LogistEC

Logistics for Energy Crops' Biomass

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Recommendations for the valorisation of process residues by biomass crops

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Summary

The evaluation of pretreatment systems based on wet torrefaction was a key objective of the FP7 LogistEC project for enhancing the logistics of energy crops. The wet torrefaction is a two-stage pretreatment process consisting in a prewash followed by a high temperature Torwash treatment, which allows to obtain a cookie with a higher heating value and a lower ash content compared with the initial biomass. The residues of these treatments are two liquids: one from prewash (PW) and one from Torwash (TW), characterized by a high mineral content.
A pot experiment was carried out to evaluate the effects of PW and TW on the growth of micropropagated plantlets of giant reed, on soil properties and on leached water quality. A scarce effect of K on plant growth was observed, with an increase of the aboveground dry yield (AGB). The lower AGB observed in TW probably depended on the limited evapotranspiration capacity of TW plants, which responded to stress by increasing their production of roots.
Regarding the soil, the electrical conductivity (EC) at the end of the trial was higher in PW-TW treatments than in the control treatment and it varied accordingly to the ionic content of the wastewaters (PW>TW), while the untreated soil did not differ markedly from the control treatment. Consistently with the reduced evapotranspiration, higher drainage volumes were observed in wastewater treatments. The main finding about leached water quality concerns nitrate content, which was markedly lower in PW and TW treatments than in the control. Since the treatments did not differ in nitrogen supply, it might be hypothesized that the differences in nitrate leaching originated from organic matter mineralization and from nitrification.
In conclusion, while the PW could be reused for irrigation and for restoring the K content into the soil, the TW seems to be not suited for fertigation, and its high content of volatile fatty acids suggests a better reuse for other applications (such as anaerobic digestion).

Mis en forme : Anglais (Royaume-Uni)

<u>Objectives</u>
The objective of this work was to analyze the effects of fertigation on giant reed, using two wastewaters originated from wet torrefaction of biomass from this crop. To achieve this objective, crop growth, leached water and soil proprieties were monitored in a plot experiment carried out on young plants for 18 weeks.

<u>Geographical areas covered:</u> Mediterranean countries

Abbreviations

Mis en forme : Anglais (Royaume-Uni)

AGB: aboveground biomass

Mis en forme : Anglais (Royaume-Uni)

BGB: belowground biomass

CK: tap water + potassium fertilizer

FM: fresh matter

PW: prewash

TW: Torwash

UT: untreated soil

Liquid residues from wet torrefaction of biomass for fertigation

Mis en forme : Anglais (Royaume-Uni)

Substantial challenges for the development of biomass supply chains include the distributed and bulky nature of biomass, as well as its potential for degradation during transport and storage. For these reasons, the densification of biomass prior to transport is a key requirement, in order to produce an energy carrier easier to be handled and stored. Thermal pre-treatments (i.e. torrefaction) are a way to obtain such carriers, in wet or in dry processes.
The evaluation of pretreatment systems based on wet torrefaction was a key objective of LogistEC, aiming to enhance the logistics of energy crops, with a focus on perennial energy grasses. In particular, the wet torrefaction is a two-stage pre-treatment which consists in a washing phase (prewash, 50°C for 15 minutes) followed by a high temperature treatment ('Torwash', 200°C for 30 min) which allows to obtain a solid biofuel characterized by a higher heating value and a lower ash content compared with the original biomass. In fact, the use of biomass from perennial grasses for combustion shows some difficulties, owing to transport and storage but also to its chemical characteristics, such as high ash, alkalis and chlorine contents, causing corrosion, fouling, and slagging problems. These issues are particularly critical for some crop species, such as giant reed (*Arundo donax* L.), whose ash and alkali content are usually high.
Two kinds of wastewaters are originated from the two treatments: one from prewash and one from Torwash. Recycling the wastewaters obtained from wet torrefaction would allow to recover the nutrients removed from the biomass and to return them to the soil. Therefore, not only the characteristics of the solid biofuels are improved, but also the overall sustainability of the process can be increased through an improved nutrient management, involving a proper handling of the wastewaters.

1. Evaluation of the effects of Prewash and Torwash wastewaters on giant reed growth

Mis en forme : Anglais (Royaume-Uni)

In order to assess the direct reuse of wastewaters on energy crops, a pot experiment was carried out on micro propagated plantlets of giant reed. A particular focus was put on this crop, since this species is very promising for bioenergy purposes, given its remarkable yield potential under low input management and rainfed conditions. In particular, the distribution of Prewash (PW) and Torwash (TW) wastewaters was investigated, in terms of effects on plant growth and on soil and leachate properties. Noteworthy, wastewaters were obtained from the thermal pretreatment in a batch test of giant reed biomass, thus reflecting at most the composition of such wastewaters when obtained from biomass harvested and processed at the scale of giant reed-based supply chain.

