling.

Correspondence to: blandine.journel@cehtra.com

IMPACT OF ORGANIC WASTE TREATMENTS ON THE FATE OF PHARMACEUTICALS AND PERSISTENT COMPOUNDS

Marjolaine Bourdat-Deschamps, Nicolas Sertillanges*, Sabine Houot*, Claire-Sophe Haudin**, Nathalie Bernet*, Valentin Serre*, Ghislaine Delarue*, Dominique Patureau**

**INRA*
***AgroParisTech*

The fate of 37 pharmaceuticals, 13 polycyclic aromatic hydrocarbons (PAHs), 3 nonylphenol ethoxylates (NPEs) was assessed during anaerobic digestion, composting, liming and dewatering. Samples came from industrial plants treating one or a mixture of various organic residues such as sewage sludge, manure, food waste, crop waste. The novelty resides in the side-by-side comparison of a variety of micropollutants sampled on seven industrial sites with different treatment processes, particularly agricultural sites on which very few data have been recorded.

Not all pollutants were found on all sites. Particularly none of the sulfonamides was found in the samples excepted sulfadiazine in one sample; the same for lincomycin, ivermectin, eprinomectin, levamisol, tylosineB, ketoprofen, marbofloxacin and acetamidophenol. In agricultural sites, treating manure and slurry, mainly fluoroquinolones, tetracyclines, trimethoprim and tylosine were quantified. PAH and NP, as persistent and ubiquitous contaminants, were also quantified at low level in these samples. By comparison, urban samples contained many of the targeted contaminants excepted those listed above. The territorial sites that treated mixture of wastes were similar in terms of contaminants patterns to both agricultural and urban sites.

Concerning the fate of pharmaceuticals during anaerobic treatments, it seemed that many compounds were removed independently of the organic residue types, i.e., norfloxacin, ciprofloxacin, doxycycline, anhydro-chlortetracycline, anhydro-tetracycline, trimethroprim, tylosine, spiramycine were removed up to 70% whereas other compounds like erythromycin, fluoxetine, carbamazepine, diclofenac and ibuprofen presented removals between 30-70%. For NP, it seemed that NP1EO was transformed into NP during the anaerobic treatments. PAHs, particularly the low molecular weight PAHs were lowly removed between 0-70%.

For the dewatering processes (centrifuge, thermal dryer, filter press), an apparent removal was calculated based on the difference of concentration between the input of the process and the remaining solid fraction coming out from the process (the aqueous fraction was not sampled and analysed). If the dewatering process performs correctly, this apparent removal is null. If they are some losses of suspended solids in the aqueous fraction or if compounds are much more soluble, this removal may be positive. This was observed for PAH, some fluoroquinolones and tetracyclines in both less efficient dewatering processes. In the process using thermal drying, some losses were observed for PAH, fluoxetine, carbamazepine and diclofenac, potentially due to temperature instability or volatilisation.

Many pharmaceuticals, NPEs and PAHs were removed during composting whatever the organic residue types. However, none of the output samples was free of micropollutants, meaning that whatever the treatment efficiency in removing micropollutants, the resulting treated organic residues, mainly spread on soils, contain these compounds that could impact the terrestrial ecosystem. Based on this work, micropollutants fluxes on soil could be calculated, compared between various organic residues at a watershed scale and also used for environmental risks assessment (Bourdat-Deschamps et al., 2017).

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Correspondence to: marjolaine.deschamps@inra.fr

INTERACTIVE EFFECTS OF MICROPLASTICS AND THE ANTIBIOTIC CLARITHROMYCIN ON RIVER BIOFILMS: AN ECOTOXICOLOGICAL PERSPECTIVE

Lúcia Santos, Ferran Romero*, José Castaño-Ortiz*, Julio Lopez-Doval*, Damià Barceló*, Sara Rodruíguez-Mozaz**

**Catalan Institute for Water Research (ICRA)*

Microplastics are small particles of plastics with a diameter of less than 5 mm, than can be either specifically manufactured at a micro-size (primary microplastics) or originated from the fragmentation of plastics due to physical, chemical or biological degradation processes (secondary microplastics). Microplastics comprise a very heterogeneous and persistent group of particles that vary in size, shape, chemical composition, among other properties. They have been recognized as an emerging environmental threat for aquatic and terrestrial ecosystems and, in a last instance, to human health. An important concern associated with microplastics is their ability to absorb other environmental chemical contaminants from the surrounding water column, contributing to their dissemination to new locations and facilitating their contact with non-target organisms. In this context, it is important to fill the current gap of knowledge on the interactive effects of microplastics with other emerging contaminants, especially in what concern to lower levels of food webs as river biofilms.

The present work aimed to evaluate the interactive effects of polyethylene on the toxicity of the antibiotic clarithromycin to river biofilms. For that purpose, artificial mesocosms were used to perform short-term exposure experiments (72h). Different structural and functional endpoints were selected to assess the toxic effects of clarithromycin and polyethylene to river biofilms following single and combined exposures, namely: algal biomass, in vivo chlorophyll fluorescence, extracellular enzymatic activities, and metabolic biofilm rate. The concentration of the contaminants in water was also monitored.

In general, polyethylene microplastics showed a low toxicity in river biofilms, while clarithromycin caused a pronounced decrease in photosynthetic activity and net metabolism. The co-exposure to both emerging contaminants showed a statically significant decrease in the content of chlorophyll-a. Although, microplastics did not seem to impact river biofilms, when co-exposed to other contaminants like the antibiotic clarithromycin could enhance its toxic effects. Therefore, future research is needed, since it was proved that the concomitant presence of microplastics with other emerging contaminants may modify their toxicity to river biofilms and, probably, to the entire river ecosystem.

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Correspondence to: lhsantos@icra.cat

UPTAKE OF CARBAMAZEPINE BY GREEN PEA PLANTS AND ITS TRANSFORMATION IN SOIL-PLANT SYSTEM

Radka Kodešová, Giuseppe Brunetti**, Miroslav Fér*, Antonín Nikodem*, Helena* Švecová****, Kateřina Grabicová***, Aleš Klement*, Roman Grabic****

