S4.7 - GROUNDWATER REMEDIATION: THE NEVER ENDING CONFLICT BETWEEN PUMP&TREAT AND IN SITU TREATMENT

125 - THE FEASIBILITY OF IN-SITU IRON REMOVAL IN SOUTH AFRICAN AQUIFERS AS A LOW-COST TREATMENT OPTION FOR DRINKING WATER SUPPLY

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The sustainability of many wellfields is threatened by elevated iron (Fe^{2+}) and manganese (Mn^{2+}) concentrations in groundwater. Their presence causes aesthetic and potability problems but the greatest concern is borehole clogging. Physico-chemical processes and microbiological activities cause clogging by oxidation of these ions at the borehole and aquifer interface resulting in lowered yields. In South Africa two paramount examples are wellfields in the primary Atlantis Aquifer and the fractured Table Mountain Group Aquifer. Both schemes were developed to supply domestic water to rural communities which experience semi-arid conditions and lack a proximal surface water resource. Although both aquifers are known to be able to supply reliable, good quality drinking water to the communities, the boreholes in both schemes are currently operating at less than 30% of their originally assigned yields as a result of clogging. South African research has focused on the remediation of clogging problems but knowledge is needed for preventative measures in controlling the source of the problems (i.e. Fe^{2+} and Mn^{2+}). The *in-situ* iron removal (ISIR) method involves periodic injection of oxygenated water into the anoxic/anaerobic aquifer. It has successfully been applied in Europe and elsewhere for decades in reducing the need for above-ground water removal of Fe^{2+} and Mn^{2+}. In addition, the long-term application of ISIR maintains the borehole yields by reducing Fe^{2+} and Mn^{2+} movement towards the borehole screen, spreading the oxidation processes over a larger surface area in the aquifer. Over time the precipitates stabilise into crystalline oxides, further inhibiting reductive dissolution and Fe^{2+} and Mn^{2+} mobilisation. This paper discusses the ISIR applicability in a South African context and to present the findings of a small-scale test facility in the Atlantis Aquifer.

243 - FIELD TRIALS OF SUBSURFACE CHAOTIC ADVECTION

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Chaotic advection refers to the mixing of fluid elements which arise from repeated stretching and folding of fluid parcels. Chaotic advection can be engineered in porous media by time-dependent Darcy flows and has the potential to enhance mixing under laminar conditions. Enhanced mixing has many possible applications in environmental science and engineering. Remediation of contaminated aquifers is particularly relevant where mixing between the injected reagent and contaminant is a critical step. If chaotic advection can be stimulated and controlled in situ, remediation efficiencies may be significantly increased by enhanced mixing between the injected reagents and contaminants. To assess whether chaotic advection can be invoked at scale in a natural porous medium, a field trial is being designed in the sandpit area at the University of Waterloo Groundwater Research Facility at CFB Borden located near Alliston, ON, Canada, where we propose to use a transient reoriented dipole flow for subsurface stirring. A 3 m x 10 m zone in the aquifer has been isolated by sheet piling penetrating 2 m below ground surface. A funnel and gate system is in place to assess remedial technologies. In the initial phase, we propose to study the behaviour of conservative tracers within the aquifer with undisturbed and chaotic groundwater flows. Focus will then move to the treatability of a light non-aqueous phase liquid (LNAPL) source zone by injected reagents under chaotic and non-chaotic conditions. An LNAPL will be released under controlled conditions and then allowed to redistribute under gravity, forming a residual LNAPL distribution with the vicinity of the water table. This paper will describe the design criteria associated with the various aspects of this field trial, and present modeling results for determination of key flow system parameters as well as field data from the tracer test to suggest the presence of chaotic advection in the experimental aquifer.

726 - LONG-TERM EXPECTATIONS FOR THE TREATMENT OF MGP RESIDUALS BY CHEMICAL OXIDANTS

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In situ chemical oxidation (ISCO) has been touted as a remediation technology for the treatment of manufactured gas plant (MGP) residuals. Most experimental systems explored have been ideal (e.g., excess oxidant, well-mixed, long contact times) and hence the data produced are the most optimistic. Knowledge of the long-term behaviour of dissolved phase concentrations resulting from the chemical oxidant treatment of MGP residuals is unknown. To explore the temporal treatment expectations of MGP residuals, a single cell numerical model was developed. In this model, a specified mass and composition of a non-aqueous phase liquid (NAPL) is present. The NAPL consists of 22 organic compounds accounting for 34% of the total mass and the remnant mass is considered to be bulk material. The inlet oxidant concentration is prescribed and the effluent concentrations of the known soluble constituents are estimated from mass balance considerations. The results from a series of physical model experiments using impacted sediments were used to constraint the model input parameters. A variety of long-term simulation scenarios were performed. In general, for a NAPL saturation of 6%, the results indicate that the effluent profiles over a 10-year period are reduced temporality as a result of the oxidant injection and then rebound to a profile that is coincident with a no-treatment scenario. Based on a sensitivity analyses, neither water velocity or oxidant concentration affects the long-term behaviour of dissolved phase concentrations; however, increasing the mass transfer rate coefficient have a dramatic impact. This presentation will provide an overview of the modeling approach, physical model experiments, and key findings.

743 - GROUNDWATER REMEDIATION TECHNOLOGIES: A STATISTICAL ANALYSIS FOR A DECISION-MAKING SUPPORT TOOL

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A statistical analysis was performed based on historical and current data collected from the operation of a huge amount of plants, spread throughout the Italian territory, for groundwater emergency measure and contaminated site remediation according to the Italian legislation (D.Lgs 152/06 art. 240). The following main factors, impacting the final result were evaluated: costs, efficiency, duration, aquifer type, field of applicability of the different remedial technologies. Furthermore, the reliability assigned by the Public Authorities to proposed remedial technologies and the sustainability were also considered.

At present, the most trusted method is represented by the pumping of water from the wells and the subsequent treatment of extracted waters in situ or ex situ.

The aim of the work is to provide a decisional tool able to support in the application of the site-specific best remediation technology based on aquifer typology, which should take into account not only the economic and the time factors. A focused choice, maybe oriented to the application of unconventional methodologies (Air Sparging, Bio Sparging, injections of oxidizing compounds, Monitored Natural Attenuation, etc.), could turn out to be not only more environmentally sustainable, but also more economically advantageous.

792 - MOVING FORWARD FROM P&T IN TROPICAL SOILS: HOW ISCO IS AFFECTED BY SOIL PROPERTIES

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Over the past decade, the number of identified contaminated sites has increased significantly in Brazil. Recent regulations and pressure from environmental agencies has pushed site owners towards remediation. The most common remediation technology in the State of São Paulo is pump-and-treat (35% of the sites in December 2013); however, there has been an increase in the application of in-situ technologies which have increased from 5% in 2004 to around 15% in 2013. Among all in-situ technologies, in-situ chemical oxidation is one of the most utilized. Many areas in Brazil are covered with tropical soils which pose significant challenges for many in-situ technologies. Tropical soils with their relatively high clay contents and high concentrations of aluminum and iron oxides/hydroxides are very different than the aquifer systems used to develop the bulk of the chemical oxidation scientific literature. In response to this void, our research is evaluating how the chemistry and mineralogy of these tropical soils interfere with chemical oxidants, and how these oxidants can change the intrinsic soil properties.

Batch tests using three common Brazilian soils were conducted using persulfate and percarbonate to investigate the decay of oxidants. Soil mineralogy and chemical composition were determined and compared before and after oxidation. To assess the impact of the soil composition on the efficacy of the oxidant to degrade contaminants, batch tests were conducted with anthracene. It was expected that the high iron concentration in these soils could result in natural activation of the oxidant. Fast persulfate decay was observed in all tested soils, with a strong relation to clay content. Oxidation was shown to cause significant change in mineralogy, with dissolution of minerals such as kaolinite and gibbsite, and formation of iron crystalline minerals. The presence of iron likely caused an increase in persulfate decay, but that did not translate in an increase in oxidant degradation capacity. Anthracene decay rates in batch tests were lower in the presence of the iron rich soils.

Therefore, in order to decrease our dependency on pump-and-treat systems by applying in-situ chemical oxidation, we need to develop a better understanding of how the oxidants interact with tropical soils, since these oxidants will behave differently and impacts on soils were shown to be significant.

971 - CONTAMINANT TRANSPORT PROCESSES, DIFFUSION MEASUREMENT METHODS, DGT PASSIVE SAMPLERS, LAB INSTRUMENT DEVELOPMENT

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Contaminant transport phenomena are complex and often difficult to model due to the lack of reliable transport parameters. One key element of subsurface transport processes is diffusion, where the contaminant movement is driven by concentration gradient. The proper understanding of diffusion phenomena (e.g. back diffusion) plays crucial role in the success or failure of certain contaminated site remediation actions.

Our research team started the testing operation of the DKS permeabimeter, which is a lab equipment designed to determine various components transport processes. The measurements executed with the DKS permeabimeter motivated an innovative development of a new lab equipment designed to measure effective diffusion parameter of clays sediments. The obtained testing capabilities and the industry driven research demand caused us to start testing contaminated samples, in order to examine the scope of back diffusion from the soil matrix to the fluid phase.

Besides the lab measurement we started deploying diffusion based DGT passive samplers in groundwater and sediments. DGT samplers are capable to capture labile metal forms that are likely to be bioavailable. DGT results can be directly fed in to human health risk assessment, providing more reliable risk estimates than using conventional analytical concentration of the media.

Both the lab measurements and the field tests provided remarkable data to enhance the reliability of our understanding regarding contaminant transport processes. The presentation shall highlight the pros and cons of both technics and the benefits of their deployment.

S4.4 - EMERGING ORGANIC CONTAMINANTS IN GROUNDWATER: SOURCES, OCCURRENCE AND FATE

60 - IMPACT OF DOC QUALITY ON SULFONAMIDE TRANSPORT IN NATURAL SOILS

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Sulfonamides are used world-wide in animal husbandry. Sulfonamides restrain growth and multiplication of bacteria in animals and also affect soil and aquifer microbial communities. Sulfonamides and their transformation products are non-polar and hydrophobic substances. Via application of manure they can infiltrate deeper into the soil and finally groundwater. Production and usage of thousands of tons of antibiotics make sulfonamides an environmental issue. Land application of manure introduces not only veterinary antibiotics to soils, but also dissolved organic matter (DOM). Sorption sites of soil surfaces are limited, especially when high amounts of colloids and organic contaminants are present. Under these conditions colloids will not be retarded and compete with other solutes. Hydrophobic substances have a strong affinity to sorb on colloidal particles and their transport can thus be either enhanced when sorbing to mobile colloids or reduced when sorbing to immobile colloids. Therefore, in the subsurface mobile colloids from manure can act as carriers for hydrophobic contaminants resulting in an enhanced or so-called colloid-facilitated co-transport. Existence and properties of the colloids from DOM play a key role to predict the transport and leaching of contaminants into groundwater. Currently, a systematic investigation linking both experimental and numerical analysis of these complex processes are still missing. Column experiments were conducted for three different sulfonamides and manure from multiple agricultural practices. Our research highlighted that sulfamoxole strongly adsorbed to grain surfaces, however it shows facilitated transport in the presence of DOM. Maximum breakthrough concentrations and mean travel velocities of sulfamoxole increased distinctively with manure and were highest for colloids from fattening pigs. Laboratory experiments were interpreted by process-based numerical investigations using the colloid-filtration theory, competitive kinetic sorption, and co-transport approaches. Numerical investigations with HP1 coupling Hydrus-1D with PhreeqC were able to simulate the complete range of biogeochemical reactions under variable saturated conditions.

