Micropollutants Removal in MBR Reactors: A comperative study

.

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Outline

- Introduction
- Objective ans scope
- EDC Removals in 3 MBRs
- EDC Removals in other WWTPs
- Conclusion

INTRODUCTION

- Currently over 1 billion people is estimated short of adequate potable water and this is expected to rise to 2.5 billion in the year 2025
- Over 1 billion has to live below 30 L/capita-day, which is below the human rights threshold
- Water availability in Turkey, 1500-1600 m3/capita-annum, puts her among the semi-arid countries
- Reuse of wastewaters may become a perpetual resource for cities and other settlements. Note that only 2-4 L is consumed daily for physiological needs.
- Membrane Bioreactors (MBR) are now accepted as important tools in reuse of wastewaters
- Arid and semi-arid countries can benefit immensely from this technology, provided that product water is free from contaminants
- This is debatable for water-rich countries.

INTRODUCTION

- Endocrine Disrupting Compounds, EDCs, are recently recognized pollutants often classed within ‘emerging micropollutants’
- Known to interfere with the endocrine systems of fish causing gender shifts and reduced fecundity. Also cancer suspect in humans when, and if, they get into the urban water cycle.
- Their main source in natural waters are the domestic and industrial effluents.

INTRODUCTION

- Increased usage of medication and personal care products, PPCPs, in the modern household, and pesticides in the agriculture, add up to the inventory of EDCs in the aqueous systems.
- Current view in combating EDCs in water cycle is the multi barrier approach. Where EDCs are tackled at all the fronts possible; *i.e.* during wastewater and potable water treatment.

INTRODUCTION

- Therefore, knowledge on the elimination of EDCs in wastewater treatment plants is vital for establishing sustainable reuse strategies for the future.
- In this context ability of MBRs to remove EDCs from domestic effluents have been studied here
- Currently over 80 000 possible anthropogenic compounds have been identified as possible EDCs.
- Therefore studying model compounds in place of the actual compounds is most feasible.

OBJECTIVE

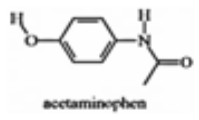
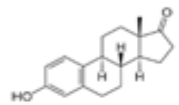
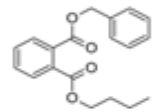
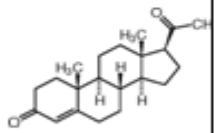
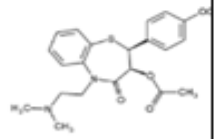
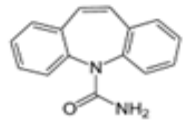
To investigate the removal of selected EDCs in MBR systems.

METHODS

- Five different EDCs, which are most frequently observed in domestic wastewaters, were selected as model compounds in this study
- Two were natural hormones:

  estrone and progesterone, which are continuously discharged by humans
- Three pharmaceuticals: carbamazepine, diltiazem and acetaminophen; which are medications widely used by the society.

- Model EDCs studied:

Compounds	CAS	Sum Formula	MW g/mol	pKa	Log Kow	Vapor pressure mm@25°C	Melting Point °C	Water solubility g/L
Acetaminophen	103-90-2	$C_8H_9NO_2$ 	151.2	9.38	0.46	6.29 E-5	196	14
Estrone	53-16-7	$C_{18}H_{22}O_2$ 	270.4		3.13		256	3,00E-02
BBP	85-68-7	$C_{19}H_{20}O_4$ 	312.4		4.73	8.25E-6	-35	2.69E-03
Progesterone	57-83-0	$C_{21}H_3O_2$ 	314.5		3.87		131	8.81E-03
Diltiazem	42399-41-7	$C_{22}H_{26}N_2O_4S$ 	414.5	0	2.80		231	1.68E-02
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$ 	236.5		2.67	1.84E-07	191	17.7E-03

Analytical

- An Agilent 6410A type LC-MS/MS spectrometer was used to detect EDCs in wastewater samples.
- Samples were pre-treated and concentrated 1000 times by using SPE technology prior to chromatography.
- 3 MBR plants with differing flow handling capacities were studied

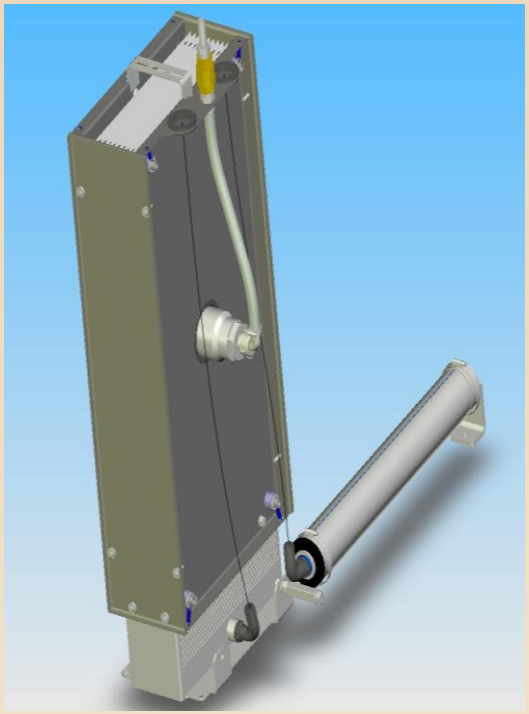
MBR Plants Studied

	Clear-Box	VRM Plant	Konacik
Storage tank volume (m^3)	0.35	10	115
Aeration Tank Volume (m^3)	0,75	85	Anox: 180 Aerobic: 600
MBR tank volume (m^3)	0,75	23	64 x 2
Membrane Type	plate and frame	plate and frame	Plate and frame
Total Membrane Area (m^2)	3	540	2560
Membrane Material	polyethersulfones	PES	PES
Nominal Pore Size (µm)	0.038	0.038	0.04
Sludge Retention Time (days)	10	10	25
Flux (L/h-m^2)	13.3-26	13.3-30	18
SRT (d)	10	10	25
HRT (h)	18	18	16
Type	Flat sheet / vacuum/ Static /Pilot plant	Flat sheet/ vacuum/ rotating	Flatsheet/positive pressure / Static
MLVSS	4-8 gL^{-1}	4-8 gL^{-1}	4 gL^{-1}
Flow	1 $m^3\ d^{-1}$	200 $m^3\ d^{-1}$	1100 $m^3\ d^{-1}$
N-Removal	NO	NO	YES
Feed	Natural domestic WW	Natural domestic WW	Natural domestic WW

Plant 1 and Plant 2 (VRM -HUBER AG.)

