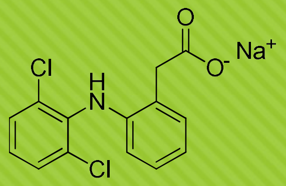
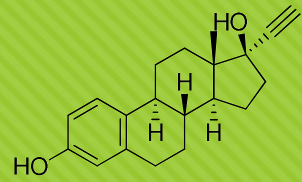
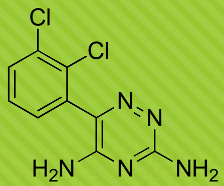
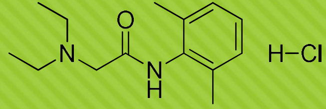
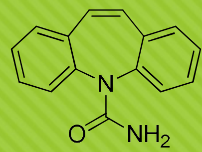
Adsorption of drugs on a hydromorphic soil as affected by their chemical properties











Lili Szabó, Attila Csaba Kondor, Tibor Filep, Gergely Jakab,
Anna Vancsik, Lilla Gáspár, Marianna Ringer and Zoltán Szalai

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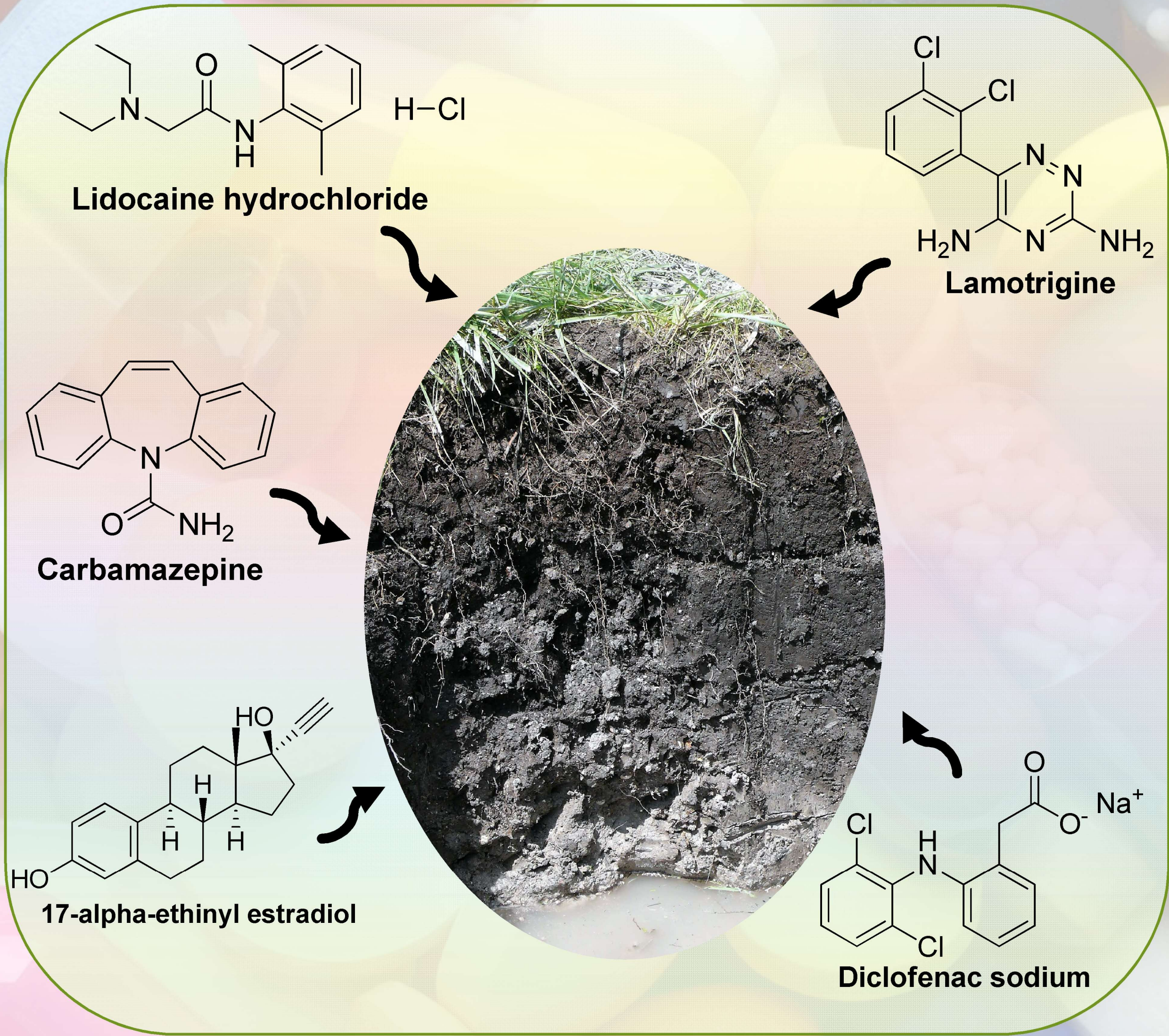
Overview

Methods

Results

Overview

- The present study focuses on the sorption of diclofenac, lidocaine, carbamazepine, 17-alpha-ethinyl-estradiol and lamotrigine on a hydromorphic soil.
- Adsorption of pharmaceuticals on the soil was examined to estimate the effect of their intrinsic chemical properties on the sorption.
- Adsorption isotherms were applied using Langmuir, Freundlich and a Polanyi-based model in a batch technique experiment under ambient conditions.



