

Changes in the biological degradability and toxicity of sulfonamide antibiotics in activated sludge and river water due to ionizing radiation treatment

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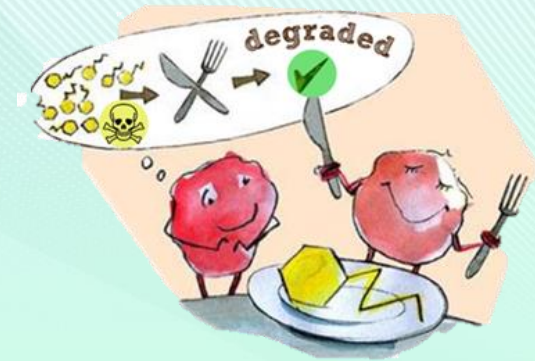


Removal of organic pollutants from municipal wastewater by conventional treatment

Secondary treatment by activated sludge:

Microorganisms metabolize the suspended and soluble organic matter.

- ✓ Removes organics
- ✓ Cost effective
- ✓ Easily maintained mechanical work
- ✓ Self sustaining system



Enzymatic processes are adapted to **biogenic** chemical compounds.

Presence of xenobiotics in activated sludge systems

Chemically synthesized compounds that **do not occur in nature**.

- Structural features to which microorganisms have not been exposed to during evolution (e.g. $-\text{CF}_3$, $-\text{Cl}$, $-\text{N}=\text{N}-$, $-\text{NO}_2$)
- Such bonds or substituents block the attack by microbial catabolic enzymes
- Inefficient removal by activated sludge
- Deterioration of wastewater effluent quality

Ionizing radiation: A promising complementary option

Urgent need for an effective technique suitable for removal of persistent organic pollutants.



Ionizing radiation treatment

offers numerous advantages
(e.g. no chemicals, process controllability,
high efficiency)



Photo: INET/Dasheng

The main basis of efficiency characterization is the pollutant removal rate.

Technological aspects!

Biological evaluation

Biological evaluation carried out by technological approach

1. Disregarding mineralization



Disregarding dose dependence of biological responses

Mineralization (irradiation) reduces the pollutant concentration that relieves the pressure from living organisms in biological tests.

Irradiation with different doses results in „dilution series”; hence, properties of product groups formed at different doses are not comparable.