98 - USING EMERGING CONTAMINANTS TO TRACE RAPID RECHARGE PATHWAYS IN URBAN GROUNDWATER: AN EXAMPLE FROM KABWE, ZAMBIA

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We explore the occurrence of emerging organic contaminants in groundwater beneath a medium-sized African town reputed to be one of the ten most contaminated places on Earth. The results represent the first investigation of many emerging contaminants anywhere within the African environment. Samples were obtained from shallow wells and deeper boreholes across peri-urban, lower and higher cost residential areas, and industrial land uses during both the dry and wet season. They were analyzed using a broad screen GC-MS method which can target over 1000 organic compounds. The insect repellent DEET was ubiquitous, with other compounds detected in less than 15% of the sources, including the bactericide triclosan, chlorination by-products and surfactants. Emerging contaminants were most prevalent in shallow wells in low cost residential areas, which were inadequately protected at the surface. Seasonal changes in DEET highlighted the aquifer is more vulnerable than previously considered and the utility of the compound as an urban wastewater tracer. There was a general absence of personal care products, life-style compounds, and pharmaceuticals which are commonly detected in the aquatic environment in the developed world. This perhaps reflects some degree of attenuation within the subsurface, but could also be a result of the current limited use of products containing emerging contaminants by locals due to unaffordability and unavailability.

229 - AN ASSESSMENT OF MICRO-ORGANIC POLLUTANTS IN GROUNDWATER ACROSS ENGLAND AND WALES

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In the last few decades there has been a growing interest in the occurrence of micro-organic (MO) contaminants in the terrestrial and aquatic environment, and in their environmental fate and potential toxicity. A large variety of MOs are used in huge quantities for a range of purposes including arable agriculture, industrial manufacturing processes, as well as human and animal healthcare. Improvements in analytical techniques have allowed identification of organic compounds at low concentrations previously undetected in the aqueous environment.

The contamination of groundwater resources by MOs is a growing concern and relatively poorly understood compared to other freshwater resources. Of particular concern are newly 'emerging contaminants' such as pharmaceuticals and life-style compounds, particularly those with potential endocrine disrupting properties. While groundwater often has a high degree of protection from pollution due to physical, chemical and biological attenuation processes in the subsurface compared to surface aquatic environments, trace concentrations of a large range of compounds are still detected in groundwater.

This study provides the first national scale assessment of micro-organic compounds in groundwater in England and Wales by analysing a national dataset to determine the relative occurrence and detected concentrations of different groups of compounds and aims to determine relationships with different land-use, aquifer types and groundwater vulnerability. MOs found included caffeine, DEET, anti-microbial agents and pharmaceuticals as well as a range of legacy contaminants including chlorinated solvents and THMs, petroleum hydrocarbons, pesticides and other industrial compounds. Temporal trends (2002 - 2012) of MOs occurrence are assessed for selected compounds.

697 - REVIEW OF THE OCCURRENCE OF EMERGING ORGANIC CONTAMINANTS AND PESTICIDES IN ITALIAN SURFACE WATER AND GROUNDWATER

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This work provides the first review of the occurrence of 161 emerging organic contaminants (EOCs) and 137 pesticides, in surface and groundwater of Italy. The reported EOCs belong to the group of industrials, pharmaceuticals, estrogens and illicit drugs. The reviewed research works have been published between 1997 and 2013. Results show that the more frequently studied EOCs are pesticide (16), pharmaceuticals (15), industrials (13), estrogens (7) and illicit drugs (2). Among the reported contaminants, those occurring with the highest concentrations in both surface and groundwater are pesticides (up to 10^6 ng L^{-1}) and industrials (up to 10^5 ng L^{-1}). Reported maximum concentrations of pharmaceuticals in surface water are about 10^3 ng L^{-1}. Whereas in the groundwater, this class of contaminants were rarely detected suggesting different contaminant sources and pathways and different degradation rates in comparison to pesticides and industrials. Both estrogens and illicit drugs appeared in surface water with concentrations lower than 50 ng L^{-1}. Groundwater concentrations for estrogens were measured to be below the detection limits, whereas illicit drugs have so far not been studied in groundwater. Apart from the national reconnaissance study carried out by the ISPRA Institute in 2013, groundwater of several regions from Southern Italy has not been collected for EOC determination. Excluding pesticides, the same applies for surface water. The present review reveals the serious contamination status of Italian surface and groundwater especially by pesticides, industrials and to a lower extent by pharmaceuticals. Moreover, this study highlights the necessity to foster the research on EOC occurrence in Italian water resources, in particular in Southern Italian areas where a very limited number of investigations exists.

S4.6 - IMPACTS OF NON- POINT CONTAMINATION SOURCES ON GROUNDWATER

552 - MULTISOPIC (B AND SR) ASSESSMENT OF BORON-RICH GROUNDWATER IN CENTRAL ADRIATIC ITALY

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The present work aims to assess the widespread boron contamination of groundwater in central-Adriatic Italy.

This research has been based on hydrochemical and statistical study of a large amount of chemical analyses on groundwater and soil samples, representing different hydrogeological domains (carbonate aquifers, intramontane basins and alluvial plain aquifers).

Boron contamination of groundwater has been detected only in the alluvial aquifers of Adriatic plains. In order to define possible origins of contamination, a new chemical survey has been executed on two sampling areas (Saline river and Vomano river alluvial aquifers), where boron and strontium isotopic ratios have also been determinated.

As already highlighted by previous analyses, the correlation between B and Cl indicates the link among these two elements and highlights the importance of salinization of groundwater in boron contamination.

In particular, the highest boron concentrations are detected in mineralized water with a Na-Cl facies and low or negative Eh values. The ion ratios between Sr and other analytes allow to clearly distinguish samples from different hydrogeological domains.

The $\delta^{11}B$ distribution show the highest values (40.5‰), related with maximum boron concentration, are due to groundwater salinization, while the lowest (8.8‰) are comparable with the known values for Italian alluvial aquifers.

Two-component mixing models indicate $\delta^{11}B$ variation is linked with mixing processes between more shallow fresh groundwater and deeper saline groundwater.

$^{87}Sr/^{86}Sr$ isotopic ratio highlights that the values observed in the more mineralized samples are similar with those known in literature for mio-pliocenic salt waters or, at least, older than the actual seawater.

In conclusion, the research results show the highest boron concentration in groundwater are referable to natural contamination related with the uprising of Na-Cl connate groundwater, excluding anthropic pollution.

707 - MODELING NITRATE TRANSPORT TOWARDS A COASTAL LAGOON UNDER THE INFLUENCE OF AQUIFER PROPERTIES, CONTAMINATING ACTIVITIES, RESTORATION POLICIES AND CLIMATE CHANGE

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Agricultural practices in the south of Portugal have highly increased the use of groundwater over the past decades, and have caused its salinization and contamination by nitrates. The highest levels of contamination are observed in the Campina de Faro Aquifer System (CFAS) located in the western part of the drainage basin of the Ria Formosa lagoon, an ecologically sensitive and economically important wetland. Groundwater abstractions from the CFAS are much higher than average annual recharge, but long-term decreasing trends in groundwater levels are not observed. This indicates that this aquifer must be in hydraulic connection with other aquifers located more to the north, a phenomenon that has not been properly assessed so far. Moreover, nitrate concentrations still show increasing trends at some locations, despite the implementation of the EU Nitrates Directive since 1997, constituting a threat to the ecological status of the coastal lagoon, as shown by previous studies. In the current study a groundwater flow and nitrate transport model is developed and used to assess how nitrate transport is controlled by intrinsic properties, human activities and restoration measures. The results show that nitrate contamination in the upper aquifer (50 m) is extremely persistent and mostly linked to unbalanced fertilization practices and irrigation return flows. The importance of agricultural practices vs. wastewater leakage was also shown by previously performed nitrate isotope analyses in groundwater of the shallow aquifer. The modeling results further show the slow response of the system to the implementation of good agricultural practices (GAP) in compliance with the European policies, indicating that good qualitative status would be impossible to reach in the entire aquifer by the required EU deadlines, even in the most optimistic scenario. Moreover, climate change scenarios for the region, when integrated in the transport model, show that despite the implementation of GAP nitrate levels could further increase in the upper aquifer due to a concentration trend caused by lower recharge, higher water demands and incomplete mixing within the aquifer.

938 - USE OF AN ARTIFICIAL SWEETENER TO IDENTIFY SOURCES OF GROUNDWATER NITRATE CONTAMINATION

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The artificial sweetener acesulfame is a potentially useful tracer of wastewater contamination in groundwater. In this study, acesulfame (ACE) concentrations were measured in wastewater and impacted groundwater at 12 septic system sites in Ontario, Canada. All samples of septic tank effluent (n =37) had ACE > 6 µg/L, all samples of groundwater from the proximal plume zones (n =93) had ACE > 1 µg/L and, almost all samples from the distal plume zones had ACE > 2 µg/L. Mean ratios of total inorganic nitrogen/acesulfame at the 12 sites ranged from 680-3500 for the tank and proximal plume samples. At five sites, decreasing ratio values in the distal zones indicated nitrogen attenuation. These ratios were applied to three aquifers in Canada that are nitrate-stressed and an urban stream where septic systems are present nearby, to estimate the amount of wastewater nitrate contamination. At three aquifer locations that are agricultural, low ACE values (<0.008 - 0.15 µg/L) suggested that wastewater contributed <1% of the nitrate in most samples. At another aquifer location that is agricultural, but where a small community using septic systems is present upgradient, slightly higher ACE values (0.06-0.14 µg/L) indicated that wastewater contributed about 2-15% of the nitrate. In groundwater discharging to the urban stream, much higher ACE values (0.2-11 µg/L) indicated that wastewater was the source of >50 % of the nitrate in most samples. This study confirms that acesulfame is a powerful tracer and demonstrates its use as a diagnostic tool for quantifying wastewater contamination in groundwater.

S8.4 - TRACER AND ISOTOPE HYDROLOGY

74 - THE IMPACT OF DOMESTIC WASTEWATER TREATMENT SYSTEM EFFLUENT ON PRIVATE WATER WELLS: AN EVALUATION OF CONTAMINATION FINGERPRINTING TECHNIQUES

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Approximately 162,000 Irish households depend on private water sources, mainly wells, for their water supply. Sampling studies of these wells for the presence of faecal indicator bacteria have shown that approximately 30% are polluted, at least intermittently, with one of the main sources of microbial pathogens believed to be domestic wastewater treatment systems (DWWTS), mainly septic tanks. DWWTS are employed by approximately 438,000 dwellings across Ireland. However, as faecal indicators are not source-specific, identifying whether the contamination is of human or animal waste origin is difficult and has not been carried out previously. Building on previous research on the extent of private well contamination in Ireland, this research is employing a range of techniques for identifying specific sources of well contamination and, particularly, the extent of the pollution from DWWTS as opposed to agricultural sources, which are also a significant issue in rural Ireland. A total of 216 private wells have been surveyed across four study areas of specific geological characteristics found in Ireland. Two areas are highly vulnerable to groundwater contamination due to the shallow depth of subsoil, with the remaining two areas displaying characteristics of inadequate percolation for DWWTS and hence low vulnerability. Individual site assessments have been conducted on each of the well sites, recording details of the well, including its wellhead, and the DWWTS. Each well is being examined for indicator bacteria and a full suite of chemical constituents during a one-off sampling regime. Of 165 wells tested to date, 67% have tested positive for total coliforms, with 17% positive for *E. coli*. Subsequently, a temporal scale study will monitor a select number of wells over the study period. Wells are currently being used to assess a range of fingerprinting techniques including fluorescent whitening compounds, faecal sterols, anion ratios, F-RNA coliphages and Bifidobacterium. The paper will present an evaluation of these different techniques for identifying contamination from DWWTS sources.

