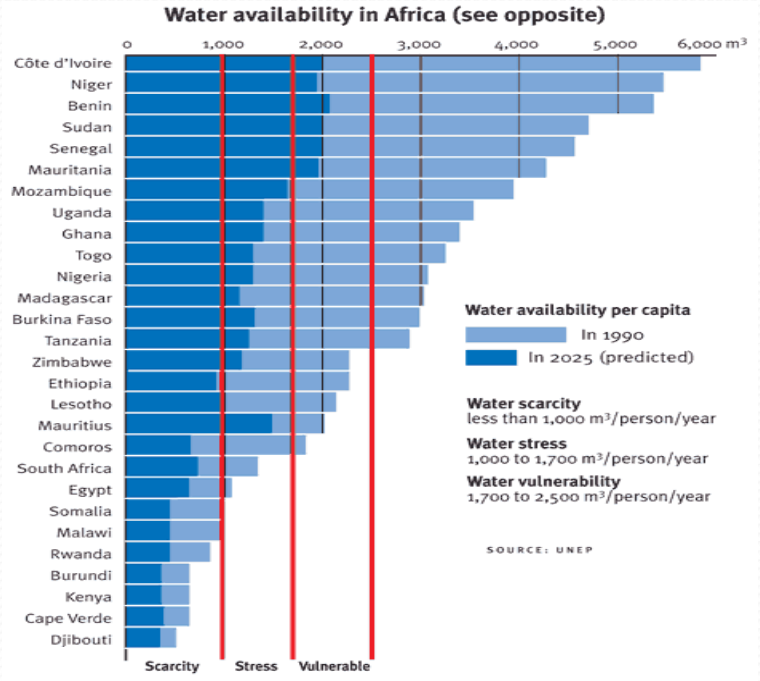
The Chemical Fate & Suggested Removal Technologies of Pharmaceutical Residues within the Israeli Aquatic Environment

D. Avisar, and his research group

Hydrochemistry Laboratory
Tel Aviv University

Hydrochemistry Laboratory

Tel-Aviv University



In addition to worldwide severe water scarcity (quantities),

the issue of **WATER QAULITY IS DRAMATICALLY AFFECT PUBLIC HEALH!**

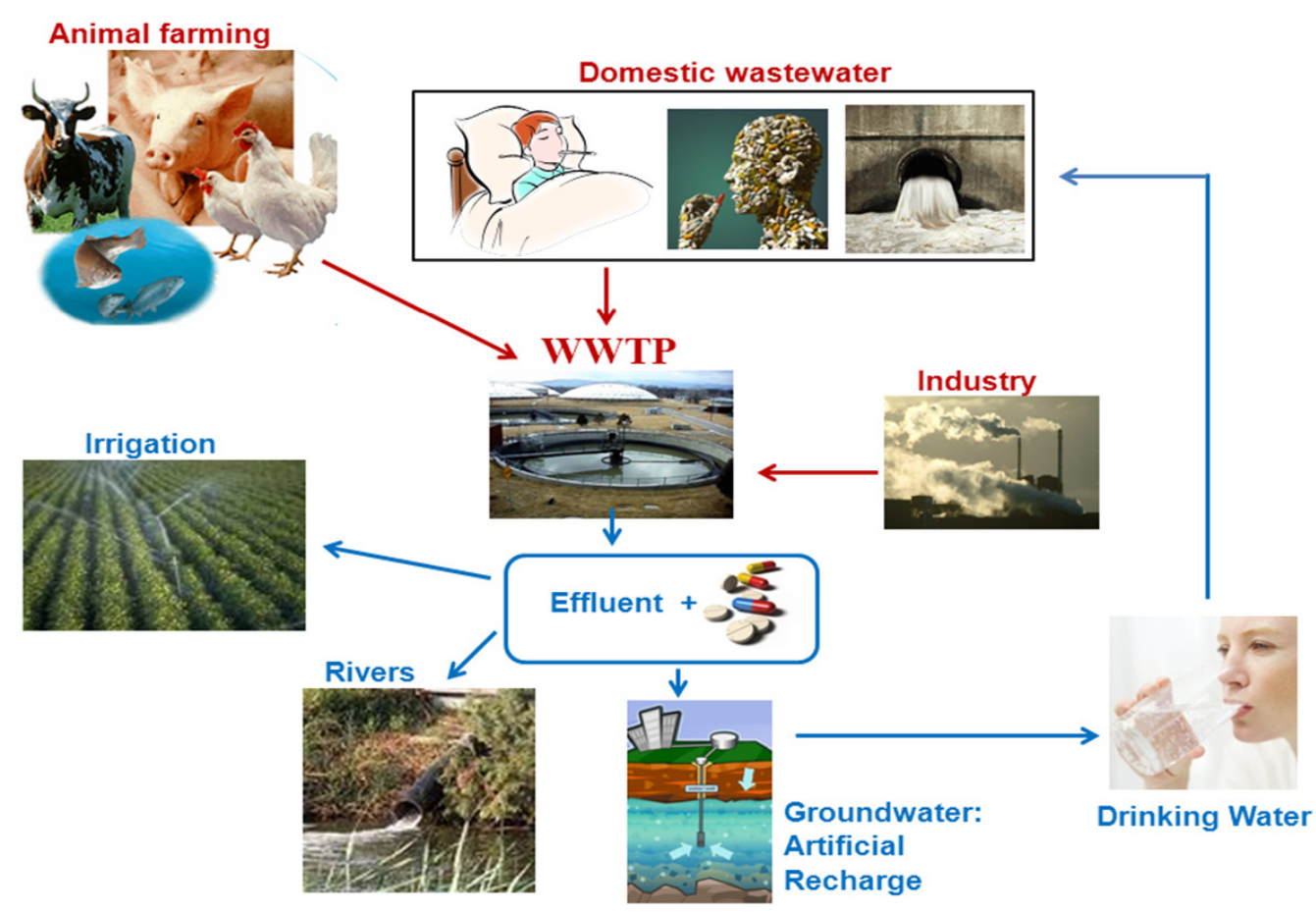
The Problem:

- **Drinking water** and **wastewater** may contain **toxic chemicals** at very low concentrations such as herbicides, pesticides, dioxins, **pharmaceuticals** and more.
- These **pharmaceuticals** are **not regulated** and **traditional treatments** do **little** to break them down.
- These compounds may cause **an adverse effects** on various ecosystems and possibly on human.

Hydrochemistry Laboratory

Tel-Aviv University

Main Sources & pathways



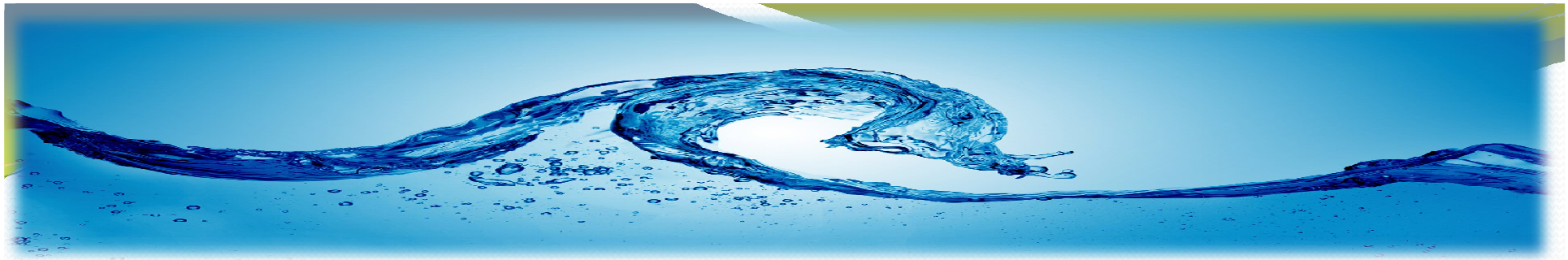
Animal Farming....

