Photocatalytic Disinfection: Fundamentals & Futures

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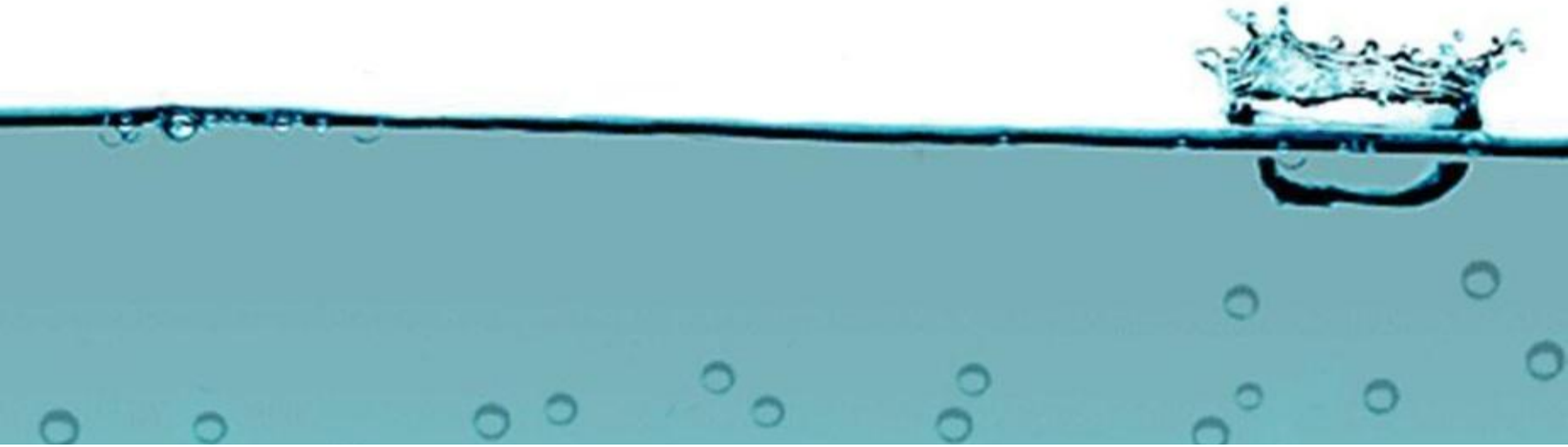

AOPs PhD School

European PhD School on AOPs, Salerno, July 2015

Presentation outline

- Short introduction to NIBEC
- Solar and photocatalytic water disinfection processes
- Developing world problems – providing safe and clean, potable water
- Developed world problems – BIG problem with antimicrobial resistance

Engineering is as important (maybe more) than chemistry/biology for real world applications!

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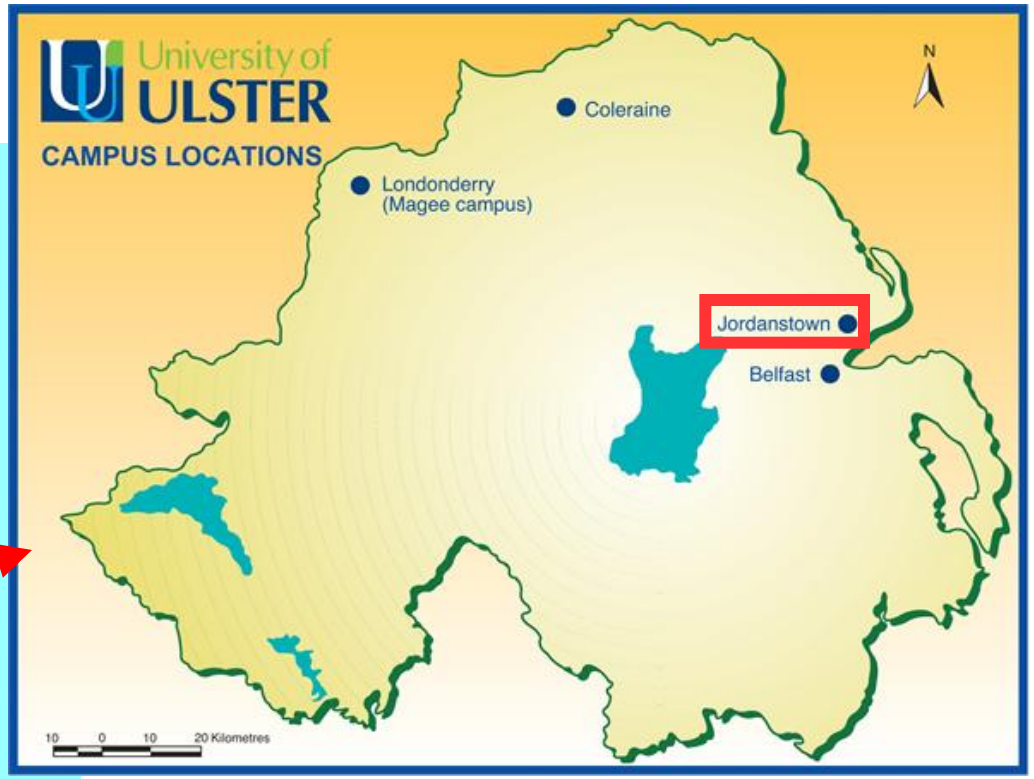


Largest university on the island of Ireland

Jordanstown campus:

Engineering, Health Science and Sports

University of ULSTER

Nanotechnology and Integrated BioEngineering Centre (NIBEC)

Multi-disciplinary R&D centre: Materials chemistry/engineering/nanotechnology/biology

Priority pollutants in drinking water sources

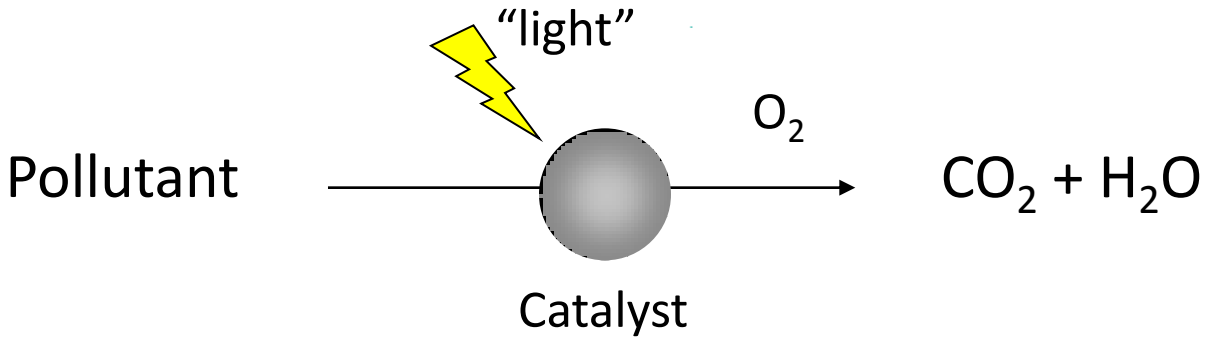
- Chemicals:
  - Persistent organic pollutants (POP'S)
  - Endocrine Disrupting Chemicals (EDC's)
  - Pharmaceuticals Personal Care Products (PPCP's)
  - Disinfection by-products (DBP's)

- Pathogens
  - Chlorine & ozone resistance, DBP formation

    e.g. Bacterial spores, protozoans, biofilms

Photocatalysis

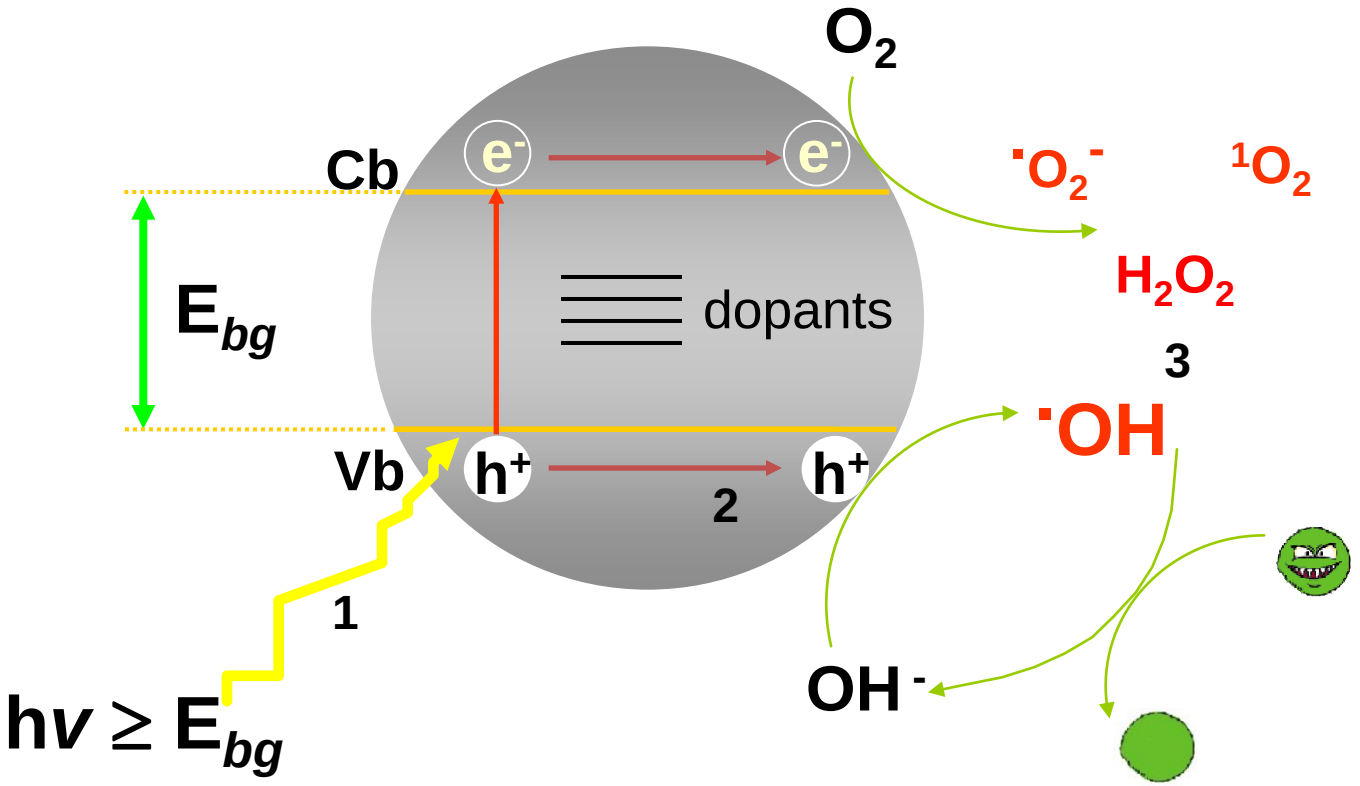
"The use of a catalyst to accelerate a photochemical process"



Pay close attention to control experiments!

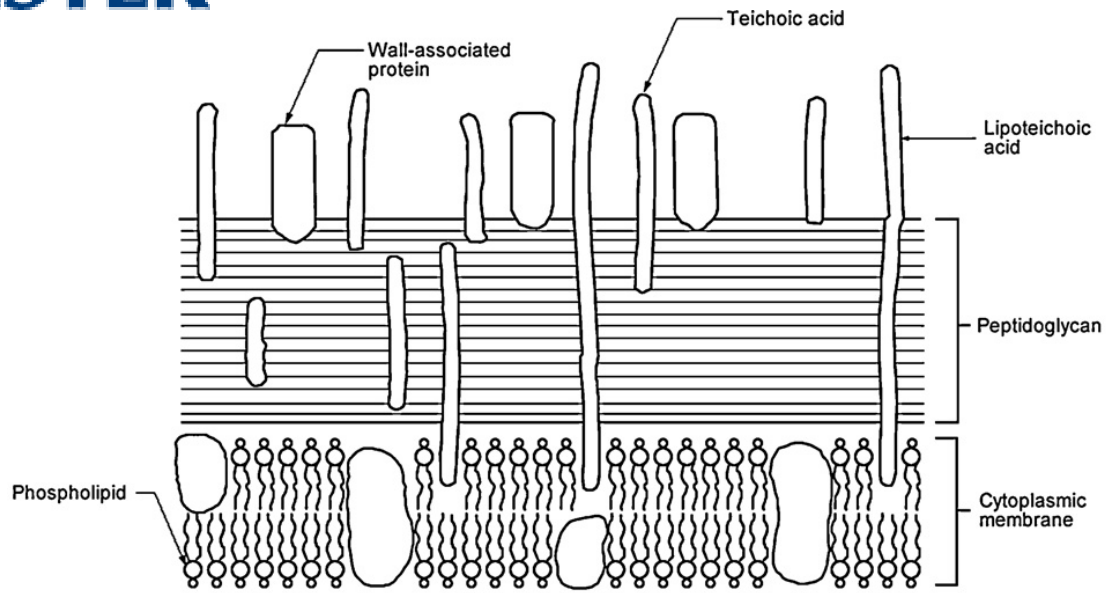
Why TiO_2?? Insoluble solid, abundant, cheap, safe E171 is non-toxic (bulk form yes, nanomaterials?)