415 - BIODEGRADATION HOT-SPOTS AT THE SOIL/ GROUNDWATER INTERFACE OF A CONTAMINATED AQUIFER

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Dissimilatory sulphate reduction represents an important process in the anaerobic degradation of organic contaminants in groundwater ecosystems.

Here, we demonstrate that a BTEX (*i.e.* benzene, toluene, ethyl-benzene, and xylenes) plume which interacts with the groundwater table leads to a zone of variable redox conditions, in which redox cycling complicates the interpretation of concentration measurements and microbial community structure to the point that reactive transport models have previously failed to reproduce observed trends. This geochemical complexity is studied through a suite of observations, including the use of sulfur intermediates such as S^0, SO_3^{2-}, and $S_2O_3^{2-}$, and microbial community analysis in conjunction with high-resolution sampling of the porous aquifer. In addition stable isotopes measurements of dissolved sulphate, hydrogen sulphide, and elemental sulphur were performed to shed light on sulphur cycling processes at the soil/groundwater interface.

The isotopically enriched $d^{34}S$ values of dissolved sulphate linked to decreasing toluene concentrations near the water table are indicative that BTEX were oxidized at the upper plume fringe under sulphate reducing conditions. The $d^{18}O$ in dissolved sulphate from the same depth suggest a re-oxidation of up to 70% reduced sulphur to dissolved sulphate. Concentrations of measured sulfur intermediates at the plume fringe were twice as high as in other sampling depth and support the interpretation of intensive redox cycling processes near the water table. An isotopic shift in $d^{34}S$ of S^0 of nearly +4‰ compared to the $d^{34}S$ values of H_2S from the same depth linked to a high abundance (~10%) of sequence reads related to *Sulphuricurvum spp.* (*Epsilonproteobacteria*) in the same depth is indicative of oxidation of S^0 to sulphate in this zone. This study documents that complementary information on the microbial population distribution and sulphur isotopes facilitate the application of sulphur stable isotopes to qualitatively describe the sulphur cycle in aquifer sediments. In the future, biodegradation of contaminants linked to the recycling of sulphur intermediates should be considered in advanced and more sustainable site-remediation schemes.

468 - ASSESSING THE EFFICIENCY OF REMEDIATION SYSTEM ON GROUNDWATER FLOW USING GROUNDWATER ISOTOPES (Δ18O, ΔD AND 3H)

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Two of the most common applications of environmental isotopes in groundwater studies are related to evaluation of sources of recharge and the role of sea water intrusion in the salinity of coastal aquifers. The present work deals with the application of isotopic techniques to assess the conceptual groundwater flow model of a contaminated coastal aquifer in an industrial area affected by seawater intrusion within the framework a permanent remediation strategy. The remediation system, located along the coast line, is composed by an Horizontal Flow Barrier (HFB), not sealed in the aquiclude, coupled with an Hydraulic Barrier (HB) represented by an alignment of 67 fully screened pumping wells. Both barriers are aligned perpendicular to the main groundwater flow direction and a complex hydrodynamic regime have been generated around the barriers.

Environmental isotopes, ^{18}O and ^{2}H have been used to evaluate groundwater sources and the magnitude of seawater intrusion and tritium has been used to estimate groundwater residence time. The isotopic investigation has been focused in the coastal portion of the industrial area, where groundwater flow is strongly affected by the remediation system.

Based on the stable isotope data it was possible to distinguish three different groundwater groups: one related to local recharge waters, one representing sea water intrusion and the third one is a mixing between the first two groups.

The tritium data show that most of the groundwater are relatively young, especially the ones at shallow depths, corresponding to recent recharge. In the coastal area, for piezometers located upgradient to the HFB, older groundwater is found along the entire profile, confirming the extension of the HB capture zone. Conversely, the piezometers located downgradient of the HB and of the HFB are influenced by recent recharge in the shallower part of the aquifer, while in the deeper part relatively older groundwater reflect the effect of seawater intrusion due to the pumping activity. The stable isotope and the tritium data provide key information to evaluate the performance of remediation system concerning the containment of the contaminated groundwater and its potential impact in the coastal areas.

839 - NATURAL ATTENUATION OF SEPTIC SYSTEM NITROGEN: A CASE STUDY IN KILLARNEY PROVINCIAL PARK, ONTARIO, CANADA

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Nutrient concentrations in groundwater have been monitored down gradient from an onsite sewage treatment and disposal system on a campsite located at the Killarney Provincial Park (Canada, On). During July and August, the study site serves both local and visitors in 142 campsites, receiving significant wastewater loading up to 25,000 L/day.

The objective of this study is to assess the processes involved in nitrogen attenuation in a well-characterized septic system plume. Isotopic and microbiological tools have been used to evaluate the role of nitrification, denitrification and anammox on the attenuation of nitrate and ammonium along the groundwater flow system.

Results showed chloride (~32 mgL^{-1}) remarkably uniform across the entire transect, suggesting that the septic system plume is composed essentially of straight sewage, excluding the effect of dilution derived by precipitation.

Ammonium content of the septic tank effluent is relatively high but it is then attenuated at the bottom of the plume, in the most distal monitoring location. Conversely, nitrate at high concentration is most present on the upper fringes of the plume, where dissolved oxygen diffusion from the water table zone promotes nitrification. Therefore, nitrogen compounds are variably distributed along the transect with high (57.5 mgL^{-1} $N\text{-}NO_3^-$, 40.5 mgL^{-1} $N\text{-}NH_4^+$) near the source and low (<1 mgL^{-1} for $N\text{-}NO_3^-$ and $N\text{-}NH_4^+$) concentrations in the distal part of the plume. Nitrate isotope signatures ($^{15}N\text{-}N\text{-}NO_3^-$, $^{18}O\text{-}N\text{-}NO_3^-$) suggest that multiple transformation processes take place at the study site: (i) nitrification in the unsaturated zone and shallow part of the plume, where high nitrate concentration is accompanied by depleted $\delta^{15}N\text{-}NO_3^-$ (57.5 mgL^{-1} and -3.2‰, respectively) and (ii) denitrification along the plume where nitrate concentration decreases (<1 mgL^{-1} $N\text{-}NO_3^-$) correlated with an enrichment trend for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (up to +44.8‰ and +26.8‰, respectively). There is a possibility that anammox is involved in the attenuation of nitrate and ammonium. The role of this process is being evaluated using microbial analysis, specifically bacterial community composition (DNA-based analysis), and $\delta^{15}N$ data in ammonium. This study has shown that ammonium associated to high sewage loads can be present in septic system plume. Nitrification, denitrification and anammox can be all involved in nitrogen transformation and attenuation in these complex septic plumes.

S8.12 - MOLECULAR BIOLOGY TOOLS, COMPOUND-SPECIFIC ISOTOPES AND NANOTECHNOLOGY IN GROUNDWATER STUDIES

452 - USE OF DUAL CARBON-CHLORINE ISOTOPE ANALYSIS TO IDENTIFY DEGRADATION PATHWAYS OF 1,1,1-TRICHLOROETHANE IN GROUNDWATER

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The high susceptibility of chlorinated aliphatic hydrocarbons (CAHs) like 1,1,1-trichloroethane (1,1,1-TCA) to be transformed via different competing pathways (biotic and abiotic) complicates the assessment of their fate in groundwater. This knowledge is necessary to evaluate contaminant degradation and potential formation of toxic intermediates. Identifying pathways is further complicated in sites contaminated by mixed CAHs because some degradation products of 1,1,1-TCA can be formed from different precursors. Here, identification of pathways based solely on substrate-product concentration relationships may lead to ambiguous interpretations.

This study investigates, for the first time, dual C-Cl isotope fractionation as a means of identifying and assessing degradation pathways of 1,1,1-TCA in groundwater. Distinctly different dual isotope trends ($L = \Delta\delta^{13}C/\Delta\delta^{37}Cl$) were observed for 1,1,1-TCA transformation via oxidation with heat-activated persulfate ($L = \infty$), reduction with zero-valent iron ($L = 1.5 \pm 0.1$), hydrolysis and dehydrohalogenation (HY/DH, $L = 0.33 \pm 0.04$) in laboratory experiments, illustrating the potential of a dual isotope approach. This approach was evaluated in an aerobic aquifer impacted by 1,1,1-TCA and trichloroethylene (TCE) with concentrations of up to 20 mg/L and 3.4 mg/L, respectively. For 1,1,1-TCA, the dual isotope slope determined from field samples ($L = 0.6 \pm 0.2$, $r^2 = 0.75$) was close to the slope observed for HY/DH in the laboratory ($L = 0.33 \pm 0.04$), indicating that HY/DH was the predominant degradation pathway of 1,1,1-TCA in the aquifer. The observed deviation could be explained by a minor contribution of additional degradation processes. This result, along with the little degradation of TCE determined from isotope measurements, confirmed that 1,1,1-TCA was the main source of the 1,1-dichlorethylene (1,1-DCE) detected in the aquifer with concentrations of up to 10 mg/L. This study demonstrates that a dual C-Cl isotope approach can strongly improve the qualitative and quantitative assessment of 1,1,1-TCA degradation processes in the field.

860 - USE OF INNOVATIVE ISOTOPIC AND MICROBIOLOGICAL TOOLS FOR ASSESSMENT OF NATURAL ATTENUATION OF MONOCHLOROBENZENE (CB) AT A COMPLEX CONTAMINATED FIELD SITE

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Chlorinated solvents contaminated sites entail costly management costs and often creates significant impacts to the environment. Innovative tools such Compound-Specific Isotope Analysis (CSIA) and Molecular Biological Tools (MBTs) can provide unequivocal information for site characterization and assessment of natural attenuation processes, particularly biodegradation.

This contribution explores the potential for the dual- element CSIA approach and MBTs to study a heavy monochlobenzene (CB) and benzene contamination at a mega-site where potential multiple sources are presents.

A significant difference in the $d^{13}C/d^{37}Cl$ and $d^{13}C/d^{2}H$ for CB and benzene respectively - in the high concentration spots - allowed distinguishing two distinct sources and plumes. Concerning natural attenuation processes, although the site is characterized by reducing conditions with high concentrations of CH_4, MBTs results indicated the presence of mainly aerobic potential degraders within the indigenous community at the site, with predominance for Pseudomonadaceae and Comamonadaceae species. In addition, the dual $d^{13}C$ /$d^{37}Cl$ data also showed that aerobic biodegradation processes are taking place (because of a unique trend presenting no $d^{13}C$ changes but a $d^{37}Cl$ significant enrichment). Finally, regarding benzene, $d^{13}C$ /$d^{2}H$ data showed that the benzene present at the site is not link to CB dehalogenation processes but is rather a primary contaminant; these data also showed benzene is being attenuated by biodegradation.

These results demonstrated the potential of combining dual-element CSIA: particularly important insights regarding CB natural attenuation were obtained by applying the dual $d^{13}C$ /$d^{37}Cl$ analysis.

