



# REMOVAL OF PESTICIDES FROM WASTEWATER BY MEMBRANE PROCESS

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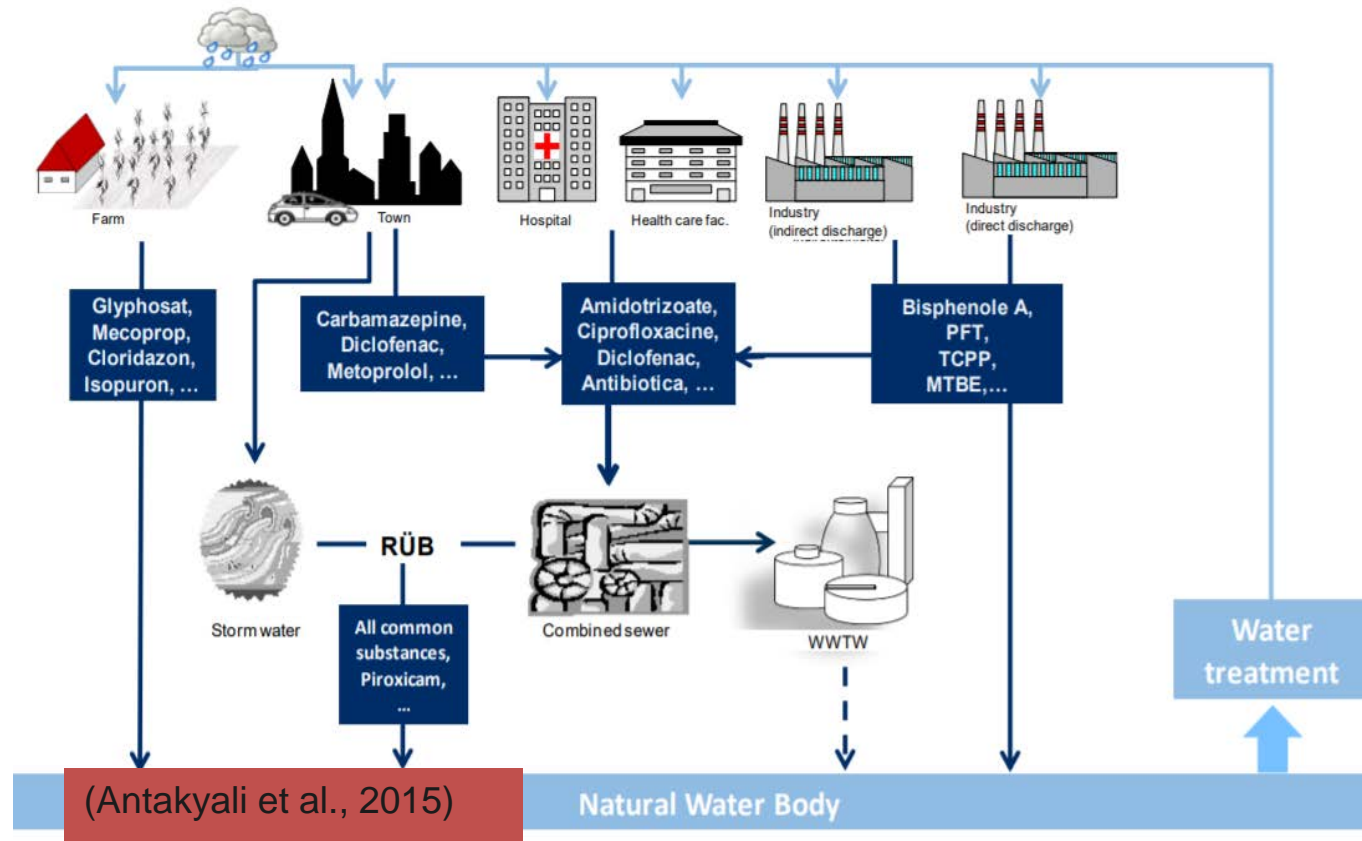
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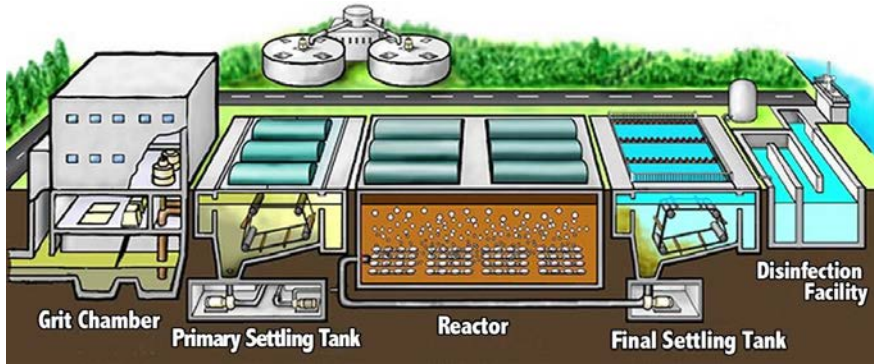
# Micropollutants

