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Nanomaterials and photonic solutions. Novel ‘at source’ approaches to stop hospital derived pharmaceuticals reaching the sewer network

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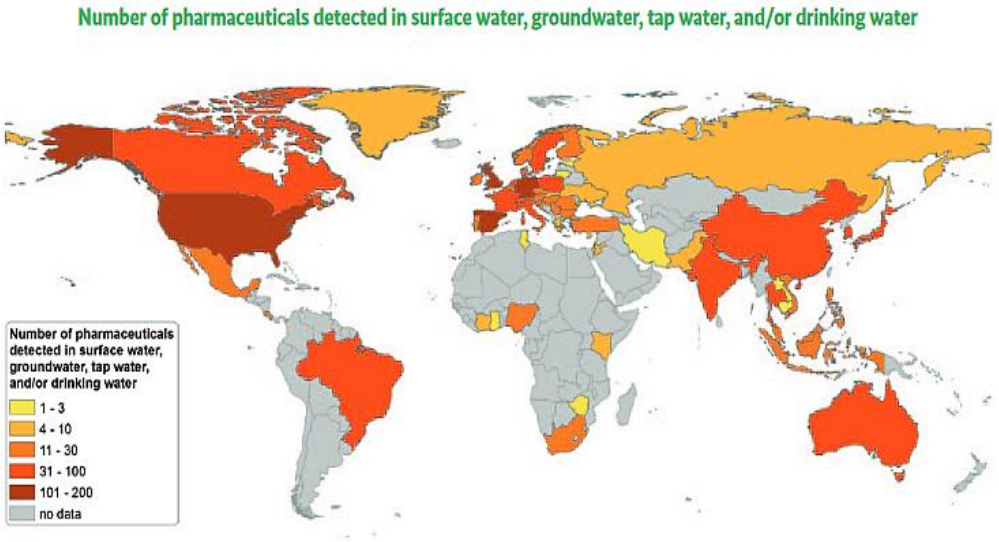
Background

630 different pharmaceuticals and their transformation products have been detected in 71 countries worldwide

Global drug prescribing volumes are increasing continuously



Active pharmaceutical ingredients (APIs) have shown detrimental toxic effects on aquatic organisms …

- Birth control pill -> Feminisation of male fish
- Analgesics, antidepressants -> Fish migration

…and may accumulate in food chains:

Diclofenac poisoning in vulture populations

Still many drug compounds are not classified or routinely monitored in surface or drinking water !

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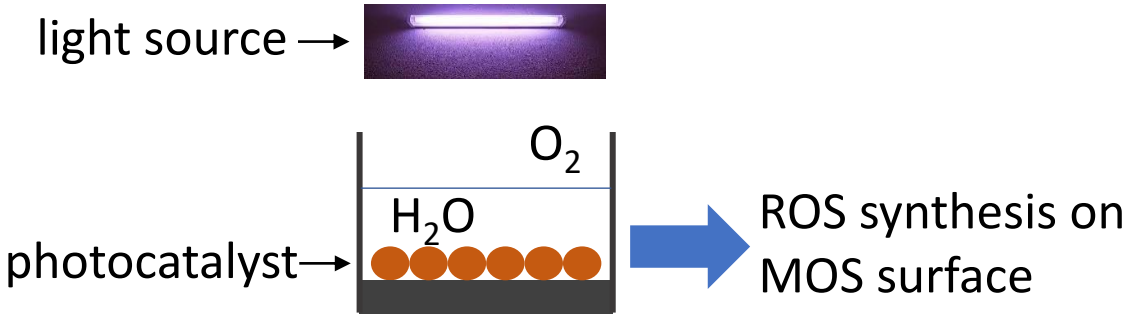
Background