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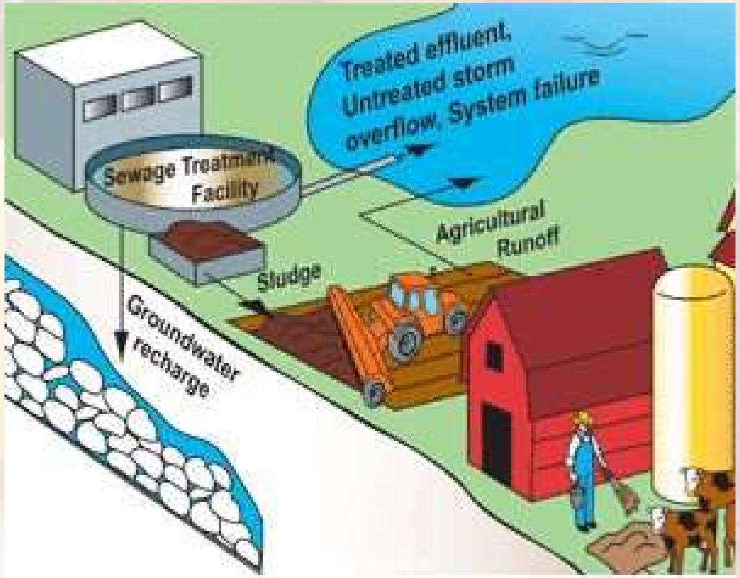
Why is it so important to investigate? 2/3

- During the sewage treatment pharmaceuticals may be adsorbed onto the sludge or remained unchanged in the water phase. Furthermore, recycled water and wastewater sludge are often used in agriculture, so these materials can be appeared in the environment not only by direct release of effluents to waterways

- The presence of pharmaceuticals is constantly increasing in the environment. The pharmaceuticals are gone through metabolic processes and then excreted from humans or animals unchanged or as active metabolites.

- They are repeatedly discharged into domestic waste waters. Their solubility in water is different, therefore the persistence and bioavailability in the aquatic environment depend on their sorption on the solid phase.



This drawing shows some of the contributions of sewage, biosolids and farms to PPCPs in the environment. (http://www.epa.gov/ppcp/basic2.html)

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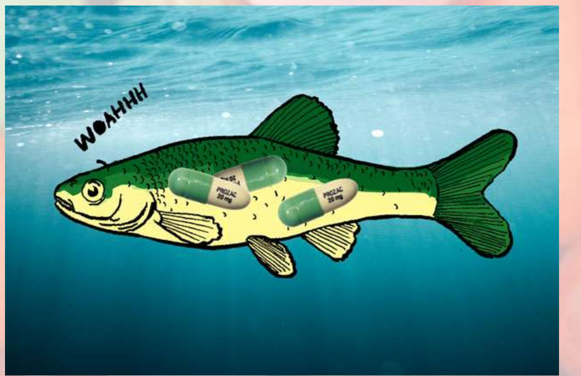
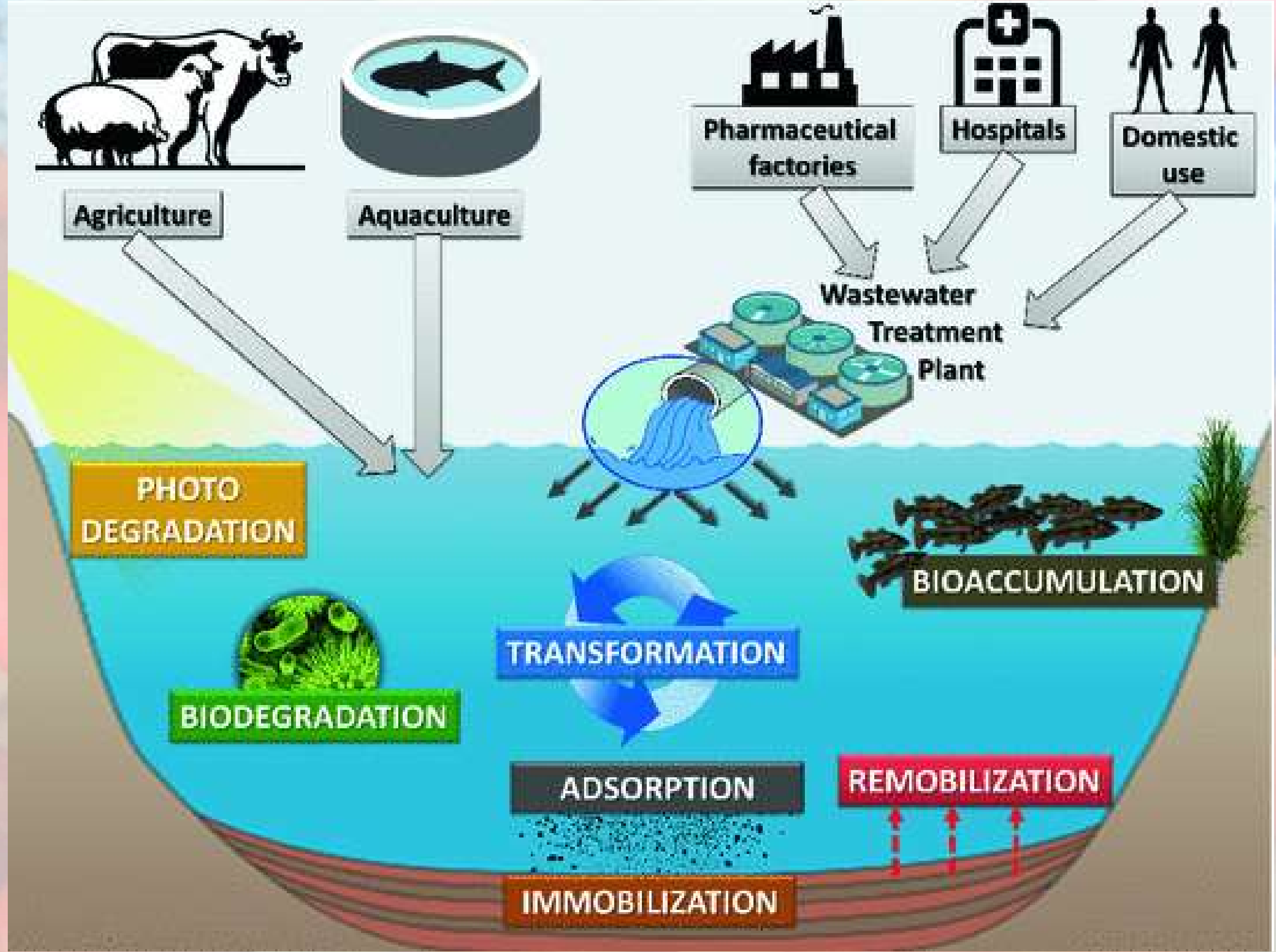
Flow chart of the pharmaceutical pollution





