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Agrosystems and Ecosystem Services: an agroenvironmental assessment of vegetated systems for phytoremediation of water from agricultural drainage

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Indice

Riassunto

Il rapporto tra servizi ecosistemici e agricoltura è di cruciale importanza, sia per investigare il flusso bidirezionale di servizi che attraversa il sistema agricolo, sia per quantificare i beni e servizi da esso derivati, indispensabili alle società umane. Le zone umide rappresentano oggigiorno un elemento di fondamentale importanza, soprattutto se localizzate in territori agricoli intensivi, come ad esempio il bacino scolante della laguna di Venezia. I sistemi *wetland*, infatti, sono in grado di erogare importanti servizi ecosistemici: regolazione, supporto, approvvigionamento; esse sono capaci di regolare il flusso di acqua ed il ciclo di nutrienti, mitigare l'eccesso di fertilizzanti e pesticidi, sequestrare carbonio, migliorare la biodiversità. Attraverso tre sperimentazioni a scala campo il presente progetto di ricerca intende valutare il servizio di *water purification* erogato da zone umide nel mitigare l'inquinamento da drenaggio agricolo; un ultimo caso, invece, vuole stimare il servizio di approvvigionamento legato alla vegetazione presente lungo il reticolo minore, stimandone l'energia potenziale derivata.

Nel primo caso di studio "a constructed wetland for water purification services from pesticide in an intensive cropping system" i risultati mostrano come il sistema possa ridurre la concentrazione di metolacloro e terbutilazina nelle acque di runoff di un fattore 45-80, anche in condizioni di eventi estremi.

Nella seconda sperimentazione "vegetated ditches as water purification systems to mitigate contamination from pesticides runoff" i risultati mostrano come canale vegetato in alveo può ridurre le concentrazioni di *runoff* contaminato almeno del 50%, anche in condizioni di eventi pluviometrici estremi; in generale, un *runoff* di 1 mm da 5 ha di bacino agricolo viene mitigato al 99% in 100 metri di canale vegetato in alveo.

Nel terzo caso "assessing phytoremediation performance of an integrated agricultural wetland" i risultati mostrano come le concentrazioni mediane di N totale siano state di 2.43 ppm in entrata e 1.79 all'uscita del sistema, mentre, a seguito di un importante evento di precipitazione, siano passate da 6.34 ppm (inlet) a 1.29 ppm (outlet). In generale, quindi, le zone umide agricole hanno mostrato una grande capacità nel purificare le acque contaminate da drenaggio agricolo, proteggendo le acque superficiali situate a valle. La ricerca, inoltre, conferma che l'implementazione di wetland costruite e dispositivi di mitigazione *off-site* possono aumentare la sostenibilità della produzione agricola.

Summary

Relationships between Ecosystem Services and agrosystems are extremely important both to understand the bidirectional flow of services from/to agriculture and to quantify goods and benefits for human societies. Wetland systems nowadays represent an important cornerstone for beneficial Ecosystem Services, especially in intensive agricultural landscapes characterized by shallow water and a dense minor channel network like the territory of the Venice Lagoon drainage system. Wetlands provide a crucial suite of regulating, supporting, provisioning and cultural services to regulate water flows and nutrient cycling, remove and detoxify excess fertilizers and pesticides, sequester carbon, enhance biodiversity and provide cultural benefits to local communities. By three experimental study cases this research present results about the assessment of the water purification service provided by wetlands in mitigating agricultural contamination; moreover, estimation of a provisioning service such as bioenergy derived from wetland vegetation was performed. In the study case "a constructed wetland for water purification services from pesticide in an intensive cropping system" results show that the system can reduce runoff concentration of metolachlor and terbuthylazine by a factor of 45-80 even in extreme flooding conditions. Herbicides retention in the constructed wetland was reversible, and the second and third floods mobilized 14-31% and 3.5-7.0% respectively, of the amount detected in the first flood. In the second experimentation "vegetated ditches as water purification systems to mitigate contamination from pesticides runoff" results show that the ditch can immediately reduce runoff concentration of herbicides by at least 50% even in extreme flooding conditions; as a general rule, a runoff of 1 mm from 5 ha is mitigated by 99% in 100 m of vegetated ditch. In the study case "Assessing phytoremediation performance of an integrated agricultural wetland" results show that median concentrations of total nitrogen were 2.43 ppm at the inlet and 1.79 at the outlet, while after an extreme rainfall event, total nitrogen concentrations were 6.34 ppm at the inlet and 1.29 ppm at the outlet. In general, wetland systems perform a high buffer capacity both for nutrient and herbicides, capable to provide water purification service, protecting downstream surface water. Moreover, this project confirms that the implementation of constructed wetlands and offsite mitigation measures like vegetated ditches in agro-systems can improve the sustainability of agricultural production.

Chapter 1

Ecosystem Services and agriculture

State of the art

The Ecosystem Services (ES) concept is constantly gaining importance since 1970, focusing on the human-environment interactions to increase the interest of people regarding biodiversity conservation and the importance of ecosystems for human life, in front of evidences of a more and more unsustainable use of natural resources. By this concept, ecosystems are considered as a "natural capital" that produces a services flow useful and often indispensable for human well-being and subsistence, and that is influenced both positively either negatively by natural and anthropic factors (Balvanera *et al*., 2001; Costanza *et al.*, 2002; MEA, 2005a; Daily and Matson, 2008; Maes *et al.*, 2012).

