Advanced Wastewater Treatment

Treating Wastewater From a Hospital WW
By Ozone based AOP

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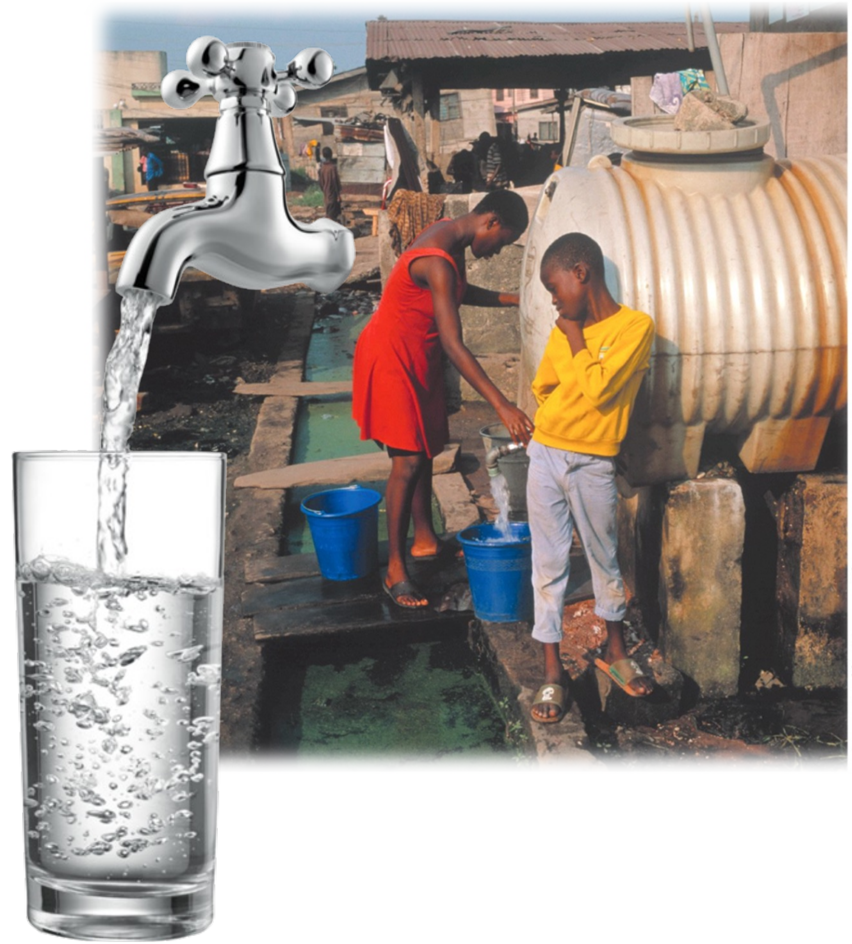
THE IMPORTANCE OF WATER

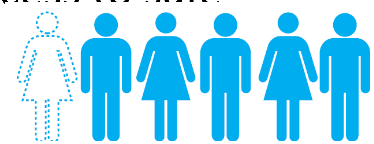
- Life on Earth would be impossible without water
  - All living organisms contain water
  - Humans are ~ 70% water
  - Uses include drinking, cooking, washing, agriculture, transportation, manufacturing, mining, energy production, waste disposal



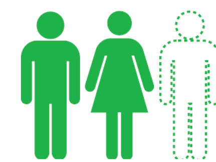
By 2025, more than 1/3 of humans will live in areas with inadequate supply of fresh water for drinking and irrigation

Water Pollution in Developing Countries

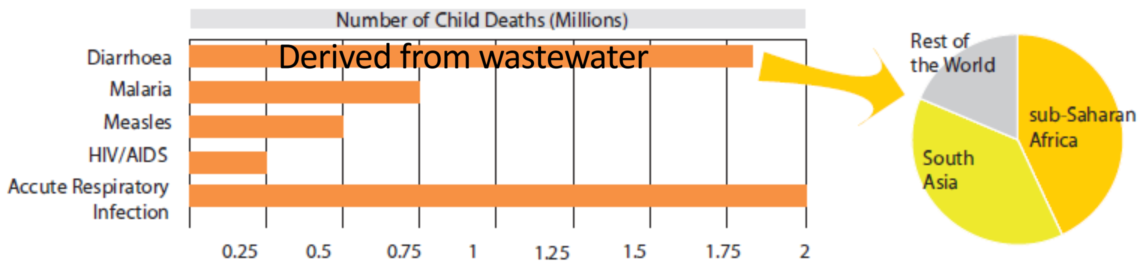
- 1.4 billion people in the world do not have access to safe drinking water



- 2.9 billion do not have access to sanitation systems (1/3 of world population)



- 250 million cases of water-related illness each year
- 5 million or more result in death—1.8 million from diarrheal illnesses alone a year.

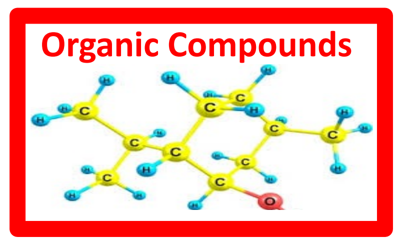


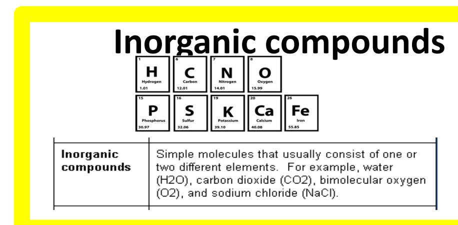
Results in…

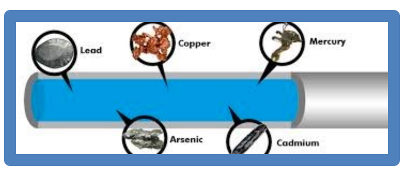
- ✓ **The need** - Increasing need for water reuse (treated wastewater)
- ✓ **The source** - Municipal WW a major source
- ✓ **The risk** - **contaminants** in treated wastewater (effluent) as pharmaceuticals, pesticides, personal care products and others…

In addition to worldwide water scarcity (**quantity**), the issue of water contamination (**quality**) dramatically effects public health

Major contamination sources:

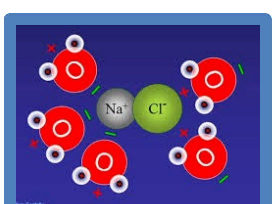


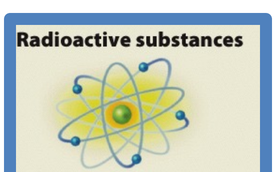


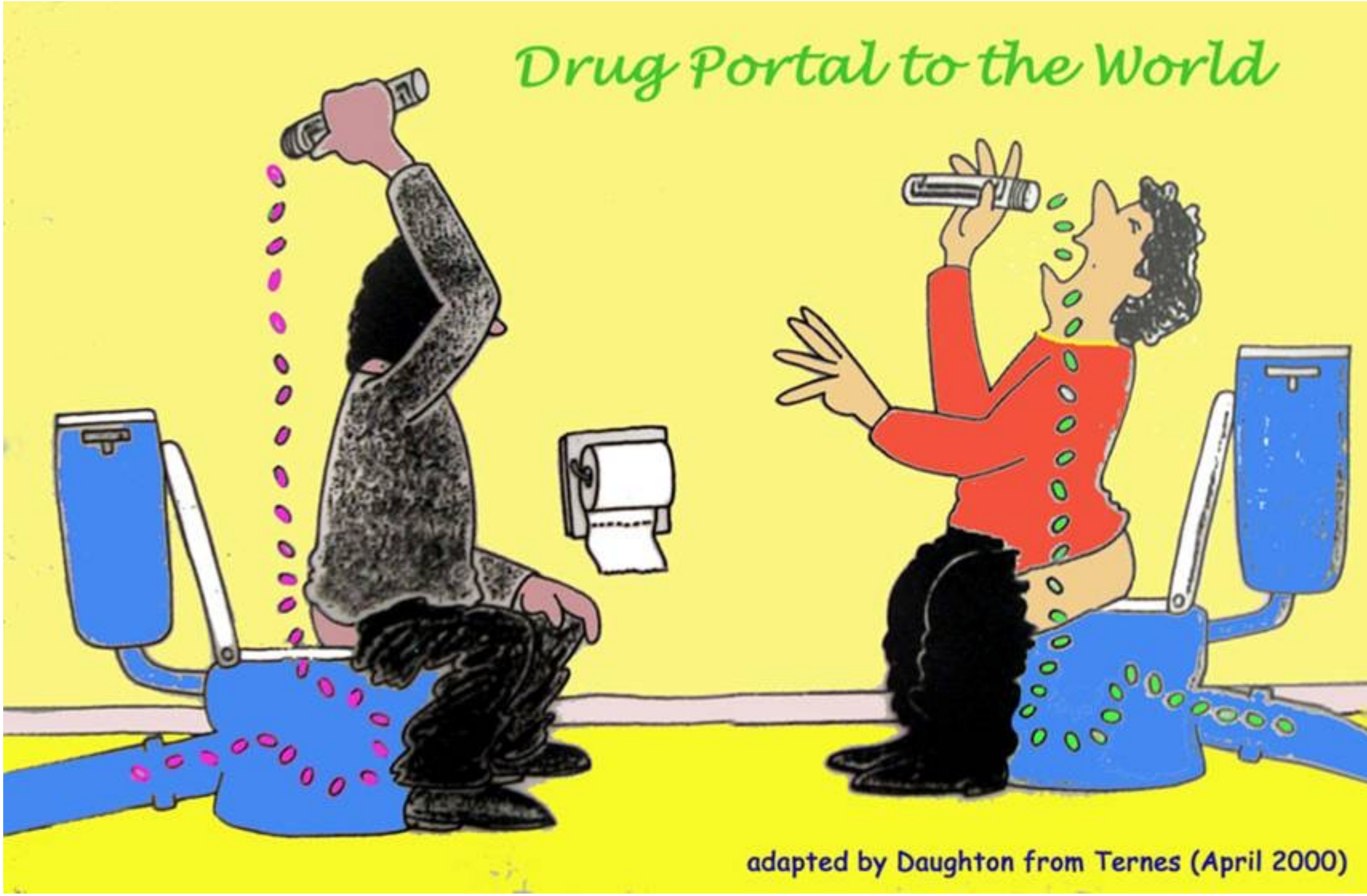


Dissolves

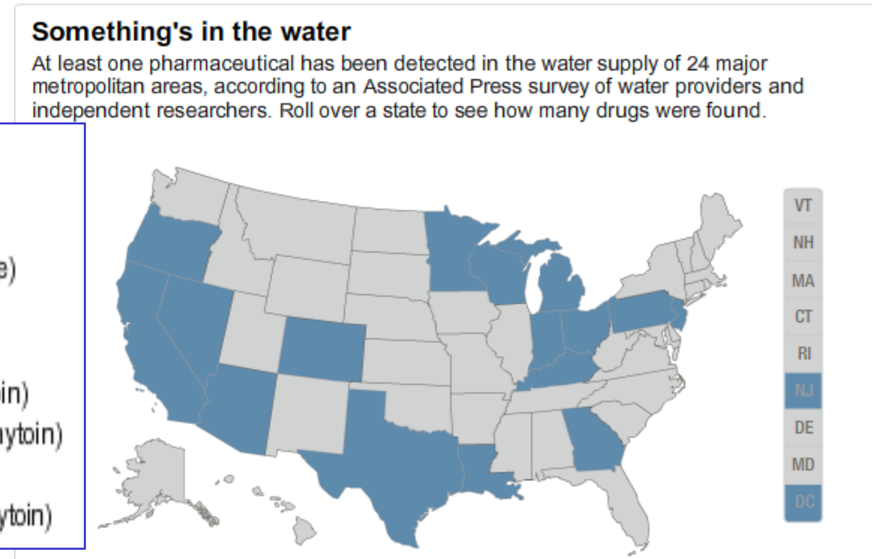
Particulate

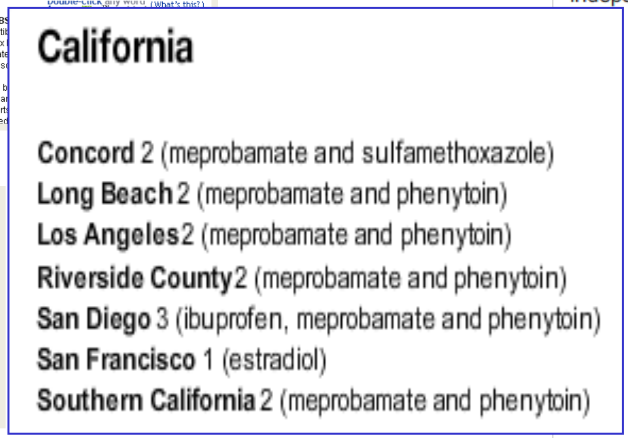


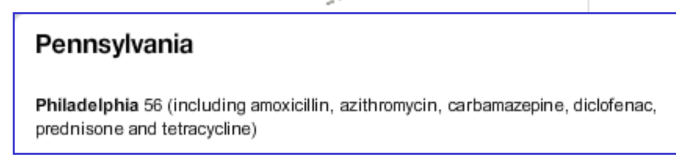



Drug Portal to the World
adapted by Daughton from Ternes (April 2000)