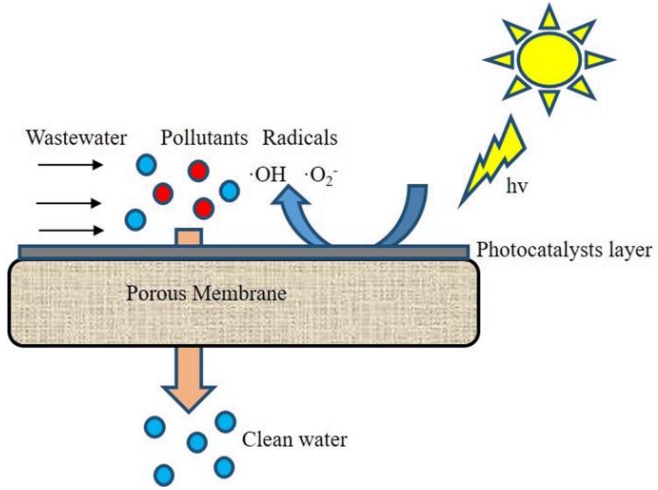
- Hospitals are a point source for ecotoxic drugs and metabolites in our environment
- Drug concentration in wastewater: ng/L – ug/L
- Conventional biological wastewater treatment eliminates APIs poorly
- Persistent, lipophilic APIs reach our water bodies, pose ecotoxic risks and may accumulate in food chains

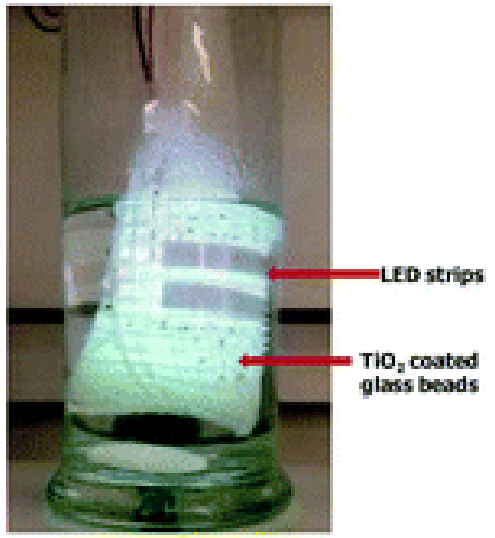
Novel at-source wastewater treatment concepts are urgently needed to eliminate a wide range of harmful organic drug compounds !

Overview photocatalysis

- Light activated oxidation of organics in the presence of water and a photocatalyst – Metal Oxide Semiconductor (MOS)
- Non-selective, holistic approach for drug elimination via generation of ROS species







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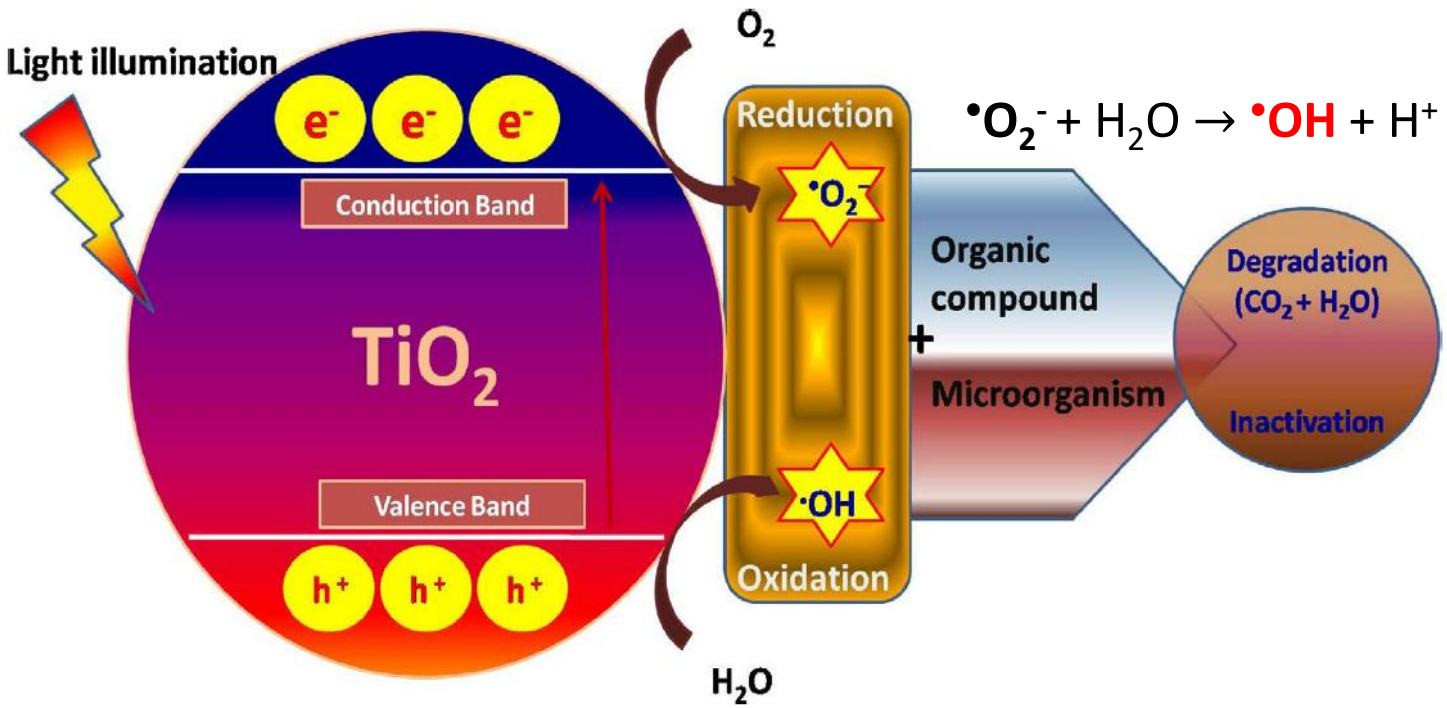
Treatment concept photocatalysis