The big boost in ES evaluation, quantification and management is related to Millennium Ecosystem Assessment (2005), after which different studies and projects are carried out to try to bring this concept from the academic side to an operational one, using different ecosystems and their services frameworks in decision making processes, land planning, natural resource management and conservation projects, among others. These efforts also bring out the need of consistent and reliable assessment, quantification, evaluation and mapping methods of ecosystems, their functions, services, trade-offs and beneficiaries at different temporal and spatial scale that integrate biophysical, socio-cultural and economical aspects. Particularly, quantification methods vary widely according to the availability of data, temporal and spatial scale, ES types and other aspects investigated, involving primary data and proxies, quantitative and qualitative data, such as statistic and survey information, data from empirical studies and/or from remote sensing, expert opinions, participatory processes.

The ES are therefore defined as the set of benefits that companies derive from ecosystems, whose taxonomy is divided into four classes: 1) provisioning services, namely the supply of services directly derived from ecosystems (eg. food, fiber, energy, biogenetic resources, fresh water); 2) life supporting services, ie all the essential mechanisms that govern the functioning of the biosphere system (eg. nutrient cycling, bio-geochemical processes, primary production); 3) regulating services, ie the services derived from the regulatory mechanisms of ecological processes (eg. climate control and the hydrological cycle, carbon sequestration, water purification and nutrient absorption, control of erosion, biological control agents and pollinators) ; 4) cultural services, ie the intangible, cultural and aesthetic

values associated with ecosystems (landscape, educational and recreational activities, ecotourism) (MEA, 2005; TEEB 2006).

The EU, through the Action 5, established to support the Aichi biodiversity targets (CBD, Nagoya, 2010) combining the implementation of scientific knowledge with operative measurements for biodiversity conservation, by the functional restoring of at least 15% of degraded ecosystems by green infrastructures, and management of natural and semi natural areas (Target 2, European Commission, 2011a). Moreover, restoring and preserving ES are clearly highlighted within the six priorities identified by the EU in the platform for the rural development, the Common Agricultural Policy (CAP, European Commission, 2011b). The research project is based on the conceptual framework and the applicative models for the agroecological assessment of the *environmental services*, defined in the last decade as Ecosystem Services (ES) (Balvanera *et al*., 2001; Costanza *et al.*, 2002; MEA, 2005a; Daily and Matson, 2008; Maes *et al.*, 2012).

Water purification services from wetland systems

The ES approach is particularly appropriate to the applied research about agricultural systems which are, at present, the largest ecosystems on earth and, at the same time, the one that has been modified and intensively transformed by anthropic activities to provide good and services to the societies (Scott et al., 2006). The agricultural system is, in fact, the dominant form of land management on a global level considering that it has presently converted about 40% of global surface (FAO, 2009).

In the *flow cascade* of ES (De Groot, 2010), cropping systems play a crucial role, both in providing goods and services to human societies and in demand of ES from other natural ecosystems. In fact, agrosystems provide the main classes of ES – provisioning and regulating services, and cultural values. Restored or constructed wetlands, and vegetated systems represent within an agricultural basin a key issue in water purification and sediment retention services (MEA, 2005b). Wetland vegetation has the ability to absorb nutrients from soil and water bodies, acting as an ecological system "plant-soil" in the process of water purification. Through such processes, pollutants (including nitrates and phosphates) are removed by a combination of chemical, physical and biological factors,

among which the main ones are sedimentation, absorption of certain molecules from the soil, nutrient absorption and extraction of heavy metals (Borin, Bonaiti, 1997).

However, since agriculture is thermodynamically an open and complex system, to optimize on-site crop production, agro-systems often represent a direct and indirect driver of environmental change off-site: soil erosion, landuse / landcover changes, run-off of nutrients and pesticides, degradation of the quality and availability of the groundwater and surface water and, on a global scale, alteration of temperature regulating mechanisms (Ruhl 2000. MEA, 2005; Swinton et al., 2006). Unsustainable agricultural practices can affect also natural ecosystems, eroding ecosystem services associated with them: loss of biodiversity and natural habitats, the release of nutrients and pesticides, excess sedimentation in the water supply, increasing the hydrogeological and greenhouse gas emissions (MEA, 2005; Power, 2010).

If, on the one hand, provisioning services derived from agriculture (food, fiber, energy) - the so-called production - are well defined, on the other hand quantification and mapping of other ES are not well explored. Among the main ES that sustain the agro-systems Supporting Services (including genetic biodiversity for the improvement of ideotypes and farmed varieties, soil structure and fertility, the nutrient cycle and the water availability) and Regulating Services (pollination, atmospheric setting, natural pest control and weed) are paramount. Among the latter, in particular, natural and seminatural ecosystems play a key role in water purification processes and water cycle self-regulation to agricultural systems. By contrast agrosystems provide, in addition to agricultural productivity in terms of ton/hectars, important ecosystem services such as supporting and regulating, including the maintenance of soil fertility (soil organic matter), the purification capacity of surface and groundwater, flood control , carbon sequestration and climate regulation, (Swinton 2007; Powell, 2010). The quality and quantity of available water are important ecosystem services that can be improved or degraded according to farming practices and the agrosystem structuring.

An evaluation of the ES related to agro-systems can provide useful information about the sustainability of agricultural practices, directing them toward a greater use efficiency of nutrients and water resources, enhancing the buffer strips and riparian zones which, for

example, can be optimized for the removal of nutrients and sediment before the runoff reaches the neighboring water bodies.

