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"IDENTIFICATION OF ABSORBED ORGANIC MICROPOLLUTANTS VIA GC/MS"

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Autor/a:
Andrea Oliver Marín

Tutor/a:
BERTRAM KUCH
JESÚS MENGUAL CUQUERELLA

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IDENTIFICATION OF ABSORBED ORGANIC MICROPOLLUTANTS VIA GC/MS

APPLICATION OF GRANULAR ACTIVATED CARBON IN MUNICIPAL WASTEWATER TREATMENT PLANTS

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STUDENT: ANDREA OLIVER MARÍN

PROFESSOR: BERTRAM KUCH

JESUS MENGUAL CUQUERELLA

University of Stuttgart

ABSTRACT

Today's world must face serious damages to ecosystems and human health due to pollution. This research focuses on a group of substances called micropollutants. The importance of these compounds is that despite of being in low concentration, they can cause significant problems in the environment because its physical and chemical properties. Wastewater Treatment Plants (WWTPs) use a technique called granular activated carbon in order to remove them. To know more about the behaviour and presence of these compounds, we have analysed samples of granular activated carbon via GC/MS from three different WWTPs: Mannheim, Emmingen-Liptingen and Eriskirch. Furthermore, we have characterized the main compounds and have established a comparison between them considering different parameters such as bioconcentration factor and mutagenicity. We have found that the carbon has high concentrations of micropollutants, especially TCPP, OTNE, HHCB Lactone 1 and MTBT, and it appears to degrade them to other forms over time. This project opens the possibility of utilizing granular activated carbon not only as a filter, but as a method to degrade some of the micropollutants considered as dangerous or not easily biodegradable in some less dangerous degradation products.

Keywords: micropollutant; wastewater; granular activated carbon; wastewater treatment plant.

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LIST OF ABBREVIATIONS

- WWTP: Wastewater Treatment Plant.
- GAC: granular activated carbon.
- BCF: bioconcentration factor.
- LC50: Median lethal dose.
- HHCB L1: HHCB lactone 1.
- HHCB L2: HHCB lactone 2.
- EBCT: empty bed contact times.

1. INTRODUCCTION

Environmental pollution is such a significant problem that the author Bary Commoner says: "Environmental pollution is an incurable disease. It can only be prevented" (Commoner, 1998). When the industry began, it was believed that every substance industrially created would be an advance. Further than that, some of the main components used during the last century (such as PCBs which were first manufactured in 1929) have caused a huge damage to the environment. This research will focus on a group of substances called micropollutants. Micropollutants are a large group of compounds found in very low concentration in the environment due to human activity. They have different characteristics and origins. We can find in this group pesticides, pharmaceuticals, household products and other industrial products. These substances, despite of their low concentrations, can cause a huge impact in the ecosystems and water bodies, because of its physical and chemical properties. Because of their differences it is difficult to stablish a common characterisation. However, some of them have found to be endocrine disruptors (capacity of cause damage in the hormonal system of living beings by altering it), induce the mutagenesis or have a high bioconcentration and bioaccumulation factors. Fortunately, some of these pollutants have been banned. Despite of that the use of some of them is no longer allowed, because of their persistence we can still find traces of them in all the countries.

It is fair enough to start talking about wastewater treatment plants (WWTP) at this point. Every day, every citizen uses a huge quantity of water to brush his teeth, to have a shower, to clean the dishes and so many other common actions. The total daily (or yearly) used water per capita depends in the country where we are. The economy, the money income and the climate are important factors that conditionate it. For example, in the United States the average is 3.794 L/(cap·day) and in South Africa is 791 L/(cap·day). All the water used has go somewhere (in most cases, a WWTP) to be cleaned and after returned to a water body.

The WWTPs are infrastructures where polluted water come and after a series of treatments, the same water can be discharged in the environment again following a legal limit values, which ones change between countries. Among all the treatments that have placed in WWTPs, the granular activated carbon (GAC) filtration is one of the last steps. Known in Germany as "fourth step", it is used to eliminate traces of substances or micropollutants such as pharmaceuticals and chemical products. It is based in the technique of carbon filtering (use of the adsorption capacity of the carbon activated to clean a water flow). The adsorption capacity of the filter is based in its crystalline, porous and chemical structure. In this research we want to analyse the most frequent micropollutants in the WWTP of Germany and characterise them to study their potential danger. Additionally, we want to demonstrate that further than just filtering these hazardous substances, the GAC filtration has the capacity to degrade micropollutants and store them in some degradation products that can be less toxic than the original compound.

2. COMPOUNDS

For this research we will focus in twelve different compounds and some of its degradation compounds, a total of twenty-six substances. The main reasons to choose these compounds over others are:

- The presence of them in our samples.
- The toxicity and danger of them.
- The possibility of degradation and its conditions.

To characterize them we have investigate different parameters such as:

- Molecular weight: in g/mol.
- Log D: phase distribution coefficient liquid-liquid (octanol-water), pH=7.40.
- Log P: phase distribution coefficient liquid-liquid (octanol-water), pH independent.
- Log Koc: phase distribution solid-liquid. It indicates the compound mobility in the solid phase. A high value indicates that the compound will remain in the solid part (soil) and not in the liquid phase.
- Log BCF: bioconcentration factor pH independent.
- Log BCF (bioconcentration factor) pH linearly dependent.
- Log BCF 2 (bioconcentration factor) pH exponentially dependent.
- Bioaccumulation factor: capacity of a substance to remain in the food chain, increasing in the trophic levels.
- Daphnia Magna LC50 mg/L: predicted median lethal dose. Concentration of a substance needed to kill half of the subjects, in this case Daphnia Magna.
- Oral rat LD50 mg/kg: predicted median lethal dose. Concentration of a substance needed to kill half of the subjects, in this case rats.
- Mutagenicity (prediction): capacity to cause mutagenicity.
- Developmental Toxicity (prediction): capacity to develop toxicity.

To compare the values of the parameters we consider the following scales:

	SCALE				
PARAMETER					
Molecular weight	< 200	200 – 250	250 – 300	300 – 350	> 350
LogD (pH=7,40)	< 2	2 – 3	3 – 4	4 – 5	> 5
LogP (classic)	< 2	2 – 3	3 – 4	4 – 5	> 5
LogKoc	< 3	3 – 3.5	3.5 – 4	4 – 4.5	> 4.5
Log BCF	< 2	2 – 3	3 – 3.5	3.5 – 4	> 4
Log BCF pH dependant (linear)	< 2	2 – 3	3 – 3.5	3.5 – 4	> 4
Log BCF pH dependant (exponential)	< 2	2 – 3	3 – 3.5	3.5 – 4	> 4
Bioaccumulation factor	< 10	10 – 100	100 – 1000	1000- 5000	> 5000
Daphnia Magna LD50 mg/L prediction	> 15	5 – 15	2 – 5	1 – 2	< 1
Oral rat LD50 mg/kg prediction	> 20 000	1000 – 2000	700 – 1000	400 – 700	< 400
Mutagenicity (prediction)	< -0.10	-0.10 – 0	0 – 0.10	0.10 – 0.20	> 0.20
Dev. Toxicity (prediction)	< 0.3	0.3 – 0.5	0.5 – 0.7	0.7 – 0.9	> 0.9

Table 1: Classification of parameters: molecular weight, log D, log P, log Koc, log BCF, bioaccumulation factor, LD50, mutagenicity and developmental toxicity.

