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Coltivazione di microalghe in reattori continui: un approccio rivolto alle applicazioni industriali

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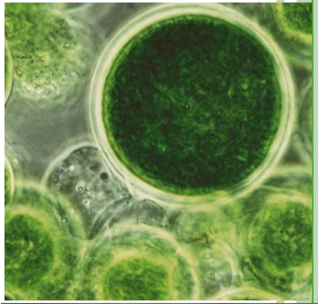
Outline

- Cultivation in a continuous photobioreactor (PBR)
- Mass and energy conservation balances
- Specific microalgae growth rate
- Photosynthetic efficiency and light supply rate
- Effects on biomass composition and production
- An energy efficient technological solution
- Nutrient supply and nutrient recycling
- Conclusions and discussion



Large scale production

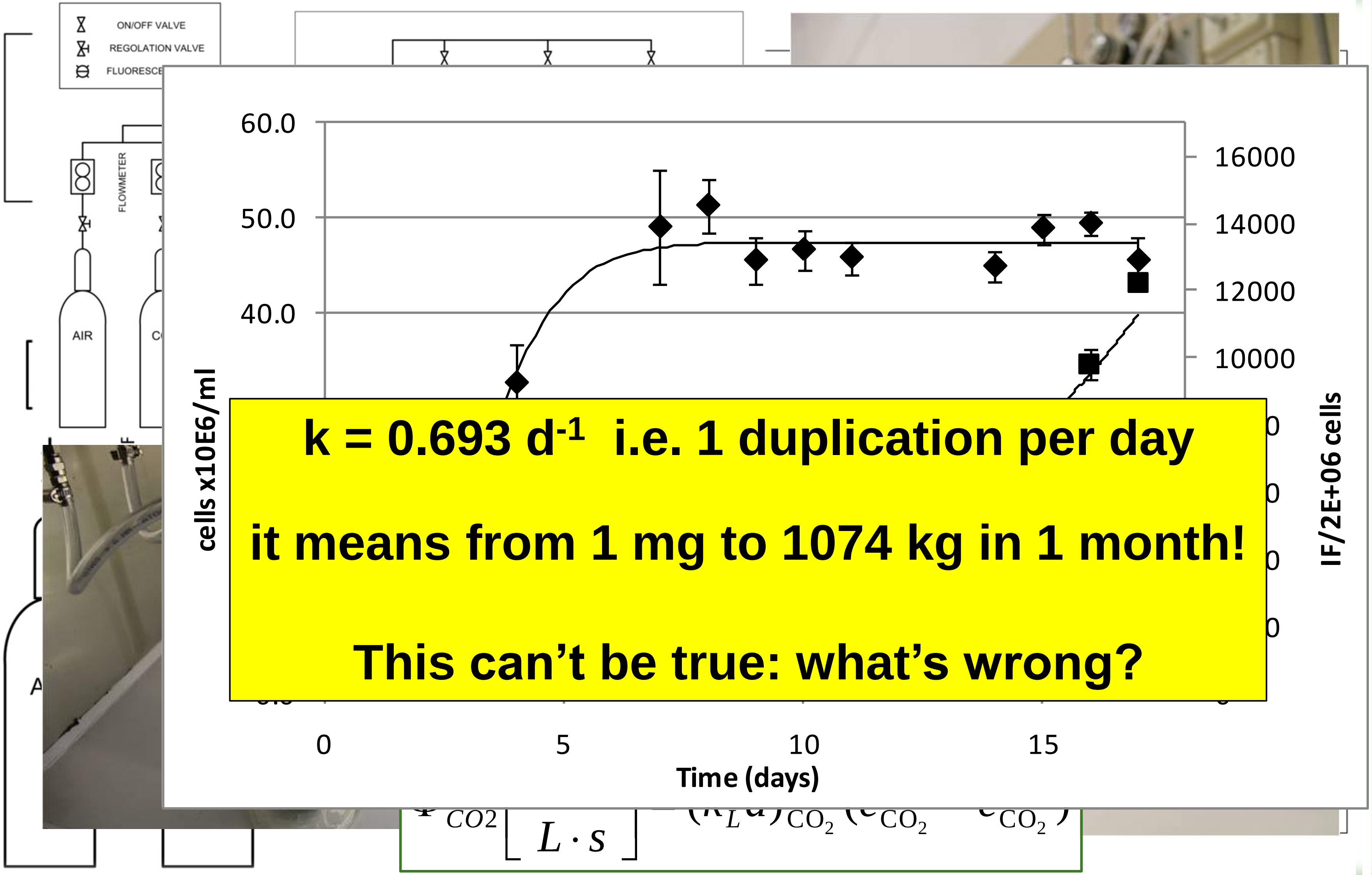
Fonte: web

Large scale production

CLOSED PHOTOBIOREACTOR SYSTEM IS THE INDUSTRIAL APPROACH TO LARGE SCALE AUTOTROPHIC MICROALGAE PRODUCTION

- First constraint: the conservation of **mass**. The desired production cannot be achieved if sufficient amounts of reactants (i.e. nutrients) are not supplied to the PBR
- Second constraint: the conservation of **energy**. The produced microalgae have a lot of internal energy (measured as Lower Heating Value, LHV) that must come from somewhere (i.e. sunlight energy)
- Both nutrients and light must be transferred from the bulk of the mixture to the cells, for the growth to occur. This requires both high **mass transfer and high transparency to light energy**
- …what about the **growth rate**?
  The measurement of microalgae growth rate is meaningful (correctly done) only if all the three points above have been properly addressed

→starting from bottom: GROWTH KINETICS MEASUREMENTS



k = 0.693 d^{-1} i.e. 1 duplication per day

it means from 1 mg to 1074 kg in 1 month!

This can't be true: what's wrong?

Large scale production: mass balances

- At a molecular level this is the stoichiometry condition. For instance, on a molar basis the composition of a microalga is:

$$C_{1.852}\,N_{0.132}\,O_{0.403}\,P_{0.005}$$

- To grow microalgae basically C, N and P have to be supplied. On a mass basis as a rule of thumb their requirements are: 100:5:0.5
- In the lab C is supplied as CO_2, N as urea/nitrates, P as phospates
- At the large scale production level the material balance is in term of flow rates (mass/time)
- To produce 1,000,000 tonn/year of microalgae (Dry Basis) we need:
  - 2,000,000 tonn/year of CO_2 (not an issue, maybe a blessing)
  - 200,000 tonn/year of urea (same as the total world production)
  - 20,000 tonn/year of sodium phosphate (exhaustion of P mines)
  - Other “micro” nutrients

NOTE every kg of microalgae produced, 2 kg of CO_2 are captured

→ THE MASS CONSERVATION BALANCE (cont'd)

- C, N, O, P (and others) are to be supplied. They are called nutrients
- concentration in the photobioreactor: not an issue, just a process operating variable to be optimized
- growth rate: to be measured in batch experiments (bottles) without any nutrients limitation. It depends upon temperature
- >99.9% of the material in the PBR is water

Large scale production

- Water
- Temperature
- CO_2

Flue gas

CO_2 absorption from combustion flue gases

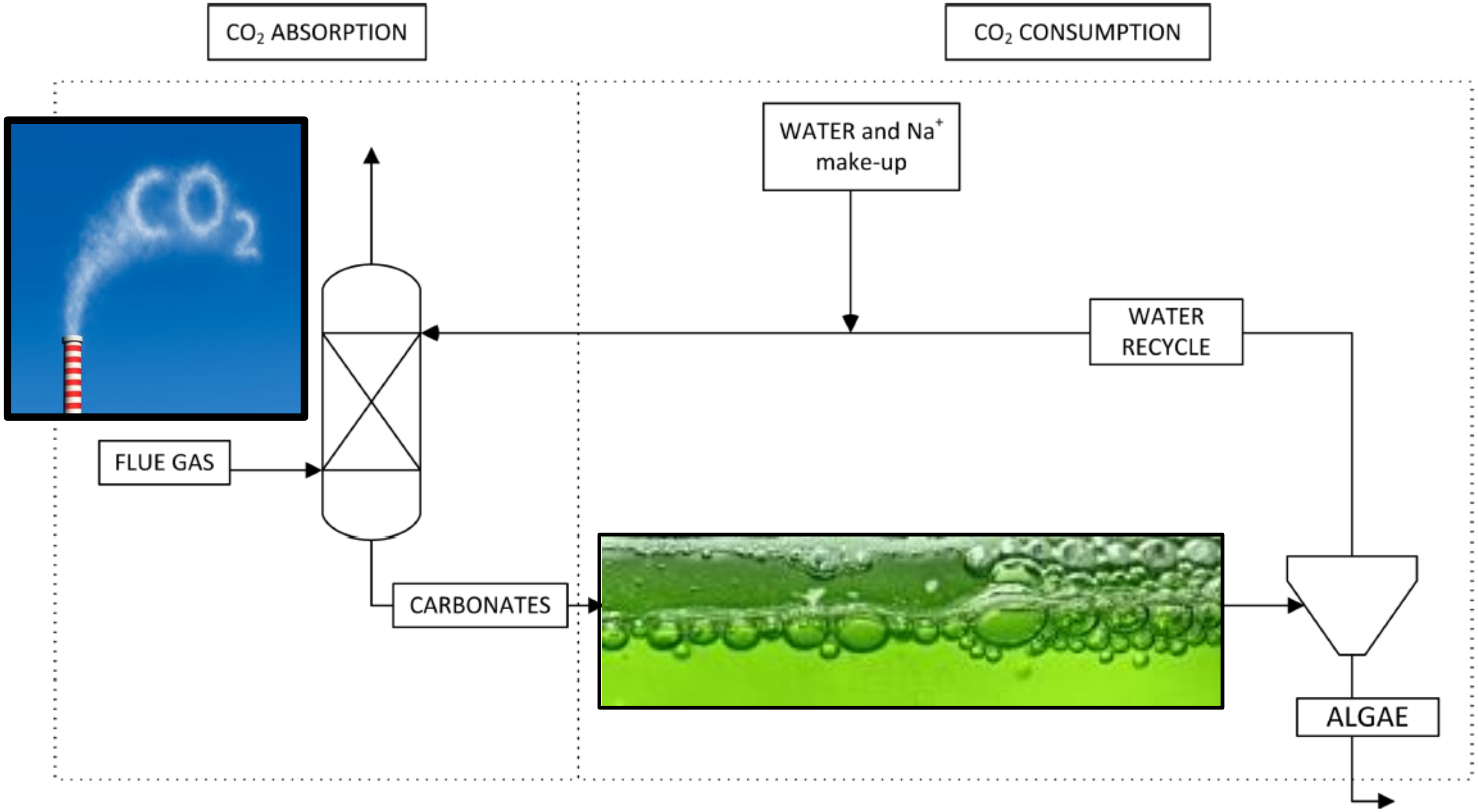


Figure 5. Scheme process proposal of CO_2 capturing from flue gas using carbonates.

Large scale production

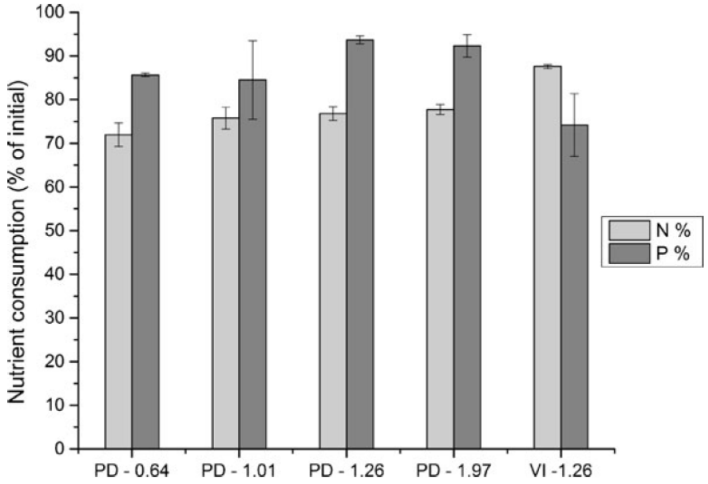
Flue gas

- Water

- Temperature
- CO_2
- Macro e micro nutrients

Wastewater treatment

Nitrogen and phosphorus from waste



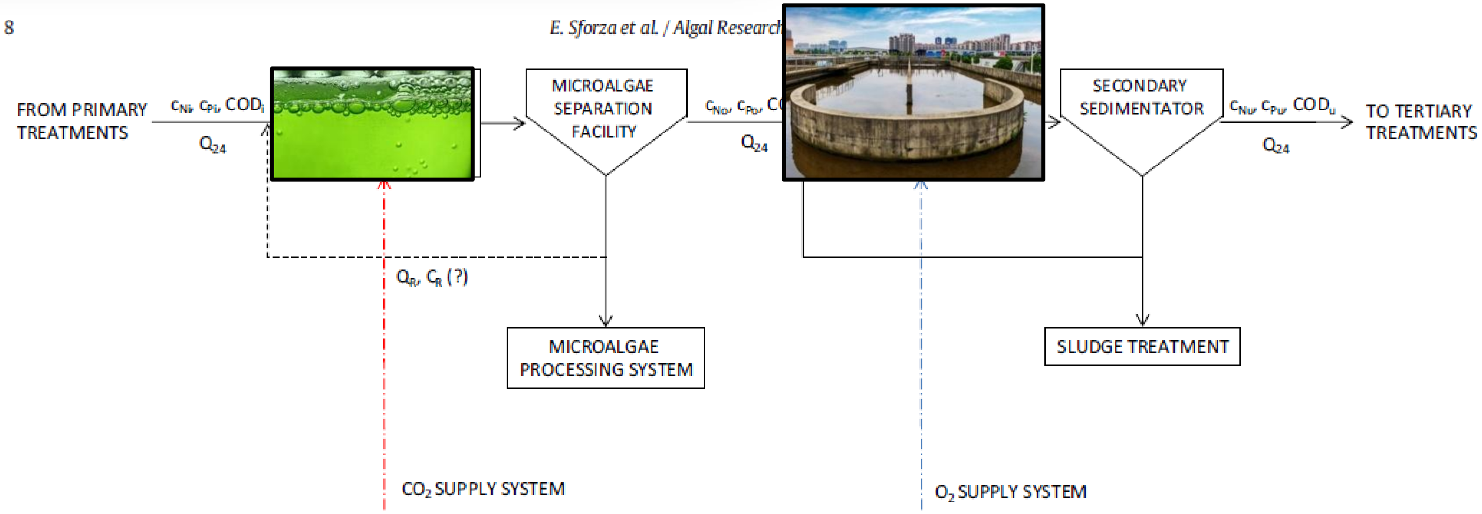


Fig. 5. Process scheme proposal: the microalgae reactor followed by conventional activated sludge process.