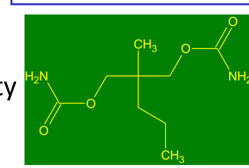
Problem Worldwide…





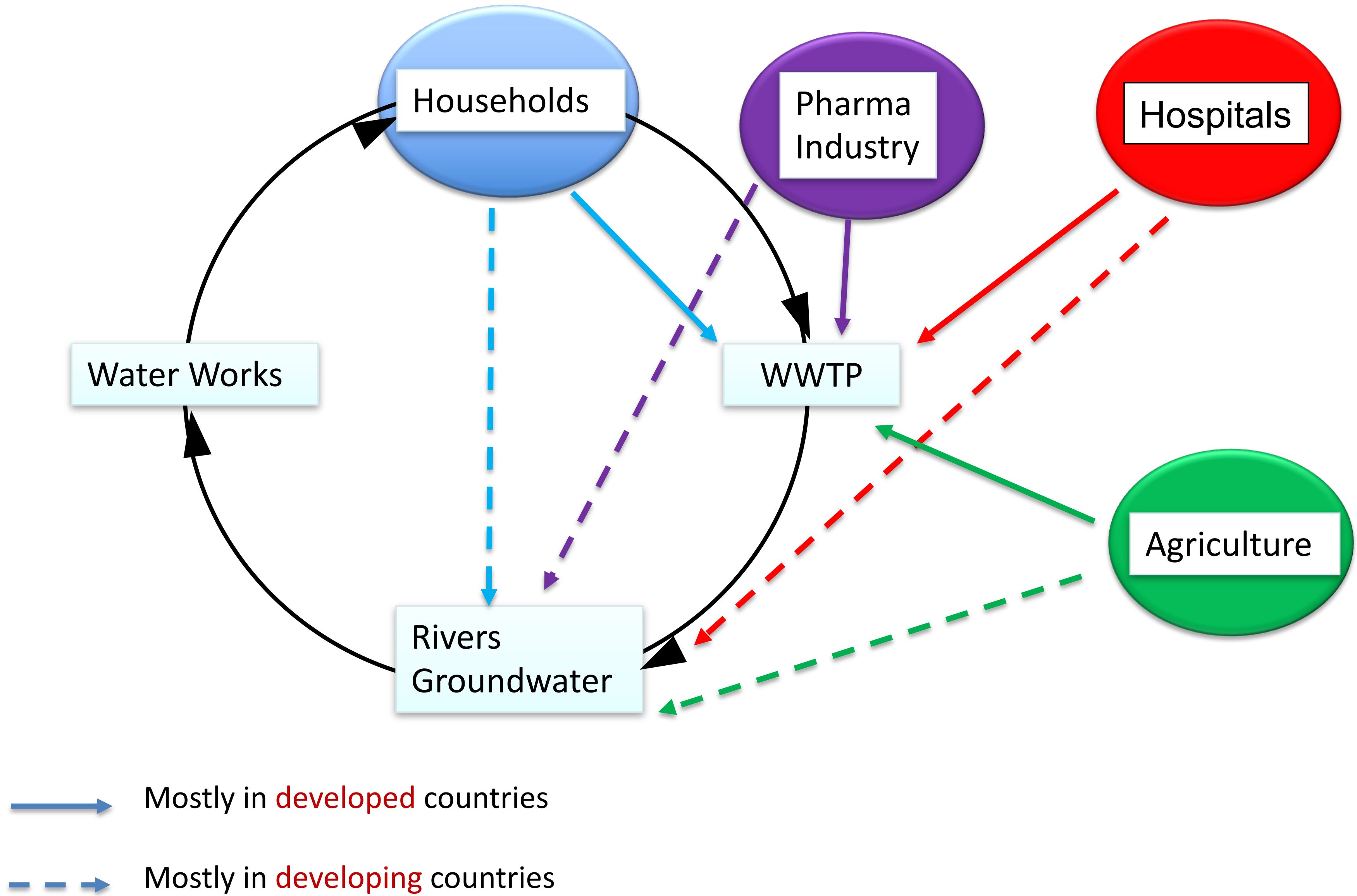


Meprobamate = Antianxiety



Various water sources may contain toxic chemicals at very low concentrations such as <u>pharmaceutical residues</u>

Main sources of pharmaceuticals in wastewater



Solutions ☺

Pharmaceuticals in the environment,

Is it really a problem ?

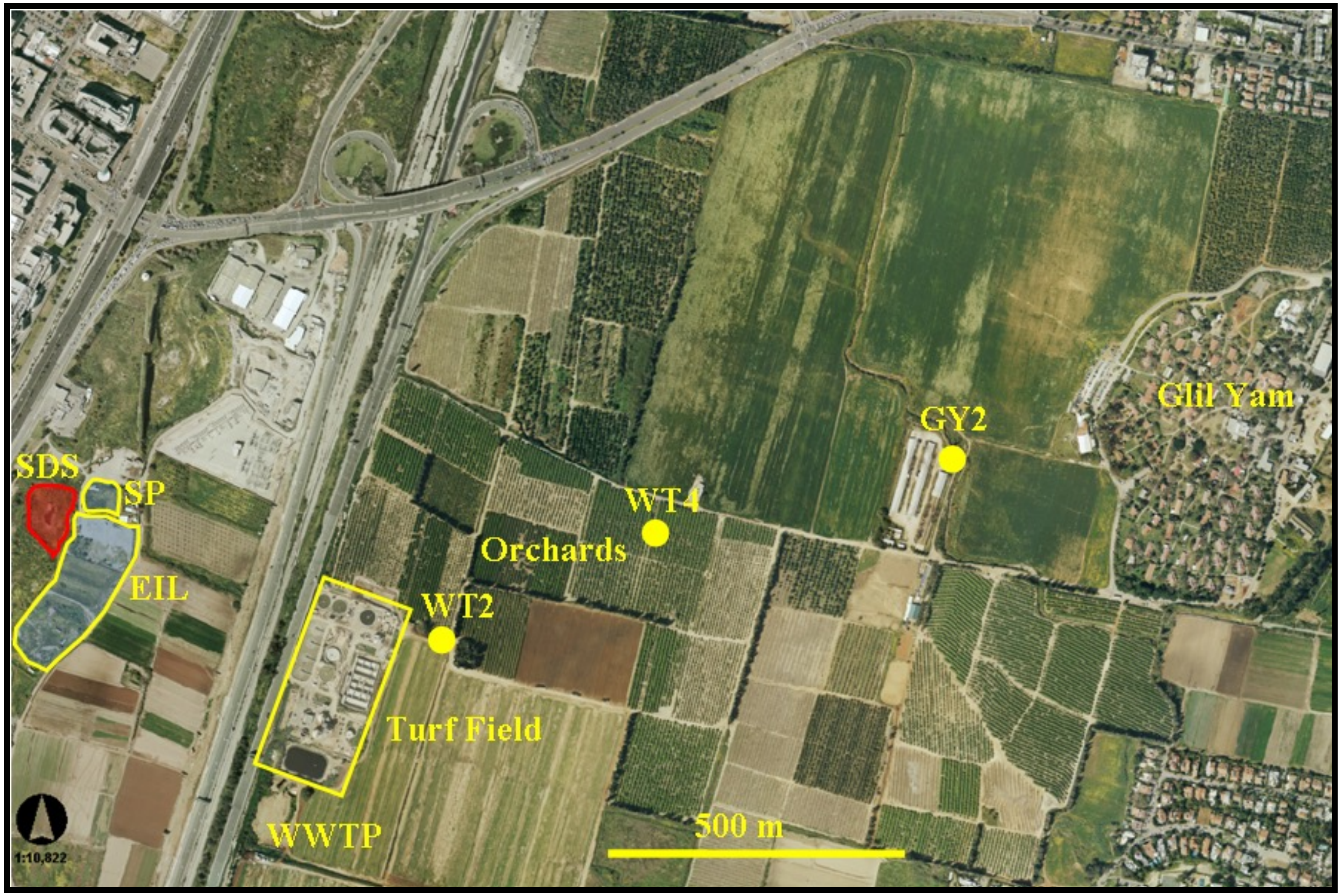
- Claim: Very low concentrations - no proven risk (yet) to man or to the environment; Answer: present as a mixture, synergetic effect)
- Claim: No regulations yet; Answer: beginning in several countries

However… Synthetic, biologically-resistant chemicals are being continuously discharged into the environment

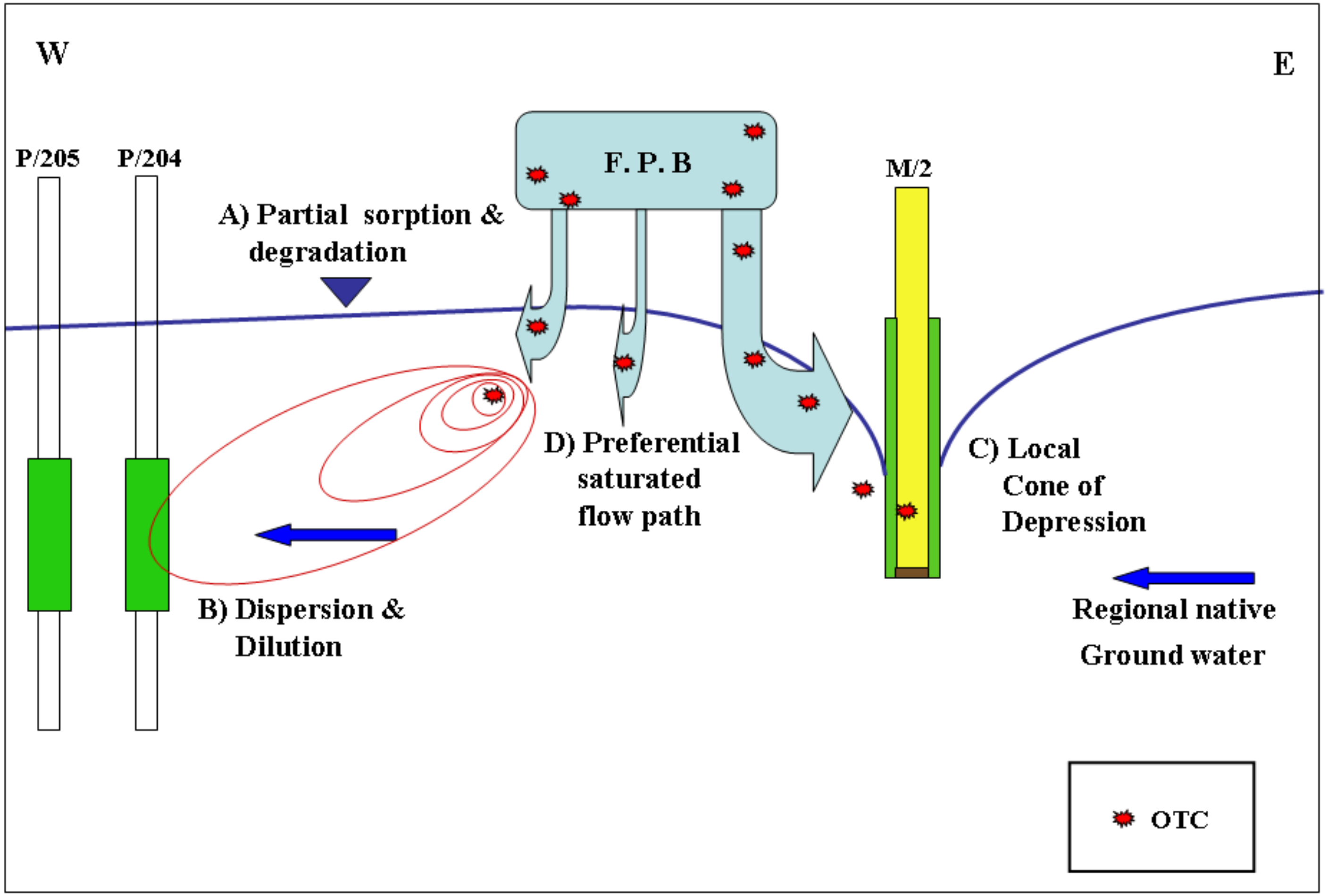
- ❑ **A non-voluntary experiment is conducted on human and on the environment**
- ❑ Estimations – only a matter of time till damage will be proven

Treatment = Act of prevention!