Wetlands and Ecosystem Services

Wetland systems are considered among the ecosystems with the highest productivity, playing a crucial role in the cycle of sediments and nutrients in the environment (MEA, 2005b). Wetland vegetation showed significant ability to absorb nutrients from soil and water bodies, acting as a "plant-soil" system in the water purification processes. Through this processes, pollutants (including nitrates and phosphates, and pesticides) are removed by a combination of chemical, physical and biological processes, among which the main ones are the sedimentation, the absorption of certain molecules to the soil composition, the absorption of nutrients and heavy metals inside the plants and the degradation of the organic molecules (Borin, Bonaiti, 1997).

The natural ability of wetlands to trap nutrients and sediments can be exploited through the use of natural, semi-natural or Constructed Wetlands (CW) for the purpose of improving the quality of water and, consequently, the biodiversity of ecotones and neighboring ecosystems. Many wetland ecosystems (natural or constructed) which are located in marginal areas or in abandoned agricultural areas can be restored and exploited within a matrix structured agricultural landscape, in order to support and implement the water purification processes and recovery of biodiversity, particularly bird life and insect fauna (Robertson, Swinton, 2007). It was estimated that, globally, the set of ecosystem services provided by wetlands, is of primary importance for the societies and economies, carrying them an environmental service from the local to the global scale, it is around at an estimated value of 'order of thousands of dollars a year (Ramsar, 2006).

Study cases

A constructed wetland for water purification services from pesticide in an intensive cropping system[1]

Ecosystem services provided by wetland systems presently play a pivotal role in intensive cropland as water purification from agricultural pollution.

A field trial was conducted in 2014 to evaluate herbicide runoff reduction and retention using a 0.32 ha constructed surface flow wetland (CSFW) at the outlet of a 6 ha agricultural basin. To simulate an extreme pulse contamination, the CSFW was flooded with a runoff contaminated with metolachlor and terbuthylazine and two other subsequent floods with pure water were applied 21 and 65 days later.

Results show that the CSFW can reduce runoff concentration of metolachlor and terbuthylazine by a factor of 45-80 even in extreme flooding conditions. Herbicides retention in the CSFW was reversible, and the second and third floods mobilized14-31% and 3.5-7.0% respectively, of the amount detected in the first flood.

The CSFW performs a high buffer capacity for herbicides, capable to provide water purification service, protecting downstream surface water. Moreover, mitigation capacity of a CSFW for a heavy runoff from a 10 ha basin is 90% for every 50 m in length of a 15 m wide wetland. This confirms that the implementation of CSFWs in agro-systems can improve the sustainability of agricultural production.

[1]Pappalardo S.E., Otto S., Gasparini V., Zanin G., Borin M., (2015), "Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland", Hydrobiologia. DOI: 10.1007/s10750-015-2375-1

Vegetated Ditches as water purification systems to mitigate contamination from pesticides runoff[2]

In intensive agricultural systems runoff is one of the major potential diffuse pollution pathways for pesticides and poses a risk to surface water.

Ditches are common in the Po Valley and can potentially provide runoff mitigation for the protection of watercourses. The effectiveness depends on ditch characteristics, so there is an urgent need for site-specific field trials. The use of a fugacity model (multimedia model) can allow recognition of the mitigation main processes.

A field experiment was conducted in order to evaluate the mitigation capacity of a typical vegetated ditch, and results were compared with predictions by a fugacity model. To evaluate herbicide mitigation after an extreme runoff, the ditch was flooded with water containing mesotrione, S-metolachlor and terbuthylazine. Two other subsequent floods with uncontaminated water were applied 27 and 82 days later to evaluate herbicides release.

Results show that the ditch can immediately reduce runoff concentration of herbicides by at least 50% even in extreme flooding conditions. The half-distances were about 250 m. As a general rule, a runoff of 1 mm from 5 ha is mitigated by 99% in 100 m of vegetated ditch.

Herbicides retention in the vegetated ditch was reversible, and the second flood mobilized 0.03-0.2% of the previous one, with a concentration below the drinking water limit of 0.1 $\mu g\ L^{-1}$. No herbicide was detected in the third flood, because the residual amount in the ditch was too low. Fugacity model results show that specific physical-chemical parameters may be used and a specific soil-sediment-plant compartment included for modelling herbicides behaviour in a vegetated ditch, and confirm that accumulation is low or negligible for herbicides with a half-life of 40 days or less. Shallow vegetated ditches can thus be included in a general agri-environment scheme for the mitigation of pesticides runoff together with wetlands and linear buffer strips. These structures are present in the landscape, and their environmental role can be exploited by proper management.