Fish ponds

From the animal farming source:

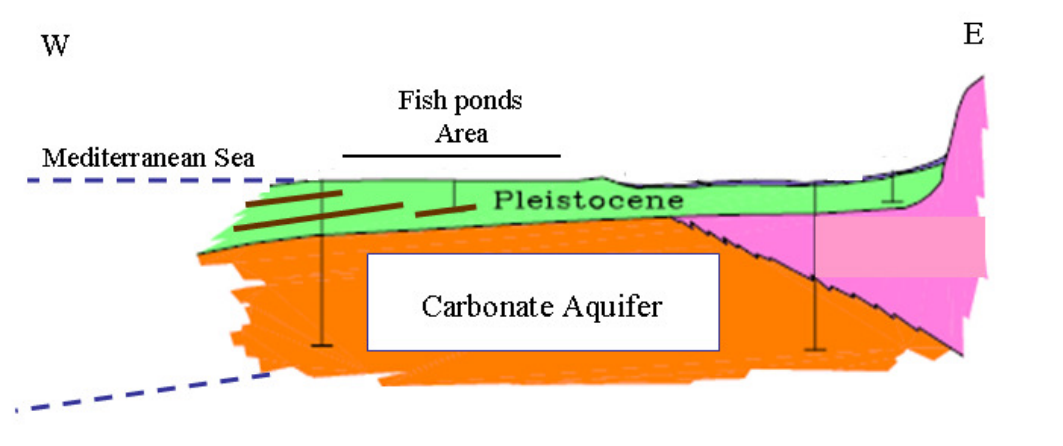
The aquaculture is one of the main contributors of antibiotic residues to the environment

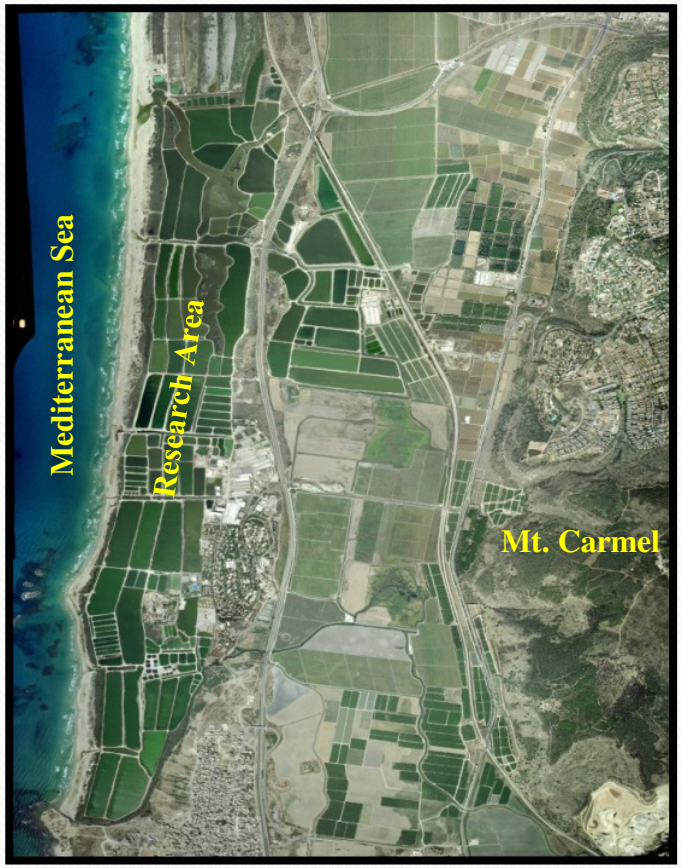
Lalumera et al (2004) found that 75% of the given drug is released from the fish body through secretions as a non-metabolite molecule and then directly discharge to the aquatic environment.



In Israel….

The intensive aquaculture industry mostly located above the sandy, phreatic coastal aquifer, a major drinking water source.





Study Area-Detailed

Locate up flow, but.. M/2 is intensively pumping production well, creating a local cone of depression

Treatment Facility

OTC Discharge

Pond B

Selected Antibiotic

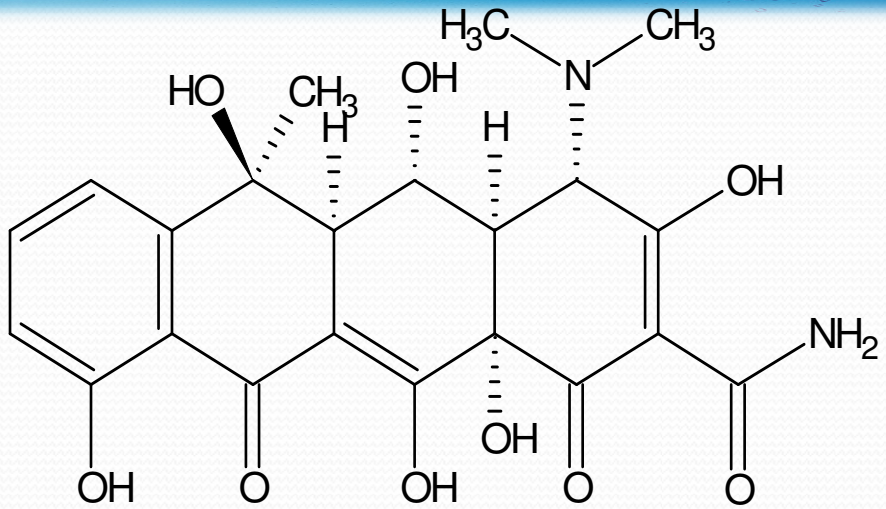
Class: *Tetracyclines*

Antibiotic: *Oxytetracycline*

Symbol: *OTC*

MW: *460 g/mol*

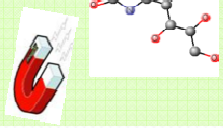
Chemical Formula: $C_{22}H_{24}N_2O_9$



OTC is an antibiotic commonly used for veterinary therapy in aquaculture, mainly as a growth promoter and to prevent infections.