Study Site

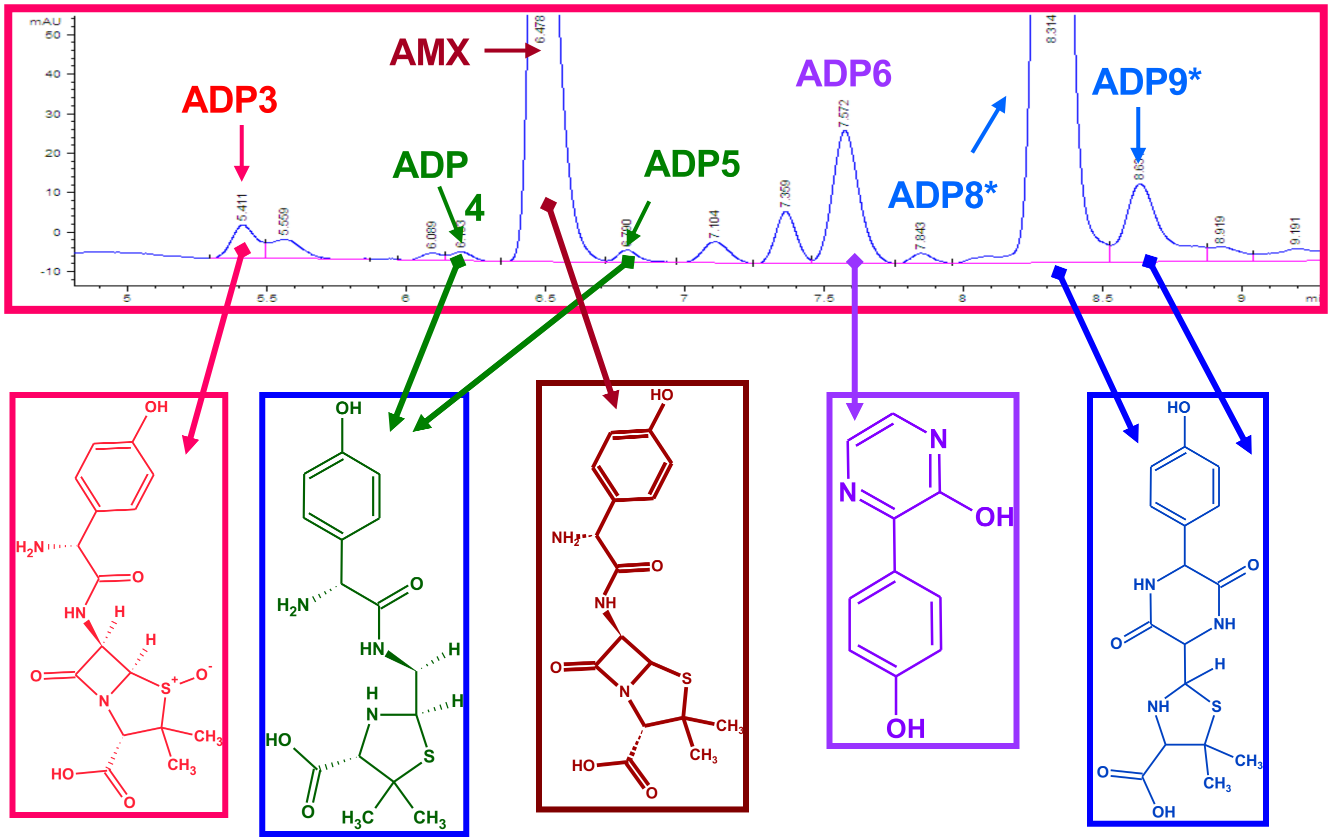


SDS
SP
EIL
Orchards
WT4
WT2
GY2
Glil Yam
Turf Field
WWTP
500 m
1:10,822



Avisar, D. Levin G. and Gozlan I. 2009. The Occurrence of Oxytetracycline (OTC) In Local Groundwater beneath Fish Pond. *Earth and Environmental Sciences* Vol. 59, 4 939-945

HPLC chromatogram **of Amoxicillin degradation products**



Lamm, A., Gozlan, I., Rotstein, A., and Avisar, D. 2009. Detection of amoxicillin-diketopiperazine-2', 5' in wastewater samples, J. Environ. Sci. Health, Part A. Vol.44, No.14.

Therefore…

There is a practical interest and need for advanced water & wastewater technologies and treatment to remove contaminants

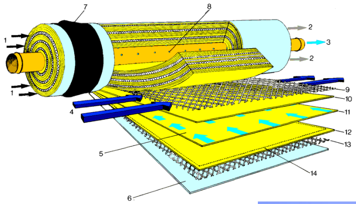
Treatment strategies and technologies – past and future

Past:

- End-of-the-pipe
- Conventional treatments: Biological (e.g. activated sludge)

Future:

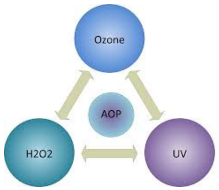
- Treatment at source



- Advanced treatments: Membrane bio-reactor (MBR)

  Membranes (NF, RO), Activated carbon

  Advanced oxidation (AOP)



Treatment methods:

Why using AOP-Ozone treatment

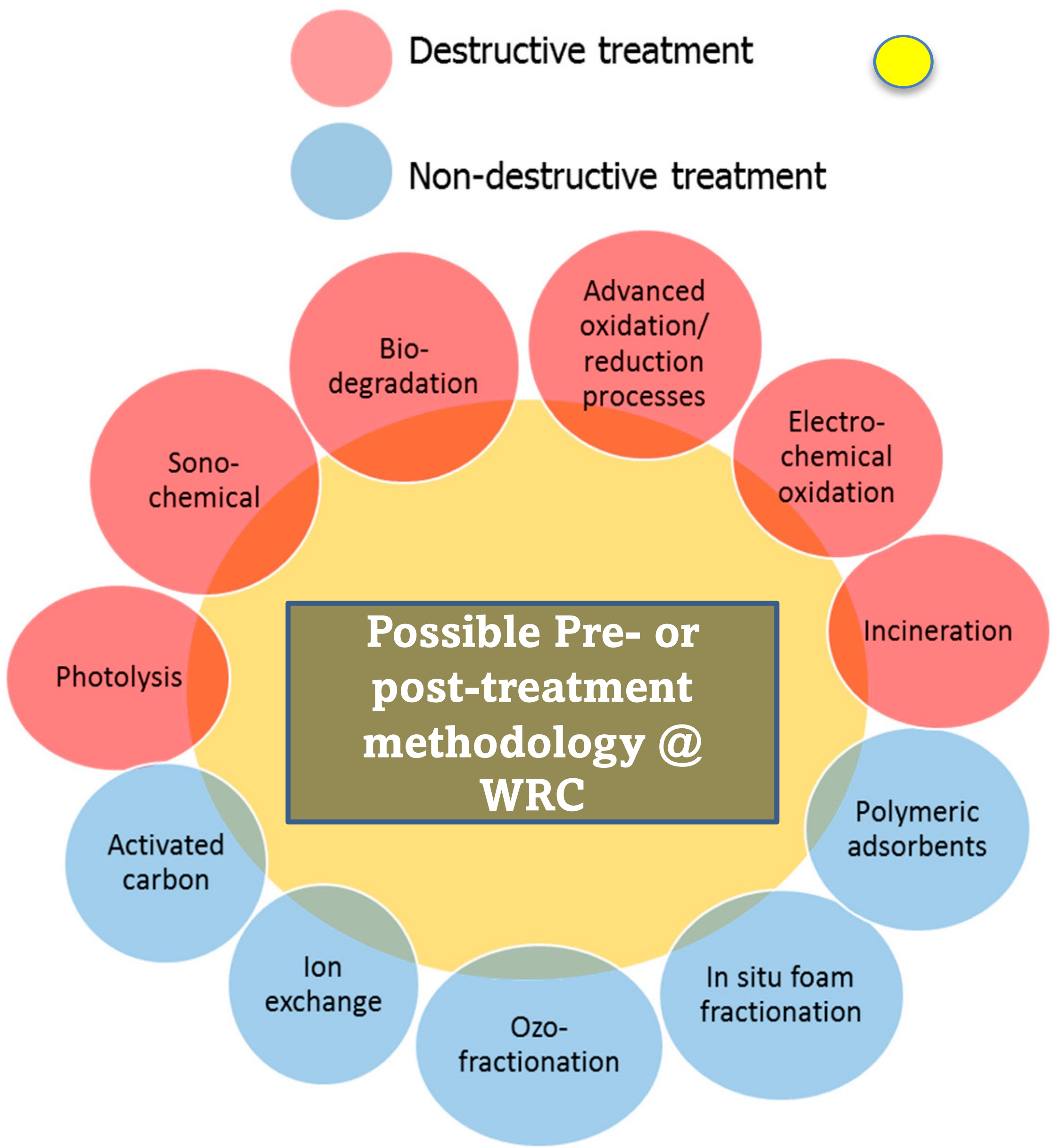
What is Advanced Oxidation processes (AOP's)?

A destructive process rather than filtration (phase transfer)

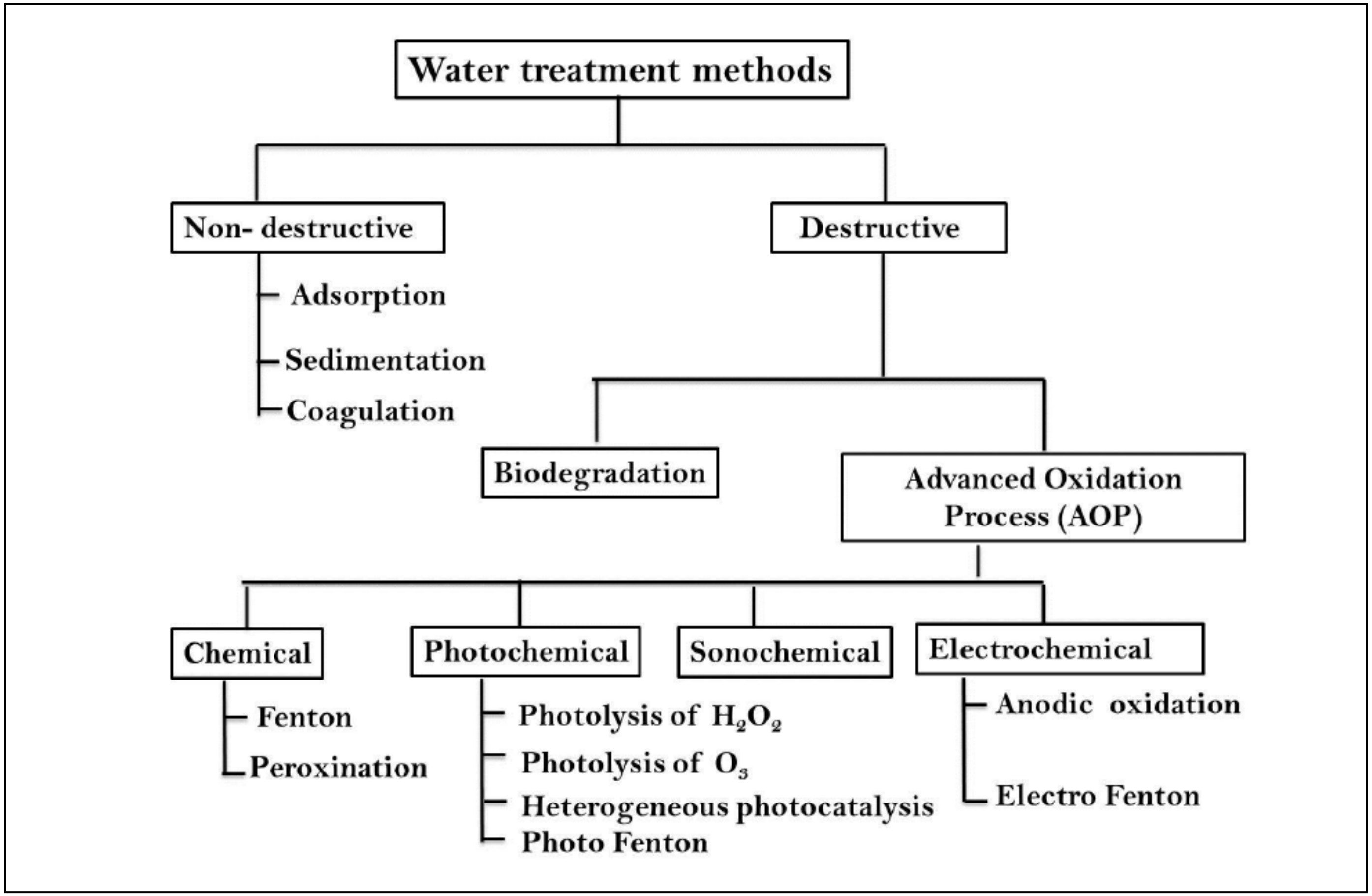
General terminology used for an array of chemical processes used to **oxidize**/mineralize various constituents of **organic pollutants** in water by a process involving the accelerated production of the **hydroxyl free radical (•OH)**

Oxidant	Oxidation potential (V)
OH• (hydroxyl radical)	2.80
O_3 (ozone)	2.07
H_2O_2 (hydrogen peroxide)	1.77
ClO_2 (hypochlorous acid)	1.49
Cl (chlorine)	1.36

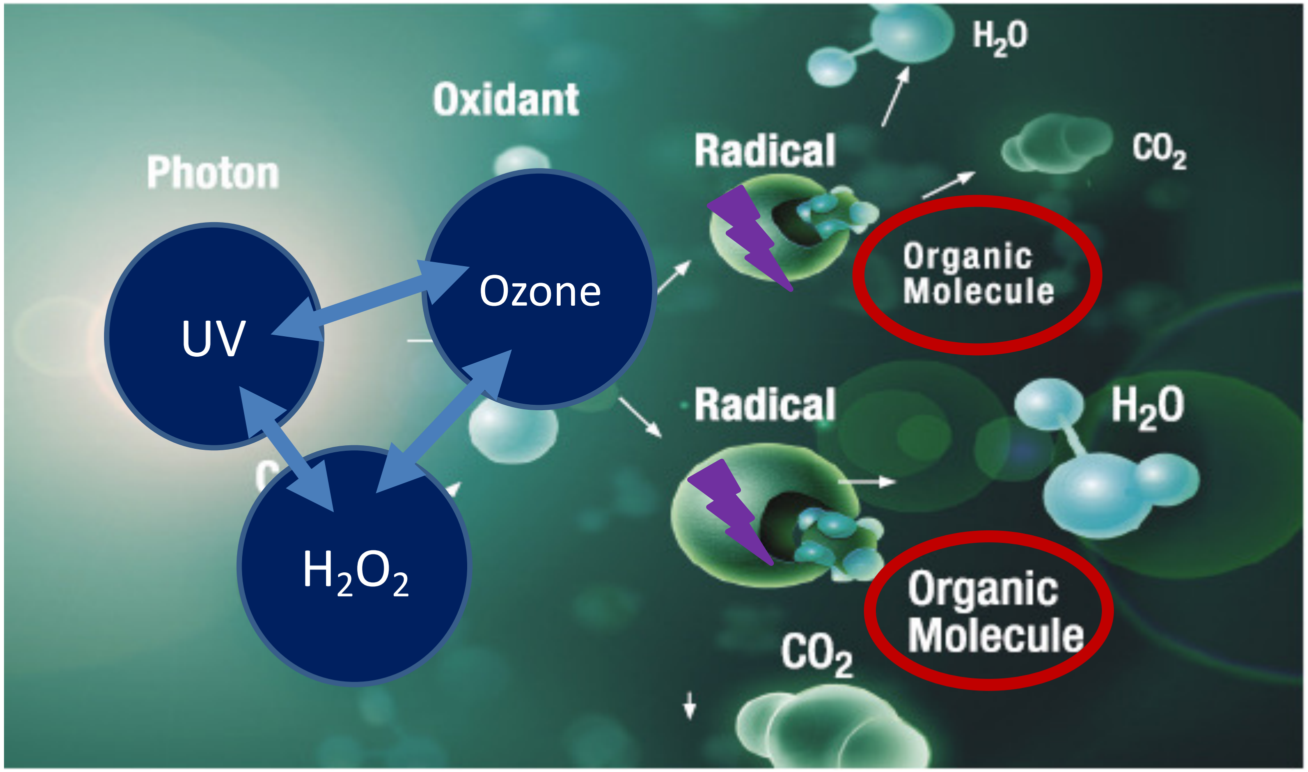
- ✓ Extremely reactive
- ✓ Short lived
- ✓ Unselective
- ✓ Very low steady-state concentration [10^{-12} to 10^{-13} M]



