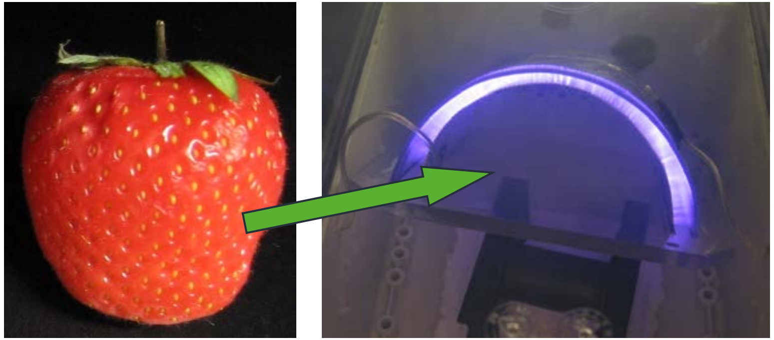
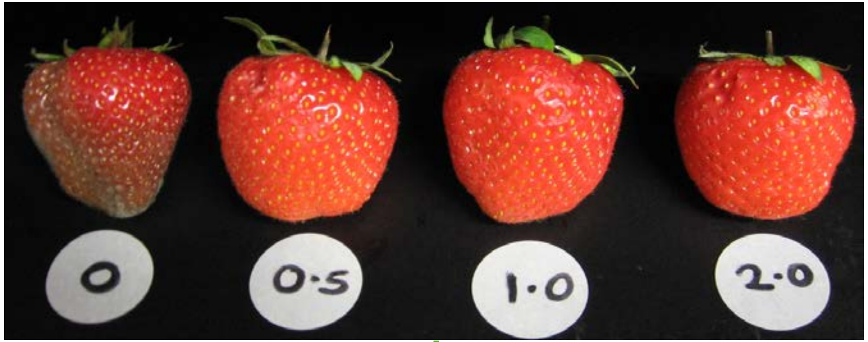
# Perspectives on the in-line decontamination of food-processing surfaces using cold atmospheric pressure air plasma

**James Walsh**

# Setting the scene







“This application shows a complete lack of awareness of the challenges faced by food producers.”

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# Setting the scene

Engaged with 100+ food producers…

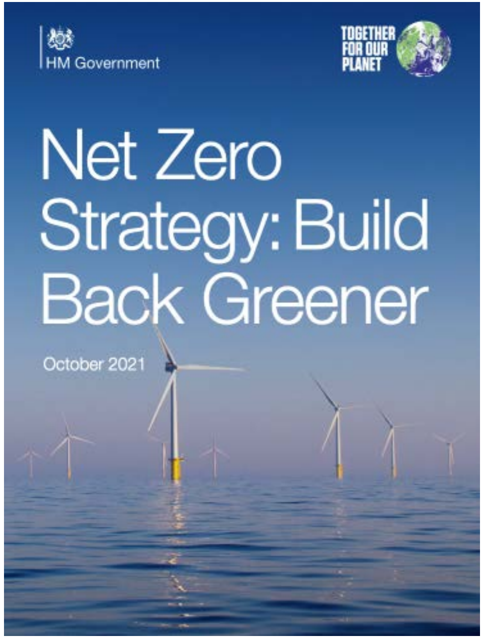
Major pain points?

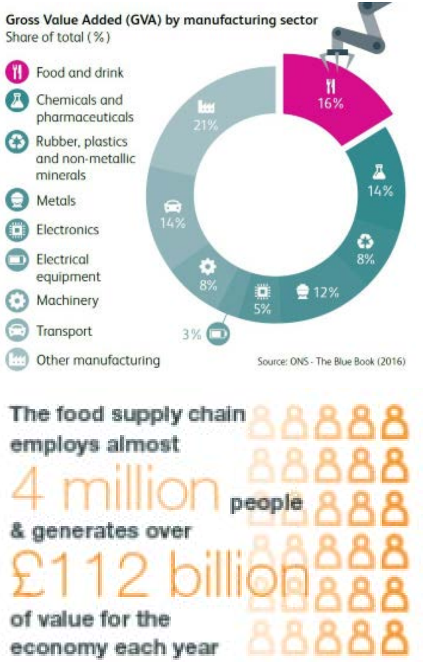
“**Resource use** – we urgently need to reduce energy and water consumption in our production facilities.”

“**Waste reduction** – it would be fantastic if we could reduce the waste generated in our facilities.”

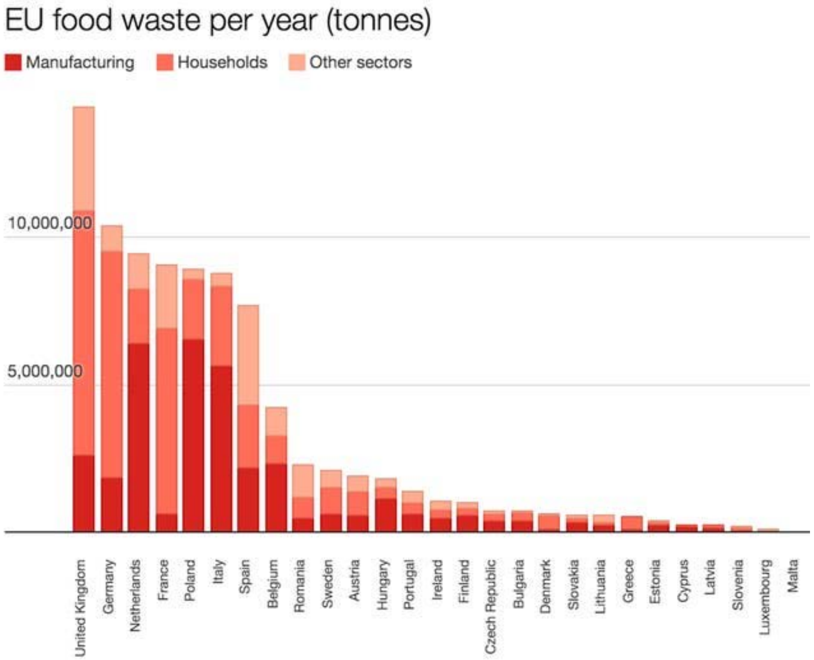
# Setting the scene

## Why reduce resource use…




## Why reduce waste…



# Challenge: Cleaning

Time consuming

Resource intensive

Prone to error

**Example:**

- 67 changeovers per day, ~20 min cleaning each time
- ~£170K per year spent on sanitiser wipes
- Drying time required to prevent wet food.
- Raw materials for disinfectants are made in Ukraine!