NOTE: All the scales are relatively because the classification was done considering the minimum and maximum only of the compounds of study. Therefore, some values can be considered high but just in comparison with the other compounds added in the present research.

Triclosan

Triclosan is an organic compound with antibacterial and antifungal activity. It is commonly used in toothpastes to prevent gingivitis and in household products such as soaps and deodorants. It has a high log D and log P. Consequently, it is more likely to be found in organic liquids than in water, it is lipophilic. The pH has a low influence in the phase distribution coefficient, but it is lower at pH 7.40. The bioconcentration factor is related with the phase distribution, therefore log BCF is also high. It is influenced by the pH, being higher in the independent pH version. Neither the bioaccumulation factor, the Daphnia Magna LD50 and the Oral Rat LD50 are high.

TRICLOSAN	
Molecular weight	289.50
LogD (pH=7,40)	5.02
LogP (classic)	5.17
LogKoc	4.19
Log BCF	3.70
Log BCF pH dependant (linear)	3.57
Log BCF pH dependant (exponential)	3.57
Bioaccumulation factor	23.06
Daphnia Magna LC50 mg/L	4.92
Oral rat LD50 mg/kg	1360.69
Mutagenicity (prediction)	0.11
Dev. Toxicity (prediction)	0.59

Table 2: Triclosan characteristic table.

Naproxen

Naproxen is an anti-inflammatory, antipyretic and analgesic compound. The phase distribution coefficient liquid-liquid is strongly influenced by the pH (0.47 at pH 7.40 and 3.00 in the independent pH version). Furthermore, the bioconcentration factor is also very influenced by the pH, decreasing in more than one unit in the pH dependent versions, being lowest in the exponentially version. The log Koc is relatively low so it will concentrate in the liquid phase. But the oral rat LD50 is relatively low, so it is more toxic. Finally, the mutagenicity and the developmental toxicity are high, and it inhibits the activity of the enzyme cyclooxygenase I and II.

NAPROXEN	
Molecular weight	230.26
LogD (pH=7,40)	0.47
LogP (classic)	3.00
LogKoc	3.01
Log BCF	2.05
Log BCF pH dependant (linear)	-0.30
Log BCF pH dependant (exponential)	0.03

Bioaccumulation factor	8.37
Daphnia Magna LC50 mg/L	10.34
Oral rat LD50 mg/kg	634.43
Mutagenicity (prediction)	0.45
Dev. Toxicity (prediction)	0.89

Table 3: Naproxen characteristic table.

Terbutryn

Terbutryn is an organic compound with a molecular weight of 241g/mol. The phase distribution coefficient liquid-liquid is not influenced by the pH, because log D and log P have the same value. The bioconcentration factors are all low and slightly influenced by the pH, being lowest in the linear version. The log Koc is also low, so it will concentrate in the liquid phase as Naproxen. Moreover, as Naproxen, the mutagenicity and de developmental toxicity are also high. It is used as herbicide and it is considered xenobiotic and environmental contaminant.

TERBUTRYN	
Molecular weight	241.36
LogD (pH=7,40)	3.44
LogP (classic)	3.44
LogKoc	3.25
Log BCF	2.38
Log BCF pH dependant (linear)	2.22
Log BCF pH dependant (exponential)	2.32
Bioaccumulation factor	11.47
Daphnia Magna LC50 mg/L	7.63
Oral rat LD50 mg/kg	N/A
Mutagenicity (prediction)	0.46
Dev. Toxicity (prediction)	0.83

Table 4: Terbutryn characteristic table.

HHCB and its degradation products (HHCBL1 and HHCBL2)

HHCB or galaxolide is a synthetic musk used basically in cosmetics and household products. Its principal degradation products are HHCB Lactone 1 (HHCB L1) and HHCB Lactone 2 (HHCB L2). All of them are present in the samples. The principal differences between them are that HHCB has the highest log D and log P followed by HHCB L1 and HHCB L2, therefore we can say that the main product is more lipophilic compared to the degradation products. Moreover, the higher phase coefficient distribution Koc is in HHCB, decreasing in the degradation products. HHCB will remain more in the solid phase than in the liquid phase. Also, HHCB has the higher BCF and bioaccumulation factor compared to HHCB L1 and HHCB L2 and it is extremely toxic to Daphnia Magna (LD50= 0.77mg/L). The mutagenicity and the developmental toxicity almost do not change between the three compounds. Finally, the HHCB L2 stands up with the relative lowest Oral Rat LD50 (705.71mg/kg).

	HHCB	HHCB L1	HHCB L2
Alternative name	Galaxolide		
Molecular weight	258.40	272.38	272.38
LogD (pH=7,40)	5.93	5.50	4.92
LogP (classic)	6.23	5.50	4.92
LogKoc	4.77	4.37	4.05
Log BCF	4.51	3.95	3.51
Log BCF pH dependant (linear)	4.59	3.98	3.48
Log BCF pH dependant (exponential)	4.52	3.95	3.49
Bioaccumulation factor	1869.78	787.22	N/A
Daphnia Magna LC50 mg/L	0.77	1.26	1.19
Oral rat LD50 mg/kg	1493.42	1285.20	705.71
Mutagenicity (prediction)	-0.11	-0.10	-0.11
Dev. Toxicity (prediction)	0.85	0.83	0.83

Table 5: HHCB and its degradation products characteristic table.

AHTN

AHTN or tonalide is an organic compound with high log D (5.75) and high log P (6.37), being higher in the pH independent version (log P). The log Koc and all the bioconcentration factors are also high, therefore we can conclude than it will remain in the solid phase and live beings. The bioaccumulation factor is relatively high, such as the developmental toxicity. The LD50 for Daphnia Magna is low, which means it is toxic to plants. It is used as synthetic musk in household products.

AHTN	
Alternative name	Tonalide
Molecular weight	258.40
LogD (pH=7,40)	5.75
LogP (classic)	6.37
LogKoc	4.84
Log BCF	4.61
Log BCF pH dependant (linear)	4.62
Log BCF pH dependant (exponential)	4.63
Bioaccumulation factor	820.35
Daphnia Magna LC50 mg/L	1.45
Oral rat LD50 mg/kg	1269.17
Mutagenicity (prediction)	-0.04
Dev. Toxicity (prediction)	0.64

Table 6: AHTN characteristic table.

