



The importance of mass balance into life cycle assessment (LCA) of Nature Based Solution (NBS) for wastewater treatment (WWT): key learning points from a case study

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EXECUTIVE SUMMARY

This study aims to perform a comprehensive life cycle assessment (LCA) of a Nature-Based Solution (NBS) for wastewater treatment, specifically focusing on a French Vertical Flow (VF) wetland. The LCA encompasses the construction phase, operational phase, and end-of-life management, with a particular emphasis on achieving a balanced mass flow for carbon, nitrogen, and phosphorus across air, water, and soil compartments. The VF wetland is evaluated for its environmental impacts and compared to a conventional activated sludge system. Key findings reveal that the VF wetland achieves substantial reductions in greenhouse gas emissions and resource use, yet requires significantly more land and exhibits higher impacts in categories sensitive to water emissions. The results underline the importance of complete mass balances in LCAs of NBS to accurately identify environmental hotspots. Recommendations for methodological improvements and system boundary definitions are provided to enhance the definition of mass balance within NBS.

1.0 Introduction

Nature-Based Solutions (NBS) are approaches that use natural processes and ecosystems to address various environmental, social, and economic challenges (European Commission, 2015). These solutions aim to protect, sustainably manage, and restore natural or modified ecosystems to provide benefits such as enhancing biodiversity, improving water quality, reducing flood risks, mitigating climate change, and promoting human well-being. NBS include a wide range of strategies, such as green infrastructure, ecosystem restoration, and the sustainable use of natural resources, tailored to meet specific local needs and conditions (Nesshöver et al. 2017). For several decades, a multitude of new NBS technologies have been developed across all continents (Castellar et al. 2021). In particular, NBS are being promoted as a way of improving the resilience and sustainability of cities in the face of a wide range of environmental challenges (Ershad Sarabi et al. 2019). In the field of urban water management, they are seen as an alternative to more centralized and "grey" treatment in order to move towards more sustainable management of water and biogeochemical cycles (Flores et al., 2019; Masi et al., 2018).

In NBS for water management, certain installations prevent flooding by diverting stormwater flow or enabling faster infiltration into the soil. This is particularly the case for infiltration basins, retention ponds, swales, and rain gardens (URBANGREENUP, 2018; UNALAB, 2019; Woods Ballard et al., 2015). Treatment wetlands can also improve urban water management and treat wastewater before its discharge into the natural environment by replicating natural processes occurring in natural wetlands involving vegetation, soils, and the associated microbial assemblages (Dotro et al., 2017; Stefanakis, 2019).

To accurately assess the environmental impacts of NBS technologies, it is crucial to consider both local impacts during the "use phase" (e.g., water quality improvement) and impacts from other life cycle phases (e.g., construction and end-of-life management) (Babi Almenar et al., 2023; Corominas et al., 2020; Larrey-Lassalle et al., 2022). Life cycle assessment (LCA) is a standardized and widely used method for evaluating the environmental impacts of products and services from a life cycle perspective (Hellweg & Mila I Canals, 2014). It is a reference method for the environmental assessment of technologies in the field of water management (Corominas et al., 2020; Larrey-Lassalle et al., 2022; Parra-Salidavar et al., 2020). Numerous water-related NBS technologies have been analyzed using LCA, including swales and ponds (Bixler et al., 2019; Bryne et al., 2017), rain gardens for rainwater or stormwater management (Flynn & Traver, 2013; Petit-Boix et al., 2015; Vineyard et al., 2015), and treatment wetlands for wastewater treatment (Flores et al., 2019; Fuchs et al., 2011; Risch, Boutin & Roux, 2021; Roux, Boutin & Risch, 2010; Pan, Zhu & Ye, 2011; Resende et al., 2019).

When focussing on the studies for wastewater treatment, system boundaries always encompass the life cycle stages related to construction, maintenance operations, and end-of-life of materials, as well as emissions to water in the water exiting the system. Greenhouse gas (GHG) emissions (CO₂, CH₄, N₂O) during the use phase are sometimes included, based on measurements or the International Panel on Climate Change (IPCC) emission factors (Fuchs, Mihelcic & Gierke, 2011; Pan, Zhu & Ye, 2011; Resende, Nolasco & Pacca, 2019). Some studies also include sludge spreading and the related soil and air emissions (Flores et al. 2019; Risch, Boutin & Roux, 2021; Roux, Boutin & Risch, 2010). However, these studies highlight a lack of harmonisation in the definition of system boundaries, and of robustness in the calculation of mass balances, as noticed in most literature review papers (Corominas et al., 2020; Larrey-Lassalle et al., 2022; Parra-Salidavar et al., 2020), who proposed a set of guidelines for carrying out the LCA of wastewater treatment technologies.

Usually, in wastewater treatment studies, only the input and output water qualities are assessed, sometimes with GHG emissions linked with the treatment activity, rarely including the fertilising effect due to sludge application. However, as nothing disappears, it is essential to carry a complete mass balance to estimate the environmental impacts of a technology for all the environmental compartments, i.e. air, water and soil (Corominas et al., 2020; Larrey-Lassalle et al., 2022) as it is widely acknowledged into grey technologies for wastewater treatment (Heimersson et al., 2016)

This paper aims to implement a complete LCA of an NBS water treatment technology, from the construction phase to end-of-life and sludge management. Particular attention will be paid to calculating a balanced mass flow for carbon, nitrogen and phosphorus in the three environmental compartments. A French Vertical Flow (VF) wetland (treatment wetland) for wastewater treatment is used as proof of concept. Comparing data and methodological choices in terms of system boundaries will allow formulating recommendations to compare NBS and grey technologies for wastewater treatment.

2.0 Material & Methods

The environmental assessment approach is based on the four standardized phases of the LCA framework (ISO 2006): (i) goal and scope definition, (ii) life cycle inventory (LCI), (iii) life cycle impact assessment (LCIA), (iv) interpretation of results with a focus on the challenges of taking into account a complete mass balance of C, N and P flows in LCA of NBS for wastewater treatment.

2.0 Goal and Scope definition

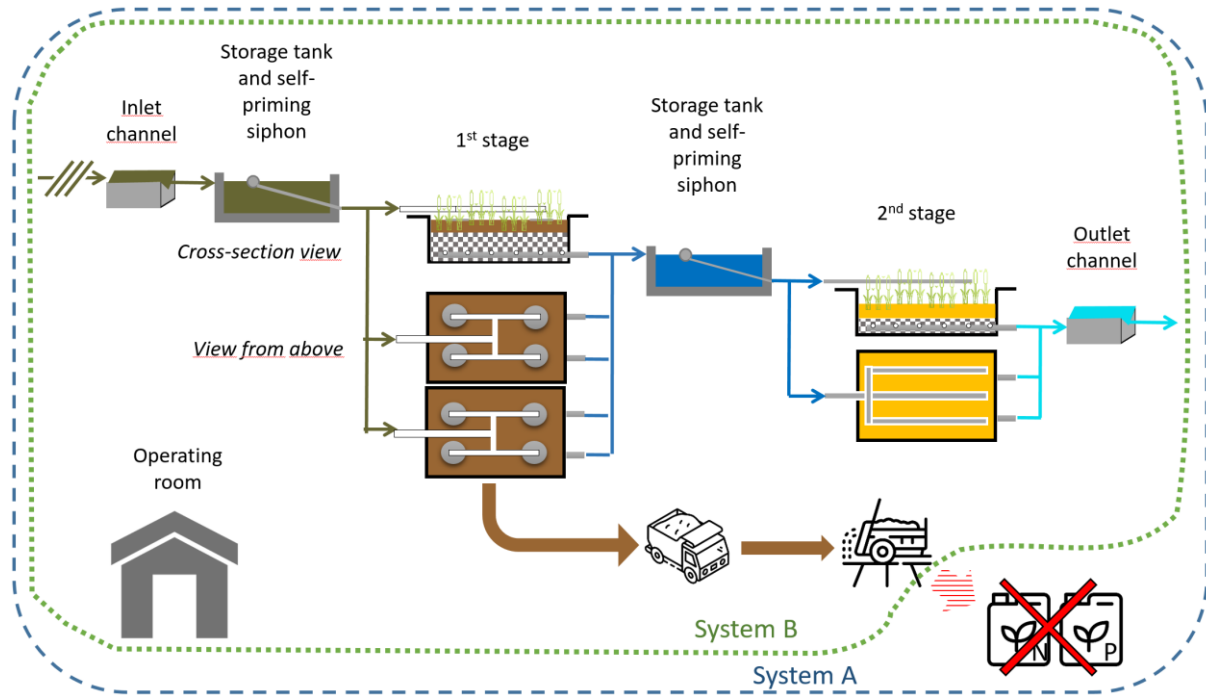
This study aims to carry out a complete LCA of a NBS for wastewater treatment, and discuss methodological choices related to system boundaries and data collection related to C, N and P mass balance. A comparison with a grey technology is also proposed for interpretation and discussion.

The LCA was applied to a French VF wetland, consisting in two treatment stages, one with gravel-based filters and the other one with sand-based filters, both planted with common reeds (*Phragmites Australis*) (see Figure 1). It is a widely distributed technology in France (Morvannou *et al.* 2015). More specifically, French VF wetlands are designed for the treatment of raw wastewater for small communities. The studied case in this paper is sized for wastewater treatment for 1000 PE (population-equivalent), with a daily wastewater emission of 150L per PE, polluted with 50g of BDO₅, and built for a 30 years lifespan. This technology is showing substantial removal rates for Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), and Total Kjeldahl Nitrogen (TKN), reaching 87%, 93%, and 84% respectively between the incoming water to the system and the treated water exiting it (Morvannou *et al.* 2015).

The functional unit was **“to treat 1 m³ of raw wastewater in France, with an abatement rate of 80% on the COD”**. This corresponds to a functional unit conventionally used for wastewater treatment, integrating the regulatory requirements of small treatment plants in France (Directive Eau Résiduaire Urbaine, 1991). Therefore, the rationale for this choice is to ensure comparisons with conventional solutions, i.e. grey technologies, such as activated sludge.

According to the recommendations of Corominas *et al.*, 2020 and INRAE Transfert 2022, a wide perspective is adopted for system boundaries that encompass the wastewater treatment technology, and sludge treatment, transport and application (Figure 1, system B). As the sludge is considered as a coproduct of the wastewater treatment, it is recommended by the ISO 14044 that a system expansion should be encompass to estimate the impacts of this co-production generation, with the integration of avoided mineral fertiliser production (Figure 1, System A). For wastewater treatment technology, construction, including excavation, material for the filters and surrounding equipment, and operation and maintenance of the filters during all the lifetime, up to the dismantlement of the NBS are considered. A particular focus is put on the use phase through N, P and C flow mass balances and sludge spreading.

Figure 1 Constructed Wetland facilities and system boundaries, adapted from Risch & Boutin 2020, presenting the system boundaries including (System A in blue) or excluding (system B in green) the substitution of mineral fertilisers due to sludge spreading



2.1 Data collection and Life Cycle Inventory (LCI)

- General information about the French VF wetland

Figure 1 presents the successive treatment stages of the French VF wetland and Table 1 gives the main building construction properties according to the 1st and 2nd stage. The presence of filters in parallel for each treatment step allows rotation in feeding, leaving some filters resting. Indeed, wastewater is poured during a feeding period (3.5 days) in a first filter. Then a technician changes the flow direction to feed another filter. The resting period is essential not only to complete the treatment of the interstitial water remaining in the filter, but also to partially degrade and mineralize the surface deposit formed during the feeding period, thus partially restoring the infiltration capacity. The second stage has only two compartments that are successfully fed during 7 days and then let to rest for 7 day. Both are covered with a geomembrane and a geotextile to ensure waterproofing.

