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Spiliotopoulou, Aikaterini; Martin, Richard; Andersen, Henrik Rasmus

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An innovative way to determine on-site ozone delivery efficiency

Aikaterini Spiliotopoulou[1,2], Richard Martin[3], Henrik R. Andersen[1]

[1]Department of Environmental Engineering, Technical University of Denmark, Miljøvej 113, 2800 Kongens Lyngby, Denmark

[2] OxyGuard International A/S, Farum Gydevej 64, 3520 Farum, Denmark

[3] Water ApS, Farum Gydevej 64, 3520 Farum, Denmark

Abstract

In recirculating aquaculture systems (RAS), the water quality changes continuously due to fish feed, excretions and makeup water or piping system, affecting system's equilibrium. Accumulation of organic and inorganic compounds, where proteins, ammonia and heavy metals are the most pronounced; creates toxic conditions for aquatic organisms, leading to system failure. The dissolved organic matter (DOM) varies among the different water sources, affecting the reaction rate of ozone and consequently its lifetime.

Ozone is a strong oxidizing agent, reacting rapid and in low concentrations, first with the easily degradable DOC (Eq.1) and inorganic pollutants, and then with the decreasingly reductive pollutants. If more ozone is dosed than the immediate demand by reducing pollutants, it will be decomposed to hydroxyl radicals (Eq.2), which are non-selective, highly reactive species oxidizing a range of recalcitrant dissolved pollutants (Eq.3).

$$DOC + O_3 \rightarrow DOC_{\text{selectively oxidized}} \quad \text{Eq. 1}$$
$$H_2O + O_3 \rightarrow O_2 + 2\,HO^{\bullet} \quad \text{Eq. 2}$$
$$DOC + HO^{\bullet} \rightarrow DOC_{\text{radical oxidized}} \quad \text{Eq. 3}$$

When ozone is introduced into water, bacteria load and dissolved organic matter (DOM) are diminished while redox level, water clarity and UV transparency are increased. Protein degradation is accelerated and coagulation, filtration and nitrification processes are improved. However, in a non-meticulously designed system, residual ozone (due to overdose) with longer lifetime will reach the culture tanks causing significant harm to cultured specie. Ozone has been reported to be toxic to a wide range of marine and freshwater organisms at residual concentrations between 0.01 mg/L and 0.1 mg/L. The risk to lose fish and the high ozonation cost are limiting parameters and contribute to a reluctance by the aquaculture industry to use ozone. Therefore, ozone should be properly delivered, efficiently dissolved and accurately controlled to ensure that it is completely consumed before returning to culture tanks.

The present study investigates the optimal technology to transfer ozone into water based on physicochemical model applied to different established delivery methods e.g. gas cone, gravitation bubble column or venturi injector. Depending on the water quality (DOC, salinity, pH, temperature, etc.), which will be analysed in advance in the laboratory, the three dissolving alternatives will be

tested in site. Based on the water flow and the disinfection needs of the facility, it will be suggested which is the optimal gas transfer method. The transfer efficiency will be monitored with oxidation reduction potential (ORP) sensors in site and by a colorimetric assay which will be developed in the laboratory.
Water samples were collected and transferred to the laboratory for further analysis. Ozone measurement in water is usually achieved by a spectrophotometer utilizing a colorimetric assay, since ORP sensors do not determine it successfully. Therefore, the possibility to determine the delivered ozone dose by utilizing the natural fluorescence caused by certain proteins, which are contained into RAS is investigated. Preliminary experiments to test this hypothesis have been conducted in wastewater effluent providing satisfactory results. Since the aquaculture water is enriched with proteins it is expected that the fluorescence effect will be greater leading to an innovative ozone determination technology. The method is evaluated by comparing it with a colorimetric assay.

Key-words: Ozone, gas solubility, fluorescence, ozone dose control

I would like the present abstract to be taken under consideration as an oral presentation. My submission is intended for the session: Waste Management and Water Quality

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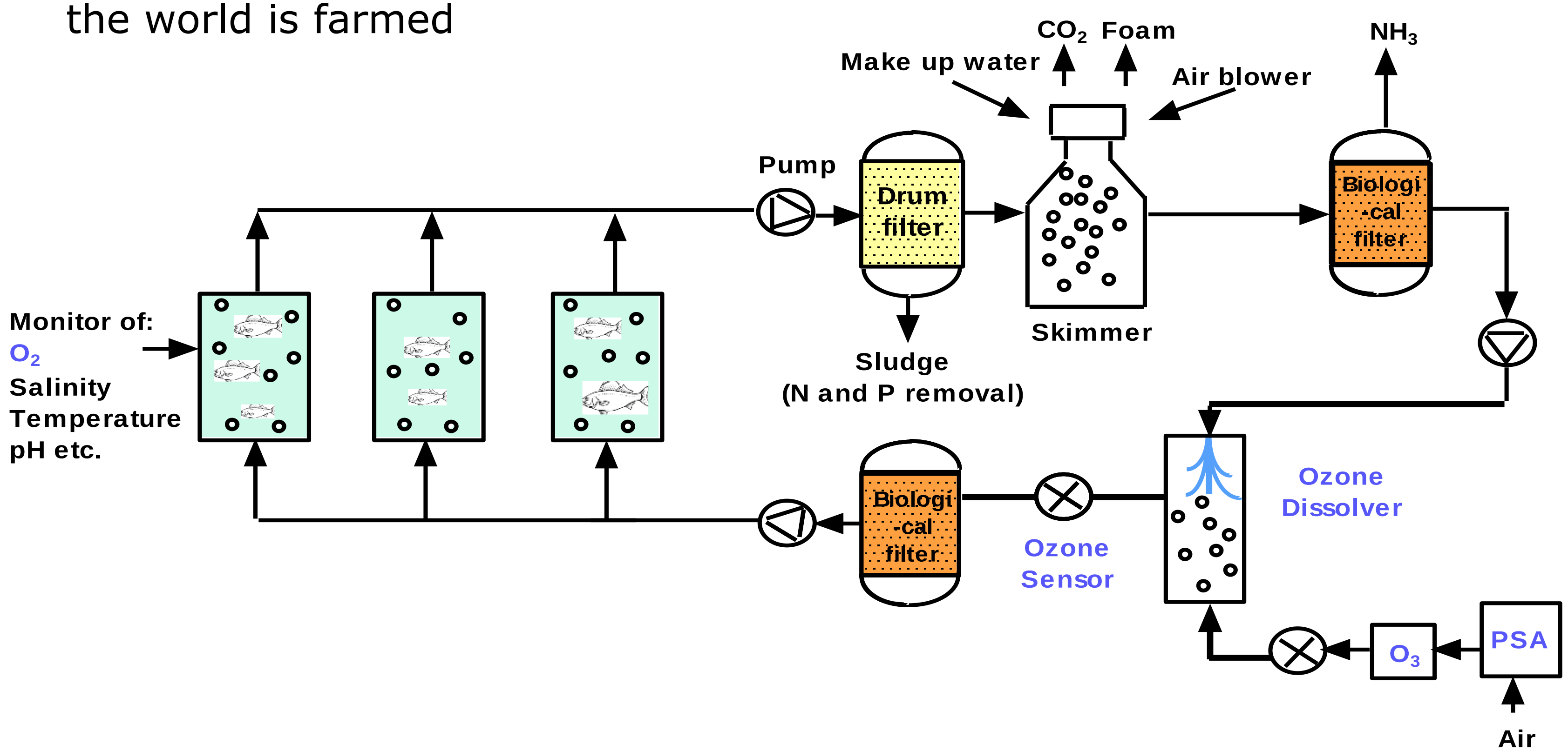
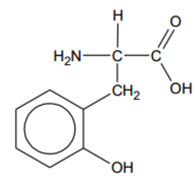
Recirculating Aquaculture System (RAS)