Biological evaluation

Biological evaluation carried out by technological approach

2. Disregarding H_2O_2 formation

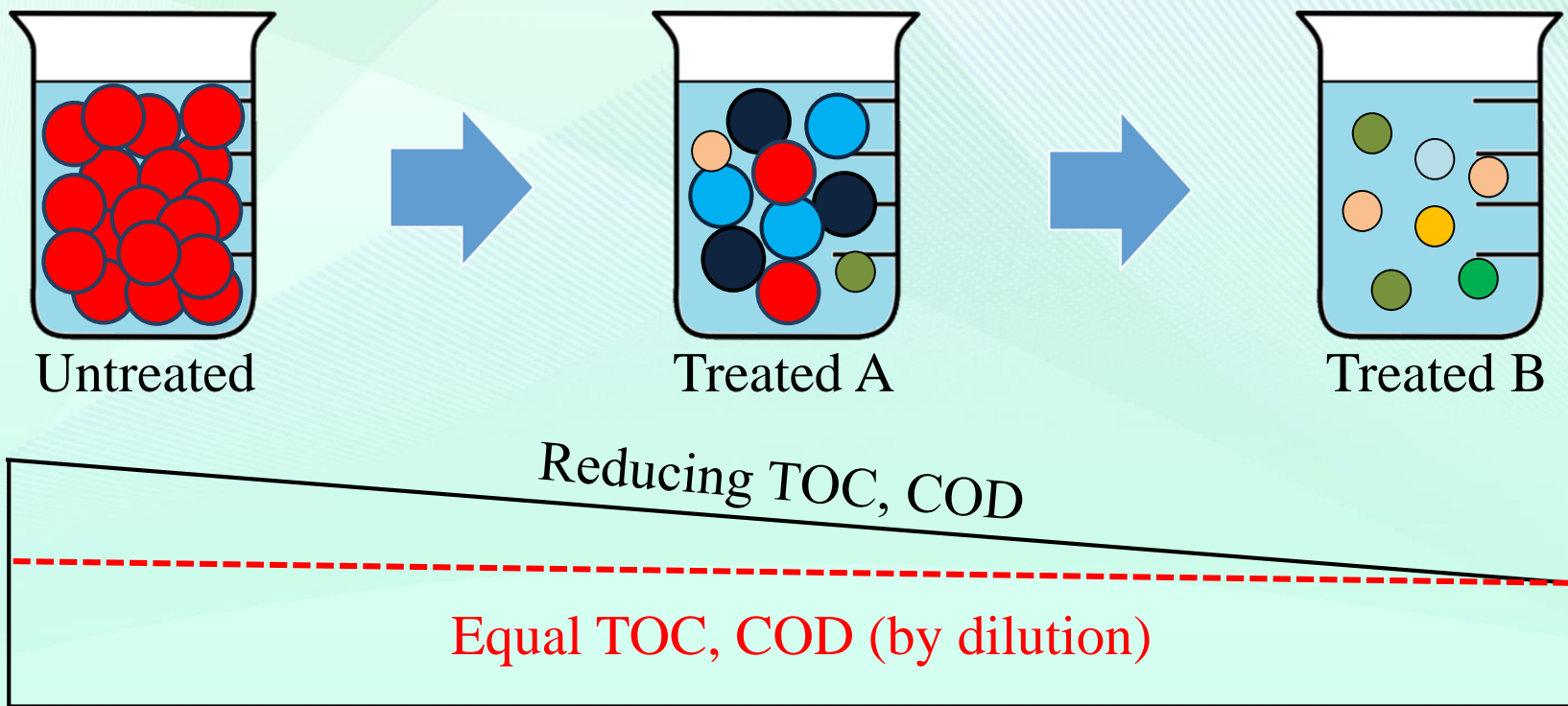
- $2 \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ ($k = 8.3 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)
- $\text{HO}_2^\bullet + \text{O}_2^{\bullet-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$ ($k = 9.7 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)
- $^\bullet\text{OH} + ^\bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$ ($k = 5.5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)



Disregarding interfering effects of oxygen liberation in manometric or respirometric experiments, and also disregarding the toxic effects.

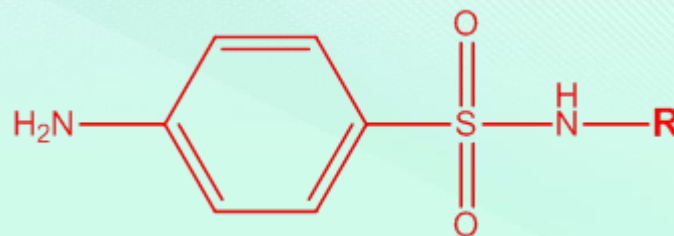
Accurate comparison of product groups formed at different doses

Adjusting the pollutant load to equal value in all biological experiments
+ H_2O_2 removal (e.g. MnO_2 , catalase).