**Czech University of Life Sciences Prague*
***BOKU*
****University of South Bohemia in České Budějovice*

Green pea plants (Pisum sativum L.) were planted in 26 soil columns (height of 20 cm, diameter of 17 cm) under greenhouse conditions. Soil was taken from the surface horizon of a Haplic Chernozem. Plants were initially irrigated by fresh water (16 days). Next plants in 16 soil columns were irrigated with solution of carbamazepine (CBZ concentration of 100 ng/mL) and 8 with fresh water. The columns were analyzed as follows. One column was dissembled 16th day to examine masses of stems, leaves and roots (depths of 0-5, 5-10, 10-15, and 15-20 cm). Next sampling was carried out 23rd, 30th, 41st and 48th day. Four columns were always analyzed to obtain an information about a plant growth (i.e., mass of stems, leaves, blossoms, pea pods and roots in different soil layers), concentrations of CBZ and its metabolites in plant tissues and concentrations of compounds in soils. One column irrigated with fresh water was similarly analyzed as control. Plant leaves were scanned and their area was evaluated using the ImageJ program. One column was also always used to analyze soil hydraulic properties on undisturbed 100-cm3 soil samples taken from the soil columns using the multistep outflow experiment. Soil water contents (at depths of 2.5 and 15 cm) and pressure heads (at depths of 5 and 15 cm) were measured in 4 columns during the entire experiment. In addition, air temperature and humidity, and potential evaporation were monitored. The sorption and degradation of CBZ was evaluated using the batch sorption and degradation experiments. The HYDRUS-1D model and a recently developed dynamic plant uptake module (DPU) for HYDRUS (Brunetti et al., 2019) were used to interpret an observed hydraulic regime in soil and a CBZ translocation and transformation in the soil-plant continuum. CBZ was freely taken up by plants. The largest concentrations in roots were observed in the top layer (depths of 0-5 cm) and gradually decreased with depth, which corresponded to the CBZ concentrations in soil. The negligible and low concentrations of a CBZ metabolite carbamazepine-10,11-epoxide (EPC) were measured in soils and roots, respectively. This indicated negligible CBZ degradation in soils and very low CBZ metabolization in plant roots. Gradual increases in the CBZ concentrations were observed in stems, blossoms and pods. The CBZ concentrations in leaves initially increased and then remained constant. At the end of the experiment the CBZ concentrations in stems were twice higher than in leaves. However, while the concentrations of EPC in stems, blossoms and pods were low, the EPC concentration in leaves were one-order magnitude higher than the CBZ concentrations. The low concentration of other 2 metabolites of CBZ (oxcarbazepine and trans-10,11-dihydro-10,11-dihydroxy carbamazepine) were measured 48th day in leaves This indicated a very high efficiency of green pea plants in metabolizing CBZ in their leaves. The DPU-HYDRUS model successfully interpreted observed data and estimated metabolization rates in plant tissues.
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Correspondence to: kodesova@af.czu.cz

THE GLOBAL DATABASE "PHARMACEUTICALS IN THE ENVIRONMENT" - UPDATE AND NEW ANALYSIS

Hein Arne, Gildemeister Daniela*, Jungmann Dirk**, Rönnefahrt Ines**

**German Environment Agency, Section IV 2.2 - Pharmaceuticals*
***Technische Universität Dresden, Faculty of Environmental Sciences, Institute of Hydrobiology*

Pharmaceutical residues occur globally in the environment. This is demonstrated in the updated database "Pharmaceuticals in the Environment". Residues of pharmaceuticals in the environment have been measured in 75 countries in all UN regions. Worldwide 771 active substances or their transformation products were reported and 596 for the European Union.

The residues of pharmaceuticals are a potential risk to the environment and their occurrence raised an increasing concern. In the last years, studies on this potential risk increased. Hence, the exposure of the natural environment is characterized much better. To organize the huge amount of information caused by the global environmental exposure situation, the German Environment Agency (UBA) initiated this project to collect all these data within one publicly available database. Besides the database evaluation on the global distribution of the active pharmaceuticals substances from the European Watch List (WL) for emerging water pollutants and the main antibiotic groups is presented in a corresponding report and exemplary on the poster.

The database now contains 178,708 entries. Most of these substances were found in the effluents of wastewater treatment plants (liquid emission – worldwide: 613, EU: 474). 528 substances were detected worldwide in surface water, groundwater and drinking water. 19 substances were detected in surface water, groundwater or drinking water in all five UN regions. For the database 1,519 publications and 240 review articles were comprehensively reviewed and analysed. Environmental concentrations of human and veterinary pharmaceutical residues could be collected for 53 matrices.

The data were transferred from the publications, reports and other data sources into the database (MEC database). You are invited to browse the 178,708 data entries from 1,519 publications in the publicly available database for download as Microsoft Excel© or as Microsoft Access© file.

Correspondence to: daniela.gildemeister@uba.de

THE GREY WATER FOOTPRINT OF HUMAN AND VETERINARY PHARMACEUTICALS

Lara Wöhler, Gunnar Niebaum**, Maarten Krol*, Arjen Hoekstra**

**University of Twente*
***University of Osnabrück*

Water pollution by pharmaceuticals is widespread, causing both environmental and human health risks from regional to global level. There are several emission sources and pathways how pharmaceutical compounds enter freshwater resources. Within this study, we assess pharmaceutical water pollution from human and veterinary pharmaceuticals at three geographical levels: global, national (considering Germany and the Netherlands) and catchment level (with a case study for the Vecht basin shared by Germany and the Netherlands). We study different substances depending on data availability, which varies across geographical levels.

The study uses the grey water footprint (GWF) concept to assess water pollution by pharmaceuticals. The method indicates the volume of water that is required to assimilate pollutants, which is the volume of water needed to dilute pollutants to the extent that the quality of the ambient water remains above water quality standards.

The GWF is estimated from pharmaceutical loads entering the aquatic environment from households, hospitals and animal husbandry considering different pathways. GWFs are thereby expressed as polluted water volumes per area, but also per community, per person, and per unit of animal product (meat, milk, egg). Further, we compare the GWF per person related to direct pharmaceutical use with the GWF per person from the consumption of animal products (in the supply chain of which veterinary pharmaceuticals were used). For the Vecht basin we additionally estimate the water pollution level (WPL) per sub-catchment by comparing the GWF to available runoff, which enables us to identify geographic hotspots. At all levels, pharmaceutical water pollution substantially adds to earlier water footprint studies that excluded this type of pollution and demonstrates the importance to include pharmaceutics in water footprint studies.

Correspondence to: l.wohler@utwente.nl

PHARMACEUTICALS IN SURFACE AND GROUND WATERS IN THE CZECH REPUBLIC

Vit Kodes, Jitka Vejvodova*, Jindrich Freisleben*, Roman Grabic***

**Czech Hydrometeorological Institute*
***University of South Bohemia in Ceske Budejovice*

Monitoring of pharmaceuticals in surface and ground waters has been recently introduced in the Czech Republic. In total 55 substances from various ATC groups have been monitored in water such as NSAIDs, antibiotics, beta-blockers, psycholeptics, antiepileptics, analgesics, diuretics, antimycotics, antidiabetics etc. using LC-MS/MS. Results of in total 7771 surface water samples from 592 sites and 4079 groundwater samples from 702 sites proved an occurrence of various pharmaceuticals in the 2016-2018 period. The most frequently found pharmaceuticals in rivers were metformin (99.6 % of 760 samples), tramadol (88 % of 3056 samples), oxypurinol (88 % of 510 samples), ibuprofen-2-hydroxy (77.8 % of 1279 samples), metoprolol (77.5 % of 3055 samples), carbamazepin (77.2 % of 7241 samples) and diclofenac (72.4 % of 7279 samples). Highest concentrations were recorded for oxypurinol (26000 ng/l), ibuprofen (15000 ng/l), iopromide (13000 ng/l) and metformin (11000 ng/l). The most frequently found pharmaceuticals in groundwater were carbamazepin (4.3 % of 4071 samples), gabapentin (3.6 % of 674 samples) and diclofenac (3.2 % of 1356 samples). Highest concentrations were recorded for paracetamol (1300 ng/l), valsartan (1090 ng/l) and gabapentin (751 ng/l). In addition POCIS passive samplers were utilized for screening of 148 pharmaceuticals in rivers at 43 sites finding 119 substances.