Water pollution has become a very important issue, especially in the last 20 years, since the presence of numerous and types of pollutants in ng/L and  $\mu\text{g/L}$  levels in aquatic environments.



Common pathways of micropollutants into water sources.

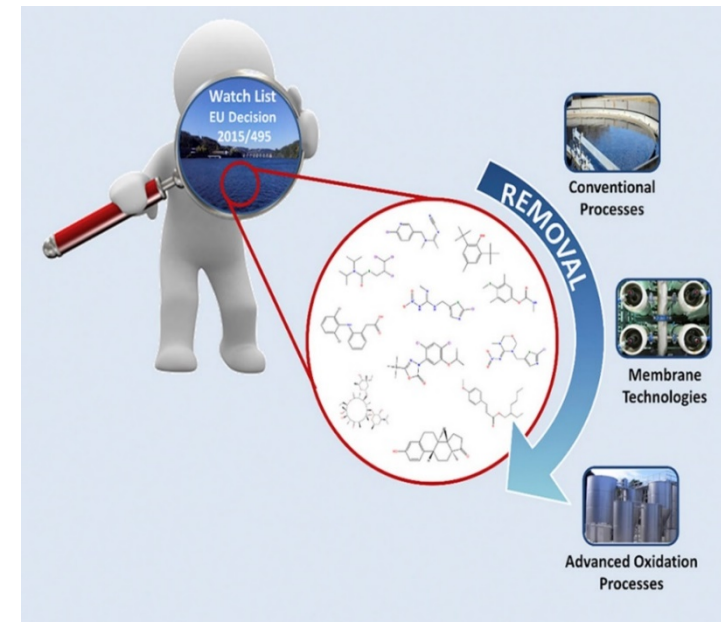
# Treatment of Micropollutants



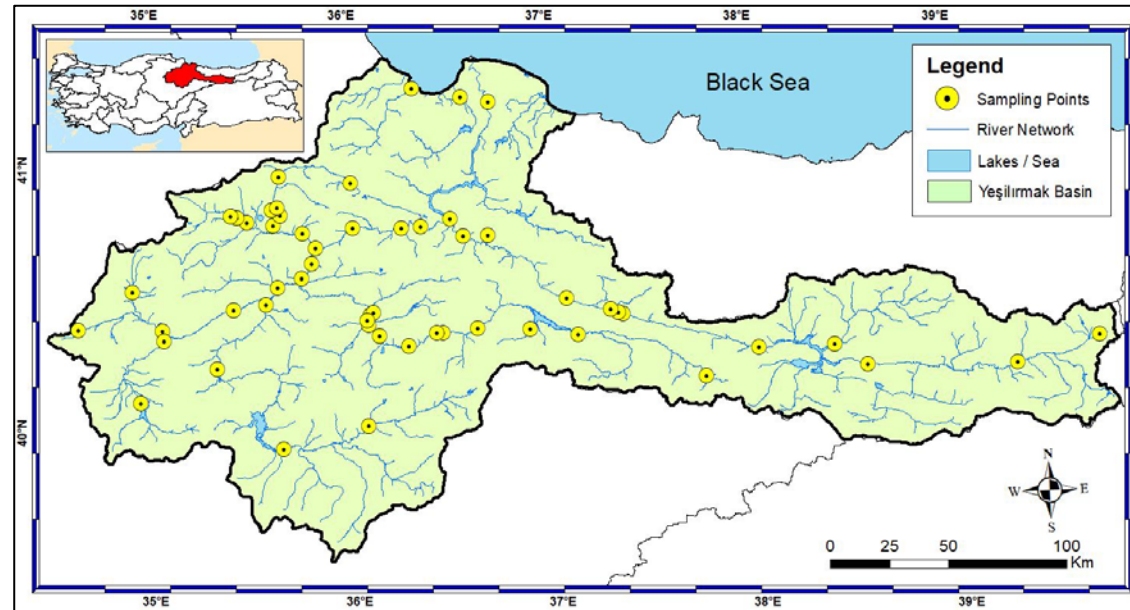
Conventional WWTPs are not designed to completely eliminate micropollutants into less harmful compounds or even to mineralize them.