[2]Otto S., Pappalardo S.E., Cardinali A., Masin M., Zanin G, Borin M. (2016), "Vegetated Ditches for the Mitigation of Pesticides Runoff in the Po Valley", PLoS ONE 11(4): e0153287. doi:10.1371/journal.pone.0153287

Assessing phytoremediation performance of an integrated agricultural wetland[3]

Wetlands are a cornerstone of beneficial ecosystem services, especially in intensive agricultural landscapes characterized by nutrient loss, and shallow and surface water bodies. Water purification services can trap 80-90% of sediments and eliminate 70-90% of entering nitrogen. An experimental wetland of 3.2 ha was created within the Venice drainage system to control nutrient loss from croplands and protect surface water bodies. The aims of this study were to assess the water purification service by monitoring nutrient runoff and testing the adaptability of seven macrophyte species in a floating treatment wetland system. Results show that median concentrations of total nitrogen were 2.43 ppm at the inlet and 1.79 at the outlet, while after an extreme rainfall event, total nitrogen concentrations were 6.34 ppm at the inlet and 1.29 ppm at the outlet. *Carex* spp. adapted best to the floating wetlands (433.13 g m^{-2} of biomass production), followed by *Lythrum salicaria* (210.32 g m^{-2}). *Carex* spp had the highest total N uptake (4.84 g m^{-2}), mostly in roots (3.19 g m^{-2}), followed by *L. salicaria* with 2.35 g m^{-2}. Constructed wetlands could therefore play a crucial role in integrated agro-environmental management to control nutrient runoff from intensive cropping systems.

[3]Pappalardo S.E., Mohammad H., Cerinato S., Borin M., (2016), "Assessing the water purification service in an integrated agricultural wetland within the Venice lagoon drainage system". Marine and Freshwater Research (In press).

Vegetated ditches as provision services systems: bioenergy potential from wetland plants along the minor channel network on an agricultural floodplain[4]

Renewable energy sources such as biomasses are presently playing a pivotal role both to preserve security for energy supply and reduce greenhouse gases by the progressive substitution of fossil fuels. At present, bioenergy is mainly derived from cultivated crops which are mirroring environmental impacts from the intensification of agricultural systems for food production. Instead, biomass from perennial herbaceous species growing in wetland ecosystems and marginal lands has recently aroused interest as bioenergy for electricity and heat, methane and 2nd generation bioethanol.

The aim of this paper is to assess, at local scale, the energy potential of wetland vegetation associated to the minor hydrographic network within a reclamation area of the North-East of Italy, by performing three different energy scenarios of combustion, methane and 2nd generation ethanol.

The research is based on a cross-methodology that combines survey analyses in the field with a GIS-based approach: the former consists of direct measurements and biomass sampling, the latter on spatial analyses and scaling up simulations at the minor channel network.

Results highlight that biomass from riparian zones could represent a significant source of bioenergy for combustion transformation, turning the problem of biomass waste disposal into an opportunity to produce sustainable renewable energy at local scale.

[4]Pappalardo S.E., Prosdocimi M., Tarolli P., Borin M. (2014), "Assessment of energy potential from wetland plants along the minor channel network on an agricultural floodplain", Environmental Science and Pollution: June 2014. Springer-Verlag Berlin Heidelberg 2014. Doi: 10.1007/s11356-014-3105-3.

Chapter 2

Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland

Introduction

The concept of ecosystem services (ES) has recently gained attention both in environmental sciences and practical applications to identify, map and quantify goods and services provided by natural and semi-natural ecosystems to human society (MEA, 2005; Daily et al., 2008; Maes et al., 2012). Among these, aquatic and semi-aquatic ecosystems such as wetlands, riparian ecotones and vegetative buffer strips are extremely important in providing, at multiple scales, the full set (Provisioning, Regulating, Supporting and Cultural) of ES (De Groot et al., 2006; Power, 2010; Brinson & Eckles, 2011). Particularly, they provide a crucial ES of water purification by pollution control, retention, removal and detoxification of excess nutrients and pesticides (Tanner et al., 2013; Tournebize et al., 2013). The water purification service is ensured by complex physical, chemical and biological interaction processes performed within the "plant-soil" system. Moreover, the water purification ES is of paramount importance, particularly in intensive agricultural landscapes that are seriously contributing to non-point source pollution mainly by soil erosion and surface runoff into water bodies, threatening potable water sources, non-target organisms and aquatic ecosystems (Vianello et al., 2005; Lazzaro et al., 2008; Otto et al., 2012). Numerous studies have confirmed that levels of pesticide concentrations in surface waters are undoubtedly linked to crop and soil management practices deployed within the agricultural basins (Dabrowsky et al., 2002; Anderson et al., 2011). To reduce the health and environmental risks associated with pesticides a number of regulations and standards have been implemented world-wide. Recently the EU, in Annex III of Directive 2009/128/EC, issued the Thematic Strategy on Sustainable Use of Pesticides that highlights the need to implement locally, through National Plans, mitigation actions to protect surface water and non-target organisms (Gregoire et al., 2008; Durel et al., 2014). Therefore, many in-field (e.g. vegetated filter strips, grassed waterways) and off-site (e.g. riparian and artificial wetlands) mitigation systems have been implemented and studied as management practices in crop production, showing significant performances in reducing pesticide loss (Reichenberger et al., 2007; Otto et al., 2012; Vylmazal & Brezinová, 2015). Specifically, Constructed Surface Flow Wetlands (CSFWs) have been tested and used extensively in the last decades, showing that they are effective in water pollution mitigation, by retaining sediments and surface runoff; however, efficiency in pesticide control is highly variable

according to the physical-chemical properties of the individual pesticide, soil texture and structure, hydraulic retention time, and wetland vegetation. It has been found that mitigation effects typically vary from average 35 to 97% (Gregoire et al., 2008; Vymazal & Brezinová, 2015). Trends in removals may be related to chemical groups and even physicochemical parameters of individual pesticides: highest average removals are performed for organochlorine (97%), organophosphate (94%) and pyrethroids (84%); middling values for triazine (63%), chloroacetamide (58%) and triazole (57%). The lowest removal efficiency has been obtained for triazinone (25%) and aryloxyalkanoic acid (35%) (Vymazal & Brezinová, 2015). Kay et al. (2009) reported that for a constructed wetland the average reduction in pesticide mass loss was 80% and varied from 25 to 100%. In a recent review Stehle et al. (2011) found that the majority of constructed wetlands retained at least 70% of the entering pesticides, while for Maillard et al. (2011) removal rates varied from 39% to 100%.