DEET

DEET is an active ingredient in insect repellent products used worldwide. It was developed by the U.S Army in 1946 and it is available to general public since 1957. We can find it different formats such as sprays and lotions. It is considered an environmental contaminant and xenobiotic. Because of its low log D, log P and log Koc, DEET will remain in the water phase. All the parameters related with toxicity are low such as de bioconcentration and bioaccumulation factors.

DEET	
Alternative name	N,N-DIETHYLTOLUAMIDE
Molecular weight	191.27
LogD (pH=7,40)	1.96
LogP (classic)	1.96
LogKoc	2.44
Log BCF	1.26
Log BCF pH dependant (linear)	0.97
Log BCF pH dependant (exponential)	1.15

Bioaccumulation factor	8.60
Daphnia Magna LC50 mg/L	51.66
Oral rat LD50 mg/kg	1662.38
Mutagenicity (prediction)	-0.04
Dev. Toxicity (prediction)	0.49

Table 7: DEET characteristic table.

TCPP

TCPP (Tris-(3-chloropropyl)-phosphate) is an organic compound with low phase distribution coefficients what means that it will remain in the water phase. Moreover, the bioconcentration and bioaccumulation factors are low. Despite of that, the mutagenicity and developmental toxicity are high and the LD50 for Daphnia Magna and rat are low, therefore we can consider this compound as dangerous. It is used as flame retardant and pesticide.

TCPP	
Alternative name	TRIS-(3-CHLOROPROPYL)-PHOSPHATE
Molecular weight	327.57
LogD (pH=7,40)	2.58
LogP (classic)	2.44
LogKoc	2.71
Log BCF	1.63
Log BCF pH dependant (linear)	1.37
Log BCF pH dependant (exponential)	1.53
Bioaccumulation factor	5.44
Daphnia Magna LC50 mg/L	0.10
Oral rat LD50 mg/kg	606.97
Mutagenicity (prediction)	0.41
Dev. Toxicity (prediction)	0.74

Table 8: TCPP characteristic table.

TDCPP

TDCPP or Tris-(dichloropropyl)-phosphate is an organic compound with a molecular weight of 430.90g/mol used as flame retardant. The phase distribution coefficient is strongly influenced by the pH, being higher at pH 7.40 (logD= 3.26) in comparison with the pH independent version (log P=1.79). Therefore, it will be more hydrophobic at pH

7.40. All the bioconcentration and bioaccumulation factors are low, and it shows a modest influence by the pH. Nevertheless, both LD50 (Daphnia Magna and rat) are low and the mutagenicity is high, therefore we can consider the compound hazardous.

TDCPP	
Alternative name	TRIS-(DICHLORPROPYL)-PHOSPHATE
Molecular weight	430.90
LogD (pH=7,40)	3.26
LogP (classic)	1.79
LogKoc	2.35
Log BCF	1.13
Log BCF pH dependant (linear)	0.82
Log BCF pH dependant (exponential)	1.01
Bioaccumulation factor	9.18
Daphnia Magna LC50 mg/L prediction	0.01
Oral rat LD50 mg/kg	607.51
Mutagenicity (prediction)	0.12
Dev. Toxicity (prediction)	0.38

Table 9: TDCPP characteristic table.

MTBT

MTBT or 2-(methylthio)benzothiazole is a xenobiotic metabolite that it will remain in the liquid/water phase because its low log P, log D and log Koc. Furthermore, it has a low BCF and bioaccumulation factor. The LD50 for Daphnia Magna is high (10.68mg/L), unlike the LD50 for oral rat (613.66mg/kg). The mutagenicity is high (0.54).

MTBT	
Alternative name	2-(METHYLTHIO)BENZOTHIAZOLE
Molecular weight	181.30
LogD (pH=7,40)	2.87
LogP (classic)	3.10
LogKoc	3.06
Log BCF	2.13
Log BCF pH dependant (linear)	1.94
Log BCF pH dependant (exponential)	2.05
Bioaccumulation factor	20.66
Daphnia Magna LC50 mg/L	10.68

Oral rat LD50 mg/kg	613.66
Mutagenicity (prediction)	0.54
Dev. Toxicity (prediction)	0.59

Table 10: MTBT characteristic table.

OTNE and its degradation product (OTNE OX)

OTNE or Patchouli ethanone is used as scent in perfumes, laundry products, and cosmetics. OTNE OX is its main degradation product. In comparison, OTNE has higher phase distribution coefficients, being the highest the log P (5.28). Therefore, the original compound (OTNE) will remain in the solid phase more absorbed than its product. As well, the bioconcentration and bioaccumulation factors are also high for OTNE compared to the ones of its degradation product. The only parameter that is higher in OTNE OX is the mutagenicity (-0.11 for OTNE and 0.11 for OTNE OX).

	OTNE	OTNE OX
Alternative name	PATCHOULI ETHANONE (ISO E SUPER)	
Molecular weight	243.38	248.36
LogD (pH=7,40)	4.72	3.54
LogP (classic)	5.28	3.23
LogKoc	4.25	3.14
Log BCF	3.79	2.23
Log BCF pH dependant (linear)	3.79	2.31
Log BCF pH dependant (exponential)	3.77	2.40
Bioaccumulation factor	313.93	22.12
Daphnia Magna LC50 mg/L	1.57	4.24
Oral rat LD50 mg/kg	4037.76	1503.65
Mutagenicity (prediction)	-0.11	0.11
Dev. Toxicity (prediction)	0.64	0.69

Table 11: OTNE and its degradation product characteristic table.

Chlorobenzenes

Chlorobenzenes are a group of compounds formed by a benzene group and different number of chlorine atoms. In this project, we analyse the following compounds with these principal applications:

- Chlorobenzene: solvent for pesticides, to degrease automobile parts and mostly chemical intermediate to make other chemicals. In the past, it was used to make other compounds such as phenol and DDT.
- 1,4- dichlorobenzene: used in deodorant and it is an insecticide fumigant for moth control.
- 1,2,4- trichlorobenzene: used as intermediate in the production of herbicides.
- 1,2,4,5- tetrachlorobenzene: building block in manufacturing of herbicides, insecticides, defoliants and other chemicals such as 2,4,5- trichlorophenol.
- Pentachlorobenzene: nowadays it has not any commercial use, but in the past, it was a fungicide and flame retardant.
- Hexachlorobenzene: currently, its use is low, but it is a by-product in the formation of other compounds. However, before, it was a pesticide in the production of fireworks and synthetic rubber.