## Advanced water treatment processes include;

- ✓ Ion Exchange
- ✓ Adsorption (e.g., GAC),
- ✓ Advanced chemical/oxidation technologies,
- ✓ **Membrane filtration**
  - Complete Removal
  - Management of by-products



# Management of Point and Diffuse Pollutant Sources in the Yeşilırmak River Basin



Monitoring studies were carried out in a total of 54 different stations in the Yeşilırmak Basin;

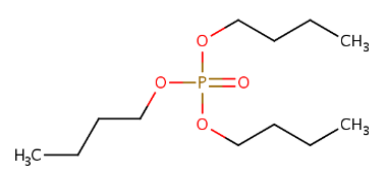
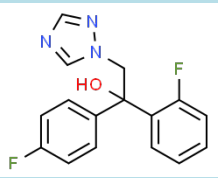
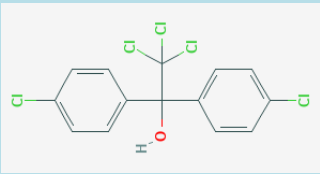
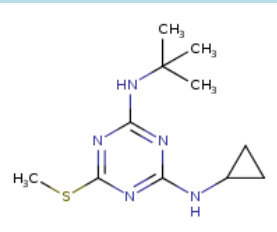
**Point Sources:** Industrial Facilities, WWTP, etc.

**Non-Point Sources:** Agricultural Activities

8 pollutants were detected in at least 3 of the monitored WWTPs at least 10 times above the EQS values;

- Carbendazim
- Malation
- Imidacloprid
- Aclonifen
- Flutriafol,
- Tributyl phosphate
- Irgarol
- Dicofol

# PESTICIDES

Pesticide	Molecular Structure	Specifications	MW	LogK <sub>ow</sub>	K <sub>H</sub> (atm. m <sup>3</sup> /mole)
Tributyl Phosphate		<ul style="list-style-type: none"> <li>~ Organophosphorus pesticide</li> <li>~ very stable in the natural environment</li> <li>~ cannot be removed in WWTP</li> <li>~ Class II, 'moderately hazardous' pesticide</li> </ul>	266.31	4.0	1.5*10 <sup>-7</sup>
Flutriafol		<ul style="list-style-type: none"> <li>~ Fungicide</li> <li>~ Not readily biodegradable but can dissolve in soil and water over a long period of time,</li> <li>~ Toxic for aquatic organisms</li> </ul>	301.29	2.3	1.63*10 <sup>-13</sup>
Dicofol		<ul style="list-style-type: none"> <li>~ Organochlorine pesticide</li> <li>~ Listed in POPs in</li> <li>~ Partially biodegradable and hydrolized, but persistent in acidic conditions</li> </ul>	370.49	5.02	2.4*10 <sup>-7</sup>
Irgarol		<ul style="list-style-type: none"> <li>~ Biocide and algicide</li> <li>~ Persistent, does not decompose easily in water</li> <li>~ Undergoes photodegradation to some permanent metabolites</li> </ul>	253.37	3.95	3.1*10 <sup>-8</sup>

# Motivation of The Study

In the scope of the Project, the pollutants detected to exceed the EQS in at least 3 WWTPs were evaluated as important pollutants for the Yeşilırmak Basin.

