



Decomposition of Carbamazepine by Ultrasound & Ozone

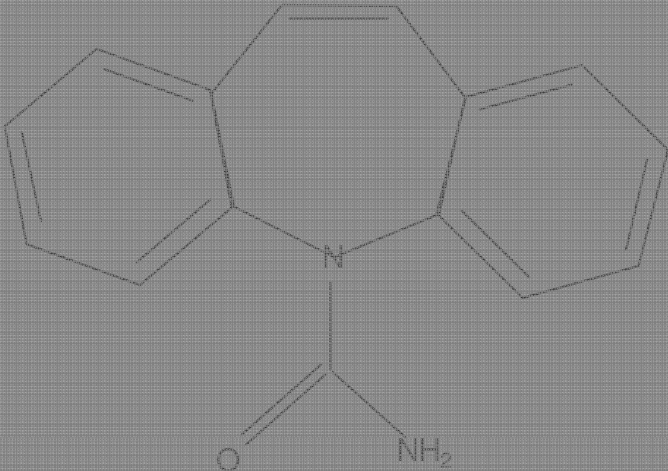
Record of Progress

Master Thesis Georg Theissen

Content

1. Carbamazepine (CBZ) and its occurrence
2. Persistence of CBZ in WWTPs
3. „Neukirchen“ and Results
4. Kinetics of the degradation of CBZ
5. Laboratory Plant in Garching and Results
6. Conclusion

General Information

Carbamazepine (CBZ)	
Structure	
Structural Formula	$C_{15}H_{12}N_2O$
Molecular Weight [g/mol]	236,27
Usage	Analgesic, antiepileptic
Water solubility [mg/l] (25°C)	17,7
LogP _(ow)	2,45
Henry's Law Constant [Pa m ³ /mol] (25°C)	$1,09 \cdot 10^{-5}$
pKa	neutral
Elimination half-life [h]	25-65
Excretion	72% of what is taken orally --> excreted in urine, 28% in feaces
Metabolites in Urine	CBZ, CBZ-epoxide, CBZ-diol, CBZ-acridan, 2-OH-CBZ, 3-OH-CBZ
Dose [mg/d]	800 - 1200

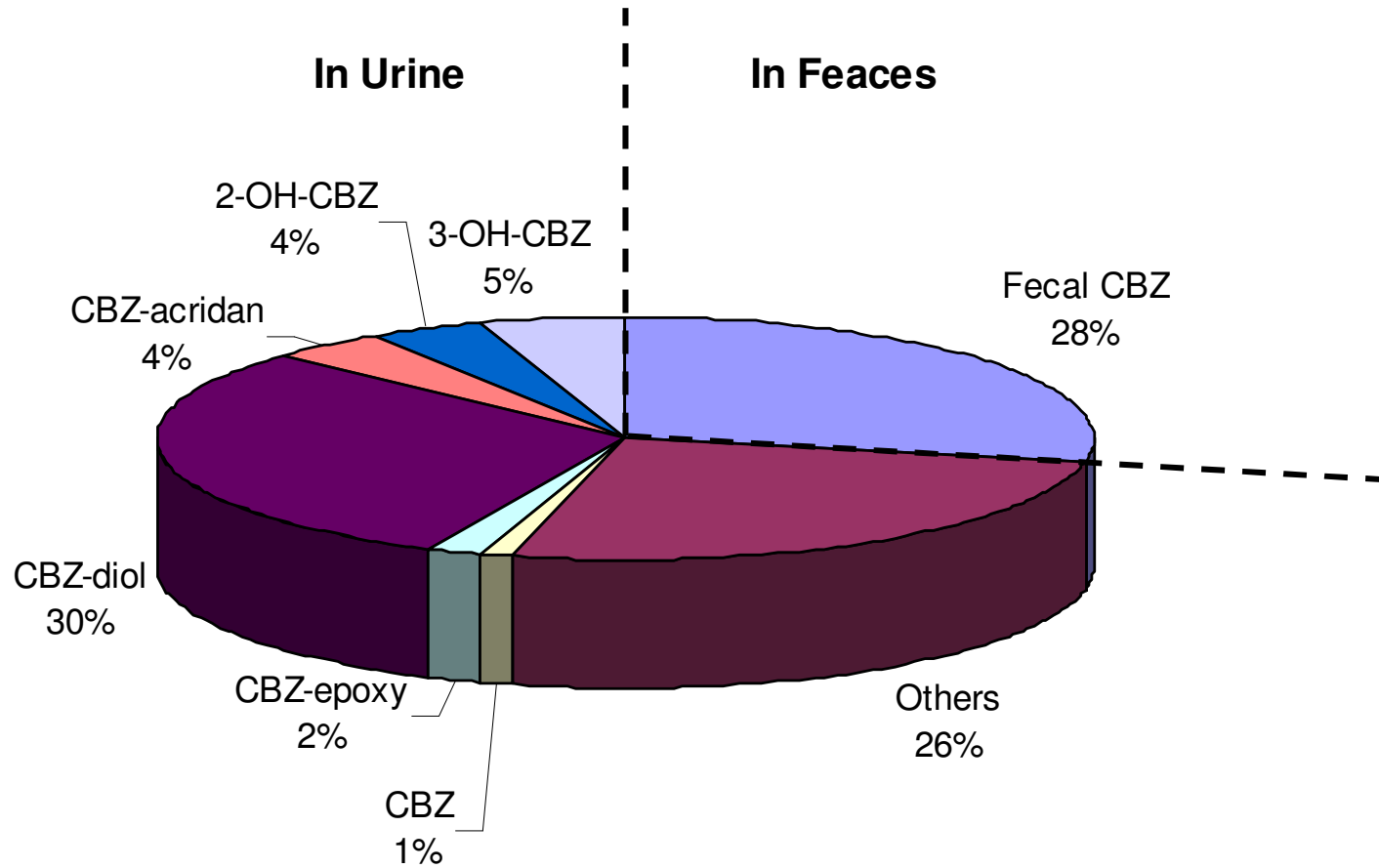
Source: Yongjun Zhang, 2008 / RxList, 2006