Photocatalytic disinfection

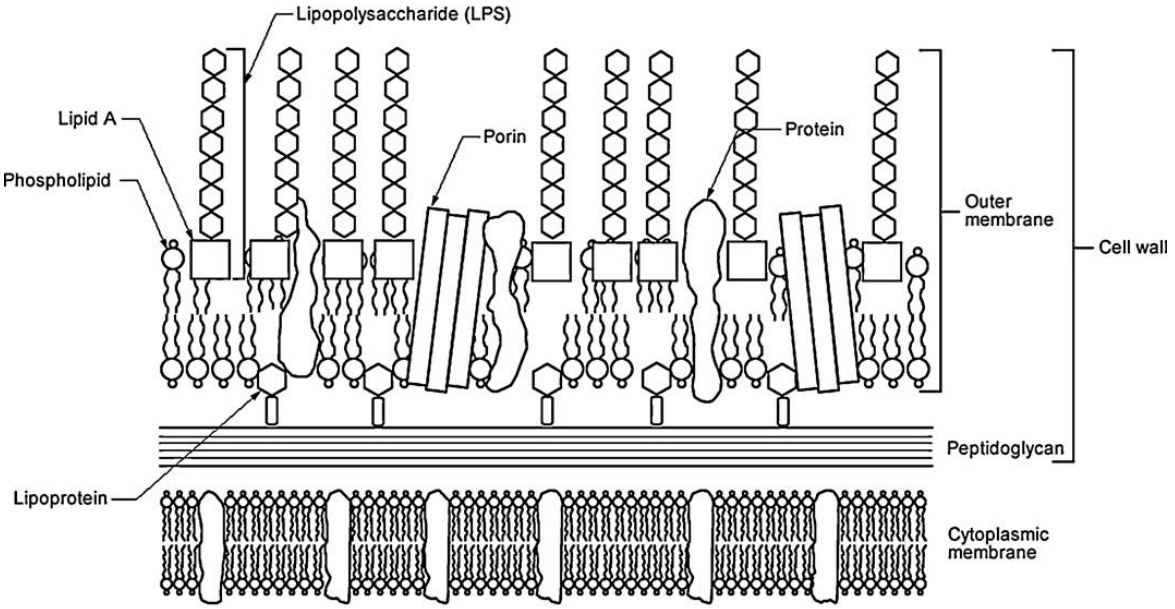


1: Activation of the photocatalyst using UV energy
2: Migration of charge carriers to the surface of the particle
3: Production of reactive oxygen species and inactivation of pathogens

Bacterial cell surface is not simple



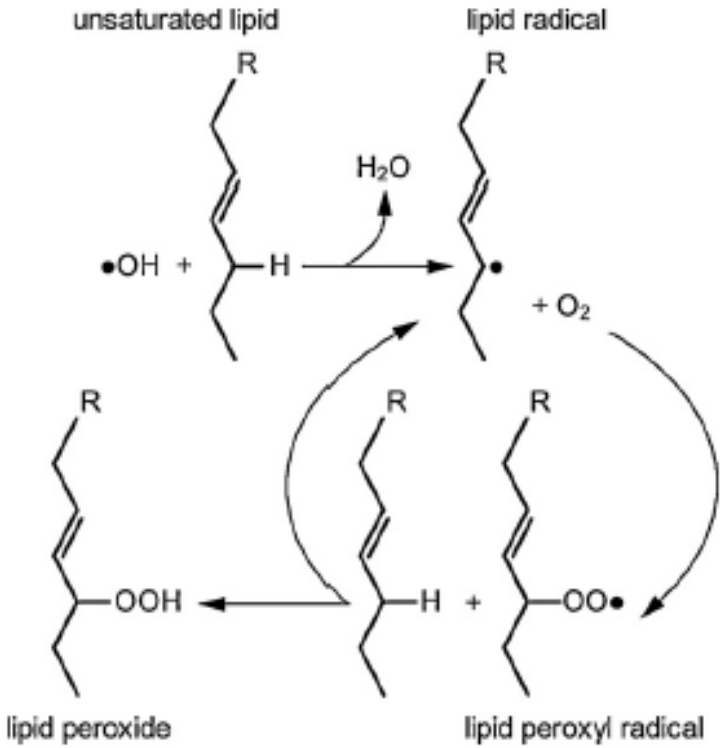
Gram positive (e.g. MRSA)



Gram negative (e.g. *E. coli*)

Photocatalytic disinfection

Main mechanism reported is lipid peroxidation of the phospholipid bylayer:



chain reaction

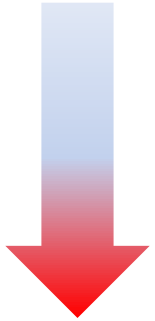
Other process can also take place using ROS, with less positive reduction potentials, e.g. singlet oxygen, super oxide radical anion, hydrogen peroxide and more radicals

(See Pulgarin / Kiwi group output for some great papers on mechanisms)

Photocatalytic disinfection

>1000 papers on PC disinfection, UU research has shown disinfection of:

- *E. coli* - Dunlop *et al* J. PhotoChem. PhotoBiol. A 2002
- Clostridium spores - Dunlop *et al* J. PhotoChem. PhotoBiol. A 2008
- Cryptosporidium - Sunnotel *et al* J. Water and Health 2009
- In real water - Alrousan *et al* Water Research 2009

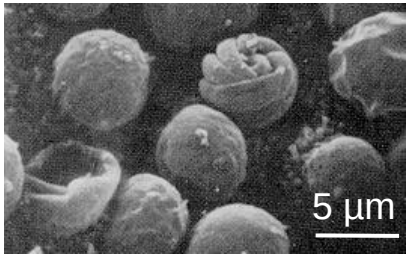


Time needed for killing increases

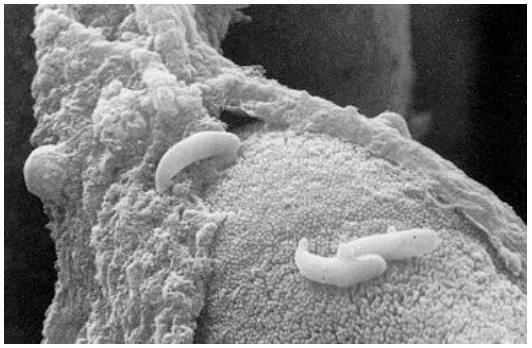
- Hospital acquired infections:

MRSA & C. diff – Dunlop *et al* J. PhotoChem. PhotoBiol. 2010
("real" bacteria respond differently than simple "lab" organisms)

Resistant pathogens - Crypto



Cryptosporidium parvum oocysts



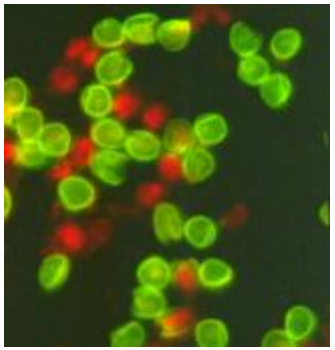
Excystation in intestine

"Illness"

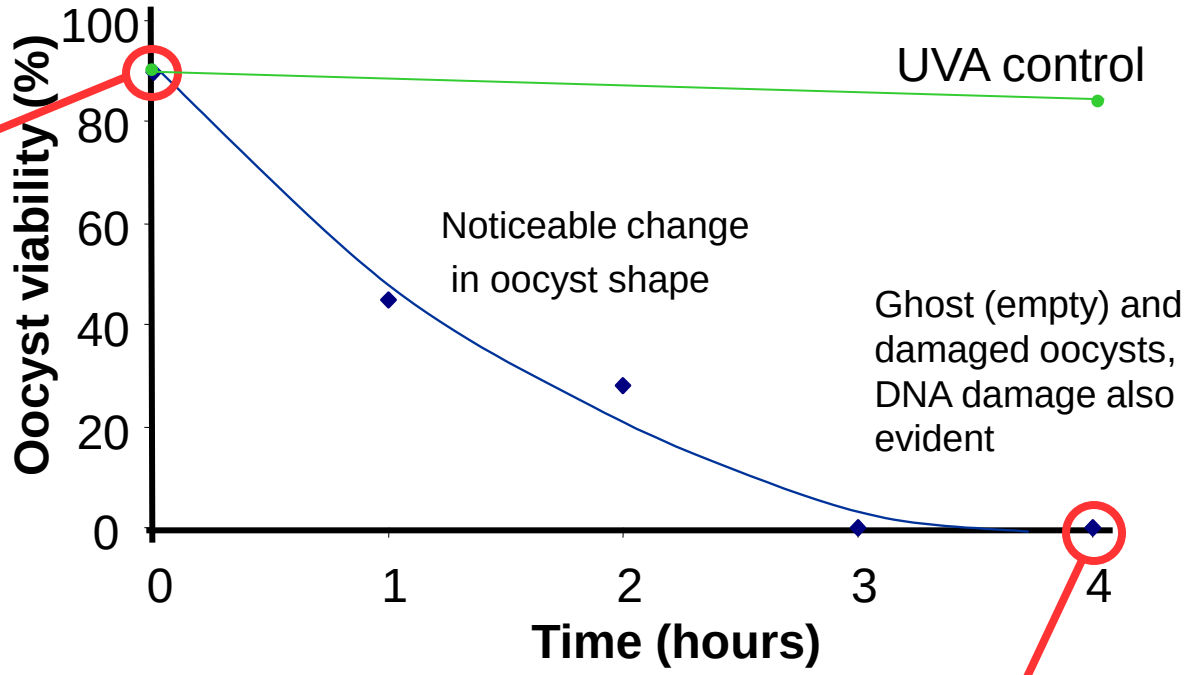
Waterborne outbreaks recorded in

America, Australia, UK and Northern Ireland!

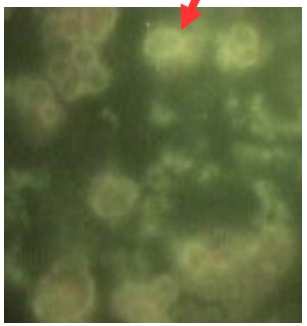
Resistant pathogens - Crypto



Vital Dye Exclusion Assay indicated 90% oocyst viability

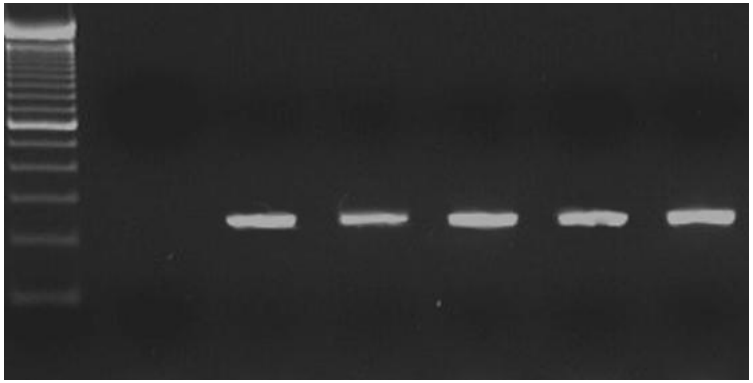


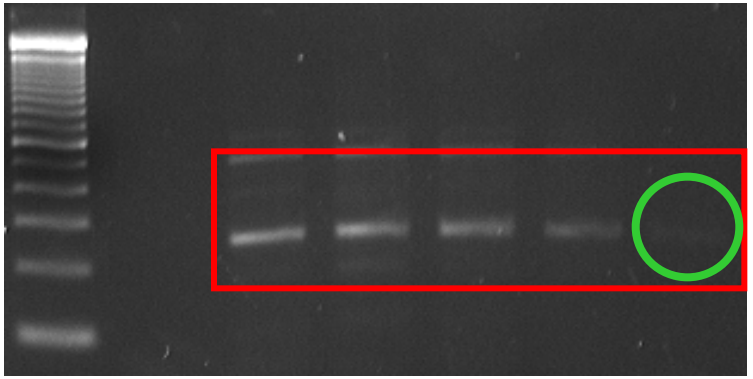
VDEA showed extensive damage to oocysts



Sunnotel *et al* J. Water and Health 2009

Resistant pathogens - Crypto





Relative mRNA expression of *Cp* LDHI coding region

Sunnotel *et al* J. Water and Health 2009

Where can we use photocatalysis?