Irradiation conditions

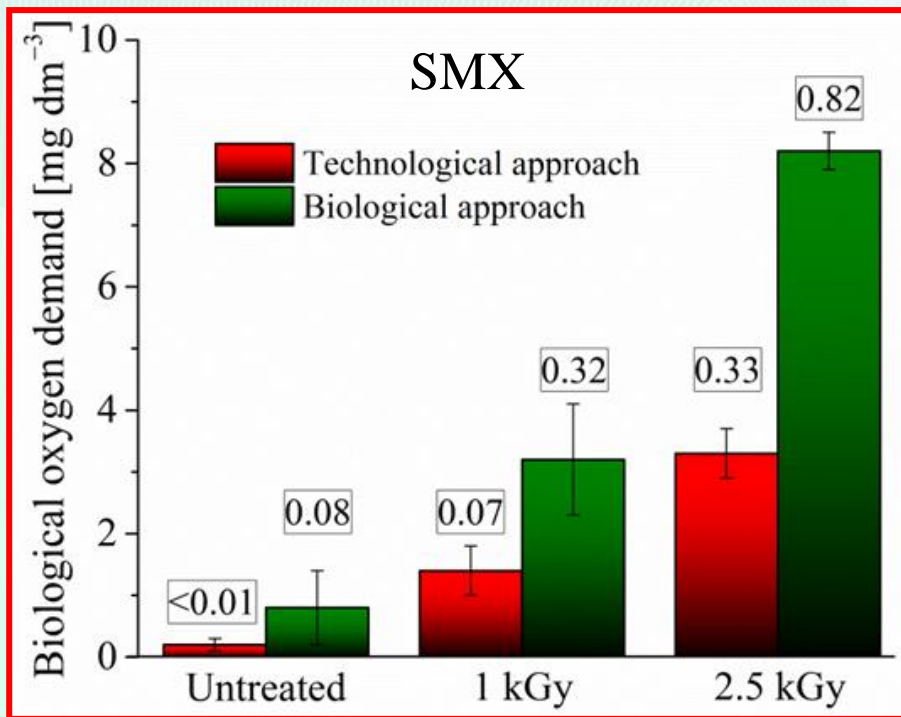
- ^{60}Co SSL-01 panoramic type pilot scale facility
 - 6 kGy h⁻¹ dose rate
 - Continuous aeration
 - Room temperature
 - Test substances: unbuffered aqueous solution of sulfonamide antibiotics
 - Sulfamethoxazole (SMX)
 - Sulfanilamide (SAA)
 - Sulfaguanidine (SGD)
 - Sulfathiazole (STZ)
- 0.1 mmol dm⁻³ initial concentration





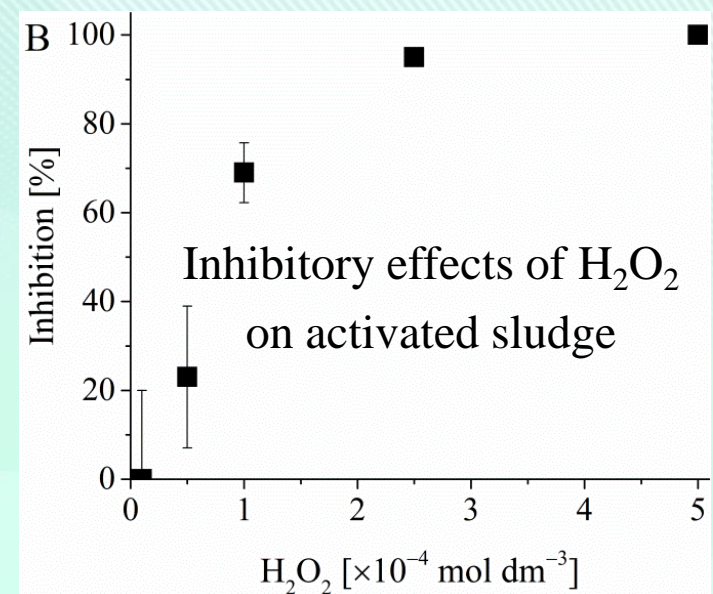
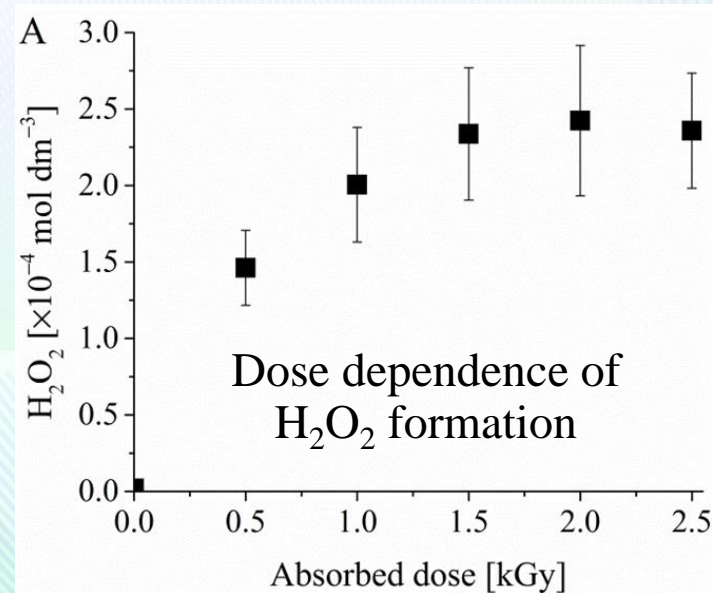
Examples on different sample application approaches