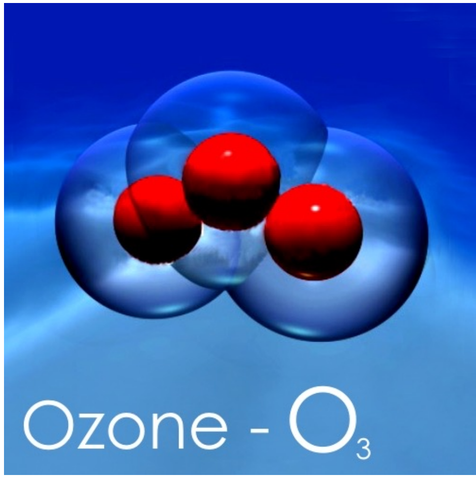
Destructive treatment
Non-destructive treatment
Bio-degradation
Advanced oxidation/ reduction processes
Sono-chemical
Electro-chemical oxidation
Incineration
Photolysis
Possible Pre- or post-treatment methodology @ WRC
Activated carbon
Polymeric adsorbents
Ion exchange
Ozo-fractionation
In situ foam fractionation


Water treatment methods
Non- destructive
Adsorption
Sedimentation
Coagulation
Destructive
Biodegradation
Advanced Oxidation Process (AOP)
Chemical
Fenton
Peroxination
Photochemical
Photolysis of H_2O_2
Photolysis of O_3
Heterogeneous photocatalysis
Photo Fenton
Sonochemical
Electrochemical
Anodic oxidation
Electro Fenton

The basics of AOP



Why ozone based AOP?

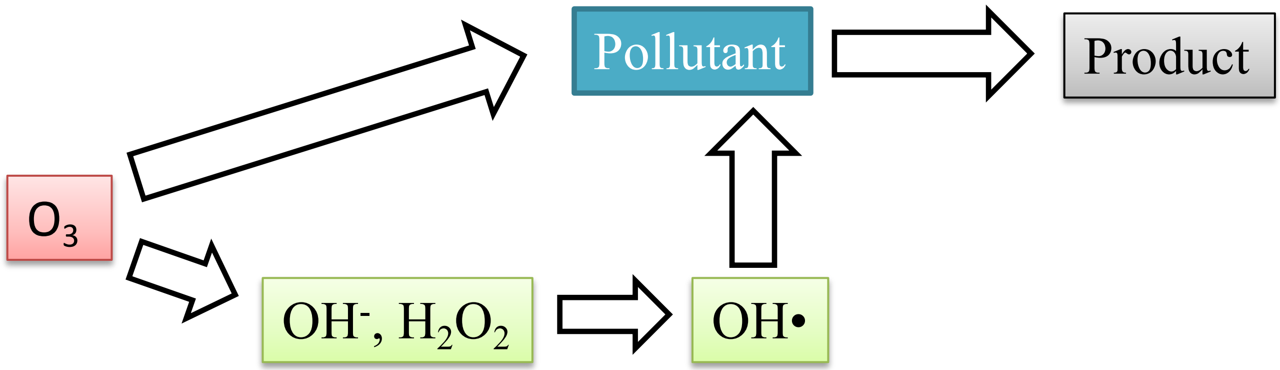


- **Electrophilic oxidant (2.07 V)**
  - Direct reaction:
    - Selectively reacts with compounds containing electron-rich moieties
  - Indirect reaction:
    - Non selective hydroxyl radical (•OH)
    - Formed from reaction of ozone with natural organic matter
- **Parameters affecting ozonation**
  - Dissolved organic carbon (DOC)
  - Nitrite
- **Advantages:**
  - Efficiently remove TrOCs
  - Increase the effluent dissolved oxygen (DO) conc.
  - Increase the biodegradability of dissolved organic matter

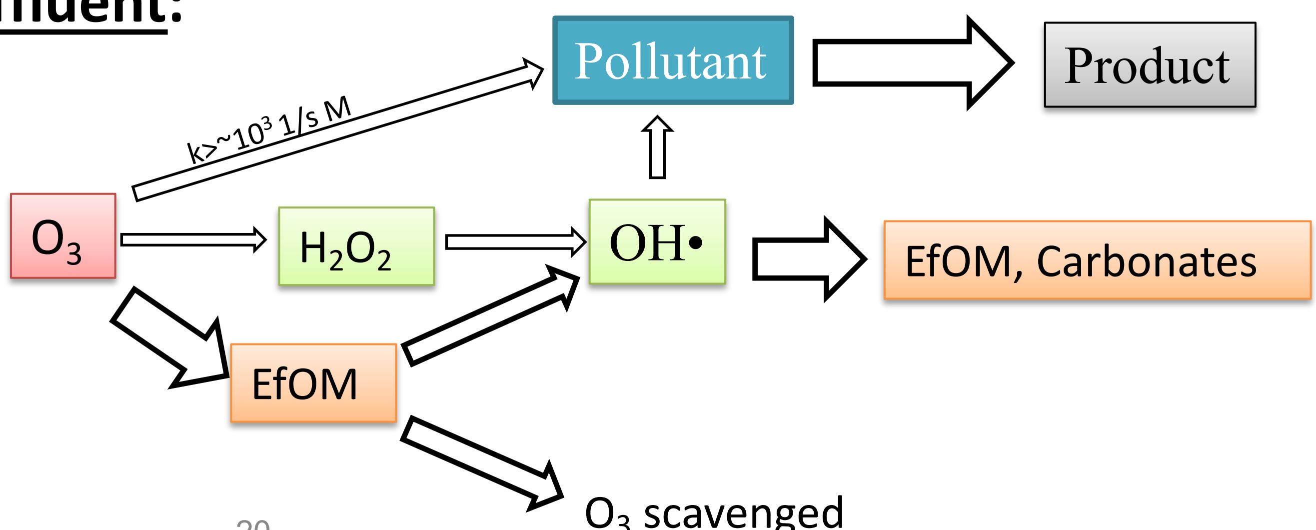
http://info.craftechind.com/

Ozone based degradation mechanisms:

In water:



In effluent:



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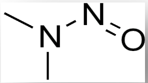
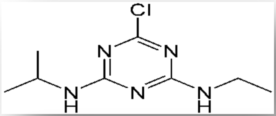
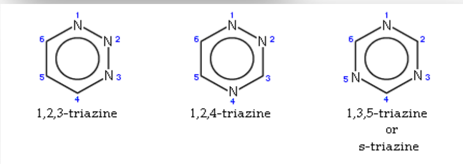
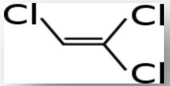
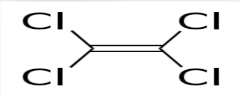
Contaminants treated by AOPs

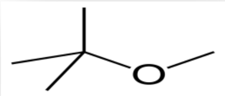
- N-Nitrosodimethylamine (NDMA) 

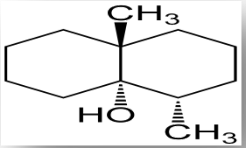
- Atrazine 

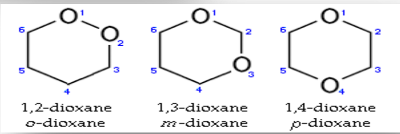
- Triazine 

- Trichloroethylene (TCE) 

- Tetracholoroethylene (PCE) 

- Methyl Tert Butyl Ether (MTBE) 

- Geosmin 

- 1,4 Dioxane 

Pharmaceuticals, Personal Care Products, EDCs

2nd Study case: Removal of pharmaceuticals from hospital wastewater (HWW) using advanced oxidation

Treatment of Hospital Wastewater (HWW)

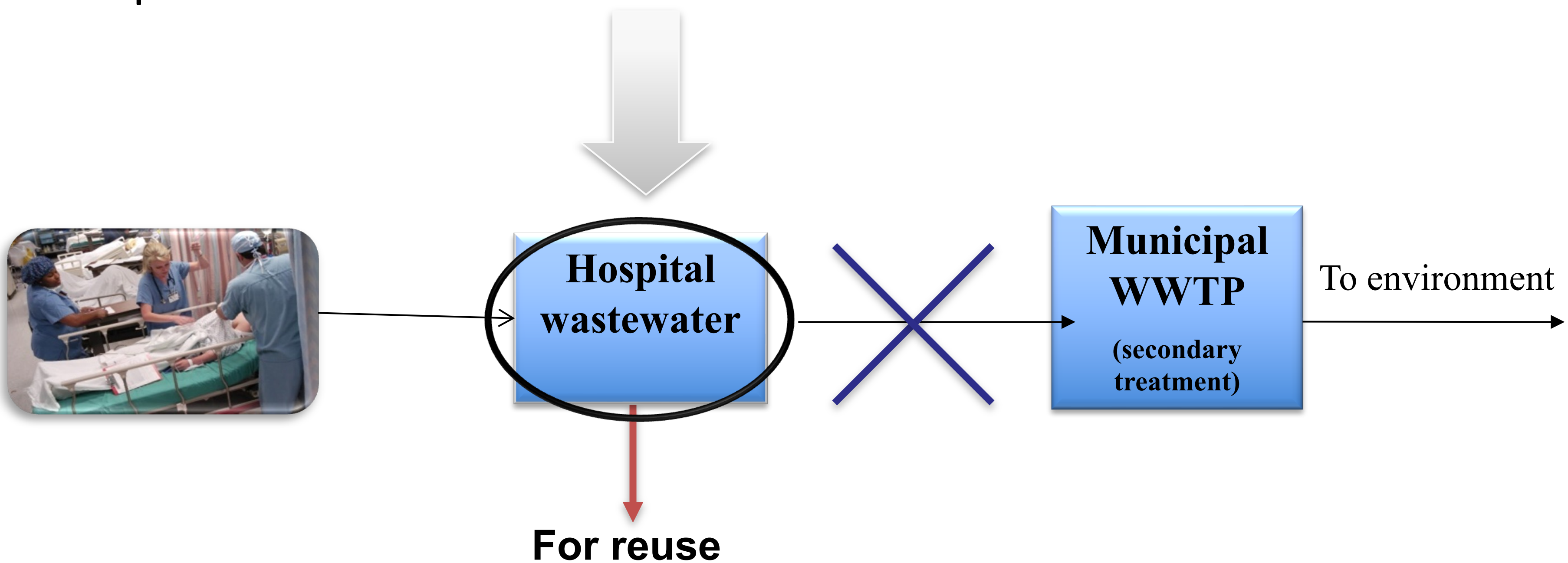
- Hospitals consume water and generate HWW
- Drugs administered to patients and metabolites are excreted to hospital sewer
- HWW contains highly concentrated toxic, carcinogenic, mutagenic, radioactive and persistent chemicals (as cytostatic, anesthetic, antibiotics, iodinated contrast media, analgesic), toxic-metals (mercury, silver, platinum) and pathogens
- Surprisingly, HWW are not considered as an industrial WW, thus no specific standard and are not treated in situ and no separate collection of urine
- Consequently are discharged to a municipal WWTPs (if present) with **NO PRETREATMENT**

The result

- Persistent, hydrophilic and non-biodegradable chemicals are not removed or partially removed in conventional WWTP and pass to the effluent
- The existing BAT biological traditional treatments solutions are far from providing a solution
- Even high quality effluent still may contain many types of pharmaceutical residues
- Contaminate water sources with drugs administered at hospital
- Adverse effects on various ecosystems and possibly on humans

Our objectives

Goal: Determine the potential of the **ozone** based Advanced Oxidation Technology **(AOP)**, as a complementary treatment, for the **removal of drugs using for chemotherapy treatment** from hospital wastewater