General Information

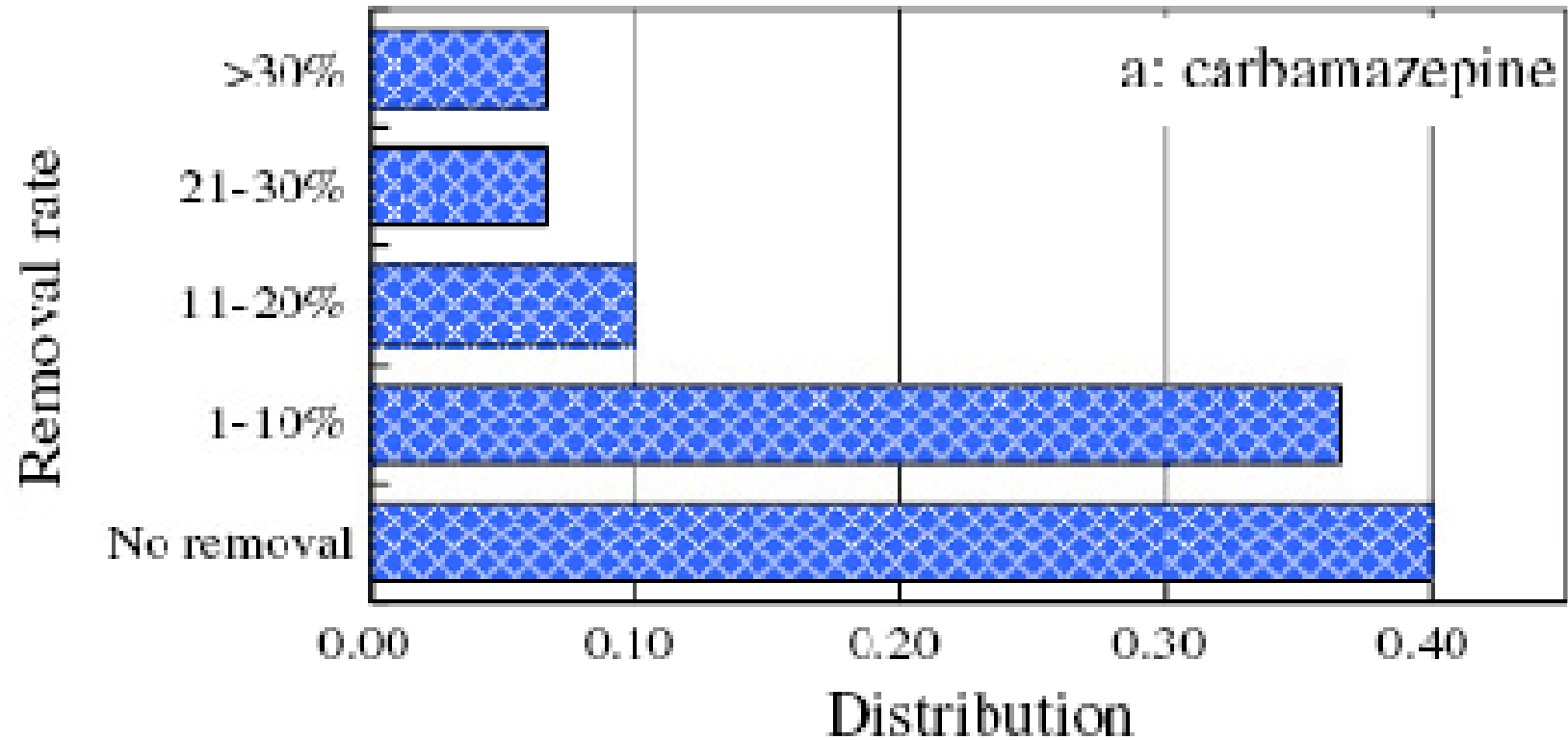
Data on the Consumption of Carbamazepine			
Region	Annual consumption [to]	Population [mio.]	DPC [mg]
Australia	10	19	526
Austria	6	8	750
Canada	28	31	903
Finland	4,6	5	920
France	40	59	678
Germany	87	82	1061
England	40	49	816
USA	43	284	151
World	1014		

Source: Yongjun Zhang, 2008

Metabolites of CBZ and their percentage of Oral Dose



Carbamazepine degradation in WWTPs



Reasons for the persistence of CBZ in WWTPs

1. Resistant to biodegradation (test of carbamazepine in CH₃COONa cultured activated sludge in both sea and fresh water → no biodegradation at low concentrations (0.5 mg/l)) (Stamatelatou, 2003)
2. It is hardly attached to sludge / The bulk remains associated with the aqueous phase

$$K_d = \frac{C_s}{C_{aq}} = 1,4 \text{ For Carbamazepine [l/kg]}$$

C_s : the content of the compound absorbed by the soil [$\mu\text{g/g}$].

C_{aq} : the concentration of the compound in aqueous phase [$\mu\text{g/ml}$].

A significant sorption onto sludge for efficient removal in WWTPs are values of around $K_d = 500 \text{ l/kg}$

Source: Ternes, 2004



Ultrasonic Systems

WWTP – Neukirchen vorm Wald

Inhabitants: 1600

Dry weather discharge [m³/day]: 300

Storm discharge [m³/day]: 1500

Existing stages:

- 1. Primary treatment**
- 2. Perculating filter**
- 3. Aerated maturation pond**