Table 1 Main characteristics for the French VF wetland studied

	1st stage	2nd stage	Surroundings area
Area (m ²)	1,200	800	3,000
Number of parallel filters	3	2	
Total depth (m)	1.1	0.85	
Depth filled with materials (m)	0.6	0.6	
Composition (depth in m)	Gravel (0.6)	Sand (0.3) + gravel (0.3)	
Construction characteristics			
Filing (Gravel) (t)	1,224	408	538
Filing (Sand) (t)	0	384	
Geomembrane (PEHD) (kg)	1,957	1,333	
Geotextile (PP) (kg)	2,221	1,512	271
Distribution pipes (kg)	(stainless steel) 1,533	(PEHD) 700	
Drainage pipes (PVC) (kg)	512	342	(evacuation) 296
Partition walls (Glass fiber) (kg)	84	20	
Excavated volume (m ³)	4,800	3,200	
Excavation time (h)	44	29	
Dosing system	Self-priming siphon	Self-priming siphon	
Operating room (concrete) (t)			25
Storm overflow (concrete) (t)			4.4
Storage tank (concrete) (t)			8.8
Inlet and outlet channels (concrete) (t)			8.8

- **Construction hypothesis**

The lifespan of such constructed wetland is 30 years. It is assumed that the previous land occupation was pasture or meadow. After the dismantlement, the land occupation would come back to this initial state. The volume of excavated soil, computed from the filters geometry, was used to estimate machine operation and energy consumption for construction and dismantlement, assuming an excavation rate of 110m³.h⁻¹ (ACV4E software, 2018; Risch, Boutin & Roux, 2021). Each hour of construction or dismantling is made up of the use of a dump truck for 0.7h, a mechanical shovel for 0.7h, a dumper for 0.3h and an excavator for 0.3h (ACV4E software, 2018; Risch, Boutin & Roux, 2021).

Surrounding the French VF wetland, a grass area of 3000m² has a buffer role and holds an operating room, a storm overflow, inlet and outlet channels and some storage tanks. These structures are made of 25t of reinforced concrete and 22t of lean concrete, assuming there are local materials for the transportation.

The various stage feed structures (self-priming siphons), as well as the manual bar screen, have been taken into account through the consumption of raw materials. They do not entail any power consumption. In addition, there is no lift station to feed the filters.

The distance hypotheses were as follow:

- For local materials: 20 km by truck between the quarry and the wetland site.

- For imported materials: 200 km by train and 50 km by truck between the manufacture and the wetland site.
- The landfill and recycling sites are located 30 km by truck from the wetland for all material.
- The incineration site is located 50 km by truck from the wetland for all incinerated material.

Table 2 Main assumptions of origin and end-of-life treatment for raw materials used in the inventory

Material	Local or imported	End-of-life treatment
Stainless steel	Imported	95% recycling + 5% landfill
Concrete	Local	100% landfill
PEHD	Imported	25% incinerated + 75% landfill
PP	Imported	25% incinerated + 75% landfill
PVC	Imported	25% incinerated + 75% landfill
Gravel	Local	100% landfill
Sand	Local	100% landfill
Glass fiber	Imported	25% incinerated + 75% landfill

- **Operation and maintenance**

This life cycle stage takes into consideration all maintenance operations that occur on the French VF wetland in its life time, allocated to 1 year of maintenance. A twice weekly routine check (changing the flow direction to parallel filter) is carried out, by car, with a distance of 20 km one-way and 17 travels happen for exceptional maintenance and operation, with the same distance, per year. The exceptional maintenance includes:

- Grass mowing around the wetland three times per year
- Reed harvesting once a year
- Sludge removal, every 10 years, but with an annual build-up of 24 t on the whole wetland.

A daily accumulation of 24.7 g of sludge (or surface deposit) for 1,000 PE was estimated in the 1st stage. No sludge gets accumulated in the 2nd stage, as all suspended elements are collected into the 1st stage. 100% of the collected sludge is spread on fields, generating emissions to the soil due to its chemical composition (trace metal elements (TME), indirect gaseous emissions (N₂O and NH₃) as well as some emissions to water through lixiviation (NO₃⁻ and PO₄³⁻). These indirect emissions were estimated using agricultural references for fertilisation emissions (IPCC, 2006; Prasuhn, 2006). Storage area is located 35 km away from the filter and the fields are 2 km from the storage (ECODEFI, 2011). The sludge is transported by lorry, before being spread using a tractor and a spreader, considering a dose of 9.01 tMS.ha⁻¹. This dose was calculated using barley as the reference crop, one of France's main cereal crops (Ministère de l'agriculture et de la souveraineté alimentaire, 2023)). Barley cultivation in central France requires 115.4 kg N.ha⁻¹, 131.5 kg P₂O₅.ha⁻¹ and 100.25 kg K₂O.ha⁻¹ for a correct fertilisation (Pradel, Pacaud & Cariolle, 2009). The dose was estimated considering the P and N content in the removed sludge and, these elements were considered completely bioavailable for the long-term fertilisation.

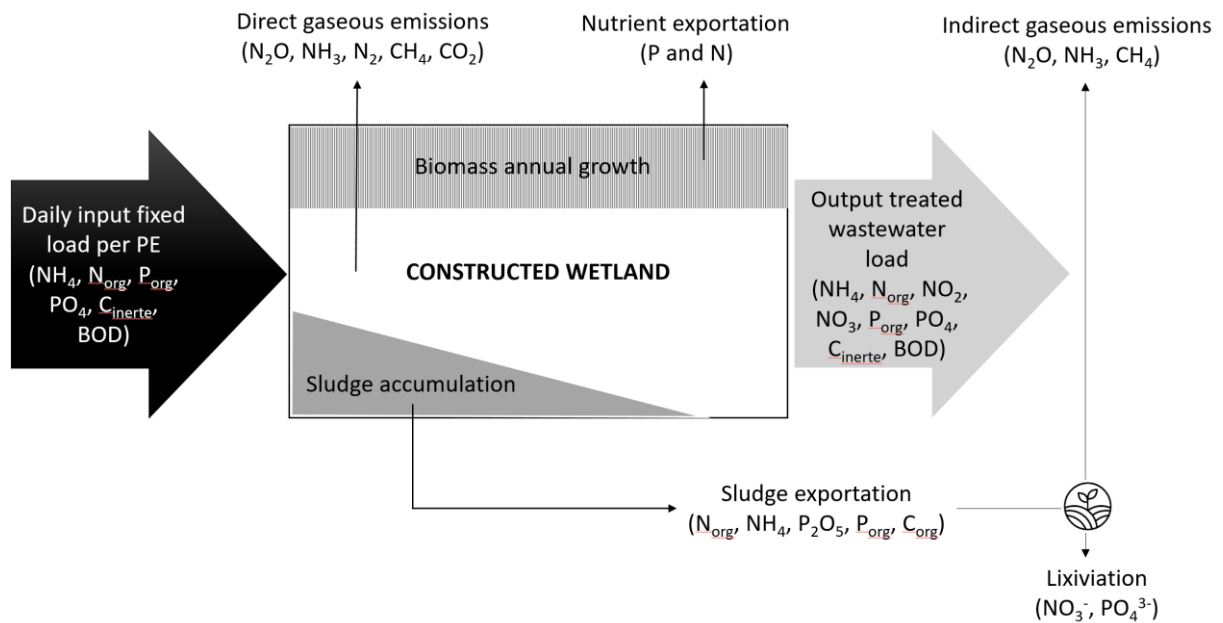
An annual harvest of 1 kg/m² was considered for the reed biomass. This biomass is then composted into industrial site. Grass cut-off are left on site, without any impact considered beyond the mowing.

- **Focus on Mass balance for C, N & P flows**

French VF wetland is a treatment technology that primarily aims to reduce the organic pollution (measured by the COD or BOD content) and the pollution associated with reduced forms of nitrogen,

depending on the size of the treatment plant. As a small-scale installation (1,000 PE), the case study must comply with current regulations and ensure 80% removal of COD from incoming wastewater before it is released into the natural environment. Not particular threshold is set on nitrogen removal. Even if not specifically targeted, Phosphorous is also partially removed by assimilation and adsorption.. Following the first rule of thermodynamic “nothing is lost, nothing is created, everything is transformed”, it was crucial to gather a complete picture of the mass balance happening daily into the different stages and compartments of the French VF wetland. Figure 2 reports the main C, N and P flows occurring in the compartments of French VF wetland.

Figure 2 Schematic representation of a mass balance for a French VF wetland



The input wastewater quality was determined through experts’ knowledge, starting from the regulatory value of 60 g of BOD per day per people equivalent (PE) and assuming that the wastewater production is 150 L per PE per day, the wastewater composition was estimated as shown in Table 3. A summary of this mass balance is presented in the Table 3 below, and detailed calculations and references are available in the supplementary material. The outputs were calculated by experts and using compilation of multiple references on equivalent technologies. The complete procedure is available in supplementary materials. To ensure the balance of elements between input and output when necessary, adjustment variables are used, derived from the subtraction between the total element entering the system and the different outputs measured in different forms. These adjustment variables are N_2 and CO_2 .

Table 3 Mass balance for a French VF wetland for 1,000 PE, on nitrogen, phosphorus and carbon flows, from input wastewater load (1st column) to the repartition between the different categories of outputs as direct water and air emissions, or sludge and reed accumulation.

		Inputs (g.PE ⁻¹ .d ⁻¹)	Outputs (g.PE ⁻¹ .d ⁻¹)			
			Wastewater	Direct emissions		By-products
				Water	Air	Sludge
Nitrogen	N-NH ₄	12.00	2.16	-	-	-
	N _{org}	3.50	0.21	-	0.11	0.49
	N-NO ₂	-	0.01	-	-	-
	N-NO ₃	-	6.5	-	-	-
	N-N ₂ O _{dissolved}	-	0.02	-	-	-
	N-N ₂ O	-	-	0.04	-	-
	N-N ₂	-	-	5.96	-	-
	Total	15.50	8.90	6.00	0.11	0.49
Phosphorus	P _{org}	0.52	0.17	-	0.25	0.07
	P-PO ₄	1.58	1.58	-	-	-
	P-P ₂ O ₅	-	-	-	-	-
	Total	2.10	1.75	0	0.25	0.07
Carbon	C _{inerte-soluble}	2.10	2.10	-	-	-
	C _{inerte-particulate}	13.10	-0	-	-	-
	C _{org}	37.20	4.72	-	6.91	-
	C-CO ₂	-	-	38.43	-	-
	C-CH ₄	-	-	0.24	-	-
	Total	52.40	6.82	38.67	6.91	0

It is assumed that 5% of the input wastewater is lost through evaporation (Risch *et al.*, 2014).