Water and health in developing countries

- Approx 1 billion people without access to safe water
- 4 Billion cases of diarrhoea (88% due to unsafe water)
- 1.8 Million die each year (majority under 5 yrs)

Typical drinking water sources:

Water for Life – Making it Happen. WHO/UNICEF

Household water treatment options

1) Gravity filtration

Katadyn (ceramic filters) €10-20 each

Vestergaard (Lifestraw ®) €2.50 / 1000L

2) Chlorination

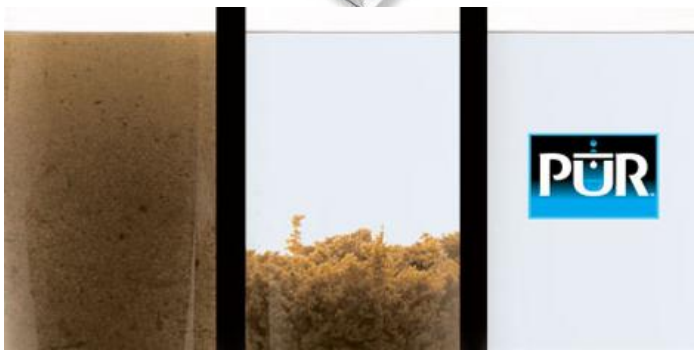
Medentech (Aquatabs®) €0.35 / 1000L

PSI (Water Guard®) €0.30 / 1000L

3) Flocculation/Chlorination

Procter & Gamble (PUR®)

€8.00 / 1000L



Household water treatment options

4) Solar water disinfection (SODIS):

- ✓ Recommended by WHO
- ✓ Easy to use
- ✓ No chemicals
- ✓ Inexpensive
- ✓ Maintenance free

Solar disinfection (SODIS)

1 Wash the bottle well the first time you use it

Fill the bottle 3/4 full with water

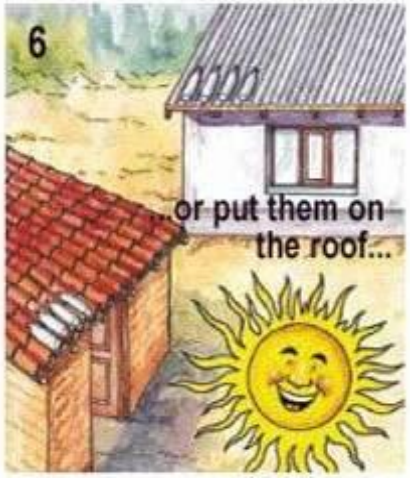
Shake the bottle for 20 secondes

4

Now fill up the bottle fully and close the lid

Place the bottles on a black iron sheet

6



Expose the bottle to the sun from morning until evening for at least six hours

The water is now ready for consumption

SODIS used daily by 4.5 million people across 30 countries

How does SODIS work?

SODIS is a synergistic process:

a) solar UV-A radiation (cell damage)
b) solar IR (increased temperature)
c) production of oxygen radicals

Problems:

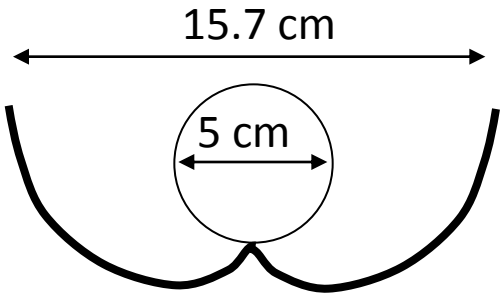
- Some pathogens are resistant to SODIS
- Slow process, 6 hours solar exposure recommended
- Low volumes in current “reactors”

Can we use engineering to enhance SODIS??

“Pilot scale” SODIS – larger volume

In collaboration with Dr Pilar Fernández, Plataforma Solar de Almería-CIEMAT, Almería, Spain

Low cost enhancement technology: CPC reflectors

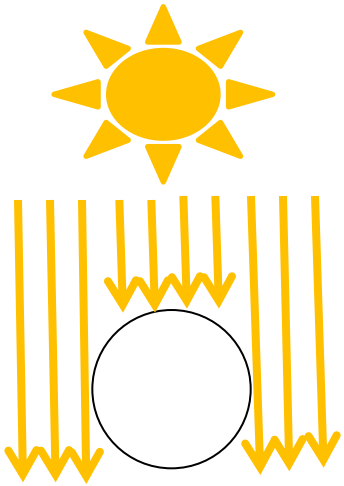


Length (irr.) = 128.0 cm

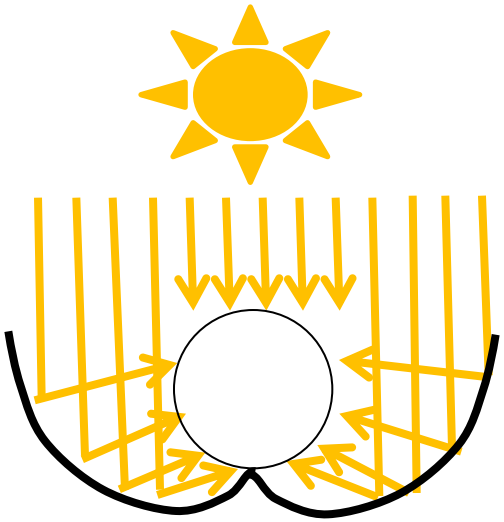
Aperture$_1$ = 15.7 cm /CPC

Irr. Area$_1$ = 0.21 m^2 /CPC

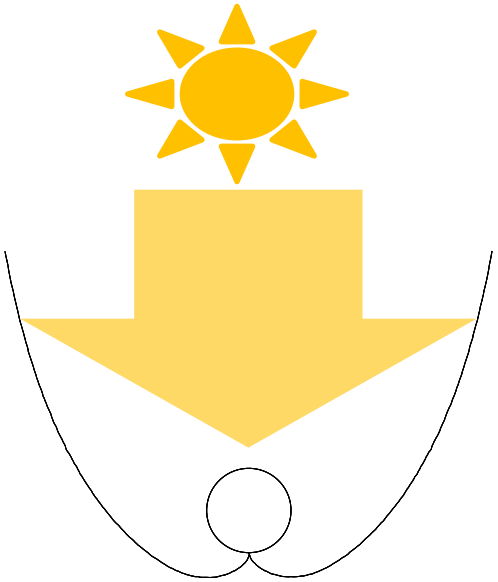
Low cost enhancement technology: CPC mirrors



Concentration factor = 0.5



Concentration factor = 1



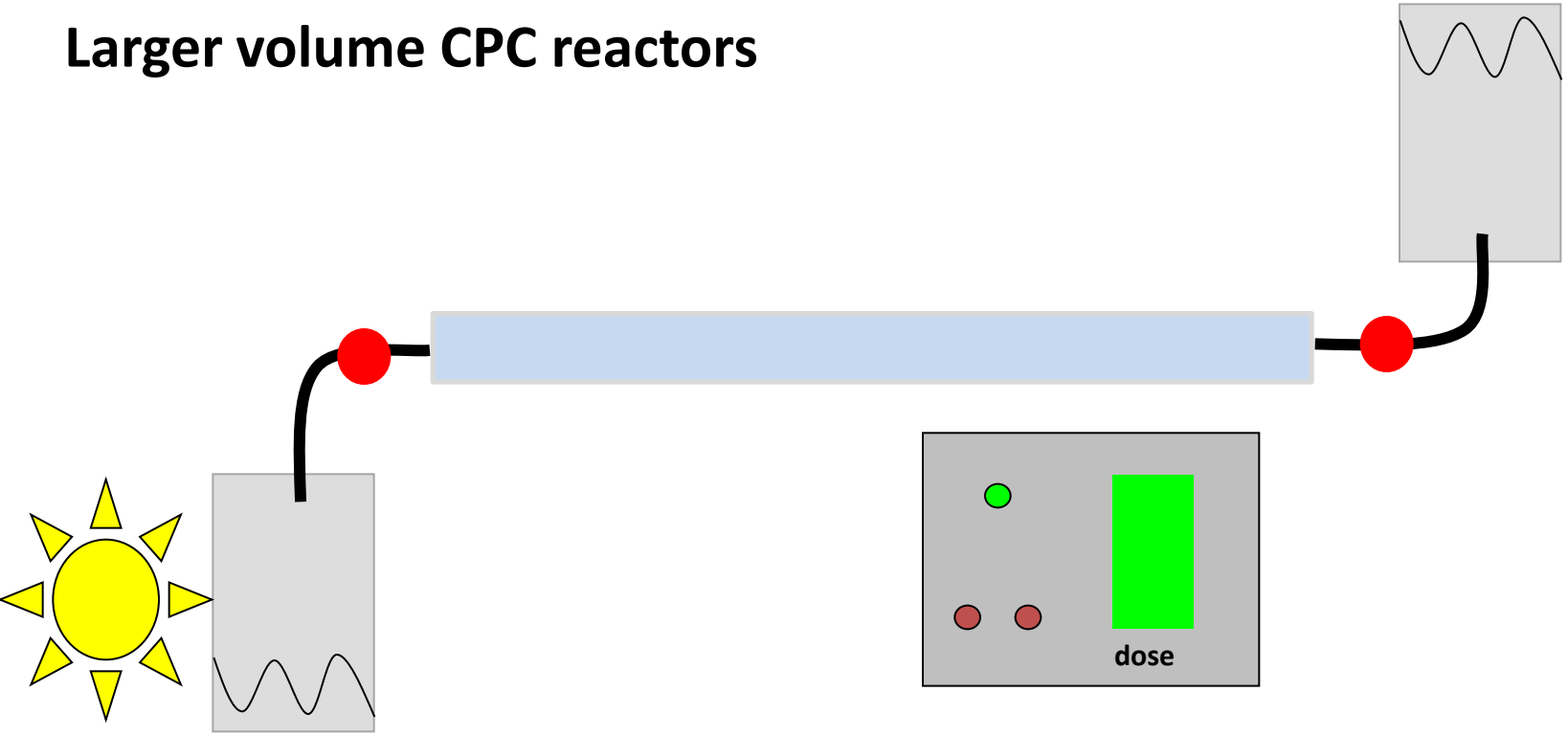
Concentration factor = 2

100% more energy collected with each doubling of the CF

More photons = more disinfection (my level of physics!)

Sequential batch “SODIS”

Larger volume CPC reactors



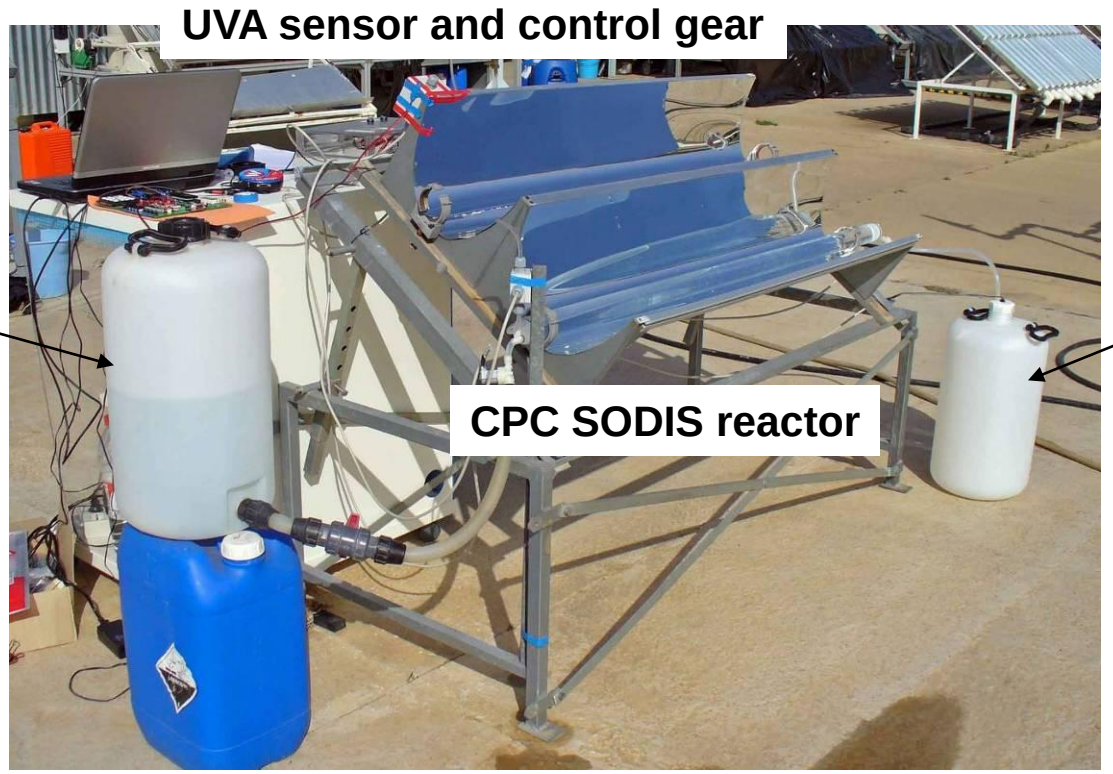
Full reservoir, minimum UV level - Fill

Measure intensity and calculate “lethal dose”

When “lethal dose” reached - Empty and restart

Polo Lopez *et al* J. Haz. Mat. 2011

Sequential batch “SODIS”