Klimaszyk P., Rzymski P. (2018) Water and Aquatic Fauna on Drugs: What are the Impacts of Pharmaceutical Pollution?. In: Zelenakova M. (eds) Water Management and the Environment: Case Studies. WINEC 2017. Water Science and Technology Library, vol 86. Springer, Cham

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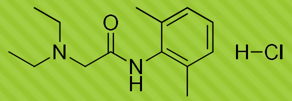
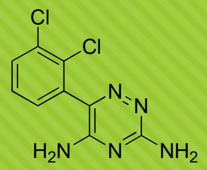
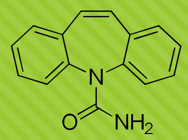
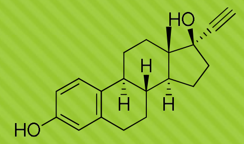
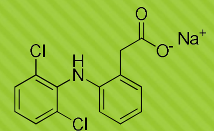
Methods











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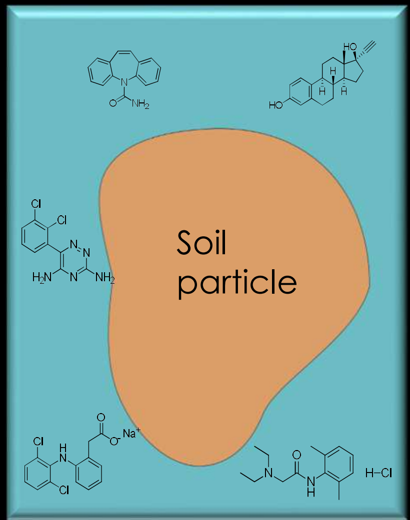
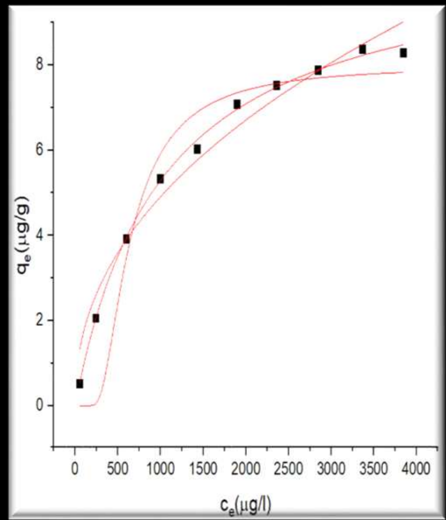
Results