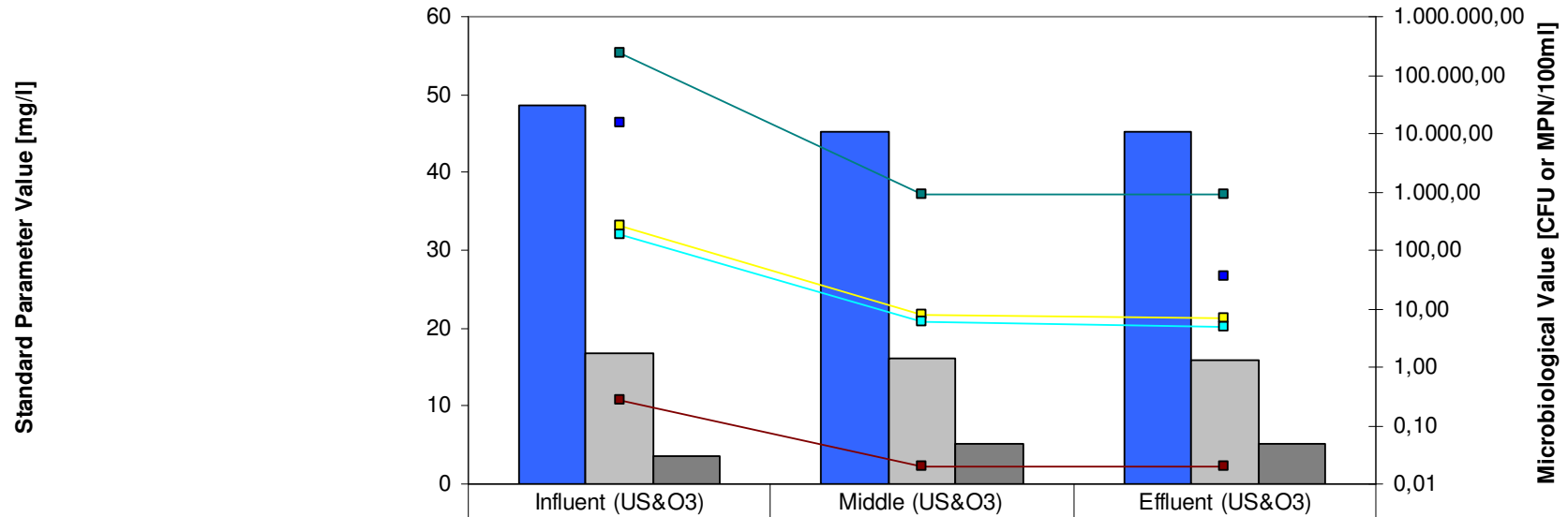


Date: 02.07.08,

flow-rate [m³/h]: 17,7,

O₃ [g/m³]: 8,00,

ultrasound [Wh]: 5.932,5



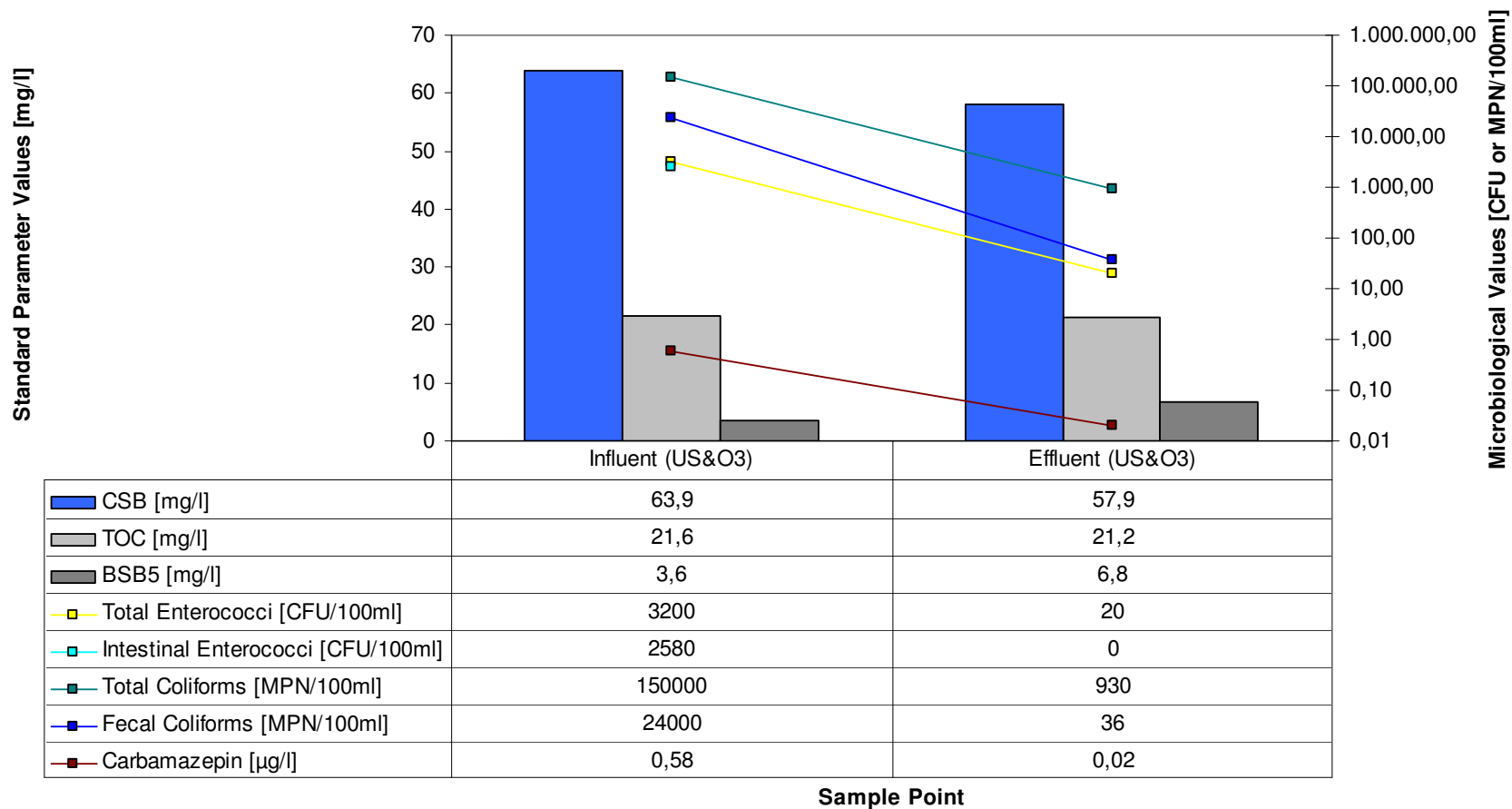
	Influent (US&O3)	Middle (US&O3)	Effluent (US&O3)
CSB [mg/l]	48,5	45,2	45,2
TOC [mg/l]	16,7	16,2	15,9
BSB5 [mg/l]	3,6	5,2	5,2
Total Enterococci [CFU/100ml]	260	8	7
Intestinal Enterococci [CFU/100ml]	186	6	5
Total Coliforms [MPN/100ml]	240000	930	930
Fecal Coliforms [MPN/100ml]	15000	0	36
Carbamazepin [µg/l]	0,27	0,02	0,02