- **Metallic trace elements, hypothetical mass balance**

To have the broader picture on the environmental impacts generated from the French VF wetland, trace metal elements mass balance has to be included in the study. Quantities of TME are derived from Catel *et al.*, 2017 as follows: Cadmium ($2.86 \cdot 10^{-5}$ g.PE⁻¹.day⁻¹), Mercury ($9.11 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹), Nickel ($6.85 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹), Lead ($1.18 \cdot 10^{-3}$ g.PE⁻¹.day⁻¹), Cobalt ($1.58 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹), Arsenic ($6.27 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹), Molybdenum ($4.40 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹), Zinc ($2.23 \cdot 10^{-2}$ g.PE⁻¹.day⁻¹), Barium ($6.28 \cdot 10^{-3}$ g.PE⁻¹.day⁻¹), Copper ($8.19 \cdot 10^{-3}$ g.PE⁻¹.day⁻¹), Chromium ($4.46 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹) and Vanadium ($2.45 \cdot 10^{-4}$ g.PE⁻¹.day⁻¹).

The following assumptions, by expert's knowledge, is made regarding the distribution of TME in the different outputs: 50% of the trace metals are found in the water exiting the filter, 25% remain in the sludge that will be spread, and 25% are captured by the reeds that will be composted. Thus, the latter two contribute to the emission of TME to the soil.

- **Avoided products: mineral fertilisation**

In order to have a complete picture of all the effects of a French VF wetland, it is necessary to take into consideration the fertilizing and amendment effect due to the sludge spreading, as a coproduct of the wastewater treatment. An extension of the system boundaries is then considered to include the avoided mineral fertilizers.

The avoided mineral fertilization is based on the amount of nitrogen and phosphorus that is supplied to the soil through sludge, and therefore will not be provided by mineral forms of fertilizers. Spreading the accumulated sludge over 15 years allows for organic fertilization of 9 hectares of barley crops, with a total of 131.5 kg P₂O₅ per hectare and thus 66.7 kg N per hectare, as the limitation factor to calculate the spreading dose was the P content in the sludge. The same amounts of fertilization were substituted from the system using average mineral fertilizers for France from the Ecoinvent database. Additionally, the emissions associated with these fertilizers were calculated using the same frameworks as for sludge (IPCC, 2006; Prasuhn, 2006) to substitute them in the system as well. Thus, 116.14 kg N₂O, 17.47 kg NH₃, and 191.13 kg NO₃⁻, as well as 3.822 kg P, would have been emitted for this mineral fertilization, which will not occur thanks to the spreading of sludge.

- **Reference for comparison**

In order to interpret and discuss the results, a comparison of the environmental impacts of the NBS technology and a grey technology is performed. A grey process is selected for a small-scale wastewater treatment plant (806 PE) from the Ecoinvent database. This plant relies on three water treatment stages (mechanical, biological, and chemical), and the sludge is digested before being spread and incinerated. Emissions associated with this technology include direct emissions from wastewater treatment, emissions from incineration and spreading of sludge, as well as certain emissions related to sewer overload discharge. This reference was then slightly modified to adapt to the French context: the origin of electricity was changed to French, as well as the water source. The system boundaries are comparable except for the avoided products from the grey technology (substitution of mineral fertilization by sludge spreading and energy recovery from sludge incineration) that are not included within the reference boundaries. The system B boundaries (Figure 1) for French VF wetland was thus used for the comparison, based on the same volume of wastewater treated within both technologies (1 m³).

3.0 Life Cycle Impact Assessment (LCIA)

The software SimaPro 9.5 was used with the ecoinvent 3.9.1 allocation, cut-off by classification and the EF 3.1 method (Andreasi Bassi *et al.*, 2023) to characterise the environmental impacts as this is the LCIA method recommended by the European Commission.

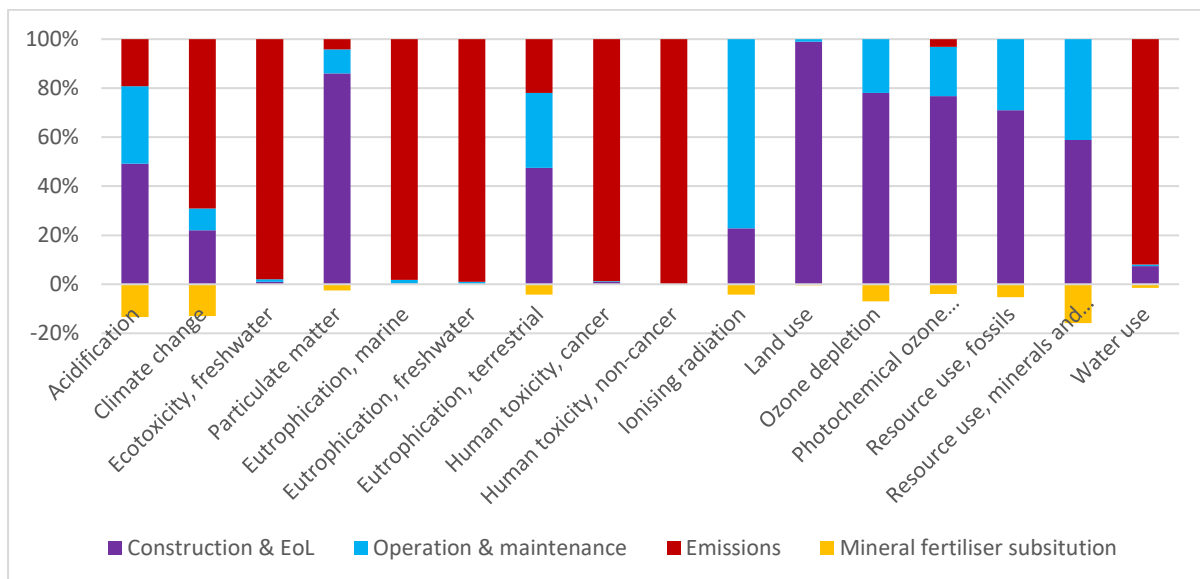
4.0 Results & Discussion

4.0 Analysis of the French VF wetland including the mineral fertilisation substitution

- Overview

Figure 3 below reports the results of the contribution analysis of the French VF wetland according to the impacts of the construction and end-of-life stage, the operation and maintenance stage, and the direct emissions related to the use phase computed from the mass balance for N, P and C flows, as well as TME. Additionally, the end-of-life of co-products (sludge and reed biomass) has also been included with operations within the Operation & maintenance category and emissions to air, soil and water within the Emissions category. The contribution of substitution of mineral fertilization due to the spreading of sludge is also highlighted.

Figure 3 Analysis of the French VF wetland using the EF3.1 method, over 16 categories of environmental impacts and the single score. Main life cycle steps are presented: construction and end-of-life (purple), operation and maintenance without the emissions linked (blue), emissions from operation and maintenance (red) and the substitution of mineral fertiliser (orange).



Emissions into the air, water, and soil contribute to 11 out of 16 impact categories according to the EF 3.1 method (Figure 3). While their contribution is relatively moderate for 4 categories, it is significantly predominant for 7 impact categories: climate change (69%), water use (92%), freshwater ecotoxicity (98%), marine eutrophication (98%), freshwater eutrophication (99%), human toxicity cancer (99%) and non-cancer (100%).

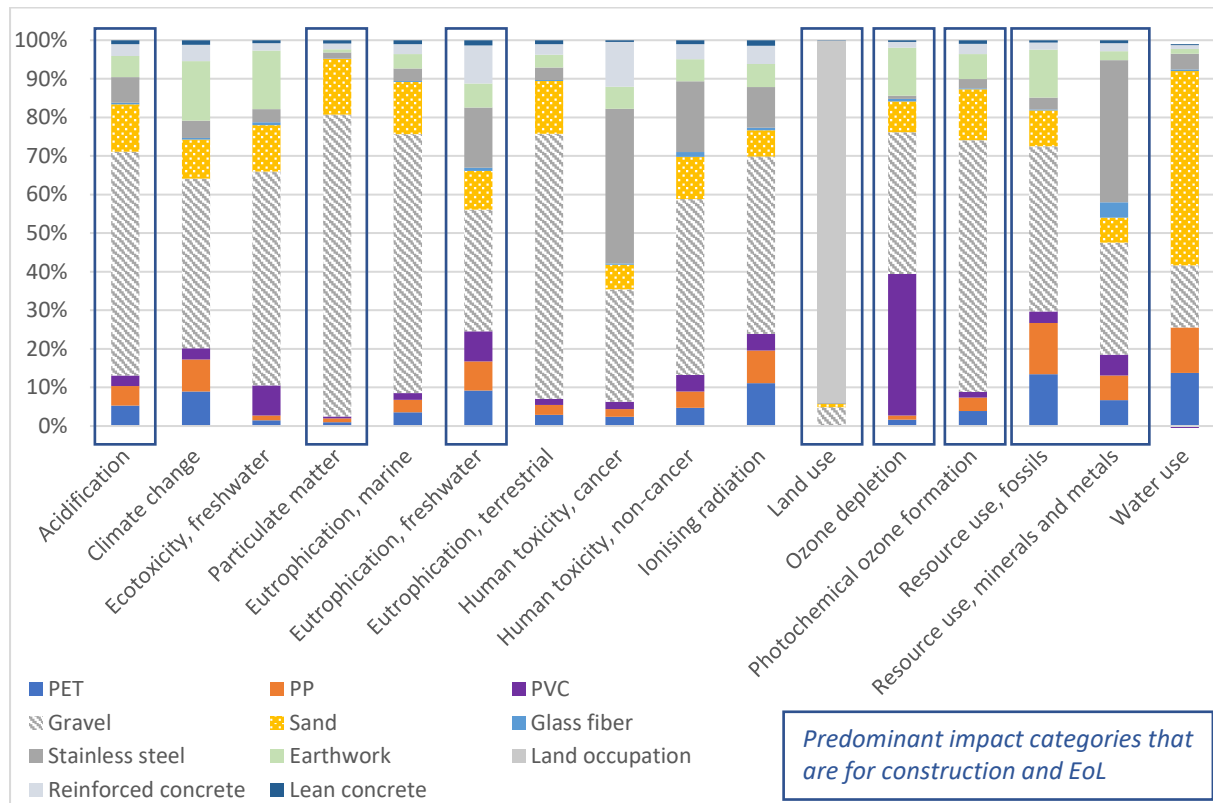
Wastewater management (inflow and outflow of the system, as well as 5% evaporation) is managed in the emissions stage, making it this stage contributing most to the impact. The Land Use category is dominated by the construction stage, as this is where land occupation is accounted for in the inventory.

- Construction and end-of life stage

The construction & end-of-life stage (in purple in Figure 3) dominates terrestrial eutrophication (48% of the total impact), acidification (49%), resource use impacts (59% and 71%), photochemical ozone formation (77%), ozone depletion (78%) and particulate matter (86%).

Raw materials, notably gravel and in a secondary manner sand, stainless steel and plastics (PET, PP and PVC), contribute the most to these impacts as presented in Figure 4 below. Earthwork also contributes to most impact categories, due to the intensive use of combustion-motorized engine.

Figure 4 Construction step analysis, using the EF 3.1 method and presenting the raw material used to build the French VF wetland



- Contribution of operation and maintenance, without emissions

Looking at the contributions of the operation and maintenance stage (in bright blue in Figure 3), the impact categories to which they contribute significantly are ionising radiation (77%), mineral and metals resource use (41%), acidification (32%), terrestrial eutrophication (31%), fossils resource use (29%), ozone depletion (22%) and photochemical ozone formation (20%).

The primary sources of these impacts are the use of motorized equipment, primarily for regular maintenance and secondarily for sludge spreading. Additionally, the composting of biomass significantly contributes to acidification and terrestrial eutrophication. The other processes (reed mowing, mechanical weeding, and sludge dredging) comprising the operations and maintenance have very low to negligible contributions to the impacts. It is important to highlight that emissions to water, air, and soil (except for diesel combustion) are not accounted for in this stage; they are studied separately in the “emission” category.