| Size of company<br>Chemical cost /year | | |
|---|---|---|
| Small<br>£30,000+ | Medium<br>£100,000+ | Large<br>£1,000,000+ |

# Cleaning: Requirements

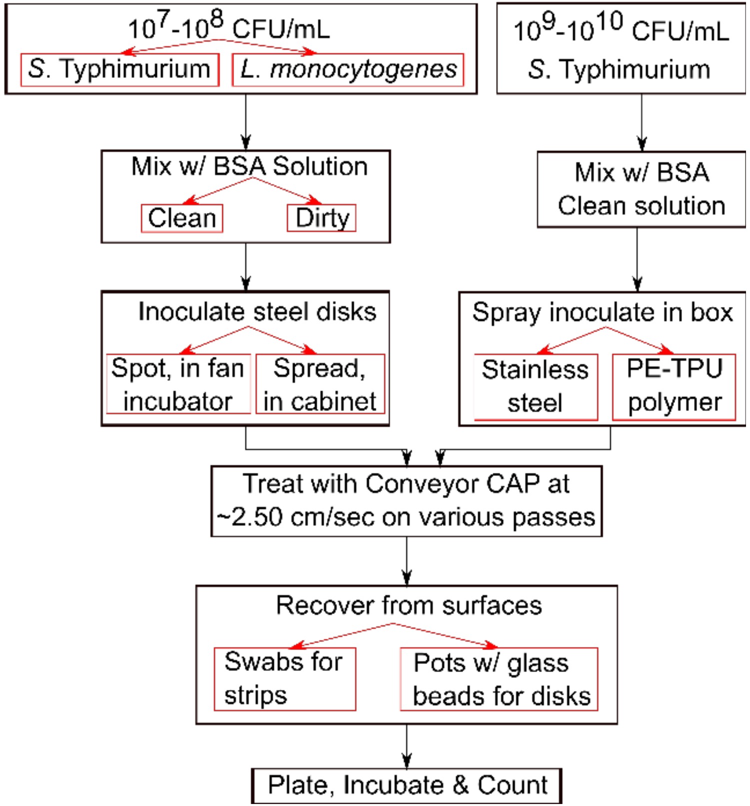
- Conveyor speed: 10 – 100 mm/s
- Contact time: few seconds maximum
- Conveyor width: 700 – 1000 mm
- Microbial reduction: >5 log CFU/mL

~ 10 mm / sec

~ 100 mm / sec

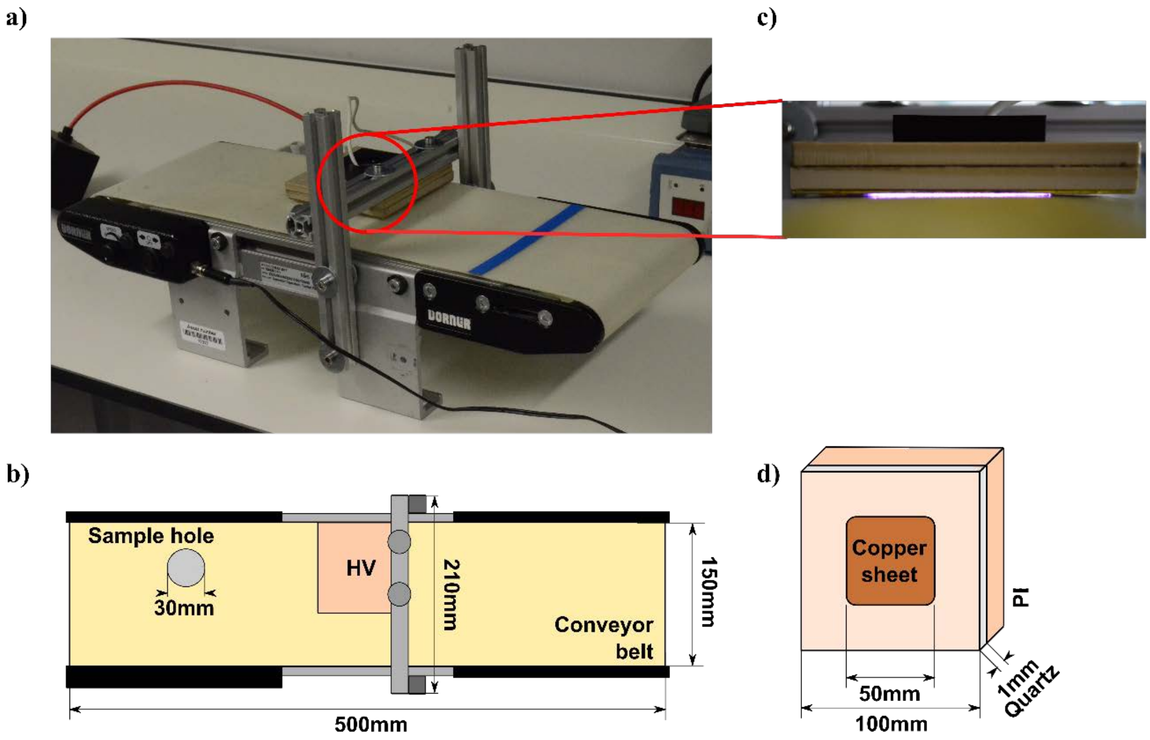
# Cleaning: Testing protocol

- **EN 13697:2015** Chemical disinfectants and antiseptics – Quantitative non-porous surface test for the evaluation of bactericidal and/or fungicidal activity of chemical disinfectants used in food, industrial, domestic and institutional areas.
- ✓ Up to 60 mins contact time.
- ✓ Interfering substances to be used.
- ✓ 5 log bactericidal or 3 log fungicidal.