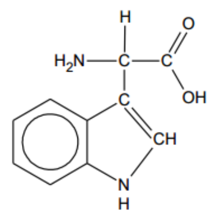
- 16% of animal derived protein is from fish
- More than 2,6 billion people get more than 20% of their protein intake from fish
- A few years ago: more than 60% of the fish consumed around the world is farmed

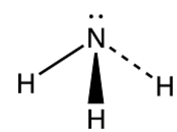


RAS implications

- Low exchange RAS (90% or more of water is recycled)
- Accumulation of:
  - Dissolved organic mater (DOM)
  - Micro-particles
  - Dissolved N-compounds (e.g ammonia)
  - Heavy metals
  - Microbial abundancies
- Potentially leading to:
  - Suboptimal conditions

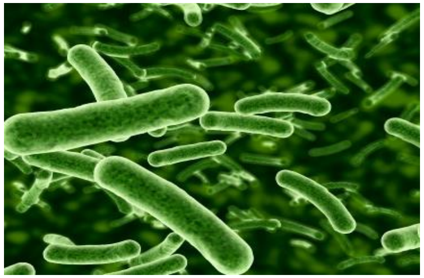


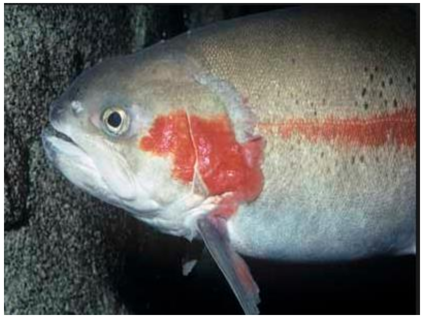




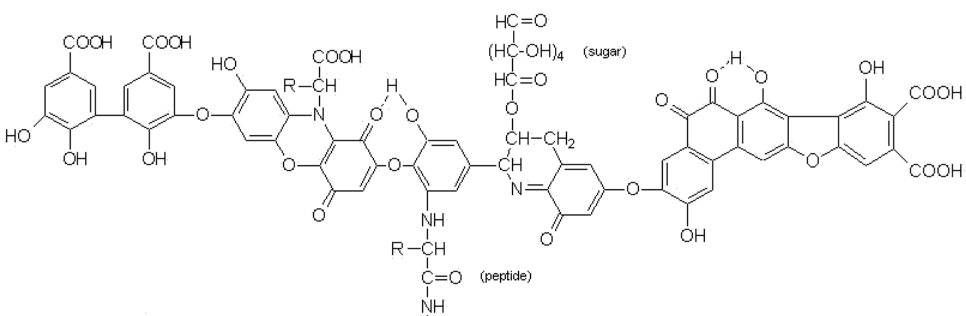
Hg

Cd^{2+} Cu^{2+}





Pb^{2+} As^{3+}



Model structure of humic acid (Stevenson 1982)

Dual Functions of Ozone

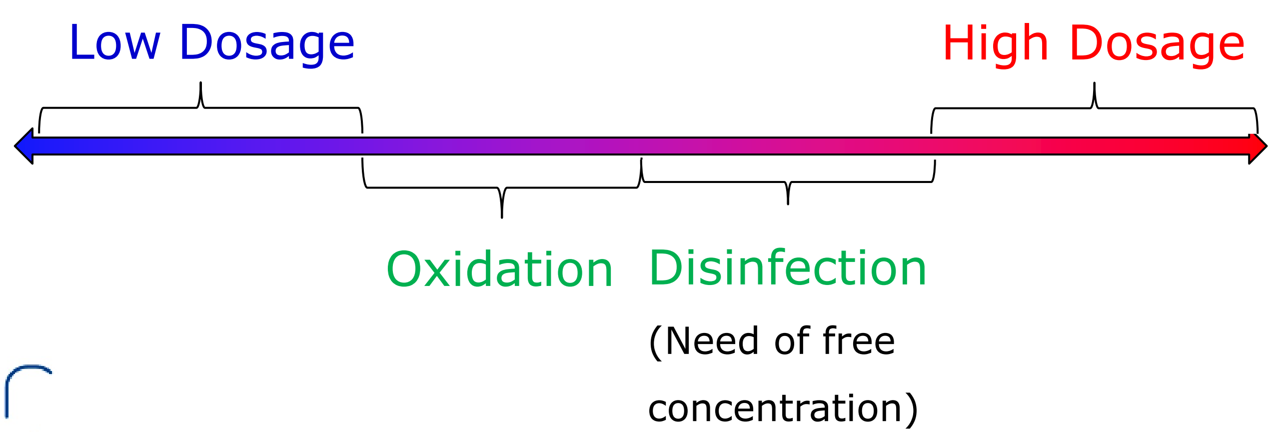
- Oxidation
  - Strong oxidizing agent
    - Rapid reactions
    - Removal of natural DOM
    - Acceleration of protein degradation
    - Increased water clarity and UV transparency
    - Improve
      - coagulation
      - filtration and
      - nitrification processes.