- Contribution of the emissions occurring during operation and maintenance

The emissions into the air during the filter operation contribute to 84% of the climate change impact, with 42% attributed to N₂O, 22% to CH₄, and 20% to CO₂. The remaining contribution to climate change from emissions comes from sludge fertilization (16%). Aquatic eutrophication and ecotoxicity impacts are

due to the composition of the water treated by the technology returning to the ecosystem. Marine eutrophication is attributed to the quantity of NO_3^- (73% of the emissions impact) and NH_3 (24%). Freshwater eutrophication stems from the quantity of PO_4^{3-} (90% of the impact) and Porg (10%). Lastly, freshwater ecotoxicity arises from NH_3 emissions (63%) and the presence of zinc (36%). TME into the soil through sludge spreading and biomass composting are responsible for all human toxicity impacts (especially mercury for more than 90% for both impacts), whereas the same elements emitted into the water have a negligible impact on these human toxicity impact categories.

- **Substitution of mineral fertilizers**

Substitution of mineral fertilizers (in orange in Figure 3) has a moderate effect on impact categories. It significantly reduces the impacts of acidification (-13%), climate change (-13%) and mineral resources (-16%). Its contribution is lower (<7%) or even negligible for other categories.

While emissions in the field are relatively similar for both types of fertilization, the mechanized operations for fertilization are vastly different. Sludge, being a viscous substance, requires more resources for handling, whereas mineral fertilizers are concentrated in fertilizing elements and optimized for easy spreading. However, mineral fertilizers have impacts related to their production, while sludge introduces trace metals into the soil.

Taking into account the substitution of mineral fertilizers by sludge spreading helps offset some of the impacts associated with sludge spreading. This offset is moderate for acidification (53% of what is emitted by sludge spreading) but becomes significant in terms of climate change (87%) for the sludge emissions only. For mineral resource use, the impact is almost twice as high for mineral fertilizer use as for sludge spreading.

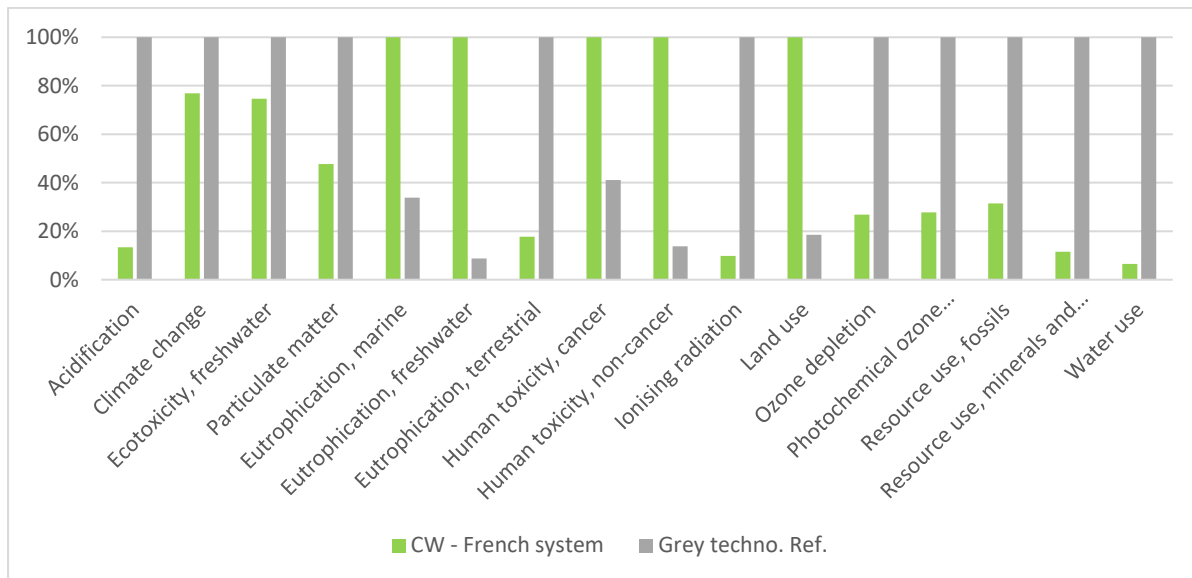
4.1 Comparison of the French VF wetland and a grey reference

Figure 5 provides a comparison between the environmental impacts of the green technology system, French VF wetland, and a grey technology reference, activated sludge based on the FU. To make the results comparable, the same system boundaries are used and the substitution of mineral fertilizers was not included in French VF wetland (System B in Figure 1). However, the mass balance as presented previously, along with trace metal emissions and sludge spreading, are included. The French VF wetland technology achieves better results for 11 impact categories out of the 16 categories of the EF 3.1 method.

The activated sludge technology emits more emissions (notably NH_3 , NO_x and SO_2) than the French VF wetland, which significantly contributes to impact categories such as acidification, particulate matter, terrestrial eutrophication, ozone depletion, and photochemical ozone formation. Additionally, this technology requires the use of electricity, predominantly derived from nuclear sources in France, thus explaining the impact of ionizing radiation 10 times higher than for the French VF wetland. This green technology also allows a mitigation of 23% and 25% on the climate change and freshwater ecotoxicity impacts respectively.

In terms of land footprint, the French VF wetland utilizes significantly more space than the grey technology for the same amount of treated water. This results in a land use impact over 80% higher for the French VF wetland. The impacts on marine and freshwater eutrophication, as well as on human toxicity, can be explained by N and P emissions to the output water source, as well as the TME emitted to the soil, as described previously.

Figure 5 Comparison of green NBS technology for wastewater treatment (French VF wetland) and grey equivalent technology (Activated Sludge), using the EF 3.1 method.



4.2 Data for mass balance

Through this detailed study, it is evident that the LCA results of the French VF wetland are dominated by air emissions during operation, the treated water output from the filter, and the trace metal emissions into the soil from sludge spreading and composting. The impacts related to the construction and end-of-life of the filter, as well as maintenance operations, are secondary according to the impact categories. Therefore, it is necessary to perform a complete mass balance, especially for C, N and P flows, to obtain results that highlights the system hotspots, to avoid missing out important pollution and to allow for comparison with other technologies (Corominas *et al.*, 2020; Larrey-Lassalle *et al.*, 2022).

Table 4 Comparison of GHG emissions from the French VF wetland case study with IPCC emission factors

Mass balance element	Proposed value in this paper	Estimation using IPCC methodology	Recommendations for missing value
CH ₄	0.272 g CH ₄ .d ⁻¹ .PE ⁻¹	0.393 g CH ₄ .d ⁻¹ .PE ⁻¹	IPCC emission factors allow a fair estimation of CH ₄ emissions, based on DCO in the input wastewater. Emissions factors are available only for generic treatment wetlands.
CO ₂	Adjustment value of C mass balance	Adjustment value of C mass balance	It is obtained by subtracting the total incoming carbon with all other carbon fluxes exiting the system (sludge, treated water, and CH ₄). Note that biomass fixes carbon through photosynthesis and does not take carbon from the filter. A COD or BOD abatement rate for the outgoing water is usually available for the technology, but assumptions need to be made for the carbon content in the sludge.
N ₂ O	0.04 N-N ₂ O.d ⁻¹ .PE ⁻¹	0.003565 g N-N ₂ O.d ⁻¹ .PE ⁻¹	IPCC emission factors trends to underestimate greatly the N ₂ O emissions, applied to the case study. Other references in literature provide emission

			<p>factor 30 times higher than the ratio proposed by the IPCC for similar wetland (Filali <i>et al.</i> 2017).</p> <p>Due to its high contribution to climate change, sensitivity analysis has to be carried out if measurements are not available.</p>
--	--	--	---

Regarding GHG emissions, IPCC is providing emissions factors that can help to fill incomplete mass balance (IPCC, 2014, 2019) (Table 4). These factors are only available for some wastewater treatment NBS, especially treatment wetlands. Whereas they provide a good estimate of CH₄ emission, the proposed calculations for CO₂ remained incomplete if DCO in output treated water or C content in exported sludge remains unknown. For N₂O emissions, the estimate differs greatly from the value proposed in the case study and from values in literature. There is significant uncertainty regarding N₂O emission factors due to a limited number of studies and in situ measurements (Corominas *et al.*, 2020, IPCC 2014). Therefore, it is essential to emphasize that more research and measurements are crucial to improve estimate N₂O emissions, regardless of the NBS used for wastewater, as it can contribute enormously to climate change impacts.

In this study, all indirect gas emissions were not taken into account. Indirect emissions, originating from nitrogen discharged into surface waters and nitrogen in the form of NH₃ from sludge spreading that is released into the atmosphere and then redeposited, will undergo nitrification and denitrification processes in the receiving environments (Hélias, 2019). Similarly, the COD contained in the treated water can release CH₄. Thus, additional emissions of N₂O and CH₄ should be accounted for, depending on the receiving environment (INRAE Transfert, 2022, IPCC, 2019).

Regarding sludge exports, there are very few references in the literature to obtain generic reference data according to the filters. Some data can be found in Canler (2009) and Brockmann, Pradel & Helias (2018). The latter reference provides the necessary elements for calculating emissions related to sludge spreading. Therefore, it is feasible to incorporate this element within the system boundaries. It will also be interesting to consider carbon storage in the soil related to sludge spreading to achieve a more comprehensive balance.

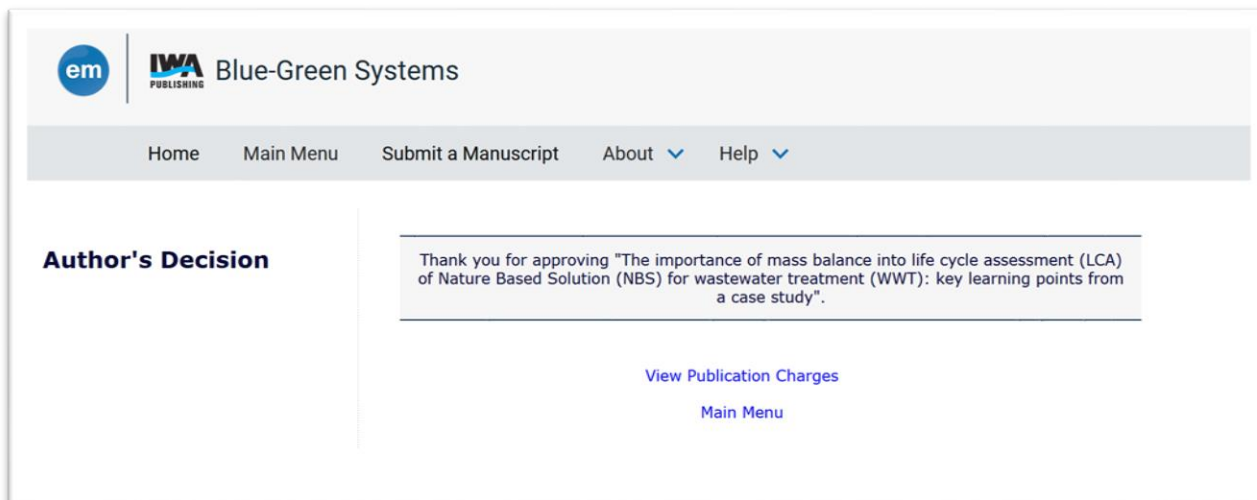
Finally, TME play a significant role in the LCA results of NBS. However, there is limited knowledge about these elements and their impact on ecotoxicity. In the absence of rapidly improving the robustness of toxicity and ecotoxicity indicators, it is crucial to better understand their distribution among sludge, biomass, and treated water to enhance the inventory of wastewater treatment technologies.