1.1. Materials and methods

From May 2014, the pot experiment was carried out at the Agro-Environmental Research Centre of the University of Pisa (Central Italy). Pots (20 L capacity) were filled with sandy soil collected in the same area (Table 1). One micro propagated plant of giant reed (four green leaves, 24 g FM) was transplanted in each pot and five pots were assigned to each treatment. The crop water requirement was determined, according to crop coefficients reported in the literature (Triana et al., 2015). Wastewater characteristics are listed in Table 2.

pH	7.38
EC (µS cm^{-1})	42.7
N tot (mg g^{-1})	0.72
SOC (%)	1.05
P_{olsen} (ppm)	17.06
K (ppm)	136
Clay (%)	4.99
Silt (%)	6.04
Sand (%)	88.97

Table 1: Physical and chemical properties of the soil used for the pot experiment

The following treatments were carried out:

(i) fertigation with PW mixed with tap water (30%) to provide 7.4 g K $plant^{-1}$ and 30 L $plant^{-1}$ of water (10 L Prewash and 20 L tap water);

(ii) fertigation with TW mixed with tap water (30%) to provide 2 g K $plant^{-1}$ and 30 L $plant^{-1}$ of water (10 L Torwash and 20 L tap water);;

(iii) control, no potassium fertilization, irrigation with 30 L $plant^{-1}$ tap water (C);

(iv) control + K, fertilization with K_2SO_4 at transplanting with the same amount usually provided at crop establishment in field condition (15 g $plant^{-1}$) and irrigation with 30 L $plant^{-1}$ of 100% tap water (CK).

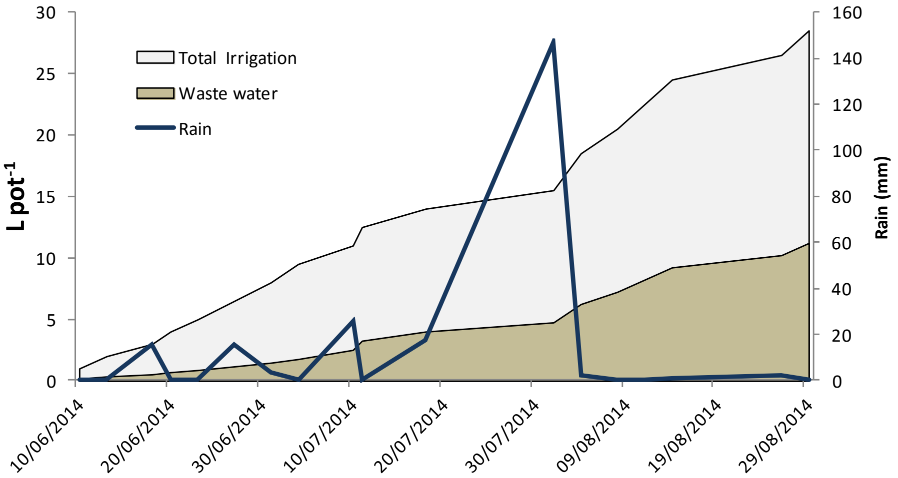
Mis en forme : Anglais (Royaume-Uni)

	PW	TW
K	743	198
Mg	121.3	61.1
Mn	1.44	1.11
Ca	177	118
Ba	0.24	0.34
Na	20.48	6.14
P	69.5	35.4
S	149.1	61.7
Si	-	323
Sr	0.48	0.41
Zn	0.75	-
Cl	472	64
Total C	6750	13504
pH	3.4	3.1
EC (µS cm^{-1})	3580	1750

(v)

(vi) Table 2: Mineral and carbon concentrations ($mg.L^{-1}$), pH and Electrical Conductivity (EC) of the residues from prewash (PW) and Torwash (TW) treatments.

Plants were grown on outdoor conditions and daily rainfall was recorded during the study period. Irrigation was scheduled according to the crop evapotranspiration coefficient (Kc) and to rainfall (Fig. 1).
Plant growth was observed for 18 weeks and after this period fresh biomass plant of each plot was measured and partitioned among different aboveground (AGB, leaves and stems) and belowground (BGB, roots and rhizomes) organs. Stem diameters and heights were also measured, and the number of shoots and belowground buds (i.e. rhizome buds) were determined. Simple biometric ratios (i.e. foliar mass ratio, root mass ratio) were calculated, as well as the total bud number (emerging buds + belowground buds, where the emerging buds were considered equal to the number of shoots).
A one-way ANOVA was applied to test the effect of the treatments analysed. Where significant effects were observed, post-hoc LSD tests were performed at the $P<0.05$ level.