Date: 30.07.08,

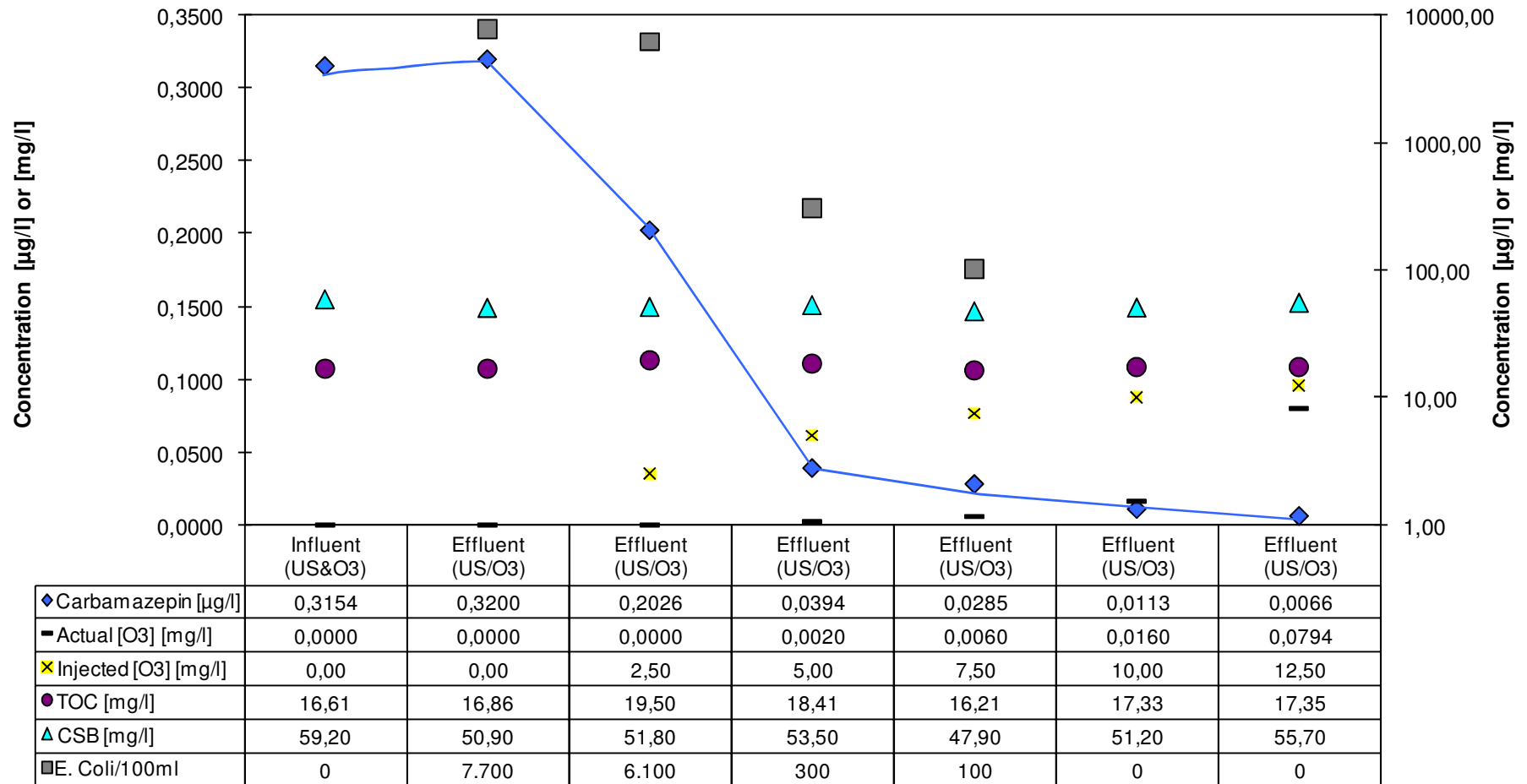
flow-rate [m³/h]: 12,9,

O₃ [g/m³]: 8,00,

ultrasound [Wh]: 2.205,5

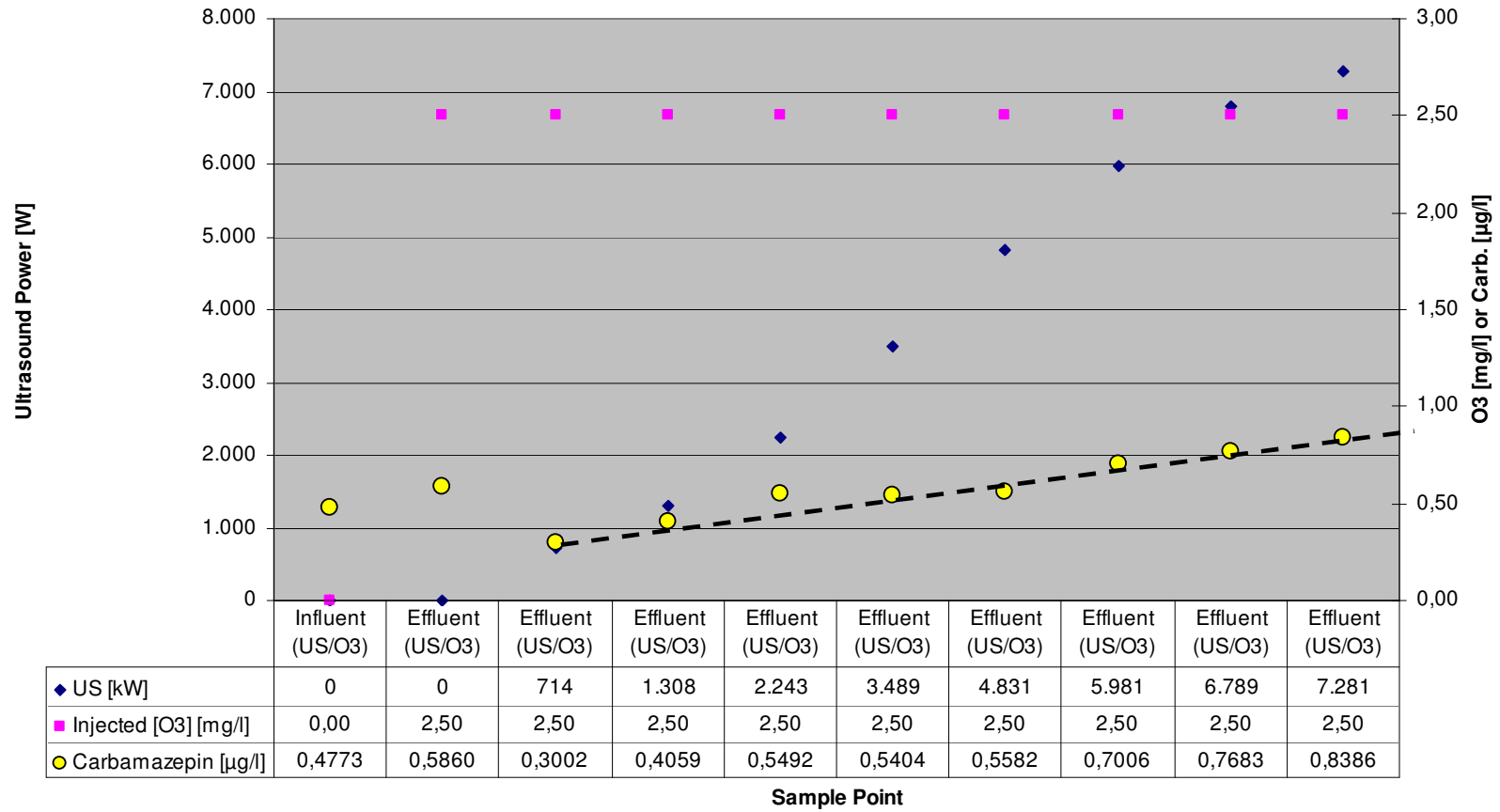


Parameter values at different O₃ - concentrations and constant ultrasound [Wh]: 2.240,0

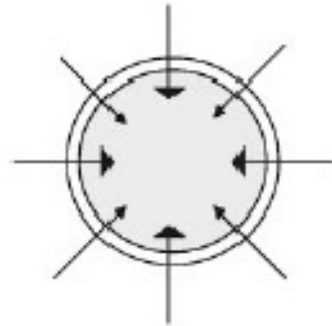


Sample Points

Parameter values at constant O₃ - concentrations [mg/l] 2.5 and varying ultrasound [W]



Cavitation Bubble



As ultrasonic waves propagate through liquids, cavitation bubbles form during the rarefaction, or negative pressure, periods of the sound waves.