5.0 Conclusions

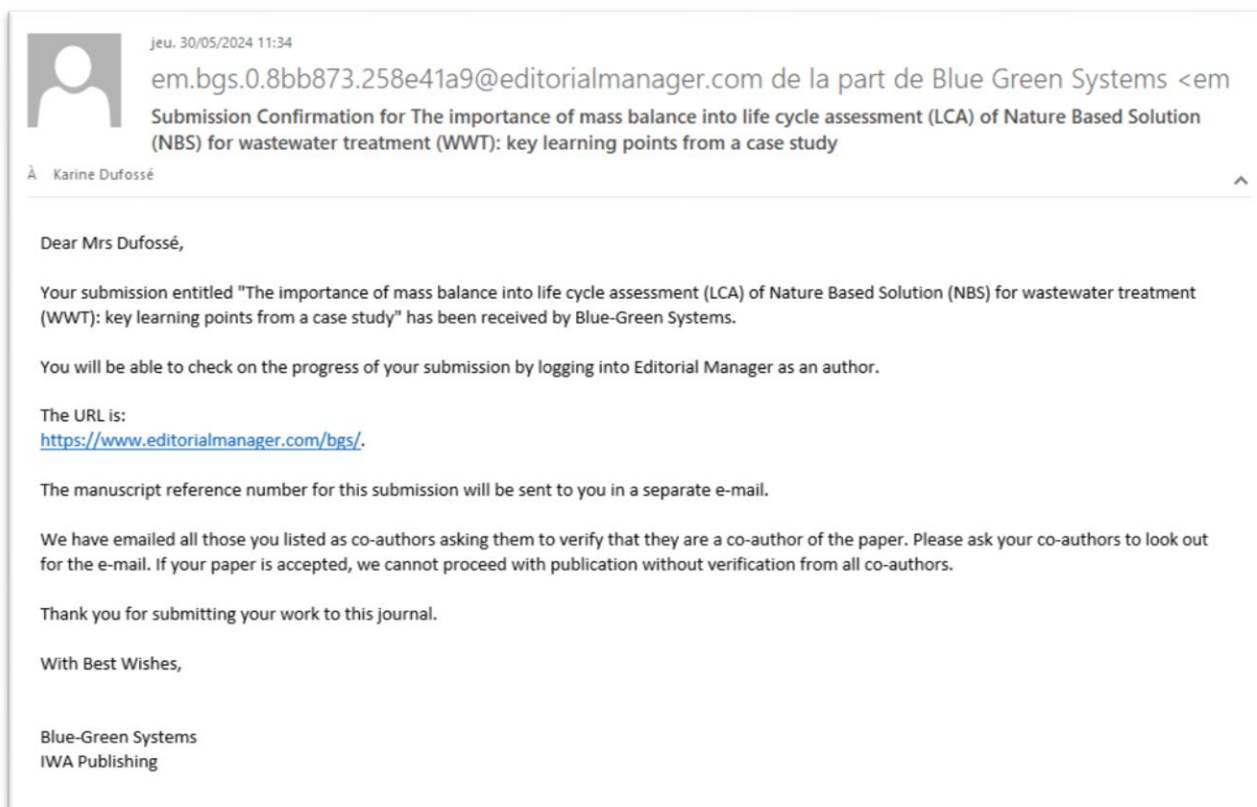
The French VF wetland could achieve a reduction in GHG emissions by more than 20% compared to the activated sludge reference, as well as significant reductions in the use of electrical energy and mineral, metal, and fossil resources. However, when considering more impact categories, these positive results must be weighed against poorer performance in impact categories sensitive to water emissions due to the absence of denitrification and dephosphatation. Additionally, it is important to consider that the land footprint is much higher for this NBS technology compared to conventional technology. Therefore, integrating all these elements into a single score does not favour the NBS technology. However, this result must be put into perspective because some of the impact categories that carry the most weight are based almost exclusively on the mass balance of TMEs, which is done approximately, and these impact indicators are also quite weak.

These lacks of information or uncertainties can be a critical barrier limiting the adoption of NBS by decision makers (Ershad Sarabi *et al.*, 2019). Risch *et al.* (2015) conducted a study that included both sewer systems and wastewater treatment plants. They have shown that the sewer system contributes significantly to several midpoint indicators: human health, ecosystems and resources. This study highlights the potential benefits of implementing a decentralized wastewater treatment approach, which limits the extent of the sewer network. The present study focused exclusively on the technology but further study should place the NBS technology within its context of use. However, besides environmental impacts, NBS are support of multiple ecosystem services and address many urban challenges (Castellar *et al.*, 2021). These services and challenges deserved to be thoroughly assessed in further researches in order to provide a better guidance to decision makers.

ANNEX A: PROOF of SUBMISSION



The screenshot shows the top navigation bar of the Blue-Green Systems website. The navigation menu includes: Home, Main Menu, Submit a Manuscript, About (with a dropdown arrow), and Help (with a dropdown arrow). Below the navigation bar, on the left, is the heading "Author's Decision". On the right, a message box contains the text: "Thank you for approving 'The importance of mass balance into life cycle assessment (LCA) of Nature Based Solution (NBS) for wastewater treatment (WWT): key learning points from a case study'". Below this message are two links: "View Publication Charges" and "Main Menu".



The screenshot shows an email confirmation from Blue-Green Systems. The sender is identified as "em.bgs.0.8bb873.258e41a9@editorialmanager.com de la part de Blue Green Systems <em.bgs.0.8bb873.258e41a9@editorialmanager.com>". The subject line is "Submission Confirmation for The importance of mass balance into life cycle assessment (LCA) of Nature Based Solution (NBS) for wastewater treatment (WWT): key learning points from a case study". The recipient is "Karine Dufossé". The email body contains the following text:

Dear Mrs Dufossé,

Your submission entitled "The importance of mass balance into life cycle assessment (LCA) of Nature Based Solution (NBS) for wastewater treatment (WWT): key learning points from a case study" has been received by Blue-Green Systems.

You will be able to check on the progress of your submission by logging into Editorial Manager as an author.

The URL is:
<https://www.editorialmanager.com/bgs/>.

The manuscript reference number for this submission will be sent to you in a separate e-mail.

We have emailed all those you listed as co-authors asking them to verify that they are a co-author of the paper. Please ask your co-authors to look out for the e-mail. If your paper is accepted, we cannot proceed with publication without verification from all co-authors.

Thank you for submitting your work to this journal.

With Best Wishes,

Blue-Green Systems
 IWA Publishing

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ANNEX C: Nitrogen mass balance of French vertical flow treatment wetlands

Nicolas Forquet, Pascal Molle, Karine Dufossé

Last modified May, 2024

This notebook describes the carbon mass balance estimation for French Vertical Flow (VF) wetlands. It is based on the first LCA inventory carried out by Risch *et al.* (2010). This updated version aims to take better account of experimental data. In particular, it focuses on data collected from a large number of full-scale French VF wetlands.

The mass balance is expressed in $g\ N \cdot pe^{-1}d^{-1}$.

C.1. Incoming nitrogen flux

Mercoiret *et al.* (2009) estimated the incoming COD flux to $15.5\ gO_2 \cdot d^{-1} \cdot PE^{-1}$.

$$F_N^{inlet} = 15.5\ [g \cdot d^{-1} \cdot pe^{-1}] \quad (1)$$

```
N <- list(inlet = list(total = set_units(15.5, g/d/pe)))
```

Mercoiret *et al.* (2009) also provided the ratio of NH₄-N/TKN at the inlet of the VF wetland. The average value is 0.74.

Therefore, the mass balance of the inlet can be completed:

```
bilan.N["water - NH4-N", "inlet"] <- N$inlet$total * 0.74
bilan.N["water - Norg", "inlet"] <- N$inlet$total * 0.26
```

C.2. First treatment stage

Water

The TKN removal rate between the inlet and the outlet of the first treatment stage is obtained from Morvannou *et al.* (2015) : 59%.

The average value of the ratio NH₄-N/TKN at the outlet of the first treatment stage has been obtained from an INRAE database and equals 0.79.

```
TKN.1st.removal <- 0.59
bilan.N["water - Norg", "first.stage"] <- (1-TKN.1st.removal)*N$inlet$total *
0.21
bilan.N["water - NH4-N", "first.stage"] <- (1-TKN.1st.removal)*N$inlet$total
* 0.79
```

NO_x-N are produced by the nitrification of part of the removed TKN. The NO₂ – N emission is set to 0.005 $gN/d/pe$. For the first treatment stage, Molle *et al.* (2008) observed a nitrification rate of 55%.

```
bilan.N["water - NO2-N", "first.stage"] <- 0.005
bilan.N["water - NO3-N", "first.stage"] <- TKN.1st.removal * N$inlet$total *
0.55- bilan.N["water - NO2-N", "first.stage"]
```

Biosolids

Molle (Molle, 2003) measured the N content in the surface deposit of treatment wetland. The estimate is 0.9% of nitrogen in the dry matter.

The biosolids accumulation rate has been estimated in the C mass balance notebook to $M_{\text{biosolids}} = 0.02764901$ [kg/d/pe].

```
M.biosolids <- set_units(0.02764901, kg/d/pe)
bilan.N["solid - biosolids", "first.stage"] <- 0.9/100*M.biosolids
print(bilan.N["solid - biosolids", "first.stage"])
0.2488411 [g/d/pe]
```

Reeds

The nitrogen content in reeds is estimated to $58 \text{ gN} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ by Tanner *et al.* (1996). The surface area of reeds per person is $1.35 \text{ m}^2 \cdot \text{pe}^{-1}$. Therefore, the nitrogen content in reeds is $0.21 \text{ gN} \cdot \text{pe}^{-1} \cdot \text{d}^{-1}$ for the first stage.

```
bilan.N["solid - reed", "first.stage"] <- 58 * 1.35 / 365.25
```

Nitrous oxide emissions

Gaseous emissions on French VF wetlands have been measured by (Filali *et al.*, 2017). For the first stage, gaseous nitrous oxide emissions have been estimated to:

$$N_2O - N = 0.34\% N_{\text{input}}$$

and dissolved nitrous oxide emissions have been estimated to:

$$N_2O - N = 0.25\% N_{\text{input}}$$

```
bilan.N["gas - N2O-N", "first.stage"] <- 0.34/100 * N$inlet$total
bilan.N["water - N2O-N", "first.stage"] <- 0.25/100 * N$inlet$total
```

N2 emissions

The emissions of N_2 have been estimated by difference:

```
bilan.N["gas - N2-N", "first.stage"] <- N$inlet$total - sum(bilan.N$first.stage)
```

C.3. Second treatment stage

Water

The TKN removal rate between the inlet and the outlet of the two stages is obtained from Morvannou *et al.* (2015) : 84%.