Katsigiannis *et al.* Comp. Rev. Food Sci. (2022) **21**, 1086
Katsigiannis *et al.* Food Control. (2021) **121**, 107543

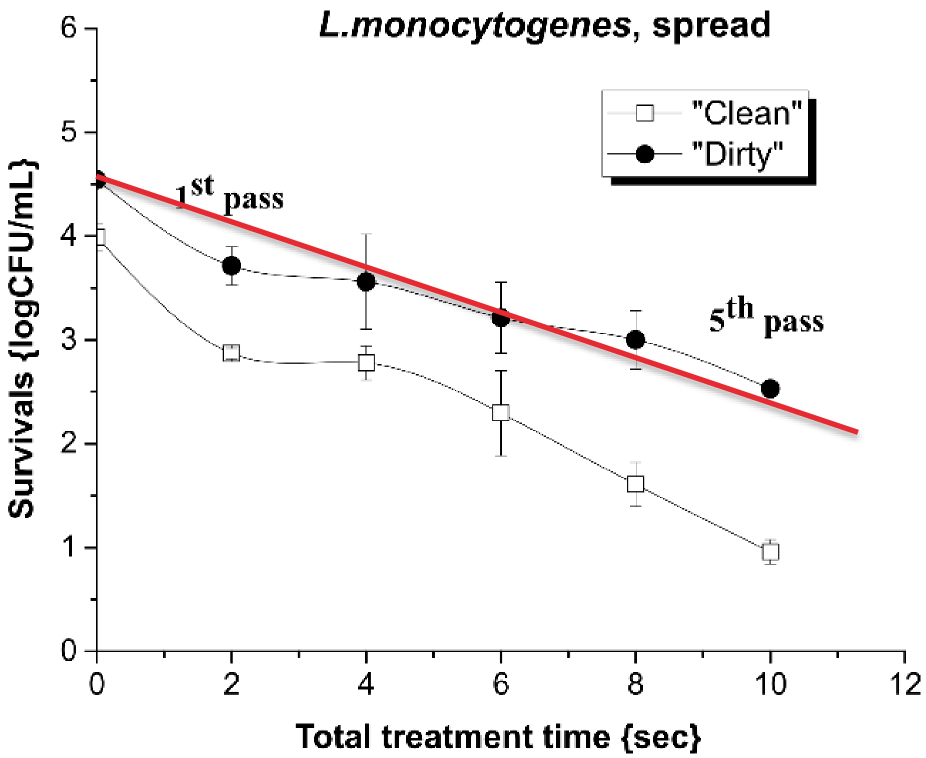
# Cleaning: Direct DBD.




- Small scale demonstrator
- Frequency: 33 kHz
- Voltage: 15 kV
- Separation: 2 mm
- Electrode: 50x50 mm
- Velocity: 25 mm/s
- Contact time: 2 s

Katsigiannis *et al.* IFSET. (2022) **81**, 103150

# Cleaning: Conveyor Belts.




## Scale-up example

5 Log reduction, ~20 s
Electrode size: 250 mm
Belt speed: 25 mm/s
Contact time: 10 s
Passes required: 2
10m belt: 6.7 mins/pass
**Total time: 13.3 mins**

Katsigiannis *et al.* IFSET. (2022) **81**, 103150

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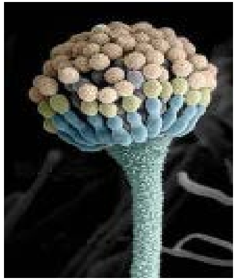
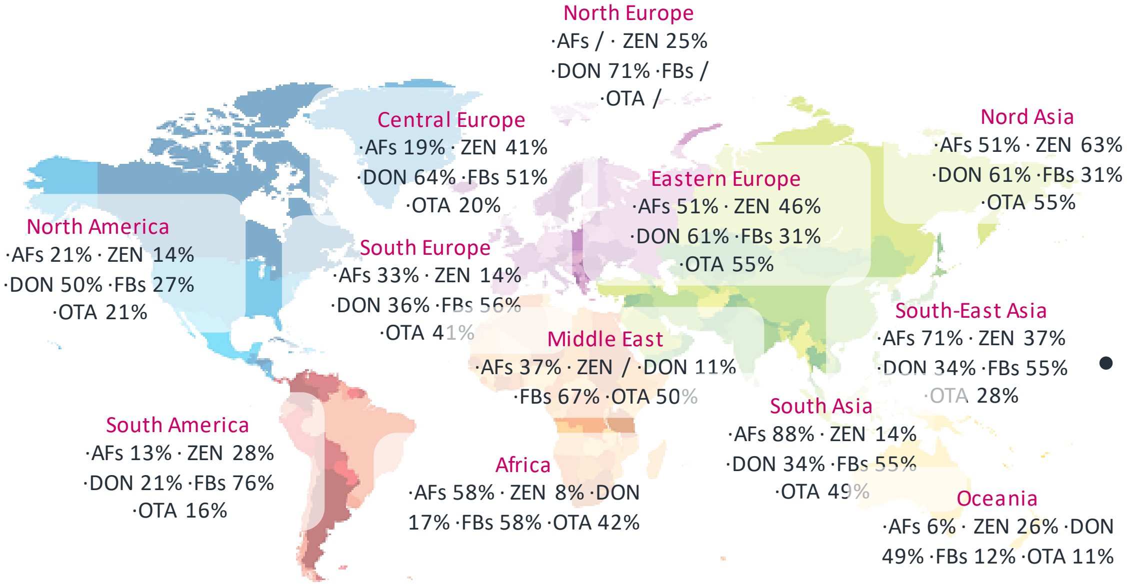
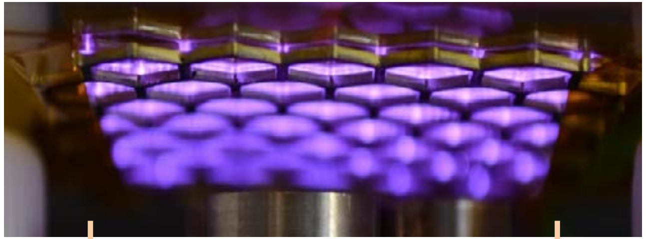
# Challenge: Reduce waste

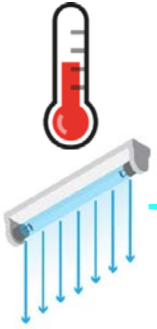





- Post-harvest fungal diseases incurs the loss of a large percentage of crops reaching 50% in some fruits.
- Many fungal species produce extremely harmful mycotoxins. 400 different structural types, giving a wide range of toxicities.
- 60% to 80% of the global food crops are contaminated with mycotoxins [Eskola et al. (2019)]