	EQS (µg/L)	Min (µg/L)	Max (µg/L)	in WWTP	Exceed Times
Tributyl Fosfat	53	571	2143	5	10-40
Flutriafol	25	129	202	3	5-8
Dicofol	0.0013	1.88	3.08	2	1500-2000
Irgarol	0.0025	0.42	0.87	4	170-350

# Objective of the Study

The removal of tributyl phosphate, flutriafol, dicofol and irgarol which are four different micropollutants contributing the industrial pollution were investigated by reverse osmosis (RO) process.

# Materials and Methods

- ✓ Three different membranes (**BW30-LE**, **SW30-XLE** and **GE-AD**) were selected for the removal of pesticides and removal tests were carried out at two different pressures (**10 and 20 bar**).

**Properties of the membranes used in this study**

Membrane Type	Polymer Structure	Rejection (% NaCl)	Pure water flux/pressure (L/m <sup>2</sup> -h)/(bar)	Contact Angel (°)
BW30-LE	Polyamide	99.0	63-78/17	26
SW30-XLE	Polyamide	99.6	30-40/55	49
GE-AD	Polyamide	99.75	20-32/55	38

- ✓ Micropollutants spiked in effluent wastewater:
  - ✓ 100 µg/L for tributyl phosphate and flutriafol (GC/MS Analysis)
  - ✓ 1000 µg/L for dicofol and irgarol (HPLC analysis)

# Flux Development

Membranes	Pressure (bar)	JW <sup>1</sup> (L/m <sup>2</sup> .h)	JWW <sup>2</sup> (L/m <sup>2</sup> .h)	JCW <sup>3</sup> (L/m <sup>2</sup> .h)	Flux Decline (%)	Flux Recovery (%)
<b>TRIBUTHYL PHOSPHATE</b>						
SW30	10	3.90	3.25	4.15	0	100
	20	13.48	12.82	12.39	8	92
GE-AD	10	6.37	4.91	5.65	12	88
	20	18.31	15.53	18.51	0	100
BW30	10	32.47	20.21	24.68	24	76
	20	72.18	41.65	52.25	28	72
<b>FLUTRIAFOL</b>						
SW30	10	15.49	16.69	16.07	0	100
	20	36.7	35.22	40.81	0	100
GE-AD	10	11.58	10.37	14.12	0	100
	20	37.27	33.83	31.36	16	84
BW30	10	46.75	48.51	49.45	0	100
	20	98.9	107.14	128.57	0	100

<sup>1</sup>JW: Clean water flux before treatment, <sup>2</sup>JWW: Raw water flux, <sup>3</sup>JCW: Clean water flux after treatment



# Flux Development

Membranes	Pressure (bar)	JW <sup>1</sup> (L/m <sup>2</sup> .h)	JWW <sup>2</sup> (L/m <sup>2</sup> .h)	JCW <sup>3</sup> (L/m <sup>2</sup> .h)	Flux Decline (%)	Flux Recovery (%)
<b>DICOFOL</b>						
SW30	10	2.0	1.8	1.4	9	71
	20	8.0	6.5	6.8	18	86
GE-AD	10	6.7	6.1	5.9	8	89
	20	16.0	12.8	13.2	<b>20</b>	82
BW30	10	23.9	22.1	18.0	7	75
	20	53.3	52.2	50.2	2	<b>94</b>
<b>IRGAROL</b>						
SW30	10	2.2	2.1	2.0	4	92
	20	7.2	7.0	6.2	2	86
GE-AD	10	7.0	6.9	6.5	2	93
	20	15.1	14.4	13.7	4	91
BW30	10	16.9	16.3	16.6	3	<b>98</b>
	20	43.2	40.9	37.4	<b>5</b>	86