The average value of the ratio $\text{NH}_4\text{-N}/\text{TKN}$ at the outlet of the first treatment stage has been obtained from an INRAE database and equals 0.79.

```
TKN.overall.removal <- 0.84
bilan.N["water - Norg", "second.stage"] <- (1-TKN.overall.removal)*N$inlet$total * 0.21
```

```
bilan.N["water - NH4-N", "second.stage"] <- (1-TKN.overall.removal)*N$inlet$total * 0.79
```

The $NO_2 - N$ concentration is assumed to be unchanged and equal to 0.005 gN/d/pe .

```
bilan.N["water - NO2-N", "second.stage"] <- 0.005
```

In the PlanteDefi database, the average value of the ratio $\frac{NO_3-N_{outlet}}{TKN_{inlet}}$ is 0.477.

```
bilan.N["water - NO3-N", "second.stage"] <- N$inlet$total * 0.477
```

Reeds

The nitrogen content in reeds is estimated to $58 \text{ g N} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ by Tanner *et al.* (1996). The surface area of reeds per person is $0.90 \text{ m}^2 \cdot \text{pe}^{-1}$. Therefore, the nitrogen content in reeds is $0.14 \text{ gN} \cdot \text{pe}^{-1} \cdot \text{d}^{-1}$ for the second stage.

```
bilan.N["solid - reed", "second.stage"] <- 58 * 0.9 / 365.25
```

Nitrous oxide emissions

Gaseous emissions on French VF wetlands have been measured by (Filali *et al.*, 2017). For the first stage, gaseous nitrous oxide emissions have been estimated to:

$$N_2O - N = 0.43\% N_{input}$$

and dissolved nitrous oxide emissions have been estimated to:

$$N_2O - N = 0.21\% N_{input}$$

```
bilan.N["gas - N2O-N", "second.stage"] <- 0.43/100 * N$inlet$total
bilan.N["water - N2O-N", "second.stage"] <- 0.21/100 * N$inlet$total + bilan.N["water - N2O-N", "first.stage"]
```

Biosolid accumulation at the second stage is negligible and therefore not taken into account.

N₂ emissions

The N_2 emissions have been estimated by difference:

```
bilan.N["gas - N2-N", "second.stage"] <- bilan.N["water - Norg", "first.stage"] +
  bilan.N["water - NH4-N", "first.stage"] +
  bilan.N["water - NO3-N", "first.stage"] +
  bilan.N["water - NO2-N", "first.stage"] +
  bilan.N["water - N2O-N", "first.stage"] -
  sum(bilan.N$second.stage)
```

C.4. Summary

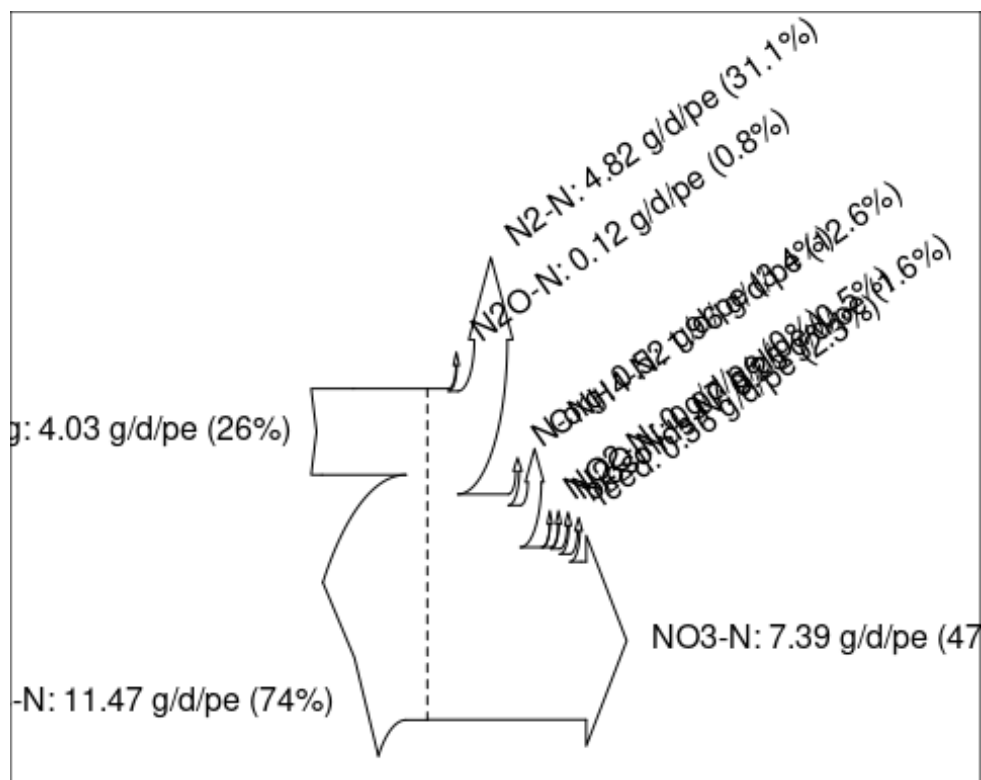
```
kable(bilan.N)
```

	inlet	first.stage	second.stage
water - Norg	4.03 [g/d/pe]	1.3345500 [g/d/pe]	0.5208000 [g/d/pe]
water - NH4-N	11.47 [g/d/pe]	5.0204500 [g/d/pe]	1.9592000 [g/d/pe]
water - NO3-N	0.00 [g/d/pe]	5.0247500 [g/d/pe]	7.3935000 [g/d/pe]
water - NO2-N	0.00 [g/d/pe]	0.0050000 [g/d/pe]	0.0050000 [g/d/pe]
water - N2O-N	0.00 [g/d/pe]	0.0387500 [g/d/pe]	0.0713000 [g/d/pe]
gas - N2O-N	0.00 [g/d/pe]	0.0527000 [g/d/pe]	0.0666500 [g/d/pe]
gas - N2-N	0.00 [g/d/pe]	3.5605852 [g/d/pe]	1.2641342 [g/d/pe]
solid - biosolids	0.00 [g/d/pe]	0.2488411 [g/d/pe]	0.0000000 [g/d/pe]
solid - reed	0.00 [g/d/pe]	0.2143737 [g/d/pe]	0.1429158 [g/d/pe]

Results can also be presented using a Sankey plot:

```
Inputs <- as.numeric(c(bilan.N$inlet[1],
                      bilan.N$inlet[2]))
Inputs <- round(Inputs,2)
Losses <- as.numeric(c(
  bilan.N$second.stage[6]+bilan.N$first.stage[6],
  bilan.N$second.stage[7]+bilan.N$first.stage[7],
  bilan.N$second.stage[1],
  bilan.N$second.stage[2],
  bilan.N$second.stage[4],
  bilan.N$second.stage[5],
  bilan.N$first.stage[8],
  bilan.N$first.stage[9]+bilan.N$second.stage[9],
  bilan.N$second.stage[3]
))
Losses <- round(Losses,2)
Labels <- c("N-org", "NH4-N",
           "N2O-N", "N2-N",
           "N-org", "CNH4-N",
           "NO2-N",
           "N2O-N", "biosolids-N",
           "reed", "NO3-N")

SankeyR(inputs = Inputs,
        losses = Losses,
        unit = "g/d/pe",
        labels = Labels
        )
```



C.5. References

- Filali, A., Bollon, J., Molle, P., Mander, Ü., Gillot, S., 2017. High-frequency measurement of N₂O emissions from a full-scale vertical subsurface flow constructed wetland. *Ecological Engineering* 108, 240–248. <https://doi.org/10.1016/j.ecoleng.2017.08.037>
- Mercoiret, L., 2009. Qualité des eaux usées domestiques produites par les petites collectivités. ONEMA.
- Molle, P., 2003. [Filtres plantés de roseaux : limites hydrauliques et rétention du phosphore](#) (PhD thesis).
- Molle, P., Prost-Boucle, S., Lienard, A., 2008. Potential for total nitrogen removal by combining vertical flow and horizontal flow constructed wetlands: A full-scale experiment study. *Ecological Engineering* 34, 23–29. <https://doi.org/10.1016/j.ecoleng.2008.05.016>
- Morvannou, A., Forquet, N., Michel, S., Troesch, S., Molle, P., 2015. Treatment performances of French constructed wetlands: Results from a database collected over the last 30 years. *Water Science and Technology* 71, 1333–1339. <https://doi.org/10.2166/wst.2015.089>
- Risch, E., Boutin, C., 2010. Rapports d'ACV et données d'inventaire.
- Tanner, C.C., 1996. Plants for constructed wetland treatment systems A comparison of the growth and nutrient uptake of eight emergent species. *Ecological Engineering* 7, 59–83. [https://doi.org/10.1016/0925-8574\(95\)00066-6](https://doi.org/10.1016/0925-8574(95)00066-6)

ANNEX D: Phosphorous mass balance of French vertical flow treatment wetlands

Nicolas Forquet, Pascal Molle, Karine Dufossé

Last modified May, 2024

This notebook describes the carbon mass balance estimation for French Vertical Flow (VF) wetlands. It is based on the first LCA inventory carried out by Risch *et al.* (2010). This updated version aims to take better account of experimental data. In particular, it focuses on data collected from a large number of full-scale French VF wetlands.

The mass balance is expressed in $g N \cdot pe^{-1}d^{-1}$.

D.1. Influent

Production par EH : 2.1 g de P/j (source Mercoiret)

Mercoiret *et al.* (2009) estimated the incoming COD flux to $2.1 gP \cdot d^{-1} \cdot PE^{-1}$.

$$F_P^{inlet} = 2.1 [g \cdot d^{-1} \cdot pe^{-1}] \quad (1)$$

```
P <- list(inlet = list(total = set_units(2.1, g/d/pe)))
```

Cette production se répartie en 75 % sous forme de P-PO4 (1.575 g/j/EH) et 0.525 sous forme organique

This production is divided into 75% in the form of $P - PO_4$ (1.575 g/d/PE) and 0.525 in organic form.

```
bilan.P["water - P04-P", "inlet"] <- set_units(1.575, g/d/pe)
bilan.P["water - Porg", "inlet"] <- set_units(0.525, g/d/pe)
```

Phosphorous organic forms are assumed to be completely removed by filtration. However part of the phosphorous leaches out after the mineralization of the organic matter.

Based on the PlanteDefi database, the overall phosphorous removal efficiency is estimated to 20% and the outlet concentration mainly consists of $P - PO_4$.

```
bilan.P["water - P04-P", "second.stage"] <- (1-0.20) * P$inlet$total
```

The difference between the $PO_4 - P$ inlet and outlet concentrations is assumed to be leached phosphorous.

```
leached.phosphorous <- bilan.P["water - P04-P", "second.stage"] - bilan.P["water - P04-P", "inlet"]
```

The rest of the P-org is either stocked in the biosolids or exported by the reeds.

```
P.stored <- bilan.P["water - Porg", "inlet"] - leached.phosphorous
```

According to Tanner *et al.* (1996), the above ground biomass production is $5 g/m^2/yr$ and the below ground production is $6 g/m^2/yr$. It is assumed that the below-ground biomass will mineralize over time and is therefore neglected.

The above part is exported by mowing.

```
bilan.P["solid - reed","first.stage"] <- set_units(5, g/m^2/yr) * set_units(
1.35, m^2/pe)
bilan.P["solid - reed","second.stage"] <- set_units(5, g/m^2/yr) * set_units
(0.9, m^2/pe)
```

Consequently, the rest of the P-org is stored in the biosolids.

```
bilan.P["solid - biosolids","first.stage"] <- P.stored - bilan.P["solid - re
ed","first.stage"] - bilan.P["solid - reed","second.stage"]
bilan.P["water - P04-P","first.stage"] <- bilan.P["water - P04-P","second.st
age"] + bilan.P["solid - reed","second.stage"]
```

Notice:

When taking into account the quantity of phosphorous that can actually be stored in the surface deposit considering the measurement done by Molle (2003), some phosphorous must be stored within the porous media of the first and second filter.