Correspondence to: vit.kodes@chmi.cz

SUBMARINE GROUNDWATER DISCHARGE AS A SOURCE OF PHARMACEUTICAL AND CAFFEINE RESIDUES IN COASTAL ECOSYSTEMS: BAY OF PUCK (SOUTHERN BALTIC SEA) CASE STUDY

Ksenia Pazdro, Beata Szymczycha*, Marta Borecka**, Anna Białk-Bielińska**, Grzegorz Siedlewicz**

**Institute of Oceanology, Polish Academy of Sciences*
***University of Gdańsk, Faculty of Chemistry*

The occurrence of pharmaceutical residues in water systems has been recognized as a potential problem for human health and aquatic organisms, nevertheless the level of knowledge of their sources and presence in the marine ecosystems is still insufficient. The presented study was designed to assess the occurrence of sixteen pharmaceutical and caffeine residues in groundwater, submarine groundwater discharge (SGD), rivers and coastal seawater in the southern Baltic Sea. The Puck Bay, which is an active groundwater discharge area, has been chosen as a model study site to assess the costal ecosystem vulnerability to the pharmaceutical and caffeine residues supply. A special focus was placed on tracing the possible sources of pollution for groundwater and SGD based on the composition of collected samples. Five pharmaceuticals (carbamazepine, sulfapyridine, sulfamethoxazole, ketoprofen and diclofenac) and caffeine were detected in all analyzed samples in varying concentrations (from below the detection limit to 1528 ng/L). Groundwater was in general enriched in the analyzed compounds and consequently SGD has been identified as an important source of pharmaceutical and caffeine residues in the Bay of Puck coastal waters. It has been recognized that chemical load associated with SGD can affect coastal ecosystems equally or even into greater extent than rivers and surface runoff. An environmental risk assessment of five most often detected pharmaceuticals and caffeine in water samples was performed based on comparison to relevant predicted no effect concentration (PNEC). This preliminary risk assessment revealed that the presence of the most often detected compounds, like diclofenac and caffeine, may be of high ecological relevance.

Correspondence to: pazdro@iopan.gda.pl

HOW PREDICTABLE ARE PHARMACEUTICAL LOADS IN WASTEWATER TREATMENT PLANT INFLUENTS AND EFFLUENTS?

Gunnar Niebaum, Lara Wöhler**, Jörg Klasmeier***

**Institute of Environmental Systems Research, Osnabrück University*
***Twente Water Centre, Faculty of Engineering Technology, University of Twente*

Comprehensive monitoring of chemicals in the environment is time consuming and expensive. Therefore, geo-referenced simulation models such as GREAT-ER and PhATE can be used to support chemical exposure assessment in whole watersheds. In these models, sewage treatment plants are implemented as point sources in the river network. The outcome of the models, however, relies on the quality of the input parameters defining the emission load via treated effluents into the river system. A well-established approach to predict pharmaceutical loads entering a wastewater treatment plant (WWTP) (L_in) is based on the assumption of constant average consumption (application) per person and excretion percentages. The load discharged into the receiving waterbody is finally calculated by applying a percent WWTP removal efficiency for the predominant wastewater treatment types. The aim of this study is to evaluate the uncertainty of this approach for different pharmaceuticals and WWTPs to be used in geo-referenced exposure models. Predicted loads are estimated based on national prescription data (purchased), excretion rates and WWTP removal rates (both literature research). The predicted loads are compared to a data set for 10 pharmaceuticals in inflow and effluent of 18 Dutch sewage treatment plants for winter and summer season. The logarithmic ratio of predicted to measured loads (log Δ) was used to examine prediction accuracy of L_in. Calculated removal efficiencies are also compared to literature values. Preliminary results show good agreement for metformin (MTF), metoprolol (MPO), sulfamethoxazole (SMX) and oxazepam (OXA) (more than 70% of measured loads in a two-fold range around the predicted load), an overestimation of azithromycin (AZI), carbamazepine (CBZ), diclofenac (DCL) and erythromycin (ERY) (more than 30% log Δ > log 2) and an underestimation of valsartan (VAL) (more than 50% log Δ < log 0.5) indicating the need for calibration of the respective input parameters. Overall prediction accuracy was calculated summing up absolute log Δ values for each compound. This resulted in the order MPO < MTF < OXA < SMX < CBZ < DCL < AZI < CLA < VAL < ERY. Calculated median removal efficiencies agree reasonably well with literature values. For azithromycin, clarithromycin and valsartan there are indications of seasonal differences in the removal efficiencies.

Correspondence to: gniebaum@uos.de

NUCLEAR MEDICINE ACTIVITIES AND PRESENCE OF RADIONUCLIDES IN THE BARCELONA METROPOLITAN AREA URBAN WATER CYCLE

Dani Mulas, Antonia Camacho*, Ricard Devesa**, Maria Amor Duch**

**INTE*
***AGBAR*

The Barcelona metropolitan area (BMA; 3.2 M inhabitants) has an integrated urban water cycle management. In order to achieve the water quality standards different type of treatment plants are located along the drinking, sewerage and reuse networks.

In nuclear medicine (NM), radionuclides are administered to patients in diagnosis and treatment procedures, excreting part of the radionuclides into the urban water cycle through the wastewater and released partially into the environment. Thus, the levels of NM radionuclides in waters and materials (sludge, sand, granular activated carbon) from the urban water cycle treatment plants must be experimentally checked to perform a risk assessment. A total of 196 samples were taken at 7 wastewater treatment plants (WWTPs), 1 reclaimed water treatment plant (RWTP) and 1 drinking water treatment plant (DWTP). The concentrations were determined by gamma-spectroscopy techniques and reported in Bq (disintegrations per second).

A total of 5 different NM radionuclides were found in the analysis performed in the BMA urban water cycle. In the case of water (Bq/L) and sludge (Bq/kg dry weight) from the WWTPs samples, the highest maximum values and detection frequencies corresponded to Tc-99m (50 Bq/L; 9530 Bq/kg d.w.) and I-131 (17 Bq/L; 2840 Bq/kg d.w.). Ga-67 (0.7 Bq/L; 206 Bq/kg d.w.), In-111 (0.4 Bq/L; 155 Bq/kg d.w.) and I-123 (0.6 Bq/L; 80 Bq/kg d.w.) were also found but showed significantly lower levels. Regarding reclaimed water for reuse from the RWTP and materials from DWTP, I-131 was found showing maximum concentrations of 0.9 Bq/L and 36 Bq/kg d.w. respectively.

Radiological assessment was carried out considering the very conservative scenarios of direct ingestion of water and radioactive waste exemption levels of solid materials. Despite the fact that the results in waters and materials does not represent a significant radiological risk, I-131 was pointed out at the most significant NM radionuclide from the radiological protection point of view. Novel methods of I-131 partitioning analysis as well as prognosis models capable to predict the I-131 sewage effluent levels at WWTPs were adapted successfully to a WWTP. I-131 partitioning results pointed out that the settling fraction predominates in the reactor while in the rest of the WWTP samples dissolved iodide fraction predominated. Furthermore the activated sludge reactors from WWTPs were revealed as the most significant step for I-131 removal from the urban water cycle. Reactors line with the highest total nitrogen kjeldahl removal (92%) were also the most effective in I-131 removal (76%).