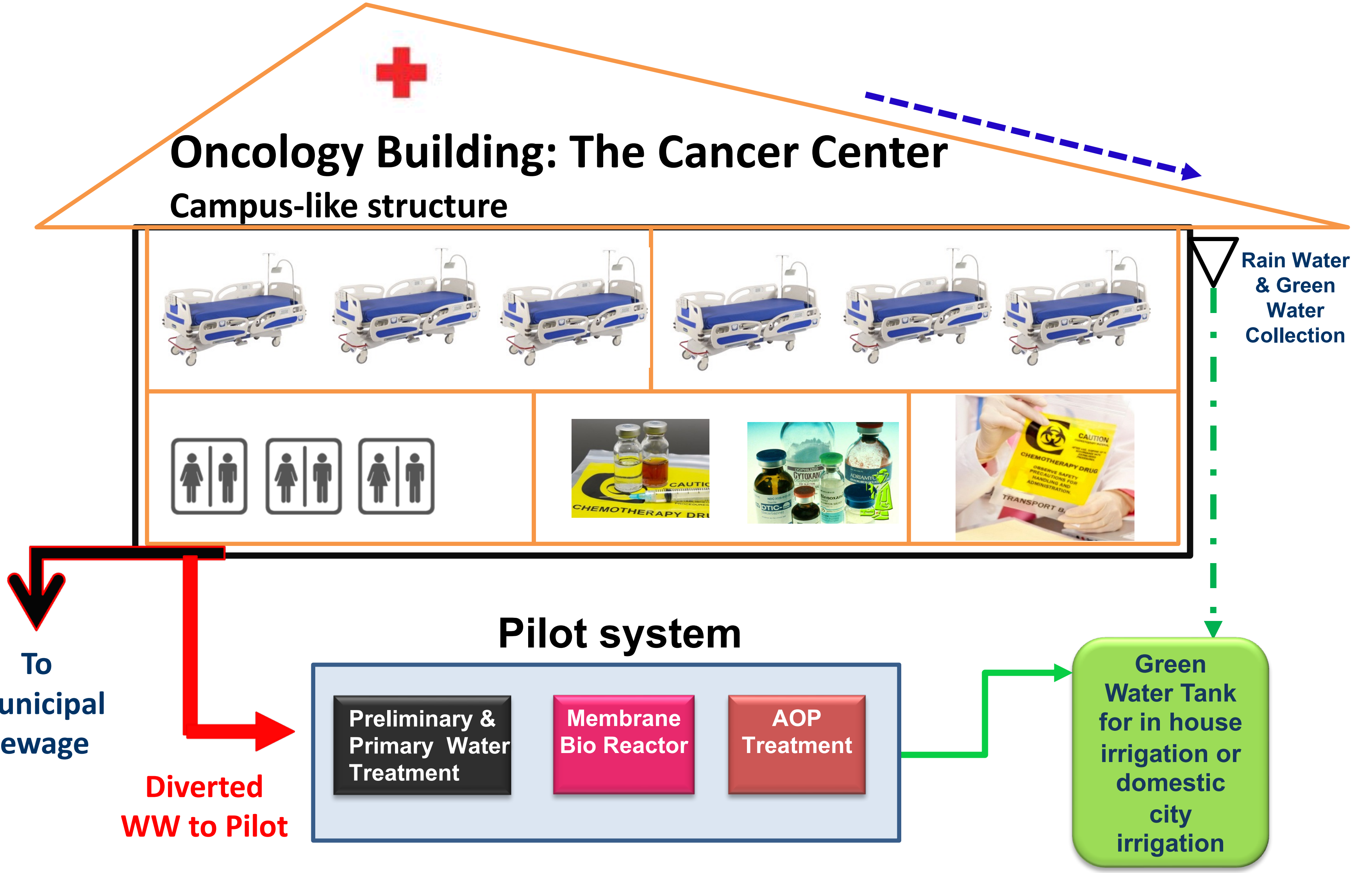


Treat hospital wastewater **in-situ** for reuse purposes

Data on the activity of oncology departments + Hemato-oncology at Tel Hashomer Hospital

- An average of 250 patients per day in the ambulatory department
- Routine treatment - reception at 8 am, beginning chemotherapy at 9 am, peak time 10:30-14:30
- Urination starts at about 1.5 h after treatment begins
- Approximately 1500 L/month of chemotherapy drugs are mixed with general wastewater
  - In addition, an oncology department has been established over the last year, with several dozen patients at a given time
  - Laboratories, clinics and radiation institutes are located in the building and contribute pollutants to the building's sewage.
  - The Department of Oral and Maxillofacial (Civil and Military) is near the Oncology Department and supplies wastewater to the treatment facility

Treatment is given daily to 250 patients at the cancer center-day care, additionally to the oncology department. Treatment peak time 10:00-15:00



Approximately <u>1500 L/month</u>!!! of chemotherapy active compounds are mixed with general wastewater

The system container

Anoxic Tank

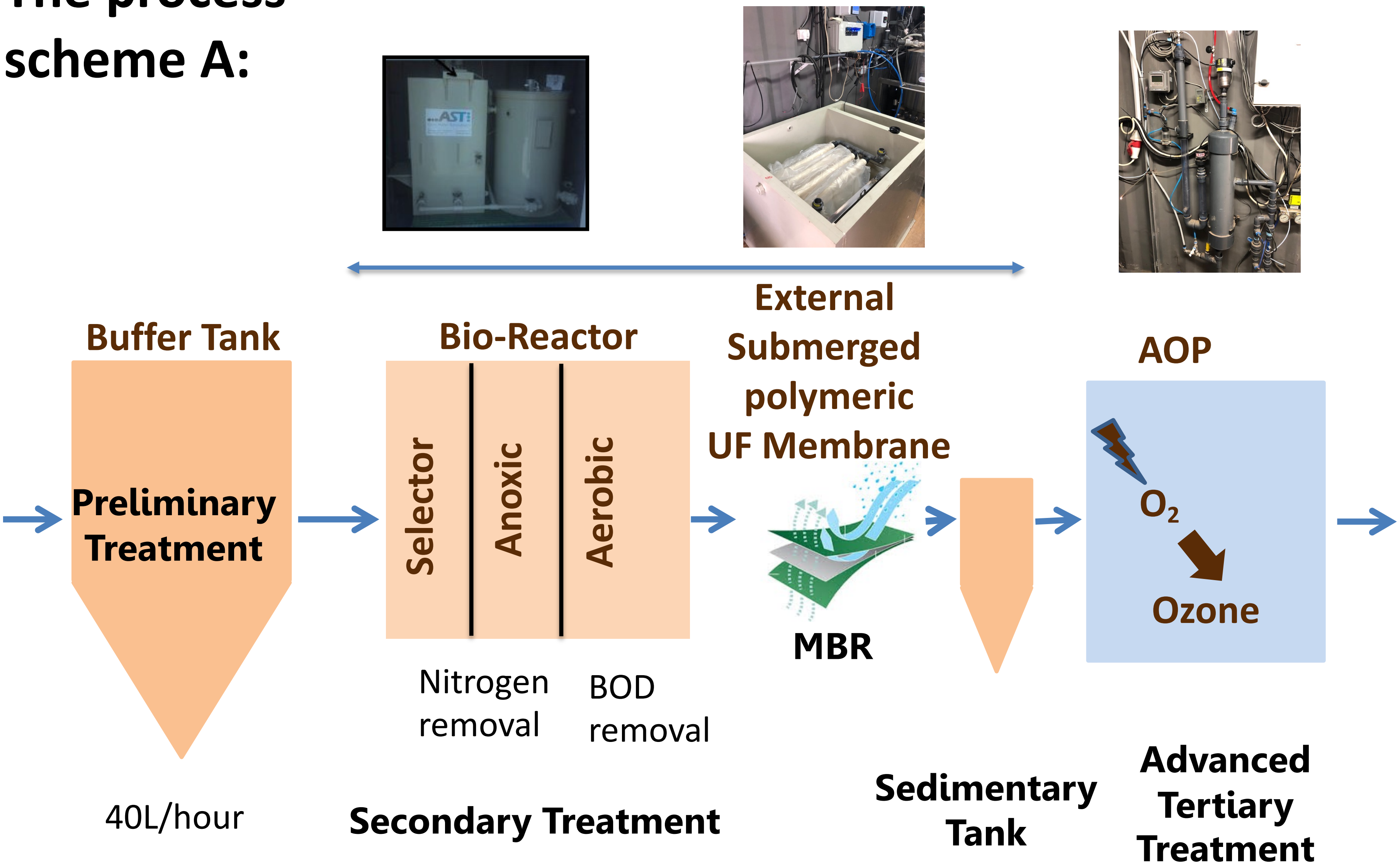
Anoxic Tank

Aerobic Tank

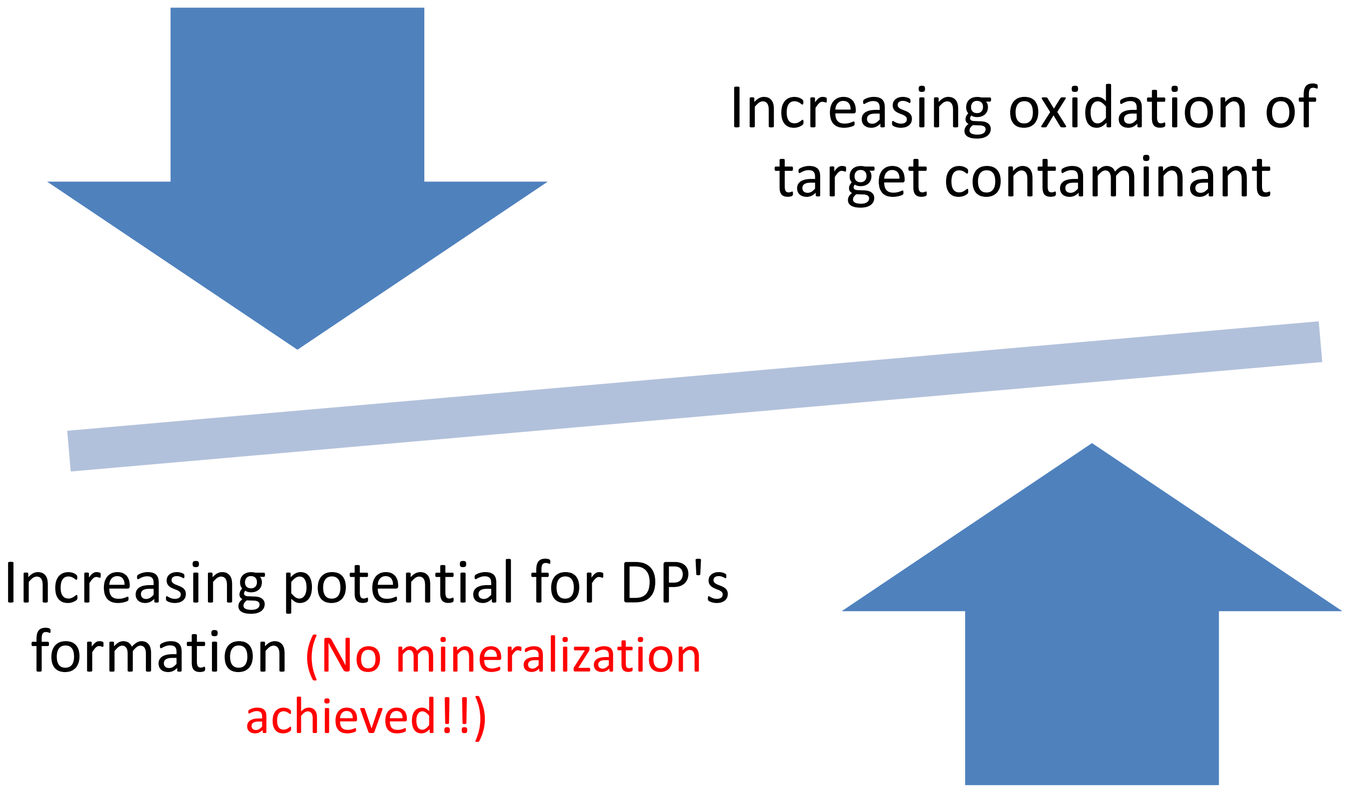
Membrane

Ozonation

The process scheme A:



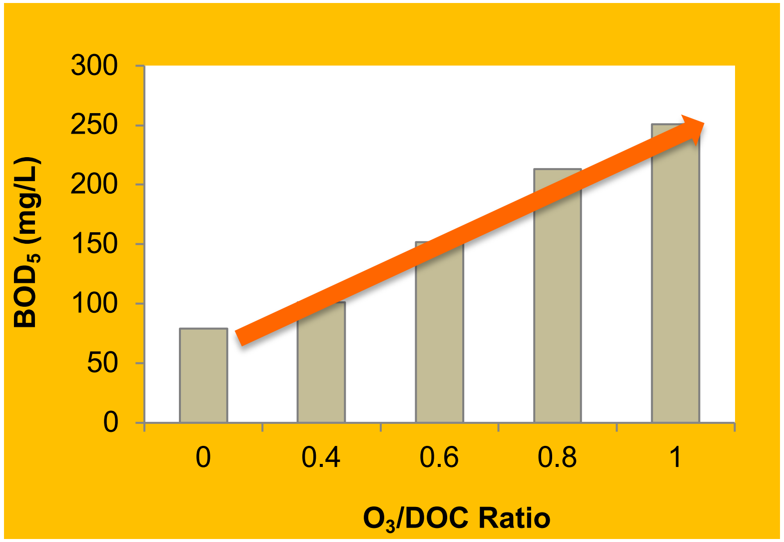
Hydroxyl radicals (indirect) and ozone (direct) are non-selective and can result in DP’s formation



Thus…

Ozone influence on biodegradability (BOD_5)

Goal: We will use the ozonation to chop the persistent molecules forming more biodegradable DP's