METU and Konacık

Plant 3
Clearbox-HUBER AG. Pilot Plant



Analytical

- 24h Composite sampling was administered throughout the study with triplicates.

RESULTS

All three plants were operating upto the design specifications

Figure 1. COD Removals in ClearBox-pilot (Plant 3) and VRM full-scale (Plant 1)

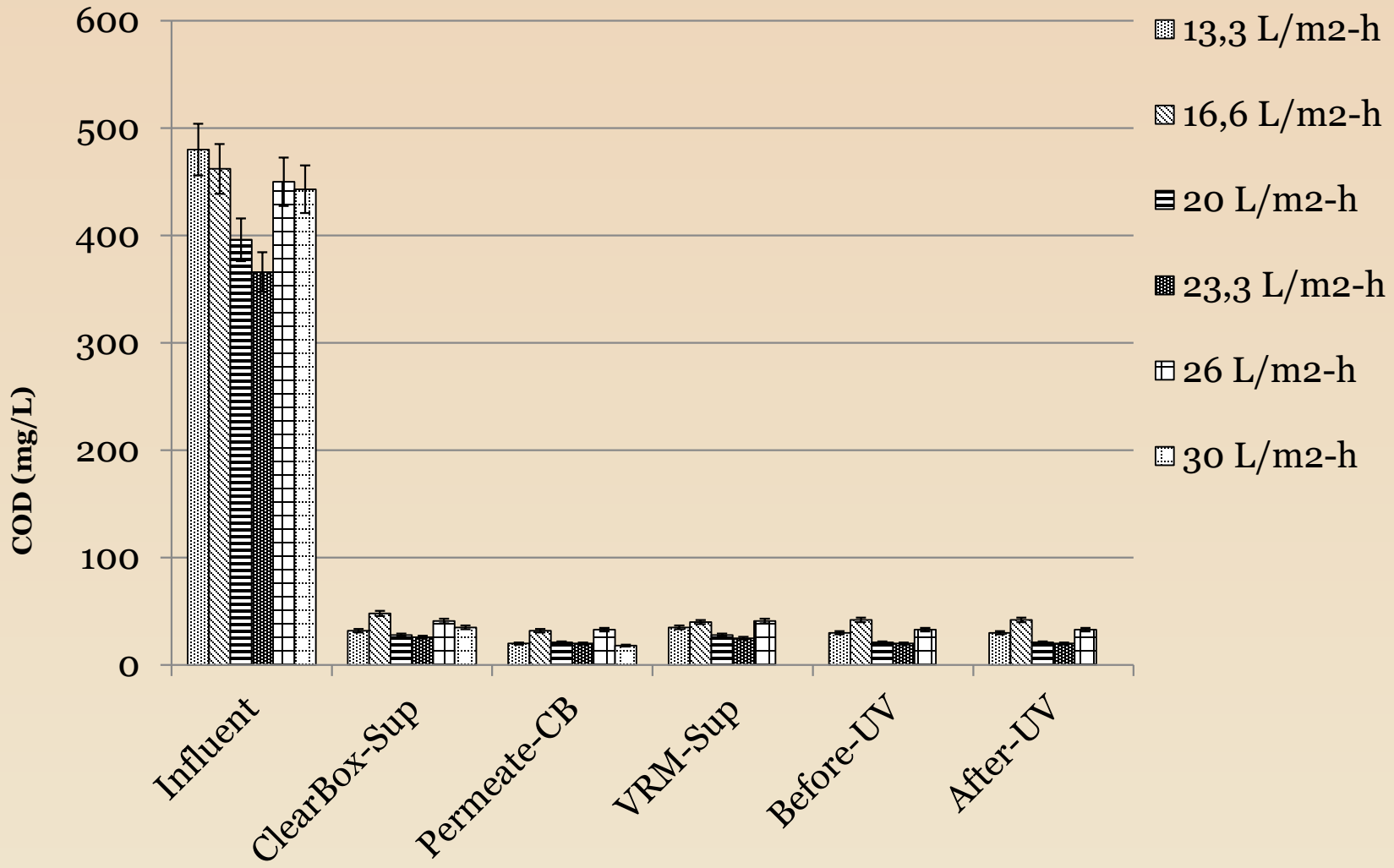
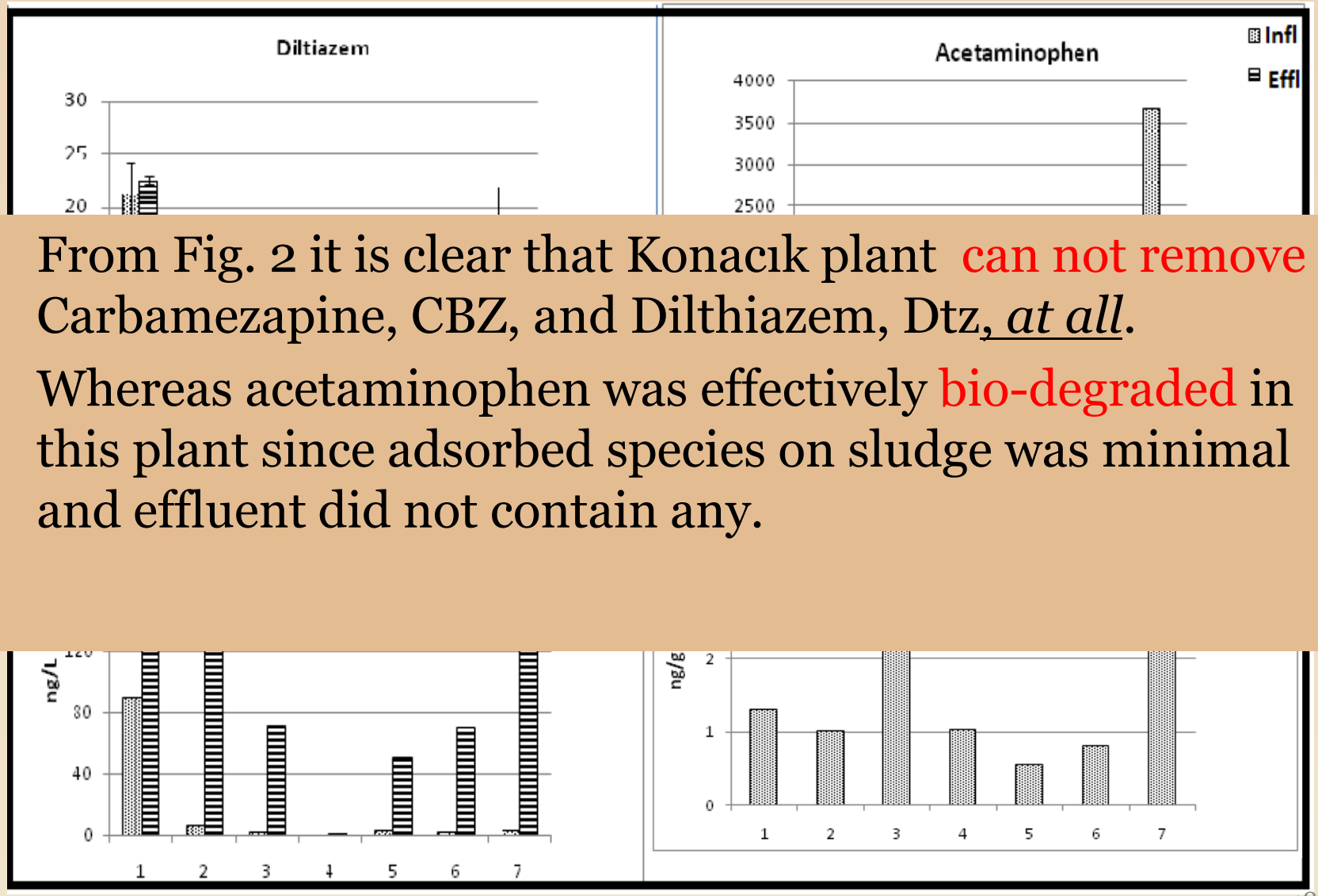