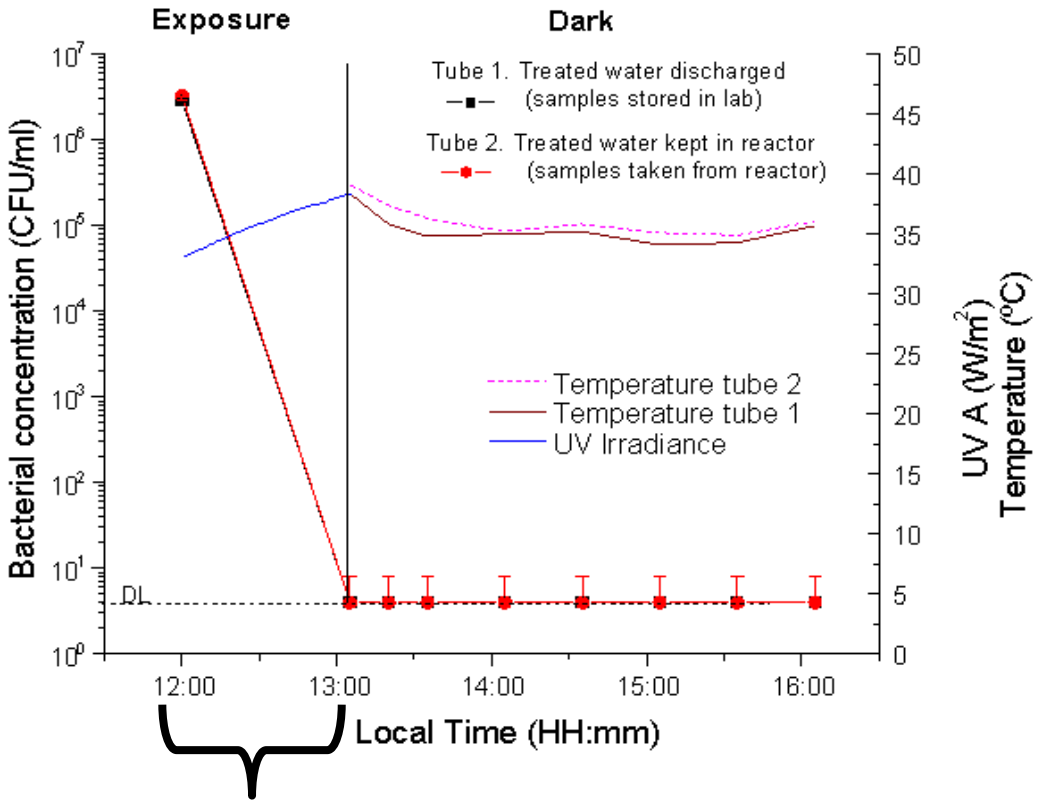
Fully automatic, gravity fed, low power consumption, low cost

Polo Lopez *et al* J. Haz. Mat. 2011

Sequential batch "SODIS"

Did the system work?

Accumulated UVA dose = **68.0 W·h/m²**



Treatment time 1.0 hour …. NO bacterial regrowth!

"Large" 6 tube reactor: initial cost €450, 100 L/day, €0.15 for 1000L

Polo Lopez *et al* J. Haz. Mat. 2011

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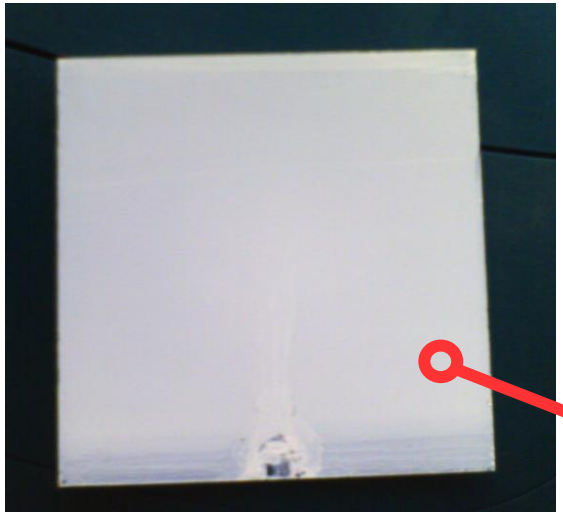
OK, SODIS works
but some organisms are resistant,
and we'd like to speed it up

Why not try photocatalysis …
remember developing world can't
afford the technology to
remove TiO_2 powder!

Immobilisation of photocatalysts

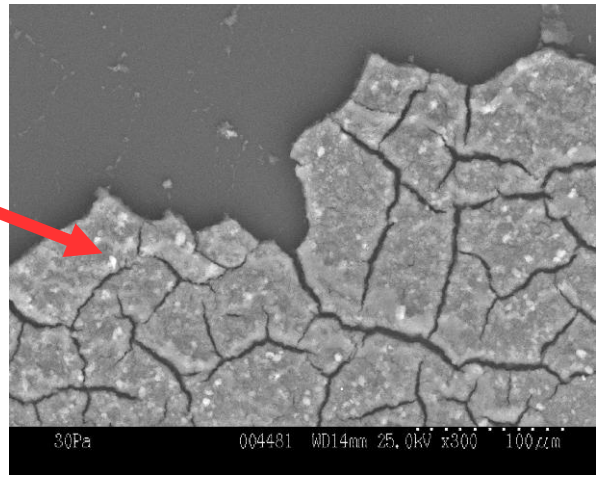
TiO_2 powder

- Commercial sources
- Particle 5 nm – 5 μm



TiO_2 coated glass

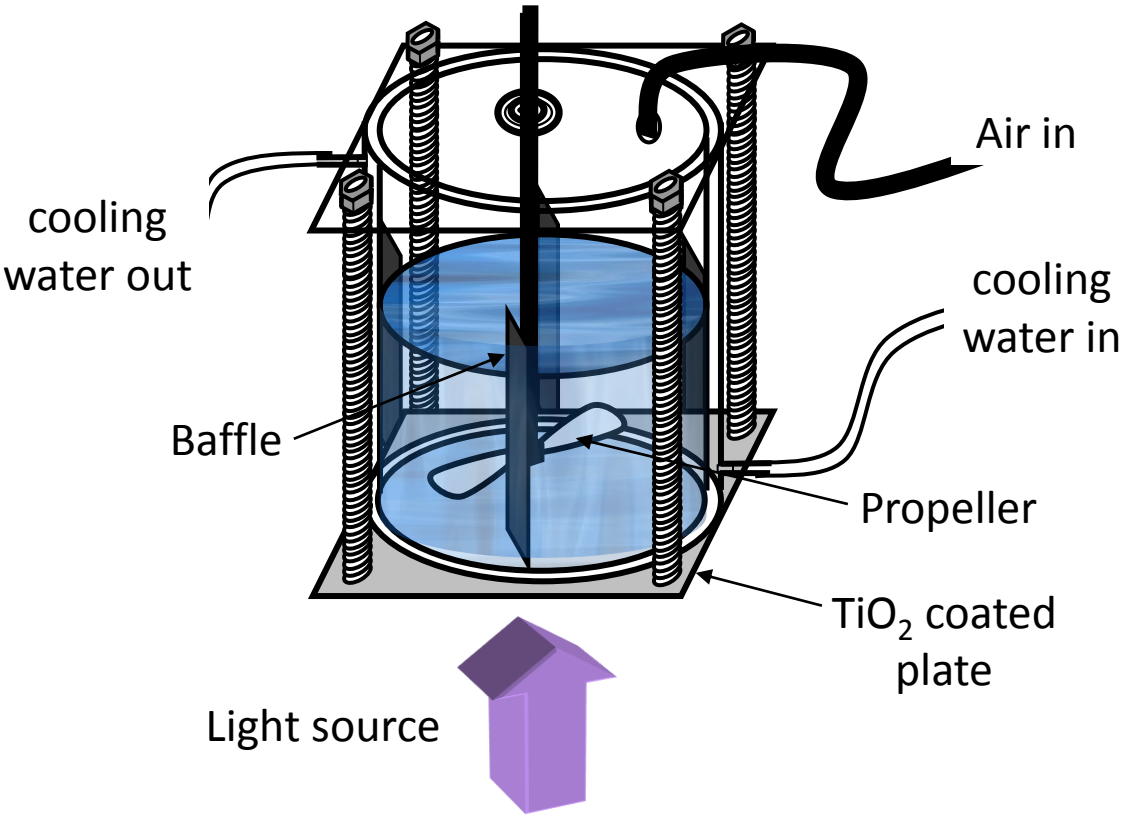
Techniques:
Dip and spray coating

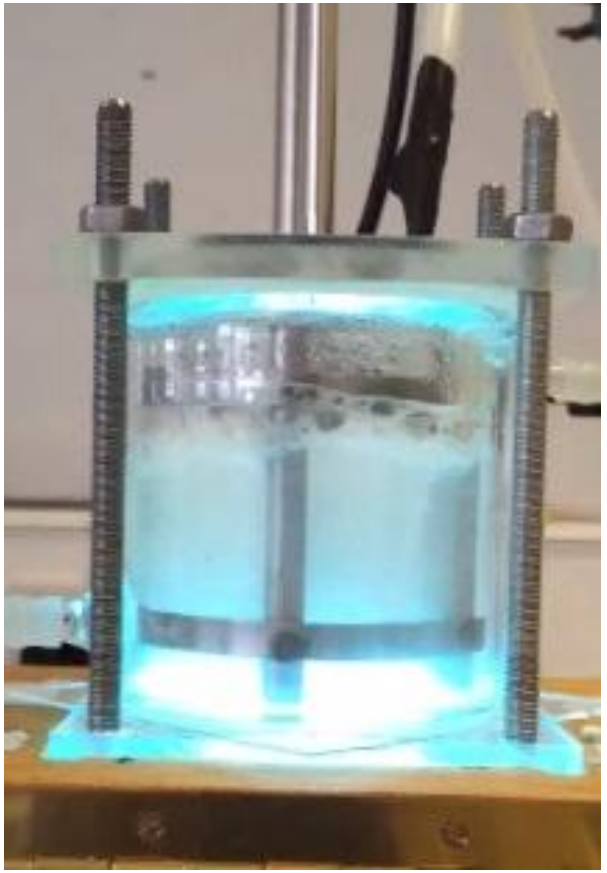


Nanostructured,
high surface area,
mesoporous film

NOTE: Mass transfer is a BIG issue in thin film based photocatalytic systems!

Assessment of photocatalysts



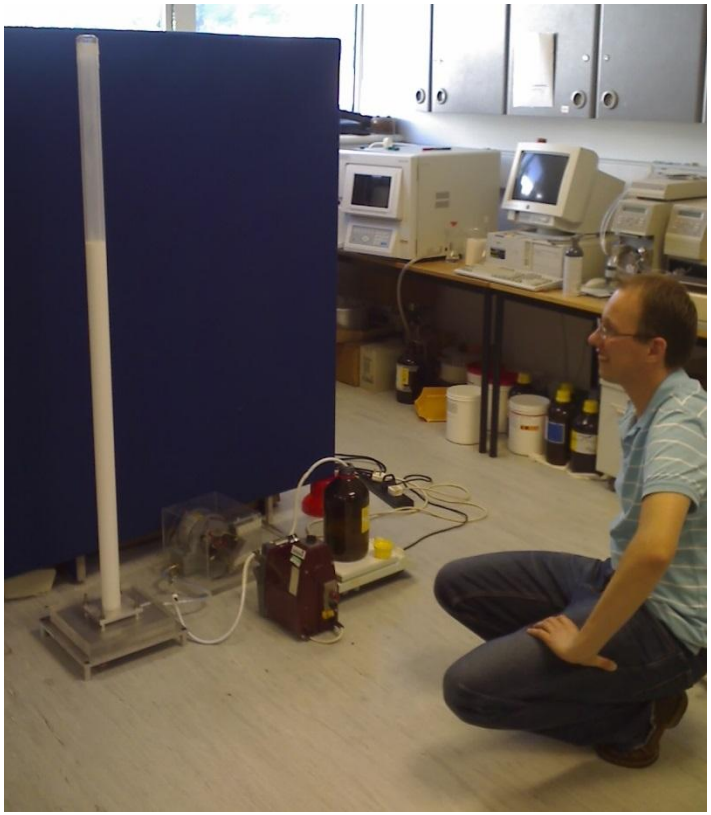


Stirred Tank Reactor – gives very efficient mixing for our lab studies

Immobilisation of photocatalysts

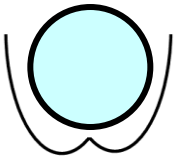
Scale-up for solar excitation – Dip coating Degussa P25 from methanol suspension

1.5 M long Pyrex glass tubes

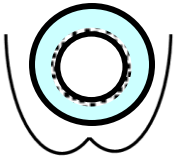


Automated coating system (approx 60 coating cycles)

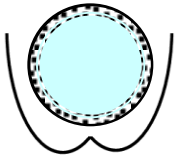
0.5 mg TiO_2 / cm^2



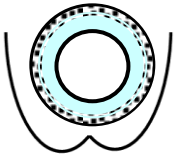
Uncoated external



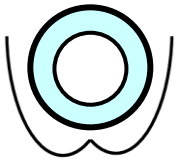
Uncoated external, TiO_2 coated internal