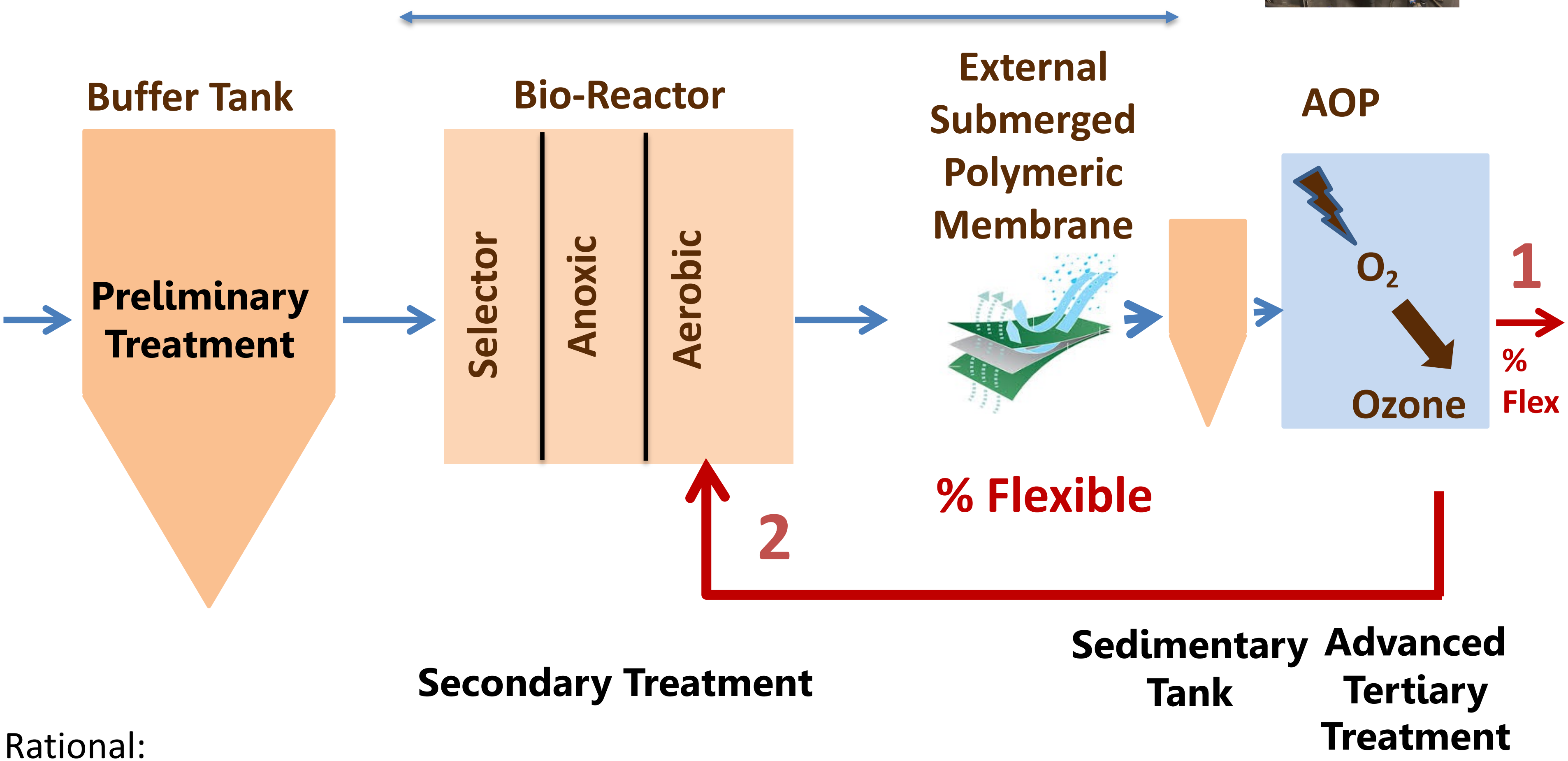
1. As the **DOM mw decrease**, the **BOD values increase**! Thus..

1. Degradation products are more **biodegradable** than the parent compounds
2. Highly important for the required **subsequent biological treatment**
3. **Meaning of that is: Smaller & chopped DOM are easier to degrade by bacteria!**

Therefore:

Lester, Y. Mamane, H. Zucker, I. and Avisar, D. 2013. Treating Wastewater from a Pharmaceutical Formulation Facility by Biological Process and Ozone. *Water Research 47,4349-4356.*

The process scheme B:

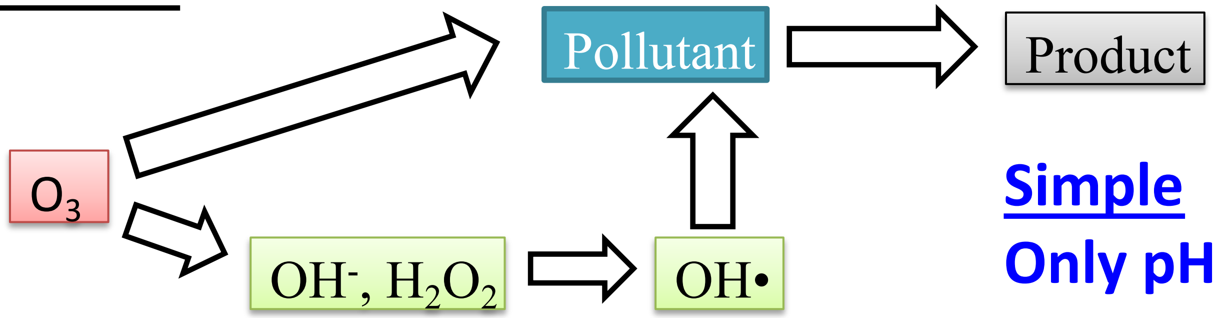


Rational:

1 Chopping the MP (aromatic rings & double bonds) - Increasing biodegradability of MP & NOM
The chopping molecules are much more easier to degrade for microbes - Aerobic Tank

Ozone based degradation mechanisms:

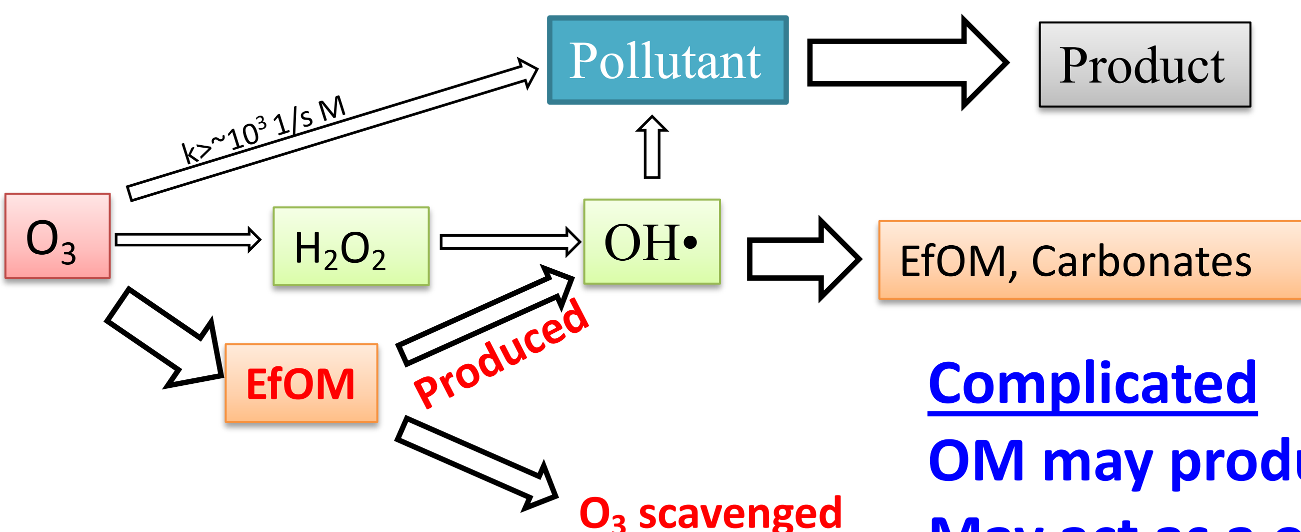
In water:



Simple

Only pH dependent

In effluent:



Complicated

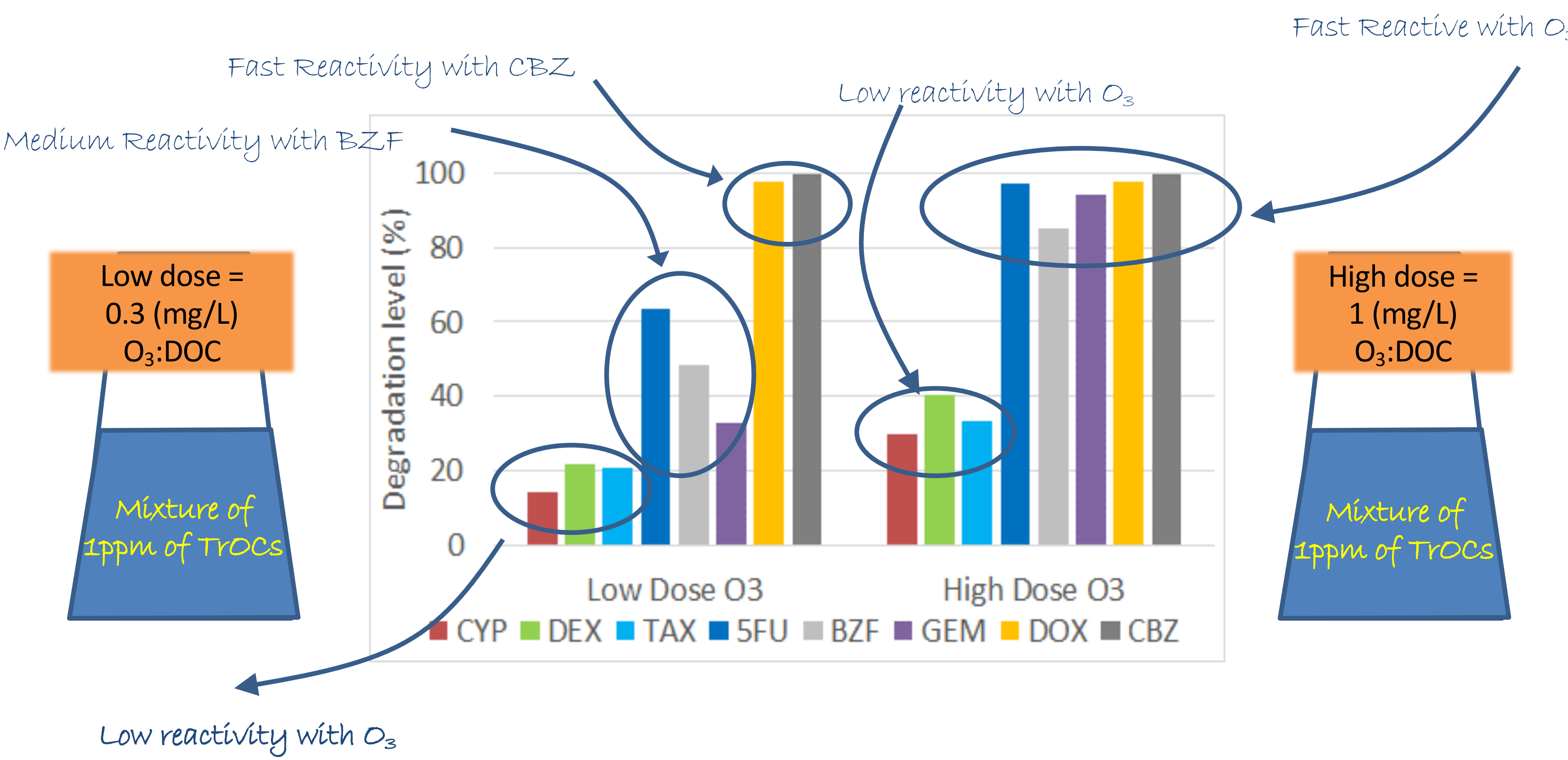
OM may produced radicals &

May act as a ozone scavengers

Thus, the kinetics is very important and complex:

The K_{O_3} & K_{OH} (degradation rate constant) values of the compounds may differ from each other, therefore, will define the ratio between **Direct** **Vs** **indirect** path treatments

OMPs oxidation kinetics- ko_3 - Preliminary:



Two step treatment:

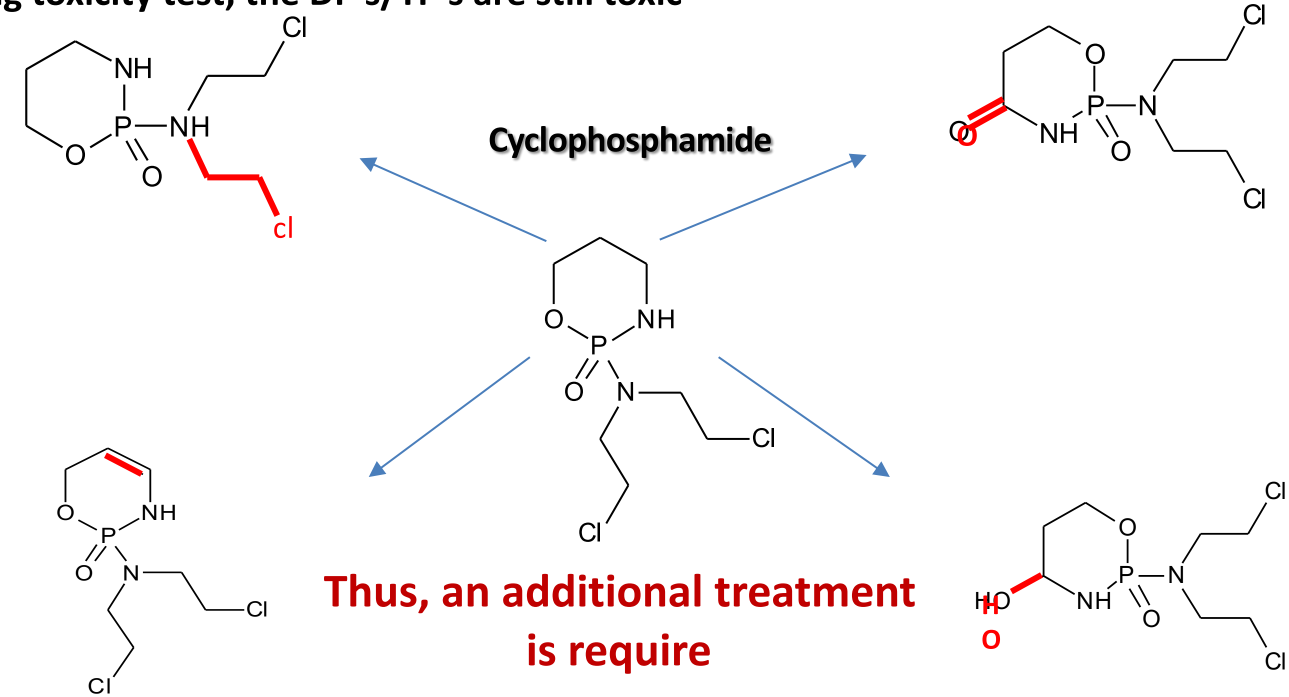
1) Direct by ozone: for fast reacting compounds
2) In direct by OH Radicals: for resistant compounds by adding H_2O_2 (for increasing OH yield), but, <u>only after we degraded the fast organic compounds</u> (natural and synthetic)

New findings – DPs Vs. TPs (under publication)

<u>However</u>, We have to be careful, sometime we only assume that the parent compound was fully degraded after oxidation!!