The danger of the chlorobenzene increases with the number of chlorine atoms, therefore hexachlorobenzene has the highest bioconcentration and bioaccumulation factors. Also, the phase distribution coefficients (log D, log P and log Koc) are higher in the chlorobenzenes with more chlorine atoms, consequently hexachlorobenzene and pentachlorobenzene will remain strongly absorbed in the solid phase instead in the water phase. Hexachlorobenzene has the lowest LD50 for Daphnia Magna (0.39 mg/L) and 1,4-dichlorobenzene has the lowest for oral rat (719.86mg/kg). The mutagenicity and developmental toxicity decrease with the number of chlorine atoms.

	Chlorobenzene	1,4-dichlorobenzene	1,2,4-trichlorobenzene
Molecular weight	112.56	147.00	181.45
LogD (pH=7,40)	2.81	3.34	3.82
LogP (classic)	2.81	3.34	3.82
LogKoc	2.91	3.19	3.45
Log BCF	1.91	2.31	2.67
Log BCF pH dependant (linear)	1.69	2.14	2.55
Log BCF pH dependant (exponential)	1.82	2.24	2.62
Bioaccumulation factor	87.63	386.46	1115.26
Daphnia Magna LC50 mg/L	7.51	4.16	2.88
Oral rat LD50 mg/kg	1435.27	719.86	1053.56

Mutagenicity (prediction)	0.07	0.01	-0.04
Dev. Toxicity (prediction)	0.50	0.55	0.52

	1,2,4,5-tetrachlorobenzene	Pentachlorobenzene	Hexachlorobenzene
Molecular weight	215.89	250.34	284.80
LogD (pH=7,40)	4.23	4.60	4.89
LogP (classic)	4.23	4.60	4.89
LogKoc	3.68	3.88	4.04
Log BCF	2.98	3.26	3.49
Log BCF pH dependant (linear)	3.90	3.21	3.46
Log BCF pH dependant (exponential)	2.94	3.23	3.46
Bioaccumulation factor	3355.42	6004.91	9996.19
Daphnia Magna LC50 mg/L	1.90	0.65	0.39
Oral rat LD50 mg/kg	1426.86	1219.61	728.40
Mutagenicity (prediction)	-0.05	-0.02	-0.04
Dev. Toxicity (prediction)	0.34	0.30	0.15

Table 12: Chlorobenzenes characteristic table.

Diclofenac and its degradation products

Because of its anti-inflammatory activity diclofenac is used as non-steroidal anti-inflammatory drug and painkiller in order to reduce the pain and inflammation in chronic illness such as arthritis. However, it is considered xenobiotic and environmental contaminant.

The diclofenac degradation products found in the samples are:

- 2,6- dichloroaniline.
- 2- [2,6-dichloro-4- hydroxy- anilino] benzaldehyde.
- 2- [2,6- dichloro- anilino] benzaldehyde.
- 2- [2,6- dichloro- anilino] benzylalcohol.

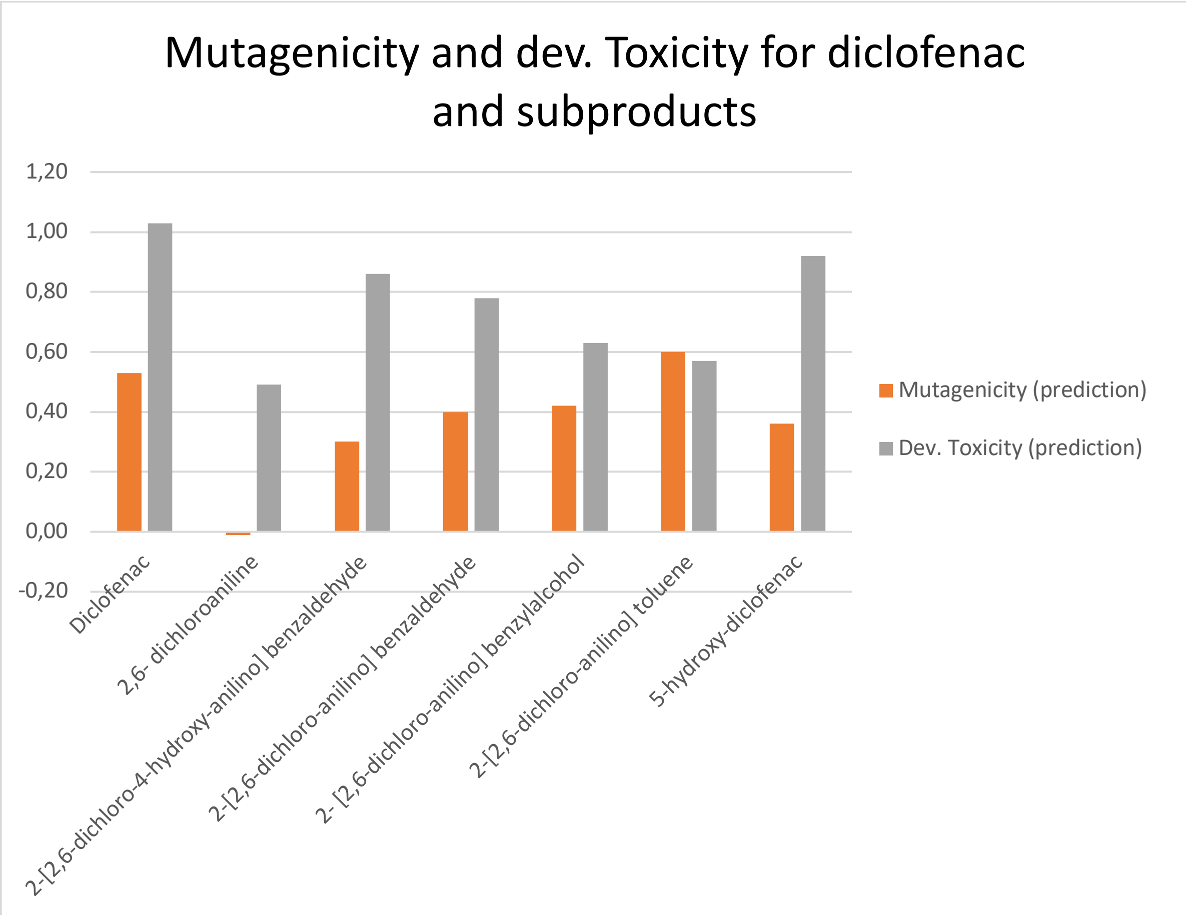
- 2- [2,6- dichloro- anilino] toluene.
- 5- hydroxy-diclofenac.

The compounds that will be strongly absorbed by the solid phase are 2-[2,6-dichloro-4-hydroxy-anilino] benzaldehyde (log Koc= 4.39), 2-[2,6-dichloro-anilino] benzaldehyde (log Koc= 4.12), and 2-[2,6-dichloro- anilino] toluene (log Koc= 4.22). Diclofenac (log Koc= 3.60) and 5- hydroxy-diclofenac (log Koc= 3.51) will be absorbed also in the solid phase but will less intensity.