- Generation of excited electrons and holes via illumination of semiconductor materials
- ROS production via redox reactions on the electrolyte interface of the photocatalyst
- Oxidation of organic drug compounds – Transformation of APIs into likely non-toxic compounds

$$O_2 + H^+ + e_{cb}^- \rightarrow {}^{\bullet}\mathbf{HO_2} + H^+ + e_{cb}^- \rightarrow \mathbf{H_2O_2} + H^+ + e_{cb}^- \rightarrow {}^{\bullet}\mathbf{OH} + H_2O$$



$$^{\bullet}O_2^- + H_2O \rightarrow {}^{\bullet}OH + H^+$$

$$2H_2O + 2h_{vb}^+ \rightarrow \mathbf{H_2O_2} + 2H^+ \rightarrow \mathbf{2}{}^{\bullet}\mathbf{OH} + 2H^+$$

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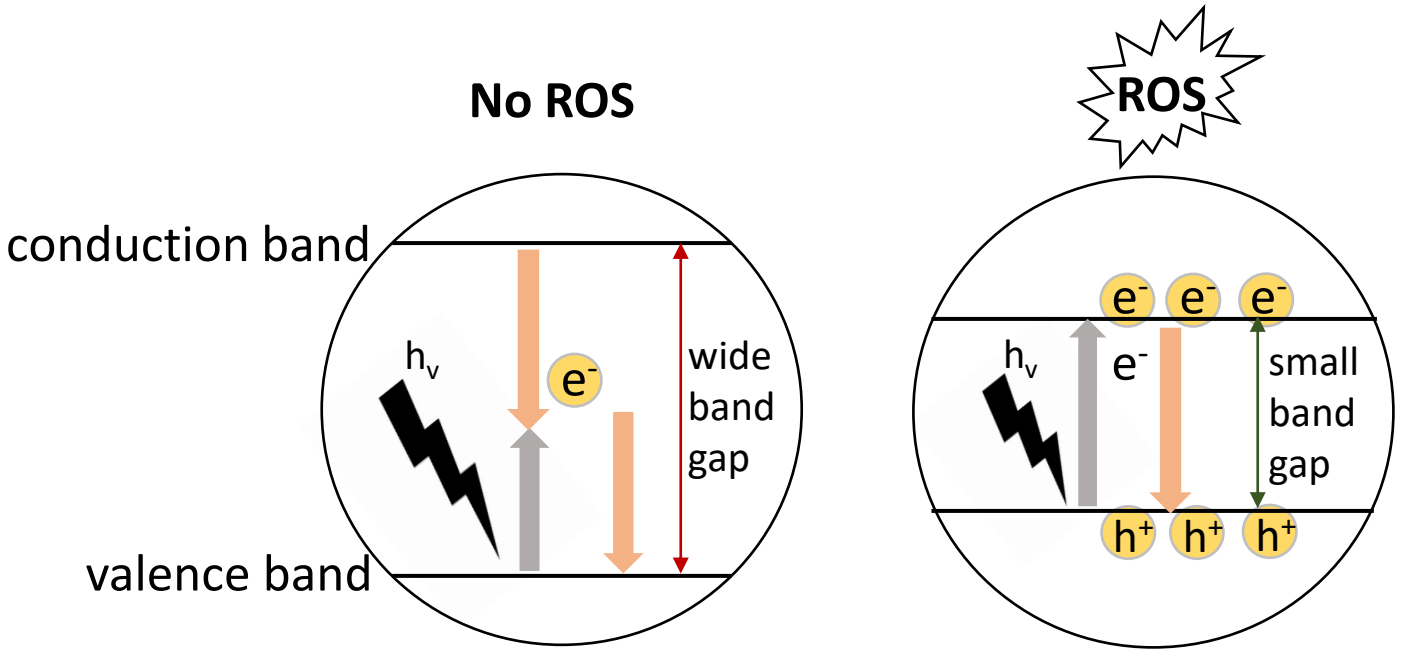
Current limitations of photocatalysis