30
25
20
15
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5
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160
140
120
100
80
60
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L pot-1
Rain (mm)
Total Irrigation
Waste water
Rain
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20/06/2014
30/06/2014
10/07/2014
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09/08/2014
19/08/2014
29/08/2014

1.2. Results

On average, the above ground biomass (AGB) of giant reed in the untreated pots (C) was about 150 g, while the below ground organs (BGB) reached 125 g (Fig. 2). Comparing the control with the treatments, a significant effect of PW and TW on AGB was observed ($p<0.001$). AGB was reduced of about -20% when giant reed was treated with PW, while TW led to a higher yield decline (-50%); conversely, no significant effects were observed on BGB. Some differences were observed also on above ground biomass partitioning, since the leaf mass ration in TW-treated plants was significantly higher than in C and in the other treatments (+14%) ($p<0.001$). However, no remarkable effects were noticed on partitioning of the below ground fractions (rhizomes and roots).

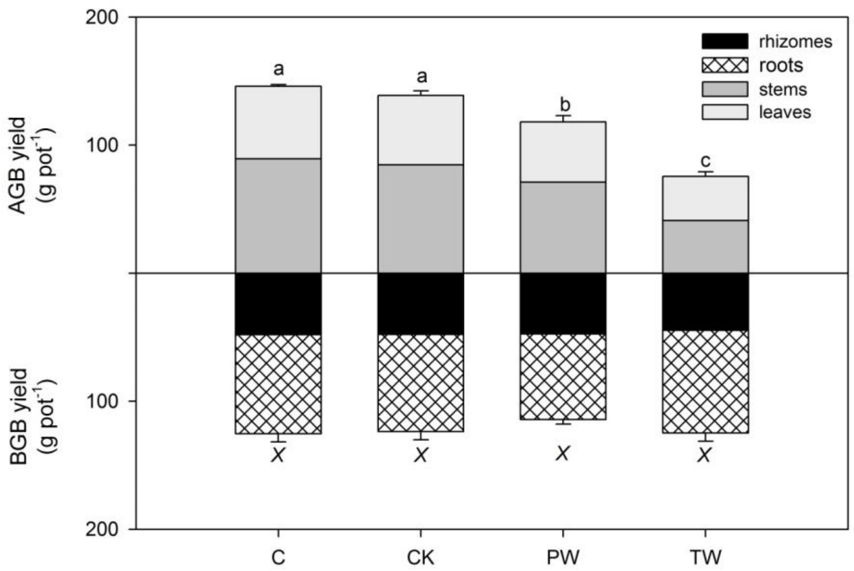

Figure 2: Aboveground (AGB) and belowground (BGB) biomass partitioning, according to different treatments (CK, PW, TW) and compared with the control (C). Lower case letters are for mean separation of aboveground yields, while upper case italic letters are for belowground biomass.

Noticeable effects were also shown on crop biometrics (Fig. 3). Significantly taller shoots were observed in the control, while the application of wastewater treatments caused a height reduction of about -20% in PW and -35% in TW ($p<0.001$). Also the high level of K fertilization determined a significant reduction of plant height and diameter (CK -15%). Shoot diameters were also lowered by TW (-21%) ($p<0.05$). In general, both the wastewater treatments showed marked effects in reducing crop growth parameters.

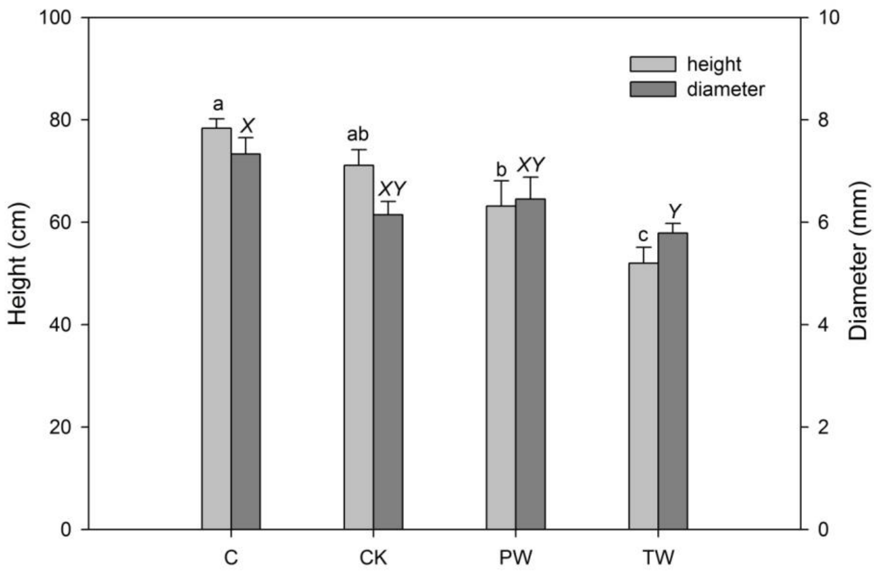

Figure 3: Biometric parameters, according to different treatments (CK, PW, TW) and compared with the control (C). Lower case letters are for shoot heights, upper case italic letters are for shoot diameters.