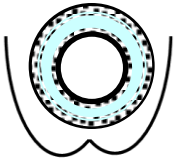
TiO_2 coated external



TiO_2 coated external, uncoated internal



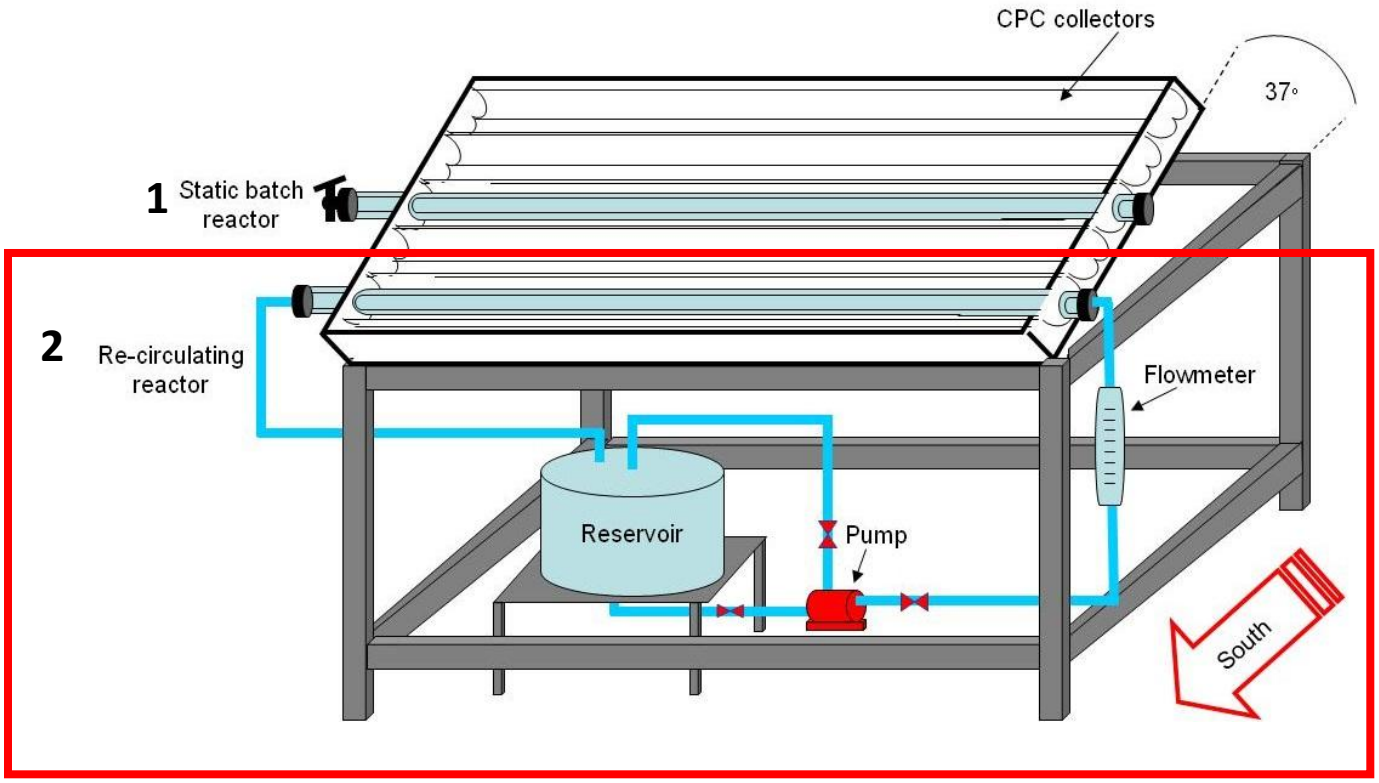
Uncoated external, uncoated internal



TiO_2 coated external, TiO_2 coated internal

Alrousan *et al* Appl. Cat. B 2012

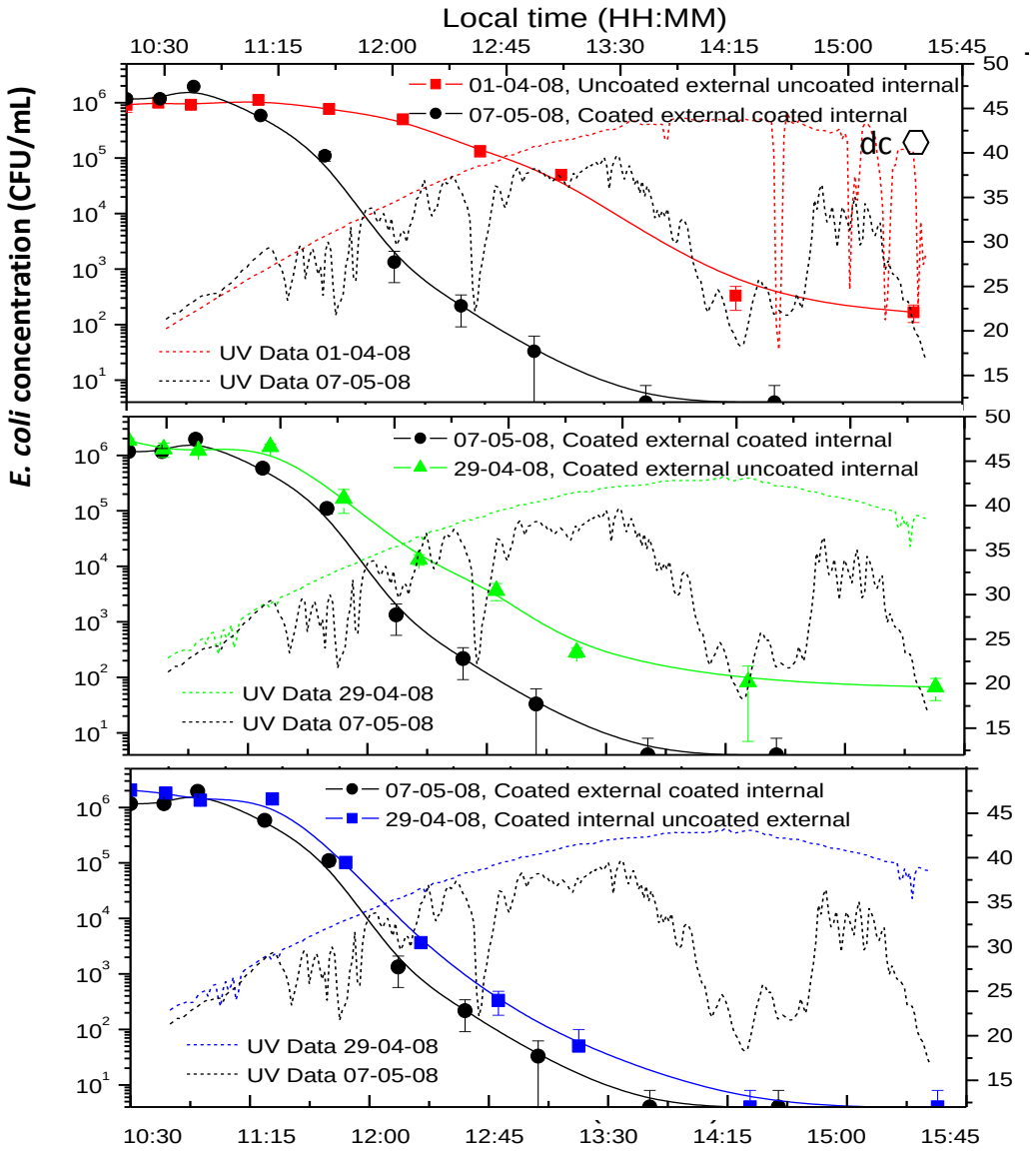
“Photocatalytic” SODIS

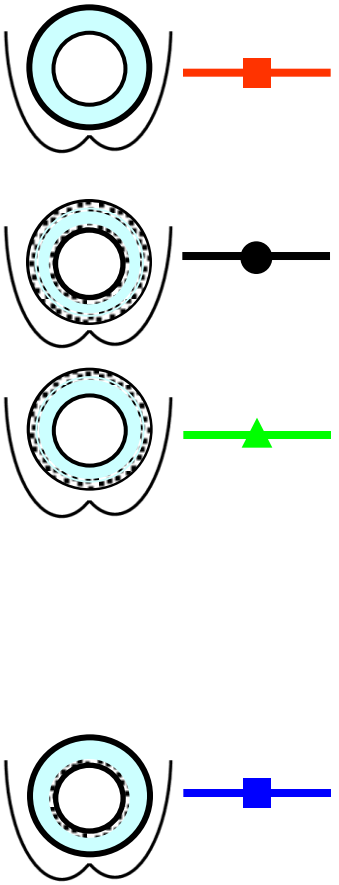


E. coli bacteria spiked into 7L natural well water and measured as a function of solar exposure time by standard microbiological tests.

Alrousan *et al* Appl. Cat. B 2012

“Photocatalytic” SODIS





Alrousan *et al* Appl. Cat. B 2012

Antibiotic resistance

- Pharmaceuticals widely used in human and animal medicine
- PPCP's "Emerging" & "Priority" pollutants in DWT & WWT
- Antibiotic resistance bacteria (ARB) - "Super-bugs"
- Healthcare acquired infections (HAI's) e.g. MRSA and C.diff
- Standard water treatment methods can inactivate ARB …
  … but ARB are widely found within WWTP and the environment
- Can AOP's inactivate ARB, preventing release to the environment?

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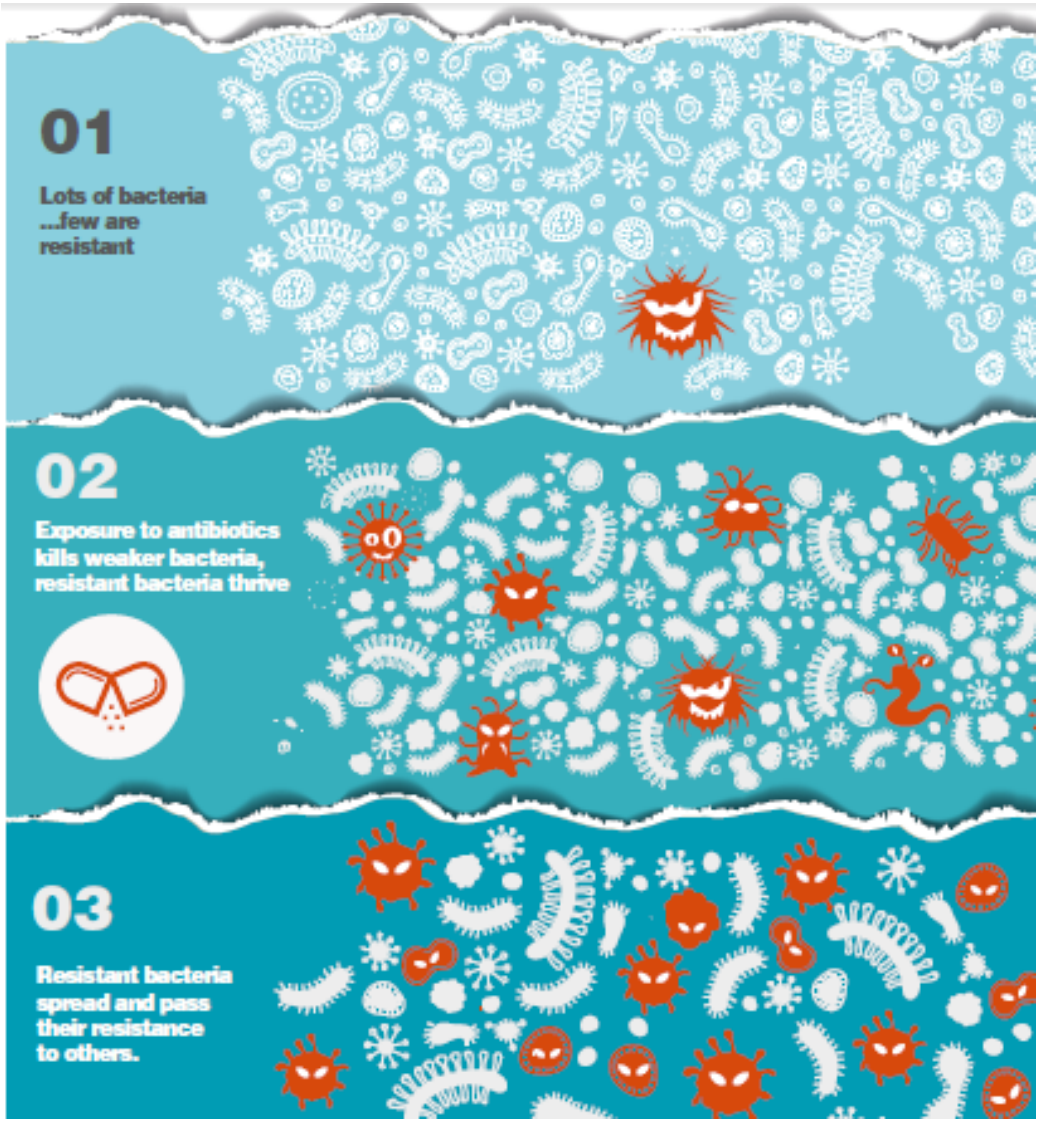
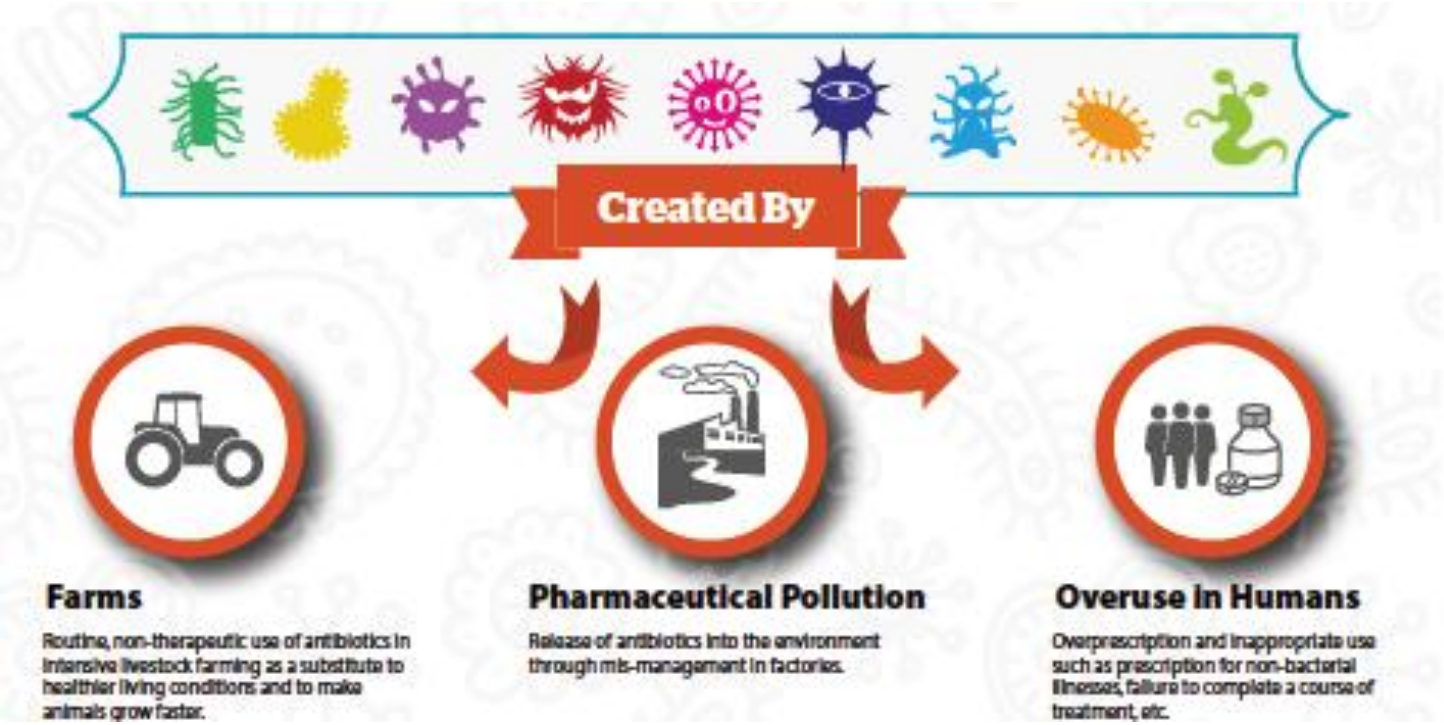
Antibiotic resistance