Temperatures in excess of 5500°C

Pressures in excess of 300 atm

Source: Leigh Hagenson Thompson

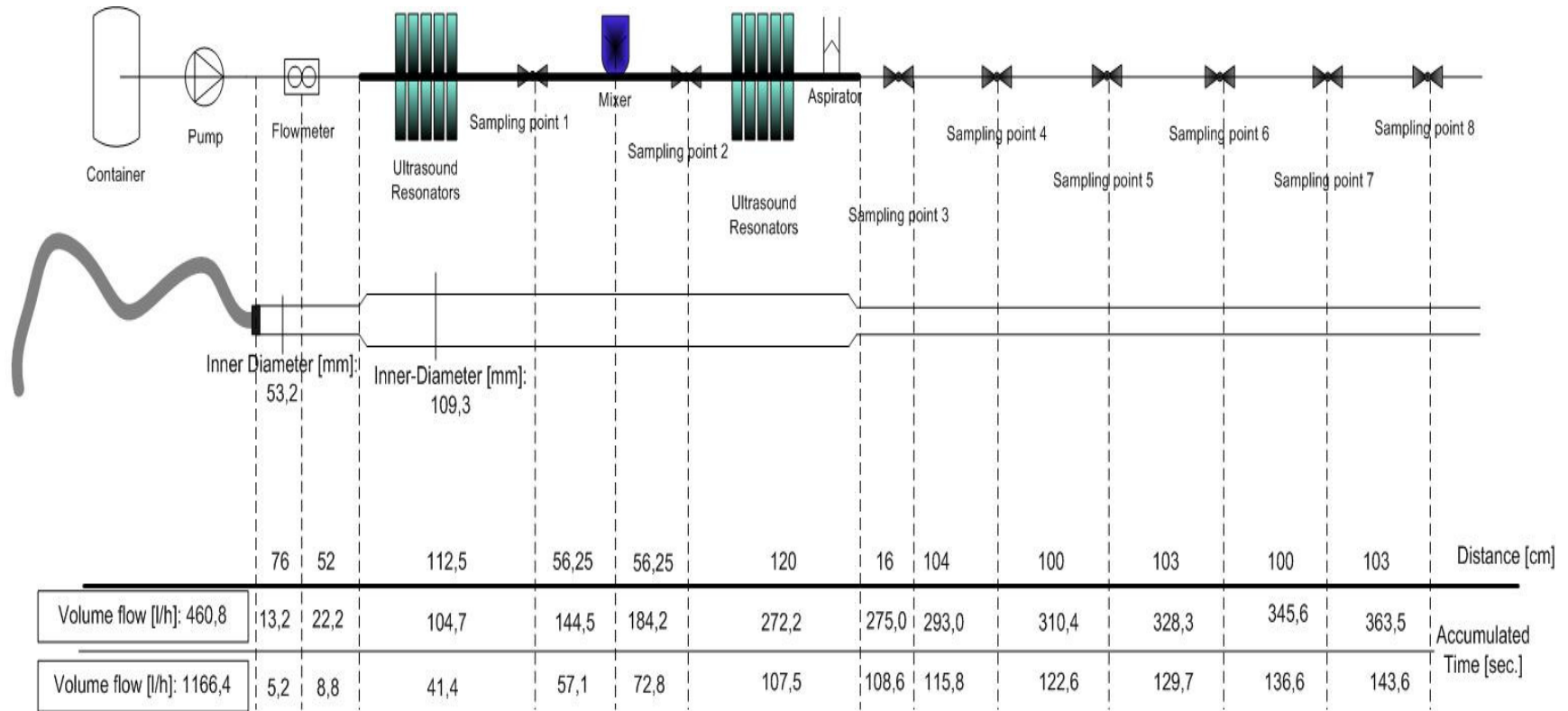
The sorption of Carbamazepine

- Sorption – attributed to the hydrophobic nature of CBZ
- When a cavitation bubble collapse occurs near a porous material the jet which is generated is able to force liquid into the bulk material.