- Disinfection
  - Efficient against
    - Bacteria
    - Viruses
    - Parasite

Challenges

- Ozone overdose
  - **Never present in culture tank**
  - Significant harm to cultured species
    - > 0.01 mg/L
- In case of saltwater system:
  - Hypobromous acid formation
    - toxic
- Reluctance to use ozone due to:
  - Risk of losing fish
  - Cost

Need for an operational method to **monitor the ozone demand** in the water phase!!!



Water
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Traditional residual ozone determination

- Dissolved (actual) ozone into water
  - Off-line colorimetric method (e.g. DPD, indigo trisulfonate)
    - Spectrophotometer
      - complicated method
    - Test kits
      - expensive
  - Online measurement
    - Potentiometric principle probe
      - quite expensive
    - Oxidation potential reduction (OPR)
      - cheap
      - do not measure ozone
      - non specific (cannot distinguish e.g. O_3 from Cl_2)
      - risk of failure when exposed to high ozone concentration

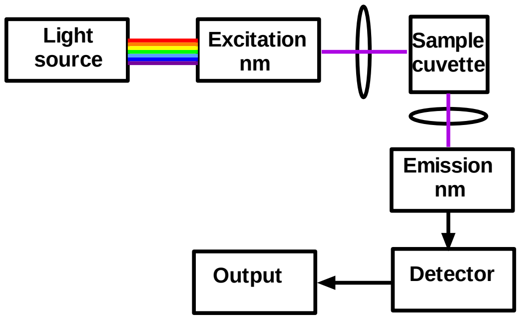
Delivered Ozone determination

We propose a new method to determine how much ozone dosage is added into water

- Fluorescence
  - Based on natural fluorescence of DOM
    - rapid detection
    - precise characterization of DOM composition
  - Tested in wastewater, river water, seawater, etc.
  - **Never used to control ozone in aquaculture until now**

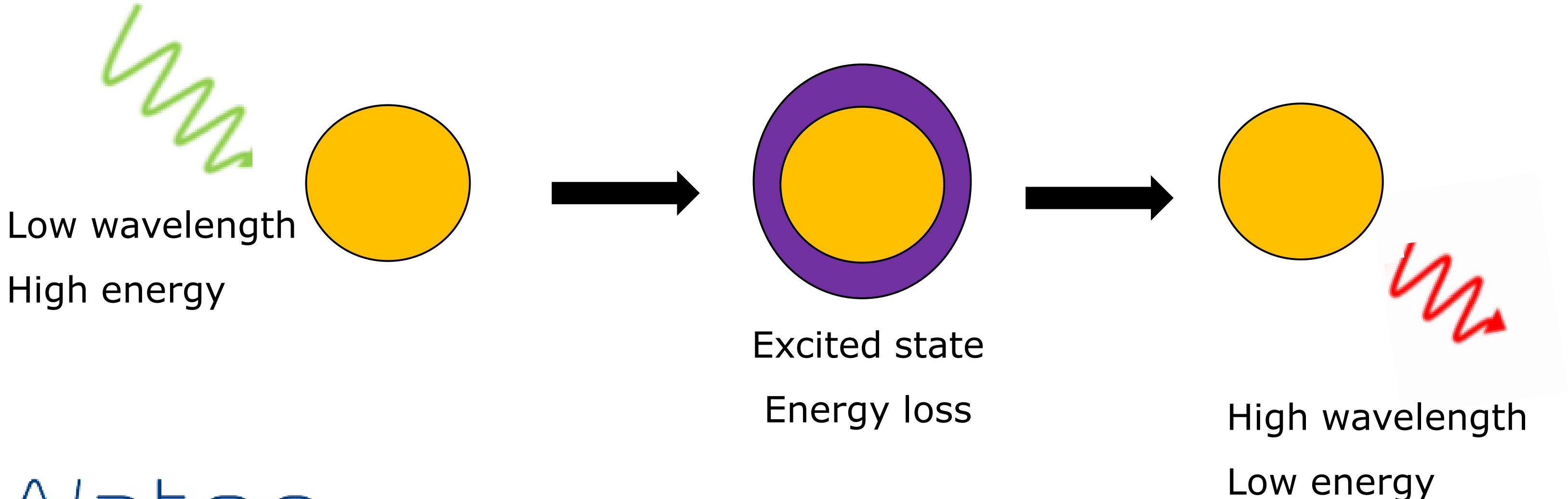
Fluorescence

- DOM contains:
  - Chromophores (absorb light)
  - Fluorophores (re-emit light)
    - Humic substaces (plant origin)
      - Refered as humic-like
    - Amino acids (proteins)
      - Refered as protein-like



(Fluorescence principle)

Photon



Fluorescence transitions

- Based on fluorescence transitions published in an wastewater overview paper (Hudson et al., 2007)
  - To characterized micro-pollutants in waste water
- We use the same wavelength pairs

Fluorophore type	Excitation/Emission wavelength (nm)
Protein-like (Tyrosine-like)	231/315
Protein-like (Tryptophan-like)	231/360
Humic-like	249/450
Protein-like (Tyrosine-like)	275/310
Protein-like (Tryptophan-like)	275/340
Humic-like	335/450

Our Aim

- Does naturally fluorescent DOM exist in RAS?
- Is the natural fluorescence in RAS reacting with ozone?
- How could this knowledge be implemented in real life applications?