Parameters of the soil samples

Chemical parameters of drugs



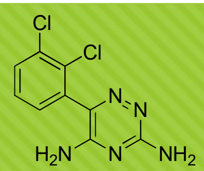
Adsorption experiments

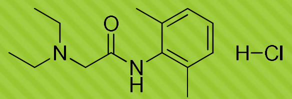


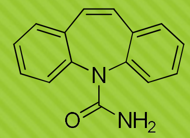
Isotherm models

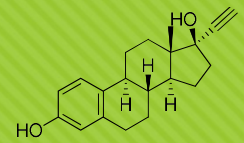
HPLC methods

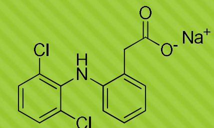
Parameters of the soil samples











Sampling:
Location: Hungary, Ceglédbercel,
47° 12' 30.0954'', 19° 40' 45.4074,,

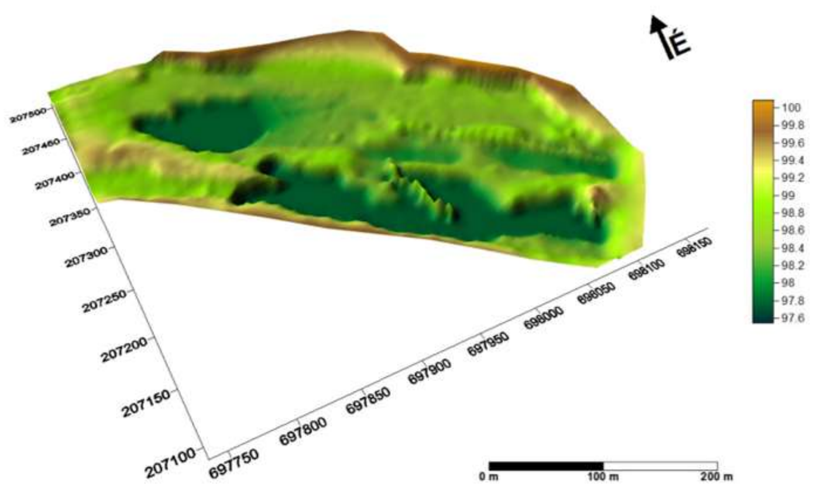
Equipment: Edelman type hand auger

Sorbent	pH (H_2O)	pH (KCl)	SOC (%)	C/N	$CaCO_3$ (%)	Fe (%)	SSA-N_2 (m^2/g)
H_20	7.5	7.2	24.4	8.0	55.4	1.2	5.6

More information of the study area

Study area

Topography of the study area



- Our study focuses on an approx. 8 ha marshy meadow located in the former floodplain of the stream Gerje. The history of the area is documented in contemporary reports and also confirmed by the land owner. The primary surface consisted of a succession of low ridges of sand dunes and shallow troughs along the stream, with progressing peat formation in the hollows. The settlement and regular dredging of the Gerje riverbed as part of waste water management happened in the 1970s. Consequently, the groundwater level ebbed to a mean of approx. 30 cm below the surface but still has a wide-range seasonal fluctuation.
- The meadow area is inundated by water for meanly 5-9 months of the year. The topsoil is almost permanently water saturated, exceeding field capacity.
- In a higher relief , some tens of meters away from the stream lies an area utilized as plough field. The soil of this plough field evolved on the same calcareous sand which functioned as parent material of the studied meadow soil but in the total absence of water saturation. During our investigations we used this material as a reference.

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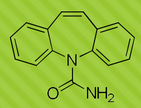
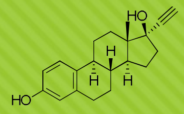
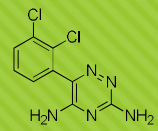
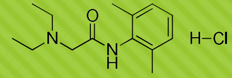
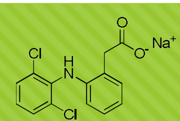
Chemical parameters of drugs

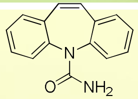
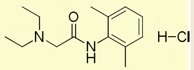
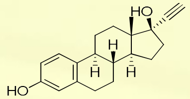
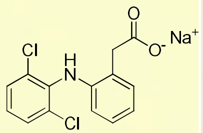
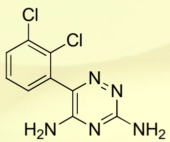










Pharmaceuticals	Structure	Drug and Medication Information	Molecular Weight (g/mol)	Water Solubility (mg/l)	Octanol/Water Partition Coefficient ($logk_{ow}$)	Dissociation Constants (pKa)
Carbamazepine		For the treatment of epilepsy and pain associated with true trigeminal neuralgia	236.274	17.7	2.45	13.9
Lidocaine-HCl		A local anesthetic and cardiac depressant used as an antiarrhythmia agent.	234.343	4100	2.4	7.75
Ethinyl-estradiol		It is a semisynthetic estrogen which is used widely in birth control pills and menopausal hormone therapy.	296.41	4.8	3.9	10.33
Diclofenac-Na		A nonsteroidal anti-inflammatory drug (NSAID) which is used to relieve pain, swelling (inflammation), and joint stiffness caused by arthritis.	296.147	2.37	1.56	4.15
Lamotrigine		Antiepileptic drug belonging in the phenyltriazine class used in the treatment of epilepsy and bipolar disorder.	256.09	170	2.19	8.53 pKa2= 9.21

Adsorption experiments

- The sorption of the selected drugs was measured at room temperature (25+- 1°C) by a batch equilibration method.
- Adsorption experiments were executed in 15 ml polypropylene centrifuge tube which were placed in a tube rotator for 2h at 50 rpm.
- Mixtures were centrifuged at 5200 rpm for 10 min to separate the liquid from the sediment. The supernatants were filtered through 0,45 μm glass filter and transferred to 1.5 ml amber short thread vials for HPLC analysis (HPLC- FL/PDA detector (Shimadzu Prominance LC-20AR)).
- According to the results from the preliminary kinetic experiments, this amount of time was enough to achieve the corresponding equilibrium.
- The soil/solution ratios were set to be 1:12 g/ml. The applied doses were as follows: 100, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500 and 5000 μg/l.