In relation to the bioconcentration and bioaccumulation factors, the compounds with higher values are also the ones with the highest values of phase distribution coefficients: 2-[2,6-dichloro-4- hydroxy- anilino] benzaldehyde (BCF= 3.98), 2-[2,6-dichloro-anilino] benzaldehyde (BCF= 3.60), and 2-[2,6-dichloro- anilino] toluene (BCF= 3.75).

The mutagenicity is high for all the compounds (2-[2,6-dichloro- anilino] toluene has the highest, 0.60) except for 2,6- dichloroaniline (-0.01). The developmental toxicity follows the same behaviour having the lowest value for 2,6- dichloroaniline (0.49) and the highest for diclofenac (1.03).

Graph 1: Mutagenicity and developmental toxicity for diclofenac and its degradation products.



	Diclofenac	2,6-dichloroaniline	2-[2,6-dichloro-4-hydroxy-anilino] benzaldehyde
Molecular weight	296.15	162.02	282.12
LogD (pH=7,40)	0.95	2.90	5.52
LogP (classic)	4.06	2.90	5.54
LogKoc	3.60	2.95	4.39
Log BCF	2.90	1.97	3.98
Log BCF pH dependant (linear)	0.11	1.77	3.99
Log BCF pH dependant (exponential)	0.35	1.89	3.96
Bioaccumulation factor	42.76	26.97	N/A
Daphnia Magna LC50 mg/L	4.19	1.16	1.46
Oral rat LD50 mg/kg	244.02	360.92	2265.98
Mutagenicity (prediction)	0.53	-0.01	0.30
Dev. Toxicity (prediction)	1.03	0.49	0.86

	2-[2,6-dichloro- anilino] benzaldehyde	2- [2,6-dichloro- anilino] benzylalcohol
Molecular weight	266.12	268.14
LogD (pH=7,40)	5.04	3.59
LogP (classic)	5.04	3.59
LogKoc	4.12	3.33
Log BCF	3.60	2,50
Log BCF pH dependant (linear)	3.58	2.35
Log BCF pH dependant (exponential)	3.58	2.44
Bioaccumulation factor	N/A	118.32
Daphnia Magna LC50 mg/L prediction	1.07	2.59
Oral rat LD50 mg/kg	4318.68	569.72
Mutagenicity (prediction)	0.40	0.42
Dev. Toxicity (prediction)	0.78	0.63

	2-[2,6-dichloro- anilino] toluene	5-hydroxy-diclofenac
Molecular weight	252.14	312.15
LogD (pH=7,40)	5.23	0.73
LogP (classic)	5.23	3.91
LogKoc	4.22	3.51
Log BCF	3.75	2.74
Log BCF pH dependant (linear)	3.75	-0.08
Log BCF pH dependant (exponential)	3.73	0.18
Bioaccumulation factor	319.76	23.94
Daphnia Magna LC50 mg/L prediction	0.41	3.21
Oral rat LD50 mg/kg	818.63	250.79
Mutagenicity (prediction)	0.60	0.36
Dev. Toxicity (prediction)	0.57	0.92

Table 13: Diclofenac and its degradation products characteristic table.

3. METHODOLOGY

Information about plants

We use samples of three different Wastewater Treatment Plants:

Mannheim

Mannheim is third-largest city in Baden-Wurttemberg (state of Germany) with approximately 310000 inhabitants. The WWTP is in the North of Sandhofen and treats 87000m3 of wastewater. The design capacity of the WWTP is for 725000 total inhabitants. The total inhabitants are the sum of inhabitants of the area plus equivalent inhabitants (commercial and industrial wastewater). The phosphorus is treated by the addition of iron salts and since July 2016, 90% of the annual inflow is treated with activated carbon (known as fourth step). The sludge is also treated through four steps and then it is utilized by the cement industry. The water, after all the treatment, is discharge in the Rhine river.

We run two different types of samples, S1 and S2. The high of the column is approximately the same in both carbons (S1= 1.26m and S2= 1.28m). The filter operates downstream and the samples are from different highs:

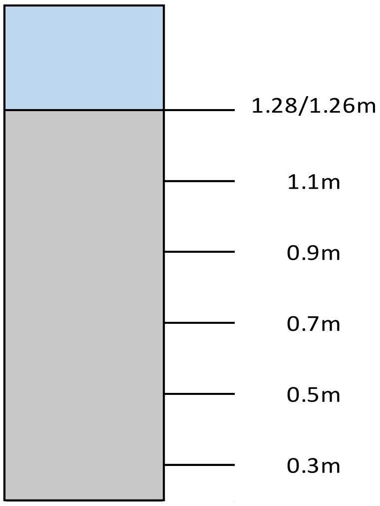


Figure 1: Operation information about the carbon filter activated of Mannheim WWTP.

The difference between the two samples is the flow rate, which results in different filter velocities and different empty bed contact times (EBCT). The contact time is higher in sample S1, consequently we can expect higher concentrations. In the following table, we can observe the values of the parameters:

	S1	S2
Flow rate [L/s]	0.41	1.1
Filter velocity [m/h]	4	11
EBCT [min]	20	7

Table 14: Operational data about Mannheim WWTP.

Emmingen-Liptingen

Emmingen-Liptingen is a municipality located in the federal state of Baden-Württemberg with a population approximately of 5000 inhabitants. The WWTP has a design capacity of 7500 total inhabitants and it eliminates the micropollutants with a granular activated carbon filtration. The maximum design inflow is 70m^3/h.

We run two different type of samples: Emmingen-Liptingen 159 and Emmingen-Liptingen 175. The difference between them is the bed volumes and the date they were taken: 100000 bed volumes and 04.06.2019 for 159 (it was in the system for 1 year) and 15000 bed volumes and 18.11.2019 for 175 (it was in the system for 2 months).

Eriskirch

The WWTP of Eriskirch treats the wastewater of 50000 inhabitants from three different areas:

- City of Tettnang: 29660 total inhabitants.
- Communities of Meckenbeuren: 14840 total inhabitants.
- Communities of Eriskirch: 5500 total inhabitants.

We run just one sample of this WWTP.