Antibiotic resistance



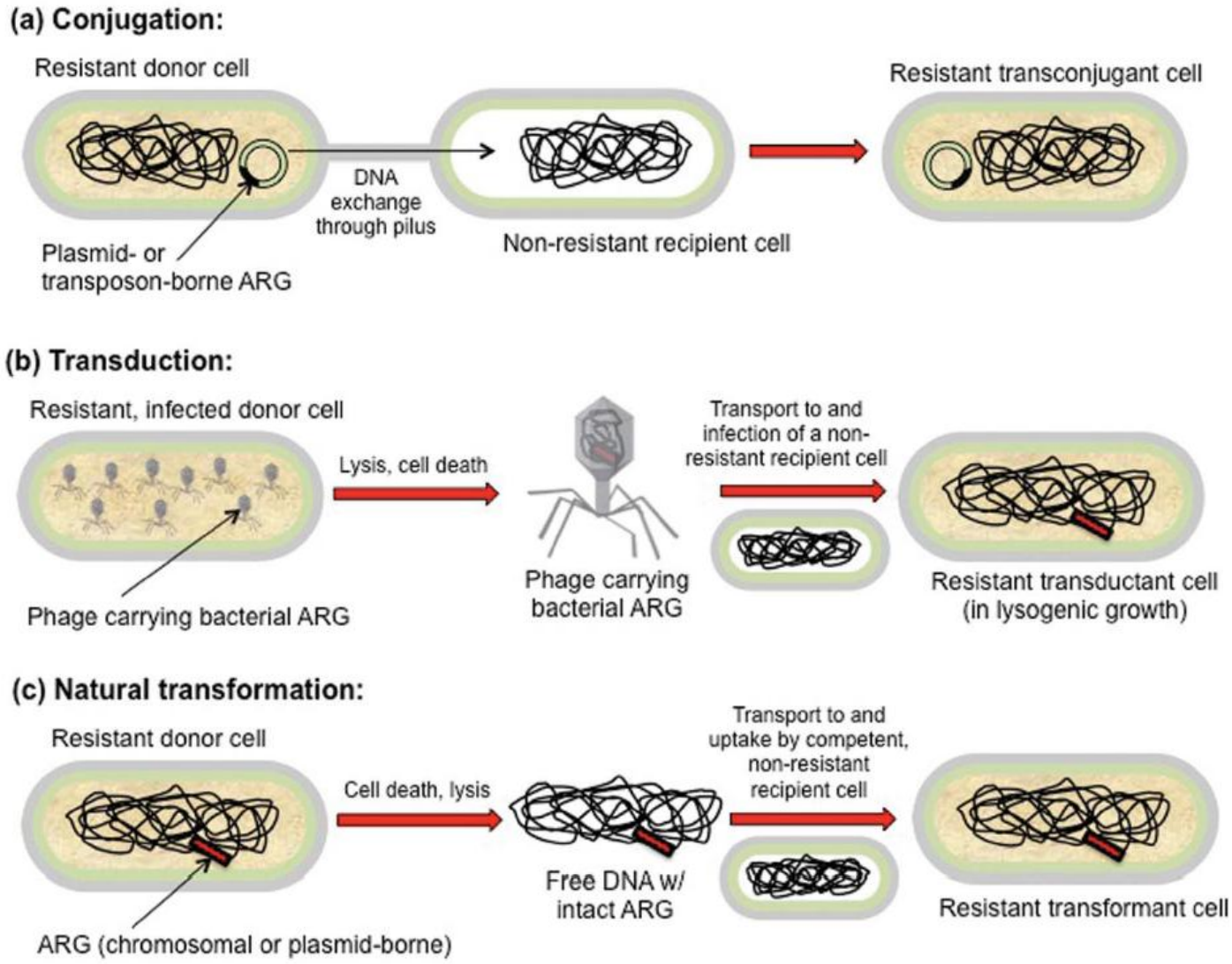
How is AMR spreading around the world?

Drug-resistant bacteria are able to travel far and wide. They can be passed on in meat, spread via contaminated manure or water used to grow food crops, travel through the air, or flourish in the bodies of people who have been contaminated. We have moved beyond the stage where resistant bacteria were rare and mostly contained to hospital environments. Today, everyone is at risk.

The resistant bacteria, carrying the genetic code New Delhi Metallo-beta-lactamase-1 (NDM-1) that was first identified in India has already been found in France, Japan, Oman and the United States. With globalisation and modern means of travel, any local health problem can soon become a disaster of global proportions.

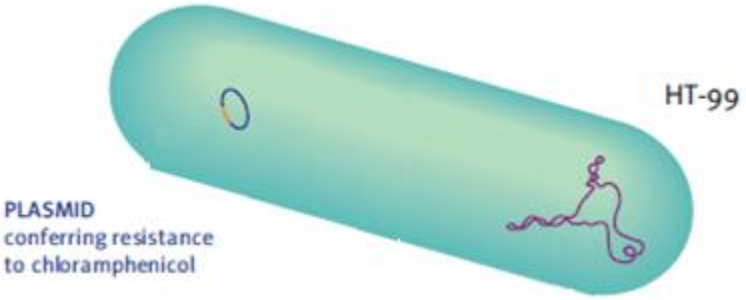
Sum Of + Us

Gene transfer mechanisms



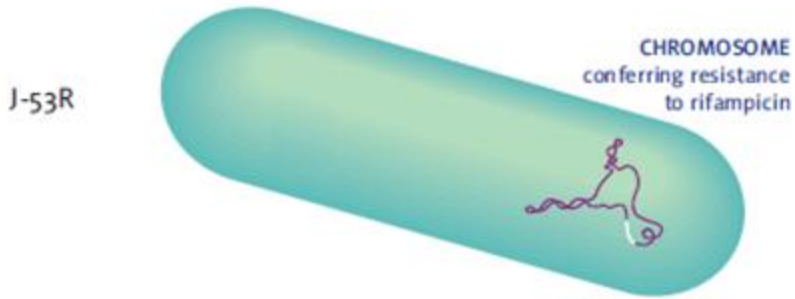
Dodd J. Environ. Monit. 2012

Antibiotic resistant bacteria



Can grow on chloramphenicol containing agar

Cannot grow on rifampicin containing agar

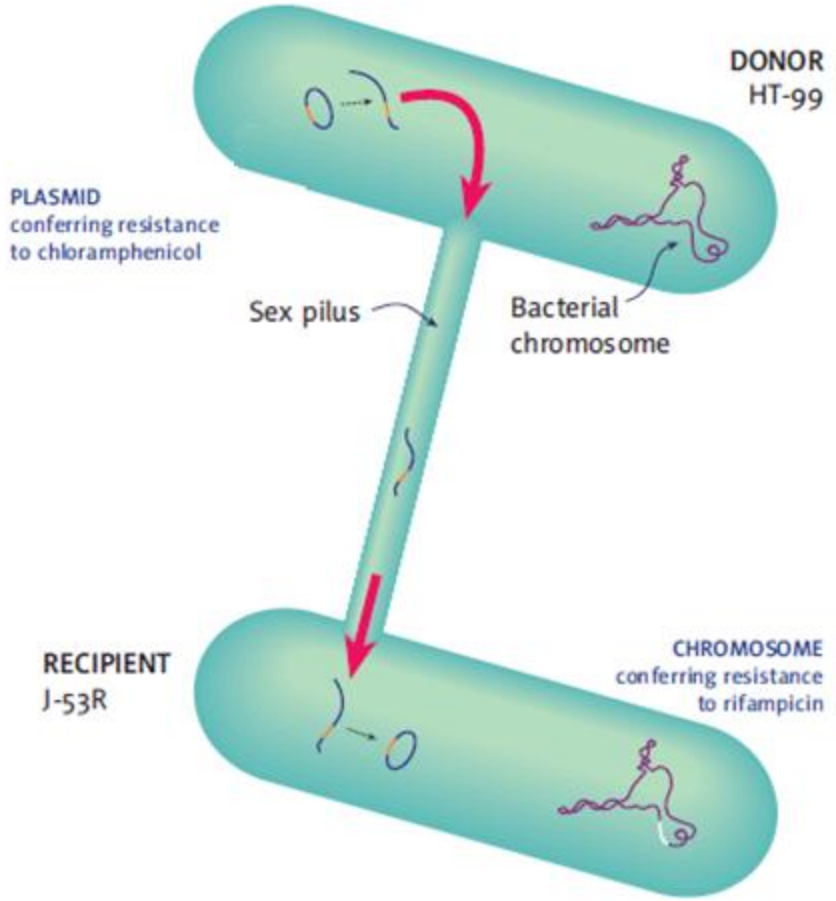


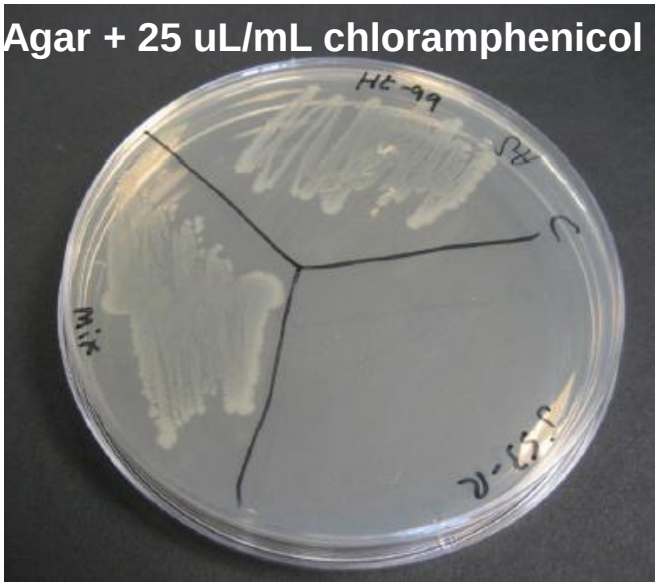
Can grow on rifampicin containing agar

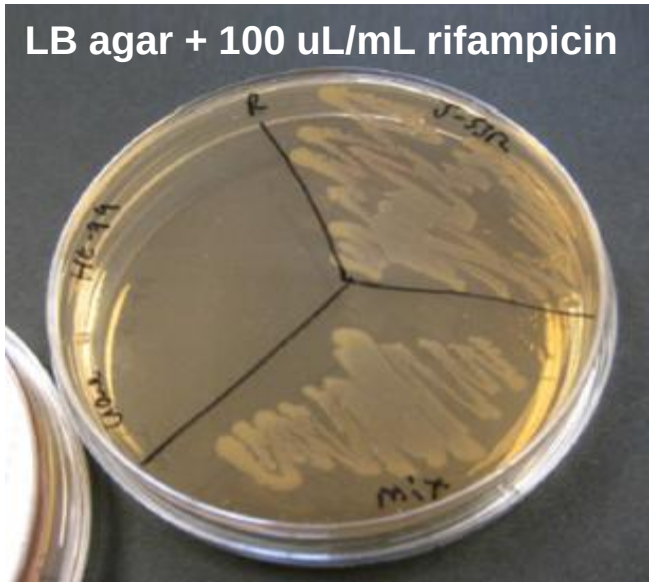
Cannot grow on chloramphenicol containing agar