However, some effects were also shown in overall crop morphology (Fig. 4). In particular, the PW treatment seemed to affect the shoot number per pot, which was higher than the control (18.6 *vs* 13.8, p=0.08), while TW and CK treatments did not show significant differences. Similarly, significant changes were observed in the number of belowground buds, which was raised in TW (18.0) compared with the other treatments (12.9) ($p<0.01$). Analysing the total number of buds (emerging + belowground), both PW and TW resulted in a significant increase in budding (32.0 and 33.0 total buds, respectively) compared with C and CK (27.2 and 26.6, respectively)($p<0.05$).

Therefore, despite a reduced crop growth observed in wastewater treatments, an increase in shoot and bud number was recorded. This observation could be explained in terms of increased crop stress, which caused a lower growth while promoting a higher organ differentiation, both in aboveground (PW) and in belowground (TW) parts.

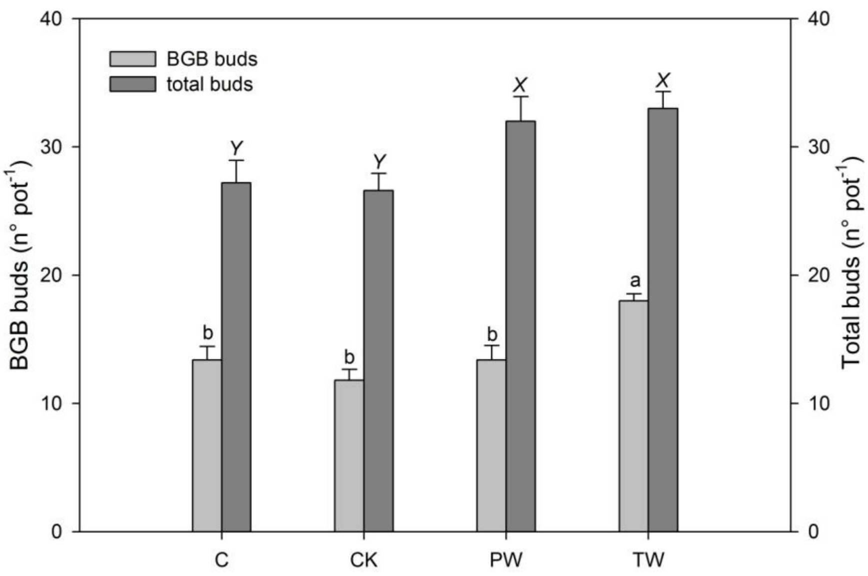

Figure 4: Belowground (BGB) buds and total buds, according to different treatments (CK, PW, TW) and compared with the control (C). Lower case letters are for BGB buds, upper case italic letters for total buds.

2. Effects of prewash and Torwash wastewaters on macronutrient uptakes

2.1. Materials and methods

At the end of the pot experiment, plant samples were taken, dried at 60°C until constant weight and then milled and used for chemical analysis. Nitrogen concentration was determined using the Kjeldahl method, while phosphorus and potassium were obtained by ammonium-molybdate colorimetric assay and by flame photometry, respectively. Nutrient uptake in each plant organ was calculated as the product of nutrient concentration by dry biomass yield. Aboveground nutrient uptakes were calculated as the sum of the nutrient uptakes in leaves and stems, while belowground nutrient uptakes were calculated as the sum of the nutrient uptake in roots and rhizomes. A one-way ANOVA was applied to test the effects of the treatments on nutrient concentration and uptakes. Where significant differences were observed, post-hoc LSD tests were performed at the $p<0.05$ level.