Biological oxygen demand

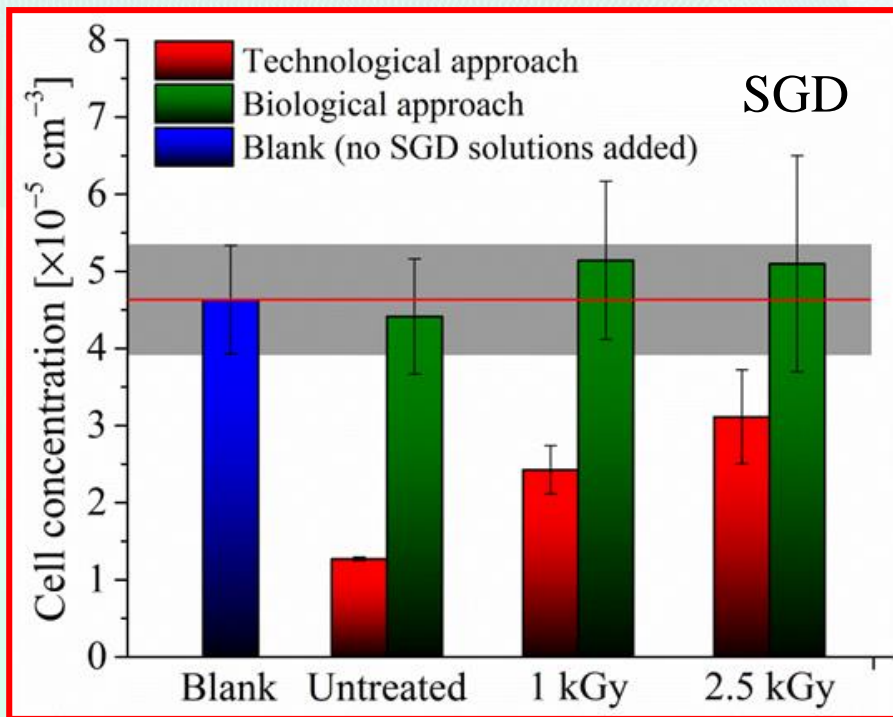


DIN EN 1899-1

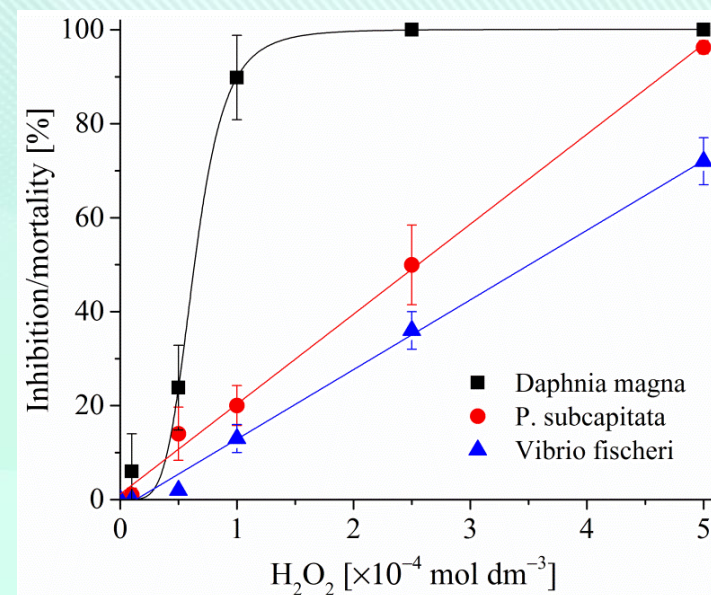
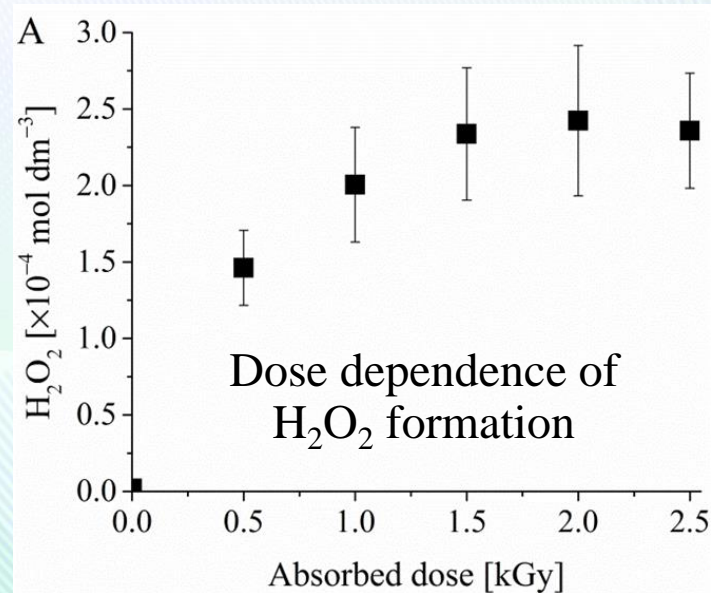
OxiTop[®] Control Respirometer System