Procedure

The procedure to determine the concentration of the study compounds is:

1) We measure approximately 2g of the carbon sample with an analytical balance.
2) We extract the substances using the Soxhlet technique using 100mL of dichloromethane (DCM).
3) We reduce the liquid sample until approximately 3 mL by heating it.
4) We divide every liquid sample in 3 and we add the selected standards in every part:
    - T series: analysis of chlorobenzenes, addition of 100μL chlorobenzenes 1-6, 100μL PCB-Mix and 50μL PBDE-Mix
    - M series: acidic sample, addition of 50μL naproxen-d^3, 100μL triclosan-d^3, 100μL bisphenol-A-d^{10}, 50μL mecoprop-d^3 and 50μL diclofenac-d^4. Analysis of triclosan, naproxen, terbutryn and diclofenac and some of its degradation products:
        - ✓ 5-hidroxy-diclofenac.
        - ✓ 2- [2,6- dichloro-anilino] benzylalcohol.
        - ✓ 2,6- dichloroaniline.
    - U series: neutral sample, addition of 200μL AHTN-d^3, 200μL DBP-d^4, 50μL Terbutryn-d^5, 50μL Lidocain-d^{10} and 50μL Carbamazepine-d^{10}. Analysis of HHCB and degradation products HHCBL1 and HHCBL2, AHTN, DEET, TCPP, TDCPP, MTBT, OTNE and degradation product OTNE OX, and some of the degradation products of diclofenac:
        - ✓ 2-[2,6-dichloro-4-hydroxy-anilino] benzaldehyde.
        - ✓ 2-[2,6-dichloro- anilino] benzaldehyde.
        - ✓ 2-[2,6-dichloroanilino] toluene.
5) In the acidic samples, we add trimethylsulfonium hydroxide solution to convert R-COOH → R-$COOCH_3$.
6) We analyze every sample in the Mass Spectrum.

4. RESULTS

All compounds

T series

In the samples of the WWTP of Mannheim (S1 and S2) 1,4- dichlorobenzene has the higher concentrations, 564.59 ng/g in S1 0,9m and 831.87 ng/g in S2 1.1m. Next, we found chlorobenzene and 1,2,4- trichlorobenzene with relatively high concentrations, 36.97ng chlorobenzene/g and 37.07ng 1,2,4- trichlorobenzene/g in S1 0.9m and 91. 64 ng chlorobenzene/g at 0.3m and 48.47ng 1,2,4- trichlorobenzene/g at 1.1m for S2 samples. Pentachlorobenzene and hexachlorobenzene have low concentrations in all samples and there is no detectable 1,2,4,5- tetrachlorobenzene in any sample of Mannheim WWTP.

In Emmingen-Liptingen WWTP the concentrations are lower in all cases compared to Mannheim WWTP and there is no significant change in the concentration between the two samples (159 and 175). Chlorobenzene has the highest concentration (9.15ng/g in 159 and 8.85ng/g in 175) and pentachlorobenzene the lowest (0.59 ng/g in 159 and 0.44ng/g in 175). It is remarkable that in both samples there is 1,2,4,5- tetrachlorobenzene (0.64 ng/g in 159 and 0.63ng/g in 175), unlike Mannheim WWTP.

In Eriskirch WWTP the concentrations are lower than Mannheim WWTP, but higher than Emmingen-Liptingen WWTP, in most cases. 1,4- dichlorobenzene is the highest concentration (159.93ng/g) as Mannheim WWTP and we also find 1,2,4,5-tetrachlobenzene (0.80ng/g) being the lowest concentration.

	C (ng/g)					
	Chloro benzene	1,4-dichloro benzene	1,2,4-trichloro benzene	1,2,4,5-tetrachloro benzene	Pentachloro benzene	Hexachloro benzene
S1 0.3m	42.54	296.36	19.29	0.00	2.02	2.88
S1 0.5m	23.85	349.01	25.59	0.00	3.32	4.13
S1 0.7m	35.53	441.85	31.01	0.00	3.79	1.14
S1 0.9m	36.97	564.59	37.07	0.00	5.83	1.43
S1 1.1m	35.73	553.69	36.65	0.00	5.35	2.41
S2 0.3m	91.64	379.13	18.56	0.00	2.08	0.70
S2 0.5m	62.24	589.45	27.30	0.00	2.83	1.21
S2 0.7m	3.35	564.46	28.29	0.00	2.67	0.69
S2 0.9m	54.69	689.80	40.68	0.00	3.76	1.70
S2 1.1m	76.68	831.87	48.47	0.00	4.08	0.99
Emmingen-Liptingen 159	9.15	2.57	2.43	0.64	0.59	0.64
Emmingen-Liptingen 175	8.85	6.29	5.19	0.62	0.44	1.39
Eriskirch	28.46	159.93	13.78	0.80	2.24	1.41

Table 15: Chlorobenzenes concentrations.

M series

	INFLOW M SERIES			
WWTP	MANNHEIM S1	MANNHEIM S2	EMMINGEN-LIPTINGEN	ERISKIRCH
Triclosan (µg/L)	0.12	0.01	0.02	N/A
Naproxen (µg/L)	0.40	0.41	0.16	0.16
Terbutryn (µg/L)	0.06	0.04	0.01	0.09

Table 16: Inflow concentrations of the M series compounds in the three WWTPs.

As we can see in the table 16, the inflow concentrations are higher for naproxen in the three WWTP (Mannheim S1: 0.40µg/L, Mannheim S2: 0.41µg/L, Emmingen-Liptingen: 0.16µg/L, and Eriskirch: 0.16µg/L). In comparison, Mannheim has the higher inflow concentration in all the compounds and between Mannheim S1 and S2 the most significant difference in with triclosan: 0.12µg/L in S1 and 0.01µg/L in S2. The reason because Mannheim has higher values can be that is a bigger WWTP connected to a very big city. The lifestyle and the income of the population have a great impact on the amount and properties of the wastewater discharged into the sewer system.

In this series we find three different compounds. In the first WWTP, Mannheim, triclosan has the highest values (398.39ng/g in S1 1.1m and 336.50ng/g in S2 0.7 m). Terbutryn is also high at S1 1.1m (220.38ng/g) and S2 0.7m (283.35ng/g). Naproxen has the lowest values, unlike the inflow values.

Emmingen-Liptingen has the lowest values in triclosan (32.24ng/g in 159 and 75.92ng/g in 175), unlike Mannheim. The values of naproxen are higher (313.09ng/g in 159 and 317.32ng/g in 175) than in Mannheim. There is a significant difference between the values of terbutryn: 267.13ng/g in 159 and 1526.88ng/g in 175.

Eriskirch has the highest values of triclosan (544.05ng/g). The values of naproxen (224.51ng/g) and terbutryn (610.96ng/g) are higher than Mannheim values but lower than Emmingen-Liptingen values.

	C (ng/g)		
	Triclosan	Naproxen	Terbutryn
S1 0.3m	157.61	35.43	186.97
S1 0.5m	229.39	76.08	182.86
S1 0.7m	285.55	126.21	187.41
S1 0.9m	362.64	177.63	208.93
S1 1.1m	389.39	148.91	220.38
S2 0.3m	187.15	35.38	187.53
S2 0.5m	218.15	43.45	186.67
S2 0.7m	336.50	102.38	283.35
S2 0.9m	271.08	75.22	199.29
S2 1.1m	308.67	84.10	205.74
Emmingen-Liptingen 159	32.24	313.09	267.13
Emmingen-Liptingen 175	75.92	317.32	1526.88
Eriskirch	544.05	224.51	610.96

Table 17: Concentrations of the M series compounds in the three WWTPs.