2.2. Results

Relevant differences in nutrient concentrations were evidenced among the different treatments (Table 3). In particular, the TW treatment led to higher [N] and [P] in giant reed leaves compared with the control. The PW treatment also led to a significantly higher [P] in leaves, while C and CK did not differ for nitrogen and phosphorus concentrations. Expectedly, higher [K] were found in giant reed leaves when potassium-enriching treatments (PW and CK) were applied. Foliar potassium contents were similar in PW and CK, averaging 2.8%, and also TW and C did not differ remarkably between each other, averaging 1.7%.
No significant differences were observed in [N] and [P] of giant reed stems, while a noticeable effect was found in [K]. Similarly to the leaves, the stems were richer in potassium when PW wastewaters were applied, and these values were rather similar to those observed in CK (1.5%), while TW treatment did not lead to significantly different concentrations from C (0.7%).
Interestingly, belowground organs showed a remarkably different trend in nitrogen concentrations compared with the aerial parts. The highest [N] was found in the control and CK did not differ significantly from it, while the lowest values were observed in PW and TW. However, this behaviour was not observed in [P], whose differences were not statistically significant. The highest [K] was observed in CK, not significantly different from PW; the lowest value was found in TW, not significantly different from C.

	Treatment	[N] g kg^{-1}			[P] mg kg^{-1}			[K] g kg^{-1}		
			***			***			***	
Leaves	PW	16.82	(0.31)	b	1633.60	(104.18)	b	27.40	(0.94)	a
	TW	20.38	(1.08)	a	2123.00	(132.56)	a	15.62	(1.02)	b
	CK	16.04	(0.36)	b	1301.80	(46.87)	c	29.48	(1.62)	a
	C	16.52	(0.24)	b	1282.60	(48.44)	c	17.94	(0.85)	b
			ns			*ns*			***	
Stems	PW	5.94	(0.33)		492.20	(84.57)		13.22	(1.16)	a
	TW	6.50	(0.32)		402.20	(86.87)		7.58	(0.84)	b
	CK	6.00	(0.24)		532.20	(73.83)		16.42	(1.21)	a
	C	5.62	(0.22)		381.40	(57.55)		6.42	(1.28)	b
			**			*ns*			**	
Belowground organs (rhizomes + roots)	PW	8.88	(0.38)	c	885.64	(74.98)		9.35	(0.71)	ab
	TW	9.74	(0.26)	bc	759.00	(40.41)		6.04	(0.75)	c
	CK	10.18	(0.23)	ab	851.98	(166.23)		12.04	(0.94)	a
	C	10.82	(0.48)	a	760.10	(80.44)		8.74	(1.33)	bc

Table 3: Nitrogen, phosphorus and potassium concentrations in giant reed organs, according to different treatments. Standard errors are reported in brackets. *p< 0.05, **p< 0.01, ***p< 0.001.

Regarding nutrient uptakes, the highest aboveground nitrogen uptake was observed in C (1.4 g pot^{-1}), while significant reduction was recorded in all the other treatments (-10% in CK; -20% in PW and -30% in TW). Moreover, slight differences were found for nitrogen uptakes related to the belowground biomass (-10% in PW) (Fig. 5a). Only a slight reduction in aboveground P uptakes was observed in TW-treated plants, while the other treatments were not significantly different (Fig. 5b). Moreover, regarding phosphorus, no significant differences were observed in belowground uptakes. On the contrary, K uptakes showed a different behaviour with significant higher values of the aboveground K uptake in CK and PW compared with the control, while a reduction of about -50% was observed in TW. A similar trend was observed in the belowground K uptakes, with the exception of PW, which showed similar values as C (Fig. 5c).