# Challenge: Reduce Waste





Comparison to **UV-C irradiation/thermal treatment**

$AFB_1$, $AFB_2$, $AFG_1$, $AFG_2$, DON, T-2, HT-2, $FB_1$, $FB_2$, ZEN

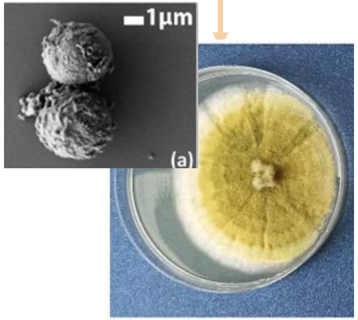
**Mycotoxins**

HRMS, MS/MS, NMR

MTS assay, comet assay

Decontamination efficiency: concentration determination

HPLC-MS, HPLC-MS/MS




Contamination with *A. flavus* spores

**Fungal spores**

Chemical modification to matrix

WCA, ATR-FTIR, XPS, SIMS

Decontamination efficiency:

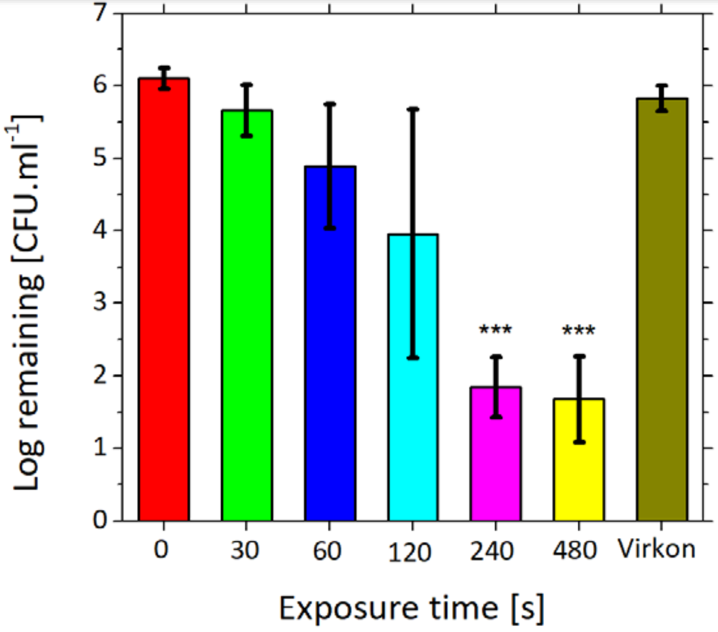
MTT, CFU counts

Morphological modification to matrix

SEM, AFM

# Challenge: Reduce Waste

Initial proof of concept*

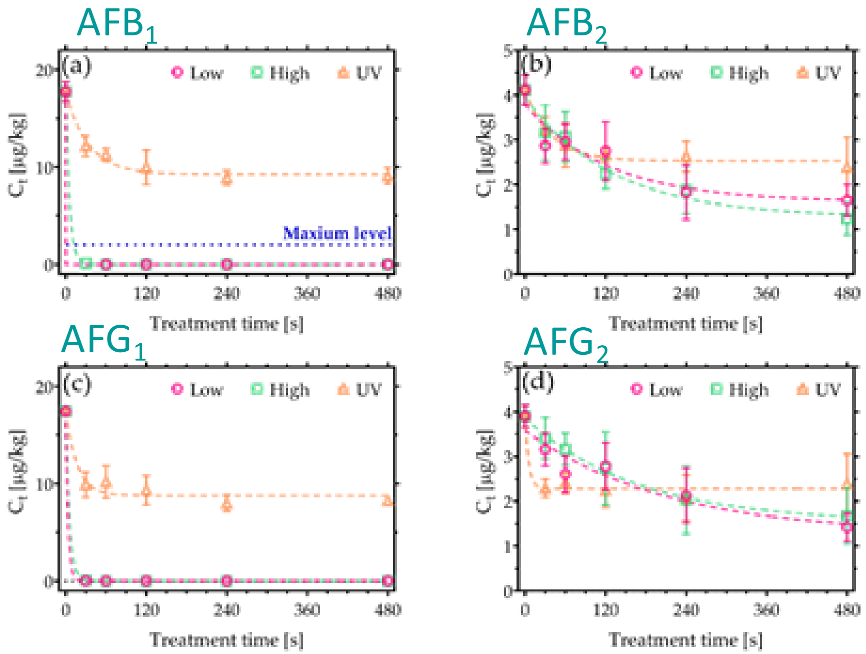



Scale up

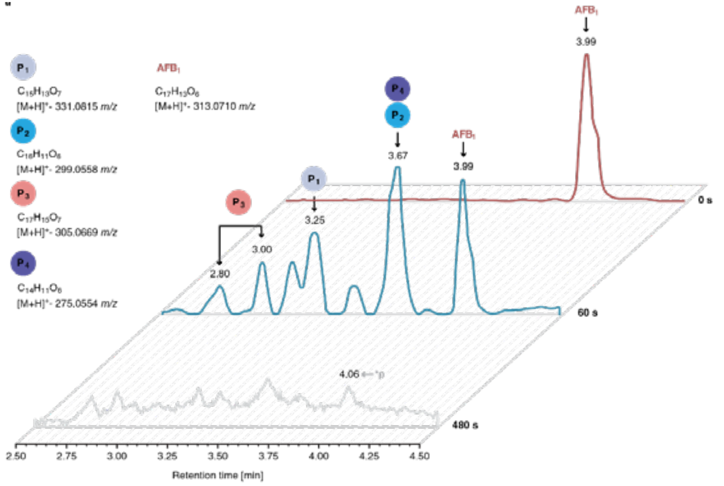

*Hojnik *et al. Environ. Sci. Technol.* 2019, 53, 4, 1893–1904

# Challenge: Reduce Waste

Mycotoxin reduction…




**HPLC/HRMS + $^1$H NMR + 2D NMR**



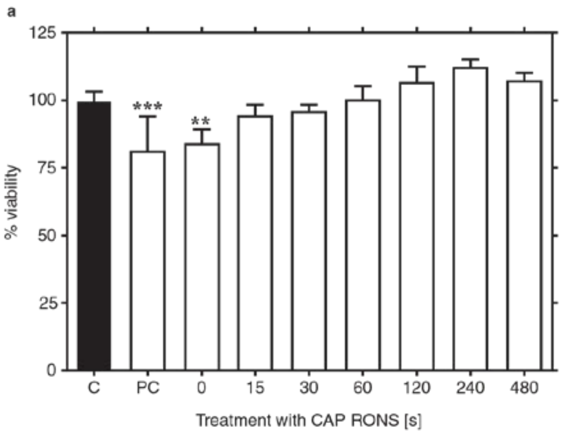

Rapid degradation of $AFB_1$, four primary by-products are formed… takes a prolonged treatment to eliminate all formation products.