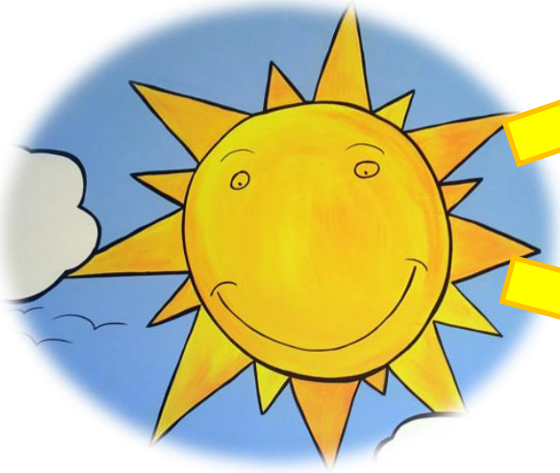
Large scale production

- Water

Flue gas

- Temperature
- CO_2
- Macro e micro nutrients

Wastewater



- LIGHT

→THE ENERGY CONSTRAINT

- Microalgae as an organic material store biochemical energy. This is measured in terms of LHV, Lower Heating Value
- In photoautotrophic cultivations this biochemical energy comes from sunlight energy
- Only part of the solar spectrum can be exploited by photosynthesis: basically blue and red wavelengths
- This photosynthetically Active Portion (PAR) is transformed into biomass with lower energetic efficiency (theoretical limit is around 25%)
- The photon energy is the process driver (this is the limiting “nutrient”!):

$$1\ \mu\text{Einstein}/(\text{m}^2\ \text{s}) = 0.225\ \text{W}/\ \text{m}^2$$

Sunlight energy flux intensity ranges from zero to 2000 μEinstein/(m^2 s)

- Photosynthetic efficiency strongly depends on irradiation intensity: microalgae grow better when shaded

→ 2nd BASIC POINT: THE ENERGY CONSERVATION BALANCE

- This is the first principle of thermodynamics. No question about it
- When the energy for biochemical reactions to occur comes from sunlight, this is always limiting, exactly as a limiting nutrient. It means that the productivity depends upon it, regardless the reaction rate
- Overall solar energy hitting the ground at Venice of 5000 MJ/(m^2 y)
- max fraction of solar energy exploitable is 12%, i.e. 600 MJ/(m^2 y)
- LHV of microalgal biomass equal to 20 MJ/kg
- maximum production results in 600/20 = 30 kg/(m^2 y) = 300 ton/(ha y), if all the incident PAR energy is exploited
- In general the production per unit PBR area, in kg/(m^2 s), is given by:

$$P_A = \frac{E_{sun} * \eta}{LHV}$$

- and the maximum concentration in the PBR for a given photosynthetic efficiency η is:

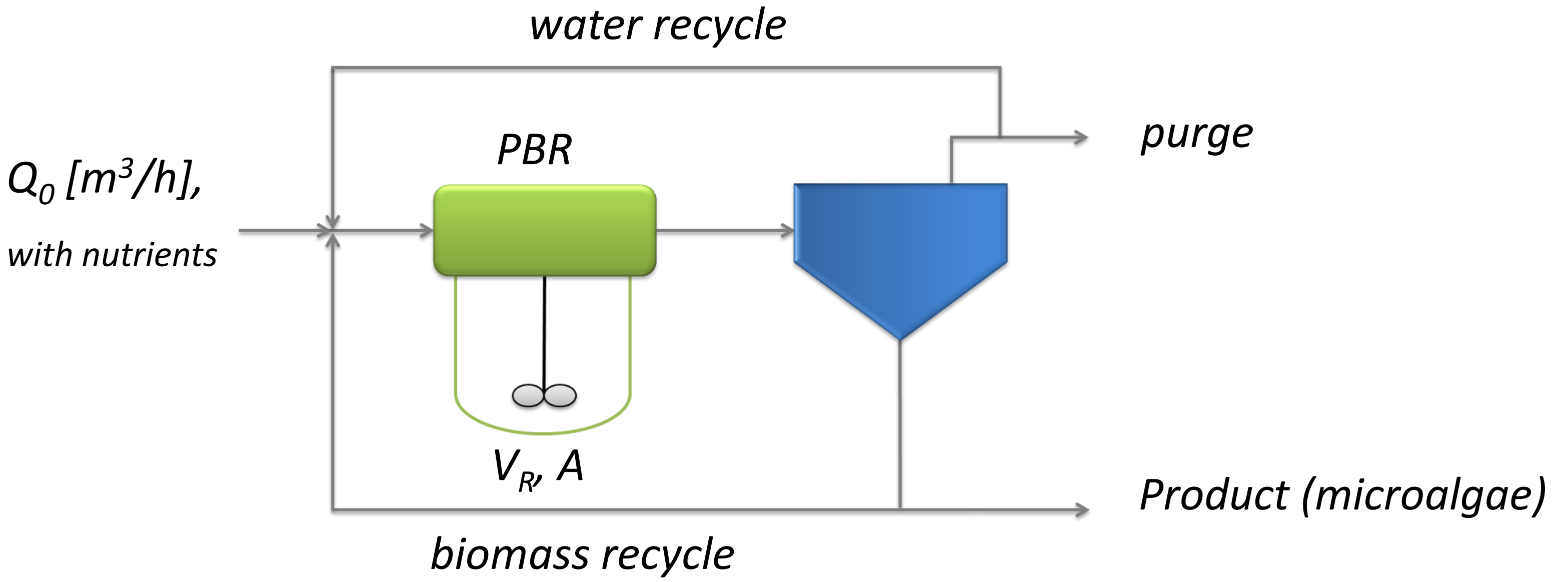
$$C_X = \frac{P_A}{Q_0/A}$$

→ THE ENERGY CONSERVATION BALANCE (cont'd)

- with a kinetic constant of 0.8 d^{-1}, and a biomass concentration of 1 kg/m^3 the expected productivity is 300 $kg/(m^2\ y)$
- The production per unit PBR volume is related to P_A by: $P_V = \frac{P_A}{H}$,

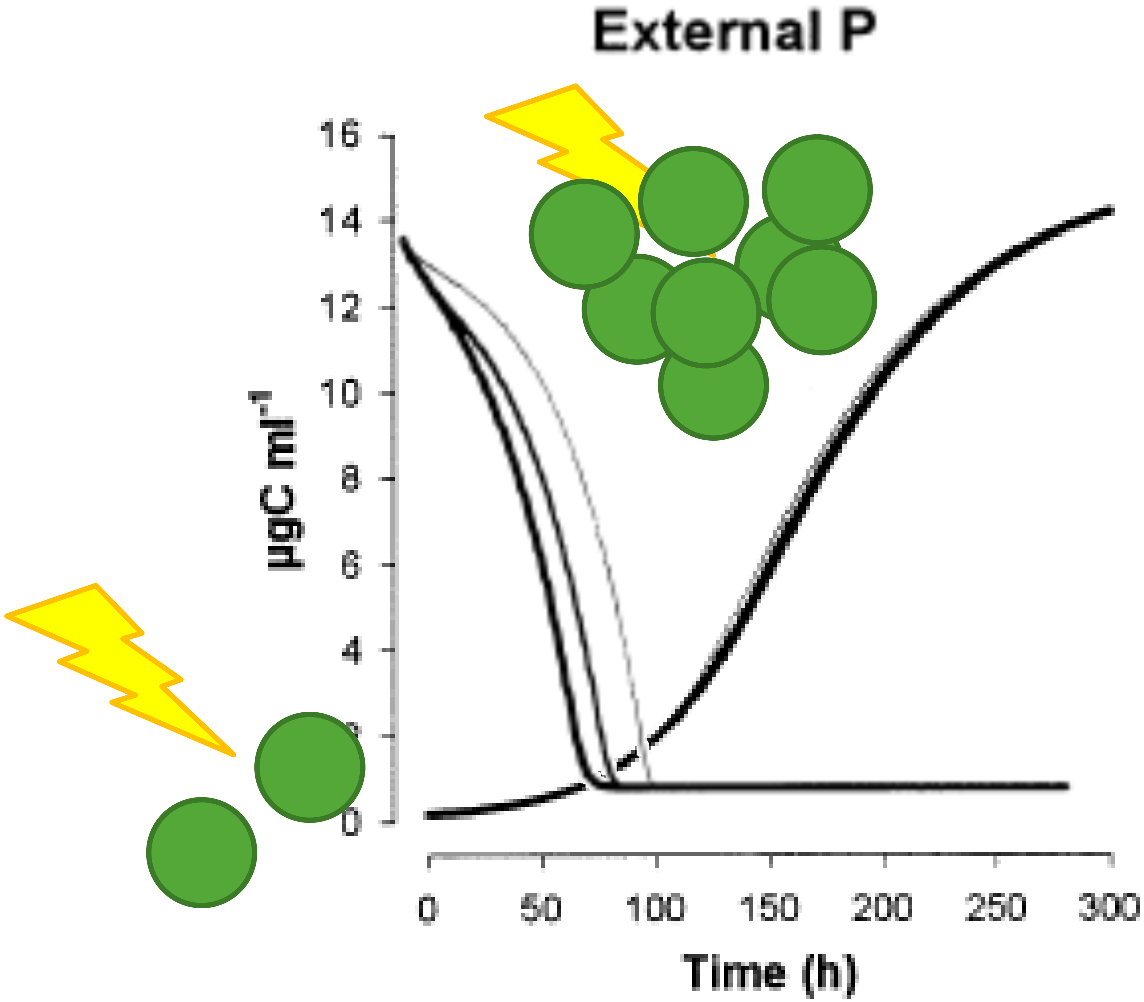
  where H is the PBR thickness, i.e. the light path length in the PBR
- Therefore, with the assumed volumetric production rate, all the light energy available is exploited in a 30/300 = 0.1 m =10 cm layer
- Note that the photosynthetic efficiency η is much lower than 12% in large scale photobioreactors, so that the current practical limit of productivity is 80 $kg/(m^2\ y)$
- This is quite a huge issue for microalgae exploitation, especially because the other way of catching solar energy (photovoltaics) is technologically far ahead (commercial PV modules are already able to transorm 20% of sunlight energy into electricity)
- Other issues: high dilution, large nutrient requirements, contamination,...