Table 2. Treatment performance of Konacik plant (Plant 2)

-N	65	< 15	>75

Clearly all three MBR plants were removing classical pollution parameters, COD, NTU, very effectively

Figure 2. Removals of selected micropollutants in Plant 2- Konacik



- From Fig. 2 it is clear that Konacık plant can not remove Carbamezapine, CBZ, and Dilthiazem, Dtz, *at all*.
- Whereas acetaminophen was effectively bio-degraded in this plant since adsorbed species on sludge was minimal and effluent did not contain any.

Figure 3. Diltiazem concentrations observed in the Plant 1 and flux effects (θ_c=10 days)

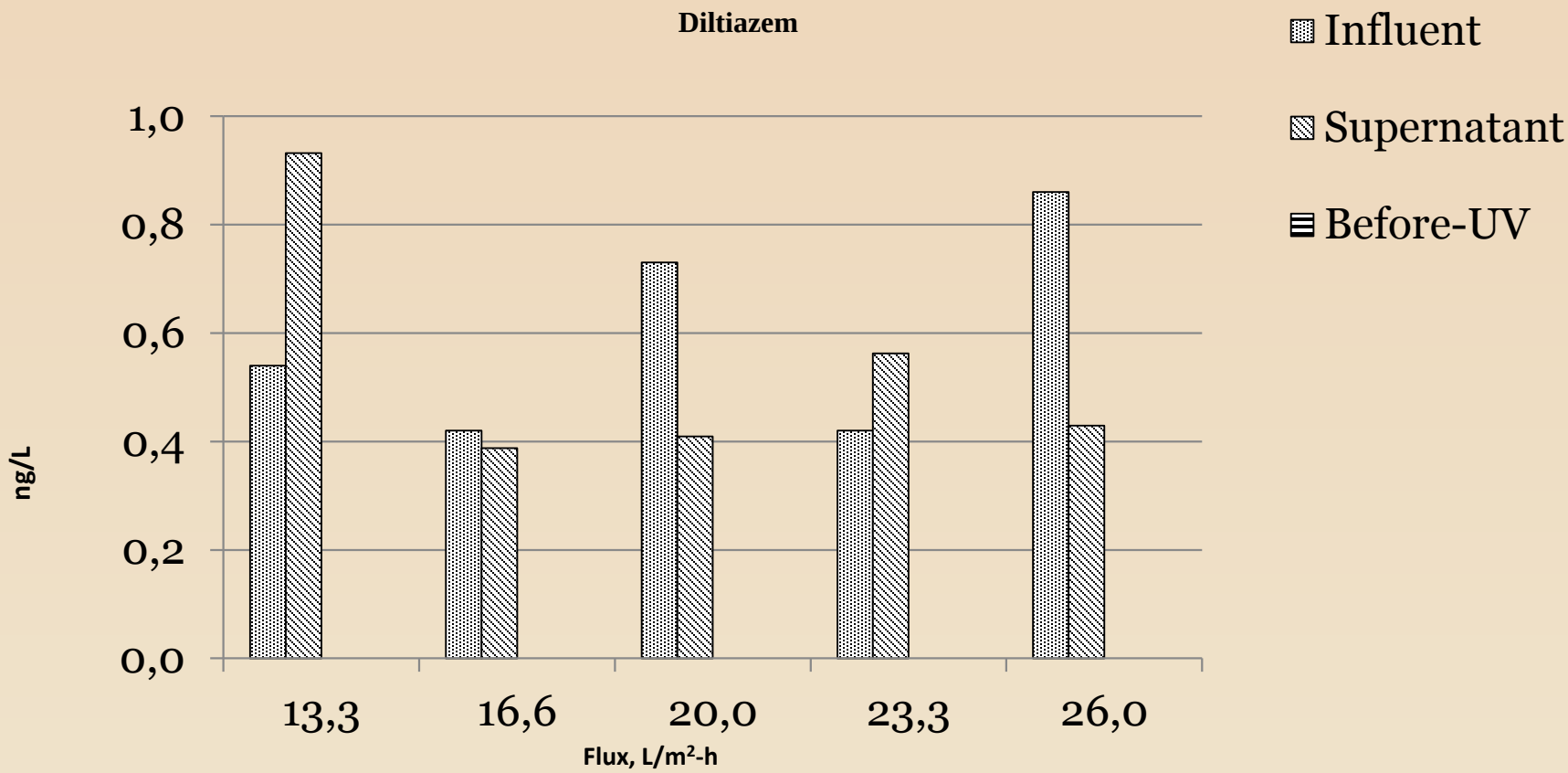