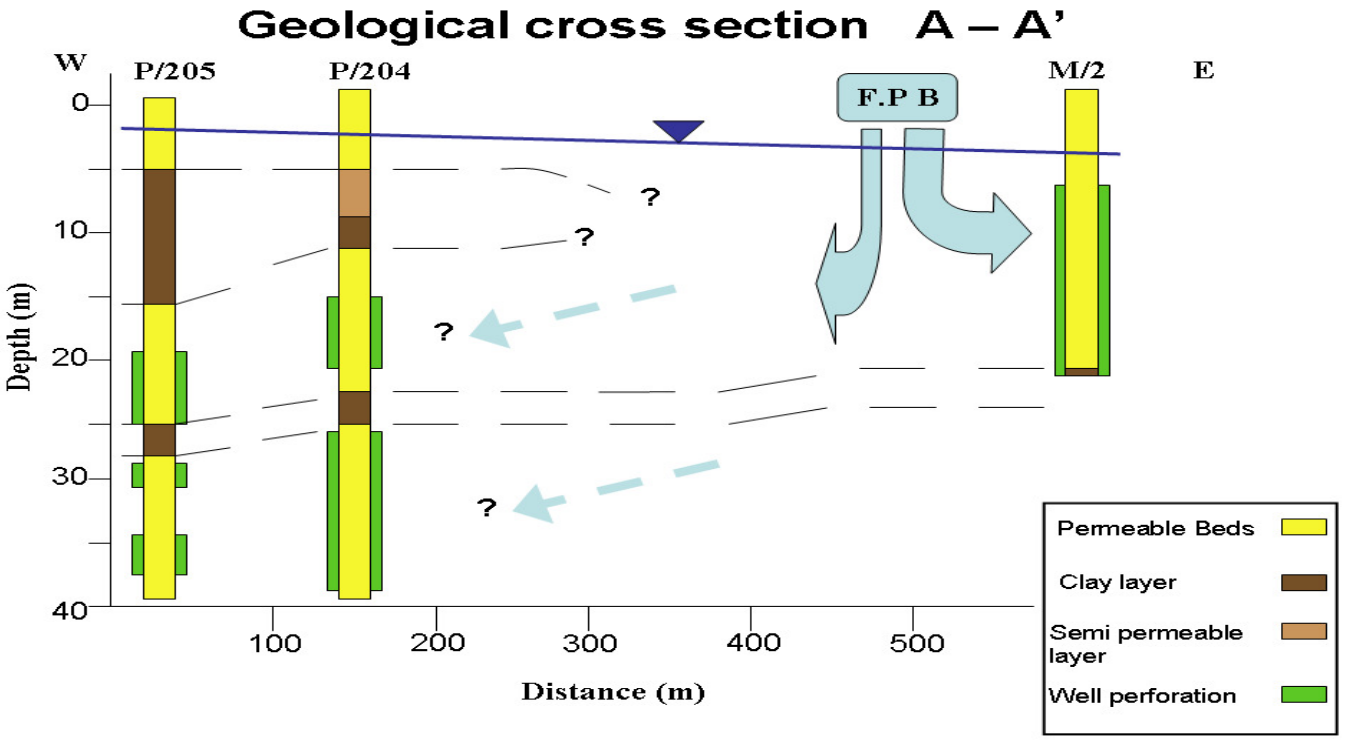
Tetracycline's are strong chelators that sorb strongly to soil (Lindsey et al, 2001, Primor, 2008, Avisar et al, 2009).

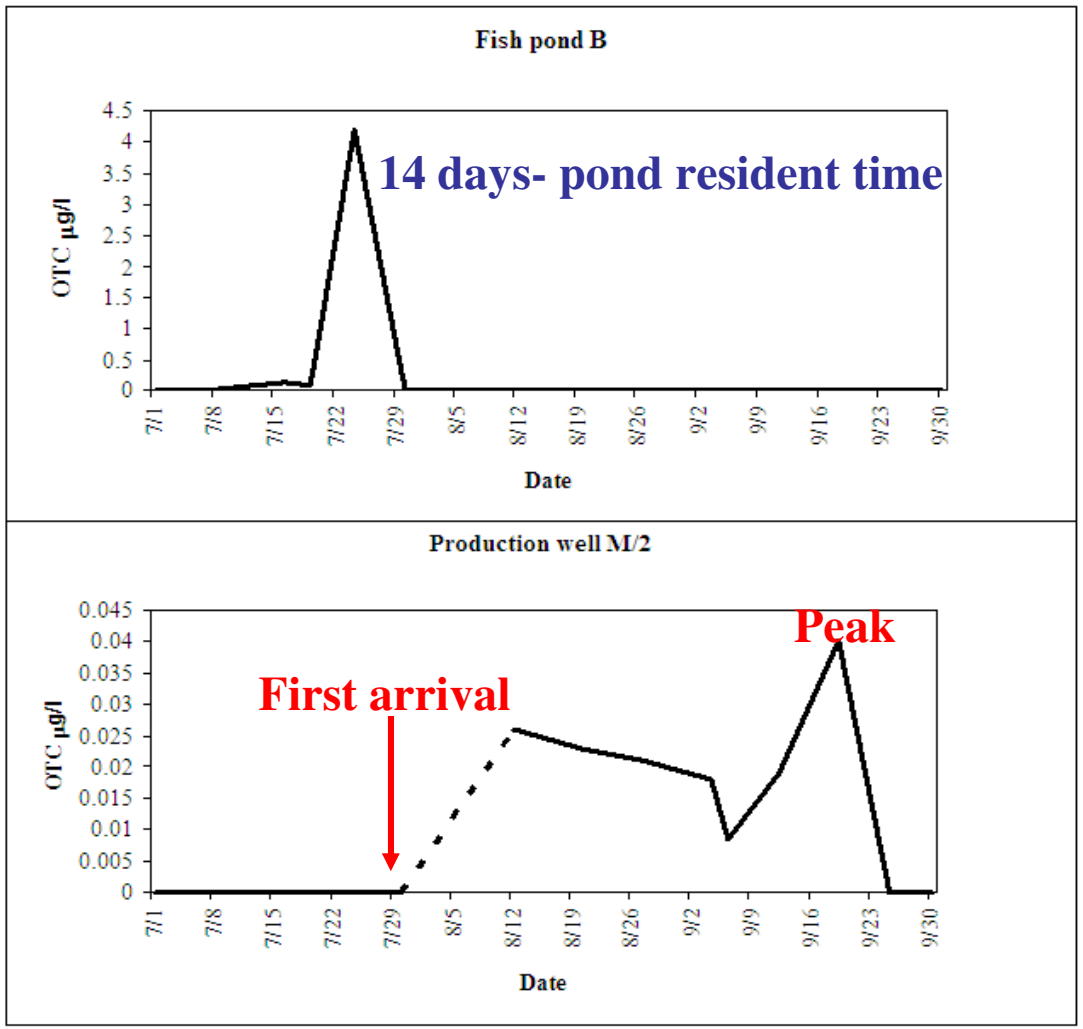
Studies indicated that these molecules are preferentially partitioning into solid phase rather than water



Main objective

This study examines the potential recharge of OTC towards groundwater wells located in a vicinity to a fish pond (B), which functioned as point source for antibiotic pollution.