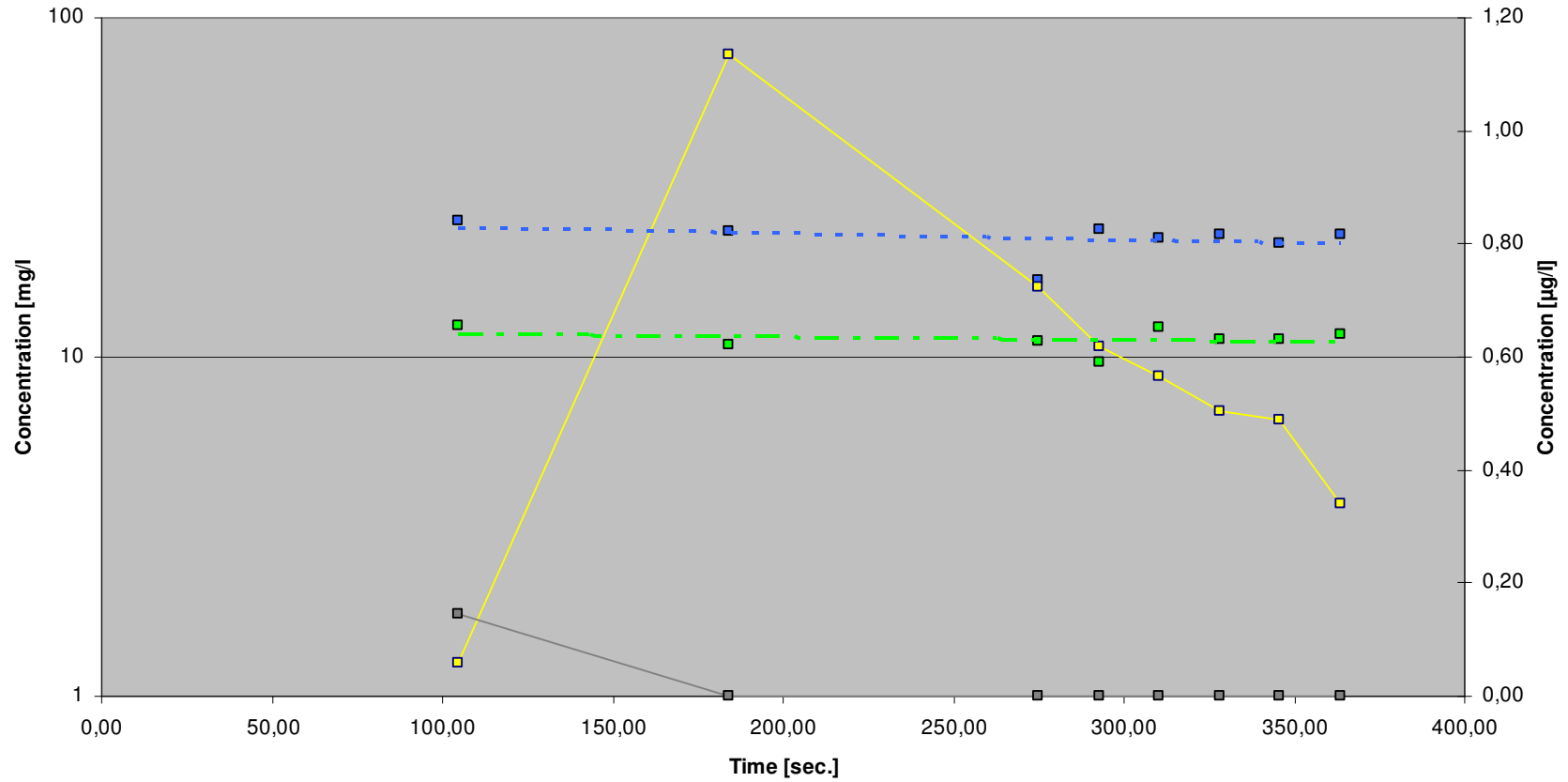
Source: Timothy J Mason

- Ultrasonic solvent extraction/ impregnation
- In this way more CBZ is solved
- The solvent around collapsing cavitation bubble will exist as a supercritical fluid shifting equilibrium to solve more solute

Retention Time / Sample Points



Ozone [mg/l]: 12, No Ultrasound



■ CSB [mg/l] ■ TOC [mg/l] ■ O3 [mg/l] ■ Carbamazepin [µg/l] - - - Linear (CSB [mg/l]) - - - Linear (TOC [mg/l])

Kinetics of the degradation of Carbamazepine

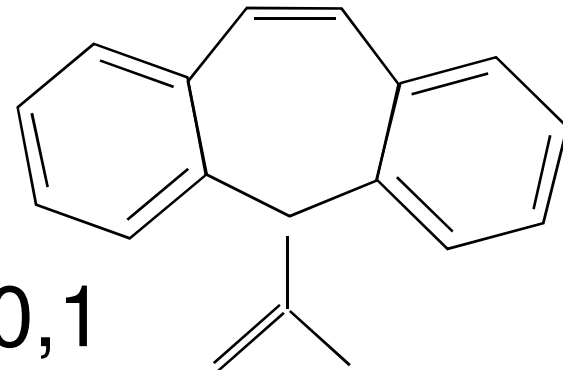
- $-d[S]/dt = k_{O_3} [S][O_3] + k_{OH} [S][^*OH]$

- [S]= the conc. of Carbamazepine
- [O₃] = the conc. of Ozone
- [OH] = the conc. of OH-radicals

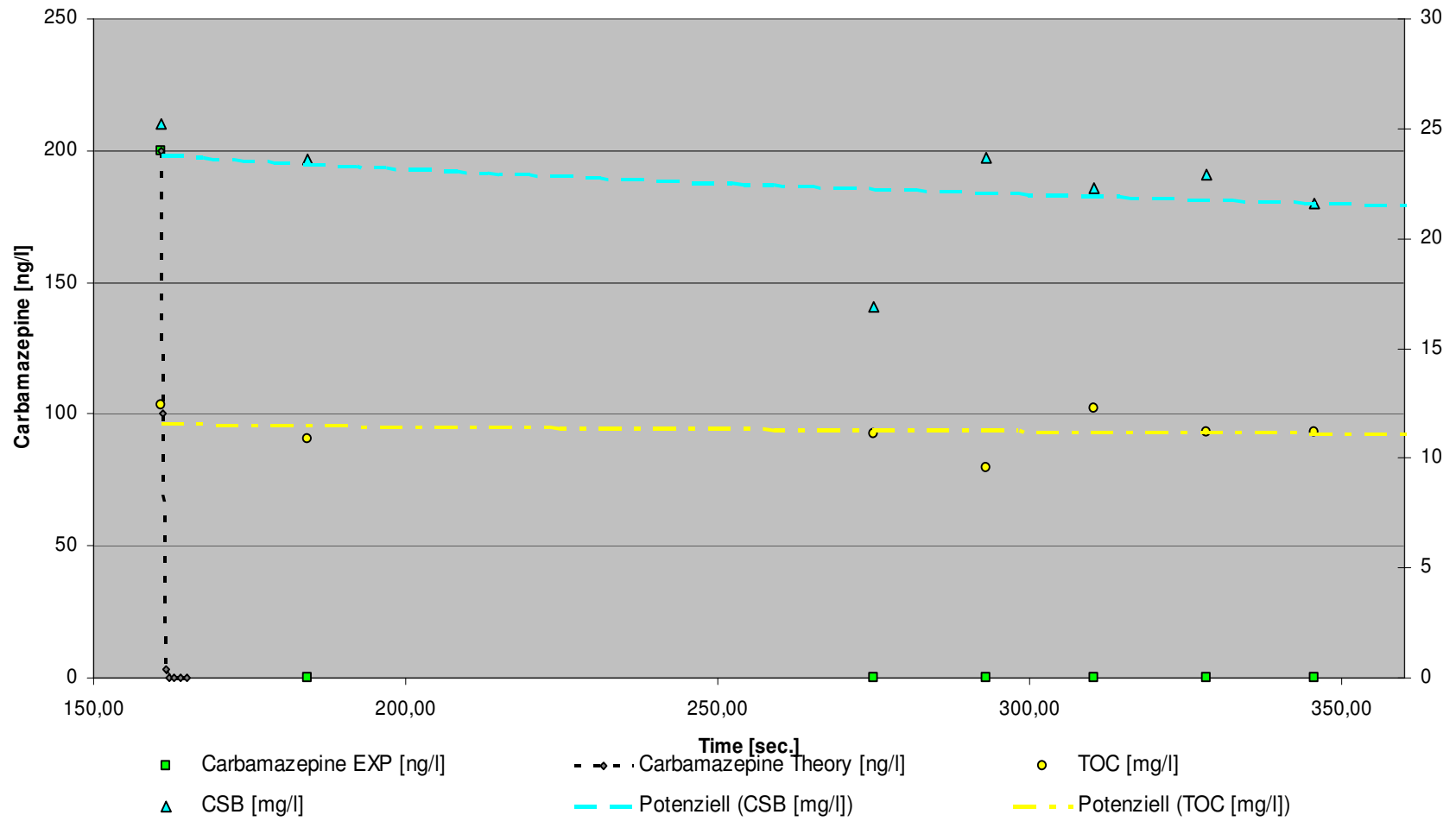
- Efficient Oxidation via O₃ when compounds contain:

- Amino group
- Activated aromatic system
- Double bond

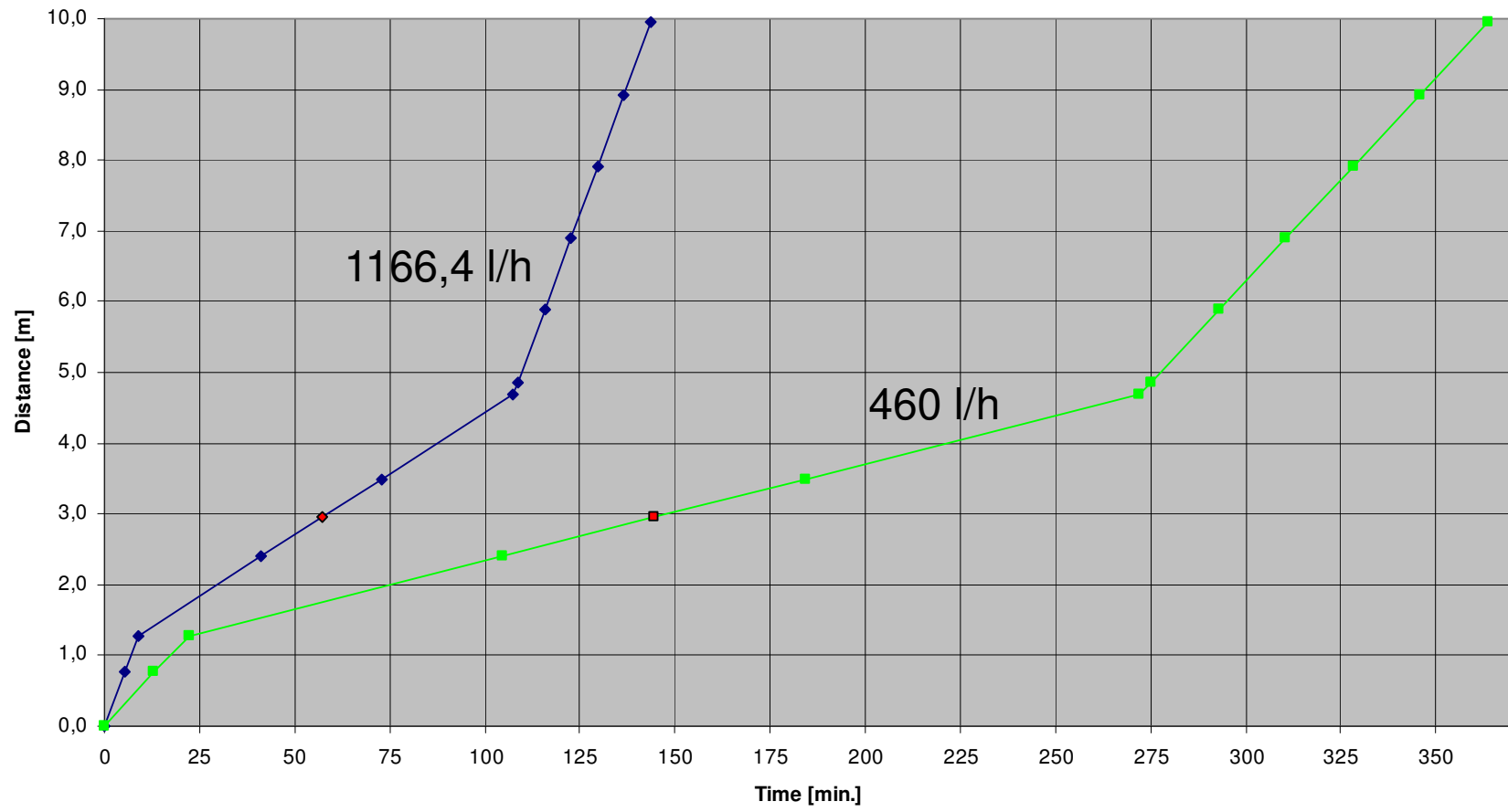
- $\text{Halflife}_{\text{carbamazepine}} [\text{sec.}] = 0,1$