→ CONTINUOUS OPERATION OF A PHOTOBIOREACTOR

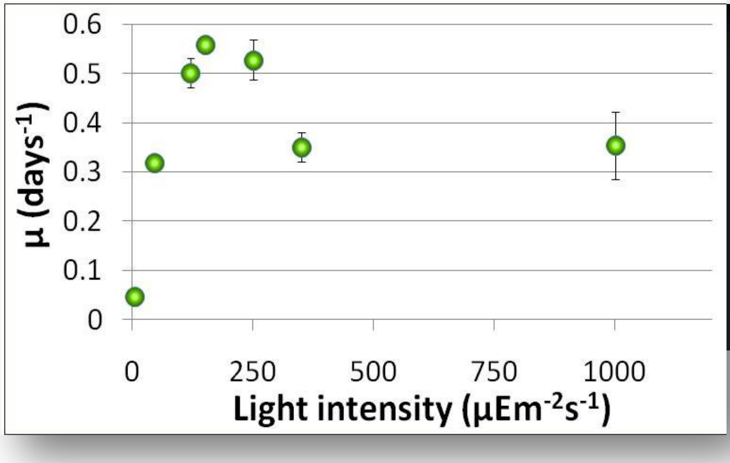


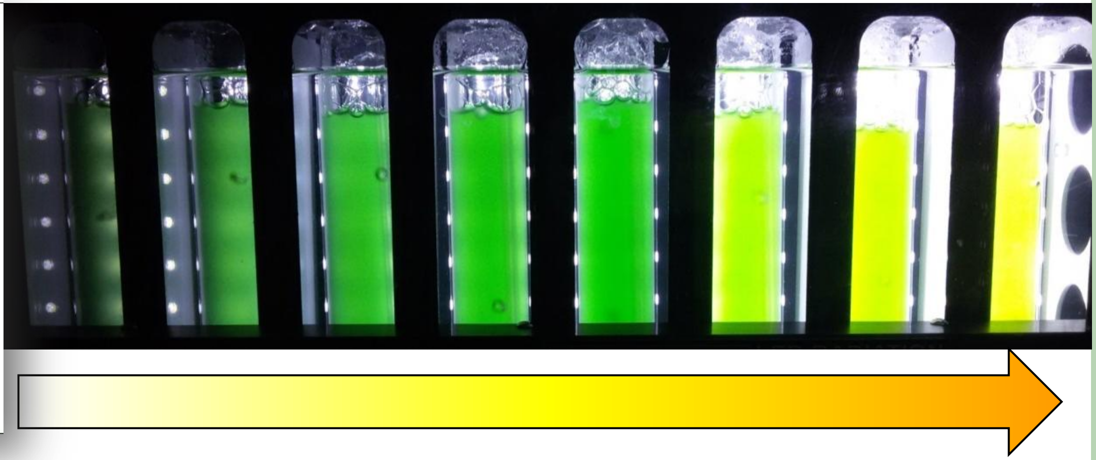
- At the large scale continuous-flow systems ensure larger productivity, easier operation control and constant quality production than batch ones, thanks to steady-state operation
- Steady-state is achieved spontaneously by any biological reactor, and easily maintained, as long as none of the reactor inputs is subjected to disturbances (the Chemostat concept holds also for PBR)
- Steady-state production depends on two variables only: residence time τ ($=V_R/Q_0$) and (less) degree of mixing in the PBR