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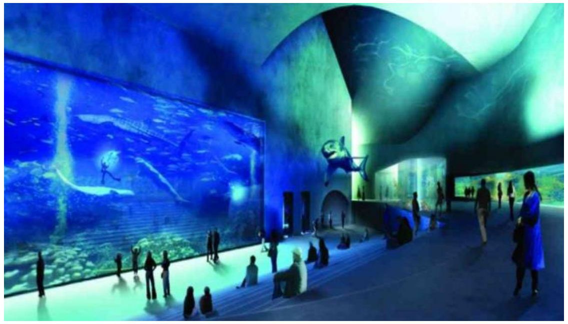
Sampling sites



Model trout farm

Tivoli

Eel fish farm

Pilot scale RAS

The Blue Planet

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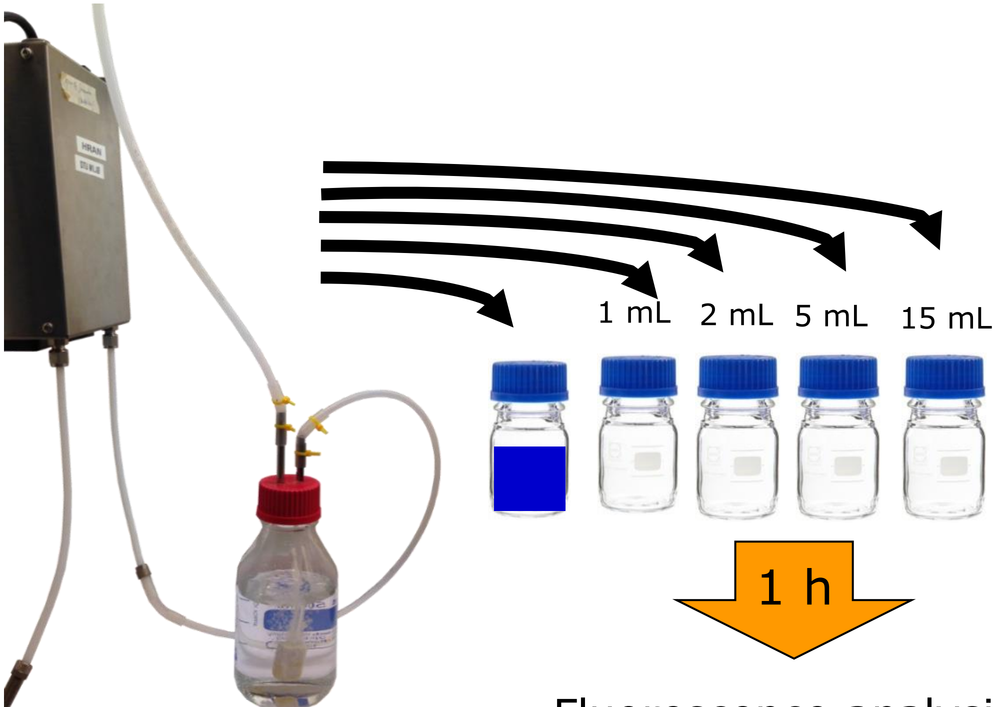
Experimental setup-lab scale