U series

WWTP	INFLOW			
	MANNHEIM S1	MANNHEIM S2	EMMINGEN-LIPTINGEN	ERISKIRCH
HHCB	0.13	0.08	0.34	0.40
HHCB L1	1.79	0.99	N/A	2.95
HHCB L2	0.47	0.31	N/A	0.53
AHTN	0.02	0.05	0.82	0.06
DEET	0.10	0.14	N/A	N/A
TCPP	2.39	1.47	0.51	0.56
TDCPP	0.06	0.12	0.09	0.09
MTBT	0.28	0.35	0.03	0.28
OTNE	0.19	0.37	0.31	0.25
OTNE OX	0.22	0.23	N/A	0.39

Table 18: Inflow concentrations of the U series compounds in the three WWTPs.

According to table 18, in Mannheim the highest inflow concentrations are HHCB L1 (S1: 1.79µg/L, S2: 0.99µg/L) and TCPP (S1: 2.39µg/L, S2: 1.47µg/L). The inflow concentrations are similar between the two samples, S1 and S2. Regarding Emmingen-Liptingen, AHTN is the highest value (0.82µg/L) and for Eriskirch is HHCB L1 (2.95µg/L).

In the table 19, in Mannheim WWTP we find that HHCB L1 has the highest concentrations (46507.47ng/g in S1 0.9m and 51247.58ng/g in S2 0,7m). Followed by TCPP (peak at S1 1.1m 17925.29ng/g and S2 0.7m 23144.36ng/g) and OTNE (peak at S1 0.9m 29050.08ng/g and S2 0.9m 27175.58ng/g). MTBT also has high concentrations: 21598.08ng/g (S1 1.1m) and 12077.24ng/g (S2 0.9m). HHCB and HHCB L2 have similar values between 2800ng/g and 6200ng/g. HHCB is high at S1 0.9m (4553.96ng/g) and S2 0.9m (4160.28ng/g). HHCB L2 is high at S1 1.1m (5344.46ng/g) and S2 0.7m (6121.80ng/g). AHTN, DEET and OTNE OX have concentrations between 1300ng/g and 3500ng/g. The highest concentration of AHTN is 2513.52ng/g (S1 0.9m), of OTNE OX is 3457.08ng/g (S2 0.9m) and of DEET is 3495.97ng/g (S2 0.7m). Finally, TDCPP has the lowest concentrations (between 330ng/g and 770ng/g).

In Emmingen-Liptingen all the concentrations are higher in 175 sample. The HHCB concentration is similar to Mannheim in 159 (2787ng/g) and higher in 175 (6110.11ng/g). For HHCB L1, HHCB L2, AHTN, TCPP, TDCPP, MTBT, OTNE and OTNE OX the concentrations are lower compared to Mannheim. For DEET the concentration in 159 is lower than Mannheim (943.70ng/g) and is higher in 175 (4336.48ng/g).

For Eriskirch, HHCB L1 has the highest concentration (19856.61ng/g), followed by TCPP (12582.15ng/g), MTBT (5973.05ng/g), DEET (5887.27ng/g) and HHCB (4520.63ng/g). TDCPP (2851.18ng/g), HHCBL2 (2821.53ng/g) and OTNE (2271.03ng/g) have lower concentrations, and AHTN (1182.38ng/g) and OTNE OX (1664.84ng/g) have the lowest values.

	C (ng/g)				
	HHCB	HHCB L1	HHCB L2	AHTN	DEET
S1 0.3m	2976.36	28732.13	2895.76	1360.73	1378.48
S1 0.5m	3721.99	39439.87	3809.39	1747.48	1857.01
S1 0.7m	4402.94	43063.64	4634.04	2252.04	1931.49
S1 0.9m	4553.96	46507.47	5110.43	2513.52	2235.17
S1 1.1m	4060.08	44137.69	5344.46	2370.17	1973.30
S2 0.3m	3013.00	39992.95	3784.48	1738.81	2358.89
S2 0.5m	3254.99	47291.86	4591.14	2106.65	3023.44
S2 0.7m	2898.81	51247.58	6121.80	2464.61	3495.97
S2 0.9m	4160.28	41369.57	4973.94	2221.93	2702.16
S2 1.1m	3500.02	33263.78	4535.86	2028.94	2266.69
Emmingen-Liptingen 159	2786.66	4229.35	482.57	355.50	943.70
Emmingen-Liptingen 175	6110.11	6720.48	733.00	445.70	4336.48
Eriskirch	4520.63	19856.61	2821.53	1182.38	5887.27

	C (ng/g)				
	TCPP	TDCPP	MTBT	OTNE	OTNE OX
S1 0.3m	10190.89	331.55	4559.76	18240.25	1492.57
S1 0.5m	13913.79	463.99	6752.77	22942.00	2274.19
S1 0.7m	15970.30	521.50	7051.11	22384.78	2520.63
S1 0.9m	17431.41	730.52	17711.70	29050.08	3255.94
S1 1.1m	17925.29	766.74	21598.08	25275.78	2848.89
S2 0.3m	17863.17	508.38	6564.60	27065.84	2534.18
S2 0.5m	20989.11	554.34	9649.75	26327.48	2820.95
S2 0.7m	23144.36	599.93	8087.65	22312.85	2921.23
S2 0.9m	21630.74	610.53	12077.24	27175.58	3457.08
S2 1.1m	20331.15	579.96	10366.64	25001.90	3398.20
Emmingen-Liptingen 159	1761.28	174.70	1673.52	5626.75	681.38
Emmingen-Liptingen 175	2804.93	240.67	5246.82	6294.59	822.74
Eriskirch	12582.15	2851.18	5973.05	2271.03	1664.84

Table 19: Concentrations of the U series compounds in the three WWTPs.

To summarize, HHCB L1 and TCPP are the highest inflow in Mannheim and the highest concentrations in the GAC filter. In Emmingen-Liptingen, AHTN concentration is one of the lowest, despite of being the highest inflow concentration. Finally, in Eriskirch HHCB L1 is the highest inflow and concentration in the carbon.