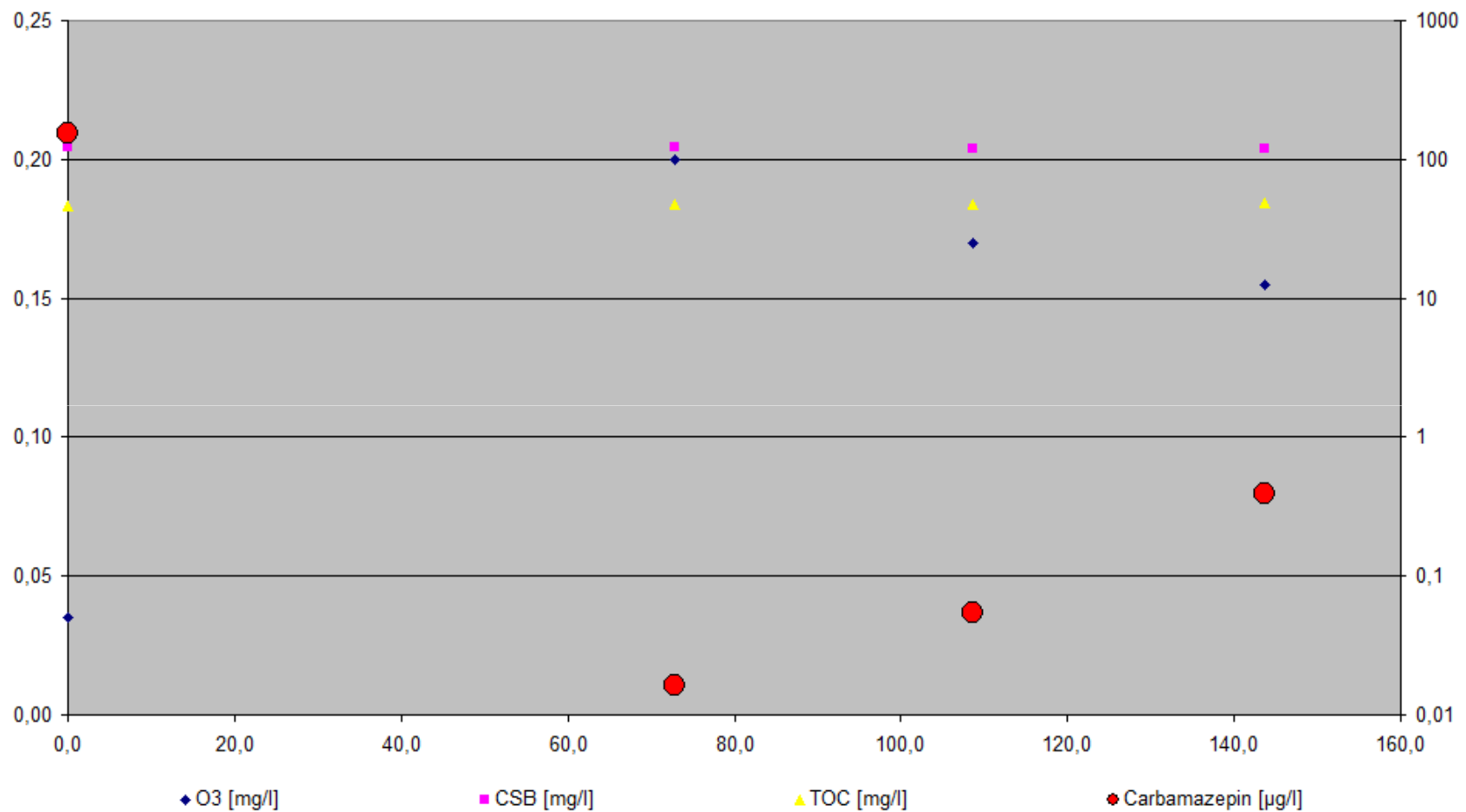
Carbamazepine Concentration Empirical Values vs. lit. values



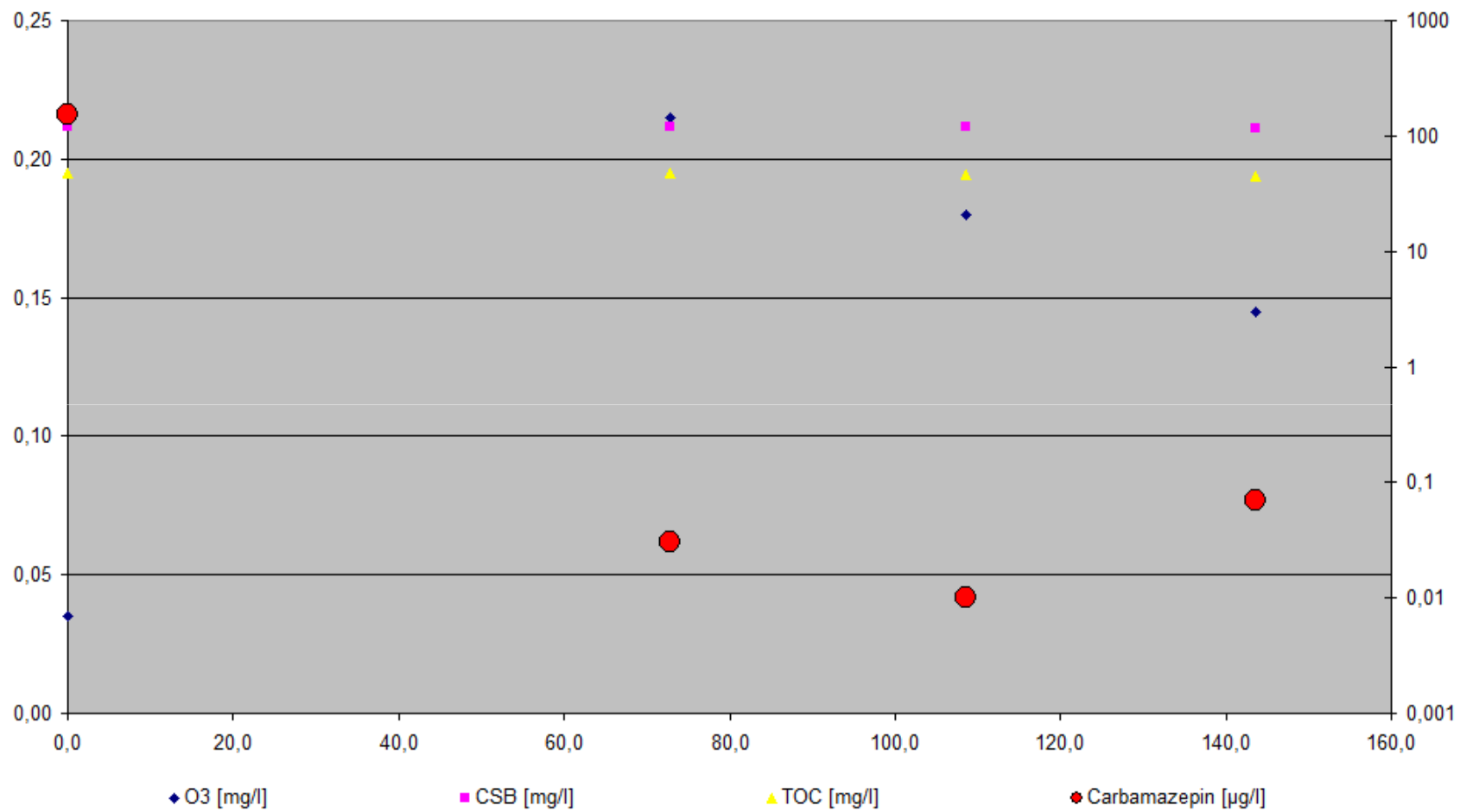
Time-Profile of the plant



O3 concentration [mg/l]: 2,0, ultrasound off, volume flow [l/h]: 1166,4



O3 concentration [mg/l]: 2,0, ultrasound off, volume flow [l/h]: 1166,4



Conclusion

- Carbamazepine is present in a large part of the aquatic environment
- The ultrasound increases the concentration of the CBZ in the aqueous phase
- Ozone oxidises CBZ very fast
- Further experiments will show how exactly ultrasound increases the elimination of CBZ

References

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- Yongjun, Z., S.-U. Geißen, and C. Gal, *Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies*. *Chemosphere*, 2008. xxx(xxx).
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