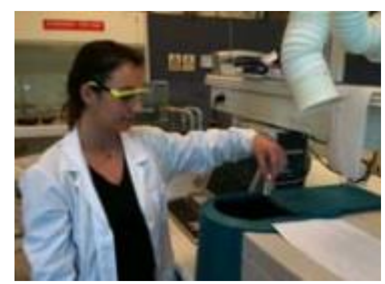


Stock solution of ozone

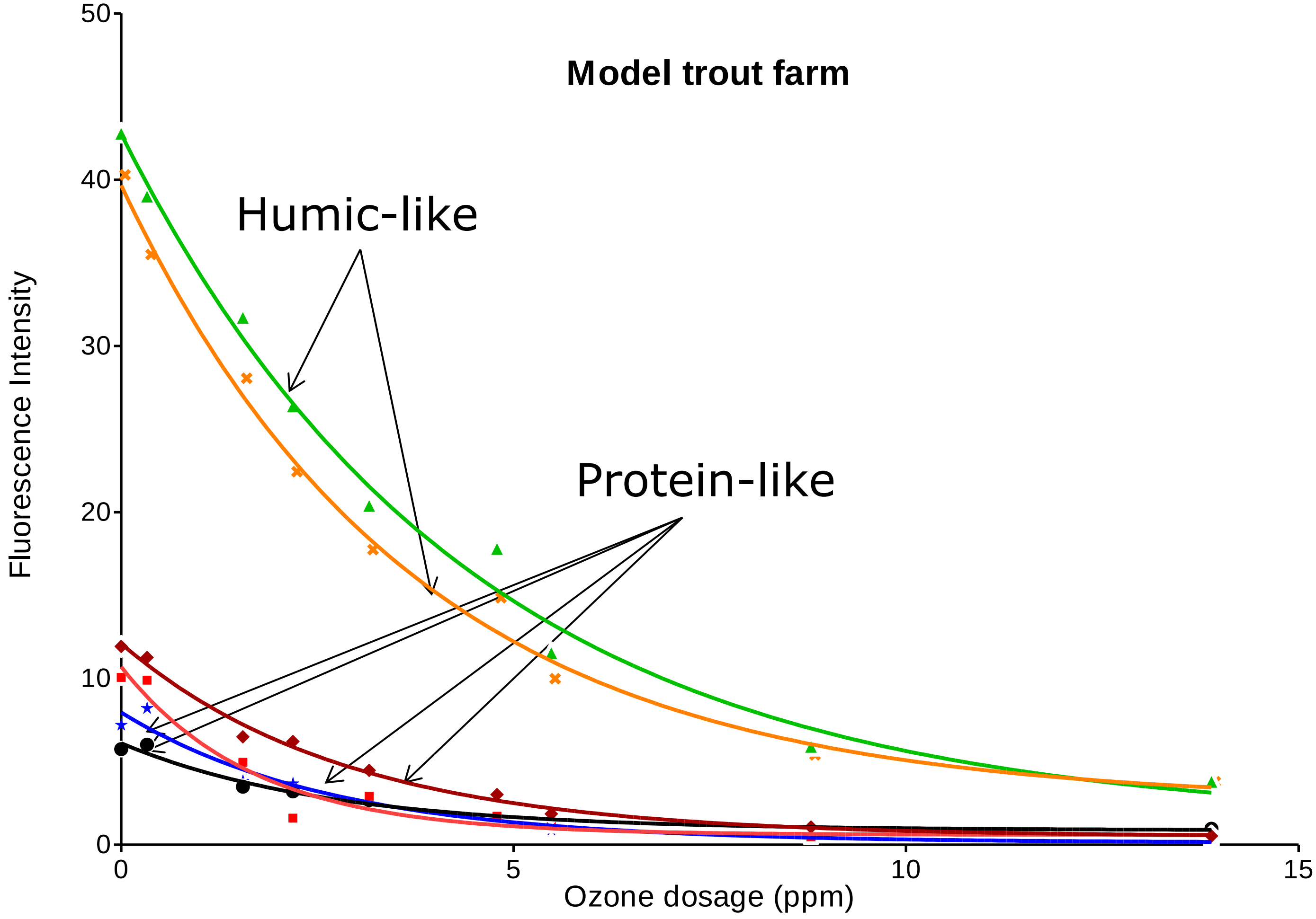
Fluorescence analysis

Water characterization

- Ozone doses
  - 0 to 20 mg O_3/L



Water characterization based on fluorescence



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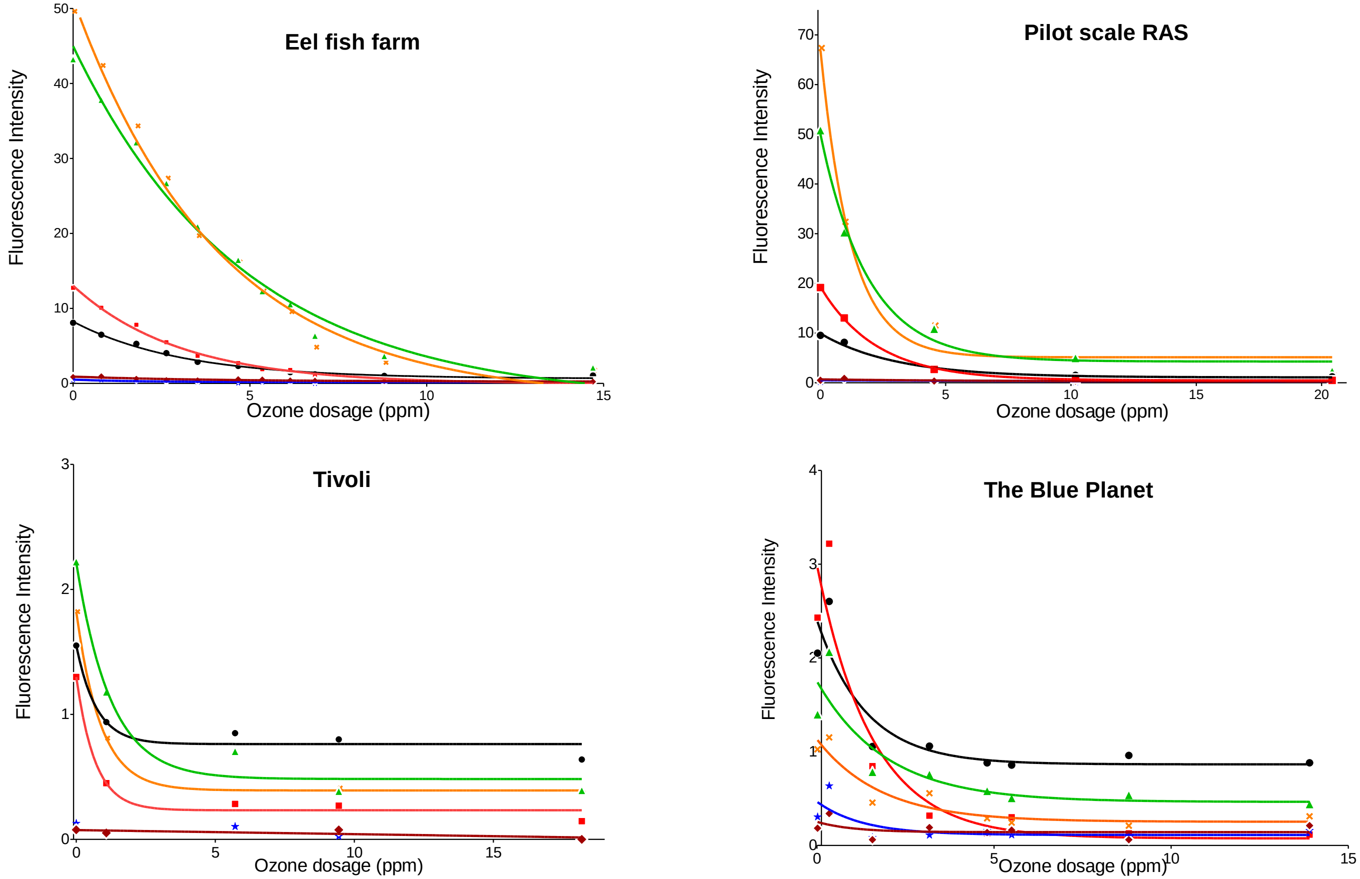
Fluorescence profile in different water samples



- Fish-farms: humic-like fluorescence dominates
- Aquariums: more diverse fluorescence
- High ozone sensitivity in low concentrations