906 - IDENTIFICATION OF BIODEGRADATION OF CHLORINATED SOLVENTS IN LOW PERMEABILITY SEDIMENTS USING COMPOUND-SPECIFIC ISOTOPE ANALYSIS (CSIA)

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As a result of improper use and disposal, chlorinated solvents are major subsurface contaminants. Due to the high density and low viscosity, chlorinated solvents migrate through the unsaturated zone into aquifer systems and often accumulate on top of low permeable sediments. With time chlorinated solvents diffuse into these low permeable units, which then potentially serve as a long-term contaminant source to the adjacent aquifer. However, due to the presence of more reducing conditions in these units, (bio)degradation might occur, which reduces the risk of long-term groundwater contamination. Compound-specific stable isotope analysis (CSIA) is increasingly used to quantify (bio)degradation processes in aquifer systems affecting organic contaminants. This method makes use of isotope effects associated with (bio)degradation. In contrast to aquifers, it is not yet clear to what extent CSIA can also be used for tracking (bio)degradation in saturated low permeability sediments, where transport is likely diffusion dominated.

To address this gap of knowledge, several detailed C and Cl isotope ratio profiles of chlorinated solvents were determined for a contaminated clayey aquitard underlying a sandy aquifer. The contaminant source originated from a controlled-solvent release on top of the aquitard 14.5 years ago. Large shifts of compound-specific isotope signatures (e.g. 20‰ for C isotopes in TCE) were measured in the aquitard profiles. The application of numerical modelling to observed shifts in isotope ratio profiles revealed that (bio)degradation of chlorinated solvents is also occurring in saturated low permeability sediments. Furthermore, the results of the numerical model allowed us to determine (bio)degradation rates affecting chlorinated solvents in the clayey aquitard.

Our findings demonstrate that CSIA is also applicable in saturated low permeability sediments for the identification of reactive processes. Moreover, our results revealed that (bio)degradation is potentially superimposed on diffusion and thus, it is difficult to identify based on concentration profiles only. Therefore, isotope information is an important complement additionally to concentration data to identify (bio)degradation in low permeability sediments.

S4.3 - THE CHALLENGES OF SOURCE APPORTIONMENT AND MANAGING CONTAMINATION AT COMPLEX FIELD SITES

903 - POTENTIAL OF MULTI ISOTOPE FINGERPRINTING FOR ANALYZING SOURCES AND SINKS OF ORGANOPHOSPHORUS PESTICIDES

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Organophosphorus pesticides (OPs) comprise a class of highly toxic compounds acting as very specific nerve agents. "Organophosphates" refers to a group of pesticides of esters of phosphoric acid and derivatives which are neuro toxic. OPs inactivate acetylcholinesterase which is essential to nerve function in insects, humans, and animals.

OPs can be degraded by hydrolysis, biodegradation and direct and indirect photodegradation. However, the persistence of OPs in the environment is of great concern, as they have repeatedly been detected in soils, sediments waterbodies as well as food and drinking water. Thus tools are needed to understand their sources, reactive transport pathways and sinks in the environment. We developed a concept for monitoring of sources and sinks of OPs making use of multi isotope analysis of hydrogen, carbon, oxygen and nitrogen for identification of sources.

The hydrogen, carbon, oxygen and nitrogen isotope composition of 40 OPs of different formulations from China, India and Europe is analysed in order to evaluate the potential for characterising sources by multi isotope analysis.

A method for carbon and hydrogen analysis for omethoate, dimethoate, parathion and methyl-parathion were developed for compound specific isotope analysis. The correlation of ^{2}H and ^{13}C isotope fractionation associated with hydrolysis of OPs at different pH were specific for the mode of hydrolysis. For example the hydrolysis of dimethoate yield characteristic correlation factor for ^{2}H and ^{13}C of lambda = 0.001 ± 0.057 at pH 7, 6.4 ± 1.7 at pH 9, 29.6 ± 5.7 at pH 12. The potential for analysis degradation mechanism is demonstrated at a field site in Denmark where is heavily contaminated by more than 100 tons of toxic chemicals, mainly OPs (e.g. parathion, malathion, sulfotep). At the parathion-contaminated field site, compared with the free phase, monitoring wells showed significant enrichment in ^{13}C and ^{2}H. 2D-CSIA concept was applied for evaluating the stimulated hydrolysis (treated by NaOH to increase the pH to 12) as well as the natural in situ degradation (pH 6-7) of parathion.

We will discuss the potential of multi isotope fingerprinting for analysing the sources and sinks of OPs in the environment, which might improve the tracing of origin, transport pathways and environmental fate of OPs.

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Fast and cost effective *in situ* derivatization method for monitoring Bisphenol-A and Estrogens in water matrices

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INTRODUCTION

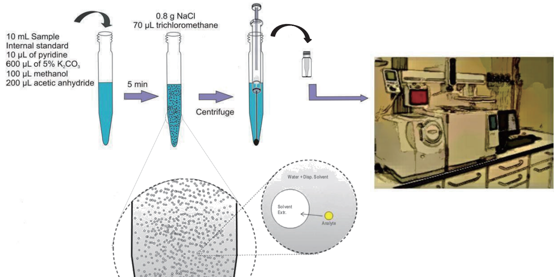
Over the last years waterborne disease risks are being altered due to higher pressures on the quality and quantity of water resources. One of the most worrying groups is that of compounds that are capable of interfering with the endocrine regulation mechanisms, called endocrine disruptor compounds (EDCs). EDCs can cause adverse effects on animals and humans at very low doses, thus requiring reliable and cost-effective strategies for monitoring evaluations. Four potent EDCs, namely: the natural estrogens estrone (E1) and 17 beta-estradiol (E2), the synthetic steroid 17alfa-ethinylestradiol (EE2) and Bisphenol-A (BPA) are, currently, classified as emerging contaminants and are under increasing scientific scrutiny.

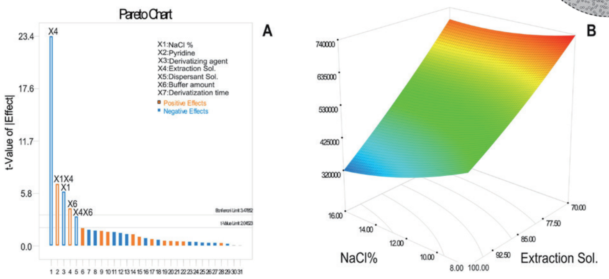
The common methods for the determination of EDCs in water are frequently time consuming, expensive and use considerable volumes of organic solvents, which stimulated the need of developing new methodologies.

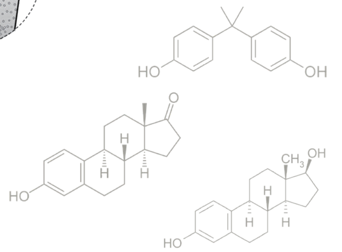
The goal of this work was the optimization of a rapid, cost effective and eco-friendly gas chromatography-mass spectrometry method (GC-MS) for simultaneous determination of the four cited EDCs in water.

MATERIALS AND METHODS

A miniaturized sample pre-treatment technique, based on a ternary component solvent system, named Dispersive Liquid–Liquid Microextraction, was developed due to a rapid equilibrium state and a short extraction time. Concerning derivatization procedure, an *in situ* methodology was tested consisting in direct addition of the derivatizing reagent in the sample solution. Derivatization and extraction parameters were optimized with the aid of experimental design approach.







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RESULTS

The proposed method was successfully validated according the International Conference on Harmonization recommendations and some European and American validation guidelines with specifications for EDCs and/or GC-MS methodologies, being able to be applied to routine analyses of BPA, E1, E2 and EE2 with excellent sensitivity, precision, and accuracy.

Ten samples of different water matrices were tested. None of the samples presented quantified levels of E2 and EE2, whereas E1 was found in two river water samples and BPA in tap water, groundwater and in river and sea water samples in concentrations of 0.0172 to 0.253µgL^{-1}.

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Research Article

Application of a fast and cost-effective in situ derivatization method prior to gas chromatography with mass spectrometry to monitor endocrine disruptors in water matrices

This work deals with the optimization of a rapid, cost-effective, and eco-friendly gas chromatography with mass spectrometry method for the simultaneous determination of four endocrine disruptor compounds in water matrices: estrone, 17β-estradiol, 17α-ethinylestradiol, and bisphenol A, that are currently considered to be of main concern in the field of water policy and that could became candidates for future regulations. The method involves simultaneous derivatization and extraction of compounds by dispersive liquid–liquid microextraction followed by gas chromatography with mass spectrometry analysis. Derivatization and extraction parameters were optimized with the aid of experimental design approach. An excellent linear response was achieved for all analytes ($r^2 \geq 0.999$). Limits of detection and quantification are 0.003–0.005 and 0.0094–0.0164 μg/L, respectively. Intraday precision ranged between 1.1 and 12.6%, whereas interday precision ranged between 0.5 and 14.7%. For accuracy, bias values varied between −15.0 and 13.7%. Recoveries at three concentration levels ranged from 86.4 to 118.2%. The proposed method can be applied to the routine analysis of groundwater, river, sea, tap, and mineral water samples with excellent sensitivity, precision, and accuracy.

Keywords: Derivatization / Dispersive liquid–liquid microextraction / Endocrine disruptors / Experimental design / Water
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1 Introduction

Over the last years waterborne disease risks are being altered due to higher pressures on the quality and quantity of water resources that shifted the focus of chemical pollution from conventional pollutants to so-called emerging contaminants [1]. One of the most worrying groups is that of compounds that are capable of interfering with the endocrine regulation mechanisms, called endocrine disruptor compounds (EDCs) [2]. EDCs can cause adverse effects on animals and humans at very low doses, which are not predicted by effects at higher doses, thus requiring reliable and cost-effective strategies for monitoring evaluations [3] to improve the knowledge about their occurrence, persistence, and bioaccumulation, and to lay down defensive and precautionary regulations [4]. The occurrence of synthetic EDCs, as well as their concentrations, in a natural ecosystem is a marker of human impact on the environment and an indicator of water quality [5]. Moreover, the finding that several EDCs presented nonmonotonicity, defined as a nonlinear relationship between dose and effect, clearly indicates that environmental exposure levels cannot be ignored, implying reliable and cost-effective strategies for monitoring evaluations [3].

Four potent EDCs, namely, the natural estrogens estrone (E1) and 17β-estradiol (βE2), the synthetic steroid 17α-ethinylestradiol (EE2) and bisphenol-A (BPA) are, currently, under increasing scientific scrutiny. In 2013, βE2 and EE2 were included in the first watch list of emerging aquatic pollutants by European legislators during the revision of the priority substances directive [6]. In the United States, E1, βE2, and EE2 were also included in the third contaminant candidate list of the Safe Drinking Water Act [7]. In the revision of Japanese Drinking Water Quality Standards, βE2 and EE2 were included in the list of items for further study with target values of 0.08 and 0.02 μg/L, respectively [8]. Steroid hormones were also reported by the World Health Organization (WHO) as chemicals of emerging concern [2, 9, 10]. BPA is a high-production-volume chemical that is ubiquitous in the environment. It is widely used mainly in the production

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Abbreviations: BPA, bisphenol-A; **CCD**, central composite design; **DLLME**, dispersive liquid–liquid microextraction; **EDC**, endocrine disruptor compound


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of polycarbonate plastics and epoxy resins. BPA is recognized to be a reproductive, developmental, and systemic toxicant [11–13]. Recently, the Environmental Protection Agency has added BPA to a key list of chemicals that will have particular uses carefully scrutinized for possible regulation or other controls [14].