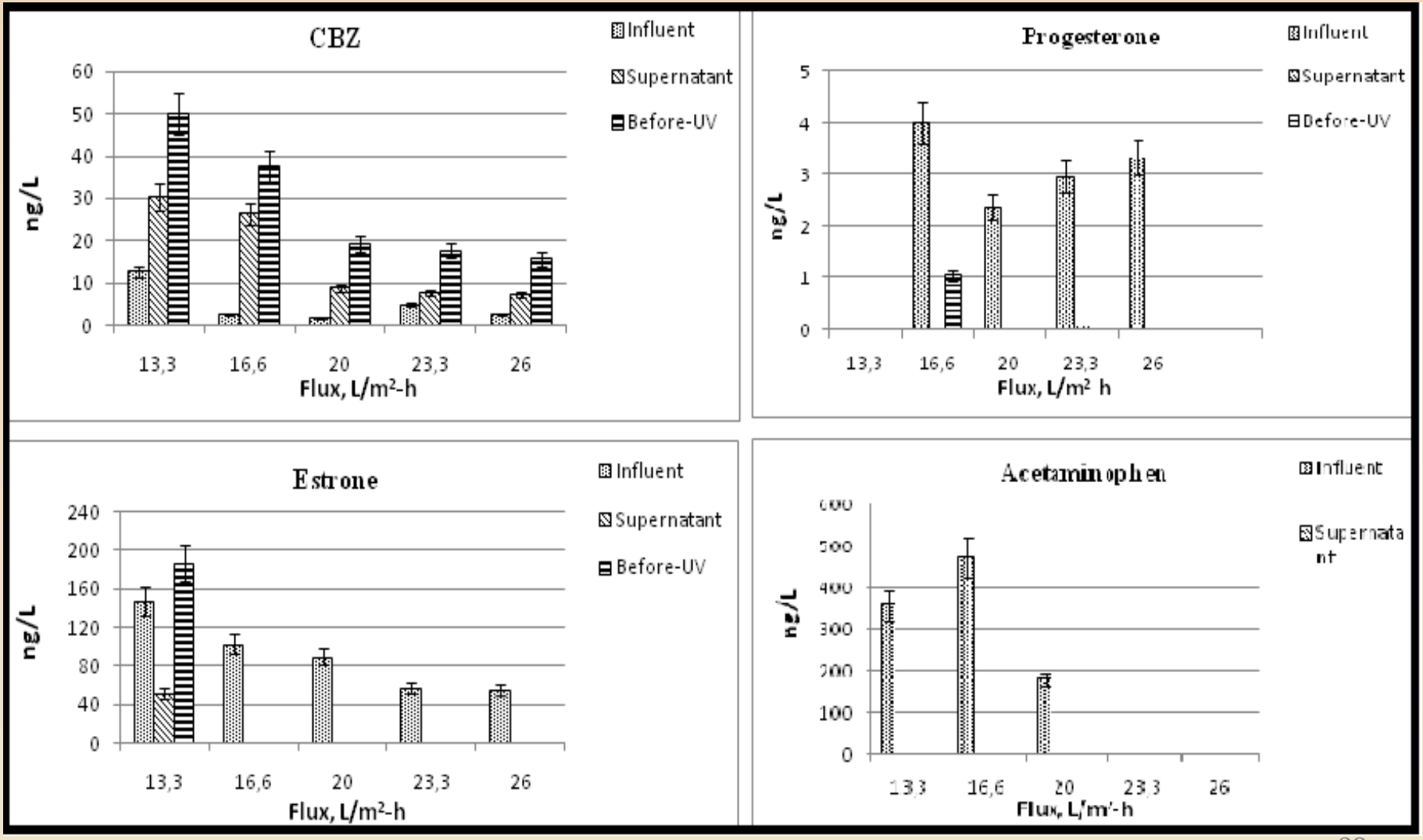


Figure 4. Removals in Plant 1



Plant 1

- Diltiazem was totally removed by this plant!
- Although supernatants did not indicate any removals, effluents contained no Diltiazem
- Possibly Diltiazem was adsorbed onto the membranes and thereby removed.
- Occasional chemical cleansings with hypo might have re-generated the membrane surfaces?
- Why not in the pilot MBR? Or Plant 2 ?
- CBZ was not removed at all in this plant too.
- Acetaminophen was totally biodegraded
- Natural hormones were, too, totaly removed. Though some effect of flux rate was noticeable, i.e. higher removals at higher flux rates