The frequencies of detection and mean levels found at the WWTPs of Ga-67, Tc-99m, In-111 and I-131 agreed with the NM radionuclides total activity administered in the region for each radionuclide. Moreover, I-131 was pointed out as the most relevant radionuclide from the radiological protection point of view, with permanence in all the steps of the BMA urban water cycle.

Correspondence to: dani.mulas@upc.edu

EMERGING CONTAMINANTS IN SOIL AND PLANT TREATED WITH WASTEWATER UNDER REAL-WORLD ENVIRONMENTAL CONDITIONS IN THE AL HAYER AREA, SAUDI ARABIA: UPTAKE, ACCUMULATION AND HEALTH RISK ASSESSMENT.

Yolanda Picó, Rodrigo Alvarez-Ruiz*, Ahmed H. Alfarhan**, Mohamed A. El-Sheikh**, Samy M. Alobaid**, Damià Barceló**,****

**Environmental and Food Safety Research Group (SAMA-UV), Desertification Research Centre CIDE (CSIC-UV-GV), Faculty of Pharmacy, University of Valencia, Av. Vicent Andrés Estellés s/n, Burjassot, 46100 Valencia, Spain*
***Department of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455, Ryadh 11451, Saudi Arabia*
****Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, C/ Emili Grahit, 101 Edifici H2O, 17003 Girona, Spain.*

During the last 60 years the development programs in various fields of Saudi Arabia, especially in the last two decades, have left clear marks on the country landscape. Moreover, there is an increase in treated sewage water which had adverse affects on the marine and terrestrial resources. In many Arid and semi arid regions, reuse of this water is a necessity for crop irrigation. The presence of organic emerging contaminants (ECs) in this water and their translocation to plants may represent a risk of human exposure. Nevertheless, information available about real field crops is scarce and focused on a limited number of compounds. The novelty of this work relays in the large number of ECs covered and the variety of crops (cabbage, barley, green beans, eggplants, chili, tomato and zucchini) analyzed. Extraction procedure developed provided an appropriate extraction yield (up to 50% of the compounds were recovered within a 70–120% range), with good repeatability (relative standard deviations below 20% in most cases) and sensitivity (LOQ b 25 ng g−1) for the model compounds. Determination by liquid chromatography quadrupole time-of-flight (LC-QqTOF-MS) is able to identify N2000 contaminants. Sixty-four ECs were identified in wastewater among which, six pharmaceuticals (atenolol, caffeine, carbamazepine and its metabolites 10,11-epoxycarbamazepine, gemfibrozil, and naproxen) and seven pesticides (acetamiprid, atrazine deethyl, azoxystrobin, bupirimate, diazinon, malathion, pirimicarb and some of their metabolites) were detected in plants also. Furthermore, one metabolite of the ibuprofen (not detected in water or soil), the ibuprofen hexoside was also found in plants. Up to our knowledge, this study demonstrates for the first time the accumulation of ECs in crops irrigated with treated wastewater under real non-controlled environmental conditions.

CHEMICAL FINGERPRINT OF SEWAGE SLUDGE : COMBINATION OF TARGET, SUSPECT AND NON TARGET ANALYSIS

Caroline Gardia-Parège, Marie-Hélène Dévier*, Eric Moïs**, Stéphanie Bémelmans**, Karyn LeMenach*, Laurent Peluhet*, Emmanuel Geneste*, Pierre Labadie*, Cécile Kech**, Hélène Budzinski**

**University of Bordeaux, CNRS, UMR EPOC, équipe LPTC, 33405 Talence cedex, France*
***Scientific Institute of Public Service (ISSeP), 4000 Liège, Belgique*

Human activities release a wide range of micropollutants (MPs) in the sewage network and consequently discharge them to sewage treatment plant (WWTP). A part of this MPs are treated by the treatment processes. However, the reduction of MPs load in the treated effluents is not directly related to the degradation of these compounds. Indeed, a part of these molecules could be transformed and/or trapped, and so accumulated in sewage sludges. Thus, the use of sludges as fertilizer in agriculture may act as an additional MP source for soil and aquatic ecosystems (after water runoff or infiltration). A better chemical characterisation of sludge obtained by various processes is thus necessary and could help to predict the potential associated release of MPs in the environment and finally the associated risks for wildlife.

For this purpose, a chemical screening was performed on thirty different sludges originating from various treatment processes (e.g. activated sludge, planted reeds, membrane bioreactor, sequencing batch reactor…). The most exhaustive screening of MPs possible, based on target, suspect and non-target analyses, has been carried out by liquid and gas phase chromatography coupled to tandem mass spectrometry (MS/MS) and high resolution mass spectrometry (HRMS – QTOF technology). For the target and the suspect approaches, 57 pollutants belonging to different classes (e.g., detergents, personal care products, perfluorinated compounds, plasticizers, flame retardants…) were screened and quantified. The list was established on various criteria such as occurrence, relevance, toxicity, regulations, …. In parallel the non target approach was undertaken to enlarge the spectrum of screened compounds using a non a priori strategy.

Phtalates, alkylphenols, perfluorinated compounds, hexabromocyclododecanes, and chloroalkanes have been detected by target analysis in several sludges, with phtalates and alkylpenols as predominant families among the observed molecules. In addition the suspect mode has brought 21 more molecules among them personal care products (musk, UV filters, antioxidants, biocides). The non target analyses have allowed establishing an overall contamination profile for each sample. The results showed the detection of thousands features in each sludge. Among these detected entities, untargeted compound classes such as polycyclic aromatics hydrocarbons, several pharmaceuticals, pesticides, steroids and transformation products have been put in evidence. The chemical fingerprints of samples were also compared by statistical means. This comparison allowed discriminating a treatment (planted reeds) as a potential promising process to reduce the number of compounds in sewage sludge.

Correspondence to: caroline.gardia-parege@u-bordeaux.fr

DETECTION, OCCURRENCE AND FATE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN A TYPICAL MEDITERRANEAN COASTAL WETLAND

Daniele Sadutto, Yolanda Picó**

**Environmental and Food Safety Research Group of the University of Valencia (SAMA-UV), Desertification Research Centre (CIDE)*

The "Anthropocene" as new geological area view as the period during which human activity has been the dominant influence on climate and the environment [1] gains defenders year after year. An important anthropogenic hazard is the environmental contamination due to the release of chemical substances affecting ecosystems that is growing parallel to the increase of population [2]. One of the most representative contaminant related to the human impact are the contaminants of emerging concern (CECs), particularly, pharmaceuticals and personal care products [3].

The work focused on determination of 35 Pharmaceuticals and Personal Care Products in water and sediment samples of 33 sampling stations located in Albufera Natural Park (an area of 21 thousand hectares, it is located in Valencia, Spain). The extraction was based on solid-phase extraction (SPE) using Strata X cartridges treated with sodium dodecyl sulfate (SDS) or mixed mode weak anion exchange cartridges. The determination was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS) with a triple-quad using two precursor product ion transitions for each compound with the exception of ibuprofen that only gave one product ion in the multiple selected reaction monitoring mode (MRM).