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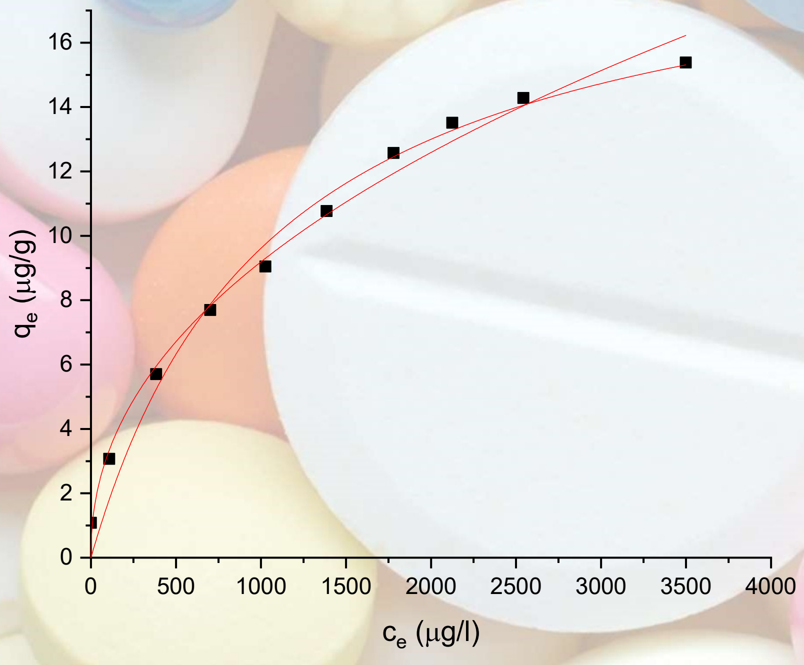
Isotherm models 1/2



Langmuir model: $q_e = Q_{max} * \frac{k_L * c_e}{1 + k_L * c_e}$

Freundlich model: $q_e = K_f * C_e^{1/n}$

q_e is the absorbed drug on the soil samples (µg/g)

K_f is the Freundlich adsorption coefficient $((\mu g/g)/(\mu g/l)^{1/n})$

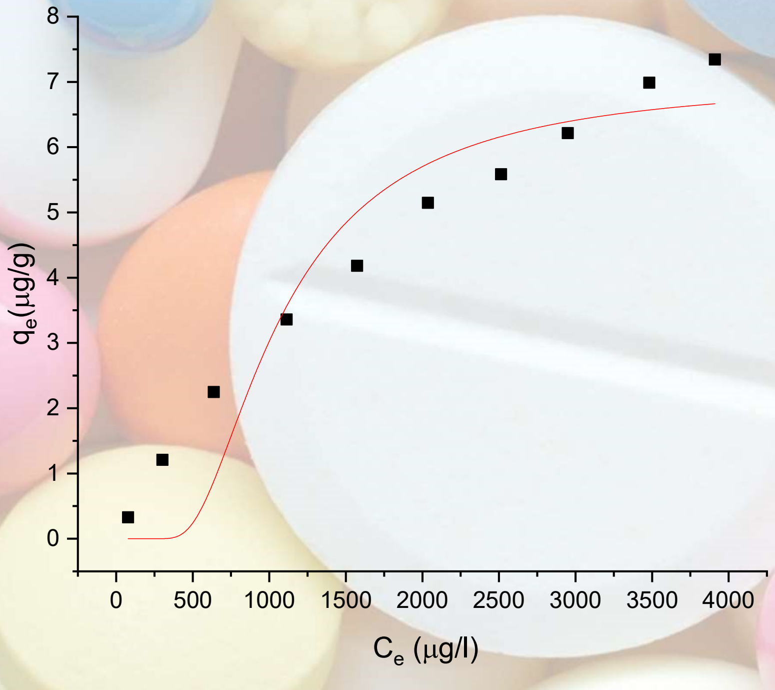
c_e is the equilibrium concentration of the aqueous phase (µg/l)

n is a dimensionless number which refers to the nonlinearity between the equilibrium concentration and the amount of adsorbed drug

Q_{max} is the maximum adsorption capacity (µg/g)

K_L is the Langmuir fitting parameter (l/µg)