Figure 5. Removals of selected EDCs in Pilot ClearBox MBR plant

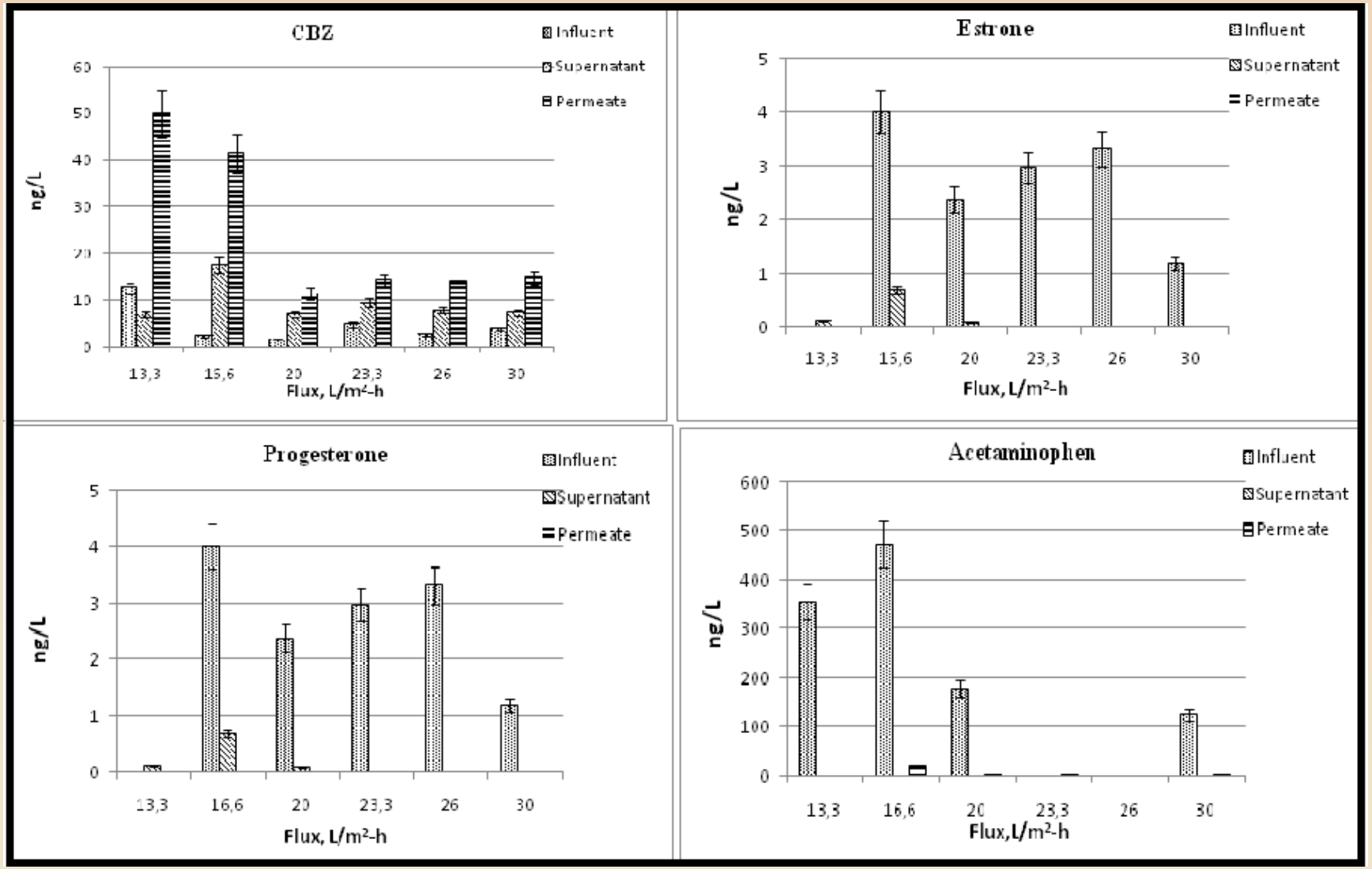
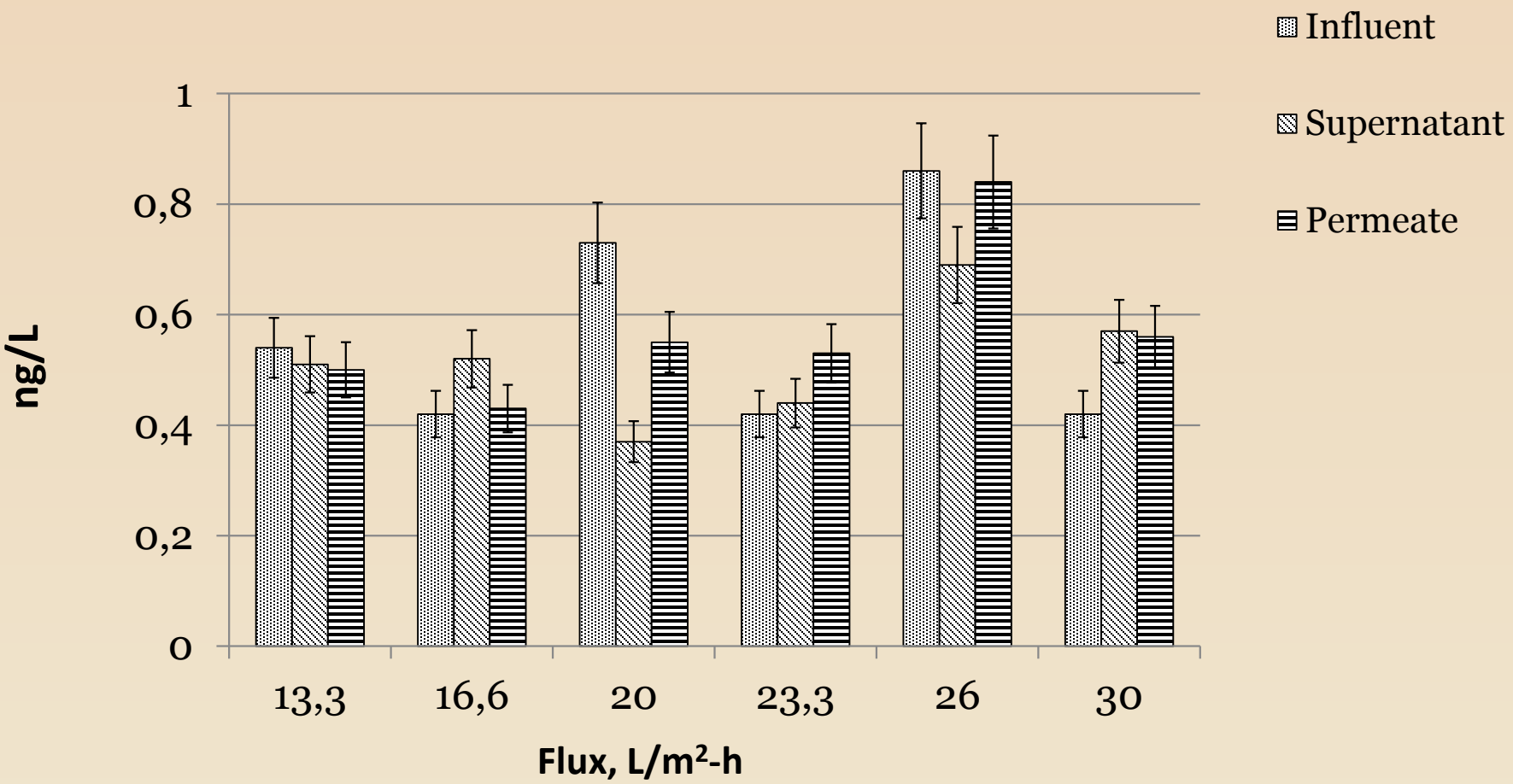