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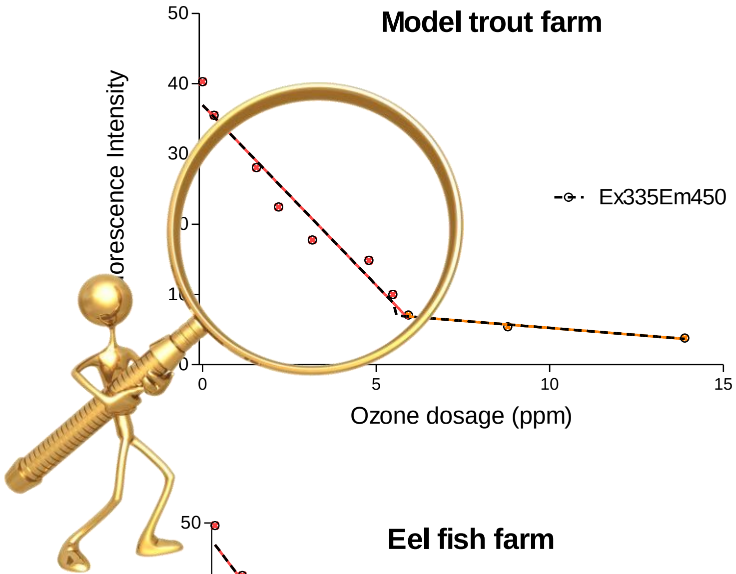
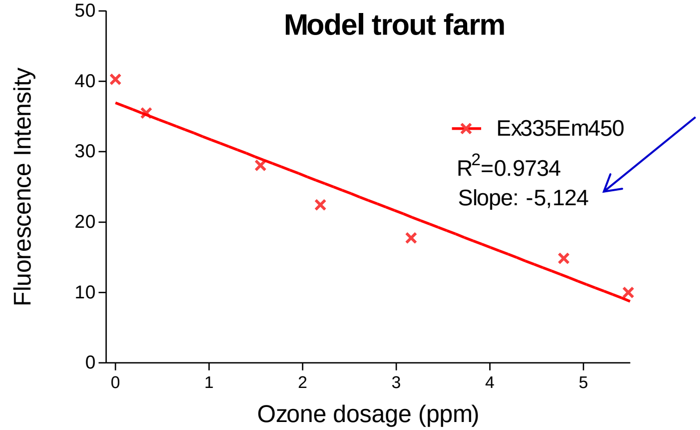
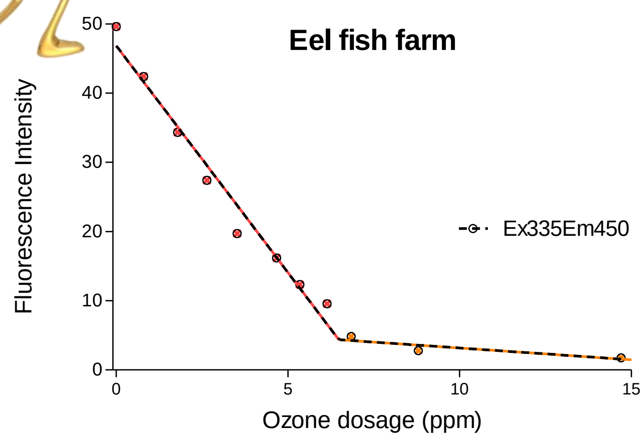
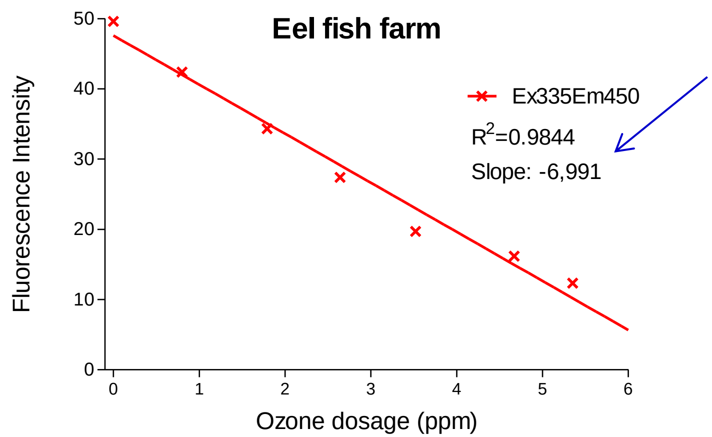
Humic-like fluorescence calibration curve