Results demonstrated:

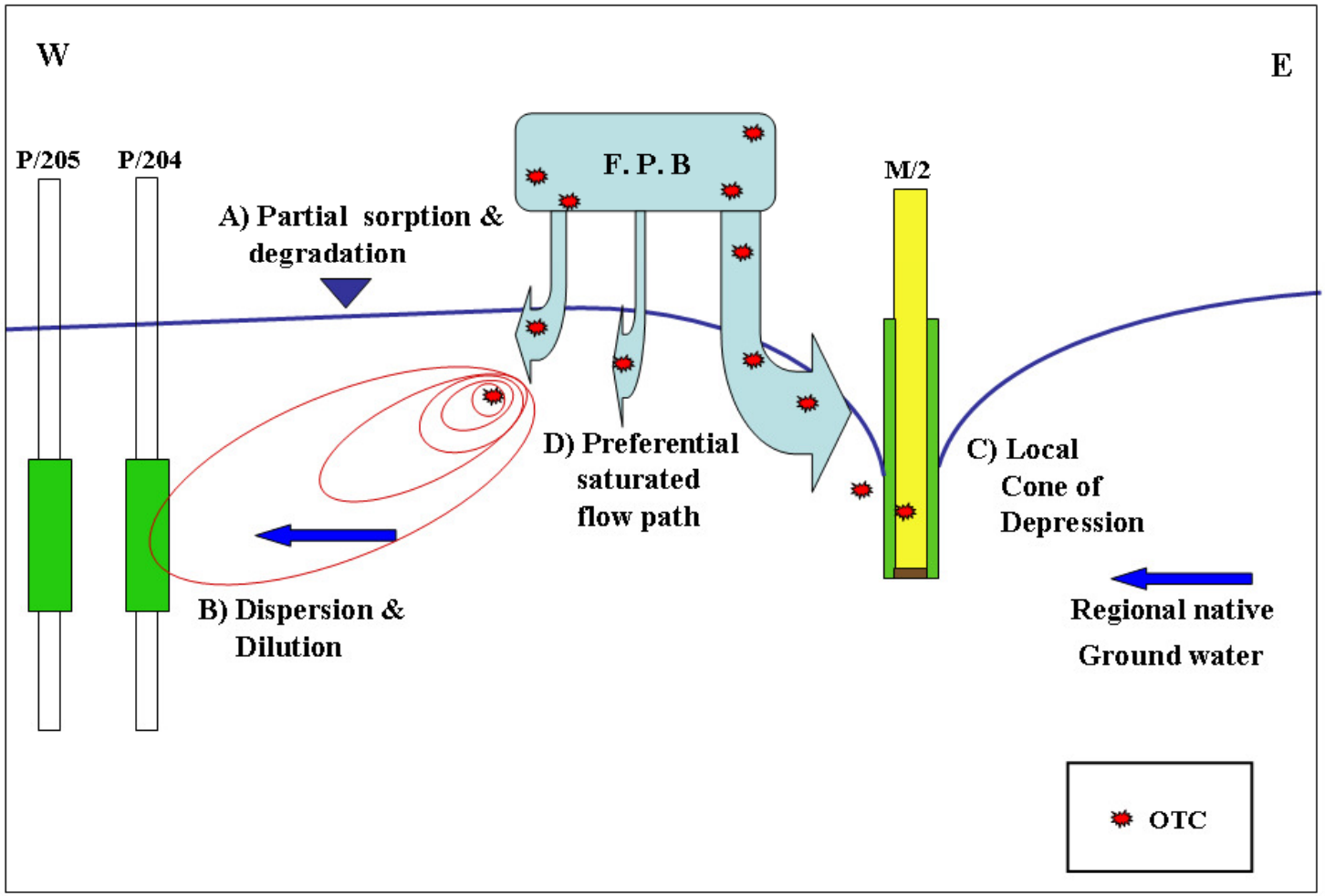
A rapid infiltration rate towards the local Groundwater

OTC detected:

33 up to 110 ng/L

For 55 days in local groundwater

Suggested mechanisms for OTC Contamination



Summary and Conclusions:

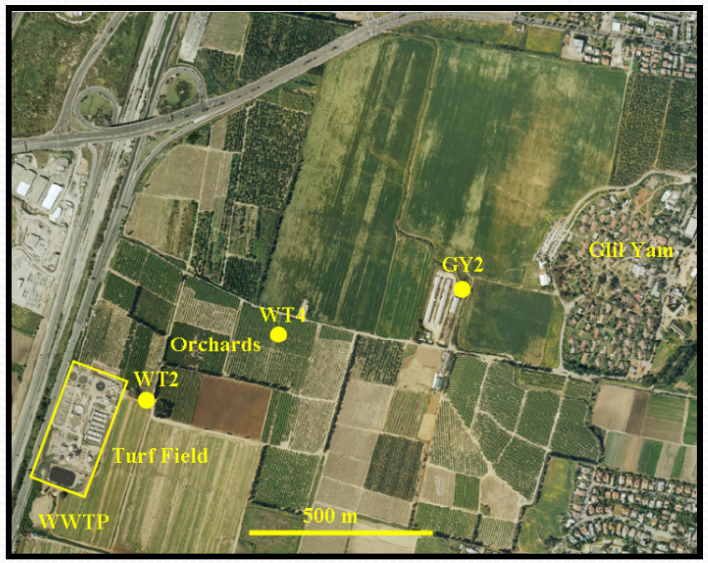
This study demonstrates the potential of groundwater contamination by antibiotic residues originated from aquaculture.

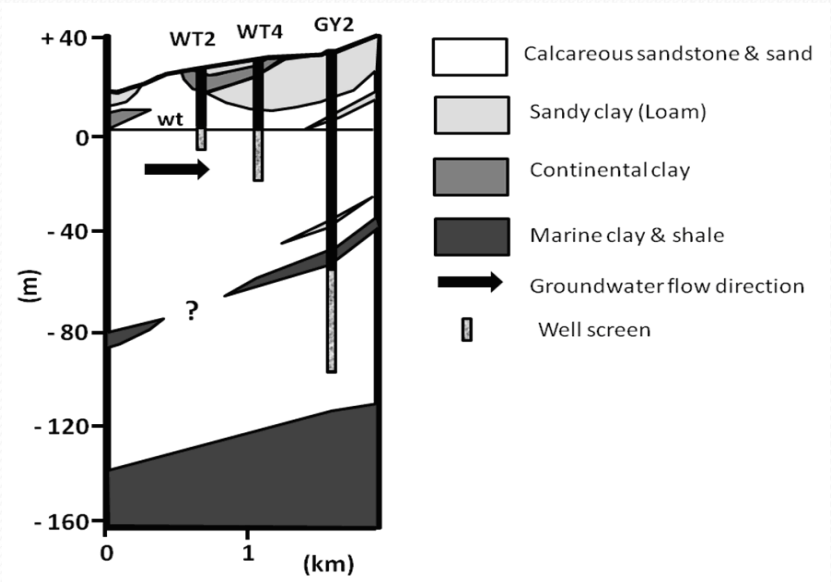
Tetracycline group is highly considered as a potential human teratogenicity factor, which may cause deformations to fetus (Friedman et al, 1990; Schardein J.L., 2000).

The OTC which usually considered as an immobile compound (strongly absorbed), shows a relatively rapid mobility, by traveling trough the pond floor and the aquifer beds towards the local groundwater due to:

The specific and unique hydrological conditions which developed under fish pond B (e.g. preferential saturated flow path), enable fraction of the OTC to leak and rapidly reach to groundwater.