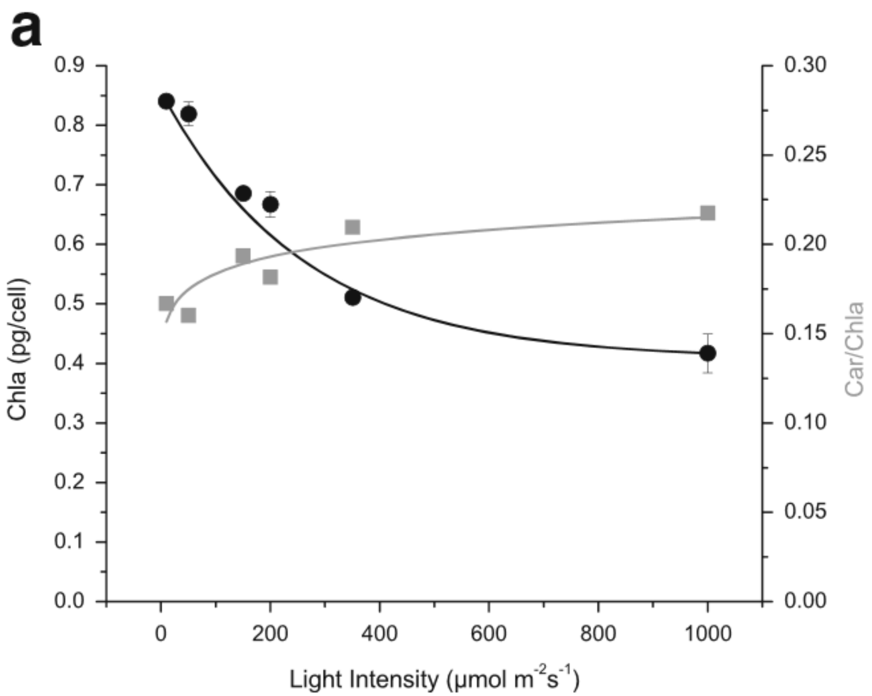
Batch experiments



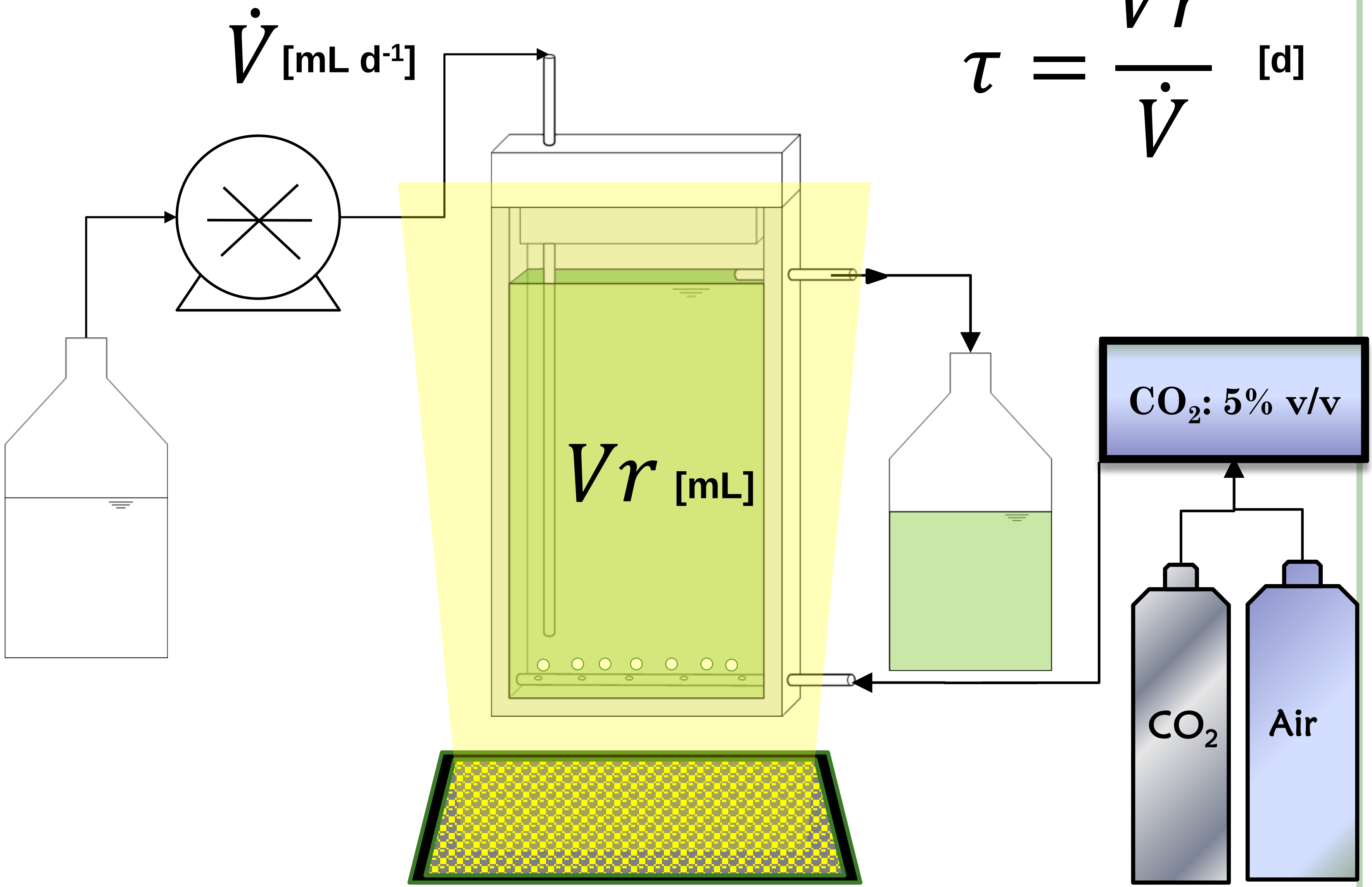
Effect of light on growth





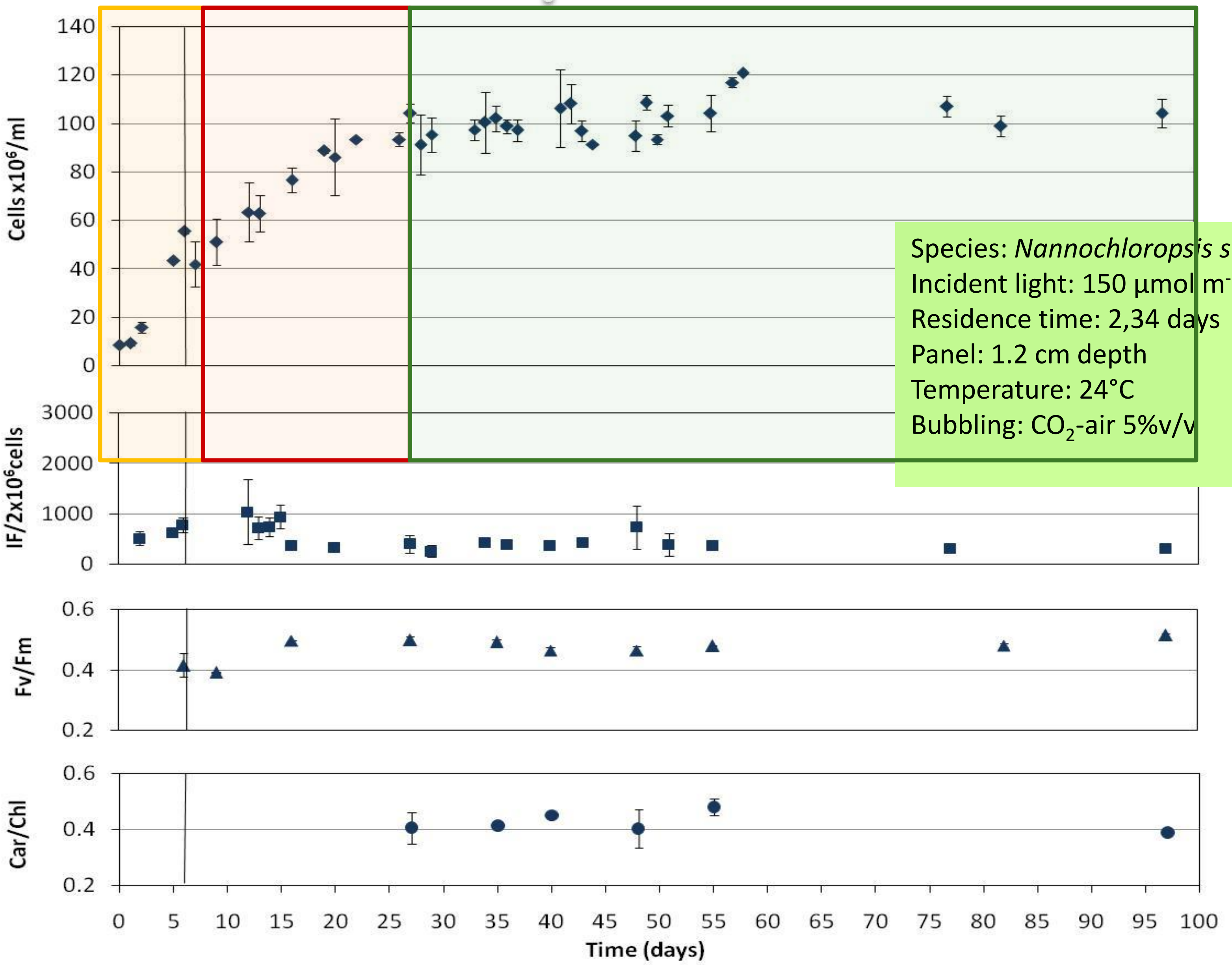


Lab continuous photobioreactor



$$\tau = \frac{Vr}{\dot{V}} \quad [d]$$

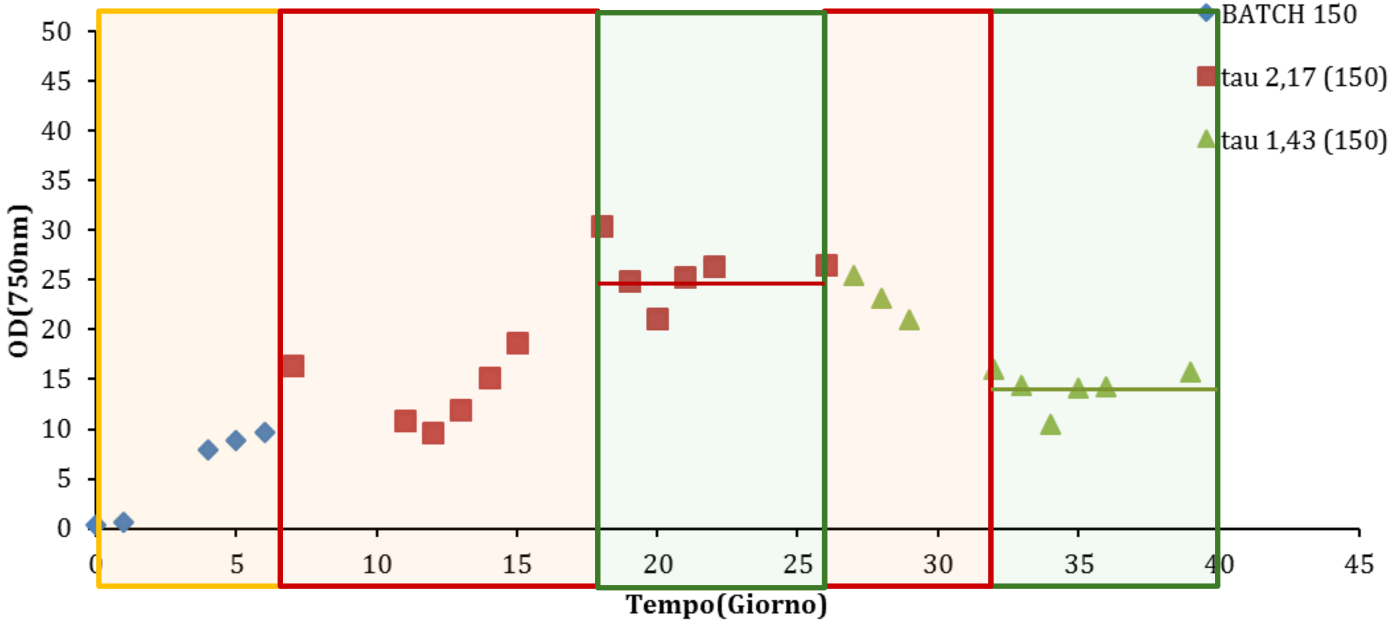
Continuous photobioreactor



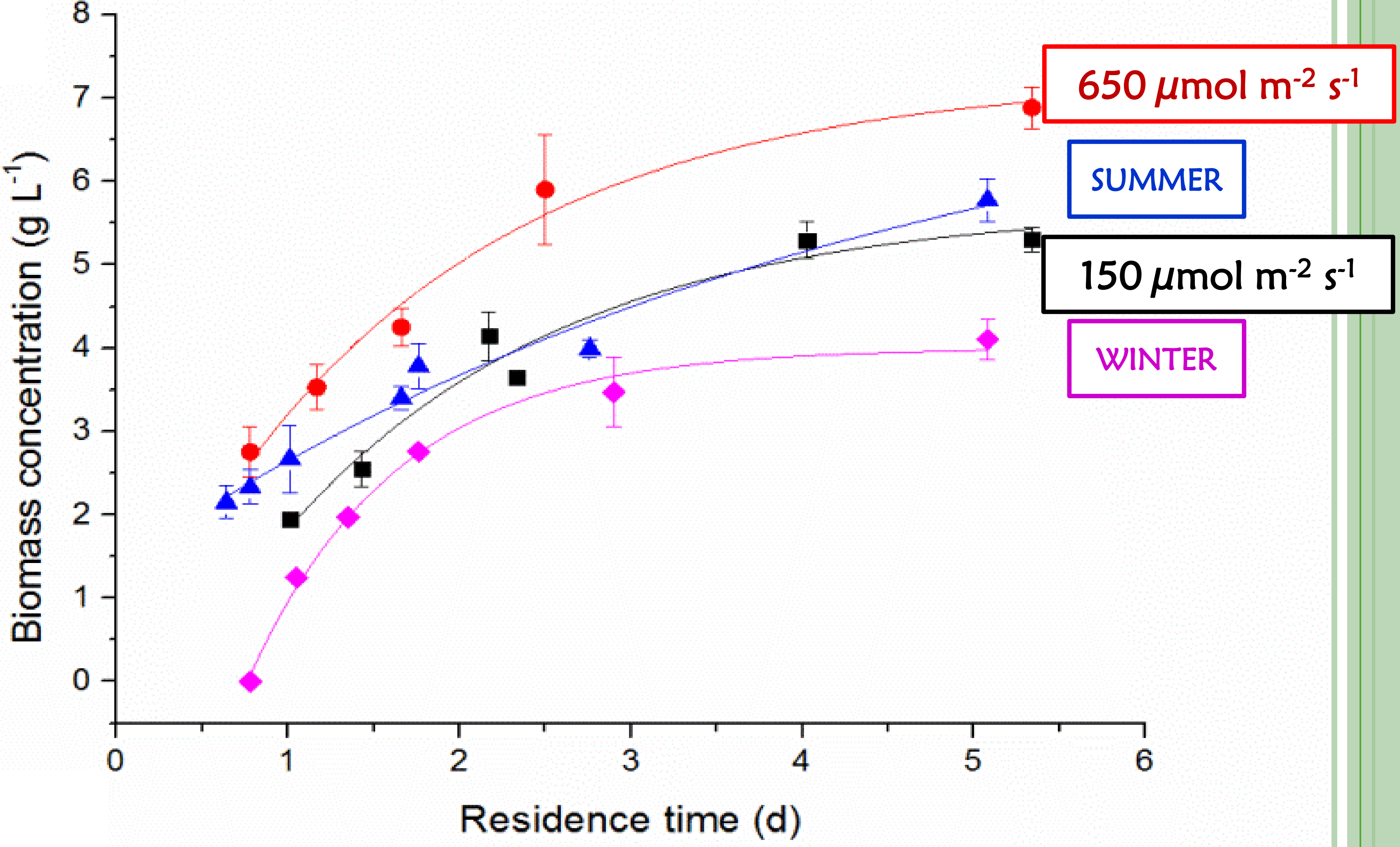
Species: *Nannochloropsis salina*
Incident light: 150 µmol m^{-2} s^{-1}
Residence time: 2,34 days
Panel: 1.2 cm depth
Temperature: 24°C
Bubbling: CO_2-air 5%v/v

Continuous photobioreactor

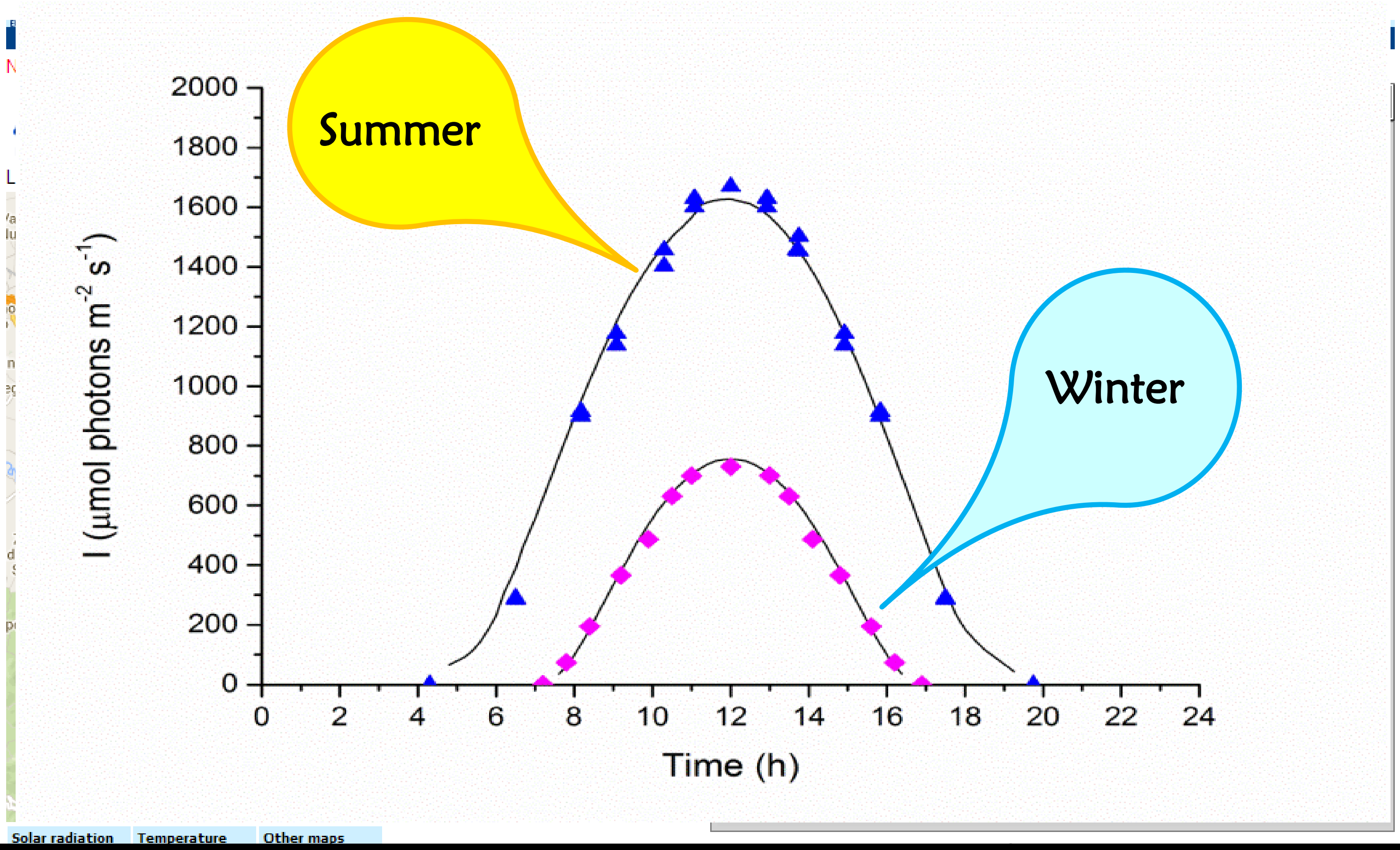
Species: *Scenedesmus obliquus*
Incident light: 150 µmol m^{-2} s^{-1}
Residence time: 2.17 and 1.43
Panel: 1.5 cm depth
Temperature: 24°C
Bubbling: CO_2-air 5%v/v