Deep look demonstrated:

1) **TOC did not changed –** no mineralization was achieved
2) **The degradation molecules path demonstrates a limited degradation – Obtained DP's/TP's** are slightly differ by structure, <u>but similar in their persistency</u>
3) **According toxicity test, the DP's/TP's are still toxic**



Thus, an additional treatment is require

Combination of Technologies

We combine AOP technologies used to produce effluent of high quality for WW reuse

Mostly based on high/low-tech **innovative ozone/photocatalysis AOP** for achieving high degradation and even mineralization of the persistent compounds

Currently, this technologies package tools were developed at TAU hydrochemistry research group as an innovative more efficient AOP technology – The new generation of AOP treatment!

Pupose: Increasing biodegradability of the obtained DP’s, follows by an effective aerobic biological treatment!

Water Research Center
Tel Aviv University

Q & A

Chemotherapy drugs derived from Hospital WW:

Doxorubicin

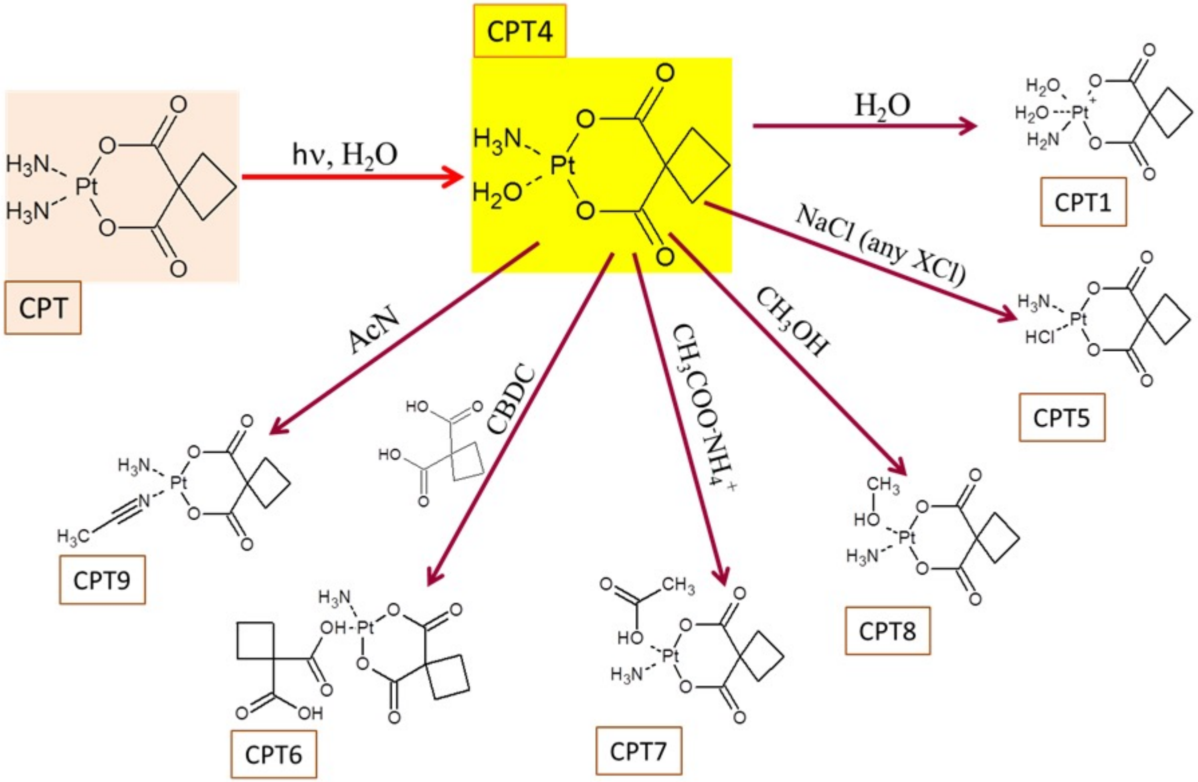
Gemcitabine

Dexamethasone

Paclitaxol

Cyclophosphamide

5-fluorouracil



The Highest toxic compounds, human ever developed!!

1ST Study case: Treating Wastewater From a Pharmaceutical Formulation Facility By Ozone based AOP Our motivations:

1) Engage Israel with **ozone** water/wastewater treatment **technologies**

Past:

- Sea of Galilee - the main source of Israel freshwater via the National Water Carrier (1964)
- Extremely high bromides concentration = **1900 µg/L**!! (highest in freshwater, worldwide)

In general: $[Br^-] > 100$ µg/L $\longrightarrow$ $[BrO_3^-] > 10$ µg/L

Recently- Israel became a bromide-free country:

- From 2000 – increasing (bromide free) alternative sources (e.g. seawater desalination**-in 2016 80% of the DW will be supplied by Desalination**; reclaimed WW)

Our motivations (cont.):

2) We have a direct approach to several major pharmaceutical firms

A small country with several big drug companies: manufacturing/formulating facilities

A confident report of the Israeli Water Authority revealed:

"Increased concentrations of **carbamazepine** were found in **groundwater** wells next to a **manufacturing facility** !"

Enable to apply our technologies in a full-scale pilots!

In addition….

OUR MOTIVATIONS (CONT.):

3) A Chance to examine & to apply the “polluter pays” principal

4) Treatment cost is (not) a problem (rich companies..?!)

Research: major question and goal

Question:

Do manufacturing facilities present a significant source of pharmaceutical pollution ?

Goal:

Determine the contribution of a manufacturing plant to environmental drugs pollution

<u>The examined plant</u>

- A formulation facility: Formulated drugs include: **<u>Carbamazepine</u>** (antiepileptic) and **<u>Venlafaxine</u>** (antidepressant)

- The <u>non-treated</u> wastewater is discharged to a local WWTP

Wastewater Treatment Plant

Question : **Do manufacturing facilities present a significant source of pollution ?**

Answer: **Yes! on a local scale manufacturing facilities are a major pollution sources**

Wastewater analysis

Venlafaxine load

1. WWTP 1: Treating wastewater -~100,000 people
2. WWTP 2: The largest plant in Israel
   Treating wastewater - over 2 million people in the Tel Aviv area

	Drug Factory	WWTP 1	WWTP 2
WW flow m^3/day	300	11000	400000
Venlafaxine concentration (µg/L)	11700	0.2[B]	0.2[A]
Venlafaxine Load[C] g/day	3500	2[D]	80[D]

[A] Gasser et al.,2012
[B] Estimated
[C] Load = Flow X Concentration
[D] Conc. due to domestic consumption

Parameter	Wastewater
TOC (mg/L)	1698 (±308)
COD (mg/L)	4765 (±1405)
BOD_5 (mg/L)	634 (±100)
BOD_5/COD	0.13
NH_4^+-N	23.5 (±8)
pH	10.2 (±0.9)
Carbamazepine (mg/L)	0.84 (±0.19)
Venlafaxine (mg/L)	11.72 (±2.2)

The examined treatment train

Drug plant

Activated Sludge Lab Reactor:

Biological Treatment

Ozonation Lab Reactor:

Tertiary Treatment

Municipal WWTP

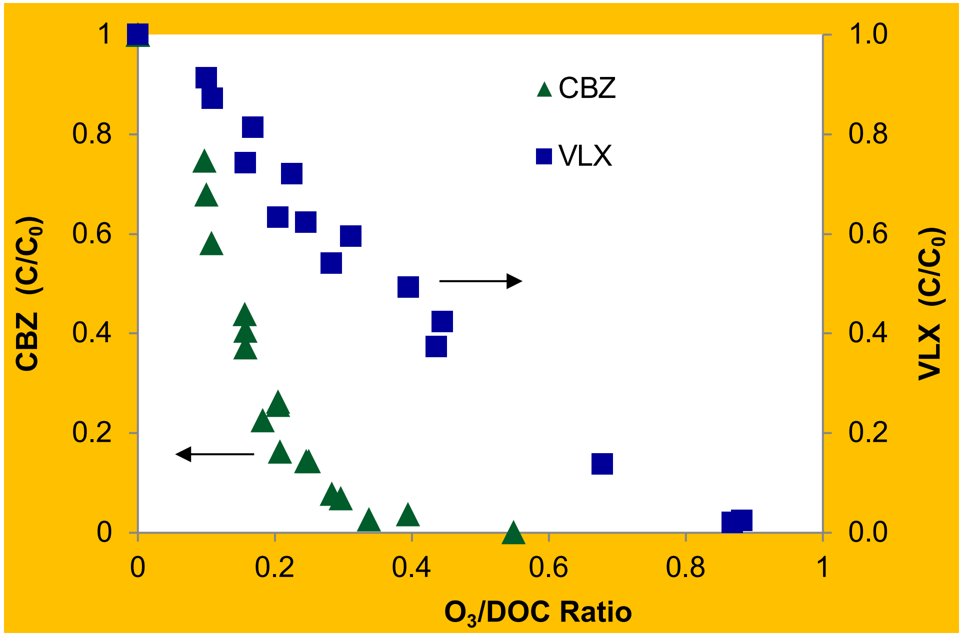
Specific goal: Reduce the concentrations of Carbamazepine and Venlafaxine

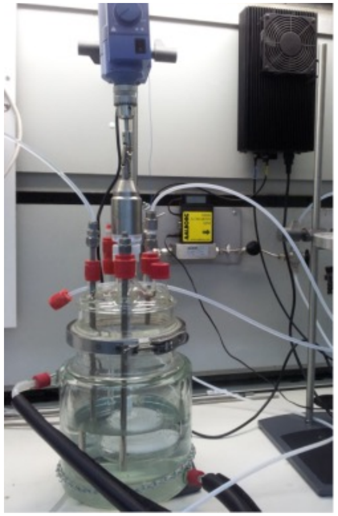
Results: Biological treatment

Parameter	Wastewater	Effluent	% removal
TOC (mg/L)	1698 (±308)	224 (±68)	87
COD (mg/L)	4765 (±1405)	741 (±253)	84
BOD_5 (mg/L)	634 (±100)	48.4 (±20)	92
BOD_5/COD	0.13	0.06	
NH_4^+-N	23.5 (±8)	17.6 (±13)	25
pH	10.2 (±0.9)	7	
CBZ (mg/L)	0.84 (±0.19)	0.83 (±0.06)	< 5
VLX (mg/L)	11.72 (±2.2)	11.34 (±1.1)	< 5

Biological treatment did not affect CBZ & VLX conc. Thus, O_3 treatment ..