Isotherm models 2/2



Dubinin-Raduskevich equation was applied to characterize the free energy of the adsorption. The equation were used to determine the type of the sorption mechanism such as physical and chemical.:

$$q_e = q_m * \exp(-\beta\varepsilon^2)$$

q_m is the theoretical saturation capacity (μg/g),
β is the isotherm constant (mol^2/kJ^2)
ε is the Polanyi potential which can be expressed by the formula below:

$$\varepsilon = RT \ln(1+1/c_e)$$

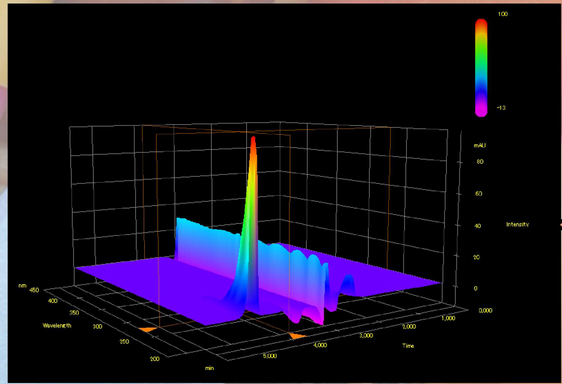
R is the gas constant (8.314 kJ/mol)
T is the absolute temperature (K).

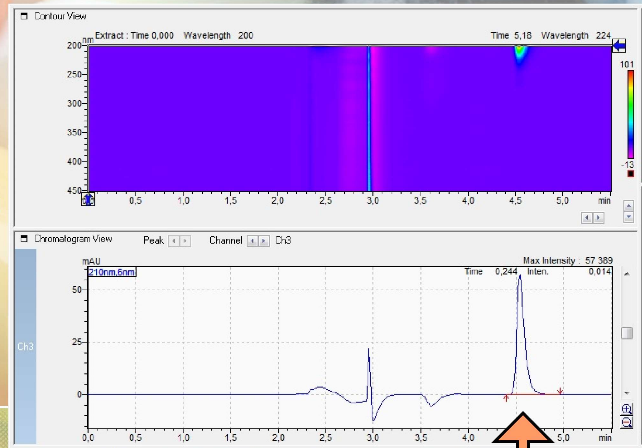
The free energy (E) can be calculated from the following relationship:

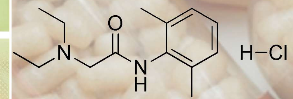
$$E = \frac{1}{\sqrt{-2\beta}}$$

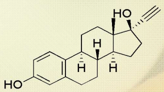
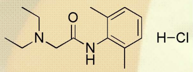
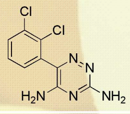
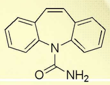
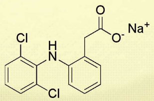
If the value of the energy is between 8-16 kJ/mol the sorption is based on chemical process. If the value is less than 8 kJ/mol, there is a physical sorption.

HPLC methods







	Total flow (ml/min)	Water/ Acetonitrile (%)	Column temperature (°C)	Ret.time (min)	UV λ (nm)	Fluorescence λ (nm)
EE2 	0.5	50/50	40	7.2	-	Ex: 280 Em: 310
Lidocaine 	0.6	80/20	30	4.5	210	-
Lamotrigine 	0.9	77/23	40	3.2	230	-
Carbamazepine 	1	50/50	40	6.5	285	-
Diclofenac-Na 	1	40/60	40	3.6	276	-