Of the 33 samples studied, 35 drugs and PPCPs of different categories have been analyzed, where analgesics, antibiotics and preservatives stand out for their variability and concentration. The most abundant ones are anti-inflammatory and analgesic drugs (salicylic acid, diclofenac and ibuprofen), antihypertensive (furosemide), anticoagulant (warfarin), stimulants (caffeine) and preservatives (parabens). Diclofenac, ibuprofen, furosemide and warfarin are at low concentrations instead caffeine and salicylic acid are at higher concentrations. In this study, the area of the natural was divided in North and South (the human pressure is higher in the north) as well as depending on the water origin in river water, irrigation channels and lake. The concentrations and pattern of pharmaceuticals was significantly different between the different sources.

The results show a deteriorated environment because of a water treatment system that is not very effective for the removal of this type of compounds. Furthermore, the results pinpointed the need of further studies on the short and long term ecotoxicological impact in animal and vegetal species.

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Correspondence to: sadutto@uv.es

DROSPIRENONE INDUCES THE ACCUMULATION OF TRIACYLGLYCERIDES IN THE FISH HEPATOMA CELL LINE, PLHC-1

Anna Marqueño, Elisabet Pérez-Albaladejo*, Cinta Porte**

**IDAEA-CSIC*

Drospirenone (DRO) is one of the most commonly used progestins reaching the aquatic environment through wastewater treatment plant effluents. It is a progesterone receptor agonist, and as such, can act primarily in the brain and reproductive organs of fish. In order to better understand and predict its effects, this work evaluates the lipidomic changes induced in PLHC-1 cells after exposure to drospirenone at concentrations below the EC10 (1 and 10 μM) by direct injection of the lipid extracts into an ESI(+/−) Orbitrap mass spectrometer. A significant accumulation of triacylglycerides, particularly long chain ones with unsaturated fatty acid moieties (TGs 46:2, 56:4–7; 58:5–8) and a concomitant decrease of diacylglycerides (DGs 32:1, 34:1–2, 36:1–2, 38:2–4) was observed after 48 h exposure to 10 μM DRO, which corresponded to an intracellular concentration of 8.3 ng·mg−1 protein. No significant alteration of PLHC-1 cell lipids was observed following exposure to 1 μM DRO. EC50 for the cytotoxicity of DRO ranged from 105-119 μM (24 h exposure) to 51-58 μM (48 h exposure). The study evidences a dysregulation of neutral lipid metabolism and increased TG/DG ratio in fish hepatic cells exposed to DRO and detects the minimal internal concentration of DRO necessary to produce this alteration (low ng/mg protein range). Considering that the entrance of DRO in the aquatic environment through waste water treatment plants is constant, it is likely that long-term exposures to low doses of DRO could lead to a similar internal concentration in the liver of exposed fish.

Correspondence to: amaqam@cid.csic.es

NON-TARGET ASSESSMENT OF THE OCCURRENCE OF ORGANIC CONTAMINANTS IN SEWAGE SLUDGE

Daniele Sadutto, Yolanda Picó**, Alejandro Cuñat**, Rodrigo* Álvarez-Ruiz**

**Food and Environmental Safety Research Group (SAMA-UV), Desertification Research Centre (CIDE-UV, GV, CSIC)*
***Environmental and Food Safety Research Group of the University of Valencia (SAMA-UV), Desertification Research Centre (CIDE)*

The human activity generates anthropogenic compounds that end up in the wastewater treatment plants (WWTPs). In these plants, part of them could be retained in the sewage sludge. The study of the presence of contaminants in this sludge involves a great challenge due to its high organic matter content. This is the reason why this matrix has not been as widely studied as the influent and effluent water of the WWTP. However, in Spain, similarly to other European countries, the 80% of the sewage sludge is used as a fertilizer for the crops, being of great interest to know the different compounds present in them and asses the environmental risk of their utilization. The sludge samples are from 8 WWTPs with different treatments. Samples were extracted using a Methanol-McIlvaine Buffer mixture, assisted by ultrasound, the supernatant was cleaned up with solid phase extraction (SPE) using StrataTMX polymeric reversed phase cartridges and then the analytes were eluted with methanol at gravity flow. To identify as many compounds as possible and obtain high quality information, non-target identification was used with a liquid chromatograph triple quadrupole time-of-flight (LC-QqTOF). 50 different compounds were identified with high degree of confidence, belonging 31 of them to the group of the pharmaceuticals, and 14 were confirmed with analytical standards. Several human metabolites (nucleotides, amino acids, etc.) were also detected. On the other hand, several compounds were tentative identified but further study and analytical standards are still needed for their confirmation. In conclusion, the results of this study demonstrate the interest of high resolution mass spectrometry to draw the profile of contaminants in solid complex matrices. Furthermore, the data obtained provides information about the potential risk of using the sewage sludge for agriculture. Further research is needed to get a complete profile of the occurrence of contaminants in the sewage sludge.

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Correspondence to: sadutto@uv.es

A SOLUTION TO THE WATER SCARCITY PROBLEM ON THE MEDITERRANEAN COUNTRIES: HYDROUSA, CLOSING THE LOOPS.

Marc Castaño, Lucia Gusmaroli*, Sara Rodríguez-Mozaz*, Gianluigi Buttiglieri**

**Catalan Institute for Water Research (ICRA) / University of Girona (UdG)*

In the later years, water scarcity has become one of the main problems for the society due to the climate change and the growing overpopulation. Even if this is a worldwide problem, some of the most affected places are the Mediterranean coast countries. Therefore, these countries need the development of new strategies to obtain fresh water from non-conventional sources. Some of these strategies are evaluated in the large-scale European project HYDROUSA. The project will provide innovative, regenerative and circular solutions for nature-based water management of Mediterranean coastal areas, closing water loops; nutrient management, boosting the agricultural profile; based on circular value chains.

One of the possibilities to obtain fresh water consists in the reuse of (waste)water from wastewater treatment plants or from other non-conventional sources (like greywater, rainwater, seawater, etc.). Nonetheless, reclaimed water can imply health problems if organic micropollutants, among the other possible concerns, are not completely removed by the wastewater treatment technologies. Micropollutants are substances that even at low concentrations can have consequences for the environment or human beings. Thus, it is very important to track them through the water cycle and determinate their origin. Eventually, less harmful substances can be proposed to substitute them. Among the most problematic organic micropollutants there are antibiotics compounds. These substances are used to stop the growth of bacteria in an organism but a continuous exposure of microbes to this kind of substances can generate the appearance of resistance genes. Many other pharmaceuticals and organic micropollutants should be considered too, like the one included in the Watch List 2018/840, including pesticides, endocrine disruptors, etc. Furthermore, an important fraction of the reclaimed water produced in the project will be used to irrigate crops. Even if most part of the micropollutants can be removed, some compounds will remain and could be transferred to the vegetables.