- Slopes among samples varied

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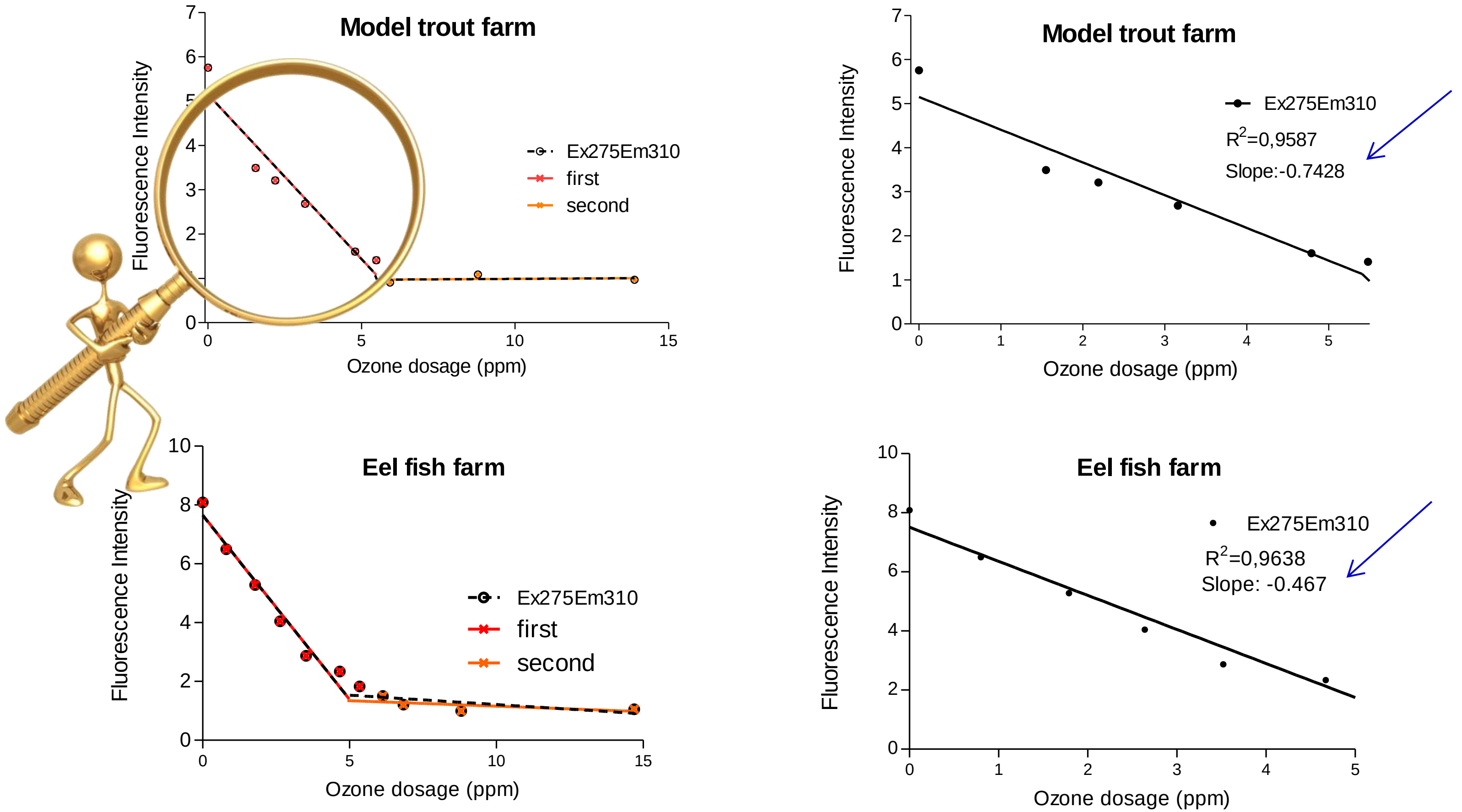
Protein-like fluorescence calibration curve



- Slopes among samples varied
  - Other OM contained in water are competing fluorescence
- Unlike to have a universal sensor controlling ozone into water

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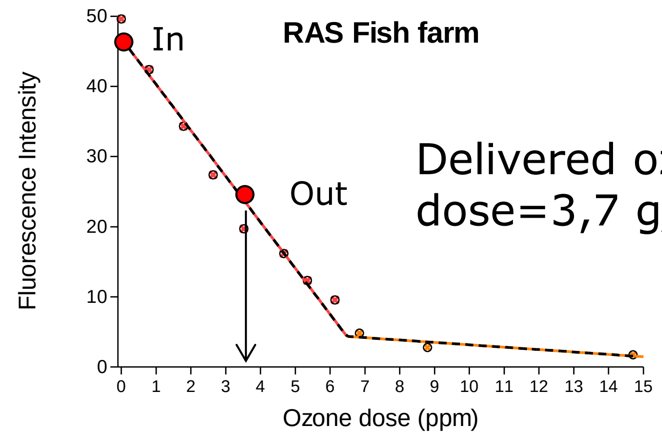
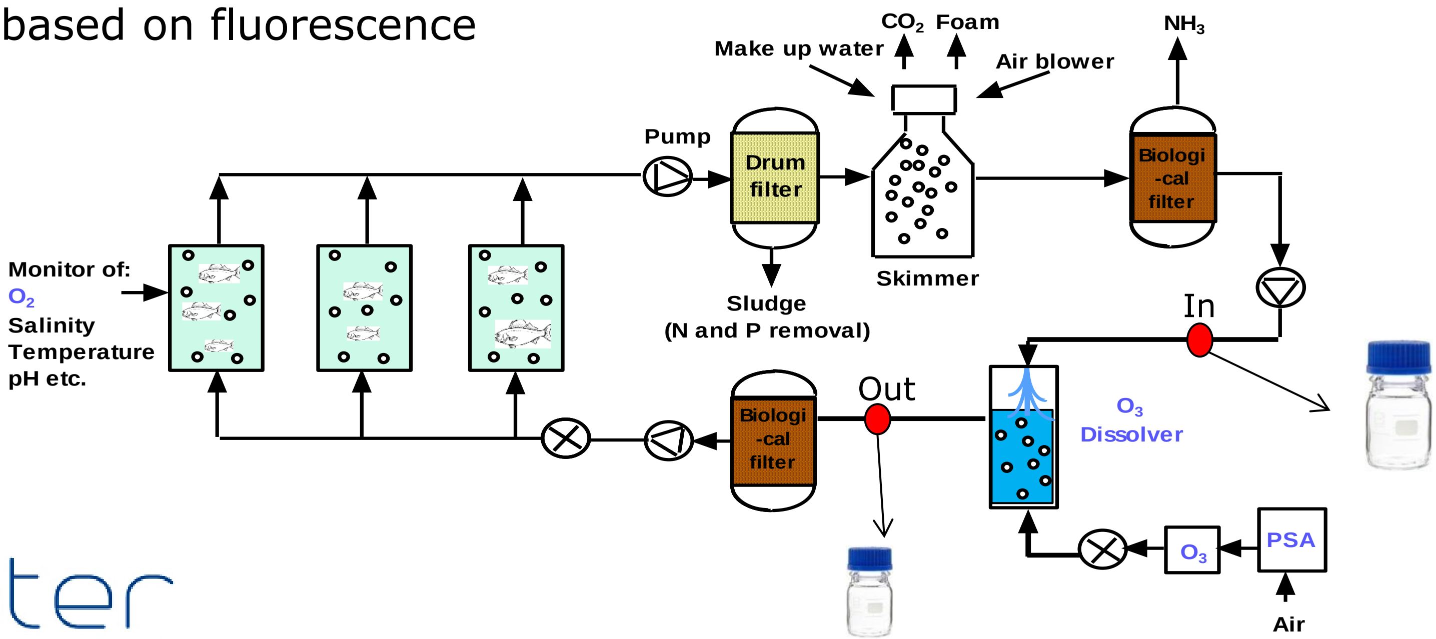
Application #1: Determination of delivered ozone dose