Ecotoxicity assay



Pseudokirchneriella subcapitata
chronic growth inhibition
OECD Test No. 202

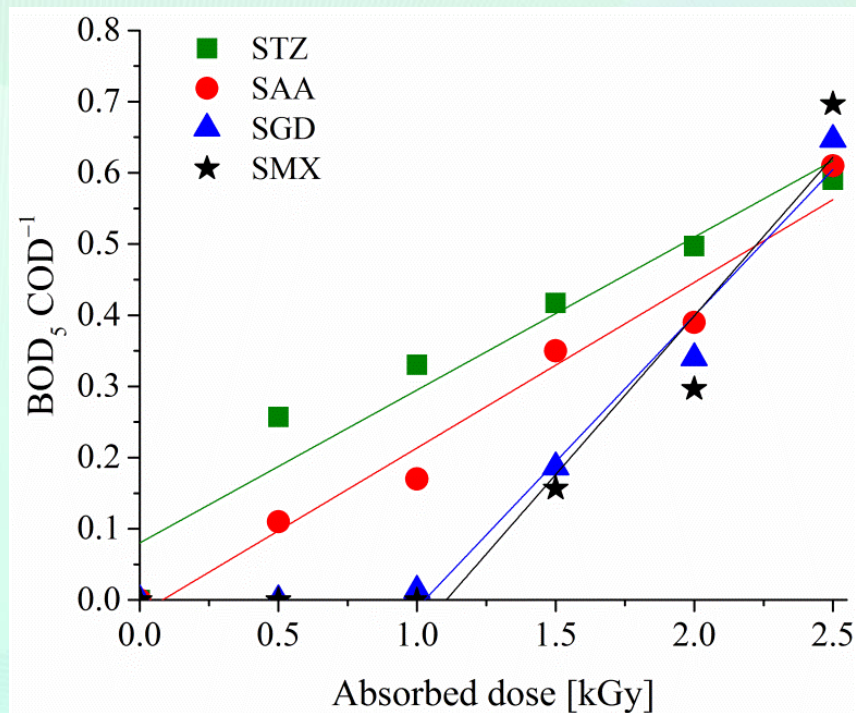




Biodegradation of sulfonamides in activated sludge and river water

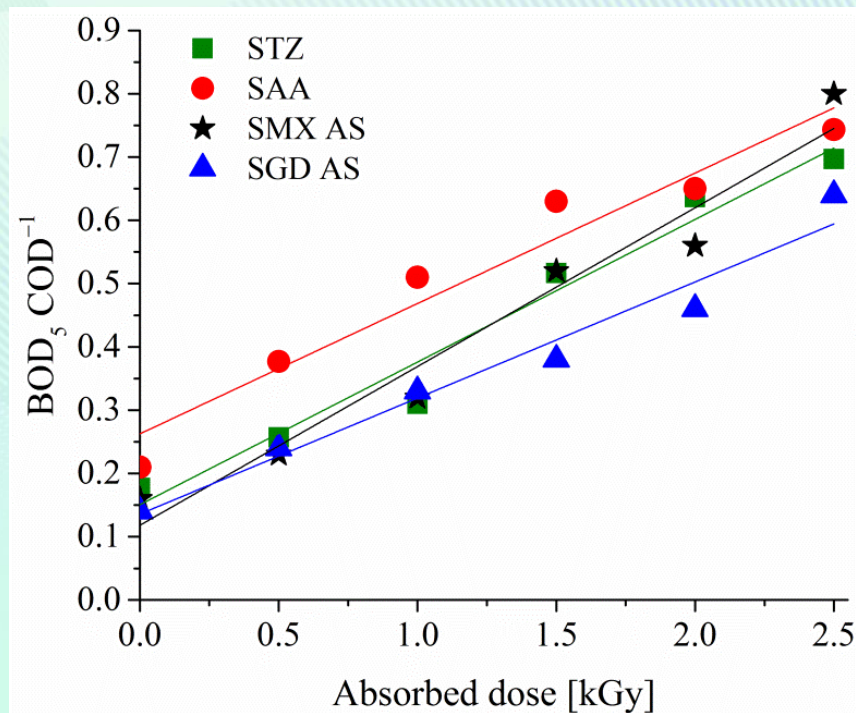