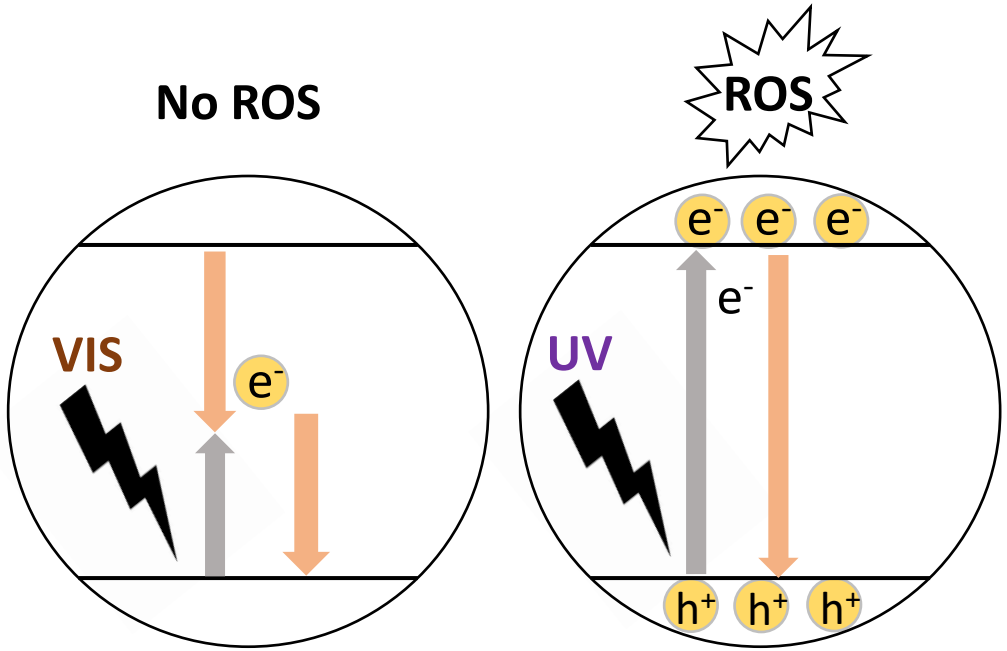
- **Recombination of charge-separated electron-hole pairs in wide band gap (≥ 3.1 eV) photocatalysts**
- Electrons do not reach the MOS-surface
- Conduction band electrons simply return to holes in the valence band



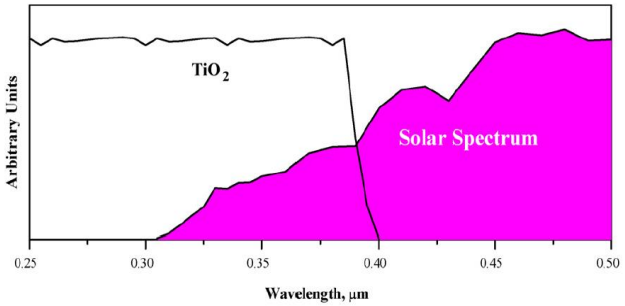
Current limitations of photocatalysis

- **Low photocatalytic activity under visible light in wide band-gap (≥ 3.1 eV) photocatalysts**
- Recombination of charge-separated electron-hole pairs