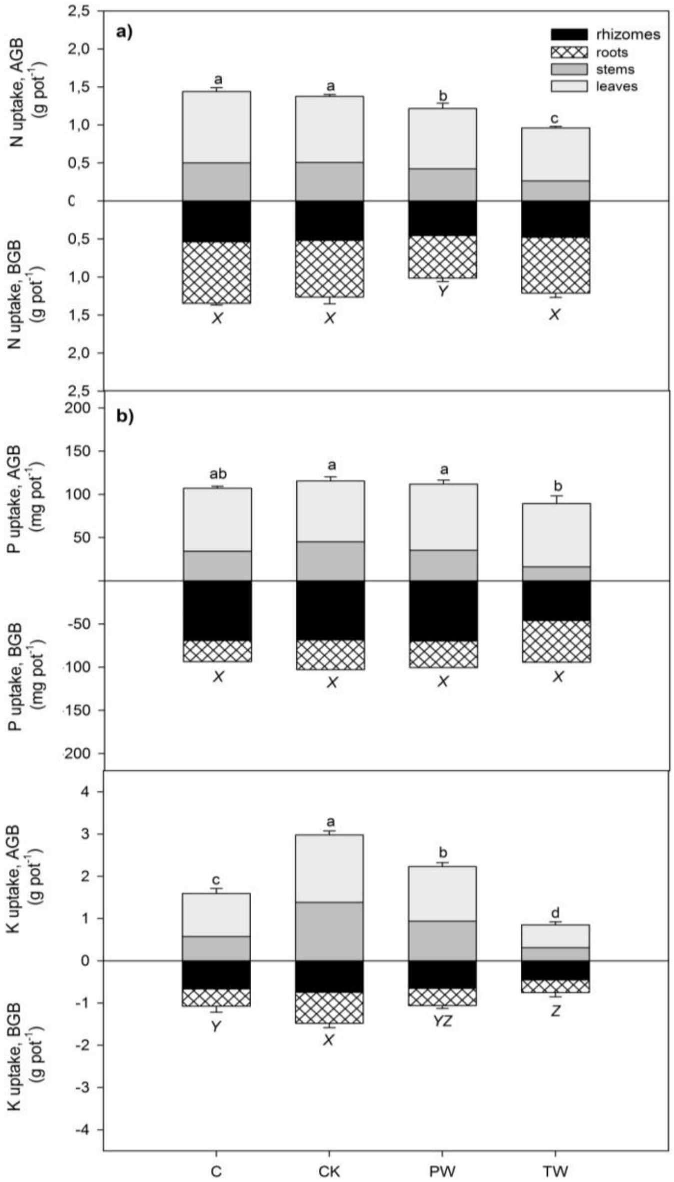

Figure 5: Nitrogen (a), phosphorus (b) and potassium (c) uptakes or each aboveground (AGB) and belowground (BGB) biomass component, among the different treatments (CK, PW, TW) and compared with the control treatment (C) set to 100%. Lower case letters are for AGB yields, upper case italic letters for BGB yields.

3. Effects of prewash and Torwash wastewaters on soil and leachate properties

3.1. Materials and methods

Throughout the crop growth, the water drained from each pot was collected and the amount of ammonium, nitrates, nitrites, phosphates and potassium were measured by atomic absorption. Moreover, drainage volumes were taken into account, in order to compute the overall amounts of nutrients lost by leaching. Other cations and anions were also considered (Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^-).

At the end of the experiment, soil samples from each experimental unit were analysed for:

- pH;
- electrical conductivity (EC);
- exchangeable potassium (K^+);
- total nitrogen (Ntot);
- soil organic matter (SOM);
- total phosphorus (Ptot).

Soil EC and pH were measured in deionized water (1:2 and 1:2.5 w/v, respectively). K^+ was determined by atomic absorption; Ntot was measured by macro Kjeldahl digestion procedure; SOM was determined using a modified Walkley-Black wet combustion method. A one-way ANOVA was carried out to compare the effect of the treatments and post-hoc LSD tests were performed ($p<0.05$ level) where significant differences were observed.

3.2. Results

Regarding nitrogen compounds, nitrites and ammonium were never detected in leachates. Therefore, the only nitrogen lost by leaching was in form of nitrates. The average nitrate concentration in leachates was significantly higher in CK than in the other treatments and TW-PW showed the lowest [NO_3^-] values (Fig. 6a). Phosphates were also not detected in leachates, while [K^+] varied largely across the different treatments. The highest concentration was by far obtained by CK leachates; PW may also have had an effect, although [K^+] it was not significantly higher in this treatment compared with C and TW (Fig. 6a).
Leachate volumes (i.e. drainage) played also a role, as they differed according to the treatments and they determine the overall amounts of leached nutrients along with nutrient concentrations (Fig.6b). Higher drainage volumes were observed in PW-TW treatments, which approached 6 L pot^{-1}, while C and CK averaged 4.5 L pot^{-1} (-22%). Lower drainage volumes observed in control treatments may be explained by a

higher water demand, i.e. higher evapotranspiration, owing to the higher aboveground biomass recorded.

Despite the higher drainage volumes, the differences in the overall mass of leached potassium were not significantly different from the control in PW and TW, due to the remarkably higher values observed in CK. Potassium fertilization timing may also have played a role, since solid K fertilizer was applied in one pass at planting, when giant reed plantlets were presumably not taking up much nutrients, while PW was distributed along the time. This noteworthy difference in the experimental set-up was intended to simulate the application of a real-scale potassium fertilization, although it produced a discrepancy in K leaching.

Regarding nitrates, the leached amounts in PW and TW treatments were markedly lower than in C and CK (36 *vs* 6 mg pot^{-1}). Since the treatments did not differ in nitrogen supply, it might be hypothesized that the differences in nitrate leaching were originated from the mineralization of organic matter and from nitrification. Plant removal should have played the opposite role, lowering the availability of nitrates for leaching in C-CK treatments, in which the N uptake was higher. Therefore, plant uptake seemed not to be the most relevant factor in determining the observed difference in nitrate leaching. On the other hand, PW and TW might have reduced the biological activity in the soil, thus affecting mineralization and nitrification.