Hence, reducing pesticide impacts by implementing off-field CSFWs is helping to face the challenge of a better sustainability of crop production in intensive agricultural landscapes.

A field-scale experiment has been ongoing since 2008 on the Experimental Farm of Padova University (north-eastern Italy) to assess the mitigation effect of a CSFW on pollution from agricultural runoff.

The aims of this study were to assess, after a simulated extreme runoff event contaminated with the herbicides metolachlor and terbuthylazine, (1) the mitigation effectiveness of a CSFW in runoff purification, (2) the herbicides and metabolites release after two subsequent controlled floods with pure water.

Data and methods

Site information and experimental layout

On the Experimental Farm of Padova University, in the Po Valley at North-East of Italy (45° 20.951'N 11° 57.132'E), a 0.32 ha CSFW vegetated with common reed (*Phragmites australis*) is located at the outlet of a 6 ha agricultural basin (Maucieri et al., 2014). The CSFW has a discontinuous free flow of water: when runoff occurs from the agricultural basin, a depth of 5-8 cm of runoff flows through the CSFW at about 0.3-0.5 m min^{-1} from

inlet to outlet 200 m apart, coming into contact with plants, litter and soil. In ordinary conditions, only the first 50 m of the CFSW are flooded, the flow is mainly horizontal and residence time is 1-2 hours before full infiltration. Geographical context and experimental design are illustrated in Figure 1.

In order to fully describe the CSFW and test its hydraulic performance in extreme runoff, a microtopography survey by DGPS and a flood with uncontaminated water had been conducted previously. The CSFW proved to be an enclosed system, without significant drainage.

Therefore a heavy runoff simulation was performed on 8th April 2014 (first flood), and the CSFW was flooded with 33 m^3 of water containing 3,800 $\mu g\ L^{-1}$ of S-metolachlor (CAS 87392-12-9) and 2,300 $\mu g\ L^{-1}$ of terbuthylazine (CAS 5915-41-3), two of the main herbicides applied to maize to control spring and summer weeds. These concentrations were planned according to the metolachlor/terbuthylazine ratio in ordinary weed control, and were about 1,000-fold lower with respect to an ordinary treatment, and 10,000-fold higher with respect to an ordinary runoff (Cardinali et al., 2013) to simulate an extreme runoff without phytotoxicity but with durable effects. The contaminated flow was followed by another 320 m^3 of uncontaminated water applied in 4.5 hours in order to flood the whole CSFW under 7-10 cm of water and uniform concentration throughout the 200 m length of the CSFW.

After standardization by the application rate, the calculated water concentrations in the fully flooded CSFW were 2,836 $\mu g\ L^{-1}\ kg^{-1}$ applied both for metolachlor and terbuthylazine. 15 geo-referenced es of 10 l surface water were then collected proceeding from the CSFW inlet to outlet, a length of about 200 m. Watertable samples were also taken. From each 10 l sample, a 1 l sub-sample was taken and placed in an aluminium bottle, sealed and stored in a cooler at +4°C during sampling, then frozen at -20°C until analysis. All water samples were geo-referenced on the field and analysed in GIS environment to perform a spatial correlation analysis.

After 21 days (second flood, 29th April) and 65 days (third flood, 12th June) the flooding was repeated with uncontaminated water, and water samples collected at the same sampling points in order to detect herbicides release according to a sponge-like effect (Otto et al., 2012).