Almost all processes operating in conventional water treatment plants were not designed to remove such compounds, leading to their occurrence in environment and in drinking, finished and/or tap waters [15]. Developing innovative, safe, efficient, and low-cost advanced methods for analysis of emerging contaminants in environmental matrices, namely contributions in the field of ultra-trace analysis of multicomponent mixtures, is of major relevance to improve data-management routines and define appropriate monitoring scales and locations for policy development/assessment [16].

The methods published for the determination of EDCs in water are frequently based on SPE followed by derivatization [17]. Although efficient, SPE is time consuming and uses considerable volumes of organic solvents, which stimulated the need of developing new methodologies. Dispersive liquid–liquid microextraction (DLLME), is a miniaturized sample pre-treatment technique based on a ternary component solvent system where the dispersion of fine droplets of the extraction solvent is accomplished within the aqueous phase, resulting in the formation of a cloudy solution where the surface area between extraction solvent and aqueous sample is considerably large. The equilibrium state is achieved quickly and the extraction time is short [18–22]. Concerning derivatization procedure it usually requires long time and effort. To obviate these problems, an in situ derivatization procedure was developed, consisting in direct addition of the derivatizing reagent in the sample solution [23]. This derivatization step converts EDCs into less polar compounds that cause an increase in the extraction efficiency [24].

The optimization of these methodologies is often performed by univariate strategies that could generate some limitations, since the interactions between factors are not considered [25]. Thus, the multivariate statistical methods have being preferred, because they explore the relationship between several explanatory variables and one or more response variables by means of a mathematical model able to properly predict the values of the response which is a very useful tool for selecting the optimum conditions [26].

In this work, a DLLME procedure prior to GC–MS analysis was optimized for the quantitative assessment of EDCs in water samples regarding the modern trends in analytical chemistry that are toward the simplification and miniaturization of sample preparation procedures, as well as the minimization of solvent and reagent consumption. Effect of certain variables on the extraction recovery of each compound was evaluated by using two-level fractional factorial design and a central composite design (CCD) that was based on the response surface methodology.

2 Materials and methods

2.1 Chemicals and materials

Bisphenol A (99%), d16-bisphenol A (BPA-d16) (98%), estrone (99%), 17β-estradiol (98%), 17α-ethinylestradiol (98%) were supplied by Sigma–Aldrich (Steinheim, Germany). Acetic anhydride (≥99%) for GC derivatization was from Fluka (Buchs, Switzerland). Methanol, acetonitrile, and acetone of HPLC grade LiChorsolv were supplied by Merck (Darmstadt, Germany). Ultrapure water was highly purified by a Milli-Q gradient system (18.2 mΩ/cm) from Millipore (Milford, MA, USA). Trichloromethane, chlorobenzene, dichloromethane, tetrachloromethane, tetrachloroethylene were high-purity solvents from Fluka for HPLC analysis. Sodium chloride (NaCl) was analytical grade from Riedel-de-Haën (Buchs, Switzerland).

Stock standards of each compound were prepared in acetonitrile by exact weighing of the high purity substances and accurate dilution and stored in amber glass-stoppered flasks at 4°C. A mixture was then prepared, in methanol, containing 1 mg/L of each compound. Working solutions were mixtures of appropriate concentrations prepared weekly and kept at low temperature in the dark. The internal standard (BPA-d16) was prepared in the same way but individually.

Calibration solutions at concentration levels ranging from 0.010 to 0.500 μg/L were prepared by spiking 10 mL of water with different volumes of the working solutions just before extraction.

2.2 Apparatus and GC–MS conditions

Chromatographic analyses were carried out in a Shimadzu GCMS-QP2010 Gas Chromatograph Mass Spectrometer equipped with an auto injector AOC-5000. Injections of 1 μL were made in the splitless mode with a 1.0 min purge-off time and the injector temperature was set at 275°C. Helium (99.9999%), at a constant flow rate of 1.74 mL/min was used as the carrier gas. Samples were analyzed using a fused-silica capillary column Zebron ZB-5MS W/Guardian (Phenomenex) coated with 5% Polysilarylene and 95% of Polydimethylsiloxane (30m × 0.25mm id, 0.25 μm film thickness) with 10 m of Guardian capillary column but not with stationary phase. The analysis were done following the oven program temperature: initial temperature 80°C (held for 2 min), increased by 20°C/min to 220°C (held for 17 min), increased again by 20°C/min to 250°C and held at this temperature for 7 min. In this device the temperature of the GC–MS interface was maintained at 250°C with an electron impact ionization of 70 eV. The transfer line was set at 275°C and source at 200°C. Positive fragment ions were analyzed over the 50–500 m/z mass range in full scan mode and in selected-ion monitoring mode.

The identification of EDCs was done according to the following conditions: (1) the selected diagnostic ions were

present at the substance specific retention time; (2) the relative retention time of the sample component matched that of the authentic compound within a limit deviation of ± 0.04 min in the chromatogram of the latest calibration standard, measured under identical conditions; and (3) the relative intensities of two of the chosen diagnostic ions measured in the sample do not deviate by more than 20% from the relative intensities determined in the reference standard working solution.

Positive fragment ions selected for quantification and identification purposes were: 213, 228, 270 for BPA, 224, 242 for BPA-$_{d16}$, 270, 312 for E1, 314, 225 for βE2 and 296, 338 for EE2.

Instrument control and MS data were managed by a personal computer with the LabSolutions GCMS software (2.50 SU3 version).

2.3 Derivatization and extraction procedure

Derivatization was carried out using a volume of 10 mL of water sample placed into a 15 mL glass conical test tube and spiked with BPA-d16 (IS) (50 ng/L of final concentration for 10 mL of sample), added with 10 μL of pyridine and 600 μL of 5% K_2CO_3 to achieve a pH≥10. Then 100 μL of methanol and 200 μL of acetic anhydride were jointed and the solution was incubated at room temperature for 5 min. The acetate derivatives were extracted by the DLLME method, after addition of 0.8 g of sodium chloride, by the injection of 70 μL of trichloromethane (extraction solvent) resulting in a cloudy solution. This solution was vigorously shaken by hand until the total dissolution of sodium chloride. Finally the conical tubes were centrifuged at 2200 rpm and 5°C for 5 min. Dispersive particles were collected at the bottom of the centrifuge tube by a glass Pasteur pipette with latex bulb. The resulting organic phase was injected for analysis.

2.4 Experimental design

A two-level (2^{7-2}) fractional factorial design was built for the screening of the main variables affecting the derivatization and extraction procedure of endocrine disruptors under analysis. Table 1 presents the seven coded variables at ranged levels of low (–1) and high (+1) concentrations in a total of 32 runs plus four center points. Afterwards, the significant variables were optimized using CCD. Its range parameters are presented in Table 2. CCD consisting of a complete 2^3-factorial design as cubic points, with six axial points at a distance of $\alpha = 1.682$ from the design center and five center points. Hence the complete design had 19 combinations, including six replicates of the center point. The response used in experimental designs was the peak area of endocrine disruptors. The statistical analyses were performed by using the software Design Expert trial-Version 7 (Stat-Ease, Minneapolis, MN).

Table 1. Factors, codes, low, and high levels in 2^{7-2} fractional factorial designs matrix for derivatization and extraction procedures

Factors	Levels	
	Low (−1)	High (+1)
(x_1) NaCl percentage (%)	10	20
(x_2) Pyridine amount (μL)	10	50
(x_3) Derivatizing agent amount (μL)	100	400
(x_4) Extraction solvent (μL)	75	250
(x_5) Dispersant solvent (μL)	100	600
(x_6) Buffer amount (μL)	0	200
(x_7) Derivatization time (min)	5	15

Table 2. Central composite design for derivatization and extraction, with independent variable levels

Standard order	Independent variables		
	X1	X2	X3
1	8.00	70.00	200.00
2	16.00	70.00	200.00
3	8.00	100.00	200.00
4	16.00	100.00	200.00
5	8.00	70.00	600.00
6	16.00	70.00	600.00
7	8.00	100.00	600.00
8	16.00	100.00	600.00
9	5.27	85.00	400.00
10	18.73	85.00	400.00
11	12.00	59.77	400.00
12	12.00	110.23	400.00
13	12.00	85.00	63.64
14	12.00	85.00	736.36
15	12.00	85.00	400.00
16	12.00	85.00	400.00
17	12.00	85.00	400.00
18	12.00	85.00	400.00
19	12.00	85.00	400.00

(x_1) NaCl percentage (%), (x_2) extraction solvent (μL), (x_3) buffer amount (μL).

2.5 Validation and QC

Validation was done mainly according the International Conference on Harmonization recommendations [27], as well as some European and American validation guidelines [28, 29] with specifications for endocrine disrupting analysis and/or GC–MS methodology.

To develop and optimize the DLLME procedure followed by GC–MS for an effective and reproducible detection of low EDCs concentrations, several parameters such as: specificity and selectivity, linearity and linear range, LODs, LOQs, precision, accuracy, and trueness (recovery) were determined. Analytical performance of the method was evaluated through matrix matched calibration, using BPA-*d16* as internal standard. Calibration curves were constructed using the least

squares linear regression model, plotting the peak area ratios of acetate derivatives and BPA-*d16* versus the concentration of each ECD. Standard calibration curves were prepared under the same conditions optimized previously, using seven calibration points for BPA, E1, and EE2 (0.010, 0.025, 0.050, 0.100, 0.250, 0.350, and 0.500 μg/L of each analyte) and six calibration points for βE2 (without 0.010 μg/L point). Each test was performed at least in five independent experiments. The LOD and LOQ were calculated based on the calibration curve parameters [30,31], where the LOD was equal to the calculated intercept of the linear regression (a) plus three times the $S_{y/x}$ and for LOQ ten times this value.

3 Results and discussion

Preliminary experiments were conducted to select the extracting and the dispersive solvents of DLLME method that enable maximum sensitivity for the four compounds under study. These preliminary experiments were performed using 10 mL of ultrapure water spiked with the four standards to obtain a final concentration of 1 μg/L each. Derivatization was performed with addition of 0.5 mL of buffer solution (5% K_2CO_3) and 200 μL of AA for 5 min; then 2 g of NaCl and 0.5 mL of acetonitrile were added. Different solvents of extraction were then evaluated by adding an experimental volume of 100 μL to form the cloudy suspension. The other procedures followed the conditions described in Section 2.3. The organic solvents tested were: trichloromethane, chlorobenzene, dichloromethane, tetrachloromethane, tetrachloroethylene. Trichloromethane presented the highest peak response for all compounds and was selected as the extraction solvent.

For the selection of the dispersive solvent it were used the previous conditions, 100 μL of trichloromethane and 0.5 mL of the different organic solvents: acetonitrile, methanol, and acetone. Methanol presented the highest peak area response for the four endocrine disrupters, thus it was preferred instead of acetonitrile (data not shown).

3.1 Optimization of extraction and derivatization conditions

After preliminary experiments the next stage was the optimization of the derivatization and extraction conditions for EDCs through a statistical design.

Firstly, the two-level (2^{7-2}) fractional factorial design was built for the screening of the main variables affecting the extraction and derivatization of the four endocrine disruptors under study. The resulting design saves 75% of trials in relation to full factorial design.