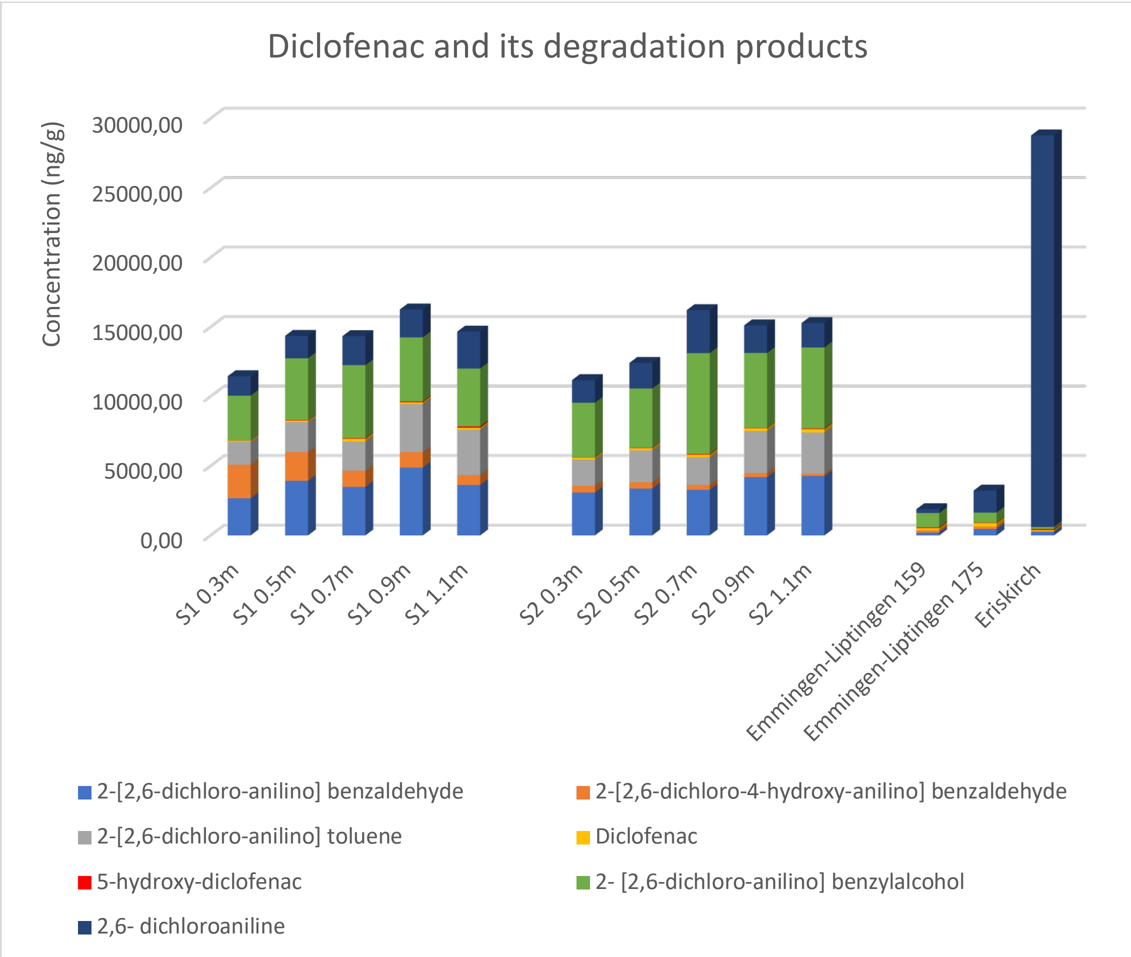
Diclofenac degradation pathway

	INFLOW			
WWTP	MANNHEIM S1	MANNHEIM S2	EMMINGEN-LIPTINGEN	ERISKIRCH
Diclofenac (µg/L)	1.37	1.32	0.92	1.92

Table 20: Diclofenac inflow concentrations.

The highest inflow concentration is highest in Eriskirch, followed by Mannheim. Emmingen-Liptingen has the lowest inflow concentration, almost half of Eriskirch's

Graph 2: Concentrations of diclofenac and its degradation products in the three WWTPs.



In graph 2, we can observe the behaviour of diclofenac in the carbon. In the samples S1 and S2, corresponding to the WWTP of Mannheim the concentration of every compound is significant. This WWTP has a high inflow but the carbon is relatively new (the degradation process has just begun). On the other hand, the samples corresponding to Emmingen-Liptingen show lower concentrations, due to a lower inflow and a lower concentration of pollutants in the inflow water. Finally, Eriskirch has the highest inflow concentration of diclofenac and is the oldest carbon, therefore, it has the highest amount of diclofenac and diclofenac products. Furthermore, we can see a high enrichment of 2,6-

dichloroaniline. It appears that 2,6- dichloroaniline is the last degradation product of diclofenac and all the inflow concentration of it will remain as 2,6- dichloroaniline.

5. DISCUSSION AND CONCLUSION

The twenty-six compounds of study have been detected in almost every sample (except 1,2,4,5- dichlorobenzene in Mannheim samples and 2- [2,6-dichloro- anilino] toluene in Emmingen Liptingen and Eriskirch samples). The concentration of these micropollutants in the granular activated carbon has shown the importance of the application of GAC filters in the process of water treatment. In the WWTPs that do not count with this fourth step are discharging pollutants to the environment that can cause a huge impact on ecosystems, due to the characteristics of them already described. For example, HHCB has a high BCF (4.51) and also a high log Koc (4.77), consequently is a dangerous substance for ecosystems that will remain in the solid phase, if the wastewater is treated with GAC filtering, the concentration of it will decrease, decreasing also its potential danger to live beings. The peak of concentration of HHCB in this research is in Emmingen-Liptingen 175 sample, with a value of 6110.11ng/g.

Focusing on peaks, the micropollutants with highest concentrations are:

- HHCB L1: 51247.58ng/g (Mannheim WWTP).
- OTNE: 29050.08g/g (Mannheim WWTP).
- 2,6- dichloroaniline: 28175.23ng/g (Eriskirch WWTP).
- TCPP: 23144.36ng/g (Mannheim WWTP).

Furthermore, regarding the difference between the samples of the same WWTP, in Mannheim it was expected that the concentrations in S1 were higher than S2, due to a higher EBCT. But the results are not very clear about this, because sometimes the samples are higher in S1 (for example HHCB) and sometimes in S2 (for example 1,4- dichlorobenzene). We can conclude that the EBCT difference between the two samples appears not to make any significant difference in the concentration value. In Emmingen-Liptingen, always the sample 175 have higher concentrations than 159. The reason can be a seasonal variations in some of the compounds, because 175 was in the system just for 2 months and 159 for one year, so 175 can be conditionate by seasonal variations.

Finally, the example of diclofenac has shown that a degradation process is occurring in the carbon. The clearest prove of that is the enrichment of 2,6- dichloroaniline in Eriskirch WWTP. This aspect of the carbon can be interesting due to the possibility of degrading pollutants into less toxic forms. The applications of that degradation process can be large and important to the urgent need of increasing the auto depurative capacity of our planet.

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