ARG transfer methods

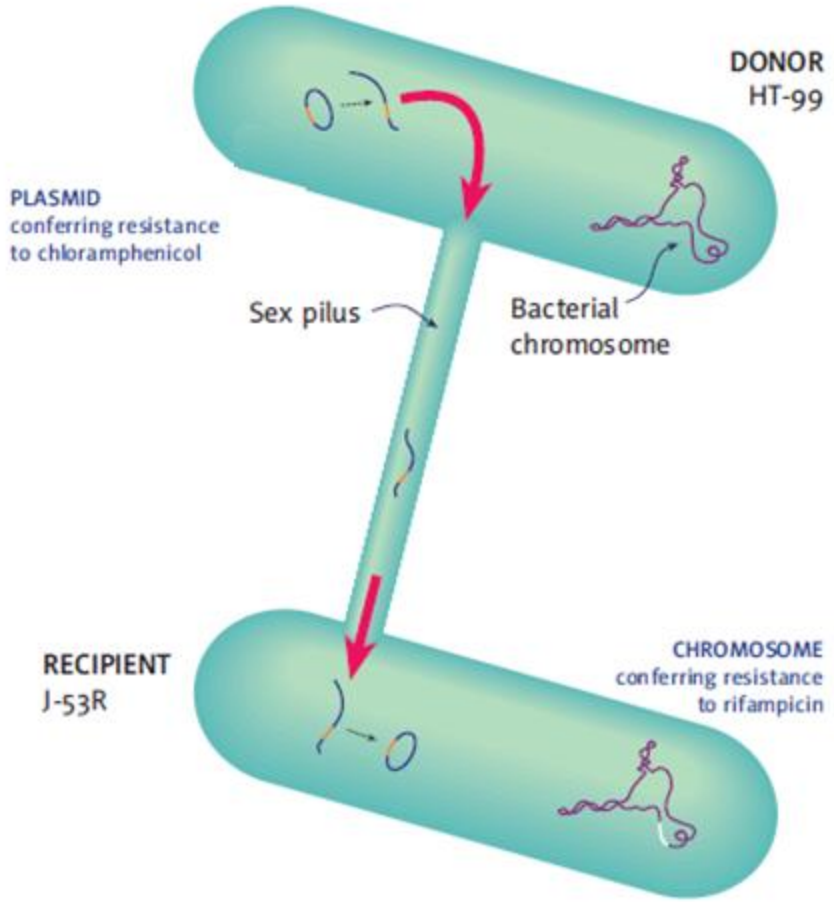
HT-99 and J-53R are a conjugated pair

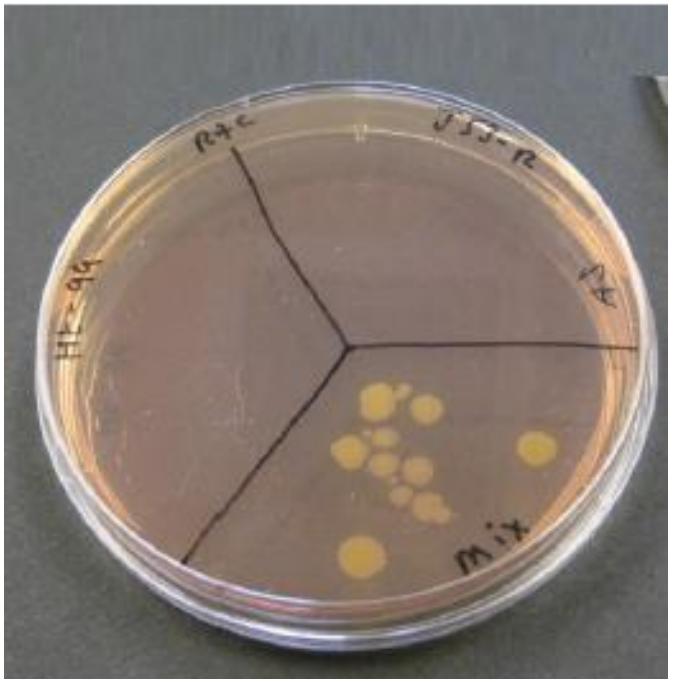






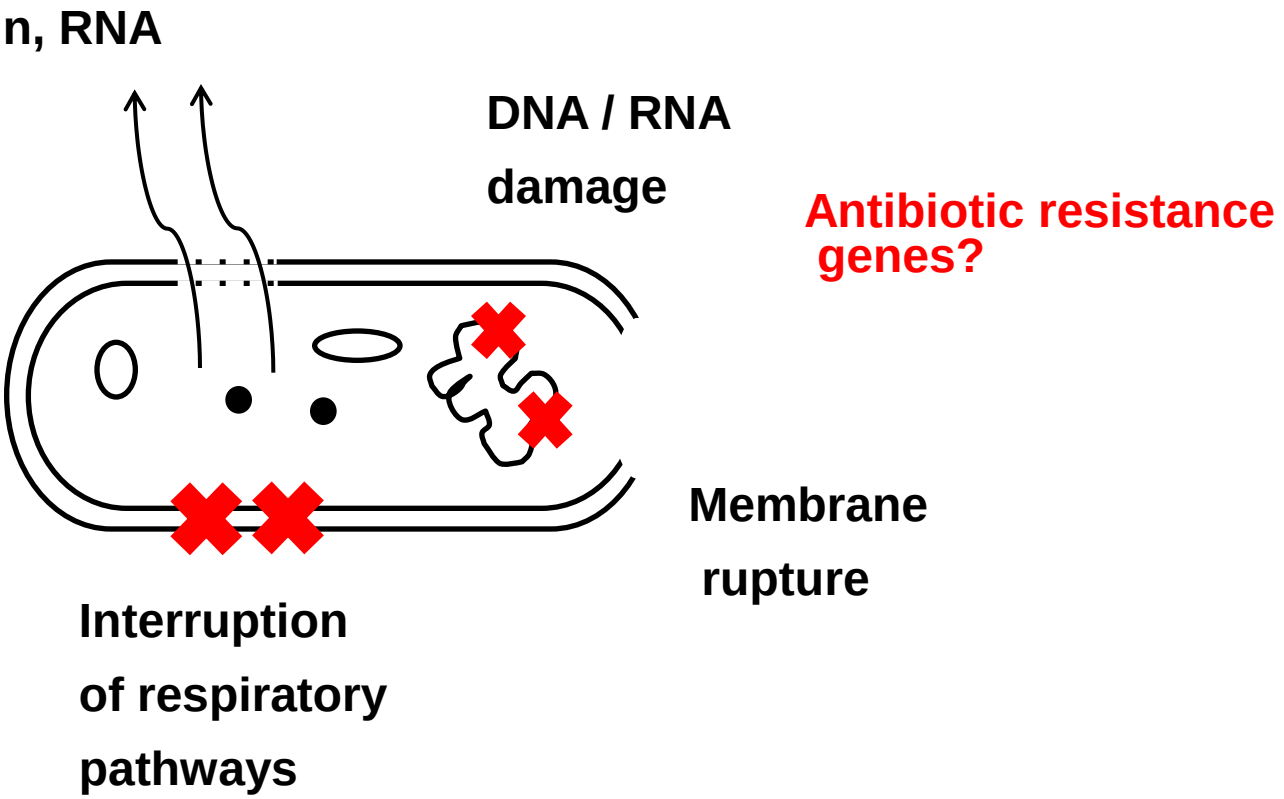
ARG transfer methods





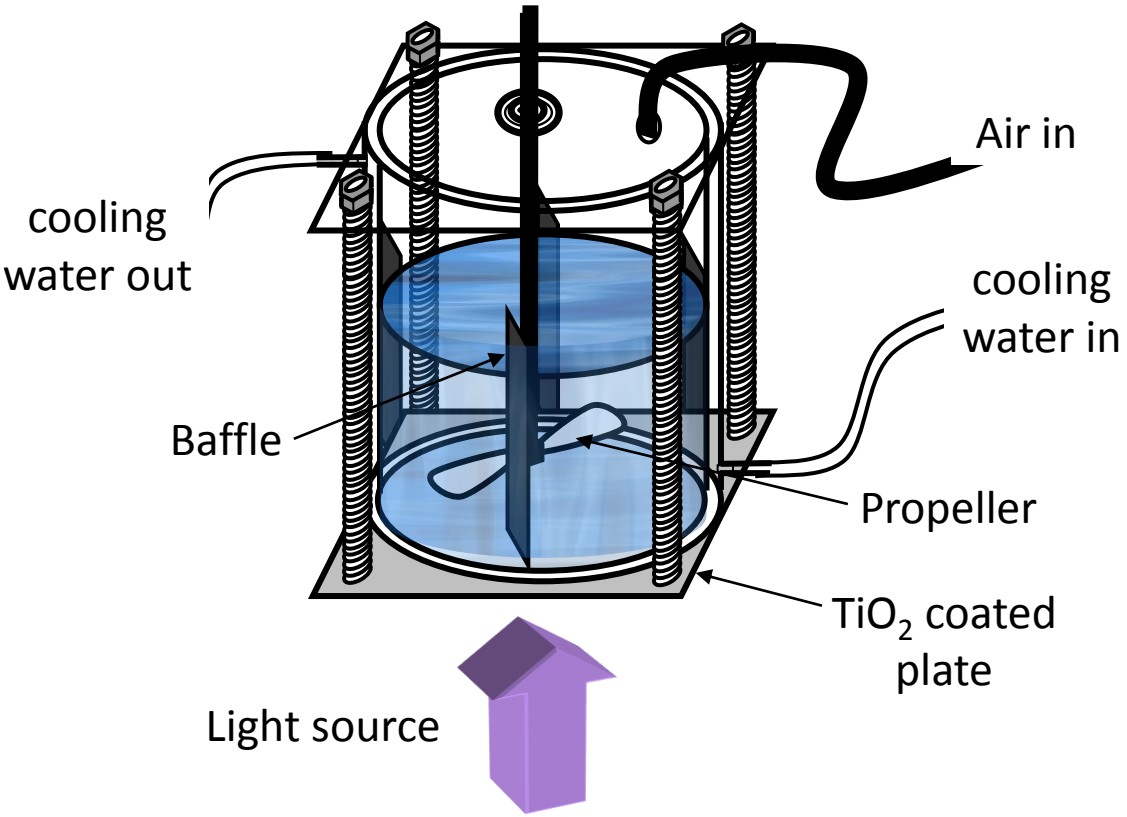
LB agar + 100 uL/mL rifampicin and 25 uL/mL chloramphenicol

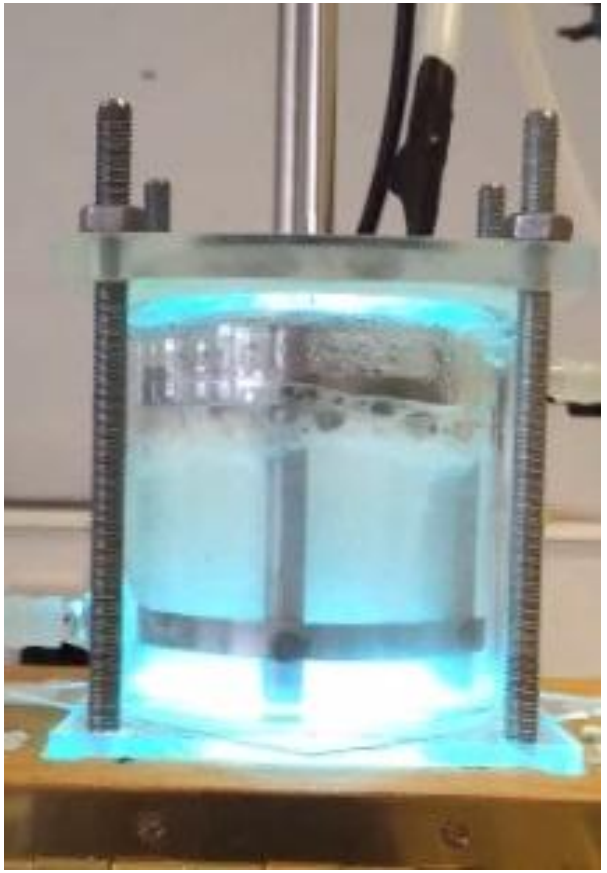
PC inactivation and stress



Organisms react to their environment – e.g. oxidative stress – and respond
What happens to cellular and genetic content released to environment?