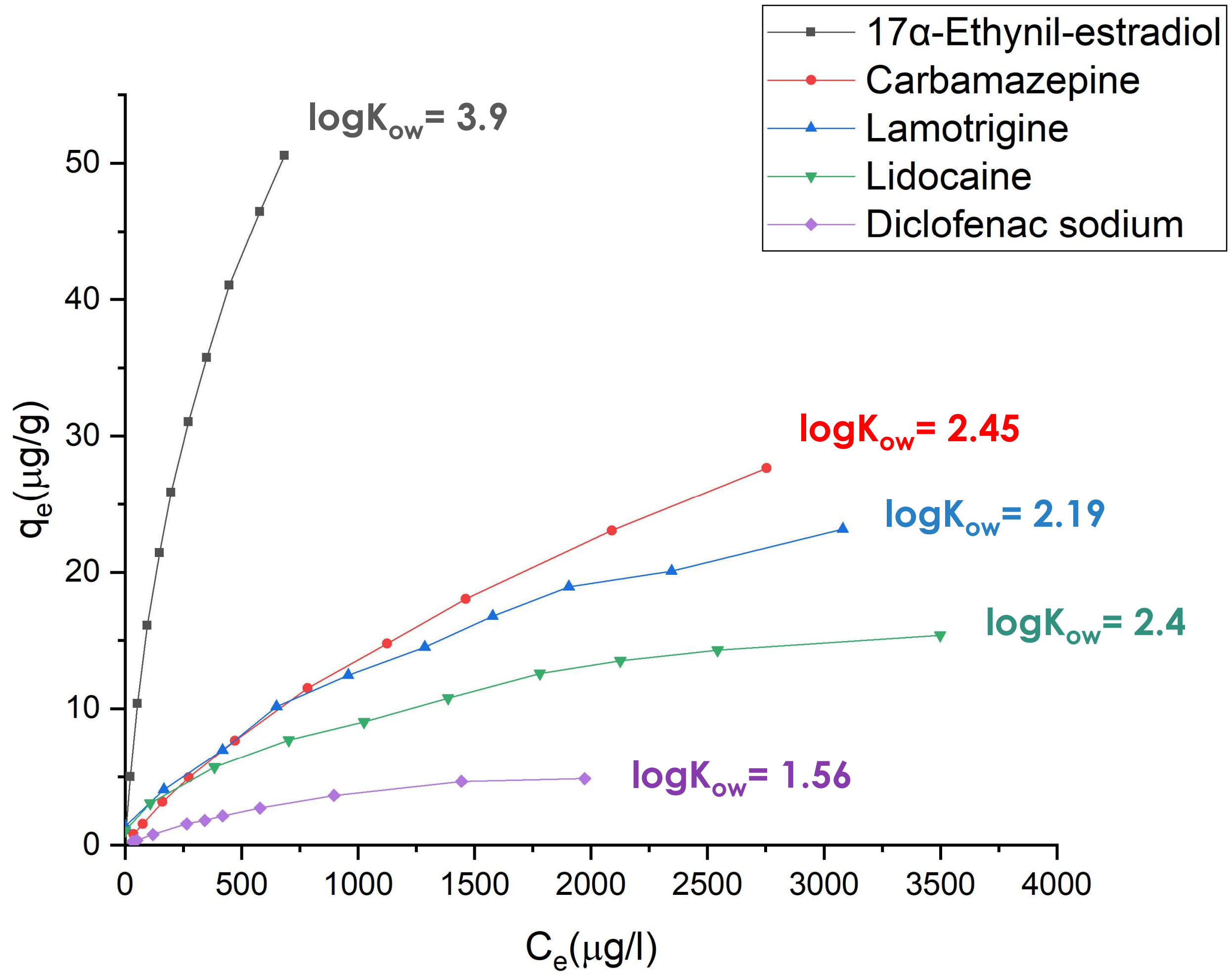
HPLC (Shimadzu Prominance LC-20AR) PDA/Fluorescence

SunShell C18 column with 2.6 μm poresize (4.6 mmx 150 mm)

Results

1/3

Adsorption isotherms



Adsorption isotherms of the selected drugs on the hydromorphic soil

Ethnynil-estradiol (EE2) > Carbamazepine > Lamotrigin > Lidocaine > Diclofenac-Na

logk$_{ow}$= Octanol/Water Partition Coefficient

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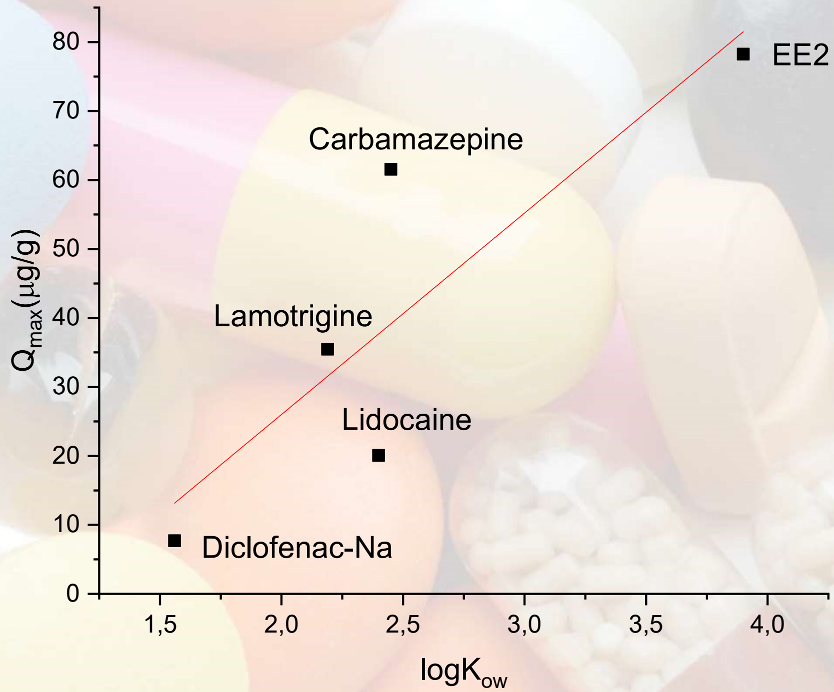
Adsorption capacity of the soil estimated by adsorption parameters

	Q (μg/g)	kF ((μg/g)/(μg/l)$^{1/n}$)	n
Lamotrigine	35.45	0.25	0.56
Lidocaine	20.07	0.39	0.45
Diclofenac-Na	7.71	0.058	0.59
Carbamazepine	61.54	0.084	0.73
EE2	78.25	1.093	0.59



- Molecules with different chemical properties were adsorbed onto the soil in varying amounts
- Strong relationship between Q_{max} and $logK_{ow}$ was found. The hydrophobic molecule has greater affinity to the soil, probably due to the large amount of organic matter and $CaCo_3$ (hydrophobic interaction)
- n were not close to 1, which meant the nonlinearity of adsorption isotherms