*Hojnik et al. Toxins.*

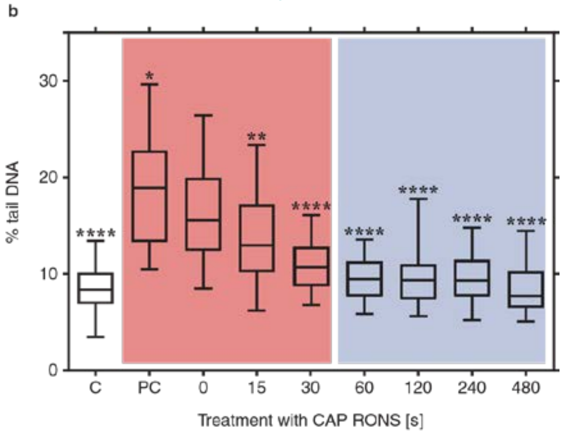
*Hojnik et al. J. Haz Mat.* 2021, 403.

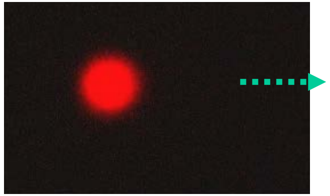
# Challenge: Reduce Waste

## MTS assay



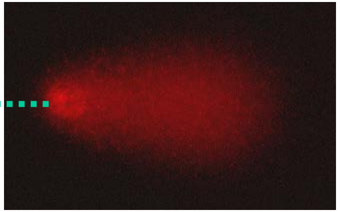

## Comet assay



No significant amount of DNA strand breaks (<7% DNA in tail)

Significant amount of DNA strand breaks (>7% DNA in tail)



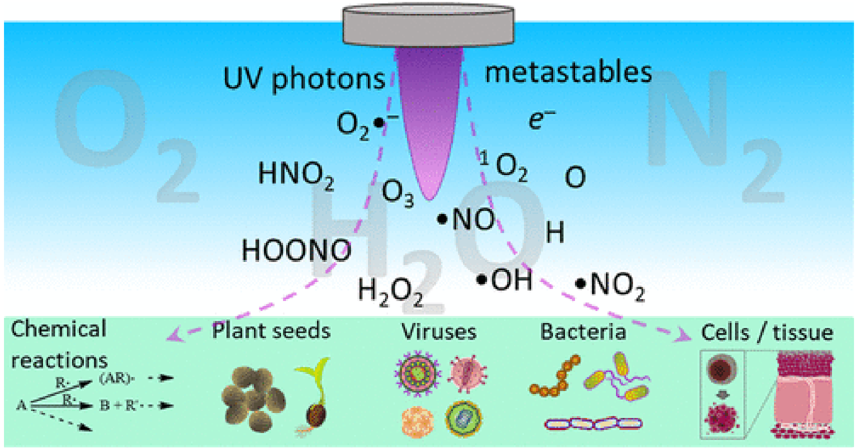
## MTS assay → cytotoxicity

The loss of the cytotoxic effect, especially after 60 s of treatent.

## Comet assay → genotoxicity

Decreasing trend in the DNA strand breaks; 60 s of treatment lead to values comparable to control.

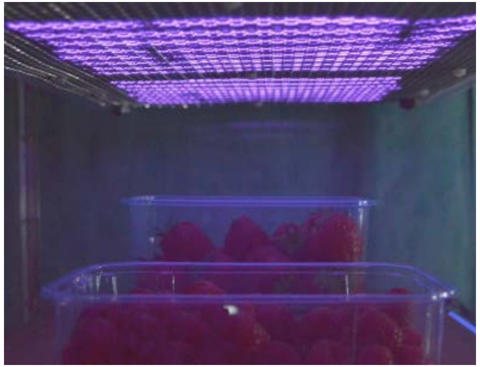
# Challenge: Understanding & Acceptance




**What is the mode of action (and is it safe)?**

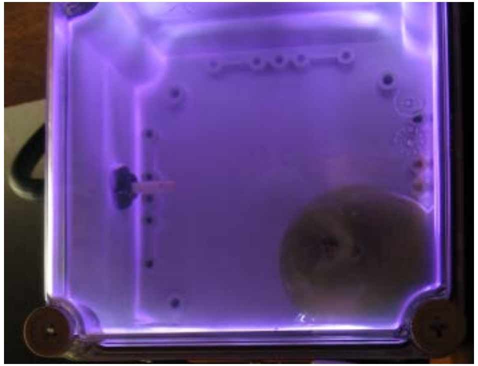
- Primarily RONS driven processes.
- Mode of action depends on composition of RONS reaching target (and what they react with on the way).