These observations are in line with some of the results obtained in soil analyses. In particular, soil organic matter and total nitrogen showed a congruent trend (higher values in PW-TW, lower values in C-CK) (Fig. 7c, Fig. 7d). Moreover, PW and TW treatments are both sources of additional carbon brought to the soils.

Concerning soil pH, an effect of the water used for irrigation may be hypothesized. A large difference was evidenced in C at the end of the experiment compared with the untreated soil (UT), expectably due to water hardness. Soil pH was kept significantly lower in CK, PW and TW compared with C (Fig. 7a). Organic carbon (acids?) and calcium displacement triggered by a relevant amount of potassium may explain these results. In fact, the amount of calcium leached from the soil is remarkably higher in CK, PW and TW treatments than in C (1073 *vs* 400 mg pot^{-1}). It should be noted that it is usually very difficult to alter soil pH, and that a coarse soil texture, rich in sand and poor in mineral colloids, has probably enhanced the effects of the considered treatments on soil chemistry. Regarding soil conductivity, this parameter varied accordingly to the EC of the applied wastewaters and, in general, to the ionic content of the applied fertilizers (PW≅CK>TW>C). The untreated soil did not differ markedly from the control (Fig.7b).

As it may be inferred from wastewater compositional data, PW is also an interesting source of phosphates, which seemed to have slightly enriched the soil compared with the other treatments (Fig. 7e). Exchangeable potassium levels were also in line with the potassium contents of the applied fertilizers. The only exception is the level observed in CK, which was relevantly higher than that of PW (Fig.7f). This might be explained with a lower retention efficiency showed by the soil in PW treatment, likely due to wastewater pH and interfering mineral elements.

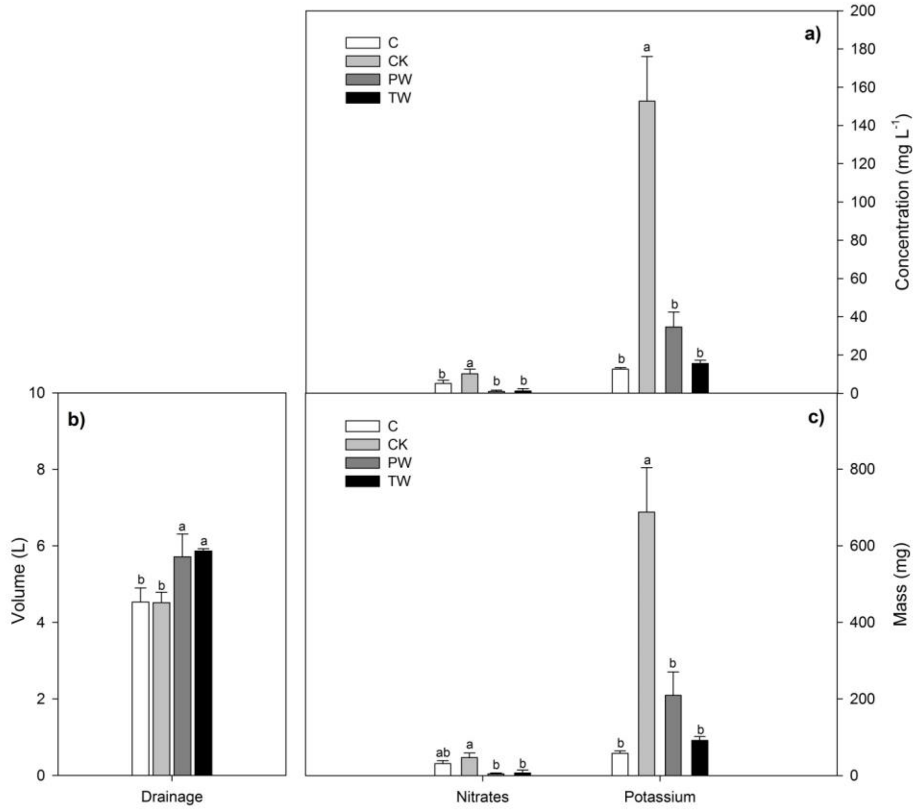

Figure 6: Nitrogen (a), phosphorus (b) and potassium (c) uptakes or each above ground (AGB) and below ground (BGB) biomass component, among the different treatments (CK, PW, TW) and compared with the control treatment (C) set to 100%. Lower case letters are for AGB yields, upper case italic letters for BGB yields.