The main effects of seven variables were studied. Results indicate that statistically significant effects on the peak areas were obtained for: the percentage of NaCl, the extraction solvent amount for E1, βE2, and EE2, and also the buffer amount for BPA. Figure 1A presents, as an example, the screening experiments, in the form of a Pareto Chart, for peak area data from BPA. The magnitude of the effects is displayed on an ordered bar-chart and the vertical axis shows the respective *t*-value. The pyridine amount, derivatizing agent amount, dispersant solvent amount and derivatization time had no significant effect on the peak area of endocrine disruptors, and thus they were fixed for further experiments at 10, 200, 100 μL, and 5 min, respectively. The pyridine amount and the dispersant solvent amount were set at the lower values used to reduce the dilution effect in experiment. Derivatization time was also set at the lower value used in experimental design. These particular designs are especially good for screening several factors and search of the vital few variables.

Afterwards, the significant variables were optimized using a CCD, as the factorial design presented a significant curvature. The range parameters for NaCl percentage (X_1), extraction solvent (X_2), and buffer amount (X_3) are shown in Table 2. The experiments were performed in a random manner at different combinations of these parameters using statistically designed experiments. It was also used the quantification of peak area of EDCs as response factor for CCD. The complete design had 19 combinations, including five replicates of the center point.

Regression analysis was performed to fit the response function, and the final model was obtained to the four EDCs. All models presented a good fitness for quadratic interaction, with R^2pred values for BPA, E1, EE2, and βE2 of 0.8888, 0.7934, 0.7976, and 0.8389, respectively, which are in reasonable agreement with the R^2adj values of 0.9553 for BPA, 0.9168 to E1, 0.8676 for βE2, and 0.8861 for EE2. The achieved S/Ns were 22.705, 17.228, 12.173, and 14.400 to BPA, E1, EE2, and βE2, respectively, which indicates adequate signals of the designs. Adequacy and significance of the quadratic model was evaluated by analysis of the variance by means of Fisher's *F* test.

It was obtained a Model *F* value indicating the high significance of the model to the four different responses with only 0.01% possibility that a large Model *F* value could occur due to noise.

The significant terms for each response were those that presented a value of Prob>*F* lower than 0.05. In the case of BPA the significant terms were X_1, X_2, X_3, X_1X_2 and $X_1{}^2$, for E1 were X_1, X_2, X_1X_2, X_2X_3 and $X_1{}^2$, to EE2 were X_1, X_2, X_3, X_2X_3 and $X_2{}^2$, and for βE2 were X_1, X_2, X_3 and $X_1{}^2$. It was also evaluated the "Lack of fit value" for all responses and was obtained a Prob>*F* of 0.4986, 0.5047, 0.9124, and 0.9350 to BPA, E1, EE2, and βE2, respectively, indicating nonsignificant lack of fit ($p > 0.05$), that means that the model is valid for the present study.

Curve analysis of response surfaces for all experimental designs allowed prediction of response function (EDCs peak area) of the effects of the three variables under study. Surface and contour plot demonstrating the effects of NaCl percentage and extraction solvent from BPA data are shown in Fig. 1B. The third variable (buffer amount) was kept constant at the higher level on the response function. According to this optimization study, higher responses were obtained with lower NaCl percentage and lower extraction solvent for

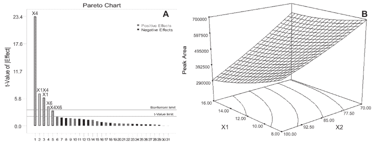

Figure 1. (A) Pareto chart with the magnitude of the chosen main effects (X1: NaCl%; X4: extraction solvent; X6: buffer amount) in derivatization and extraction procedure. Vertical axis shows the *t*-value of the absolute effects. (B) Response surface estimated for the central composite design for extraction procedure. Combined effect of NaCl% (X1) and extraction solvent volume (X2) at constant buffer amount (600 μL).

all EDCs, as well as with high amount of buffer, except for E1 that presented a higher response for a lower amount of buffer (data not shown). Therefore it was established as optimized conditions: 8% w/v of NaCl, 70 μL of extraction solvent and 600 μL of buffer amount that represent a compromise regarding the achievement of the better global response for the target compounds

3.2 Method performance

To ensure that the optimized procedure was suitable for application in routine analysis, the basic analytical performance parameters such as specificity and selectivity, linearity, and linear range, LODs and LOQs, precision, accuracy, and trueness (recovery) were determined and assessed.

Specificity and selectivity were evaluated by comparing the chromatograms of matrix-blank samples (different samples of ultrapure water and glass bottled mineral water) with an aqueous solution of the analytes at concentrations near the LOQs. No significant interferences have been detected at the retention time of the estrogens. Regarding BPA, it was observed a very small chromatographic peak even in the glass bottled mineral water that was used as blank during samples analysis. This fact was probably due to the equipment used in sample preparation [32]. Blank contamination is a common problem in the determination of BPA at these low levels [33]. To reduce blank problems and control the presence of BPA, at level of concentration <5 ng/L, the use of detergents and plastic materials was avoided. All the glassware was carefully washed with ultrapure water, acetone and methanol before use.

Regression parameters obtained after application of the weighting factors were calculated and presented in Table 3.

An excellent linear response was achieved for all analytes, where the lower correlation factor determined was equal to 0.9992 for EE2. The experimental LOD based on the calibration curve parameters ranged between 0.003 and 0.005 μg/L, and LOQ ranged between 0.0094 and 0.0164 μg/L. For BPA, the LOD and LOQ of the proposed method were below those found in the scientific literature regarding miniaturized sample pretreatment techniques coupled to GC–MS [34, 35] and slightly lower than a similar method of DLLME–LC–ESI-MS/MS [33]. For estrogens the proposed methodology presents very lower LOQ and LOD when comparing with a methodology of DLLME–HPLC–UV [36], and only slightly worse than the values presented with SPE–LC–MS/MS [37, 38]. However SPE has a high cost, is time consuming and has high sample consumption.

Evaluation of repeatability and accuracy was performed (Table 4). Results expressed as RSD ranged between 1.1 and 12.6% for intraday precision and between 0.5 and 14.7% for interday precision. Concerning accuracy, bias values varied between –15.0 and 13.7%. These values were below the 20% recommended by regulatory authorities and major international bodies [27, 28] in all three concentration levels.

The applicability of the proposed method was tested in five different types of water samples (groundwater, river, sea, tap water, and mineral water) analyzed according to the developed methodology. In situ derivatization and extraction by DLLME was performed as described in Section 2.3. None of the samples presented detected levels of estrogens, whereas BPA was found in a concentration of 0.0172 μg/L in sea water and detected, but not quantified, in tap water. Recovery studies were performed at three levels of concentration (0.025, 0.100, and 0.500 μg/L). The mean recoveries ranged from 86.4% in E1 for tap water to 118.2% for βE2 in groundwater (Table 5). For each concentration, Student's *t*-test was performed for each type of water, and the comparison between the expected and experimental concentration showed no statistical difference ($p > 0.05$). These results confirm the accuracy of the method in these different types of matrices.

Table 3. Calibration parameters of the purposed method for endocrine disruptors analysis

	LR (μg/L)	$b \pm t_{(n-2)}S_{(b)}$	$a \pm t_{(n-2)}S_{(a)}$	r^2	LOD (μg/L)	LOQ (μg/L)	S (y/x)
BPA	0.010–0.500	0.0242 ± 0.0001	1.6765 ± 0.0181	0.9999	0.005	0.0123	0.0296
E1	0.010–0.500	0.0095 ± 0.0000	0.0113 ± 0.0084	0.9999	0.004	0.0123	0.0296
βE2	0.025–0.500	0.0004 ± 0.0000	-0.0044 ± 0.0004	0.9994	0.005	0.0164	0.0006
EE2	0.010–0.500	0.0014 ± 0.0000	0.0035 ± 0.0007	0.9992	0.003	0.0094	0.0013

LR, linear range; b, slope; a, intercept; r^2, correlation coefficient; S(b) and S(a), SDs of the slope and intercept, S(*y/x*), SD of *y* residuals of regression line.

Table 4. Intraday and interday results on repeatability and accuracy of the proposed method

	Accuracy (%Bias)						Precision (RSD%)					
	Intraday			Interday			Intraday			Interday		
Spiked level (μg/L)	0.025	0.150	0.500	0.025	0.150	0.500	0.025	0.150	0.500	0.025	0.150	0.500
BPA	9.1	–4.6	1.2	–11.9	6.1	5.3	2.2	7.8	5.0	3.0	0.5	6.4
E1	–13.2	12.5	1.5	–5.4	–2.1	–2.2	8.5	1.1	2.0	5.4	13.2	5.1
βE2	9.2	13.7	5.1	4.1	–15.0	5.0	12.6	3.7	3.3	14.7	4.5	3.3
EE2	–0.9	12.1	10.8	–7.4	12.1	2.8	6.4	4.0	1.8	2.9	8.5	11.3

Table 5. Results on concentration and recoveries of the purposed method in different water matrices

		Recovery						
	Spiked level (μg/L)	Sample concentration (μg/L)	Concentration (μg/L)			Mean recovery (%)		
			0.025	0.100	0.500	0.025	0.100	0.500
BPA	Groundwater	< LOD	0.024	0.110	0.478	95.5	109.5	94.9
	River water	< LOD	0.022	0.104	0.475	88.6	103.5	95.5
	Sea water	0.0172	0.028	0.091	0.506	113.5	90.8	101.3
	Tap water	< LOQ	0.026	0.114	0.501	103.5	113.8	100.3
	Mineral Water	< LOD	0.027	0.096	0.506	109.1	96.2	101.2
E1	Groundwater	< LOD	0.026	0.114	0.547	104.8	113.6	109.4
	River water	< LOD	0.023	0.106	0.503	90.9	105.8	100.6
	Sea water	< LOD	0.028	0.092	0.498	111.4	91.6	99.5
	Tap water	< LOD	0.022	0.103	0.467	86.4	103.3	93.3
	Mineral water	< LOD	0.024	0.107	0.507	94.6	106.8	101.5
βE2	Groundwater	< LOD	0.030	0.106	0.547	118.8	106.4	109.3
	River water	< LOD	0.029	0.114	0.563	117.5	114.1	112.6
	Sea water	< LOD	0.029	0.094	0.511	114.3	94.2	102.1
	Tap water	< LOD	0.029	0.114	0.563	117.5	114.1	112.6
	Mineral water	< LOD	0.027	0.085	0.526	109.2	85.1	105.1
EE2	Groundwater	< LOD	0.026	0.108	0.560	104.7	107.7	112.0
	River water	< LOD	0.024	0.097	0.541	94.7	96.9	108.2
	Sea water	< LOD	0.022	0.094	0.528	88.5	93.8	105.6
	Tap water	< LOD	0.028	0.088	0.465	110.1	88.1	93.1
	Mineral water	< LOD	0.025	0.095	0.514	99.1	94.5	102.8

4 Concluding remarks

A quick, cost effective, and eco-friendly method was developed for analysis of four EDCs in water samples by applying in situ derivatization with acetic anhydride followed by DLLME and GC–MS analysis. Multivariate chemometric techniques were successfully used to the screening of relevant derivatization and DLLME extraction variables and to establish optimum conditions of the significant ones, namely, NaCl percentage, extraction solvent and buffer amount for DLLME. Establishment of optimal conditions was obtained with minimal number of assays to obtain maximum EDCs response.