Antibiotics and their DP's:





Detected antibiotics:

Sulfamethoxazole- S.E.-700 ng/L; G.W. 40 ng/L

Erythromycin DP's S.E.-700 ng/L; G.W. 40 ng/L

Amoxicillin DP's S.E.-700 ng/L; G.W. 40 ng/L

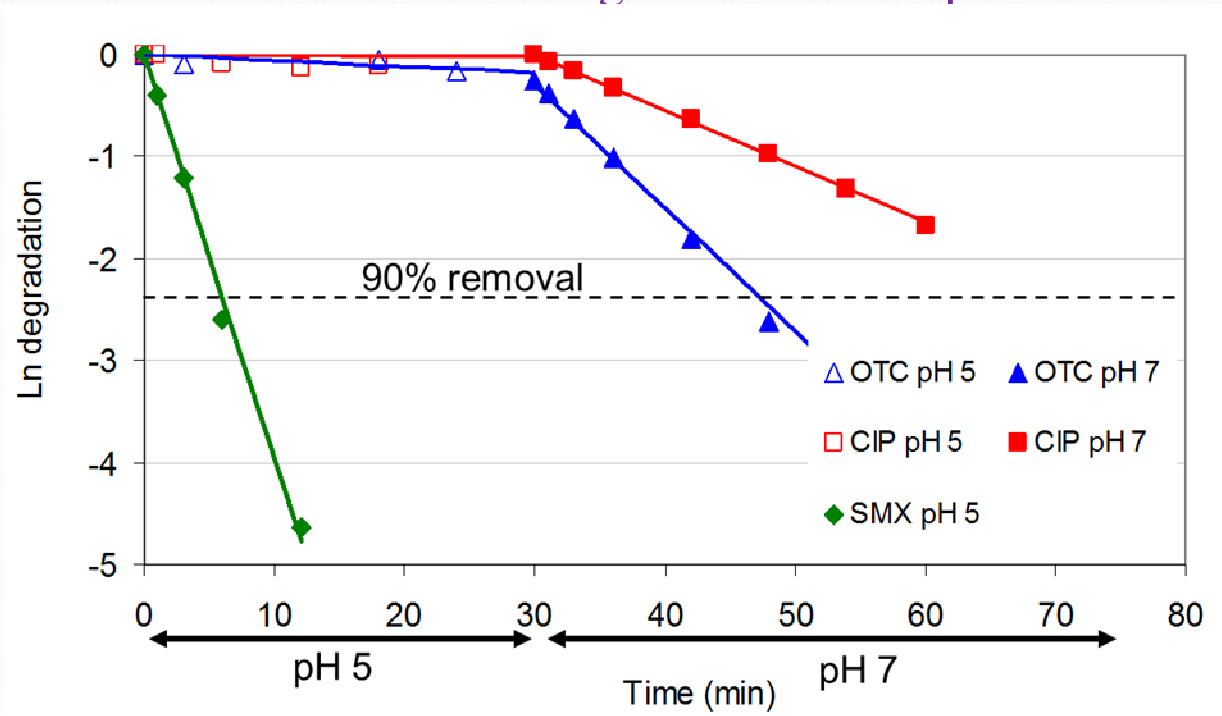
Avisar, D. Lester Y. and Ronen, D. 2009. Sulfamethoxazole Detected in a Deep Phreatic Aquifer beneath Effluent Irrigated Land. *The Science & the total Environment. Vol. 407, 4278-4282.*

Worldwide…

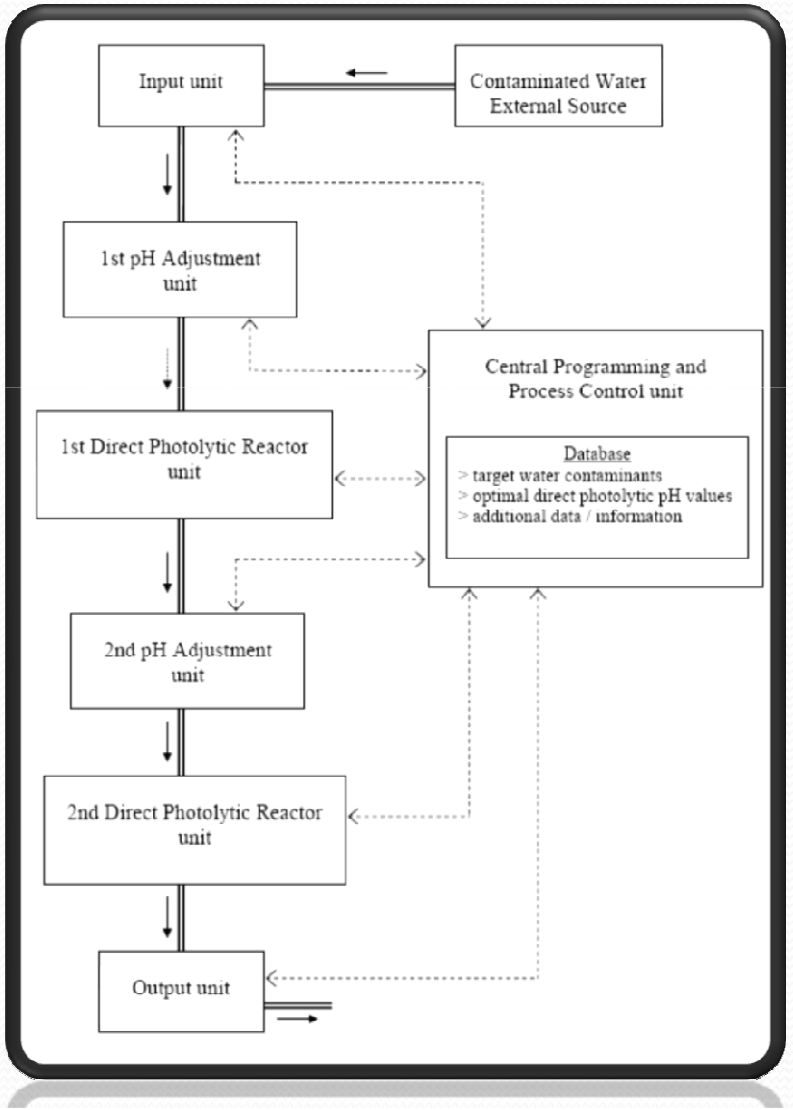
- Traditional treatments do not sufficiently break down these chemicals
- World Health Organization: ”Nowadays, even the best tertiary treatment does little to disable antibiotics activity in water”
- Thus, in some cases we need to develop technologies for treatment of contaminated waters and effluents

Suggested removal solutions: 1) pH induced direct photolysis:

Multi-contaminant water treatment 'series' configuration- Example:



pH induced direct photolysis-
Multi-contaminant water treatment-



Avisar, D., Lester Y. and Mamane, H. (2010), *Journal of Hazardous Materials*. 175, 1068-1074.

Lester, Y., Mamane, H. and Avisar, D. 2012. .Removal of micro-pollutants from groundwater, using UV light and pH modification. *Water, Air & Soil Pollution.* 223, 4, 1639-1648.