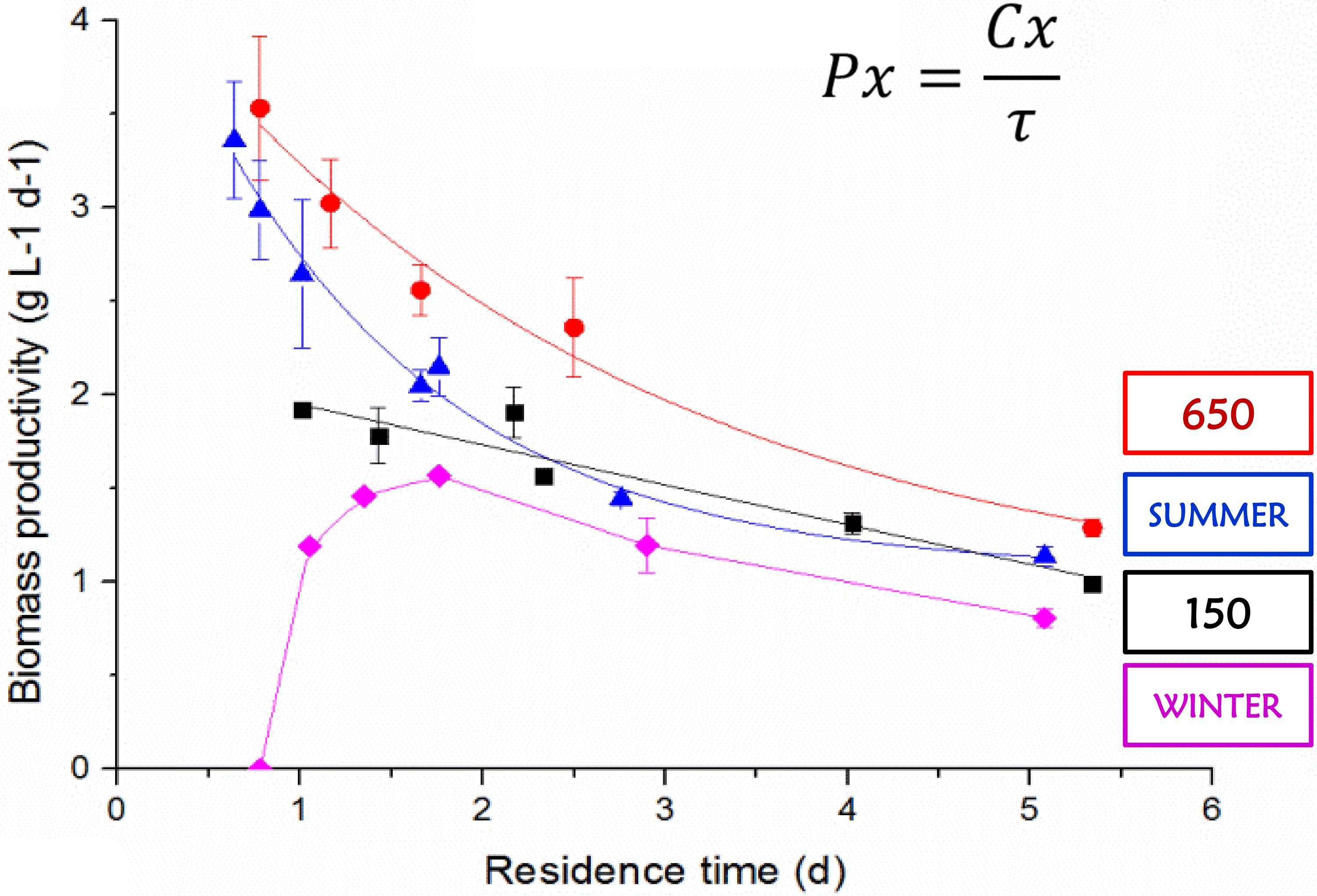
RESULTS: BIOMASS CONCENTRATION



DAY-NIGHT CYCLE: HOW REALITY IS SIMULATED IN THE LAB



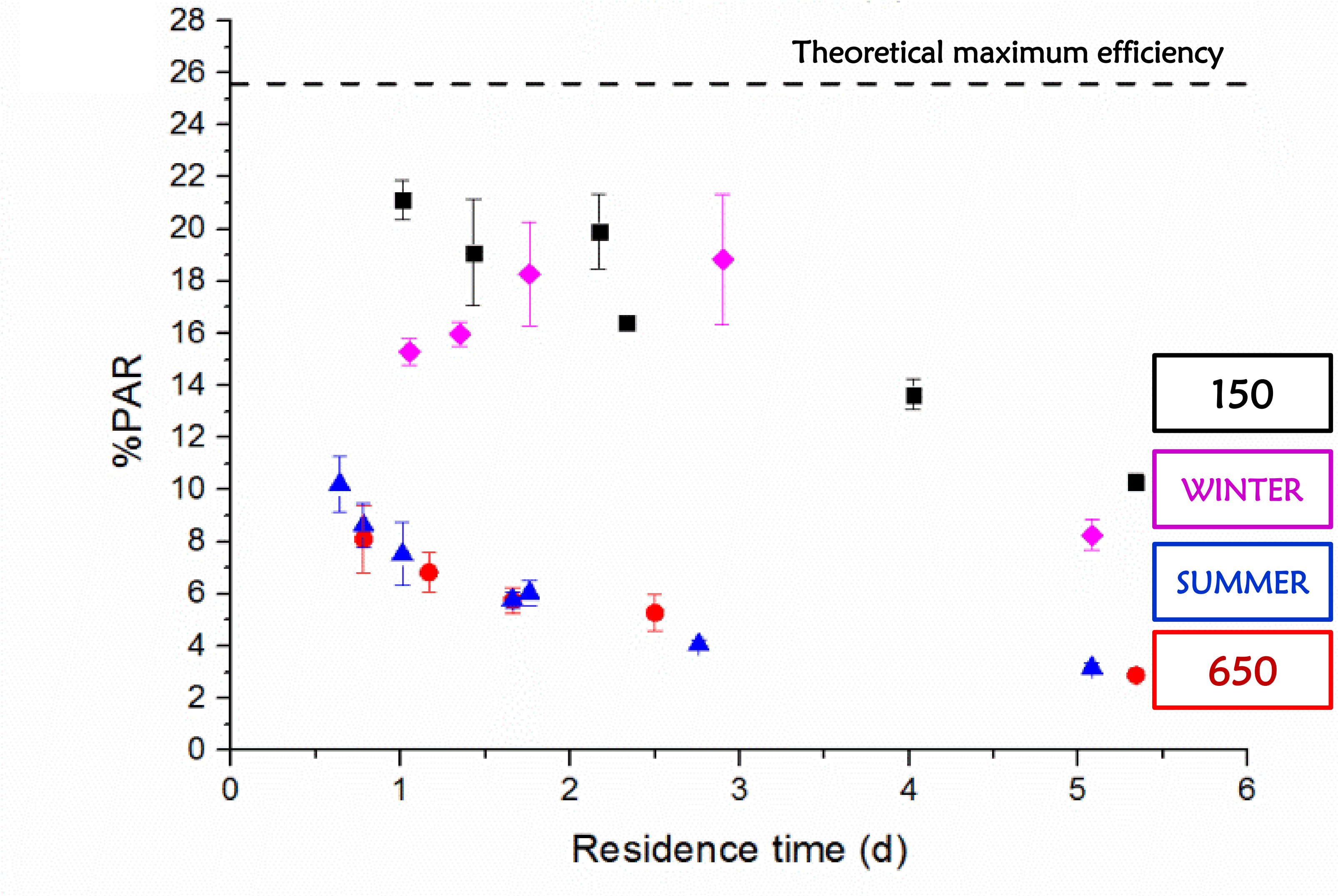
RESULTS: BIOMASS PRODUCTIVITY



$$Px = \frac{Cx}{\tau}$$

RESULTS: PHOTOSYNTHETIC EFFICIENCY

$$\%PAR = \frac{C_x * Q * LHW}{PFD_{abs} * E_p * A_{PBR}}$$

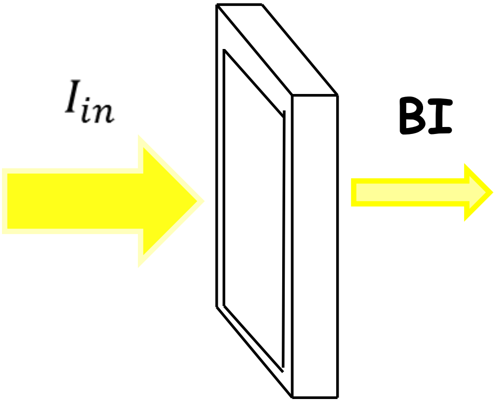


LIGHT: r_{EX}

r_{EX}= specific light supply rate (mmol g^{-1} d^{-1})

Specific light supply rate (r_{EX}): the flow rate of photons absorbed per gram of biomass (mmol photon g^{-1} d^{-1})

$$r_{Ex} = \frac{PFD_{Abs} \cdot A_{PBR}}{C_x \cdot V_{PBR}}$$



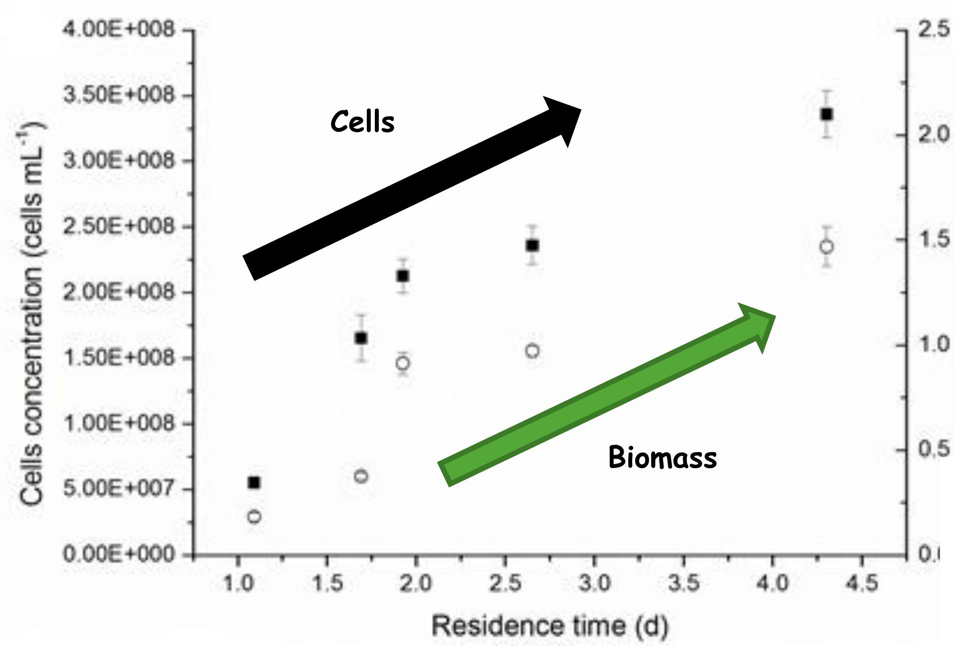
- PFD_{Abs}: absorbed Photon flux density
- A_{PBR}: PBR surface area
- C_x: biomass concentration
- V_{PBR}: PBR volume

Tempo di permanenza (giorni)	r_{EX} (mmol photon g^{-1} d^{-1})
1,09	731,41
1,69	595,21
1,94	471,50
2,65	394,92
4,3	329,20

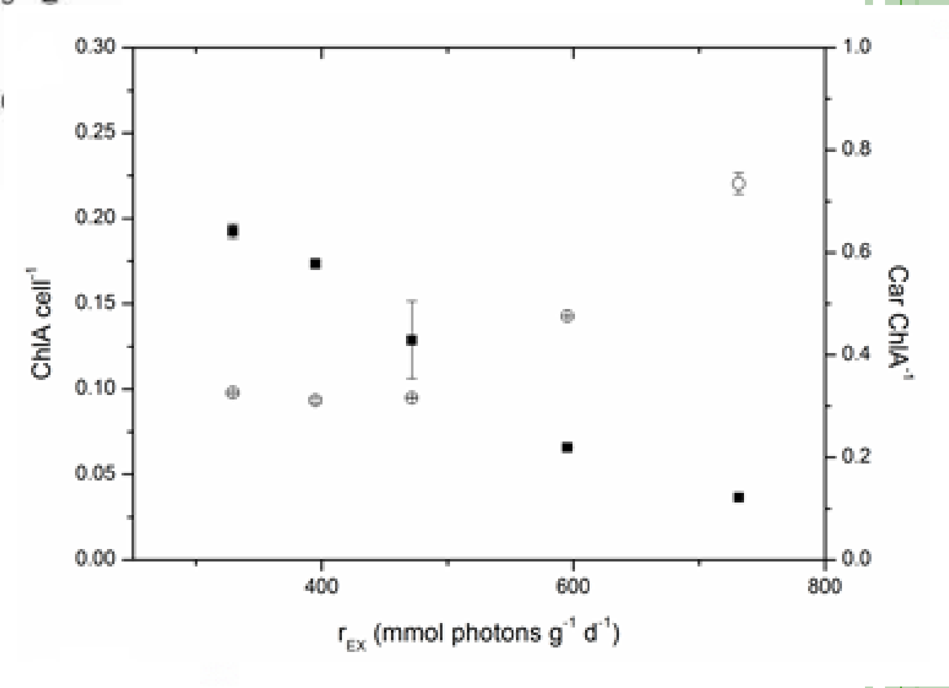
(*) a parità di luce incidente

LIGHT: r_{EX}

r_{EX}= specific light supply rate (mmol g^{-1} d^{-1})



$$r_{EX} = \frac{1}{\tau\,\eta}\;\frac{LHV}{E_P}$$



RESULTS: MAINTENANCE RATE

	Kliphuis approach		
Light regime	**m_E [mmol photons g^{-1} d^{-1}]**	**Y_G [g mmol photons^{-1}]**	**R²**
150 µmol m^{-2} s^{-1}	78.094	2.52E-03	0.98
Winter (≈ 175)	110.728	2.00E-03	0.95
650 µmol m^{-2} s^{-1}	471.469	1.13E-03	0.99
Summer (≈ 550)	543.143	1.32E-03	0.97

$$\mu = \frac{dE}{dt}\frac{1}{X} * c - \mu_e$$

GROWTH MODELING

MIXING CONDITIONS

- **CSTR :** $$\frac{dc_x}{dt} = \dot{V}c_{x,in} - \dot{V}c_{x,out} + r_x V$$
- **PFR:** $$\frac{dcx}{dt} = r_x - \frac{R+1}{\tau}\frac{dcx}{d\grave{y}}$$

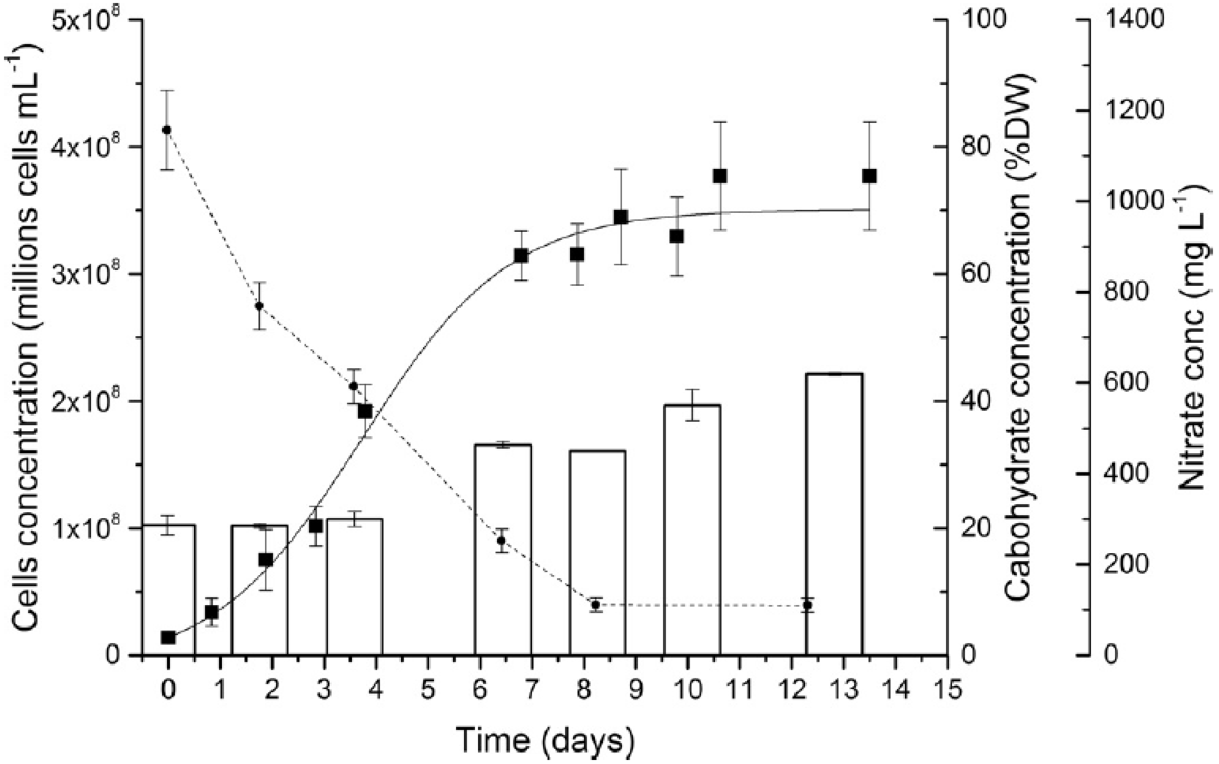
GROWTH KINETICS

$$r_{x,z} = \rho_{m\frac{K}{K+I(z)}} \Phi E_a I(z) c_x - \mu_e c_x$$

EXAMPLE 1 : HOW TO INCREASE CARBOHYDRATE PRODUCTIVITY

- Carbohydrate from microalgal biomass are a product of interest, as well as lipids
- The carbohydrate fraction of biomass changes depending of many environmental factors, such as nitrogen limitation or light intensity
- As the nitrogen limitation is the main way to boost carbohydrate fraction, in batch system a two step approach would be necessary.
- In addition, in a batch system the biomass composition changes with time
- From an industrial perspective, a simplier process would be preferred, as well as a stable product
- We have investigated the possibility to obtain a stable carbohydrate production in a single step, by optimizing the nutrient supply in a continuous system