Molle (**Molle2003?**) measured the P_2O_5 concentration in the surface deposit (biosolids) to 1.46% of the dry matter. Considering the deposit accumulation rate of 2.5 cm/y (Molle, 2014) and the biosolid density of 300 \$kg/m³ (Vincent, 2011), the mass of P2O5 accumulating in the biosolids can be estimated:

```
P205.biosolids <- 0.0146
biomass.density <- set_units(300, kg/m^3)
biosolids.growth.rate <- set_units(2.5/365.5, cm/d)
surface.1st.stage <- set_units(1.35, m^2/pe)

P205.accumulated <- P205.biosolids * biomass.density * biosolids.growth.ra
te * surface.1st.stage
set_units(P205.accumulated, g/d/pe)

0.404446 [g/d/pe]
```

Using the stocheometry of P2O5, we can convert this value to P:

```
P.surface.deposit <- P205.accumulated * 0.436
```

D.2. References :

Mercoiret, L., 2009. Qualité des eaux usées domestiques produites par les petites collectivités. ONEMA.

Molle, P., 2014. French vertical flow constructed wetlands: a need of a better understanding of the role of the deposit layer. *Water Science and Technology* 69, 106–112.
<https://doi.org/10.2166/wst.2013.561>

Molle, P., 2003. [Filtres plantés de roseaux : limites hydrauliques et rétention du phosphore](#) (PhD thesis).

Risch, E., Boutin, C., 2010. Rapports d'ACV et données d'inventaire.

Tanner, C.C., 1996. Plants for constructed wetland treatment systems A comparison of the growth and nutrient uptake of eight emergent species. *Ecological Engineering* 7, 59–83. [https://doi.org/10.1016/0925-8574\(95\)00066-6](https://doi.org/10.1016/0925-8574(95)00066-6)

Vincent, J., 2011. [Les lits de séchage de boue plantés de roseaux pour le traitement des boues activées et les matières de vidange : Adapter la stratégie de gestion pour optimiser les performances](#) (PhD thesis).

ANNEX E: Carbon mass balance of French vertical flow treatment wetlands

Nicolas Forquet, Pascal Molle, Karine Dufossé

Last modified May, 2024

This notebook describes the carbon mass balance estimation for French Vertical Flow (VF) wetlands. It is based on the first LCA inventory carried out by Risch *et al.* (2010). This updated version aims to take better account of experimental data. In particular, it focuses on data collected from a large number of full-scale French VF wetlands.

The mass balance is expressed in $g\ C \cdot pe^{-1}d^{-1}$.

E.1. Incoming carbon flux

The estimation of the incoming carbon flux is based on the COD inlet flux. Mercoiret *et al.* (2009) estimated the incoming COD flux to $157.2\ gO_2d^{-1}$.

$$F_{COD}^{inlet} = 157.2\ [g \cdot d^{-1} \cdot pe^{-1}] \quad (1)$$

```
COD <- list(inlet = list(total = set_units(157.2, g/d/pe)))
```

E.2. Unit surface area

The maximum recommended surface load (L_{COD}^{inlet}) is $350\ gCODm^{-2}d^{-1}$ (Molle *et al.*, 2023). Considering [Equation 1](#), one can derived the minimum required surface per people equivalent (S_{pe}):

$$S_{pe} = \frac{F_{COD}^{inlet}}{L_{COD}^{inlet}} \times nb.filter\ [m^2 \cdot pe^{-1}] \quad (2)$$

where $nb.filter$ is the number of filter in parallel and fed alternatively. The recommended value for $nb.filter$ is 3 for the first stage and 2 for the second stage.

```
CCTP.load <- set_units(350, g/m^2/d)
surface <- list(first.stage = list(unit = COD$inlet$total/CCTP.load,
                                nb.filter = 3),
              second.stage = list(unit = COD$inlet$total/CCTP.load,
                                nb.filter = 2)
            )
surface$first.stage$total <-
  surface$first.stage$unit*surface$first.stage$nb.filter
surface$second.stage$total <-
  surface$second.stage$unit*surface$second.stage$nb.filter
```

The recommended surface are $1.35\ m^2/pe$ for the first stage and $0.9\ m^2/pe$.

Note

The resulting surface is larger than the value usually presented in the literature: $1.2\ m^2 \cdot pe^{-1}$ (Molle *et al.*, 2005).

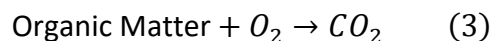
E.3. Conversion from COD to carbon equivalent

COD, BOD and TOC are all measures that can be used to estimate the quantity of organic matter present in the environment, although they are not sensitive to the same constituents (Thomas and Burgess, 2017).

Stocheometric approaches

Molar mass ratio

In Risch *et al.* (2010), conversion from COD to carbon is based on the following assumption. The degradation of the organic matter by microorganisms can be approximated by the following simplified equation:



Assuming that the consumption of 1 mole of O_2 results in the emission of 1 mole of CO_2 , the amount of carbon present in the organic matter being degraded is equal to the molar mass ratio $CO_2 - C/O_2$ (12/32) times the COD concentration. The conversion factor is then equal to 2.67g COD/g C.

Equivalent chemical formula

In Langergraber *et al.* (2007), two calculations are presented according to the equivalent chemical formula taken for the biomass ($C_5H_7O_2N$ or $C_8H_{14}O_4N$).

```
langergraber.convert <- tibble(formula = c("C5H7O2N", "C8H14O4N"),
  `conversion factor (g COD/g C)` = set_units(c(2.667, 2.917), g/g)
)
kable(langergraber.convert)
```

Table 1: conversion table from COD to C

formula	conversion factor (g COD/g C)
C5H7O2N	2.667 [g/g]
C8H14O4N	2.917 [g/g]

TOC equivalence

An alternative approach consists in converting COD into TOC. Dubber and Gray (2010) suggest the following equation:

$$COD = 49.2 + 3.00 \times TOC \quad (4)$$

The slope of the obtained relationship: 3, is very close to that of the second formula in [Table 1](#). The value of 3 (K) will therefore be retained for the time being.

```
COD_2_C <- set_units(1/3, g/g)
```

In the rest of the document, all calculations will first be performed in COD and then converted to their C equivalent using the conversion factor above.

E.4. COD inlet fractionation

The inlet COD is composed of an inert fraction and a biodegradable fraction. For the inert fraction, Gillot and Choubert (2010) indicate that it consists of:

- a soluble fraction representing 4% of the total COD
- a particulate fraction representing 25% of the total COD

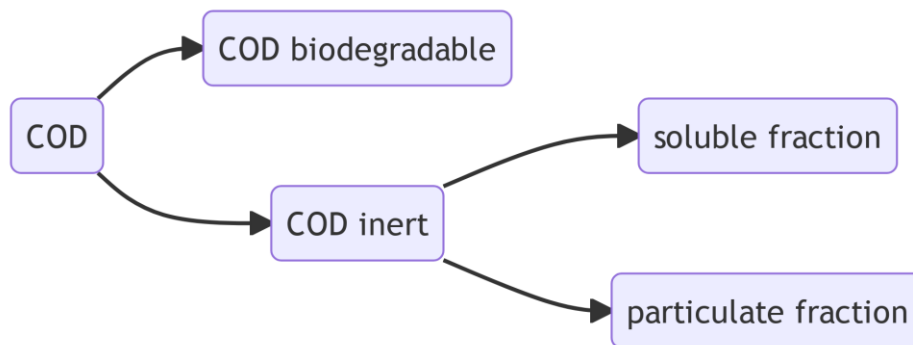


Figure 1: COD inlet fractionation according to (2010)

```

COD$inlet$inert_soluble <- 4/100*COD$inlet$total
COD$inlet$inert_particulate <- 25/100*COD$inlet$total
COD$inlet$biodegradable <- COD$inlet$total - COD$inlet$inert_soluble -
  COD$inlet$inert_particulate
  
```

Next we convert these values into their C-equivalent:

```

bilan.C$inlet[1] <- COD$inlet$biodegradable*COD_2_C
bilan.C$inlet[2] <- COD$inlet$inert_soluble*COD_2_C
bilan.C$inlet[3] <- COD$inlet$inert_particulate*COD_2_C
  
```

E.5. First treatment stage

COD removal

The COD removal rate between the inlet and the outlet of the first treatment stage is obtained from Morvannou *et al.* (2015) : 77%.

$$F_{COD}^{out} = (1 - 0.77) * F_{COD}^{in} \quad (5)$$

```

COD$first.stage$effluent <- (1-0.77)*COD$inlet$total
  
```

It is assumed that the inert soluble fraction is entirely transferred to the first stage outlet. It is also assumed that the inert particular fraction is completely removed by filtration:

$$COD_{out}^{soluble\ inert} = DCO_{in}^{soluble\ inert} \quad (6)$$

$$COD_{out}^{particulate\ inert} = 0 \quad (7)$$

$$COD_{out}^{biodegradable} = COD_{out} - COD_{out}^{soluble\ inert} \quad (8)$$

```

COD$first.stage$inert_soluble <- COD$inlet$inert_soluble
COD$first.stage$inert_particulate <- set_units(0,g/pe/d)
COD$first.stage$biodegradable <- COD$first.stage$effluent -
  COD$first.stage$inert_soluble
  
```

Conversion to C

```

bilan.C$inlet[1] <- COD$first.stage$biodegradable*COD_2_C
bilan.C$inlet[2] <- COD$first.stage$inert_soluble*COD_2_C
  
```

```
bilan.C$inlet[3] <- COD$inlet$inert_particulate*COD_2_C
bilan.C$first.stage[1] <- COD$first.stage$biodegradable*COD_2_C
bilan.C$first.stage[2] <- COD$first.stage$inert_soluble*COD_2_C
bilan.C$first.stage[3] <- COD$first.stage$inert_particulate*COD_2_C
```

Biosolids

The degraded organic matter is partly transformed into biomass and partly used to produce energy (and transformed to CO₂) (Figure 2).