Biodegradability

River water



$BOD_5 \text{ COD}^{-1}$
 $0 \rightarrow 0.59 - 0.70 (!)$

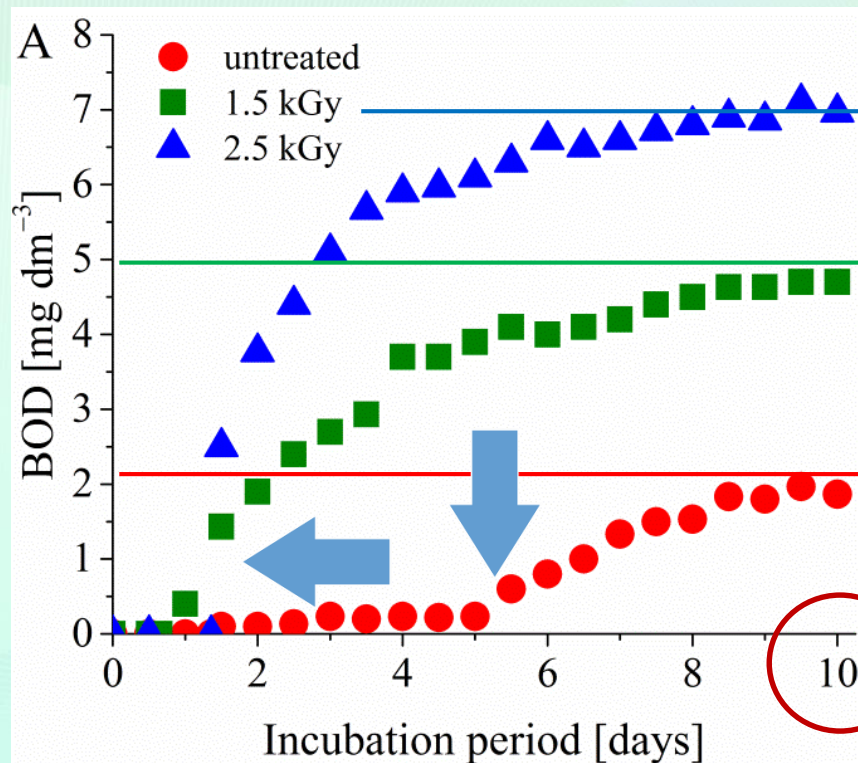
Activated sludge



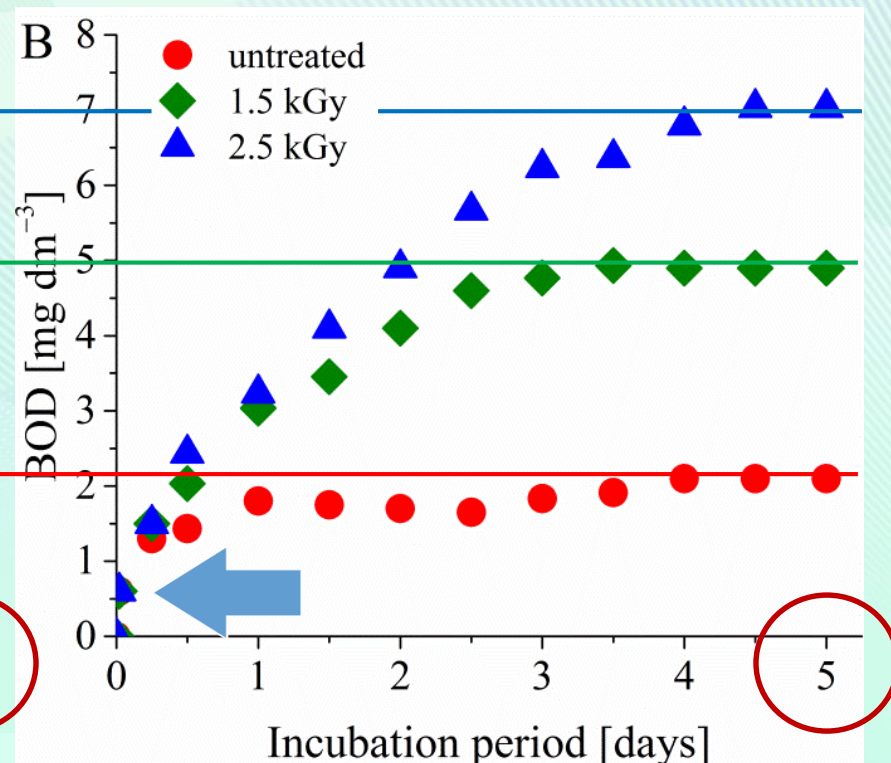
$BOD_5 \text{ COD}^{-1}$
 $0.14 - 0.21 \rightarrow 0.64 - 0.80 (!)$