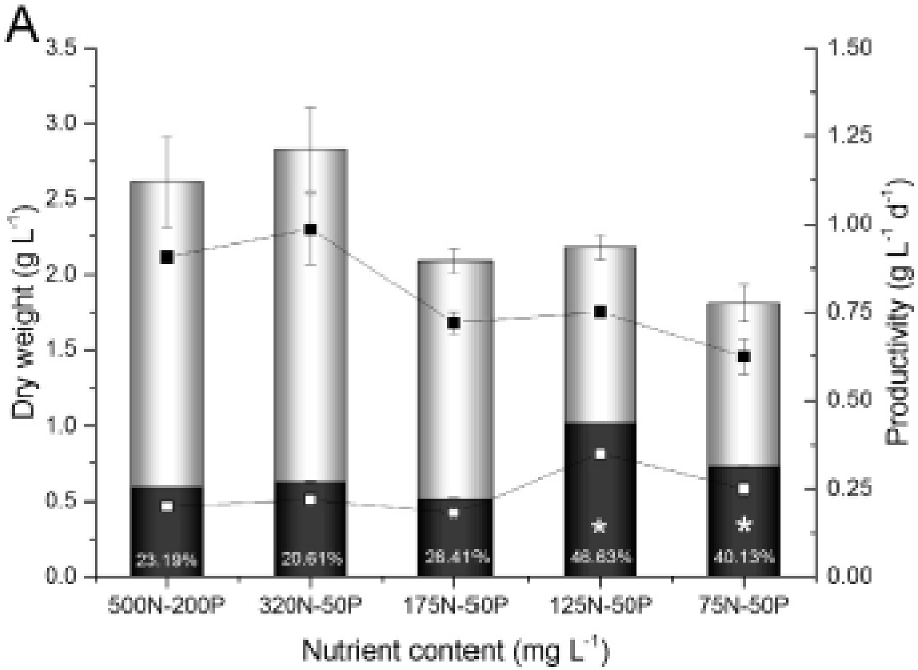
CARBOHYDRATE PRODUCTION UNDER NITROGEN LIMITATION- BATCH



The carbohydrate accumulation is triggered by nitrogen limitation. As an example, in a batch growth curve of *Chlorella vulgaris*, the external nitrogen decreases with time, and when it becomes limiting, carbohydrates start to be accumulated in cells, up to about 43% of DW)

CARBOHYDRATE PRODUCTION UNDER NITROGEN LIMITATION- CONTINUOUS

On the other hand, nitrogen limitation may affect the biomass productivity. In addition, a changing carbohydrate ratio is a major drawback toward an industrial production. Thus, in a continuous system, an optimum of nitrogen limitation can be found, without affecting the overall productivity, and also obtaining a stable biomass composition.

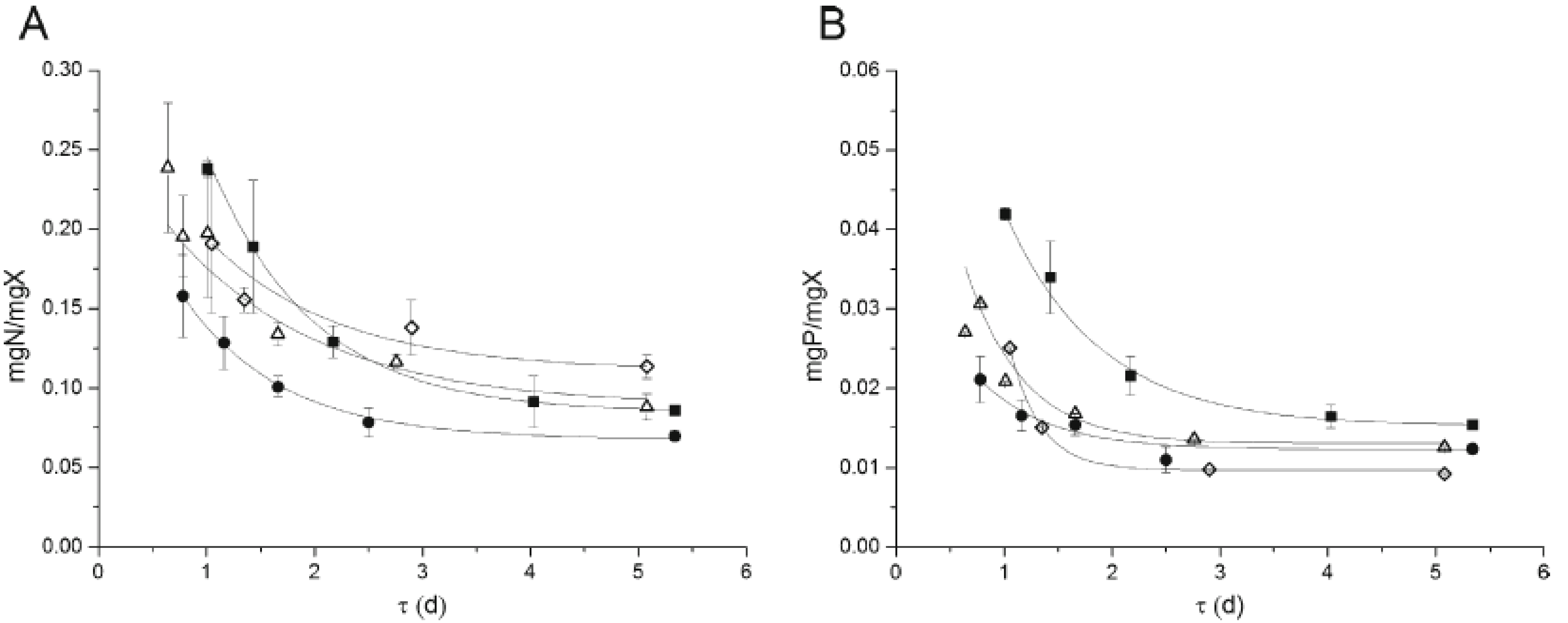


Nitrogen supply

By decreasing the inlet nitrogen concentration, a decrease of biomass productivity occurred, but it is compensated by an increased carbohydrate ratio in biomass, resulting in a higher carbohydrate productivity.

de Farias Silva C.E., Sforza E., 2016. Process Biochemistry, IN PRESS http://dx.doi.org/10.1016/j.procbio.2016.09.015

EFFECT OF RESIDENCE TIME ON ELEMENTAL COMPOSITION



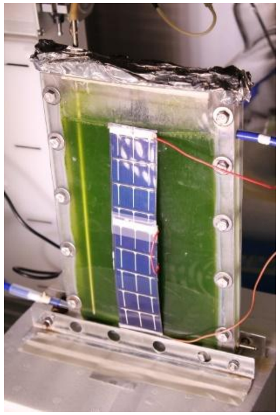
The nitrogen and phosphorus uptake by microalgal cells is affected by several process variables (environmental factors). Light plays a major role in the accumulation of phosphorus, but also the residence time may affect the uptake capabilities of P and N by biomass, as in the case of *Scenedesmus obliquus*.

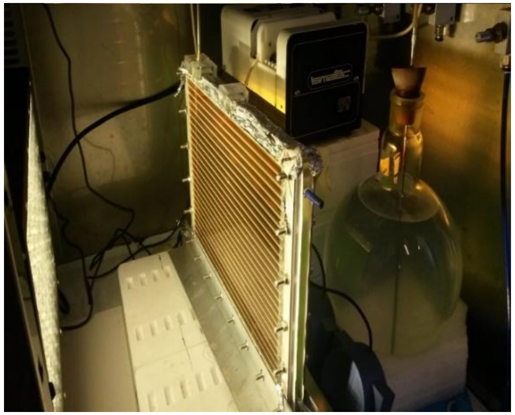
Sforza E., Urbani S., Bertucco A., 2015. Journal of Applied Phycology, 27(4), 1453-62. DOI 10.1007/s10811-014-0460-x

Increasing photosynthetic efficiency in industrial cultivation

Technological solutions

- Photobioreactor design
- Greenhouses
- PBR and photovoltaic integration

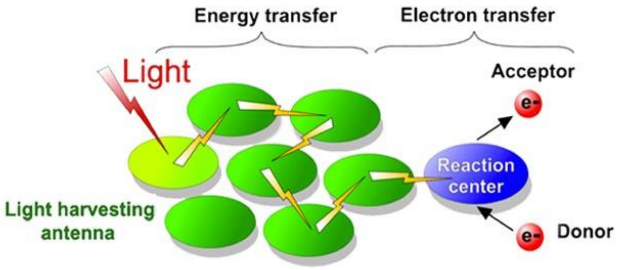


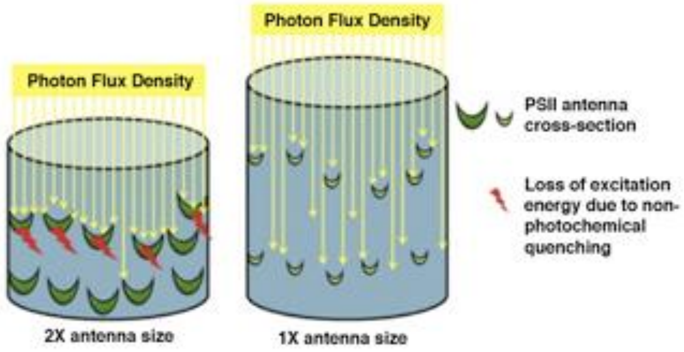


Biotechnological solutions

Genetically modified strains:

- Photosynthetic apparatus
- Less nonphotochemical quenching





Prof. Morosinotto – Dip. Biologia UniPD

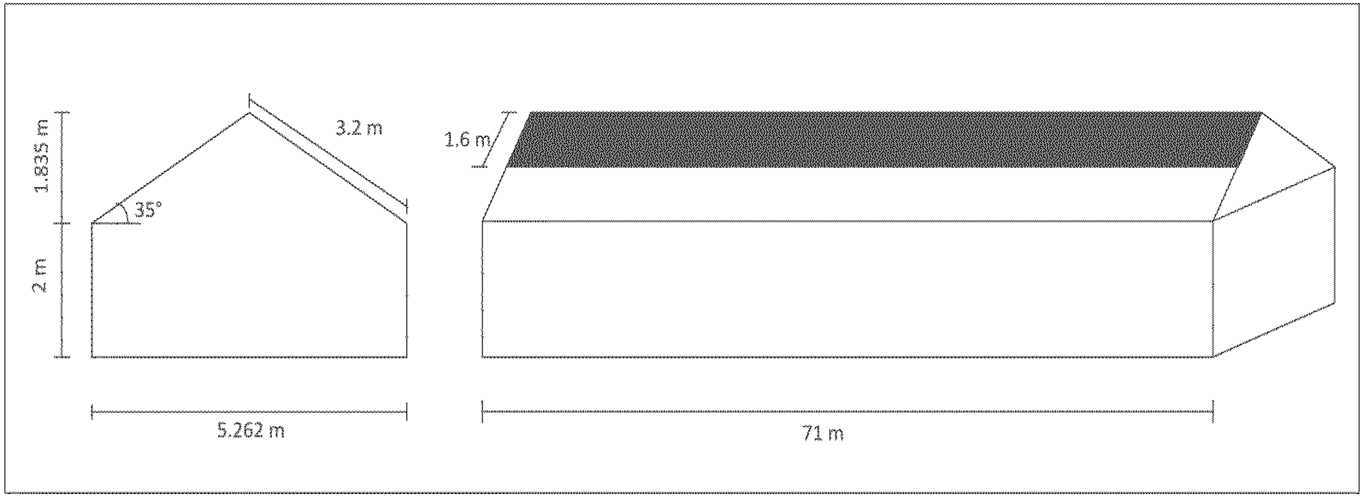
EXAMPLE 2 : HOW TO INCREASE ENERGY EFFICIENCY OF INDUSTRIAL MICROALGAE CULTIVATION

- A greenhouse is a simple way to protect the cultivation basin, by controlling the temperature and reducing contamination hazard
- Light intensity is reduced by scattering and by shades
- Photovoltaic panels can be applied on the greenhouse roof, to both shadow the pond and produce electrical power
- In this way both the energy and the economical profitability can be enhanced