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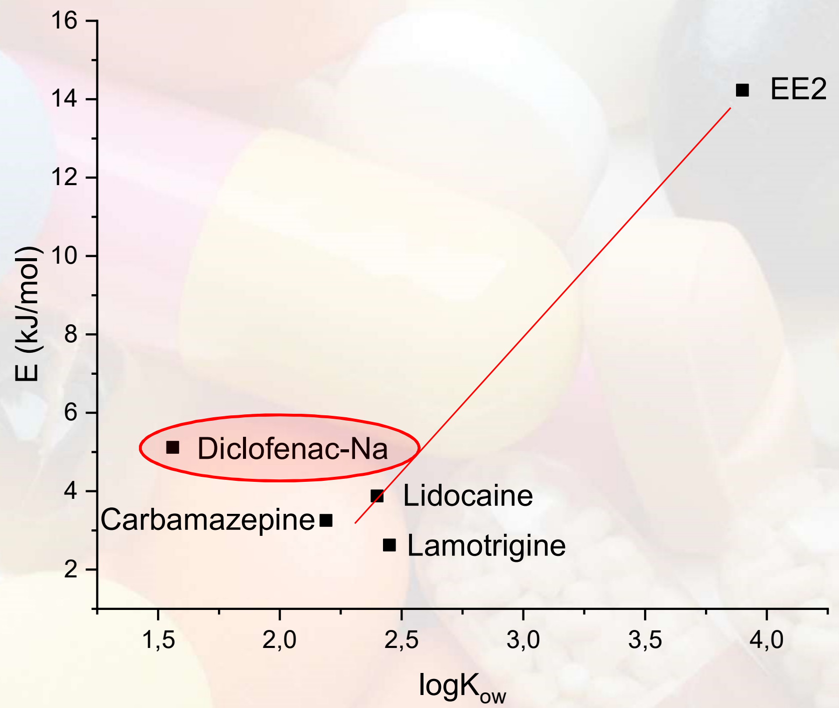
The energy of the sorption estimated by adsorption parameters 3/3

	k_L (l/µg)	E (kJ/mol)
Lamotrigine	5.81E-04	3.25
Lidocaine	9.19E-04	3.87
Diclofenac-Na	9.48E-04	5.11
Carbamazepine	2.90E-04	2.62
EE2	2.52E-03	14.23

E= free energy (kJ/mol)
Chemical process: E = 8-16 kJ/mol
Physical sorption: E < 8 kJ/mol



- The very high energy of the sorption of EE2 can be attributed to hydrogen bonding. The drugs with lower sorption energy have intermolecular interactions including hydrophobic interaction and π–π bonding which are the dominant sorption mechanisms.
- The high sorption energy of diclofenac can be explained by the ability to form Cation bridging due to the high concentration of calcium in the sample.

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Risks of some endocrine disruptors and developments for risk mitigation in Budapest Metropolitan Region

The project, supported by the Hungarian National Research, Development and Innovation Fund, focuses upon Budapest and its commuting zone (Budapest Metropolitan Region), where more than 3.2 million people live and use the highly urbanized area intensively. In this region, our researchers examine the spatial movement, accumulation, decomposition and entrapment of endocrine disruptors (EDCs) found in treated and untreated sewage. As researchers know, these materials (e.g. toxic heavy metals, hormones, certain SSRI antidepressants) can be risky for the ecosystem and people incorporating into the food chain.

During the basic research, the concentration of EDCs will be measured in the complete cycle of water in the urban and suburban area, and the way of these toxic materials will be analysed, modelled and mapped. Applied research and experimental development aim to evolve new prevention and sewage treatment methods and techniques to reduce the concentration of EDCs.

SZIE Halgazdálkodási Tanszék
AQUAPROFIT
UTB Envirotec
CSFK
MTA Csillagászati és Földtudományi Kutatóközpont FÖLDRAJZTUDOMÁNYI INTÉZET
MTA CSFK Földtani és Geokémiai Intézet
SZENT ISTVÁN EGYETEM

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MOMENTUM OF INNOVATION

MTA CSFK Laboratory for Sediment and Soil Analyses

The Laboratory for Sediment and Soil Analysis (SEDILAB) of the Geographical Institute, RCAES is the successor of the former laboratory of the same name of the Geographical Research Institute of Hungarian Academy of Sciences (MTA). Former laboratory mainly analysed loess and other sediments for Quaternary research in the 1970s and 1980s according to the researchers needs. Due to the downsizing of the institute the staff of the laboratory was decreased to one person, the instrumentation was degraded. The laboratory as a self-contained unit was ceased to exist.

The SEDILAB was re-established in 2004. The instrumentation was expanded at first with a laser particle sizer and with an NDIR-chemiluminescence TOC/TN analyzer. Further expansion of the instrumentation has been countinous since 2012. The expansion of the instrumentation implied the staff increase, which was partly filled by PhD students and trainees due to the collaboration with the Eötvös Loránd University.

CSFK

MTA Csillagászati és Földtudományi Kutatóközpont
FÖLDRAJZTUDOMÁNYI INTÉZET