*Gorbanev et al. Anal. Chem.* 2018, 90



## Indirect exposure

- Easy to scale
- Limited mass transport
- Suitable for treating 3d targets

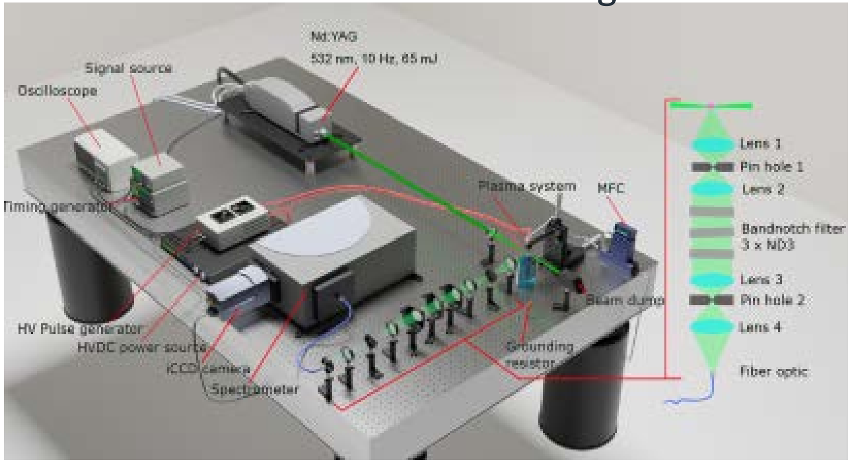


## Direct exposure

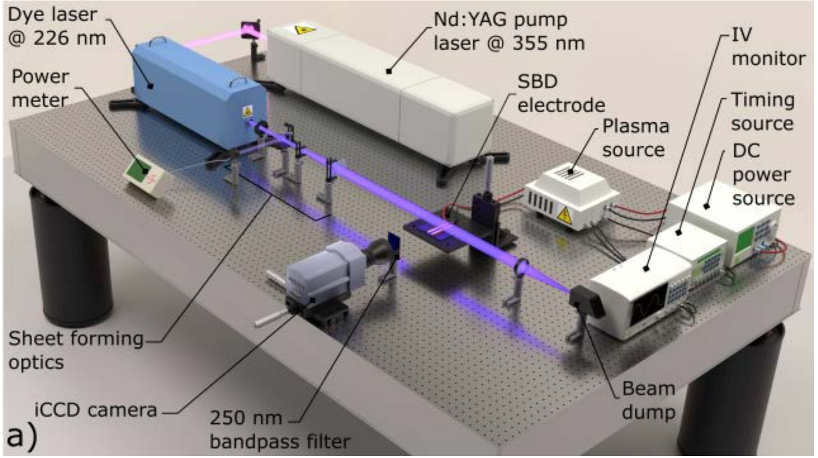
- Difficult to scale
- Efficient mass transport
- Difficult to treat 3d targets

# Challenge: Understanding & Acceptance

Thomson Scattering




Laser Induced Fluorescence




**FTIR** IR active long-lived species ($O_3$, $NO_2$, $NO_2$ etc)

**TS** Electron properties ($n_e$, $T_e$)

**LIF** Ground state molecular species (OH, NO etc)

**ps-TALIF** Ground state atomic species (O, N, H etc)

→ **Not good enough!**

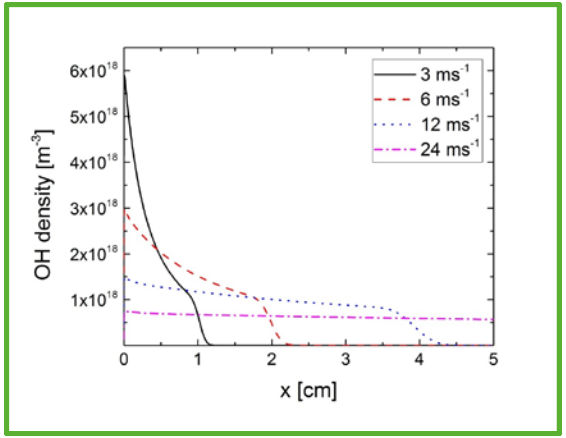

Brisset et al. (2023) Plasma Sources Science and Technology, 32 (6)
Slikboer et al. (2021) Scientific Reports, 11 (1)
Slikboer et al. (2021) Journal of Physics D: Applied Physics, 54 (32)
Ng et al. (2021) Journal of Applied Physics, 129 (12).
Morabit et al. (2020) Plasma Processes and Polymers, 17 (6)
Dickenson et al. (2018) Physical Chemistry Chemical Physics, 20 (45)
Dickenson et al. (2017) Scientific Reports, 7 (1)
Whalley et al. (2016) Scientific Reports, (6)
Ni et al. (2016) Journal of Physics D: Applied Physics, 49 (35)

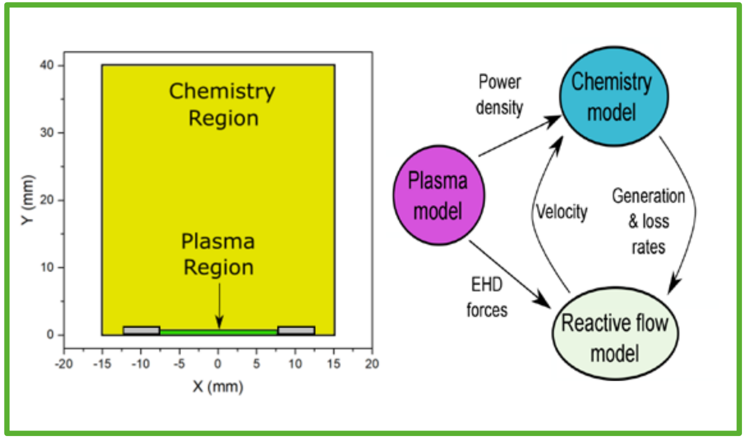
# Challenge: Understanding & Acceptance

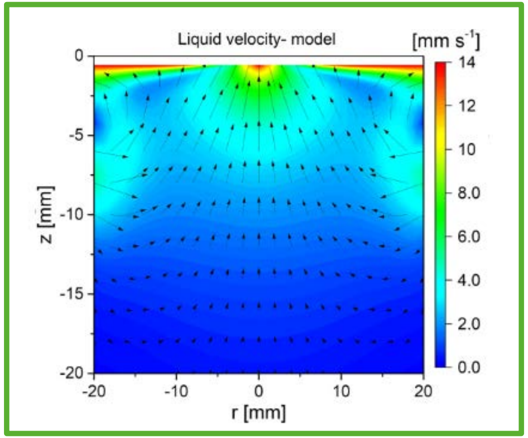
**0D + 2D air plasma fluid model:** describes the physics of the discharge in 2D, while the chemistry of the discharge is described by a combination of 0D* and 2D models through extrusion and projection methods.

*Sakiyama *et al. J. Phys. D: Appl. Phys.* **45** (2012)

1D with convective flow → 0D and 2D coupled → Interaction with substrate





Hasan et al. (2017) Applied Physics Letters, 110 (26),
Hasan et al. (2017) Journal of Physics D: Applied Physics, 50 (20).
Hasan et al. (2017) Applied Physics Letters, 110 (13).
Hasan et al. (2016) Journal of Applied Physics, 119 (20).
Dickenson et al. (2021) Journal of Applied Physics, 129 (21).
Bieniek et al. (2021) Physics of Plasmas, 28 (6).
Dickenson et al. (2018) Physical Chemistry Chemical Physics, 20 (45).