Therefore, it is of vital importance to elaborate comprehensive analytical methods capable of detect and quantify micropollutants even at concentrations of ng/L. One of our task in HYDROUSA is to develop methodologies to monitor the presence of these compounds in treated wastewater and/or the other non-conventional water source previously mentioned. This way we will also be able to evaluate the most efficient treatment train to be applied in three Greek islands, in terms of removal of micropollutants. These methods will aim to simplify the procedures and, when possible, unify them. Moreover, methods of extraction will also be developed to analyse the possible micropollutants that could leak into cultivated crops and vegetables. Different methodologies will be considered such as ultrasonication, QuECheRS or beat beating

Correspondence to: mcastano@icra.cat

IS THE MAR MENOR LAGOON (SE SPAIN) TAKING A BREAK FROM PHARMACEUTICAL POLLUTION? A DECADE OF PHARMACEUTICAL MONITORING IN A THREATENED MEDITERRANEAN COASTAL ECOSYSTEM

Jose Maria Castaño-Ortiz, Rubén Gil-Solsona*, Víctor Manuel León**, Lúcia Helena Moreira*,* Lírio Matias *Santos*,***, Damià Barceló*, Sara Rodriguez-Mozaz**

**Institut Català de Recerca de l'Aigua (ICRA), Universitat de Girona, Girona, Spain*
***Instituto Español de Oceanografía (IEO), Oceanographic Centre of Murcia*
****IDAEA-CSIC, Department of Environmental Chemistry, C/ Jordi Girona 18-26, 08034 Barcelona, Spain*

The Mar Menor is a coastal lagoon heavily impacted by surrounding anthropogenic activities. Intensive agriculture, tourism and urbanization constitute major human pressures to the lagoon, and have contributed to its deterioration in the last decades. The confinement from open sea makes coastal lagoons especially sensitive to human disturbances and the Mar Menor is no exception. In this context, El Albujón watercourse acts as the main collector of sewage effluents, as well as agricultural contaminants from irrigated crops. As it drains into the lagoon, El Albujón discharges pollutants of different types and sources, including fertilizers, pesticides or pharmaceuticals (PhACs). This adds up to direct urban discharges into the lagoon, surface runoff and groundwater inputs.

Pharmaceutical residues (PhACs) have received little attention since their early detection in the Mar Menor (2010-2011). A set of different compounds, like antibiotics and psychiatric drugs, were found in surface waters at levels ranging from low ng/L, up to tens and hundreds ng/L (lorazepam and azithromycin, respectively) [1]. Management actions have been implemented to mitigate environmental pollution in the area. An example is the reuse of effluent water from Los Alcázares WWTPs for crop irrigation purposes, thus limiting direct discharges into El Albujón watercourse. In this work, the possible impact of such management practices was assessed by determining the spatial distribution and levels of 60 pharmaceutical residues in 2018-2019 relative to the 2010-2011 period.

Surface water was collected from nine locations across the Mar Menor lagoon in 2018 (summer) and 2019 (winter). Samples were stored in glass bottles and frozen until treatment following the extraction and preconcentration procedure from Gago-Ferrero et al. [2]. Methanolic extracts were led to dryness under N2 and reconstituted to 1 mL methanol:H2O (1:9). Analysis was carried out as described in Gros et al. [3] via LC-MS/MS.

The lower occurrence and overall levels of selected PhACs in surface waters may relate to the recent implementation of management measures, such as the abovementioned, aiming at reducing the discharge of agricultural and urban pollutants into the Mar Menor lagoon. However, additional pressures have put the lagoon in a critical situation. Future research will be performed in order to determine PhACs levels in sediments and biota.

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Correspondence to: jcastano@icra.cat

INTRODUCING 'PLAS-MED' MICROPLASTICS AND MICROCONTAMINANTS IN THE MEDITERRANEAN COAST: ENVIRONMENTAL AND HUMAN HEALTH IMPACTS

Natalia Ospina-Alvarez, Lucía Helena Santos*, José María Castaño*, Rubén Gil-Solsona*, Sara Rodríguez-Mozaz*, Juan Antonio Campillo**, Víctor M. León**, Concepción Martínez Gómez**, Esteban Abad***, Marta Llorca***, Marinella Farré****

**Catalan Institute for Water Research (ICRA); University of Girona. Girona, Spain*
**Spanish Institute of Oceanography (IEO, Murcia Oceanographic Centre. Murcia, Spain*
****Institute of Environmental Assessment and Water Research (IDAEA-CSIC). Barcelona, Spain*

The so-called marine litter, and in particular microplastics (MPLs), are recognised by the scientific community as an emerging risk for the environment and human health. The aim of PLAS-MED is to assess the risks associated with MPLs and their ability to accumulate and transfer other microcontaminants to aquatic organisms, including the highly toxic and persistent marine biotoxins and persistent organic compounds (POPs), as well as contaminants of emerging concern (pharmaceuticals, personal care products, pesticides etc).
This project counts with the participation of three research institutes (Institute of Environmental Assessment and Water Research - IDAEA-CSIC, Spanish Institute of Oceanography - IEO and Catalan Institute for Water Research - ICRA) and is organised in the four research modules with specific objectives:

- Evaluation of the presence, fate and impact of microplastics in marine and freshwater systems, taking the Mediterranean coast as a case study. The project monitors the presence of MPLs, POPs and emerging organic contaminants at the Ebro Delta (NE Iberian Peninsula) and at the Mar Menor coastal lagoon (SE Iberian Peninsula).
- Assessment of the potential of adsorption of the organic contaminants to microplastics by means of mesocosms studies (marine and fluvial), in order to determine their contribution in the transference of such contaminants to the aquatic organisms.
- Study of the bioaccumulation, toxicity and metabolic changes in aquatic organisms in response to the exposure to contaminants, as well as the impact that the associated presence of microplastics might have.
- Evaluation of the potential risk for human health through the consumption of fish and seafood exposed to contaminated MPLs, including the effects from food preparation.

Update information of the action can be followed at https://www.plas-med.es/

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Correspondence to: nospina@icra.cat

PRESENCE OF ANTIBIOTIC RESIDUES IN MARINE, SURFACE AND WASTEWATERS AND POTENTIAL ANTHROPOGENIC SOURCE ASSESSMENT. A CASE STUDY IN THE VULNERABLE AREA OF THE EBRO DELTA (NE SPAIN).

Ruben Gil-Solsona, Jose Maria Castaño Ortiz*, Lucia Helena Santos*, Damiá Barceló Culleres*, Sara Rodríguez-Mozaz**

**Institut Català de Recerca de l'Aigua*

Anthropogenic activities contribute to the discharge of a wide range of xenobiotics into the environment, including pesticides, personal care products or pharmaceuticals. Among these compounds, antibiotics (ABs) can potentially cause a set of adverse ecological effects [1], as for example, the environmental emergence and spread of antibiotic resistance bacteria (ARBs) and genes (ARGs). One of the main anthropogenic sources of ABs and ARBs in natural water bodies are wastewater treatment plants (WWTPs) [2]. Therefore, the monitoring of ABs in the aquatic environment impacted by WWTP discharges is crucial in order to obtain information about their occurrence and to evaluate the potential risks they pose to ecosystems and human health. The aim of this work was the monitoring of antibiotics belonging to different families in the Ebro river and delta basin as well as the identification of possible anthropogenic sources of contamination. Seven sampling points were considered along the final part of the Ebro river (Miravet, Benifallet, Amposta and Deltebre), and eight across the Ebro Delta (four in Alfacs Bay, at south of Ebro mouth, where a WWTP is directly discharging, and four in Fangar Bay, in the north of the Ebro mouth). Moreover, influent and effluent wastewaters were collected in two relevant WWTPs from the study area. Two sampling campaigns were carried out: summer 2018 and winter 2019. Sample treatment and analysis for the analysis of antibiotics was performed according to Gros et al. [1].