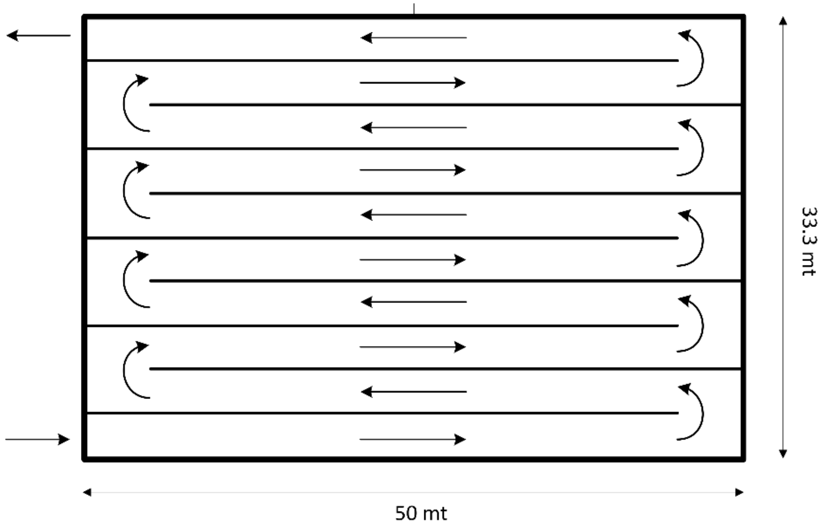
A POND IN A GREENHOUSE WITH PV

Dimension characteristics of one span of the greenhouse

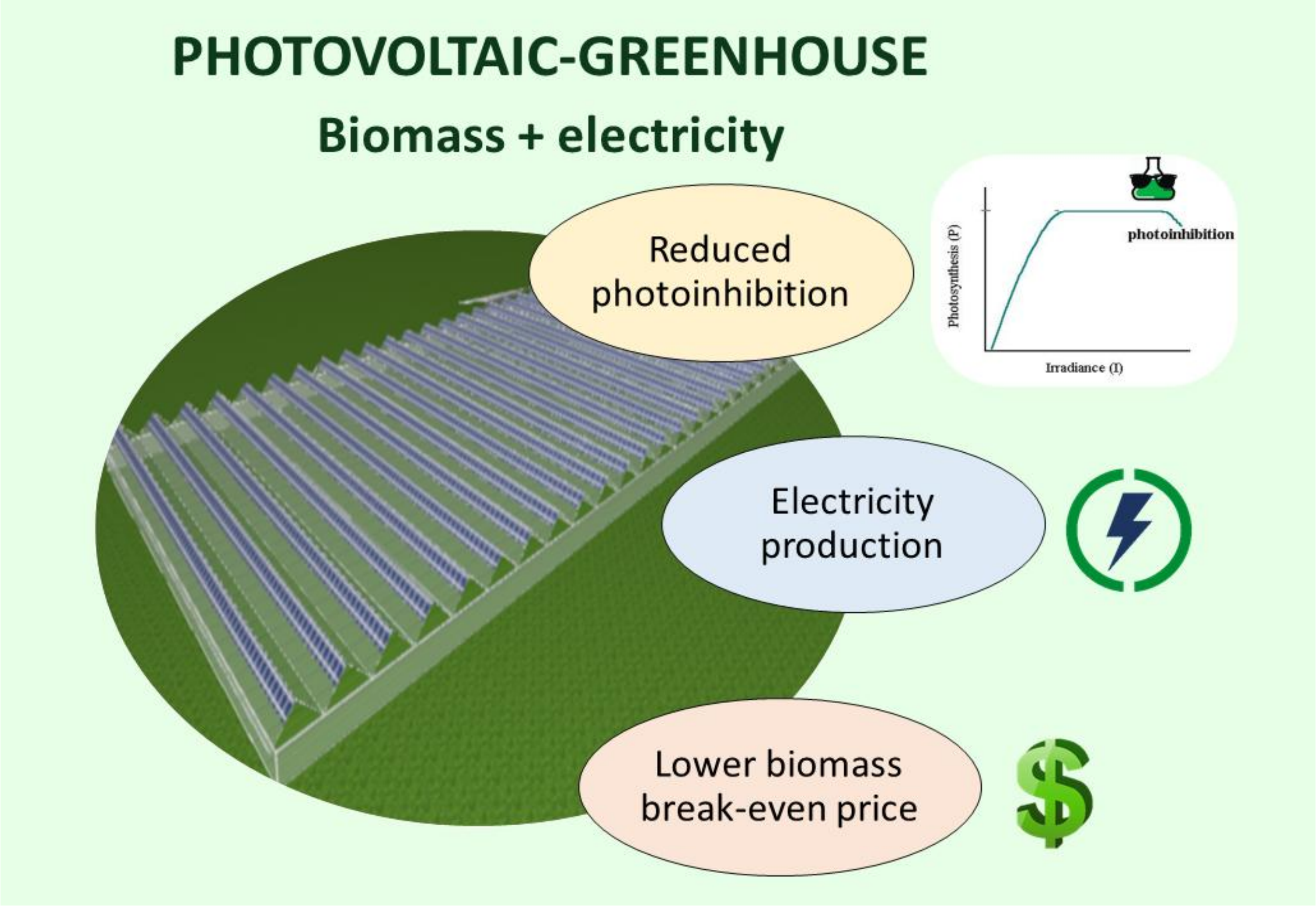
Total area: 1 ha
N° of spans: 29



Open pond module



ALGREENHOUSE©



PHOTOVOLTAIC-GREENHOUSE

Biomass + electricity

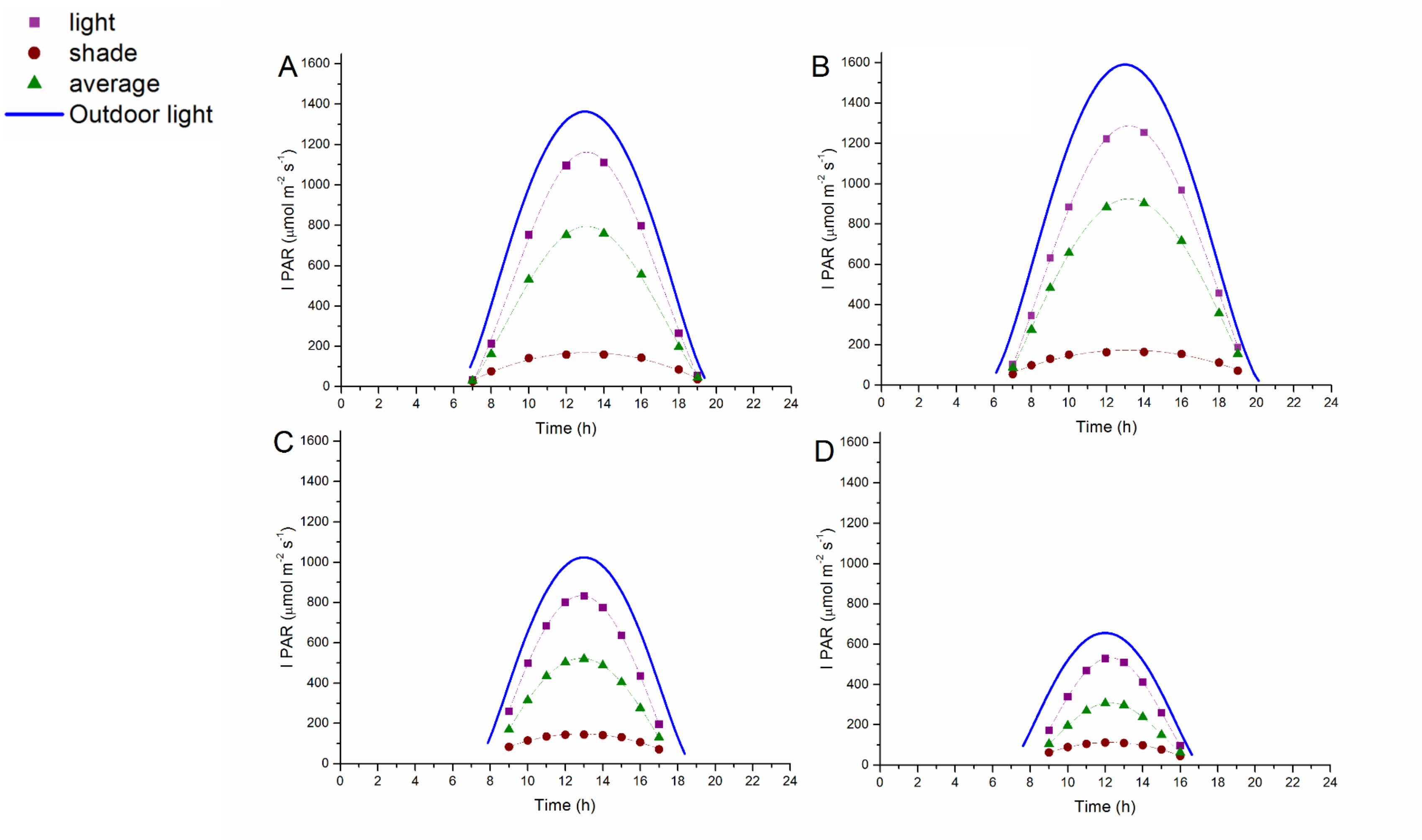
Reduced photoinhibition

Electricity production

Lower biomass break-even price

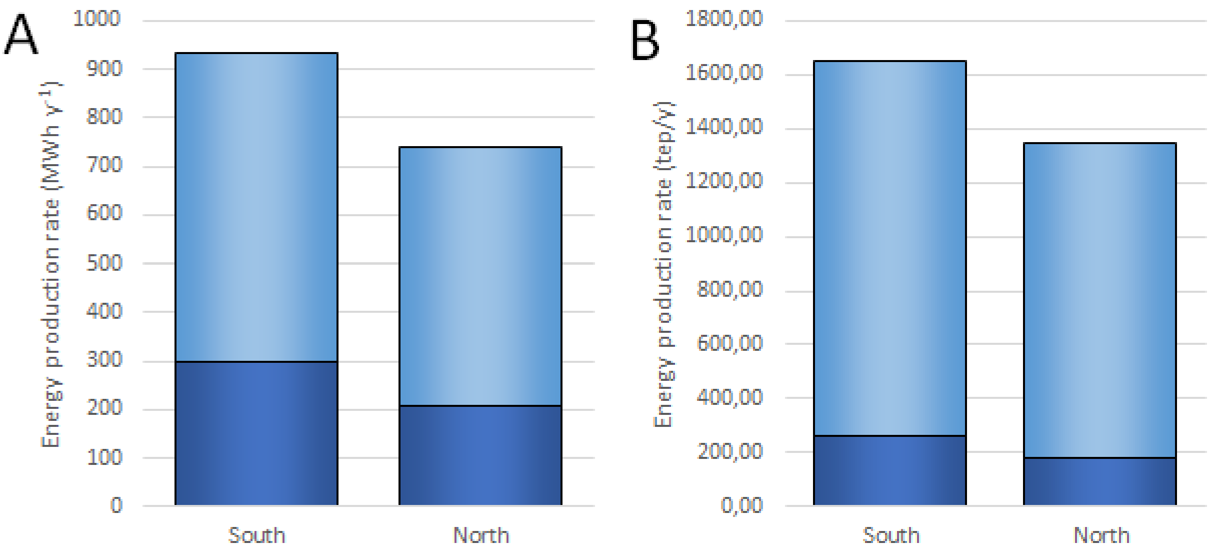
RESULTS: INDOOR SUNLIGHT INTENSITY

Sunlight intensity both outside (continuous line) and inside the greenhouse for spring (A), summer (B), fall (C) and winter (D) of Southern location



RESULTS: ENERGY CAPTURE

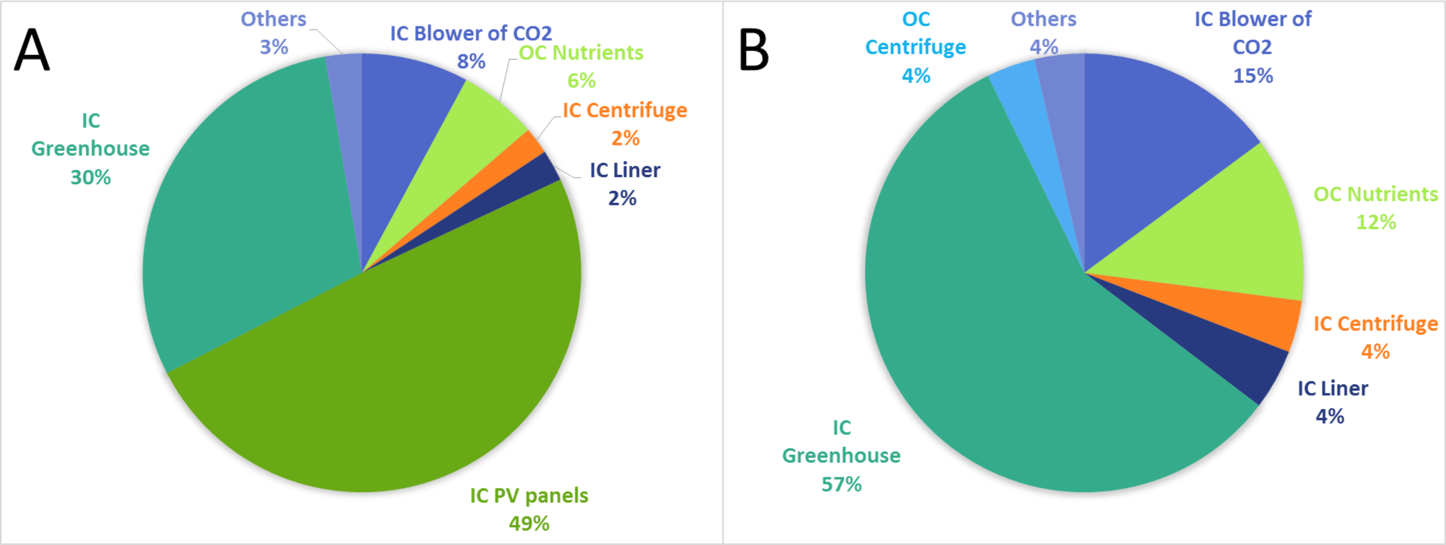
Energy produced by biomass (dark blue) and PV (light blue) for southern and northern locations in Italy.
In A the energy produced is directly compared, by using the biomass LHV value. In B a comparison based on Tonns of Oil Equivalent (TOE) is shown



Using PV modules on the greenhouse roof is highly advantageous: the ratio between electrical energy and biochemical energy produced ranges from 2.15 (North) to 2.55 (South)(**A**). These figures become 5.38 and 6.36 when accounting for the higher quality of electricity with respect to heat (**B**)

RESULTS: PRODUCTION COSTS

Annualized IC e OC for Southern location with PV (A) and without PV (B)



PV modules costs are most relevant, accounting for about 50% of the total value and increasing it by 90% with respect to the greenhouse without PV. Second in the list is the greenhouse capital cost.