The proposed method was successfully validated in terms of LOD and quantification, precision, and recovery, and it can be applied to routine analyses of BPA, E1, EE2, and βE2 in

different types of water samples, namely, groundwater, river, sea, tap, and mineral water.

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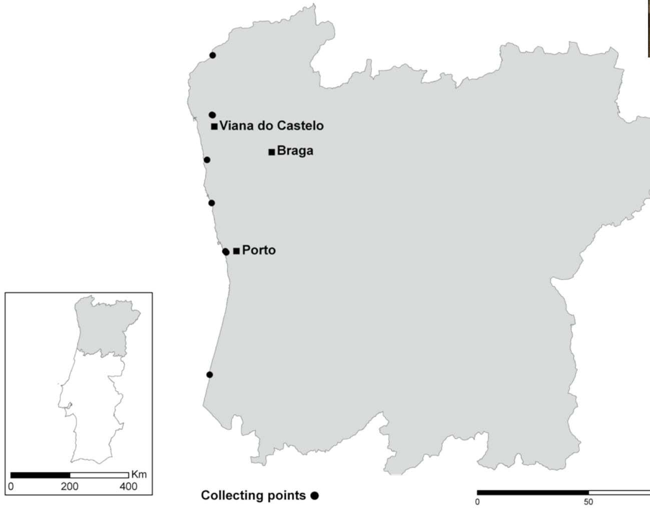


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Sample Code	Coordinates: latitude/longitude		Bisphenol-A	Estrone	17 -Estradiol	17 -Ethinylestradiol
S1 - Tap water	41° 38' 23.900" N	8° 46' 25.374" W	0,091	< LQ	nd	nd
S2 - Tap water	41° 40' 21.235" N	8° 46' 46.969" W	0,253	nd	nd	nd
S3 - Tap water	41° 38' 46.731" N	8° 48' 33.590" W	nd	0,01	nd	nd
S4 - Tap water	41° 39' 15.800" N	8° 41' 23.866" W	nd	nd	< LD	nd
S5 - River water	41° 38' 23.900" N	8° 40' 52.026" W	0,074	nd	nd	nd
S6 - River water	41° 45' 37.096" N	8° 37' 19.880" W	0,087	0,01	nd	nd
S7 - Groundwater	41° 40' 56.184" N	8° 47' 45.658" W	0,045	nd	nd	nd
S8 - Groundwater	41° 41' 27.574" N	8° 49' 49.891" W	< LQ	nd	nd	nd
S9 - Mineral water	--	--	nd	nd	nd	nd
S10 - Sea water	41° 9'15.490" N	8°40'55.070" W	0,017	nd	nd	nd

Tap water was collected in fountains for public supply

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EMERGING CONTAMINANTS
P.0462

DISTRIBUTION AND INTERACTION BETWEEN SELECTED PHARMATEUTICALS AND HYDROGEOCHEMISTRY IN GUADALHORCE AQUIFER (SOUTH OF SPAIN)

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ABSTRACT

There is a growing interest on emerging contaminants (ECs), since they are contaminants that have gone unnoticed over the years due to their low concentrations, although they have adverse effects on health and on environment, some of them behave even as endocrine disruptors. These pollutants are classified into different groups, but stands out the pharmaceuticals and personal care products (PPCPs) as the group that has probably attracted the most interest and concern in recent years. They have been found in surface water, groundwater, sediments and even in drinking water. They are mostly non regulated compounds of which relatively little is known.

The study focuses on porous aquifers of the Guadalhorce river basin (south of Spain), determining theirs distribution and the relationship with existing sources of pollution and with other environmental variables such as the hydrochemical characteristics water bodies. In addition, alternatives are proposed for their removal, because one of the main problems presented is that conventional waste water treatment plants are not designed to remove them.

STUDY AREA

The study was focused on the Guadalhorce River Basin (Malaga Province, South of Spain (Figure 1).

Figure 1. Location of the study area

MATERIAL AND METHOD

14 different PPCPs were measured in 9 sampling points distributed around the study area (Table 1 and Figure 2).

All concentrations are expressed in parts per trillion (ppt) and were sampled during the field sampling of May 2012.

Puntos de muestreo / Emergentes*	Almargen	Campillos	Sierra Teba	Vega Antequera	Vega Antequera	Bajo Guadalhorce	Bajo Guadalhorce	Bajo Guadalhorce	Bajo Guadalhorce
	Pozo Granja Aeropuerto	Pozo Granja Capitanía	Manantial de Torrox	Cortijo Las Monjas	Cruce MACO	Pozo Vega Sta María	Pozo Harinera de Pizarra	Pozo Mestanza	La Isla
	1	2	3	4	5	6	7	8	9
Ibuprofen	53 ± 0	84 ± 29	58 ± 12	97 ± 14	79 ± 7	61 ± 8	54 ± 16	60 ± 2	750 ± 229
Hidroclorothiazide	1 ± 1	-	31 ± 6	5 ± 2	26 ± 1	10 ± 0	31 ± 17	-	1 ± 1
Salicilic Acid	13 ± 0	17 ± 0	13 ± 3	13 ± 0	24 ± 2	12 ± 1	19 ± 2	16 ± 1	19 ± 6
Triclosan	12 ± 1	11 ± 10	15 ± 8	16 ± 4	11 ± 10	21 ± 7	16 ± 1	10 ± 1	17 ± 10
Mefenamic Acid	28 ± 1	33 ± 0	33 ± 5	45 ± 1	35 ± 0	33 ± 6	33 ± 6	35 ± 1	50 ± 8
Carbamazepine	-	2 ± 0	3 ± 0	-	3 ± 0	-	-	-	-
Trimethoprim	2 ± 1	-	-	-	-	-	-	-	-
Ofloxacine	-	-	-	-	-	34 ± 14	12 ± 2	8	-
Caffeine	6 ± 0	-	10 ± 2	-	47 ± 3	13 ± 8	10 ± 0	9 ± 5	61 ± 5
Metotrexato	-	-	-	-	-	4 ± 1	3 ± 0	-	-
Metronidazole	2 ± 0	4 ± 0	3 ± 0	3 ± 0	5 ± 4	-	3 ± 0	5 ± 2	-
Sulfadiazine	-	3 ± 0	-	-	-	-	-	-	-
Sulfamethazine	4 ± 1	2 ± 0	2 ± 0	-	-	-	-	-	1 ± 0
Sulfamethoxazole	-	-	3 ± 1	1 ± 0	2 ± 0	3 ± 2	7 ± 1	-	-
∑	121 ± 5	156 ± 39	171 ± 37	180 ± 21	232 ± 27	191 ± 47	188 ± 45	143 ± 12	899 ± 259

Table 1. Emerging contaminants concentrations (ppt) sampled in the Guadalhorce river basin, in May 2012.

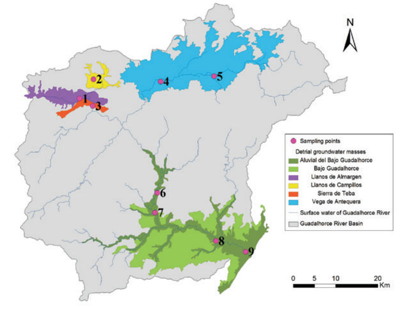


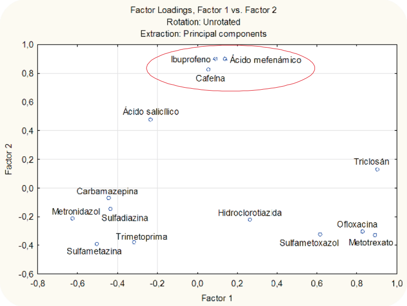
Figure 2. Sampling points in the study area.

RESULTS

RELATIONSHIP AMONG EMERGING CONTAMINANTS

A Principal Component Analysis (PCA) has been carried out (Figure 3) and results indicate that:
(1) Ibuprofen, mefenamic acid and caffeine have a direct relationship and are also linked to urban areas (Ibuprofen and mefenamic acid have a nonsteroidal anti-inflammatory medications (NSAIDs) use).

(2) Triclosan, ofloxacin and methotrexate have a direct relationship, and linked to urban areas;

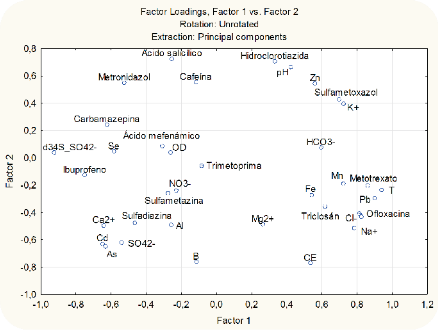


	Factor 1	Factor 2	Factor 3
Ibuprofen	0,092	0,900	-0,276
Hidroclorothizide	0,262	-0,219	0,783
Salicilic Acid	-0,236	0,478	0,655
Triclosan	0,904	0,130	-0,204
Mefenamic Acid	0,139	0,900	-0,121
Carbamazepine	-0,445	-0,068	0,635
Trimethoprim	-0,317	-0,378	-0,615
Ofloxacin	0,829	-0,304	-0,052
Caffeine	0,054	0,826	0,192
Metotrexato	0,892	-0,328	0,079
Metronidazole	-0,626	-0,214	0,613
Sulfadiazine	-0,436	-0,147	-0,004
Sulfamethazine	-0,505	-0,389	-0,543
Sulfamethoxazole	0,614	-0,325	0,543
Expl.Var	3,966	3,267	2,968
Prp.Totl	0,283	0,233	0,212

Figure 3. PCA results among emerging contaminants.

RELATIONSHIP BETWEEN EMERGING CONTAMINANTS AND HYDROGEOCHEMISTRY OF AQUIFERS

Some hydrochemical variables related directly or indirectly to the concentrations of some PPCPs (Figure 4). These relationships are not functional, if not casual relationships linked through the same source activity (**In study**).



	Factor 1	Factor 2	Factor 3
Ibuprofen	-0,751	-0,124	-0,506
Hidroclorothizide	0,332	0,707	-0,414
Salicilic Acid	-0,254	0,727	-0,395
Triclosan	0,619	-0,354	-0,278
Mefenamic Acid	-0,309	0,086	-0,489
Carbamazepine	-0,624	0,245	-0,401
Trimethoprim	-0,084	-0,059	0,952
Ofloxacin	0,812	-0,407	-0,259
Caffeine	-0,118	0,555	-0,241
Metotrexato	0,861	-0,202	-0,304
Metronidazole	-0,525	0,551	-0,222
Sulfadiazine	-0,465	-0,475	-0,286
Sulfamethazine	-0,278	-0,258	0,813
Sulfamethoxazole	0,698	0,427	-0,335
CE	0,534	-0,769	0,259
T	0,940	-0,235	-0,038
pH	0,423	0,666	0,572
OD	-0,262	0,041	-0,377
Cl-	0,824	-0,429	-0,078
SO42-	-0,541	-0,618	-0,407
HCO3-	0,594	0,076	0,747
NO3-	-0,229	-0,239	0,856
Na+	0,784	-0,511	0,011
Mg2+	0,264	-0,484	-0,249
Ca2+	-0,640	-0,492	0,003
K+	0,722	0,396	-0,389
B	-0,115	-0,758	-0,172
Al	-0,260	-0,489	-0,324
Fe	0,542	-0,273	-0,533
Mn	0,723	-0,186	-0,051
Cd	-0,649	-0,629	-0,148
Pb	0,901	-0,293	-0,190
Zn	0,561	0,547	-0,161
As	-0,630	-0,646	-0,223
Se	-0,585	0,048	-0,078
d34S SO42-	-0,924	0,039	0,157
Expl.Var	12,528	7,274	5,887
Prp.Totl	0,348	0,202	0,164

Figure 4. PCA between emergents and hydrogeochemistry

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EMERGING CONTAMINANTS
P.0462

DISTRIBUTION AND INTERACTION BETWEEN SELECTED PHARMATEUTICALS AND HYDROGEOCHEMISTRY IN GUADALHORCE AQUIFER (SOUTH OF SPAIN)

UNIVERSIDAD DE MÁLAGA
UPC
UCA Universidad de Cádiz

RELATIONSHIP BETWEEN EMERGING POLLUTANTS AND POLLUTION SOURCES

1.- Selection of pollution sources in the areas of influence (2 km) and in the direction of groundwater flow (Figure 5). Closest area to the river mouth (48 % of total sources) has the highest concentrations of emerging pollutants.