Figure 6. Diltiazem concentration in the influent, supernatants and permeates of the pilot plant 1 and flux effects (θ_c=10 days)



The Pilot ClearBox plant

- Similar to the other reactors, influent being shared with the VRM plant
- CBZ was not removed at all.
- Acetaminophen was totally removed by biodegradation.
- Natural hormones were, too, totaly removed. Though some flux rate effects was noticeable, i.e. higher removals at higher flux rates
- Unlike the other plants, Dtz was not removed at all

Treatment of Recalcitrant EDCs in Conventional WWTPs

Figure 7. Carbamezapine Treatment in Conventional Activated Sludge

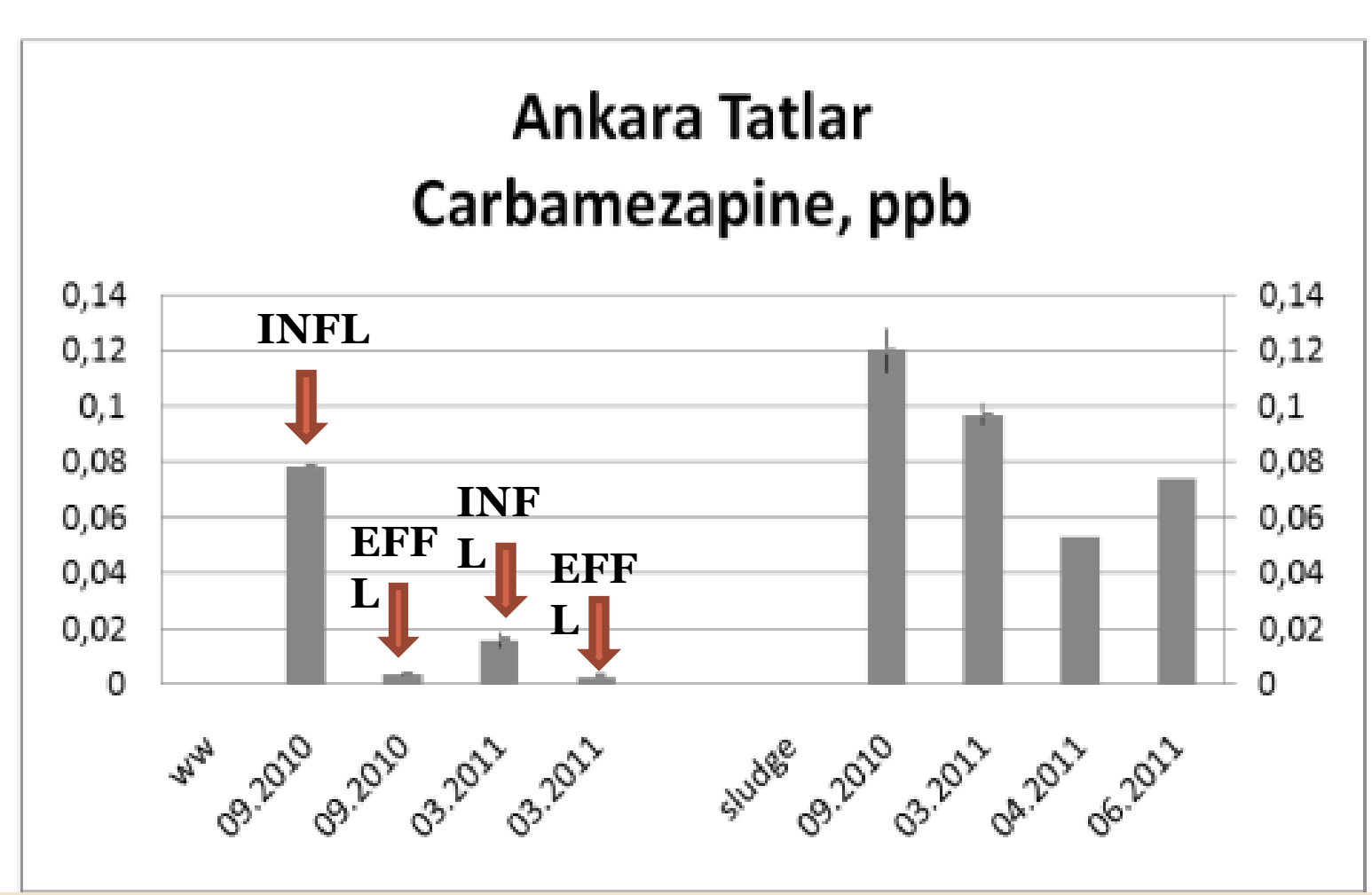


Figure 8. Carbamezapine Treatment in a BNR Plant

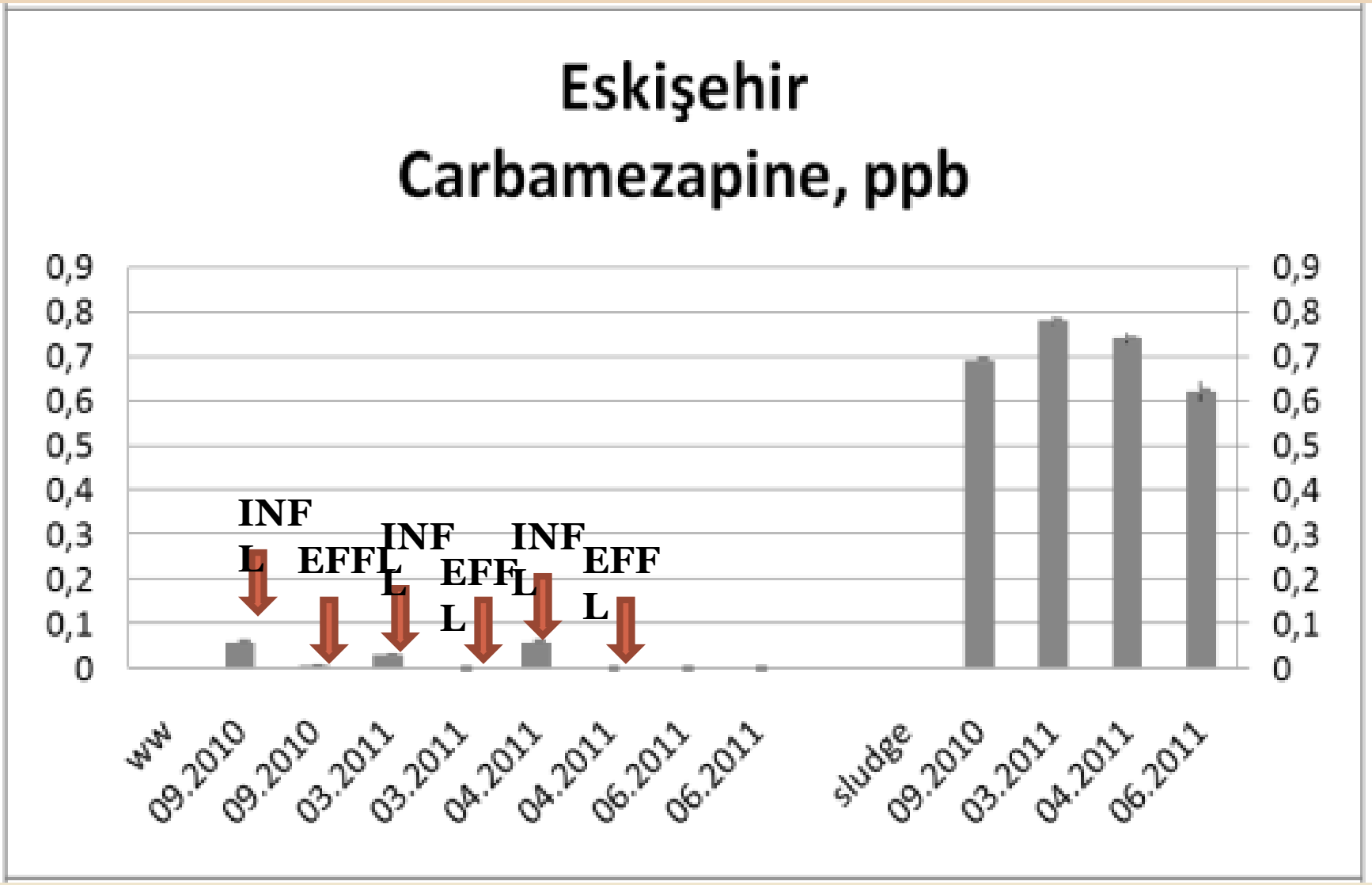