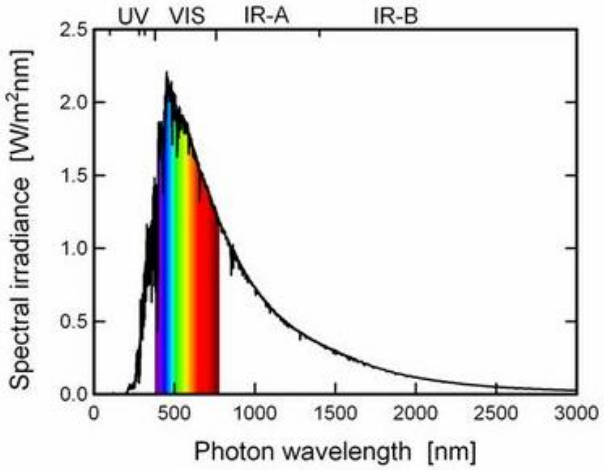
UV-A 300 – 400 nm
VIS 400 – 700 nm



TiO_2 Solar Disinfection
min. 6 hours light exposure



Solar irradiance:
UV-A 4-6% VIS 43%



TiO_2 photocatalysts only absorb a small fraction of the UV-VIS spectrum !

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Novel photocatalytic materials

Conventional MOS:

TiO_2 3.2 eV

+ non-toxic, stable, cheap
  very good UV-light performance
- Poor VIS-light performance

Novel photocatalysts:

g-C_3N_4 (graphitic carbon nitride) 2.7 eV

+ non-toxic, no metal leaching,
  thin-film layers enhance VIS-light performance
- unmodified - limited VIS-light performance

B_2O_3, $BiVO_4$, Bi_2WO_6 (bismuth-based) 2.3 – 2.6 eV

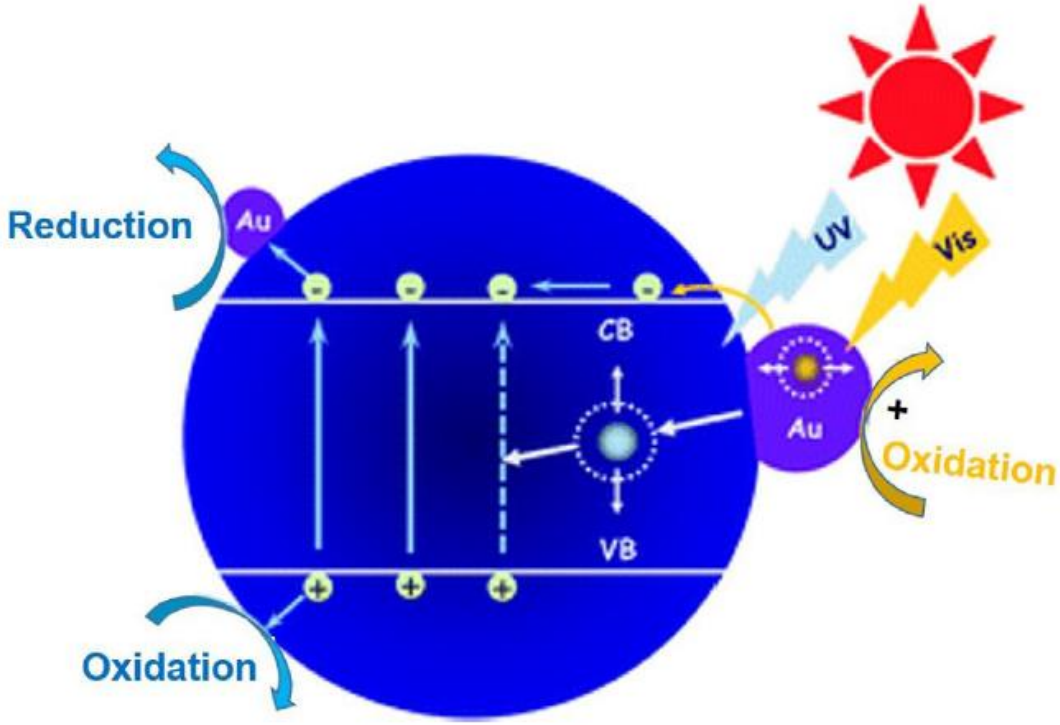
+ non-toxic, enhanced VIS-light performance