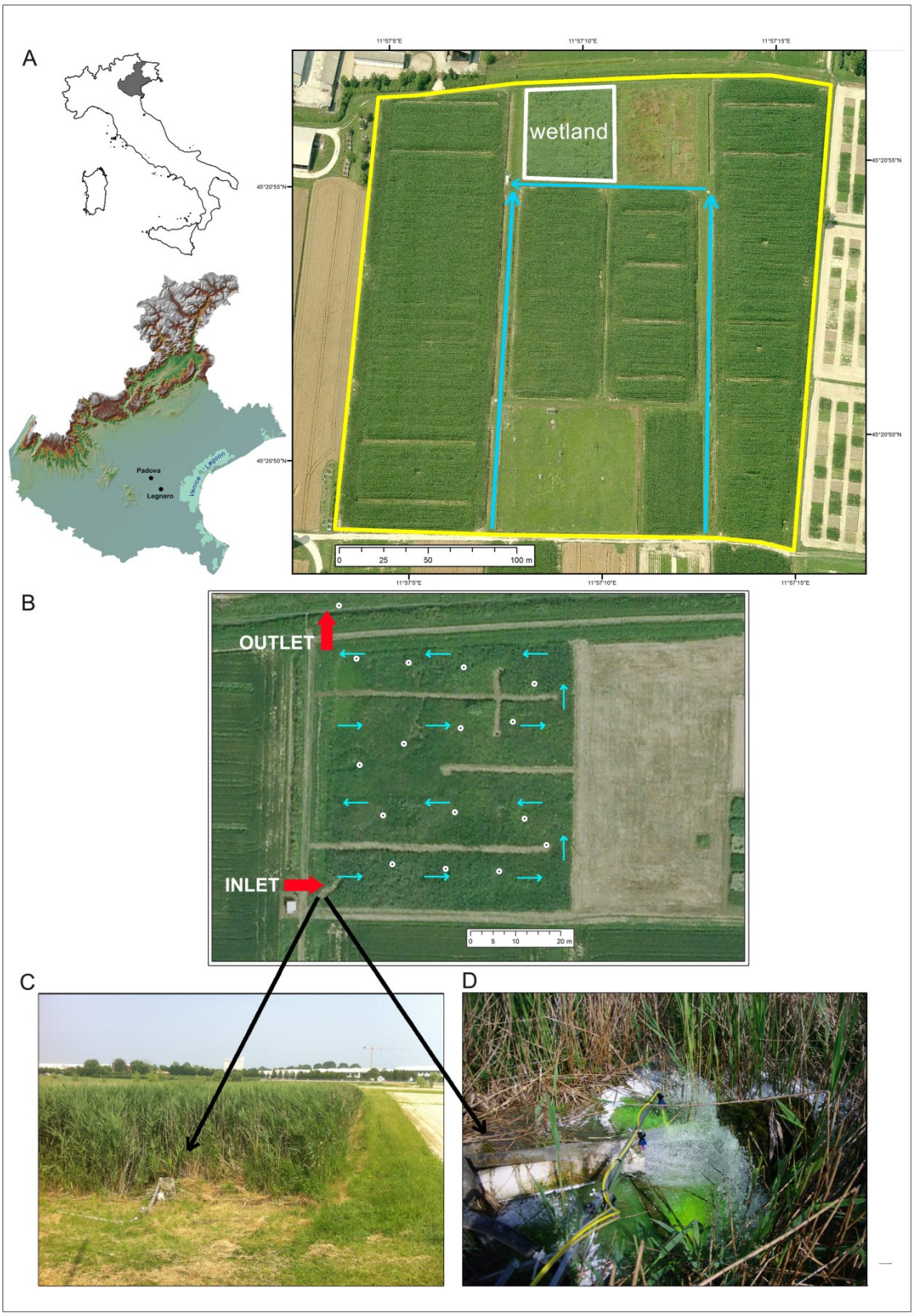


Figure 1 Agro-system (6 ha) and Constructed Surface Flow Wetland for phytorepuration at the Experimental Farm of University of Padova. Blue arrows indicate the flux direction of the agricultural water drainage.

Herbicides physico-chemical properties

Metolachlor is about 50-fold more soluble than terbuthylazine (Table 1) according to recent reviews, instead lipophilia ($logK_{OW}$) is similar or slightly lower for metolachlor.

The adsorption in soil (K_{OC}) of metolachlor is also slightly lower (215 vs 259 ml g^{-1}). Persistence of metolachlor in soil is significantly lower than terbuthylazine in a large selection of soils. Recent studies performed on the Experimental Farm of Padova University (Vianello et al., 2005; Otto et al., 2012) fully confirm this trend, and show that in field conditions of north-eastern Italy metolachlor is about half as persistent as terbuthylazine, with half-lives of 12-14 and 20-27 days respectively.

When two chemicals are applied at different rates, a proper comparison of detections is possible taking rate into account. Application rates of metolachlor and terbuthylazine in standard weed control in maize differed, being 1.25 and 0.75 kg ha^{-1} respectively, so observed concentrations in the CSFW were standardized by the application rate to ease comparison and better highlight the trend over time, and reported as μg L^{-1} kg^{-1} applied.

Parameter (units)	S-Metolachlor	Terbuthylazine	Reference
Appl. rate (kg ha^{-1})	1.25	0.75	
CAS	87392-12-9	5915-41-3	MacBean, 2012
Solubility (g l^{-1})	0.480	0.009	MacBean, 2012
$LogK_{OW}$	3.13		Mackay et al., 1997
		3.04	Di Guardo et al., 1994
	3.00	3.20	Tomlin, 2006
	3.05	3.40	MacBean, 2012
	3.06	3.21	General mean
K_{OC} (ml g^{-1})	121-309	162-378	Tomlin, 2006
	215	270	Tomlin, 2006 (mean)
	61-369	162-333	MacBean, 2012
	215	248	MacBean, 2012 (mean)
	215	259	General mean
t50 in field (days)	23	45	Di Guardo et al., 1994
	14	27	Vianello et al., 2005
	11-30	30-60	Tomlin, 2006
	21	45	Tomlin, 2006 (mean)
	6-49	6.5-149.8	MacBean, 2012
	28	78	MacBean, 2012 (mean)
	30	17	MacBean, 2012 (median)
	12	20	Otto et al., 2012
	21	39	General mean

Table 1. Physico-chemical properties of the herbicides applied to the CSFW.

Analytical procedure

The procedures used derived from previous studies (Dyson et al., 2002; Freitas et al., 2004), were already applied in Otto et al. (2012) and fine-tuned in the present study. Metolachlor (98.0% purity) and terbuthylazine (99.5% purity) standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade methanol and water were used (Fluka). All other chemicals were purchased from Merck (Germany). For all analytes, stock solutions were prepared in methanol (MeOH). The 1 l sample was filtered at room temperature using cellulose nitrate membrane filters 0.45 μm pore size. After filtration an acetate buffer solution (2.5 M) was added to the samples in ratio 1% v/v. Samples were cleaned by solid phase extraction using an OASIS® HLB sorbent cartridge (60 mg, Waters), earlier conditioned with 2 ml of MeOH followed by 2 ml of ultrapure water, and a Baker spe-24 G vacuum column processor. Once the samples were extracted, the cartridges were washed with 1 ml of MeOH-water mixture (5:95 v/v) and the excess of water removed by opening the valves of the manifold letting the air to pass through them. The analytes were eluted with 5 ml of MeOH and the aliquots reduced with a gentle nitrogen gas stream at 45°C. The extracts (50 μl) were reconstituted with 1 ml of MeOH.