Figure 9. Diltiazem Treatment in Conventional Activated Sludge

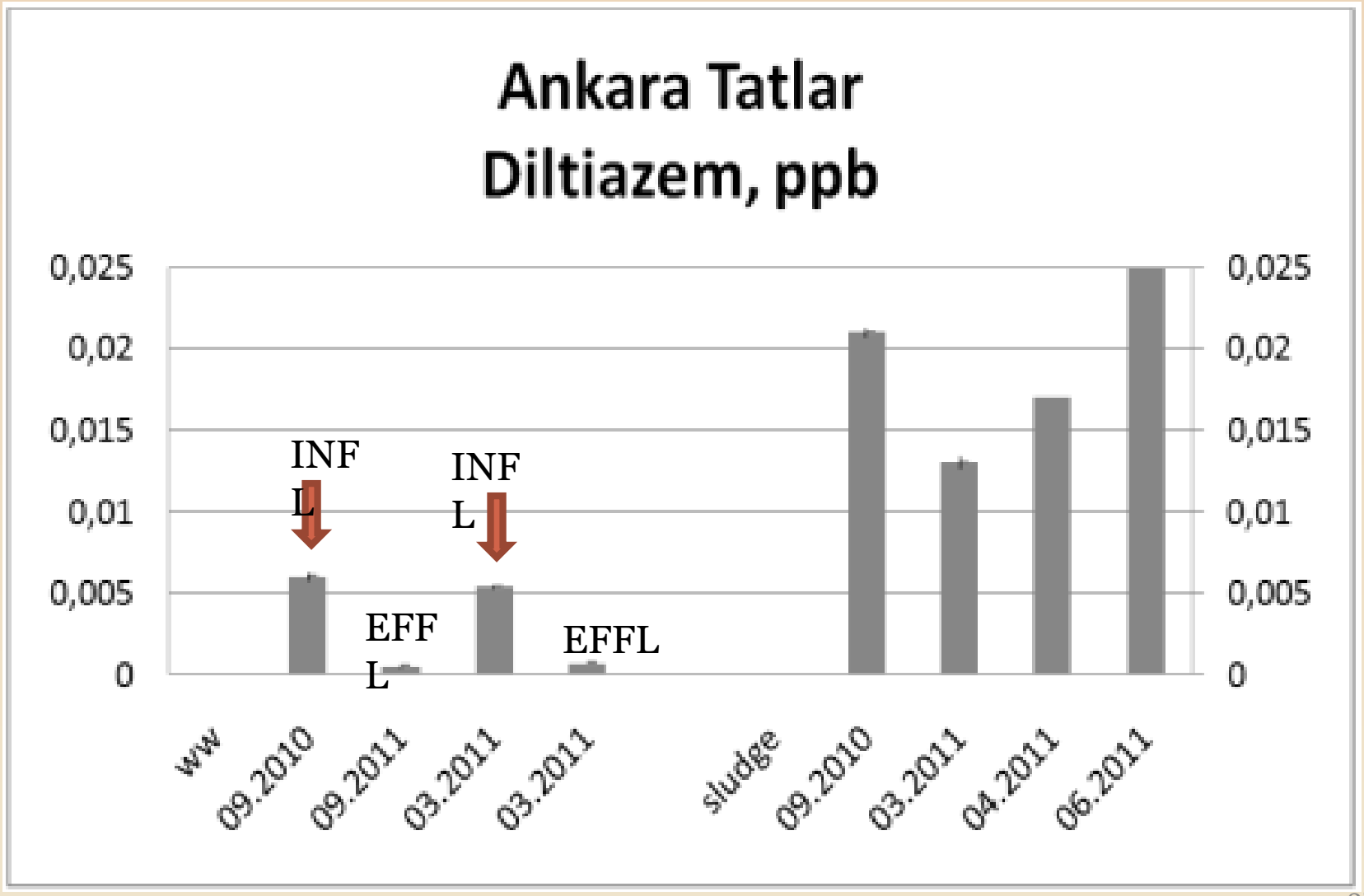
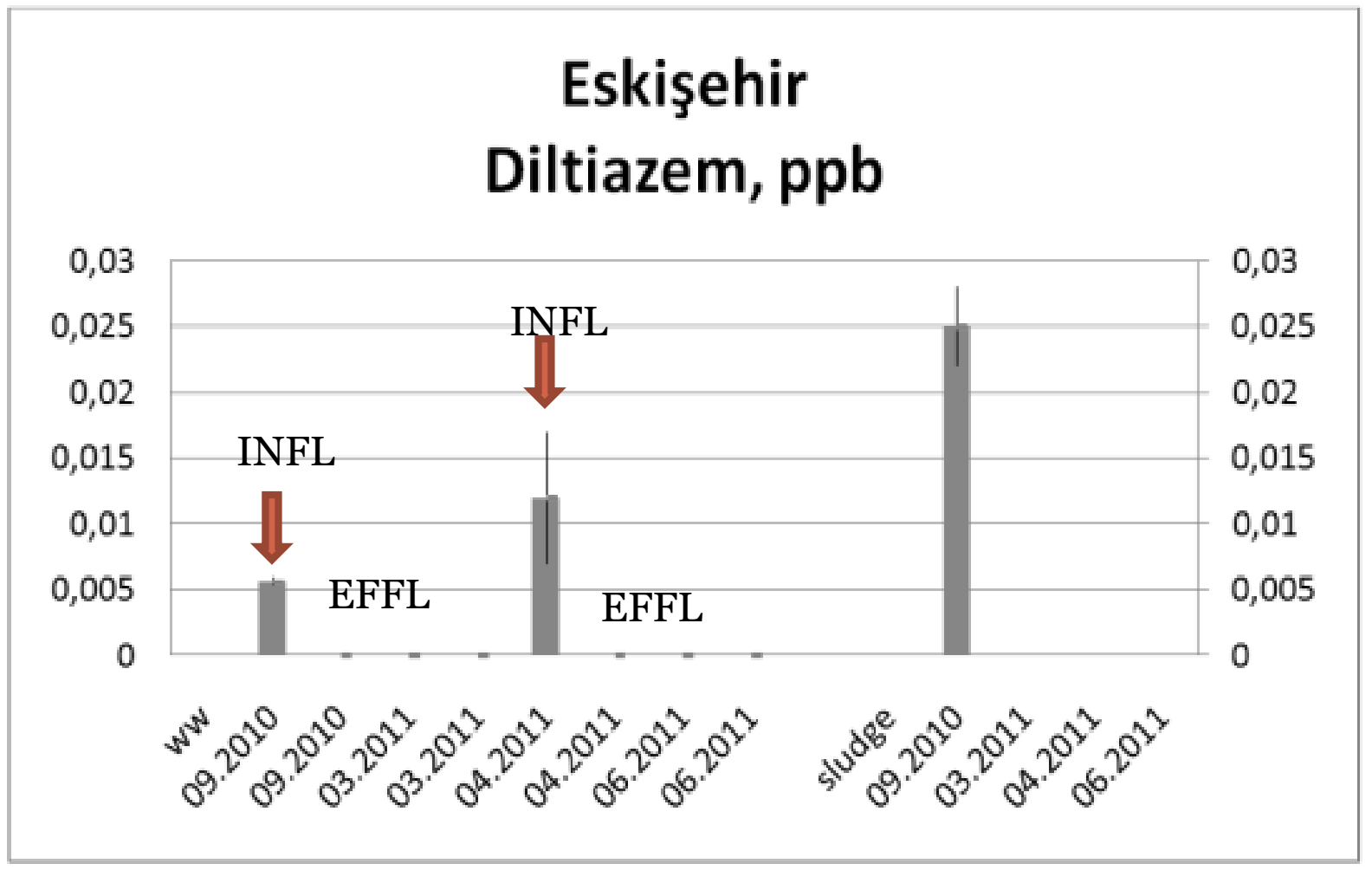


Figure 10. Diltiazem Treatment in a BNR Plant



Findings

- It is clear that CBZ and Dtz, the two non-treatable EDCs in MBRs, were totally removed in conventional biological treatment plants.
- Although it was not a biodegradation but it is clear that these compounds were adsorbed onto the sludge and thereby removed.

Conclusions

- The commonly prescribed pain killer, acetaminophen, and the natural hormones, progesterone and estrone, which are commonly present in wastewaters, were completely biodegraded in the three MBR plants sampled.

- The Carbamezapine, a commonly prescribed antiepilepthic, was not removed *at all* in any of the MBR plants.

Conclusions

- Diltiazem, a blood thinner, was non-treatable in two of the MBRs but completely treatable in the third one, in spite of the fact that two reactors were sharing a common feed and the initial culture.

- The flux rate does not have any significant effect on EDCs removal, though slight improvement in treatment of natural hormones have been noticed when flux rate exceeded 20 L/m^2-h.

Conclusions

- As compared to the MBRs, *conventional* bological treatment plants were all able to completely remove CBZ and Dtz from effluents by way of adsorption onto the sludge.
- The discrepency possibly lies in the nature of the two cultures. Where, MBR cultures were possibly less hydrophobic than activated sludge.
- This remains to be explored.

THANK YOU

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