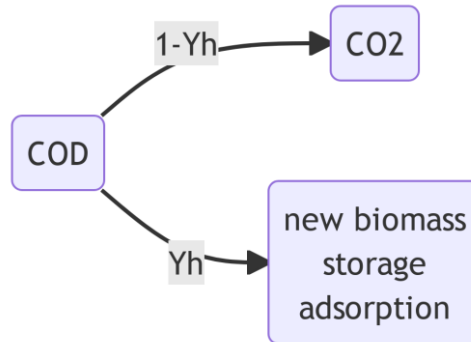


Figure 2: COD biodegradation pathways

The yield coefficient (Y_H) for heterotrophic bacteria is equal to 0.67 mg COD/mg COD (Henze et al., 2015). For sake of simplicity, new biomass, storage and adsorption will be looped into a simple term called biomass that we directly convert into C.

$$biomass = Y_H * (F_{COD}^{in} - F_{COD}^{out}) * K \quad (9)$$

$$F_{C-CO_2}^{biomass} = (1 - Y_H) * (F_{COD}^{in} - F_{COD}^{out}) * K \quad (10)$$

```
COD.degraded <- COD$inlet$biodegradable-COD$first.stage$biodegradable
YH <- set_units(0.67, g/g)
biomass <- YH*COD.degraded*COD_2_C
CO2.degradation <- (set_units(1, g/g)-YH)*COD.degraded*COD_2_C
```

There are two sources of biosolid accumulation:

- The biomass associated to the organic matter degradation (estimated above)
- The inert particulate COD

It is assumed that biosolids only significantly accumulates on the surface of the 1st treatment stage.

$$biosolids = biomass + F_{COD}^{inert\ particulate} * K \quad (11)$$

```
biosolids <- biomass + COD$inlet$inert_particulate*COD_2_C
```

However, accumulated biosolids are partly mineralized over time. This mineralization will in turn produces CO₂ and CH₄. In order to estimate the mineralized fraction, an estimate of the actual surface deposit accumulation rate will be used. Molle *et al.* (2014) reported an average

accumulation rate of $2.5 \text{ cm}/\text{m}^2/\text{y}$. Therefore, the volume of biosolids produced can be calculated:

$$V_{\text{biosolids}} = 2.5 \text{ cm}/\text{y} \times S_{\text{total}} \quad (12)$$

```
biosolids.growth.rate <- set_units(2.5/365.5, cm/d)
V.biosolids <- biosolids.growth.rate*surface$first.stage$total
```

The biosolids density is assumed to be equal to $300 \text{ kg DM}/\text{m}^3$ (source ? - **Pascal**)

$$M_{\text{biosolids}} = d_{\text{biosolids}} \times V_{\text{biosolids}} \quad (13)$$

```
density.biosolids <- set_units(300, kg/m^3)
M.biosolids <- density.biosolids*V.biosolids
```

The biosolids COT content has been estimated to $\sim 25\%$ (Kania et al., 2019)

$$M_{C \text{ biosolids}} = 0.25 \times M_{\text{biosolids}} \quad (14)$$

```
biosolids.C.content <- 0.25
bilan.C$first.stage[6] <- set_units(biosolids.C.content*M.biosolids,g/d/pe)
```

The difference between the stored biosolids ([Equation 14](#)) and the produced biosolids ([Equation 11](#)) gives an estimate of the fraction of biosolids that have been mineralized and then turned into methane or CO_2 .

```
biosolids.degraded <- biosolids - bilan.C$first.stage[6]
```

Gaseous emission

Methane emission have been measured by Molle *et al.* (2008). For the first stage, it has been measured:

- $0.1 \text{ g C-CH}_4/\text{m}^2/\text{d}$ during resting period
- $0.25 \text{ g C-CH}_4/\text{m}^2/\text{d}$ during feeding period

```
CH4.emission.feed <- set_units(0.25, g/m^2/d)
CH4.emission.rest <- set_units(0.1, g/m^2/d)
```

Consequently, over an entire feeding/resting cycle, the methane production is:

$$= \frac{\text{Production C-CH}_4}{\text{feeding duration} + \text{resting duration}} \cdot \text{m}^2 \cdot \text{d} \quad (15)$$

```
feed.duration <- set_units(3.5, d)
rest.duration <- set_units(7, d)
```

```
CH4.emission.cycle <- (feed.duration*CH4.emission.feed+rest.duration*CH4.emission.rest)/(rest.duration+feed.duration)
```

Then the production per square meter is transformed into the production per people equivalent:

$$\text{Production C-CH}_4/\text{EH} = \text{Production C-CH}_4 \times \text{Surface per PE} [g \cdot PE^{-1} \cdot d^{-1}]$$

```
bilan.C$first.stage[5] <- CH4.emission.cycle*surface$first.stage$total
```

If the mass of carbon transformed into methane is removed from degraded biomass estimated earlier, we obtain the mass of the biosolids that have been turned into CO_2 to which we need to add the mass of CO_2 produced during the biomass formation to obtain the total CO_2 emission.

```
bilan.C$first.stage[4] <- biosolids.degraded - bilan.C$first.stage[5] + CO2.degradation
```

Carbon storage in reeds

It is assumed that reeds only captured atmospheric CO_2 which in turn will be transformed into atmospheric CO_2 during composting. This lead to a neutral mass balance (biogenic CO_2).

```
bilan.C$first.stage[7] <- set_units(0,g/d/pe)
```

Cette hypothèse tend à négliger la quantité de carbone stockée au niveau des rizhomes et le carbone stocké au final après compostage. Pascal cherche le quantité de C stockée dans les roseaux et Karine cherche la quantité de C capté par photosynthèse par les roseaux

E.6. 2nd treatment stage

Effluent

COD removal

The COD removal rate between the inlet and the outlet of the second treatment stage is obtained from Morvannou et al. (2015): 87%

```
COD$second.stage$effluent <- (1-0.87)*COD$inlet$total
```

It is assumed that the quantity of inert soluble COD remains unchanged between the inlet and the outlet of the second treatment stage.

```
COD$second.stage$inert_soluble <- COD$first.stage$inert_soluble
COD$second.stage$inert_particulate <- COD$first.stage$inert_particulate
COD$second.stage$biodegradable <- COD$second.stage$effluent-COD$second.stage$inert_soluble-COD$second.stage$inert_particulate
```

Conversion to C

```
bilan.C$second.stage[1] <- COD$second.stage$biodegradable*COD_2_C
bilan.C$second.stage[2] <- COD$second.stage$inert_soluble*COD_2_C
bilan.C$second.stage[3] <- COD$second.stage$inert_particulate*COD_2_C
```

Carbon storage in reeds

Similarly to the first stage, the storage in reeds can be neglected.

```
bilan.C$second.stage[7] <- set_units(0,g/d/pe)
```

Gaseous emission

There has been no measurement performed on the second treatment stage. Therefore, it has been assumed that for both treatment stages, the methane production is proportional to the quantity of organic carbon degraded and that the ratio observed for the first treatment stage can be applied to the second treatment stage.

```
bilan.C$second.stage[5] <- (bilan.C$first.stage[1]-bilan.C$second.stage[1])/
  (bilan.C$inlet[1] - bilan.C$first.stage[1])*bilan.C$first.stage[5]
```

CO2 emission are computed by difference:

```
bilan.C$second.stage[4] <- sum(bilan.C$first.stage[1:3])-sum(bilan.C$second.
stage[-4])
```

E.7. Summary

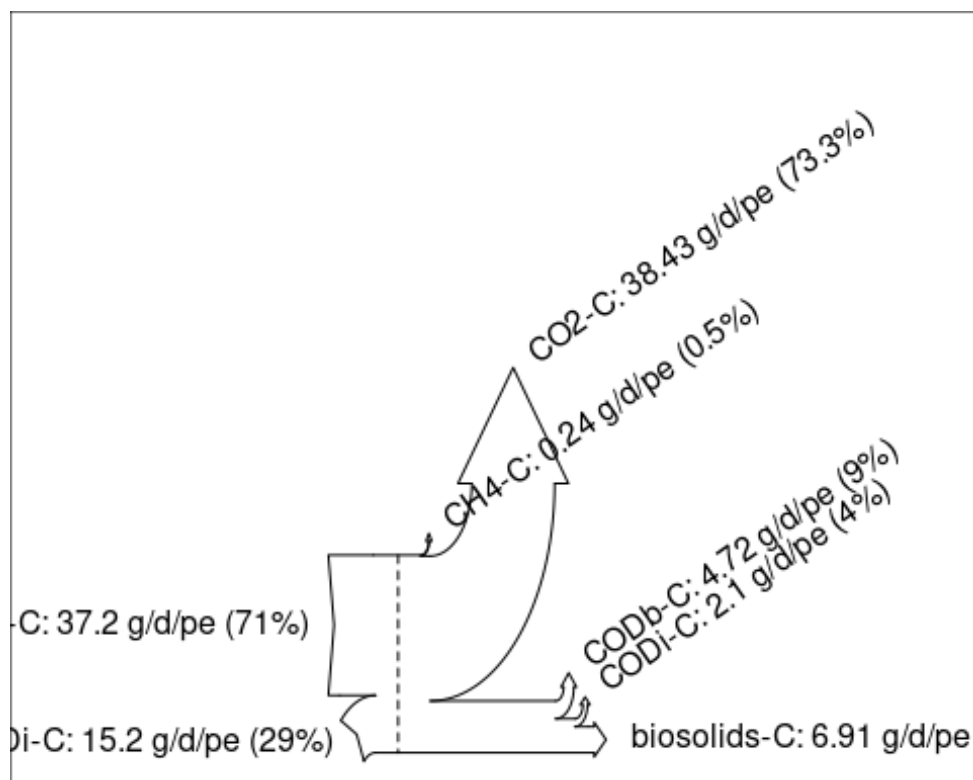
```
kable(bilan.C)
```

	inlet	first.stage	second.stage
water - biodegradable	37.204 [g/d/pe]	9.9560000 [g/d/pe]	4.71600000 [g/d/pe]
water - inert soluble	2.096 [g/d/pe]	2.0960000 [g/d/pe]	2.09600000 [g/d/pe]
water - inert particulate	13.100 [g/d/pe]	0.0000000 [g/d/pe]	0.00000000 [g/d/pe]
gas - CO2-C	0.000 [g/d/pe]	33.2336324 [g/d/pe]	5.20113187 [g/d/pe]
gas - CH4-C	0.000 [g/d/pe]	0.2021143 [g/d/pe]	0.03886813 [g/d/pe]
solid - biosolids	0.000 [g/d/pe]	6.9122533 [g/d/pe]	0.00000000 [g/d/pe]
solid - reed	0.000 [g/d/pe]	0.0000000 [g/d/pe]	0.00000000 [g/d/pe]

Results can also be presented using a Sankey plot:

```
Inputs <- as.numeric(c(bilan.C$inlet[1],
  bilan.C$inlet[2]+bilan.C$inlet[3]))
Inputs <- round(Inputs,2)
Losses <- as.numeric(c(
  bilan.C$second.stage[5]+bilan.C$first.stage[5],
  bilan.C$second.stage[4]+bilan.C$first.stage[4],
  bilan.C$second.stage[1],
  bilan.C$second.stage[2],
  bilan.C$first.stage[6]
))
Losses <- round(Losses,2)
Labels <- c("CODb-C", "CODi-C",
  "CH4-C", "CO2-C",
  "CODb-C", "CODi-C",
  "biosolids-C")

SankeyR(inputs = Inputs,
  losses = Losses,
  unit = "g/d/pe",
  labels = Labels
)
```



5.0 References

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The overall goal of MULTISOURCE is to, together with local, national, and international stakeholders, demonstrate a variety of about Enhanced Natural Treatment Solutions (ENTS) treating a wide range of urban waters and to develop innovative tools, methods, and business models that support citywide planning and long-term operations and maintenance of nature-based solutions for water treatment, storage, and reuse in urban areas worldwide. The project includes seven pilots treating a wide range of urban waters. Two individual municipalities (Girona, Spain; Oslo, Norway), two metropolitan municipalities (Lyon, France; Milan, Italy), and international partners in Brazil, Vietnam, and the USA will contribute to each of the main project activities: ENTS pilots, risk assessment, business models, technology selection, and the MULTISOURCE Planning Platform. The use of urban archetypes in the Planning Platform will enable users to quickly classify regions (in both developed or developing countries) suitable for the application of nature-based solutions for water treatment (NBSWT) and compare scenarios both with and without NBSWT.



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