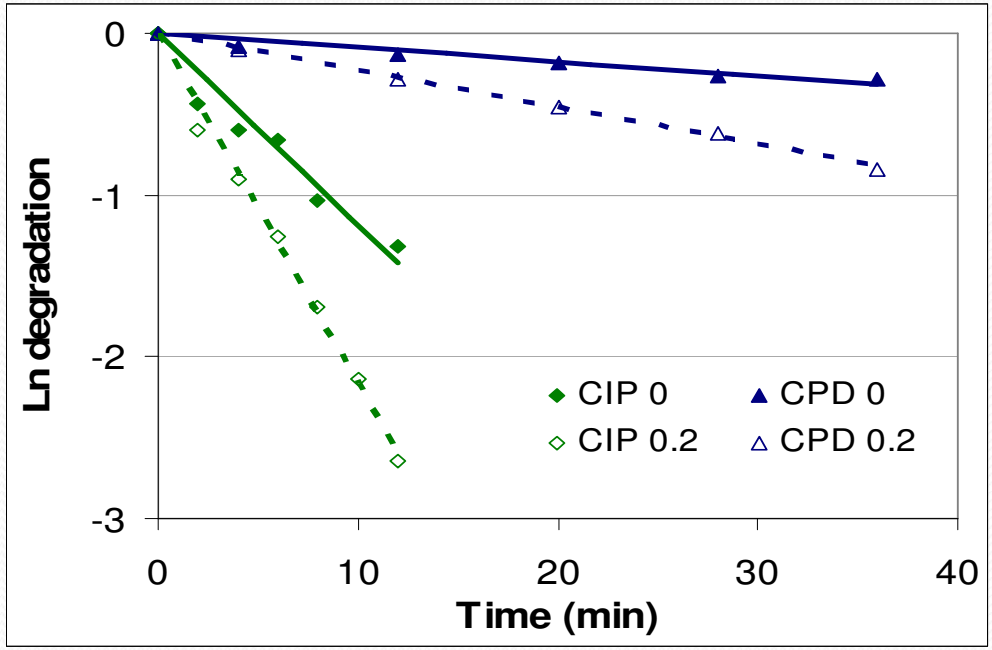
2) O_3 based AOPs:

$O_3+H_2O_2$

$2O_3 + H_2O_2 \Rightarrow 2{\bullet}OH + 3O_2$

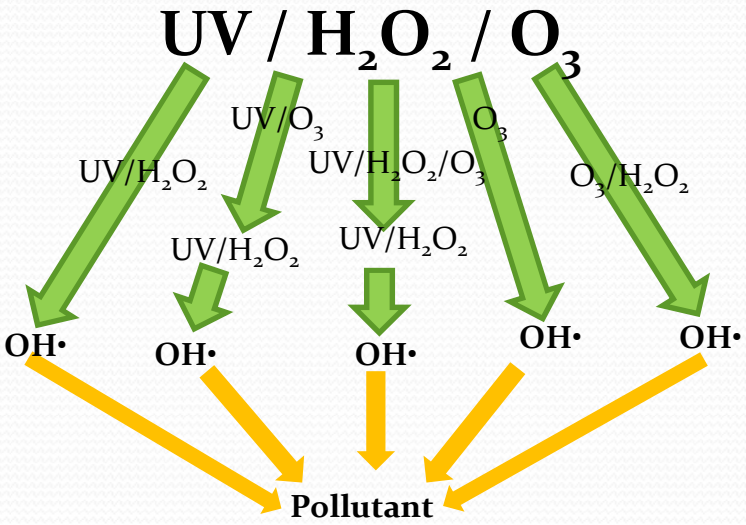
${\bullet}OH + \text{Pollutant} \Rightarrow \text{Product}$

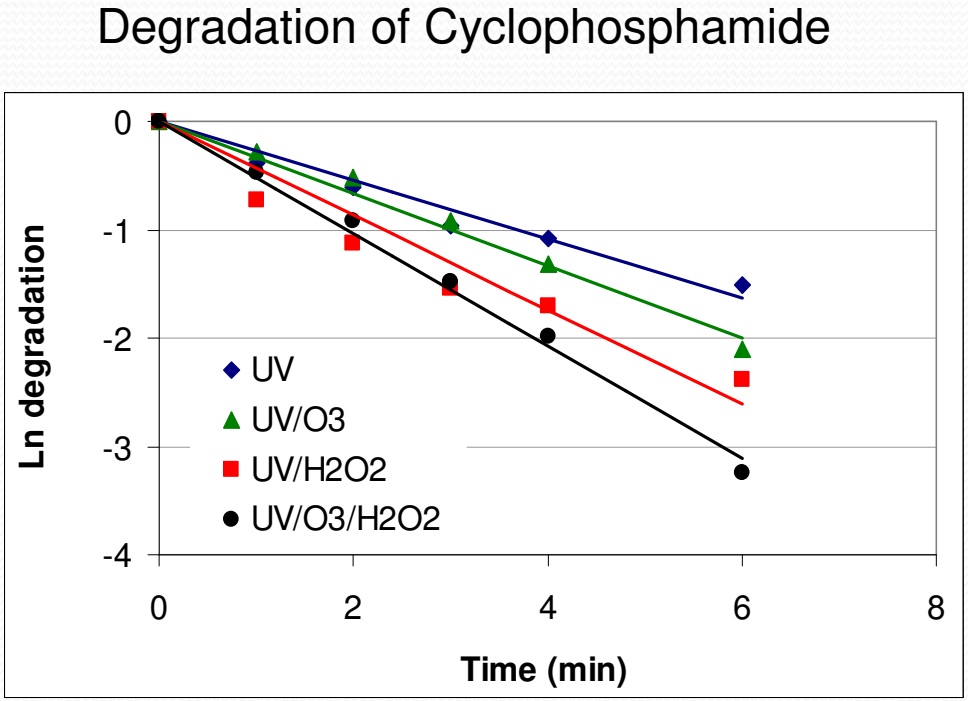
Degradation of Cyclophosphamide (CPD) and Ciprofloxacin (CIP)



Lester, Y., Avisar, D. and Mamane, H. Ozone Degradation of Cyclophosphamide – Effect of Alkalinity and Key Effluent Organic Matter Constituents. *Ozone Science & Engineering (Accepted).*

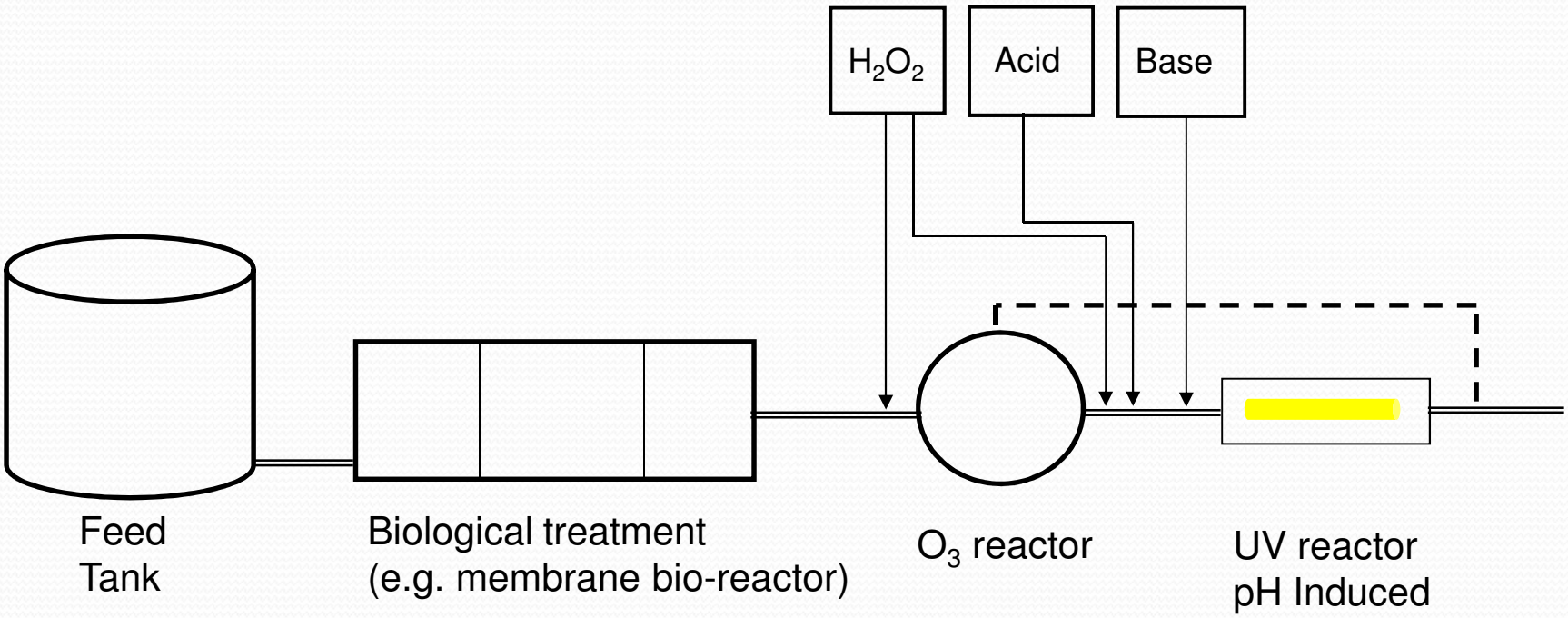
3) Combined Treatment:





Lester, Y., Avisar, D. and Mamane, H. 2011. Removal of Pharmaceuticals Using Combination of UV/H_2O_2/O_3 Advanced Oxidation Process. *Wat.Sci.Tech.* *DOI:10.2166/wst.2011.079.*

Combination of technologies



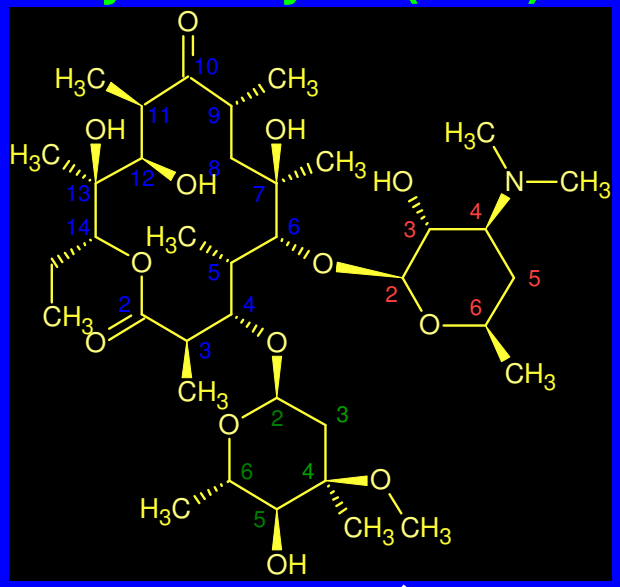
Thousands have lived without love.
Not one without water.

W.H. Auden (1907-1973)

Thank you for your attention

Erythromycin : possible degradation path in the aquatic environments

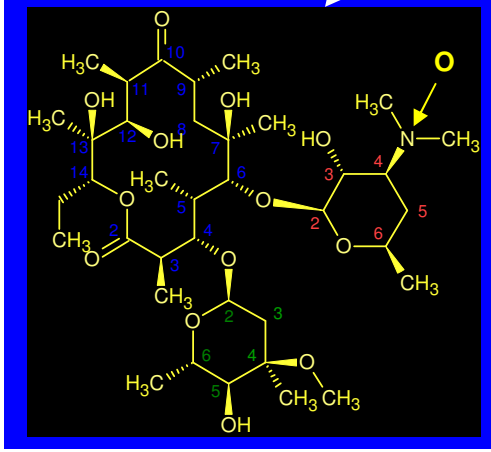
Erythromycin (ERY)



MW=733

$h\nu$, O_2

ERY-N-oxide



$-H_2O$

ERY-N-oxide Spiro ketal product

ERY-N-oxide – H_2O (other products)

MW=749

MW=731

$-H_2O$

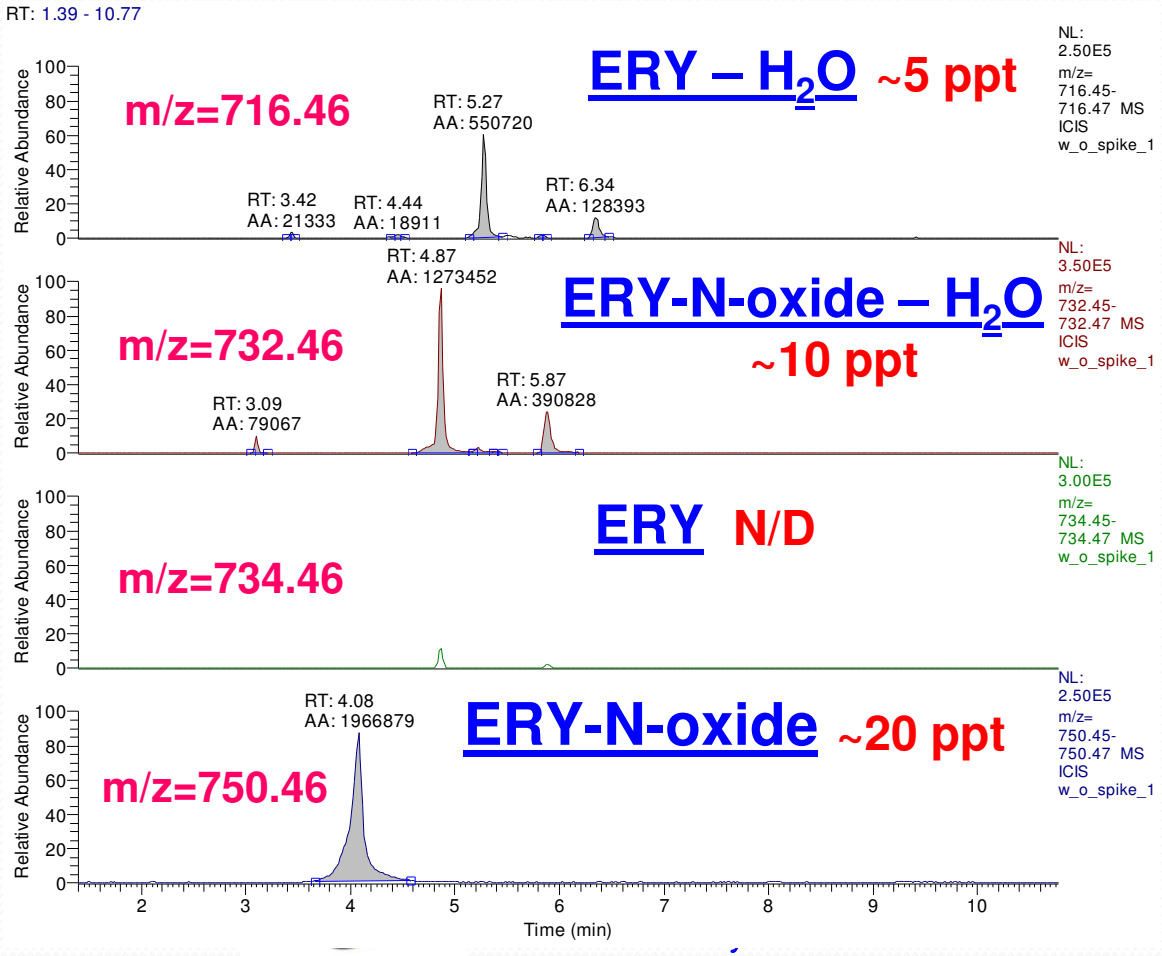
ERY Spiro ketal product

ERY – H_2O (other products)