Different antibiotics were detected in WWTP waters such as ciprofloxacin (100-300 ng/L in Influent Wastewater (IWW) and 10-30 ng/L in Effluent Wastewater (EWW)) ofloxacin (40-200 ng/L in IWW and 10-20 ng/L in EWW) or sulfamethoxazole (10-20 ng/L in IWW 5 ng/L in EWW), Sulfamethoxazole was also found in river waters (0.3-5 ng/L) and sea waters (0.01-0.02 ng/L), confirming WWTPs as anthropogenic source of ABs contamination in this area. Future research is foreseen in order to analyze antibiotics in fish captured in Ebro river waters, and to assess possible effects on their metabolism.

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Correspondence to: rgil@icra.cat

ELECTRON BEAM IRRADIATION AS A FUTURE ECO-TECHNOLOGY FOR PHARMACEUTICALS DEGRADATION AND WASTEWATER TREATMENT

Malgorzata Siwek, Thomas Edgecock**

**University of Huddersfield*

The interest in using high energy electrons for wastewater purification has been rising for the last several decades. Starting from the early 70s', there have been many laboratory- and industrial-scale plants investigating not only wastewater but also sludge, and sewage sludge disinfection with the high effectiveness. Furthermore, the electron beam has been proven to be a successful approach to various pharmaceuticals and persistent organic pollutants disposal. Nevertheless, before 2000, there were concerns about the perceived high capital costs of the accelerator and with public acceptance of the usage of irradiation for treatment purposes. Nowadays, with increased knowledge and technological development, it may not only be possible but also justified to use the electron beam technology for risk-free pharmaceuticals decomposition, sewage sludge treatment, and bio-friendly fertiliser production.

High energy electrons irradiation is reported to be efficient for the reduction of 4-chlorophenol chloroform, dichloroethane, methyl isobutyl ketone, xylene and phenol, pesticides, polycyclic aromatic hydrocarbons (PAHs) and Polychlorinated biphenyls (PCBs), various azo dyes, benzene, toluene trichloroethylene as well as numerous personal and pharmaceutical care products (PPCPs). Amongst the numerous electron beam applications, bacteria, viruses and parasites destruction is also widely known, making this technology a promising future solution for the simultaneous removal of both biological and chemical contamination from wastewater and sludge.

In this work, the chemical and physical action of the electron beam is thoroughly explained, and its applicability to pharmaceutical and personal care products, including anti-inflammatory drugs and antibiotics as well as the antibiotic-resistant bacteria neutralisation is assessed.

A separate section of the research has been devoted to the possibility of electron beam microplastics decomposition in fresh- and seawater. It has been identified that microplastics exist worldwide in sediments in the shorelines and beaches as well as in marginal seas and oceans. Moreover, municipal sewage sludge from wastewater treatment plants is suspected to be a significant source of microplastics to the environment as many pharmaceutical and personal care products contain plastic microspheres. The most common plastics such as PP, PE, PET, PS and PVC have been irradiated with various doses up to 200kGy in tap- and seawater. The materials before and after the irradiation were studied by infrared spectroscopy (IR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Additionally, the high-resolution pictures have been taken using the digital microscope in order to observe the possible material degradation signs such as commonly reported yellowing.

Correspondence to: malgorzata.siwek@hud.ac.uk

PREDICTING THE ENVIRONMENTAL RISKS OF PHARMACEUTICALS IN NORWEGIAN FRESHWATERS

Samuel Welch, Jannicke Moe*, Knut Erik Tollefsen*, Mohammad Nouri Shakirabad**, Kristine Olsen**, Merete Grung**

**Norwegian Institute for Water Research*
***Norwegian Institute of Public Health*

Pharmaceuticals have attracted much recent attention as 'pollutants of emerging concern'. However, the large-scale measurement of pharmaceuticals in the environment remains difficult due to their diversity and wide range of potential metabolites. Present day environmental risk assessment of pharmaceuticals often relies on environmental concentrations predicted from maximum daily dose and the proportion of a population using a drug. However, in Norway, where high-quality sales records are maintained, it is possible to predict environmental concentrations at a higher level of specificity.

We are working as part of ECORISK2050, a large ITN analysing and addressing future risks of chemicals, to refine a predictive model of environmental concentrations of pharmaceuticals in Norwegian freshwaters, from sales data maintained by the Norwegian Institute of Public Health. The aquatic concentrations (predicted environmental concentration, PECs) will later be used to calculate the environmental risk by comparison with predicted no-effect concentrations (PNECs). Once we have fully completed my implementation of this model, we will apply it to NIPH sales data for the years 1995 – 2019, allowing me to retrospectively calculate Risk Quotients for pharmaceuticals in Norwegian freshwaters for this period.

With this data, we hope to predict future scenarios of pharmaceutical use, and develop a list of priority substances that will pose the greatest risk to Norwegian fresh and marine waters over the next three decades. Beyond prioritisation, we will also compare predictions and measure concentrations in Norwegian cities with and without waste water treatment to assess the effectiveness of current techniques.

Finally, I intend to recreate my risk assessment pipeline in a Bayesian context, using Bayesian networks to allow me to quantify uncertainty introduced during the risk assessment process.

Correspondence to: samuel.welch@niva.no

THE USE OF QUECHERS AND LC–HRMS TO EVALUATE THE UPTAKE OF PHARMACEUTICALS BY RADISH CROPS IRRIGATED WITH RECLAIMED WASTEWATER

Andrea Peris Domes, Francesc Labad*, Rayana Manasfi**, Nicola Montemurro*, Sandra Perez**

**ENFOCHEM, Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA), Spanish Council for Scientific Research (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain*
***UMR HydroSciences 5569, HSM, Montpellier University, 15 Avenue Ch. Flahault, 34093 Montpellier cedex 5, France*

In arid and semi-arid regions, where water is a limited commodity, are using increasingly reclaimed wastewater to cover their demands. Larger part of the reclaimed water is used for agricultural irrigation. However, the reclaimed wastewater can contain salts, nitrogen and pathogens heavy metals and organic contaminants which potentially can present risk for irrigation. For instance, reclaimed water can lead to uptake and accumulate organic contaminants such as pharmaceuticals in soil plant system. Thereafter, since irrigation with reclaimed water is becoming a very common practice, there is a growing concern that the consumption of fresh crops irrigated with such water can pose a risk to human health.