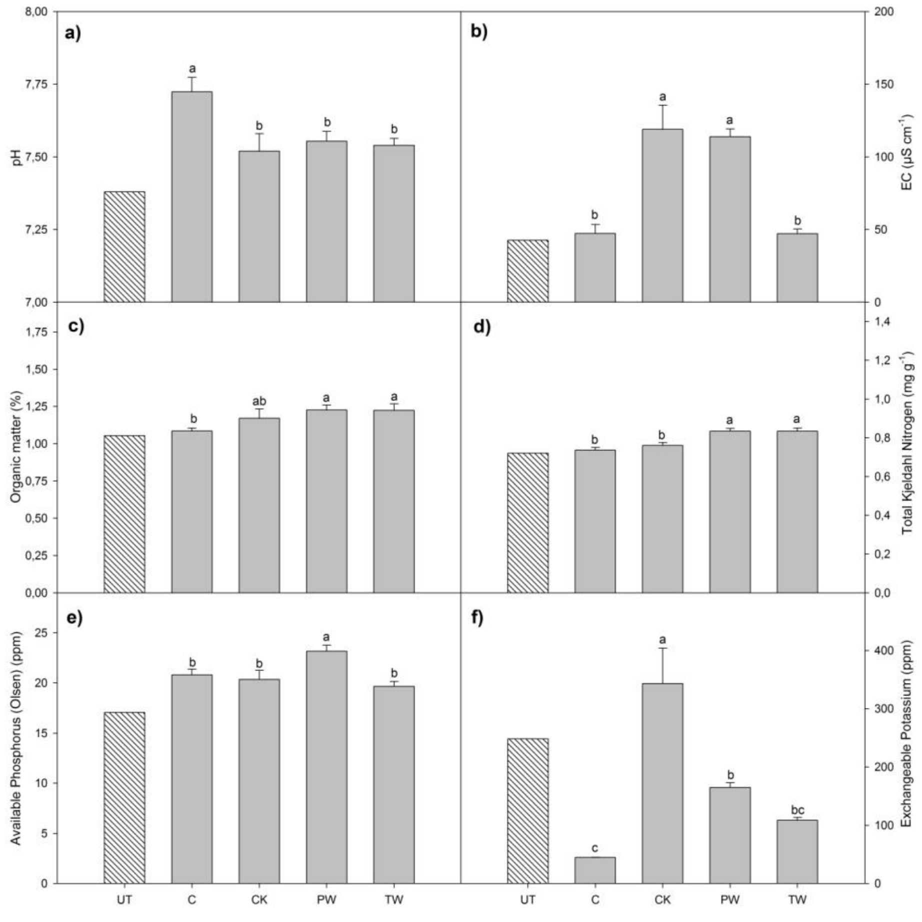

Figure 7: Soil pH (a), electrical conductivity (EC) (b), organic matter (c), total nitrogen (d), available phosphorus (e) and exchangeable potassium (f) as affected by the different treatments (CK, PW, TW) and compared with the control (C) and with the untreated soil (UT).

Conclusion

Even if giant reed is proposed as a stress-tolerant crop, potentially suitable for the valorisation of wastewaters, a negative effect of Torwash residues on biomass yield was observed. This reduction was determined by a reduced stem growth (height and diameter). The lower aboveground yield observed in TW was related to reduced evapotranspiration, as confirmed by the higher volume of leachates. However, it must be stated that the effects on giant reed growth in a pot experiment, carried out on micropropagated plantlets grown on a sandy soil, may have been exacerbated for several reasons. In fact, the experiment was purposely aimed to highlight the possible effects of wastewater treatments on the crop-soil-water system.

The high conductivity alone cannot explain the negative response of plants to TW treatment, while it was probably the most relevant factor affecting biomass productivity in PW treatment. The toxic effects of wet torrefaction wastewaters have already been assessed, but uncertainty on their effective causes still remains. Furthermore, a scarce effect of K fertilization on plant growth was also shown, the aboveground dry yield being similar in C and CK. With regard to K uptakes, a high K availability may have led to potassium luxury uptake by this crop.

Overall, both the wastewaters resulted to be poorly suitable for fertigation at crop establishment. PW could be used to restore the K content of the soil, although no increase in crop yield can be expected, unless a potassium lack in the soil is occurring. PW treatment seemed to be advisable especially in mature crops or after the end of the lifespan of the plantation, in the perspective of nutrient restoration in a whole crop rotation.

Finally, the organic compounds in TW wastewater should also be considered. Owing to the high content of volatile fatty acids, the use of TW wastewater as a substrate for anaerobic digestion could represent a relevant solution, although further evaluations are needed on this aspect. In fact, TW wastewaters showed a high content of acetic and formic acid and both the compounds are easily metabolized in the methanogenetic pathway. However, furfural (2-furaldehyde) was also found to be quite abundant in TW waters (>7 g kg^{-1}) and could hamper the anaerobic digestion process. This and other compounds are known to have an inhibitory effect on several biological processes, including methanogenesis. Considering also the low total solids content, the methane potential of TW wastewaters is expected to be quite low on a volume basis.