Assessment of photocatalysts

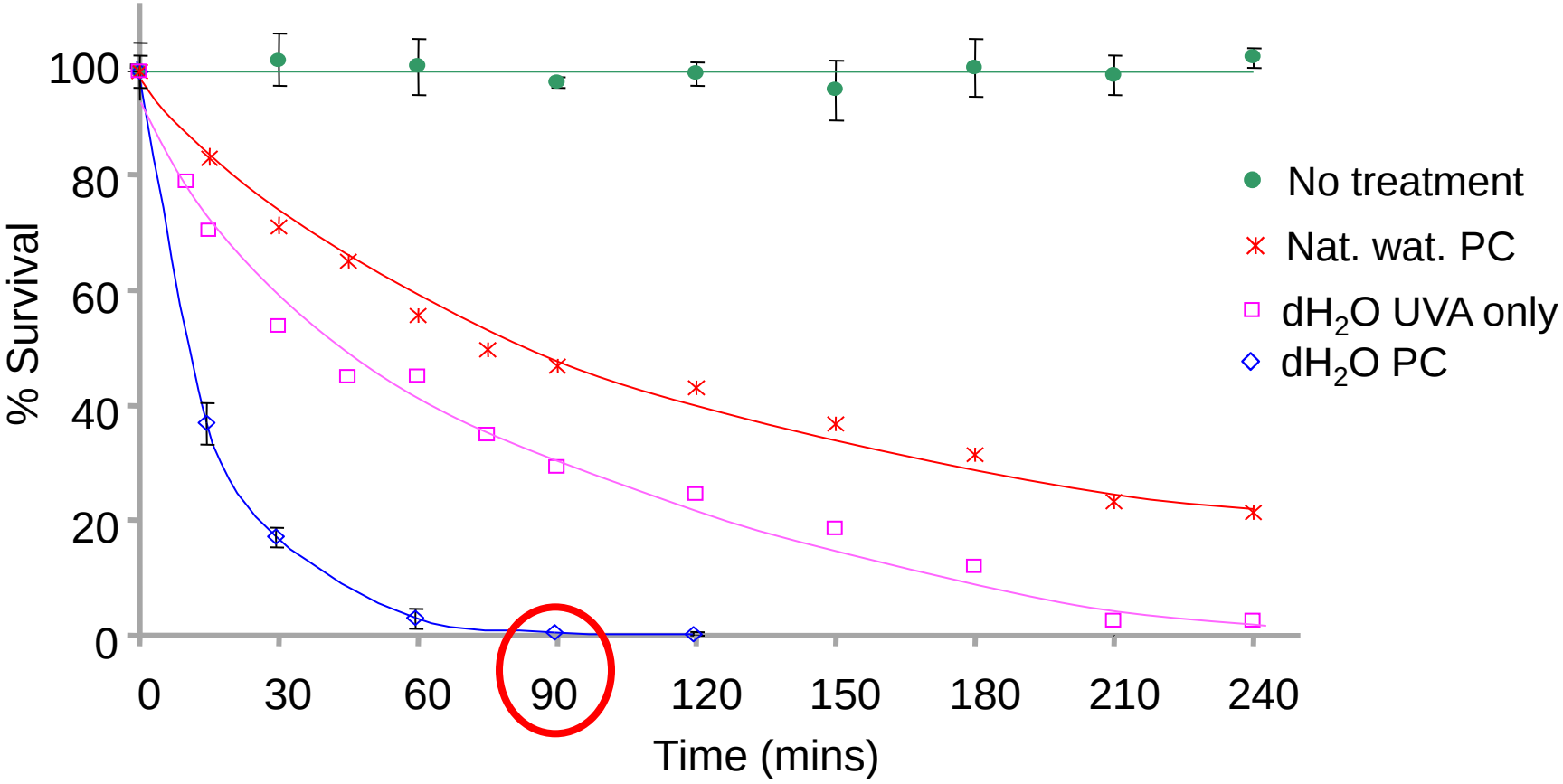




Stirred Tank Reactor – gives very efficient mixing for our lab studies

PC disinfection of *E. coli* K12

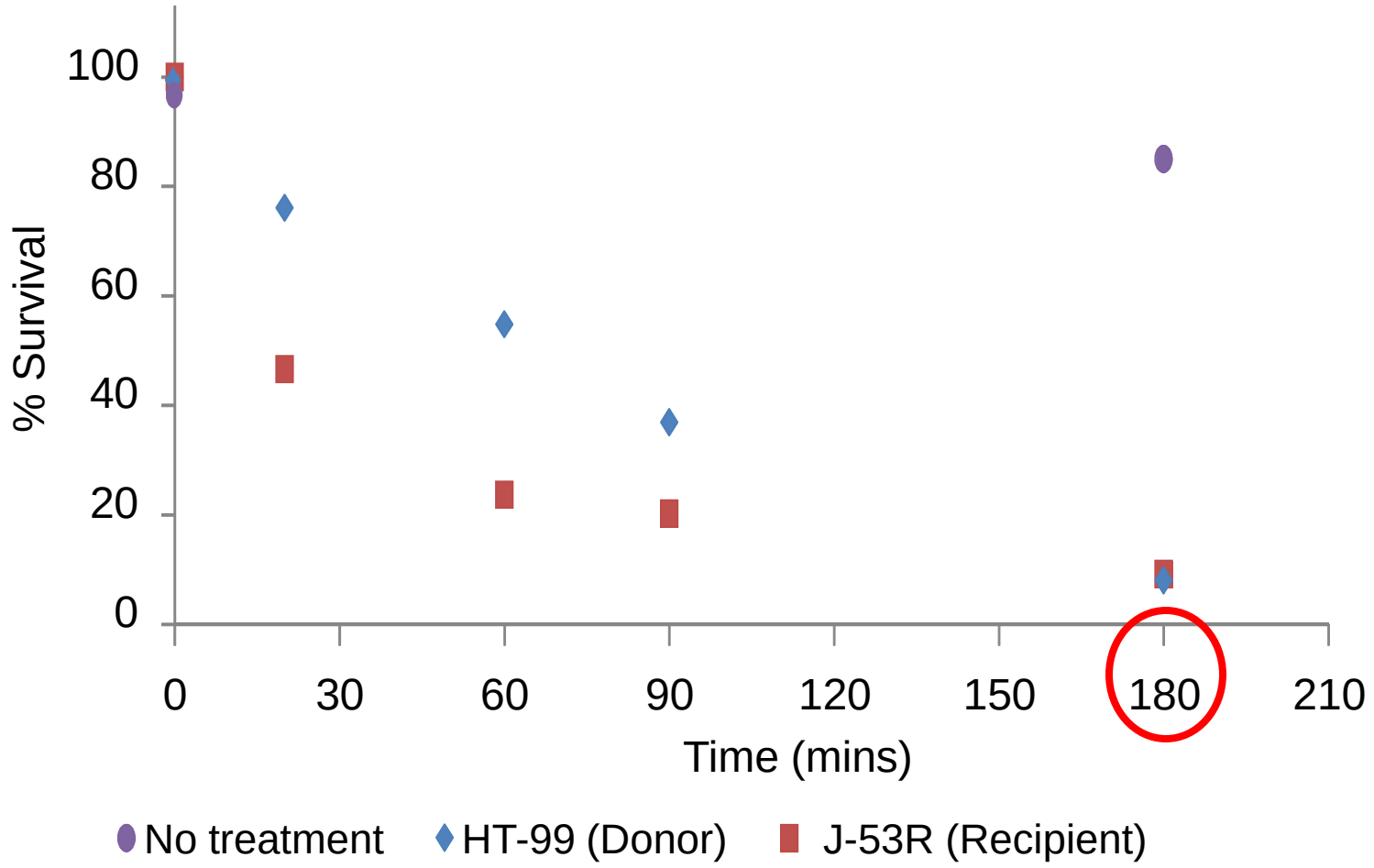
Initial bacterial loading: 1x10^3 CFU per mL



Alrousan *et al* Water Research 2009

PC disinfection of HT-99 & J-53R

Distilled water, 1 x10^3 CFU/mL (9:1 J-53R to HT-99)



Dunlop *et al* Catalysis Today 2015

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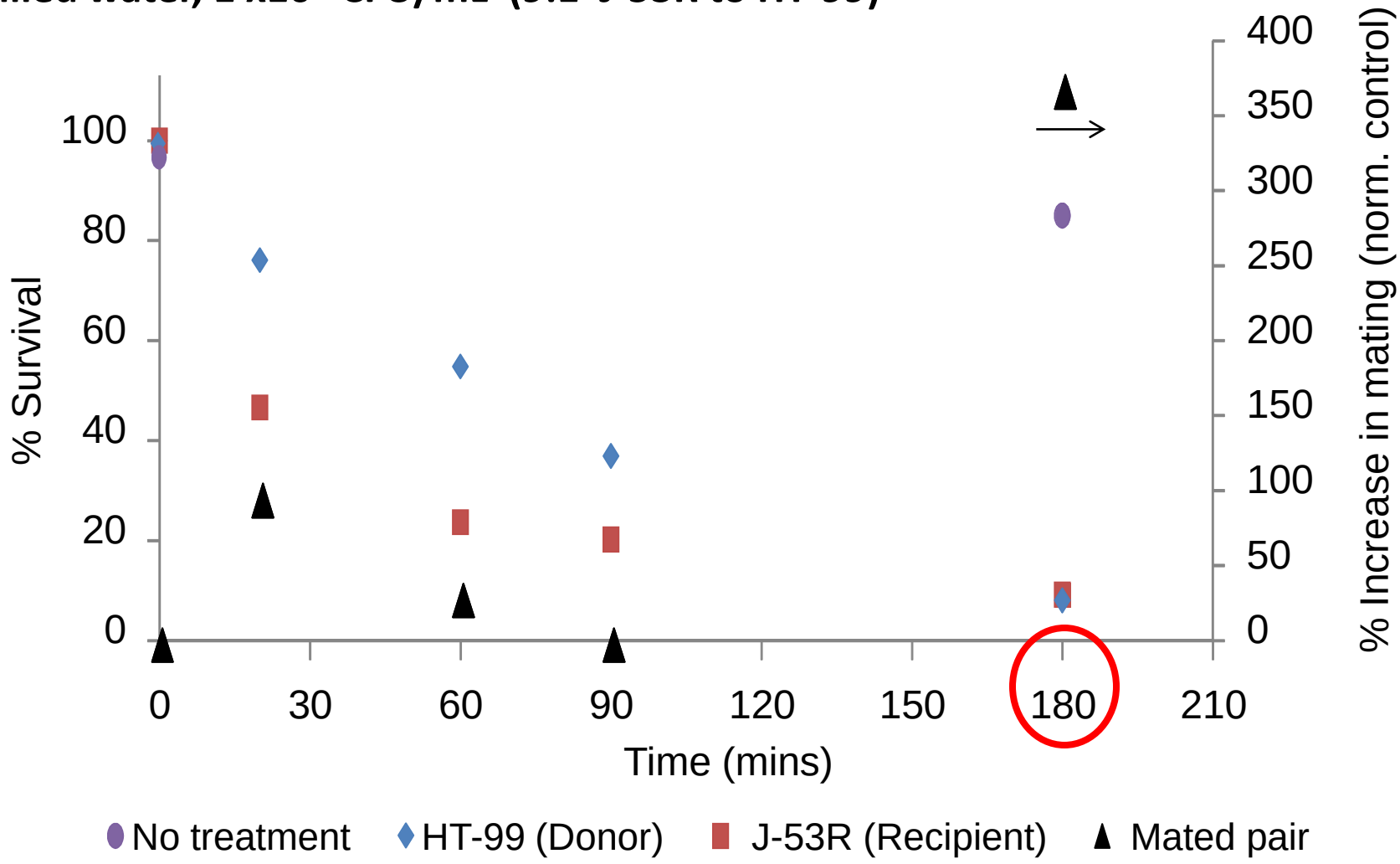


Dunlop *et al* Catalysis Today 2015

Conclusions

- Photocatalysis can inactivate a wide range of organisms, BUT we need to recognise it is slow, expensive, low volume

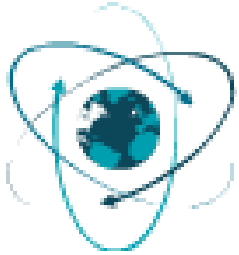
<u>We need to look for niche applications</u>

- Antibiotic resistance in the environment is a BIG problem
  - Increased PC treatment time needed for ARB
  - Important to look for re-growth and any other effects ..
    ... e.g. ARG transfer!

<u>We need to take care re ARG's – new priority pollutants?</u>

Funding acknowledgements

LED photocatalytic reactor



US-IRELAND
RESEARCH & DEVELOPMENT
PARTNERSHIP

Visible light catalysis for remediation of cyanotoxins

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PCATIE PEBCAT SODISWATER Erasmus+

University of ULSTER

Grazie per la vostra attenzione

Se vi piacciono queste foto ... e la pioggia, siete invitati a parlare con

Francesco e Marco che sarano lieti di rispondere alle domande