- Does the generator deliver the ozone dose that the specifications promise?
- Validation of ozone generator
- Without sensor installation
- How does it work?
  - Grab samples before and after
  - Calibration curve in the lab based on fluorescence

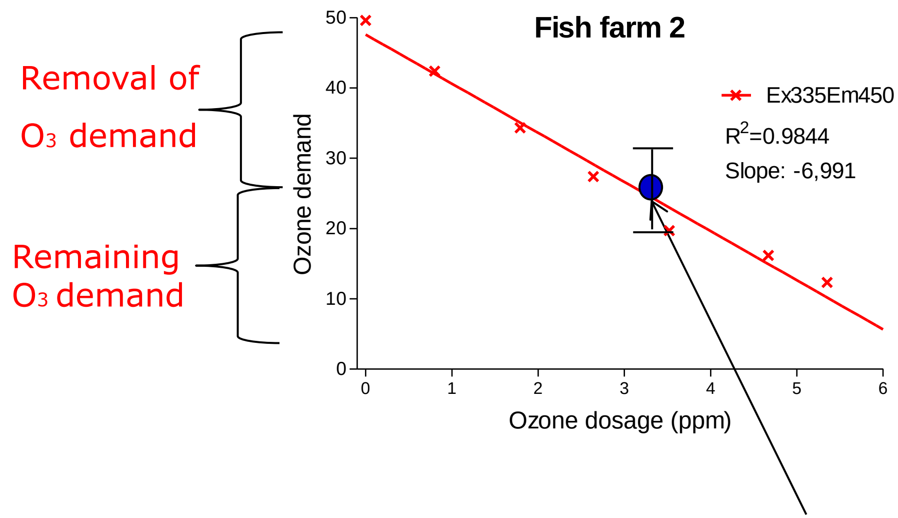


Delivered ozone dose=3,7 g/m³



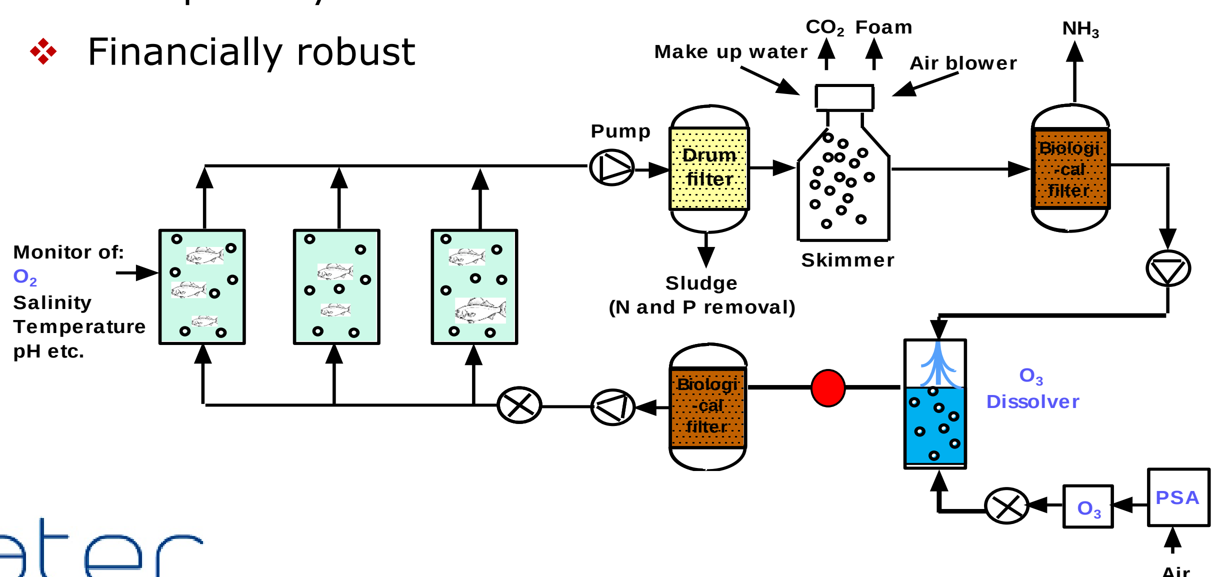
Application #2: On-line control

- Online Fluorescence sensor
- How does it work?
  - Choose a fluorescence intensity within a calibration curve and add as much ozone as needed to achieve this intensity
- Aim:
  - Ozone demand is defined
  - Low disinfection but high transparency
  - Financially robust



Control point

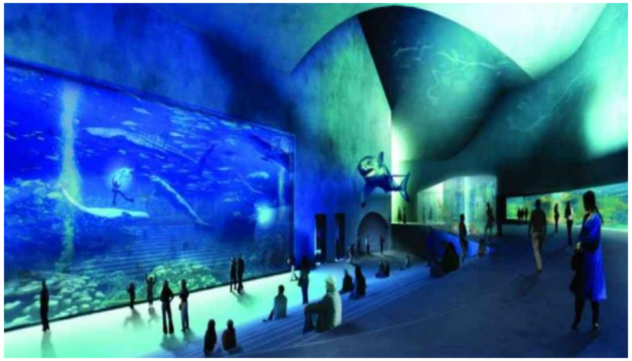
(ensuring remaining O_3 demand)



Take-home message

- Fluorescent DOM does exist in aquaculture water
- Fluorescence is highly sensitive to ozone mostly in low ranges (0-5 mg O_3/L)
- Fluorescence can be used as:
  - Off-line control verifying ozone dosage and evaluating ozone generator leading to a more robust operation
  - On-line sensor controlling ozone dosage by keeping fluorescence signal within predetermined ranges

Acknowledgements



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Thank you for the attention !!!

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