# Challenge: Understanding & Acceptance

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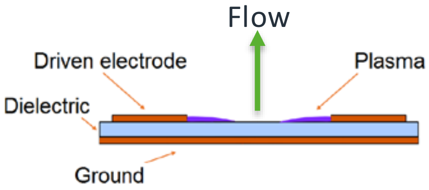
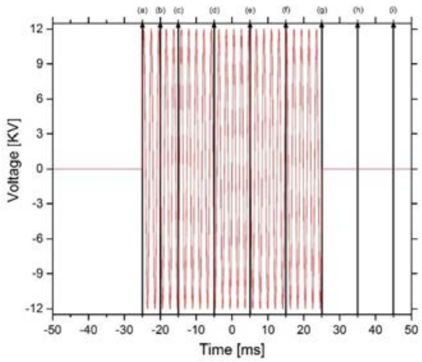
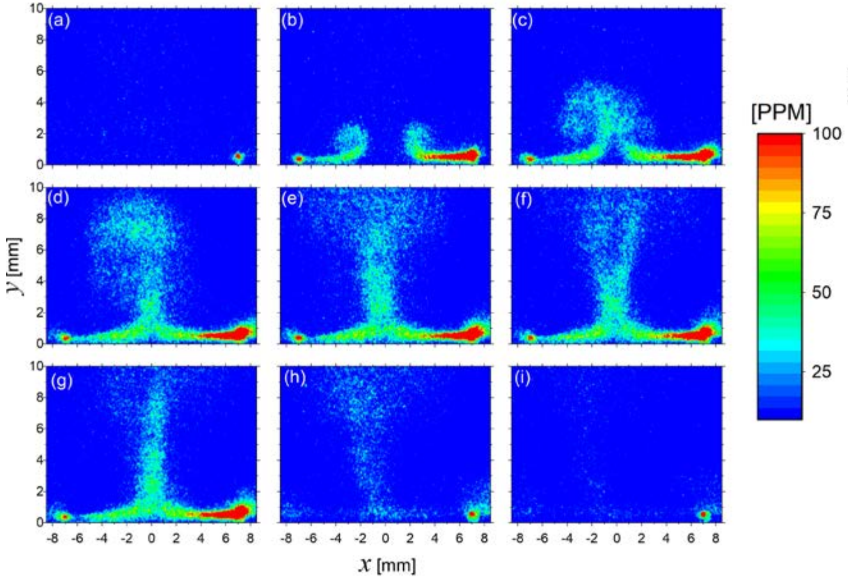
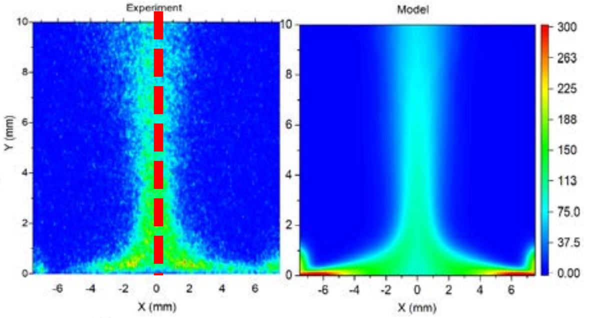
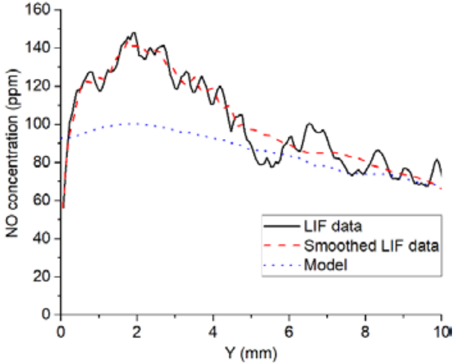



**Key points:** (1) Mass transport of reactive species driven by EHD forces created in plasma.

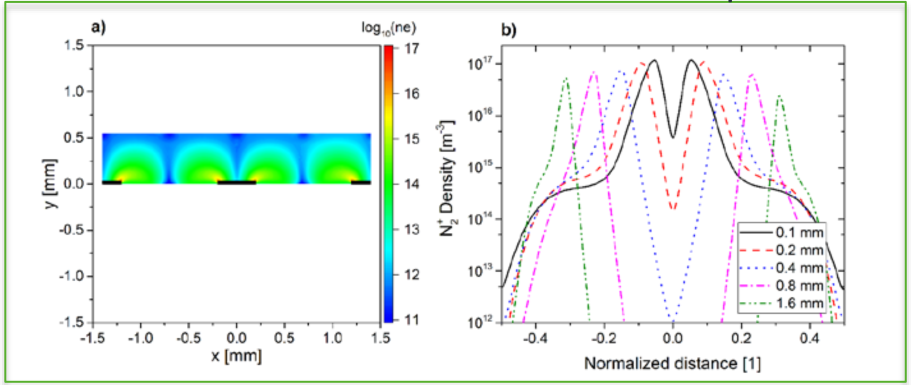
(2) Biologically relevant concentrations of NO are transported downstream.

(3) Experiments and model show good agreement.

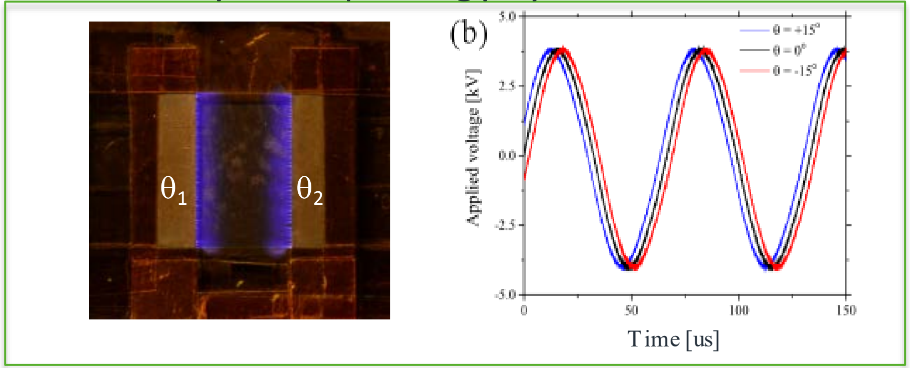
Dickenson *et al. Phys. Chem. Chem. Phys.*, **45** (2018).