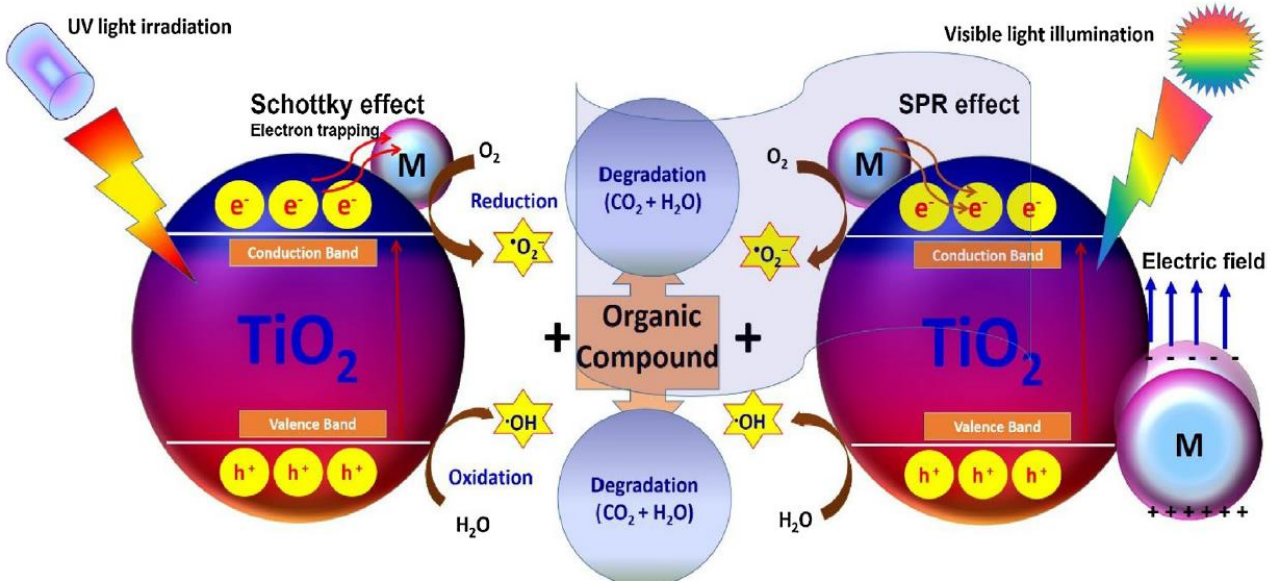
ZnO (zinc oxide) 3.37 eV

+ good surface modification properties
  excellent UV-light performance
- Poor VIS-light performance

Surface tuning to enhance UV-VIS activity

- Combination of different band gap materials for better performance
- Example: Noble metal doping





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Project Plan

<u>Aim of this project:</u> Demonstrate proof-of-principle that photocatalytic approaches can eliminate (oxidise) persistent pharmaceuticals

1. Literature review
2. Compound selection
3. Develop analytical techniques - HPLC-MS vs Raman spectroscopy to identify pharmaceuticals at low ng/L concentrations
4. Develop experimental set-up:
   Drug dilutions in tap-water with conventional photocatalysts such as powdered TiO2 (varying light, oxygen input and drug exposure time)
5. Conduct immobilisation experiments of photocatalysts on surfaces (physical deposition)
6. Test novel photocatalytic materials (Bi_2O_3, $BiVO_4$, g-C_3N_4) for better performance
7. Modify metal oxide surfaces for enhanced photocatalytic activity