Metolachlor and terbuthylazine and main metabolites (metolachlor ethane sulfonic acid (Met-ESA), metolachlor oxanilic acid (Met-OA), terbuthylazine-desethyl (TerD), terbuthylazine-2-hydroxy (Ter2H) analyses were performed by LC-MS using a 1100 Series Agilent Technologies system, equipped with binary pump, diode array detector, and MSD SL Trap mass spectrometer with ESI source. The optimum values of the ESI-MS parameters were: drying gas temperature 350°C; drying gas flow 10 l min^{-1} and nebulizing gas pressure 45 psi. The detection was carried out considering a mass range of 50–6000 m/z. A Gemini® column C18 with TMS endcapping, 150×4.6 mm i.d., 3 μm, 110 Å was used to analyse the samples, the mobile phase was composed of water (solvent A) and MeOH (solvent B) both acidified with 0.1% formic acid (60:40).

The LC gradient was: isocratic from 0 to 3 min (60% A: 40% B); from 3 to 10 min, a linear increase of B from 40 to 80%; isocratic 80% B from 10 to 13 min; a linear increase of B in 5 min from 80 to 100%. Initial conditions were re-established in 5 min and re-equilibrium time was 5 min.

The flow rate was 0.6 ml/min. A 10 µl sample volume was manually injected each time. Retention times were 11.4 min and 10.1 min for metolachlor and terbuthylazine respectively.

Herbicide concentrations were quantified by comparison with a calibration curve. Individual stock solutions were prepared in methanol/water (60/40, v/v) with concentrations of 100 mg L^{-1}. Mixture solutions were prepared in concentrations of 0.2, 0.5, 1.0 mg L^{-1}. Recoveries of the herbicides from extracted water samples were performed in triplicate at three initial concentrations.

The limit of detection (LOD) and quantification (LOQ) under the chromatographic conditions were determined from the calibration line at low concentrations (eq. 1):

$$\frac{LOD}{LOQ} = \frac{f * SD}{b} \qquad (1)$$

where *f* is factor of 3.3 and 10 for LOD and LOQ respectively, *SD* is the standard deviation of the linear regression and *b* is the slope of the calibration curve. LOQ was 30 ng L^{-1} for both herbicides. LOD varied between 0.995 and 1.002 ng L^{-1} for metolachlor and terbuthylazine respectively.

Runoff mitigation calculation

A clear definition of mitigation for CSFW has not yet been suggested. In this study the runoff mitigation of the CSFW was calculated taking into account the mass of herbicides in the floods, considering the applied mass as a reference. In general, for two values of mass A and B, with A>B, the percentage mitigation from A to B is:

$$M\% = 100 * \frac{A - B}{A} \qquad (2)$$

For example, if in the reference scenario (A) the chemical mass is 5 g, and after complete flooding (B) this amount is 2 g, the mitigation from A to B is: M%=100*(5-2)/5=60%.

Metabolites occurrence modelling

The aim of modelling of metabolites concentration over time was to outline the occurrence pattern and accumulation risk. When adsorption/desorption of parental and metabolites is not time dependent, then relative abundance is given only to transformation kinetics. Various models for metabolites occurrence are available (Rawlings et al., 1998). When one chemical (*M*) is being formed by the decay of another (*P*) at reaction rate *A*, and is itself decaying at reaction rate *B*, the simplest model of occurrence of *M* in time (*t*) is the two-exponential model (Otto et al., 1997):

$$M = (P0 - P0 * e^{-t*A}) * (e^{-t*B}) \qquad (3)$$

where *P0* is the initial amount of *P*.

Statistical analysis

Correlation between concentrations and distance or duration of flooding were tested with Pearson's *r*. For eq. (3) the fit with the experimental data was evaluated with the coefficient of determination (R^2). All analysis were performed with the software Statistica 10 (StatSoft Inc., 2011).

Results

Concentration after first flood (contaminated runoff)

After complete flooding, as expected, herbicides concentration was almost uniform throughout the CSFW, from inlet to outlet both for metolachlor (56.3±35.8 μg L^{-1} kg^{-1}) and terbuthylazine (37.8±3.77 μg L^{-1} kg^{-1}) (mean±SD). These values were 45-80-fold lower than the calculated (applied) concentration in the CSFW. The total mass of herbicide detected in the flood was 1.49 g of metolachlor (1.19% of applied) and 1.67 g of terbuthylazine (2.22% of applied). Similar concentrations were found in the water table for both herbicides. Concentrations through the CSFW were independent of distance or flooding time (Fig. 2).