<sup>1</sup>JW: Clean water flux before treatment, <sup>2</sup>JWW: Raw water flux, <sup>3</sup>JCW: Clean water flux after treatment

# Effect of TMP on Removal of TBP and FTF

Pressure	Time (min)	BW30-LE			SW30			GE-AD		
		EC* (µs/cm)	pH	Removal (%)	EC* (µs/cm)	pH	Removal (%)	EC* (µs/cm)	pH	Removal (%)
<b>TRIBUTHYL PHOSPHATE</b>										
10	0	1308	8.35	-	1194	8.62	-	1167	8.64	-
	60	53	8.03	99	77	8.19	96	45	8.02	96
	120	50	8.21	98	68	8.01	97	39	7.79	97
	180	50	8.07	99	60	8	98	26	8.17	99
20	0	1234	8.56	-	1203	8.7	-	1270	8.45	-
	60	24	7.8	99	33	8.29	96	24	8.14	99
	120	25	8.03	99	33	8.06	98	21	8.32	99
	180	19	8.15	99	31	8.11	98	21	8.34	99
<b>FLUTRIAFOL</b>										
10	0	1102	7.8	-	1066	7.6	-	1063	7.9	-
	60	144	7.8	87	37	6.9	97	14.84	7.2	99
	120	51	7.5	95	27.5	7.1	97	15.12	7.3	99
	180	26	7.2	98	16.24	7.2	99	21.5	7.2	98
20	0	1079	7.6	-	1082	7.5	-	1066	8.1	-
	60	77	7.8	93	19.18	7.3	98	19.27	7.1	98
	120	109	7.6	90	31.4	7.2	97	6.93	7.2	99
	180	86	7.6	92	11.74	7.1	99	10.27	7.2	99

# Effect of TMP on Removal of DCF and IRG

Pressure	Time (min)	BW30-LE			SW30			GE-AD		
		EC* (µs/cm)	pH	Removal (%)	EC* (µs/cm)	pH	Removal (%)	EC* (µs/cm)	pH	Removal (%)
<b>DICOFOL</b>										
10	0	1223	7.11	-	1248	7.48	-	1298	7.63	-
	60	14	8.02	99	69	8.43	95	31	7.25	98
	120	15	7.69	99	63	6.98	95	25	6.87	98
	180	19	7.96	98	60	7.22	95	15	6.46	99
20	0	1303	7.52	-	1316	7.01	-	1414	6.31	-
	60	13	8.33	99	34	7.49	97	23	7.31	98
	120	15	8.05	99	34	6.89	97	14	7.08	99
	180	13	7.78	99	31	6.91	98	13	7.06	99
<b>IRGAROL</b>										
10	0	1232	7.11	-	1355	7.48	-	1265	7.63	-
	60	26	8.02	98	62	8.43	98	84	7.25	99
	120	36	7.69	99	68	6.68	98	83	6.87	98
	180	29	7.96	98	64	7.22	98	86	6.46	98
20	0	1190	7.52	-	1532	7.01	-	1318	6.31	-
	60	21	8.33	98	54	7.49	98	98	7.31	95
	120	23	8.05	98	51	6.89	98	86	7.08	95
	180	17	7.78	98	54	6.61	98	74	7.06	95

# Conclusions

- ❑ The highest flux recovery:
  - ❑ 92 and 100% for SW30 membrane at 10 and 20 bar in TBP test
  - ❑ 98% for BW30 membrane at 10 bar pressure in Irgarol test
  
- ❑ The highest removal efficiency:
  - ❑ 98-99% of TBP for BW30 membrane at 10 and 20 bar pressures
  - ❑ 98-99% of Flutriafol for GE-AD membrane at 10 and 20 bar pressures
  - ❑ 98% of Irgarol for for BW30 membrane at 10 bar pressure
  
- ❑ In general, GE-AD and BW30 showed superior performance for the removal of pesticides with >96% performance 10 and 20 bar pressures.

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# Thank You...



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