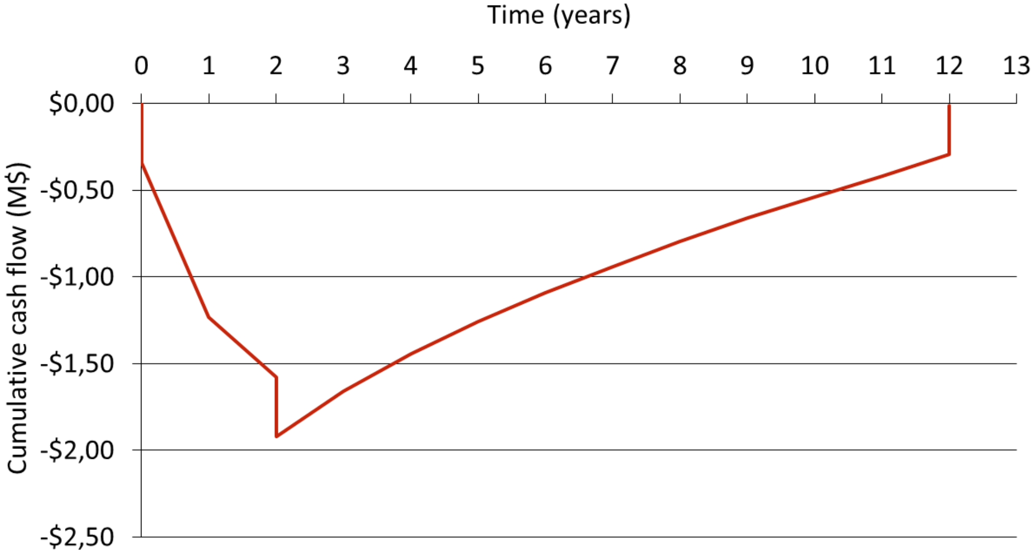
All other items are less important with PV, summing up to almost 20% of the total, and raise to about 40% when PV is not present.

RESULTS: COST BENEFIT ANALYSIS

Market price of microalgal biomass ($ kg^{-1}) to recover the capital invested within 10 years

	North		South	
	with PV	no PV	with PV	no PV
$ kg-1	22.3	23	13.8	16.4

Cash flow of plant with PV in the case of Southern location



Even though the energy produced by the PV modules is much higher than that accumulated as biomass, the revenues from biomass sale are far more relevant than those obtained from the sale of electrical energy. However, the PV plant itself has a quite fast return of investment (about 6.7 years for North and 5.7 for South), thus improving the cash balance.

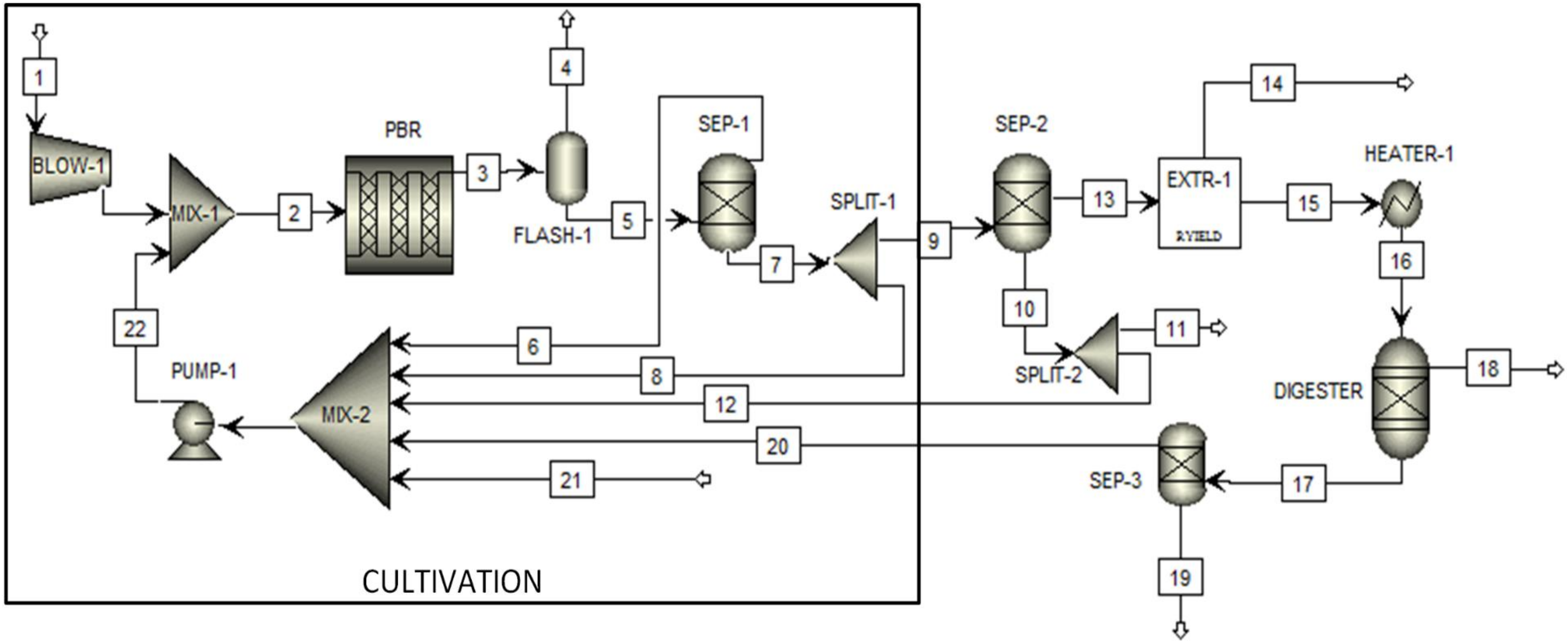
NUTRIENT RECYCLE: PROCESS SIMULATION

Anaerobic digestion

Kinetic model: Monod kinetics

$$R = \mu_{max} * C_X * \frac{C_{CO_2}}{K_{CO_2} + C_{CO_2}} * \frac{C_{NH_4^+}}{K_{NH_4^+} + C_{NH_4^+}} * \frac{C_{(HPO_4^{2-} + H_2PO_4^-)}}{K_{(HPO_4^{2-} + H_2PO_4^-)} + C_{(HPO_4^{2-} + H_2PO_4^-)}}$$

Thermodynamic model: Elec-NRTL



NUTRIENT RECYCLE: PROCESS SIMULATION

Anaerobic digestion – Base case

PBR inlet

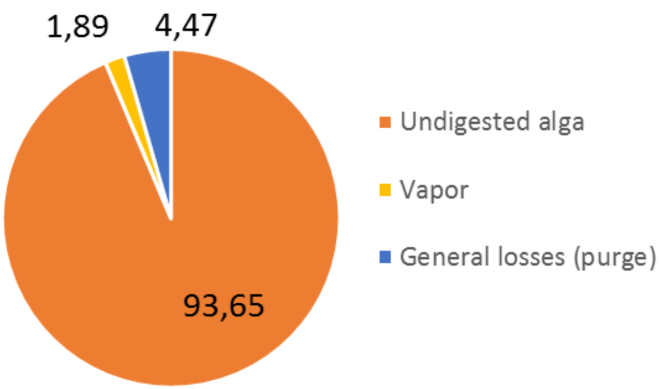
Water: 10,000 kg h^{-1}
N: 4.8 kg h^{-1}
P: 1.08 kg h^{-1}

Base case	
BD = 0.54	Lipids = 4%

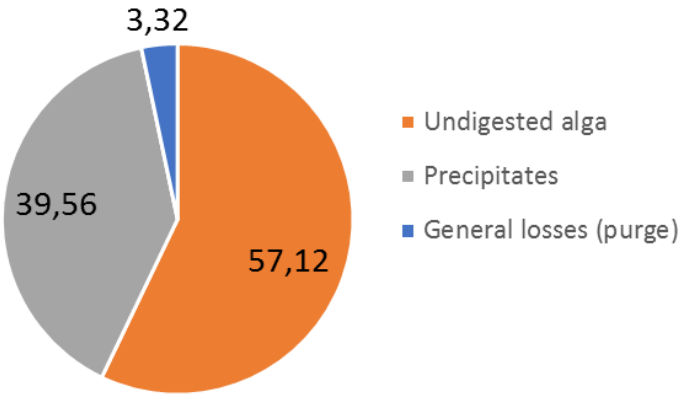
Algae production	8.2 kg h^{-1}
Nutrients make-up reduction	52% N, 21.6% P
EROEI	2.81

Nutrients losses

N



P



Our approach to industrial microalgae cultivation

Experimental measures

Kinetic models

Process simulation

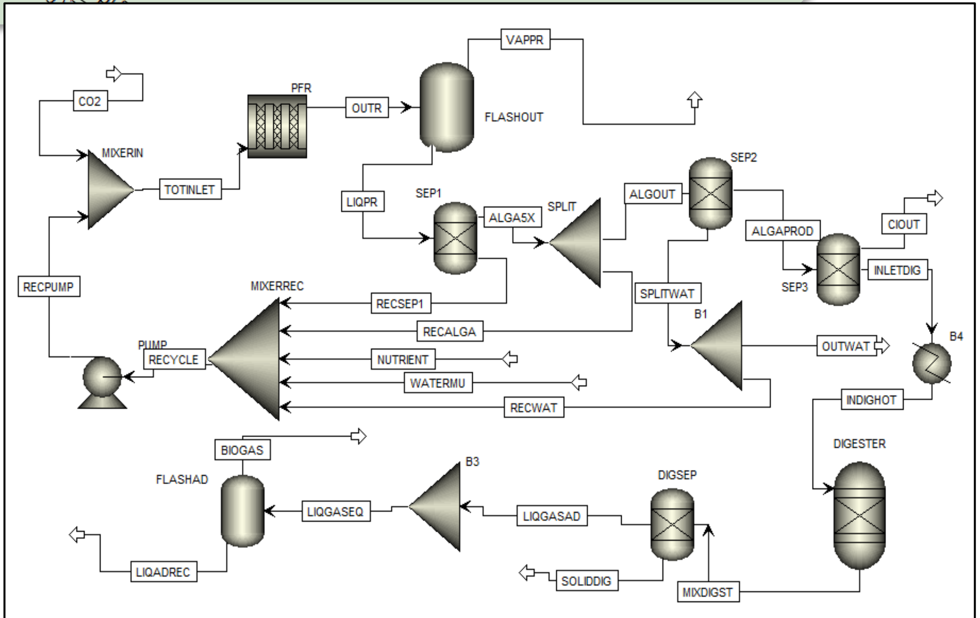
Economic and feasibility analisys

$$r_{x,z} = \rho_m \frac{K}{K+I(z)} \Phi E_a I(z) c_x - \mu_e c_x$$

$$\alpha = \sqrt{\frac{E_a}{(E_a + 2bE_s)}}$$

$$\frac{I(z)}{I(0)} = \frac{2(1+\alpha)\exp[-\delta(z-h)] - (1-\alpha)\exp[}{\cos\theta\,(1+\alpha)^2\exp(\delta h) - (1-\alpha)}$$

$$\delta = \frac{\alpha c_x}{\cos\theta}(E_a + 2bE_s)$$



CONCLUSIONS

- To develop industrial processes for autotrophic microalgae production both experimental and modelling informations are needed
- The kinetics of growth must be measured, as well as the operating conditions (temperature, pH, nutrients) of the photobioreactor.
- A quantitative analysis must then be carried out by applying mass and energy conservation balances, which allow to evaluate the process feasibility and bottlenecks
- Continuous production systems allows to achieve larger productivity, to simplify the process flow sheet and to ensure a stable product quality
- Process simulation gives the parameters required to evaluate the energy sustainability and to check the economic profitability through a cost benefit analysis
- Integrating microalgae cultivation with electricity production by PV modules located on a greenhouse roof is a promising technology to improve the process economical sustainability and to boost large scale installations

CONCLUSIONI

- Per sviluppare processi industriali basati sulle microalghe, serve un approccio quantitativo che parte dall’applicazione dei bilanci di materia e d energia, che permettono di valutare la fattibilità della tecnologia ma anche le criticità, con lo scopo di ideare soluzioni tecnologiche e sostenibili
- Lavorare in sistemi continui permette di ottenere maggiori produttività, semplificare il processo e garantire una produzione qualitativamente stabile, a seconda del prodotto di interesse
- L’integrazione di fotovoltaico alla produzione di microalghe è un promettente approccio per migliorare l’economicità del processo

GRAZIE DELL’ATTENZIONE!

Palermo, 6 e 7 aprile 2017, Palazzo Chiaramonte

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se si è **reduci da un insuccesso** tecnologico o commerciale con le microalghe o i cianobatteri,
se si è **attivi nella ricerca** o nello sviluppo di soluzioni tecnologiche riguardanti le microalghe,

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