Results: Ozone treatment





CBZ: > 99% removal at O_3/DOC = 0.55 ($k_{O3,\ CBZ}$ = 3 x 10^5 1/M s*)

VLX: 98% removal at O_3/DOC = 0.87 ($k_{O3,\ VLX}$ = 3.3 x 10^4 1/M s**)

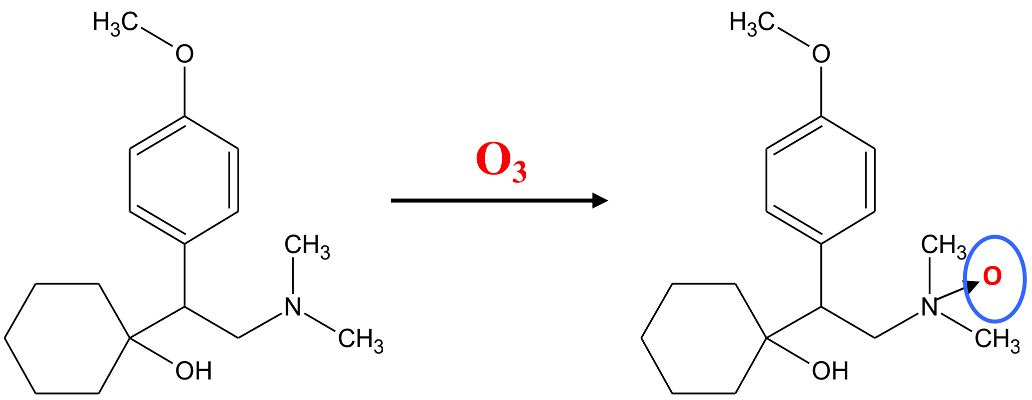
- ✓ The O_3 treatment significantly degraded both compounds
- ✓ VLX degraded slower due to its lower K_{O3} reaction constant (order of magnitude)
- ✓ Both compounds fit to the common, acceptable values: up to 1mg O_3/1mg DOC

*Huber et al., 2003; **Our study

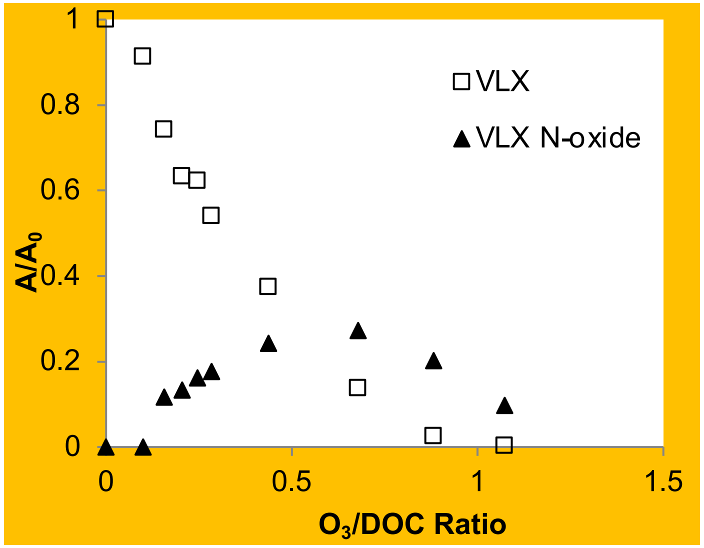
Results: degradation products

By ozone reaction with the target drugs, a degradation product obtained:

Reactants | Product



mw: 277.3 | mw: 293.2

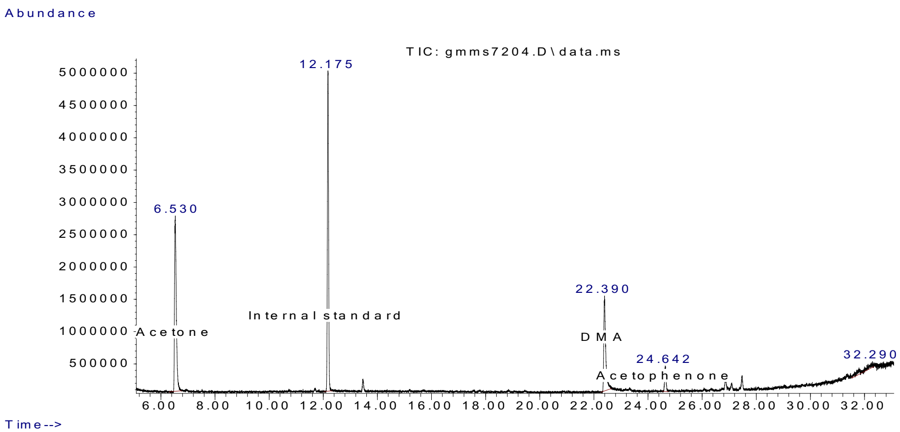


Venlafaxine *N*-oxide: **A degradation product** and also a prescribed pro-drug (slow release), which is rapidly converted in the human body **back to the parent compound**

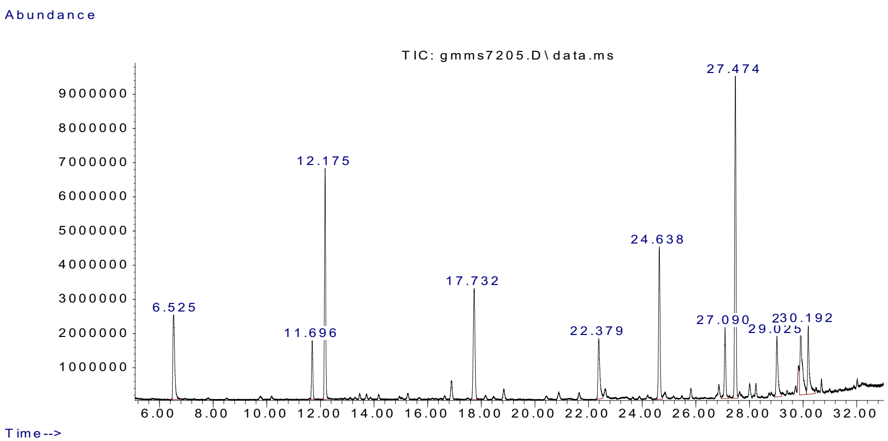
RESULTS: DEGRADATION PRODUCTS (CONT.)

Ozone reaction with DOM

Before ozonation



After ozonation (O_3/DOC = 0.8)



Compound name (Partial list)	Before O_3 (mg/L)	After O_3* (mg/L)
Acetone	7.24	11.01
Benzene	n.d.	0.037
n-Hexanal	n.d.	+
4,4-Dimethyl-2-pentynal	n.d.	+
Chlorobenzene	n.d.	0.042
Ethyl isobutyl ketone	n.d.	+
DMA	+	+
Acetophenon	+	+
Bornylene	n.d.	+
2-(2-Furyl)-2-methyl-3-butenal	n.d.	+
Nonanal	n.d.	+

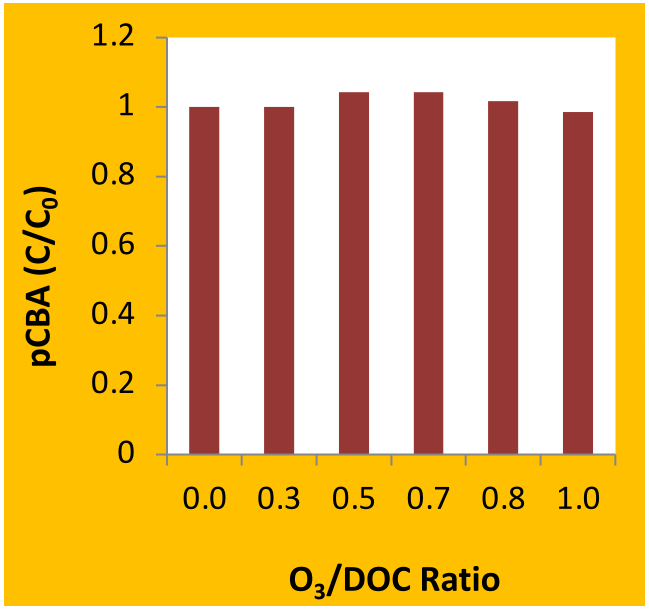
Due to the formation of various DP's, There is a need to generate an additional treatment (e.g. biological treatment at the municipal WWTP)

Results: Fate of O_3-resistant compounds (slow reactive): via OH• radical exposure

Goal: to differ between direct and non direct degradation processes

So, how can we differ?!

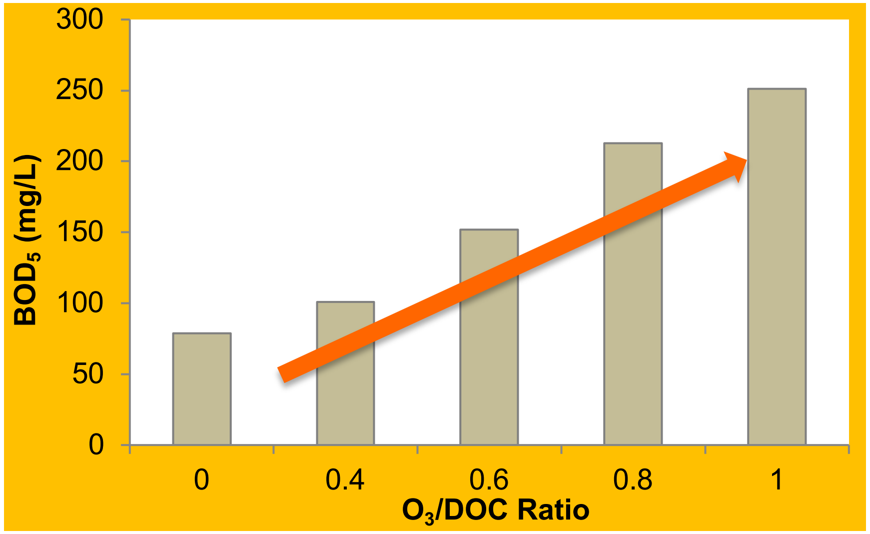
By…pCBA: This compound degrades only by OH radicals (indirect D.) and not by O_3 (direct D.) Consequently serves as an indicator for the presence of OH radicals



- ✓ Stable pCBA demonstrates **no OH radicals involve**: only direct degradation by O_3
- ✓ In municipal WW, these drugs degraded up to 50%: more OH radicals involve
- ✓ In pharmaceutical plant WW, High concentration of scavengers [e.g. Acetone > 7 mg/L], consume the OH radicals, creating only direct degradation by O_3

Results: Ozone influence on BOD_5

To characterize the degradation products



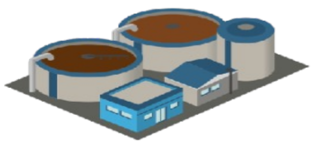
1. As the **DOM mw decrease**, the **BOD values increase**! Thus..

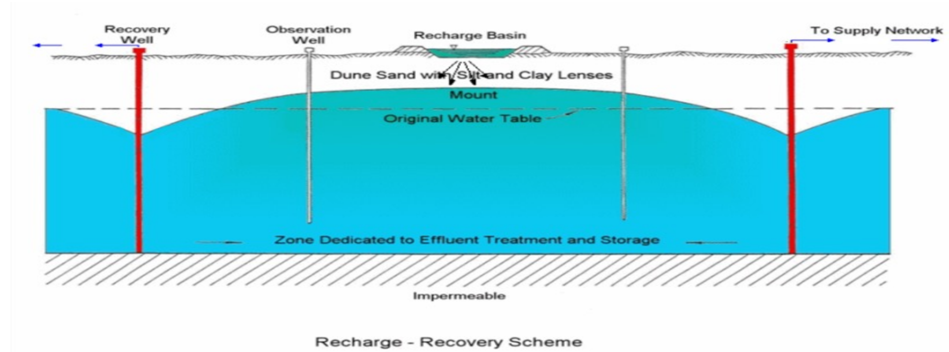
1. Degradation products are more **biodegradable** than the parent compounds
2. Highly important for the required **subsequent biological treatment**
3. **Meaning of that is: Smaller & chopped DOM are easier to degrade by bacteria!**

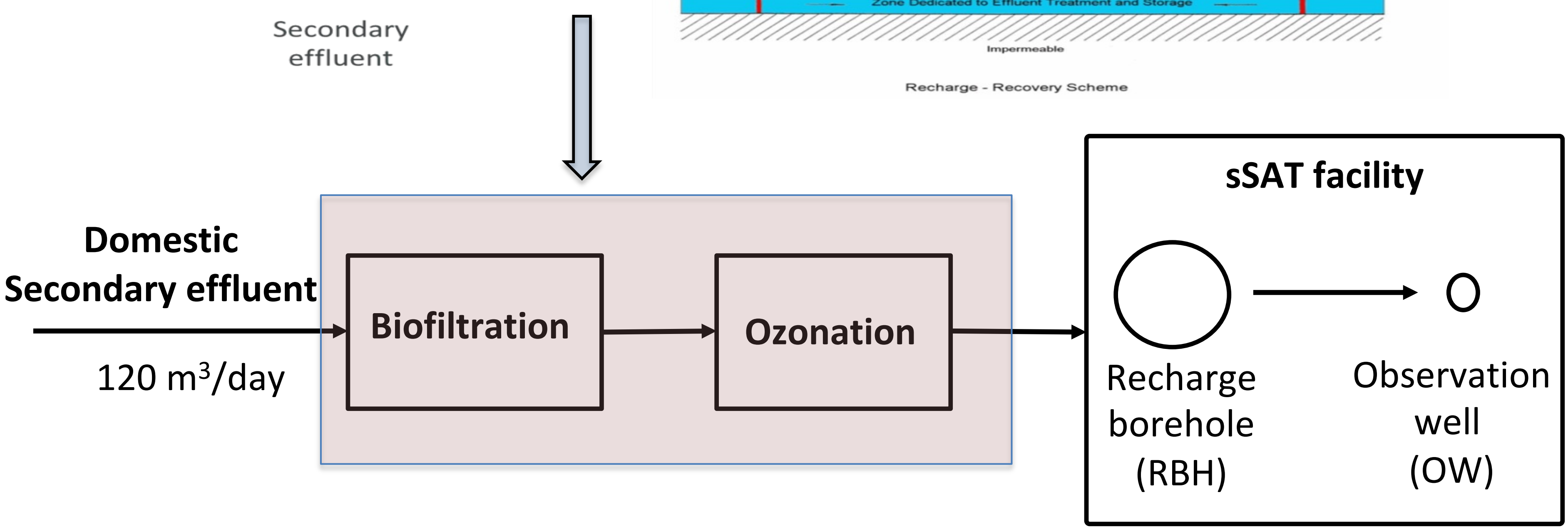
Lester, Y. Mamane, H. Zucker, I. and Avisar, D. 2013. Treating Wastewater from a Pharmaceutical Formulation Facility by Biological Process and Ozone. *Water Research 47,4349-4356.*

3rd Study case: A Hybrid Process of Ozonation and Short Aquifer Treatment for Water Reuse

Hybrid ozonation-short SAT (ssAT)







The main objective of the current study was to determine the potential of an innovative **hybrid process** consisting of flocculation, biological media filtration (Bio-filter), advanced oxidation, and short SAT (sSAT) technology **to prevent**

1) Occurrence of NH_4 (causing oxygen depletion)
2) Mn-oxide dissolution
3) Occurrence of Micro contaminants (by Increasing biodegradability), and
4) Optimize SAT infiltration capacity on the pilot scale in long-term operation mode.

PRETREATMENT