Few studies have evaluated the presence of pharmaceuticals and their metabolites in radish because of the lack of suitable analytical methods. For an innovative, rapid, simple, robust and sensitive method only few publications proposed the use of a QuEChERS (quick, easy, cheap, effective, rugged and safe)-based method for the determination of pharmaceuticals in crops1. In this work, two different QuEChERS salts (Original and CEN 15662) were used to evaluate the uptake of most detected pharmaceuticals in treated wastewater including diclofenac, carbamazepine, sulfamethoxazole and valsartan in radish roots. The detection of the target analytes was performed by means of the new quadrupole time-of-flight MS system SCIEX X500R QTOF. High resolution data were acquired using a multiple reaction monitoring (MRMHR) and the detection and quantification of the compounds was performed due to high resolution MS/MS data. The results showed that CEN 15662 method is better for leaves, whereas Original with formic acid is better for the extraction of pharmaceutical from radish roots.

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Correspondence to: apdqam@cid.csic.es

STUDY OF THE PRESENCE OF PHARMACEUTICAL COMPOUNDS DURING A TRIAL OF WASTEWATER REUSE IN THE LLOBREGAT RIVER (CATALONIA, NORTH-EAST SPAIN).

M Rosa Boleda, Agustina de la Cal*, Antoni Munné**, Mercè Aceves***, Irene Corbella****, Núria Juliachs****, Pere Serra****, Miquel Paraira**

**Aigües de Barcelona EMGCIA*
***Agència Catalana de l'Aigua (ACA).*
***Àrea Metropolitana de Barcelona.
*****Agència de Salut Pública de Catalunya*

The presence of pharmaceuticals in rivers is directly related with the discharge of treated effluents from wastewater treatment plants (WWTP) and the flow rate of the receiving waters. Mediterranean rivers are characterized by important fluctuations in the flow rates and heavy pollution levels, resulting from extensive urban, industrial and agricultural activities. The Llobregat river is one of the most important drinking water source for Barcelona and its surrounding area. Moreover, the Llobregat river basin is highly pressured by human activities (industrial and urban areas located alongside the river) which give rise to more than 30 urban wastewater treatment plants discharging into it. In this scenario, the introduction of advanced tertiary treated reclaimed waters in the river could bring an improvement of the current discharges, as well as additional water sources, which are of the upmost importance considering that the area is specially affected by droughts (that will likely increase in the future due to climate change).

In the summer of 2019, a special reuse trial was performed in the lower Llobregat river, discharging into it reclaimed water from the effluent of one of the largest wastewater treatment plants, in order to increase water availability. During this trial, a monitoring campaign was carried out, including the control of pharmaceutical compounds and related metabolites. Samples from the WWTP (secondary, tertiary and reused effluent waters), Llobregat river (before and after the discharge of reclaimed water), and intake and treated waters from a drinking water treatment plant (DWTP) located downstream were taken.

This study presents the results of the sampling campaign for the pharmaceuticals monitored. A total of 38 out of the 65 tested compounds were present in the reclaimed water, 28 in the river water intake of the DWTP, and none of them was found in the final drinking water, showing the effectiveness of potabilization treatment, as well as the safety of the reuse trial.

Correspondence to: mboledav@aiguesdebarcelona.cat

CARBON NANOTUBE SUPPORTED SLUDGE BIOCHAR AS AN EFFICIENT ADSORBENT FOR LOW CONCENTRATIONS OF SULFAMETHOXAZOLE REMOVAL

Yongfei Maa, Lie Yanga, Li Wua, Liuyang Hea, Zulin Zhanga

A novel adsorbent of sludge biochar (SBC) and multi-walled carbon nanotube (CNT) composite was synthesized (CNT-SBC) to remove low concentrations of sulfamethoxazole (SMX) from water. The key factors of dose, contact time, pH and temperature were investigated. Higher dose of adsorbents provided more active sites for SMX adsorption. The effect of pH was due to the electrostatic interaction. The thermodynamic study indicated that SMX adsorption was a spontaneous endothermic process. As pseudo-second-order, Elovich, Langmuir and Freundlich models fitted the experimental data better, this suggested that both physisorption and chemisorption played vital roles during the adsorption process. In addition, liquid film diffusion was the main rate-limiting step of adsorption. Compared with SBC (5.43×103 μg g-1), CNT-SBC-1, CNT-SBC-2 and CNT-SBC-3 exhibited better adsorption performance with up to 2.35×104, 1.49×104 and 1.22×104 μg g-1, respectively. The characterization analysis demonstrated that the stronger adsorption capacity of CNT-SBC was attributed to the larger surface area, mesoporous volume and pore diameter. Meanwhile, electrostatic interaction, hydrophobic interaction, hydrogen bonding, functional groups complexation and π-π interaction also played important roles. In summary, as the efficient and environment-friendly adsorbent, CNT-SBC has promising potential for the low concentrations of SMX and other emerging contaminants removal from water.

Key words: Sulfamethoxazole; Low concentrations; Sludge biochar; Carbon nanotube; Adsorption mechanisms

Reference:

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Correspondence to: Zulin.Zhang@hutton.ac.uk

A BASELINE STUDY TO UNDERSTAND WATER QUALITY AND THE WASTE WATER TREATMENT CYCLE IN CAITHNESS GENERAL HOSPITAL

Sharon PFLEGER, Mark Taggart, Lydia Niemi, Stuart Gibb

Context
Widespread use of human pharmaceuticals is increasing environmental pollution as they continuously enter water after human excretion or improper disposal. Current wastewater treatments are unable to remove all pharmaceuticals. Hospitals have been identified as a major point source for pharmaceuticals entering municipal sewers and waterways.

Aim
A pilot study was conducted in Wick in the Highlands of Scotland to assess the changes in water quality from the source, Loch Calder, as it travels through Caithness General Hospital (CGH) and the local waste water treatment plant (WWTP).

Methods
Sampling was carried out every day for 28 days CGH wastewater outflow, raw and final effluents at WWTP. Four samples were taken at the loch and hospital tap water.
Solid phase extraction and liquid chromatography- tandem mass spectrometry analysis were developed to monitor compounds from four classes of pharmaceuticals; analgesics (paracetamol, diclofenac and ibuprofen), antibiotics (clarithromycin and trimethoprim), psychiatric (carbamazepine and fluoxetine) and hormones (17 alpha- ethynylestradiol).

Results
All target pharmaceuticals were found in the three wastewater samples however ethynylestradiol was not observed above the limit of quantification. The highest total concentration was paracetamol in the wastewater influent. Trimethoprim, ibuprofen and fluoxetine were quantified in the three wastewater samples. Seven pharmaceuticals were found in the final effluent. A risk assessment was carried out by comparing observed environmental concentrations, ecotoxicity data and prescription rates. This suggested that the compounds of most environmental concern are paracetamol, fluoxetine, diclofenac, clarithromycin and 17 alpha- ethynylestradiol.

Interpretation
The results suggest that the hospital is an important source of pharmaceuticals entering the municipal water in Wick and support the fact that WWTPs do not effectively remove pharmaceuticals from water.

Future work is focussing on reducing the amount of pharmaceuticals being prescribed and disposed of inappropriately and further sampling to determine any changes in the levels of pharmaceuticals in the water.

Correspondence to: sharon.pfleger@nhs.net

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