MW=715

$h\nu$, O_2

LC/MS chromatograms of ERY degradation products in groundwater (Glil Yam) (instrument – MS-Executive, Thermo, high resolution)

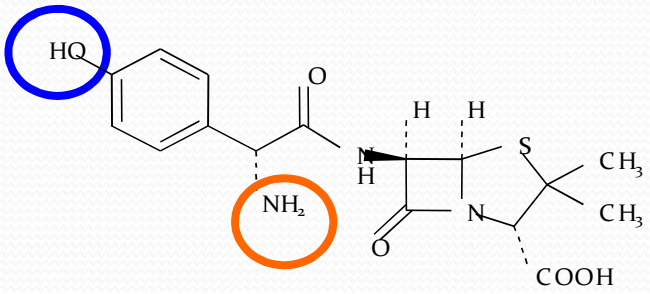


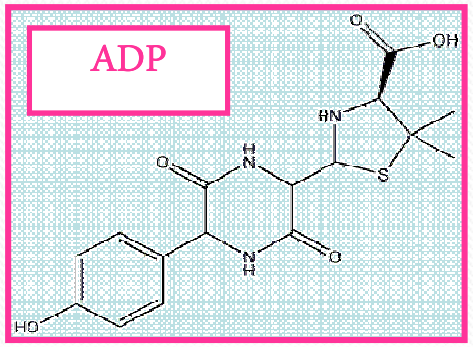
Diketopiperazine = metabolite of Amoxicillin

The most consuming antibiotic for human therapy!

1,160 ng/L Measured in Wastewater

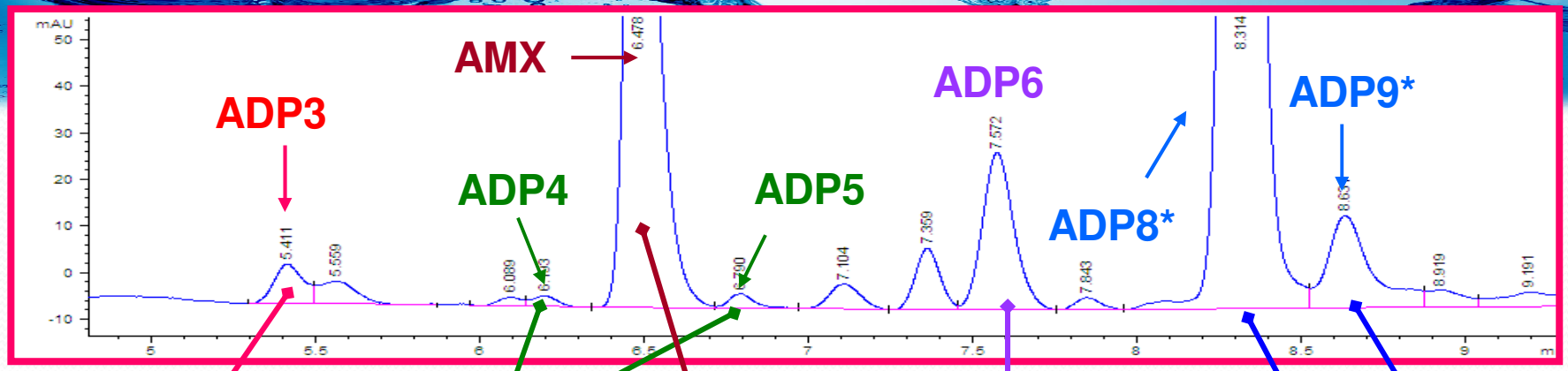
60 ± 15 ng/L Measured in S. Effluent

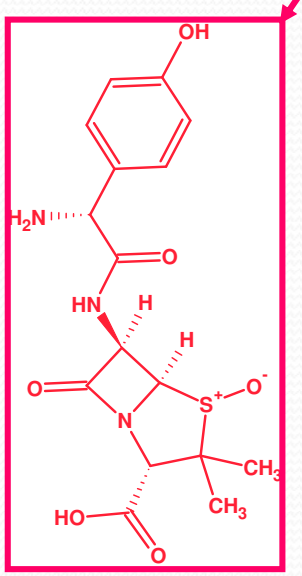


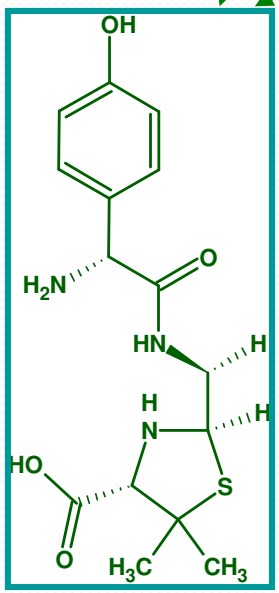


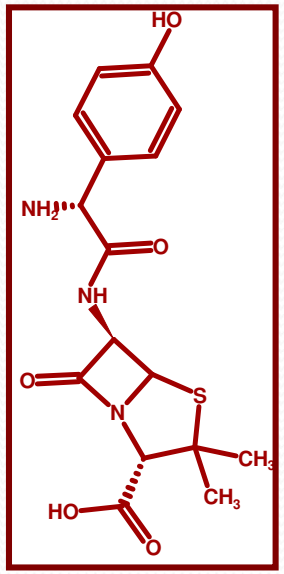
Lamm, A., Gozlan, I., Rotstein, A., and Avisar, D. 2009. Detection of amoxicillin-diketopiperazine-2', 5' in wastewater samples, J. Environ. Sci. Health, Part A. Vol.44, No.14.

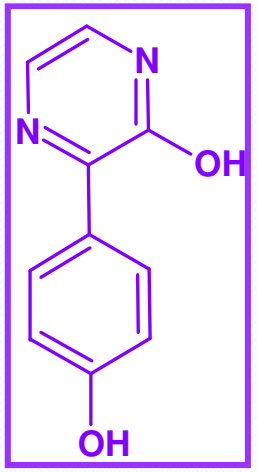
HPLC chromatogram of Amoxicillin degradation products

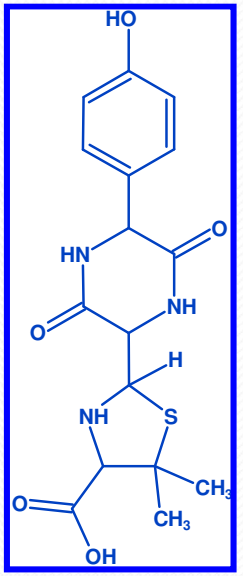












Toxic and detected in G.W!

Gozlan, I. and Rotstein, A., and Avisar, D. 2010. Investigation of Amoxicillin Oxidative Degradation Product in Environmental Condition Using Natural Sun and Ozonation Process. *Environmental Chemistry. 7,5, 435–442.*