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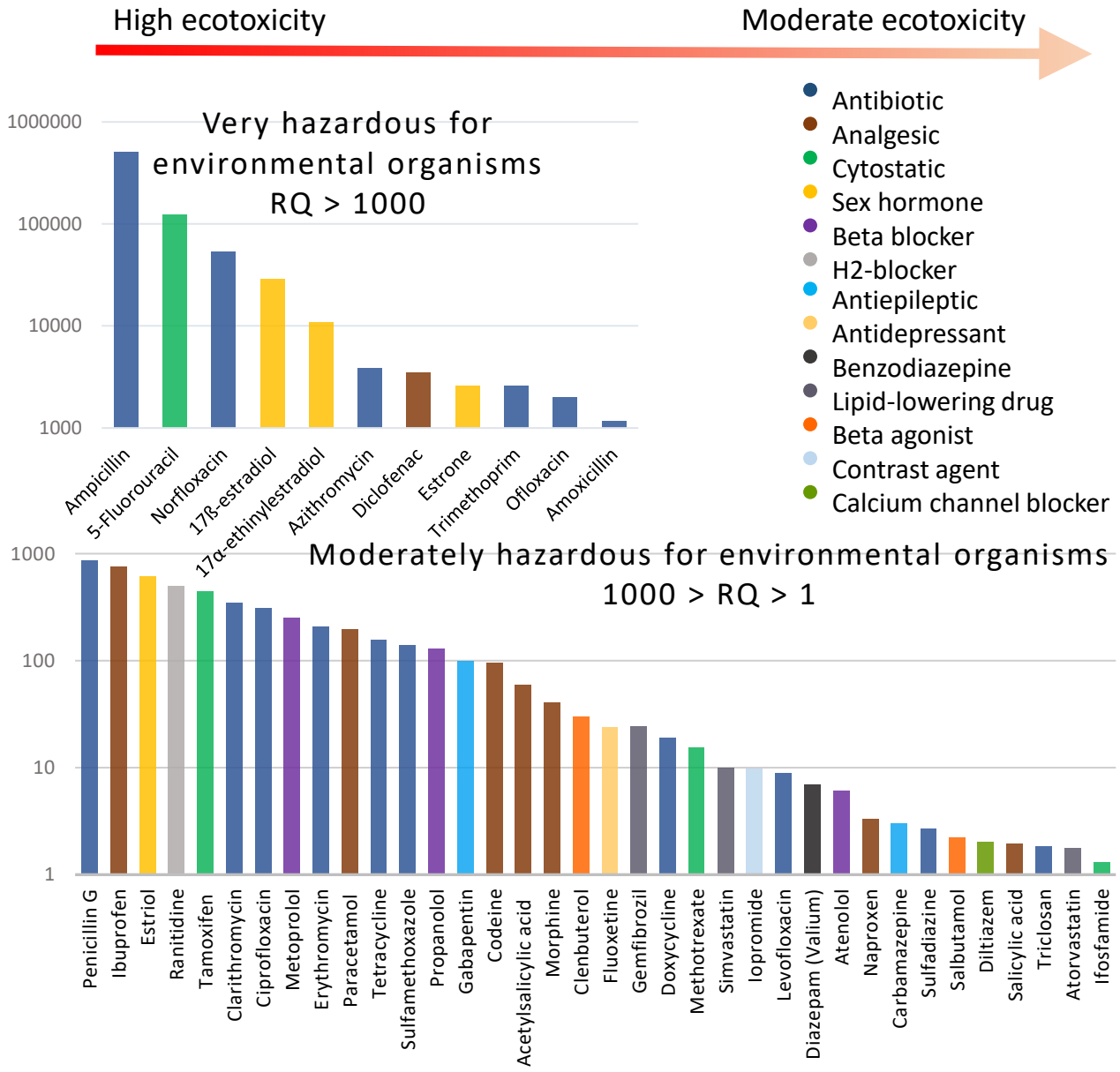
Ecotoxicity of different drugs



$$RQ = \frac{MEC_{max}}{PNEC}$$

MECmax =
Maximal drug concentration measured in hospital effluents

PNEC =
Predicted no-effect concentration (concentration below which no toxic effects in daphnia, fish, algae are observed)

Compound selection criteria

1. Ecotoxicity
2. Persistence in the environment (physico-chemical characteristics)
3. Prescribing volumes

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Development of experimental set-up for drug decay analysis

Drug dilutions in tap-water at pH 7 + UV-light + photocatalyst

Commercial powdered P25 TiO_2 in a stirred beaker suspension

- Highest possible photocatalytic activity
  –> use of maximal nanoparticle surface area
- Difficult photocatalyst recovery !

Immobilisation of P25 TiO_2 on different supports

- Glass beads: Dip-coating (sol-gel)
- Textile: Heat deposition
- Flat surfaces, diverse materials:
  Physical Vapour Deposition (PVD)

Further experiments with prototype filter set-up

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Beyond proof-of-principle:

- Toxicity studies on photocatalytic transformation products
- Surface tuning of photocatalysts

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Thank you