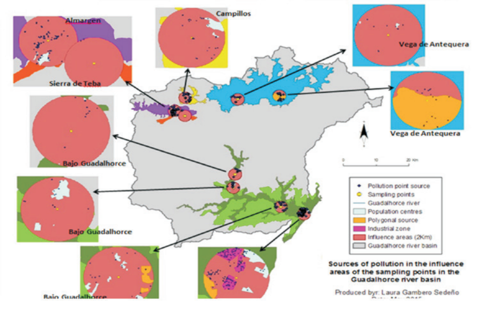


Figure 5. Influence areas around each sampling points

2.- Principal Component Analysis between emerging pollutants and pollution sources (Figure 6):

- Ibuprofen, mefenamic acid and caffeine are directly related to the amount of ECs in an area. They are the ECs that have been measured in the highest concentrations with an important influence on the total concentration of PPCPs sampled in an area.

- These have a high direct correlation with wastewater, which is the main gateway of PPCPs to the environment, either by irrigation with sewage or by direct discharge.

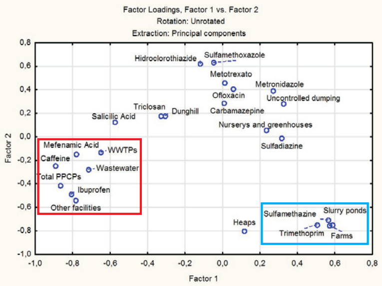
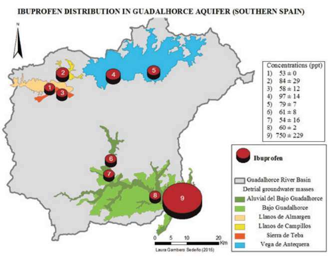


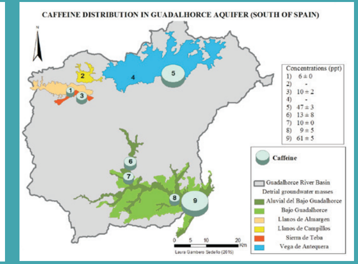
Figure 6. PCA results between emerging contaminants and pollution sources

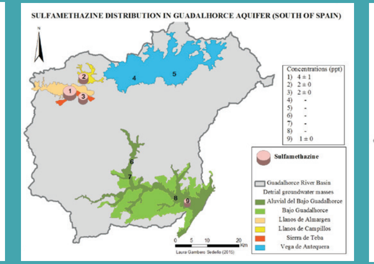
- Sulfamethazine (drug used in animals as antiprotozoal and antibacterial) and Trimethoprim (drug that can be applied against intestinal parasites in animals) are directly related to the number of farms and slurry ponds in a zone.

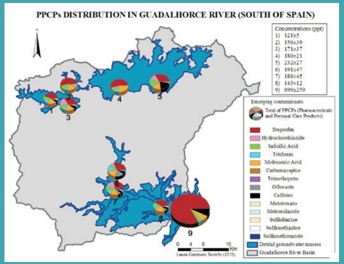
	Factor 1	Factor 2	Factor 3
Ibuprofen	-0,808	-0,486	-0,133
Hidroclorothizide	-0,119	0,625	0,140
Salicilic Acid	-0,574	0,125	0,620
Triclosan	-0,329	0,178	-0,873
Mefenamic Acid	-0,782	-0,146	-0,095
Carbamazepine	0,007	0,288	0,670
Trimethoprim	0,505	-0,747	-0,042
Ofloxacin	0,058	0,409	-0,728
Caffeine	-0,892	-0,245	0,196
Metotrexato	0,011	0,461	-0,741
Metronidazole	0,269	0,391	0,832
Sulfadiazine	0,314	-0,009	0,264
Sulfamethazine	0,563	-0,708	0,086
Sulfamethoxazole	-0,046	0,632	-0,307
Total PPCPs	-0,865	-0,413	-0,135
Wastewater Treatment Plants	-0,649	-0,129	0,472
Dunghill	-0,307	0,177	0,651
Heaps	0,116	-0,800	-0,433
Farms	0,572	-0,753	0,213
Slurry ponds	0,588	-0,747	0,026
Wastewater	-0,717	-0,276	-0,031
Uncontrolled dumping	0,327	0,282	-0,213
Other facilities	-0,784	-0,541	-0,141
Nurserys and greenhouses	0,235	0,056	0,071
Expl.Var	6,502	5,265	4,595
Prp.Totl	0,271	0,219	0,191

DISTRIBUTION OF SELECTED PPCPS IN THE GUADALHORCE RIVER BASIN (SOUTH OF SPAIN)









SOLUTIONS

1.- Increase retention time of the water in the waste water treatment plants during treatment, to eliminate higher percentage of drugs.

2.- Replacing conventional treatment in wastewater treatment plants by more advanced treatments such as membrane bioreactors and advanced oxidation processes, which eliminate higher percentage of CEs, although the main disadvantage is the high cost.

3.- Other alternatives to eliminate pharmaceutical products are artificial wetlands and ligninolytic fungi, both under examination but with good results at laboratory scale.

4.- Regulation of these ECs in the legislation would help to take better account of these substances in the environment.

5.- Avoiding certain uses of treated wastewater, as artificial recharge.

CONCLUSIONS

- Emerging contaminants (ECs), especially, pharmaceuticals and personal care products (PPCPs) have been detected, identified and quantified PPCPs in groundwater aquifers of the Guadalhorce River Basin (Malaga, South of Spain).
- There is an intense and continuous contamination of the area, mainly from urban areas and livestock originated in the northwestern part of the basin.
- The reuse of treated wastewater becomes the main entrance of contaminants into the environment, followed by livestock activities.
- The type, number and proximity of pollution sources to the sampling points strongly influence the concentrations of ECs.
- Some hydrochemical characteristics of the groundwater masses are related to the concentrations of PPCPs, linked through the same source activity.

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Variability of removal rate constants - A compilation from lab experiments on the fate of organic micropollutants within an urban water cycle

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Introduction

Owing to advanced analytical procedures an increasing number of organic micropollutants have been identified within the aquatic environment. Within urban areas, organic micropollutants are mainly introduced into the water cycle via sewage systems, since treated wastewater containing residuals of these pollutants is discharged into surface water and thus resupplied to the water cycle (see Fig. 1).
Results from field investigations evidenced the attenuation of various micropollutants to be impacted by the prevailing hydrochemical conditions [e.g. 1,2], e.g. the redox environment. In order to investigate the impact of the redox conditions on the attenuation of various organic pollutants within an urban water cycle, we simulated three stages of it by means of different experimental setups.

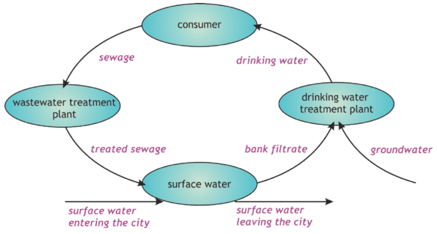
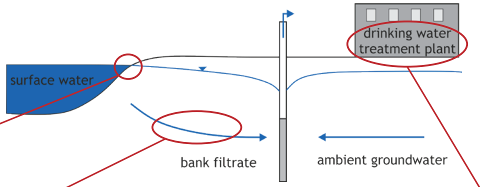


Fig. 1: Urban partly closed water cycle

Methods

1. ‘undisturbed core study‘ in order to simulate the process of infiltration of wastewater loaded surface water into the subsurface (Fig. 2)
2. ‘systematic column study’ in order to mimic conditions along the groundwater flow path within the aquifer (Fig. 3)
3. ‘tank aeration experiments’ covering one treatment step within drinking water treatment (Fig. 4)



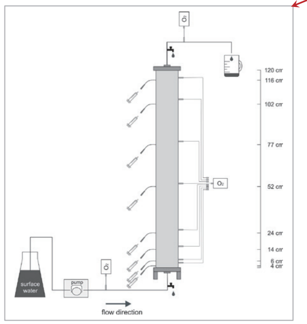


Fig. 2: Setup ‘undisturbed core study‘ [3]

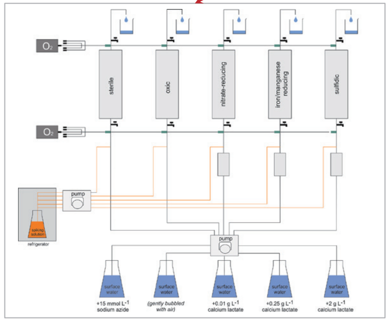


Fig. 3: Setup ‘systematic column study‘

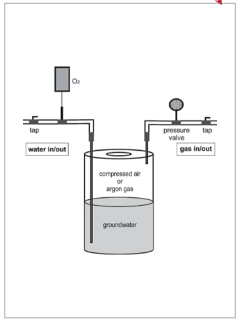


Fig. 4: Setup ‘tank aeration experiments‘[4]

Results & Conclusions

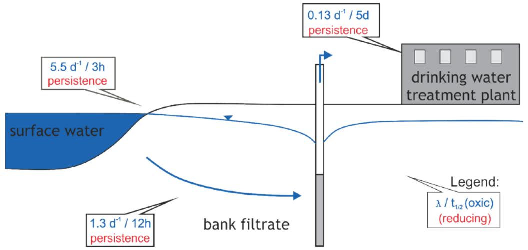


Fig. 5: Observed removal rate constants and corresponding half-life times ***exemplified*** *illustrated for the analgesic* ***phenazone***

- no degradation under of anoxic conditions, indicating the strong influence of the redox environment
- the hyporheic zone was proven to be highly reactive, as under oxic conditions a half-life time of 3 hours was observed
- proceeding along the groundwater flow path resulted in decreasing removal rate constants (1.3 d-1 and a corresponding half-life time of 12 hours for phenazone) → still indicating an efficient removal under oxic conditions
- simple aeration of anoxic groundwater within the tank experiments resulted in the removal of numerous micropollutants, but significantly lower removal rate constants compared to the aforementioned studies
- results highlight the enormous attenuation efficiency of the saturated zone compared to technical systems

$$\lambda_{infiltration\ zone} > \lambda_{gw\ flow\ path} > \lambda_{aeration}$$

- similar results were observed for other compounds (e.g. FAA, Metoprolol) while investigating the redox-sensitive degradation behavior of a total of 36 organic micropollutants classified as pharmaceuticals and industrial products

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[2] Hijosa-Valsero et al., Water Research 2010, 44(12), 3669-3678
[3] Burke et al., Science of the Total Environment 2014, 482, 53-61
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