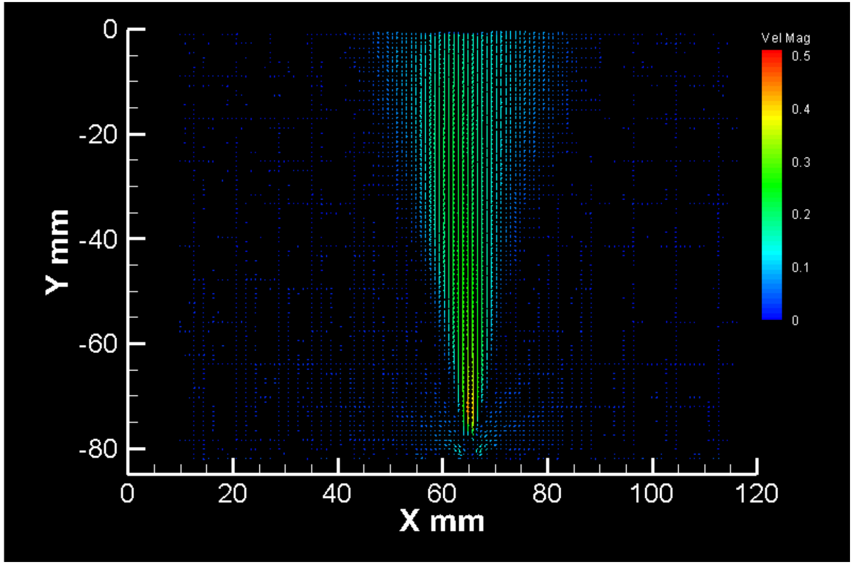
# Challenge: Understanding & Acceptance

Provide data that is inaccessible in the experiment



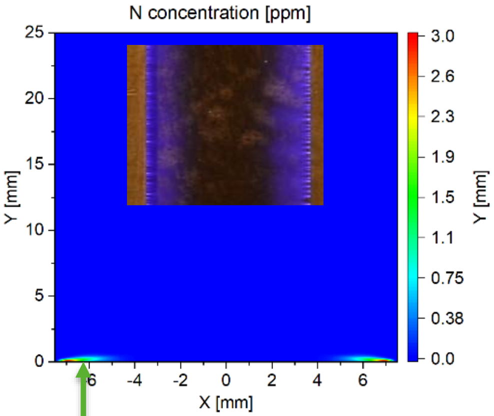

Identify underpinning physical mechanisms

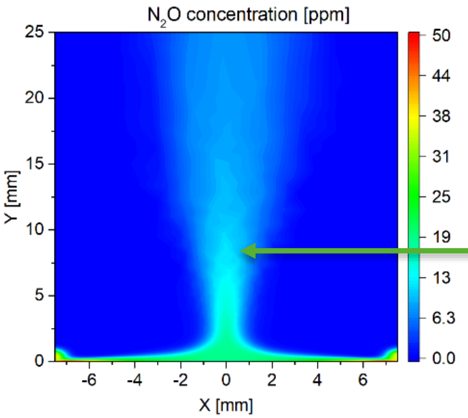


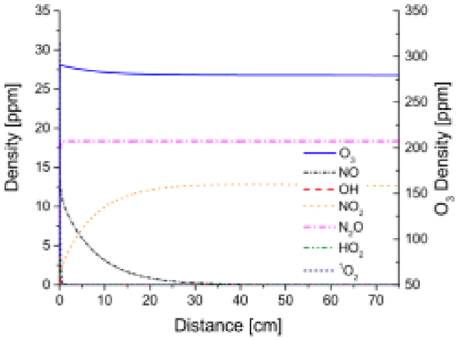

Gilbart *et al.* Plasma Processes & Polymers, 19 (2022)
Dickenson *et al.* *Sci. Rep.*, **7** (2017)

# Challenge: Understanding & Acceptance

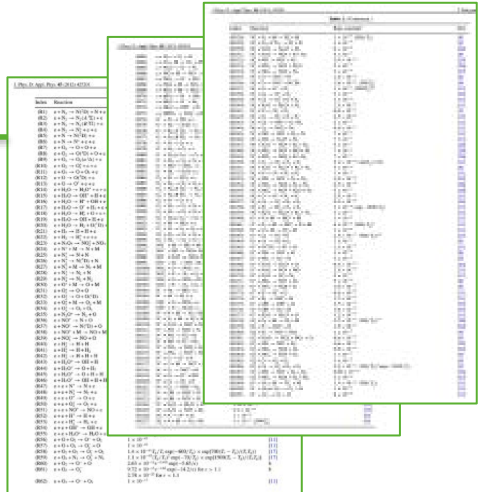



**cm above discharge**: only 7 species > 1 ppm




| Species | Predicted concentration @ 3 cm. |
|---|---|
| $O_3$ | ~0 – 100s of ppm |
| NO | ~10s of ppm |
| $NO_2$ | ~0 – 100s of ppm |
| $N_2O$ | ~10s of ppm |
| $HNO_2$ | ~Few to 10s of ppm |
| $HNO_3$ | ~Few to 10s of ppm |
| $N_2O_3$ | ~10s of ppb |
| $N_2O_4$ | ~10s of ppb |
| $N_2O_5$ | ~Few to 10s of ppm |



**In the discharge**: 50+ species, 600+ reactions, neglecting anything that comes from the product!

# Regulatory compliance: food treatment

- **Does plasma exposure have a functional and lasting effect that extends beyond what occurs naturally?**

- **NO – Plasma is a processing aide, EU Regulation (178/2002)**

"All substances used must be safe, Good Manufacturing Practices (GMP) must be followed, must have documented traceability"

- **YES – Plasma creates a novel food, EU Regulation (2015/2283)**

"Any food or ingredient not significantly consumed in the EU before May 15, 1997, must undergo a centralised safety assessment by the European Food Safety Authority (EFSA) and receive authorisation before being marketed."

# Regulatory compliance: Plasma cleaning

- **Does the controlling action take place by any means other than purely physical or mechanical action?**

- **EU Biocides Directive (98/8/EC)**

"active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means"

- **Authorisation**
  - active substance(s) need to be identified and their concentrations specified.

# Finally: SWOT analysis

## Strengths

- Consumable free.
- Active agents produced *in-situ*.
- Dry process.
- Energy efficient (compared to thermal methods).

## Weaknesses

- By-products (toxic).
- Complex to scale.
- Requires modification of infrastructure.
- Complex, mechanisms not fully understood.
- Difficult to monitor and trace.

## Opportunities

- Vast range of potential applications across the sector.
- Interesting scientific and engineering challenges remain.
- Extremely multidisciplinary.

## Threats

- Competing non-thermal methods (e.g., UV).
- Regulatory pathways unclear, may need changes made to current legislation.
- Neophobia – Producer / Consumer perceptions of plasma.