Biodegradability

River water



Activated sludge





Toxicity of sulfonamides

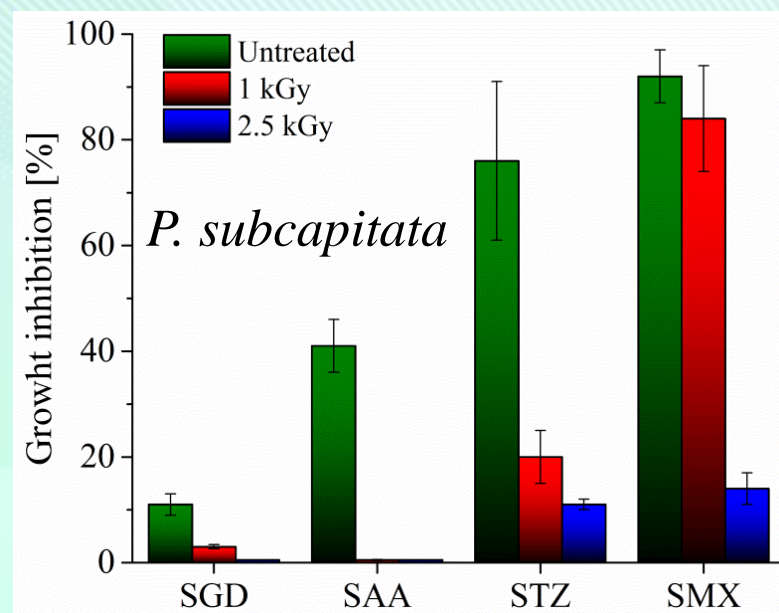
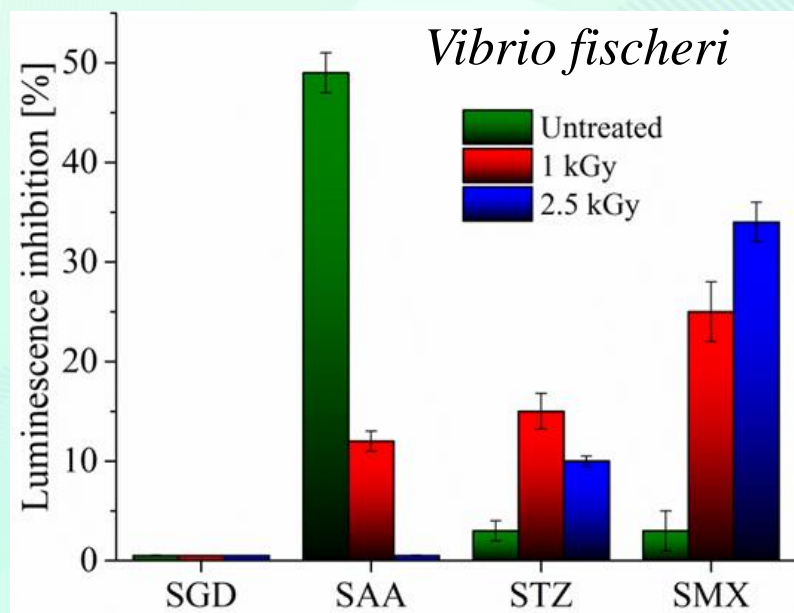
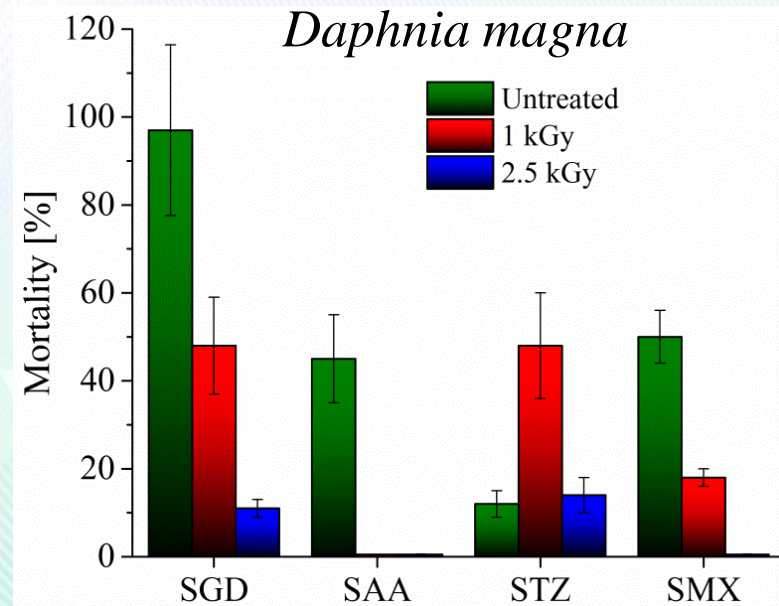
Ecotoxicity assay

Test organisms from 3 trophic levels:

D. magna (OECD Test No. 202)

P. subcapitata (OECD Test No. 201)

V. fischeri (DIN EN ISO 11348-2)



Summary

- **Methodological issues regarding sample application in biological tests**
- **Biodegradation**
 - Activated sludge shows a certain extent of adaptation to sulfonamides
 - but: irradiation is required
 - Sulfonamides may undergo biological degradation in river water
 - Significant shift in acclimatization/adaptation period
 - Enough time to exert negative effects (resistance development, toxicity)
- **Toxicity test on individual organisms showed a diverse picture**
 - A battery of toxicity experiments did not provide clear data on trend changes
 - Experiments pointed out necessity of more informative and precise biological evaluation techniques



Thank you for your attention



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