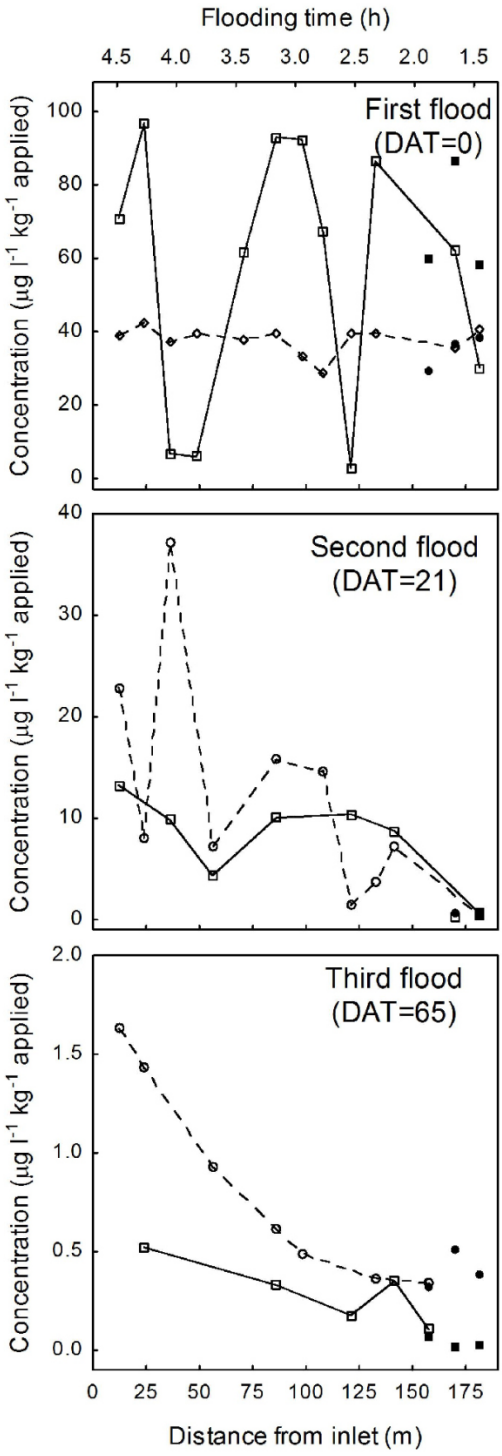


Figure 2 - Concentration of metolachlor (solid line, empty square marker) and terbuthylazine (dotted line, empty circle marker) in the three floods. Full markers are the concentrations in the water table at about 0.6 m depth. All concentrations are standardized by the application rate. The lower axis is the distance from the inlet (m), the upper axis is the time elapsed between flood start and sampling (i.e. the most distant sample was taken last). DAT=days after first treatment. Only samples with detections above the Limit of Quantification are shown.

Concentration after second flood

After 21 days, the concentrations in the second flood were lower, both for metolachlor (8.16±4.26 μg L^{-1} kg^{-1}) and terbuthylazine (11.8±11.2 μg L^{-1} kg^{-1}) (mean±SD). It is worth noting that the second flood mobilized a significant amount of herbicides in about 4.5 h, about 14-31% of the previous one. A correlation with distance and flooding duration was observed for terbuthylazine (r=-0.653, p=0.041), likely because in the first part of the flow path in the CSFW the contact time with the plant-soil complex was double and a greater mobilization occurred. For metolachlor this correlation was not significant, likely its higher solubility and slightly lower lipophilia caused a faster mobilization.

Close to CSFW outlet, concentration of the two herbicides was very similar: 0.59 and 0.37 μg L^{-1} kg^{-1} for metolachlor and terbuthylazine respectively, values well below the drinking water limit (0.1 μg L^{-1}), and the content in the watertable was also very low.

Concentration after third flood

After 65 days, the concentrations in the third flood were again very low, both for metolachlor (0.29±0.16 μg L^{-1} kg^{-1}) and terbuthylazine (0.82±0.52 μg L^{-1} kg^{-1}) (mean±SD), and the amount of herbicides mobilized was about 3.5-7.0% of the previous one. This suggests that reversibility of adsorption lasts for a very long time and is still detectable two months after application, even if the amount potentially removable from the CSFW was very low: 0.06 g of metolachlor and 0.5 g of terbuthylazine per 1,000 g applied to the CSFW. This clearly highlights its mitigation capacity.

As in the second flood, a correlation with distance and flooding duration was observed for terbuthylazine (*r*=-0.950, p=0.001) but not for metolachlor.

Close to the outlet, concentration was 0.10 and 0.34 μg L^{-1} kg^{-1} for metolachlor and terbuthylazine respectively.

Mitigation effectiveness

The CSFW was very effective in the reduction (mitigation) of herbicide concentration in runoff. For the first flood reduction was (100-1.19)=98.81% for metolachlor and (100-

2.22)=97.78% for terbuthylazine. For the second and third flood average mitigation was about 99.9%.

Metabolites occurrence

The mean concentration of metolachlor and terbuthylazine in the three floods was decreasing with time according to an exponential kinetic (Fig. 3), and this is consistent with known dissipation pattern in soil (Otto et al., 2010). For metolachlor metabolites, the Met-ESA occurrence kinetics was not clear, instead the Met-OA was the main metabolite about 30 days after application and with an increasing trend.

The two terbuthylazine metabolites show similar trends and were considered together. They occurred with a first order kinetic and the fitting of Eq. 3 was high (R^2=0.98). The metabolites concentration overtakes terbuthylazine after 35 days; however, the accumulation of metabolites in the CSFW is unlikely, because Eq. 3 predicts a concentration less than 1.0 μg l^{-1} kg^{-1} 130 days after treatment.

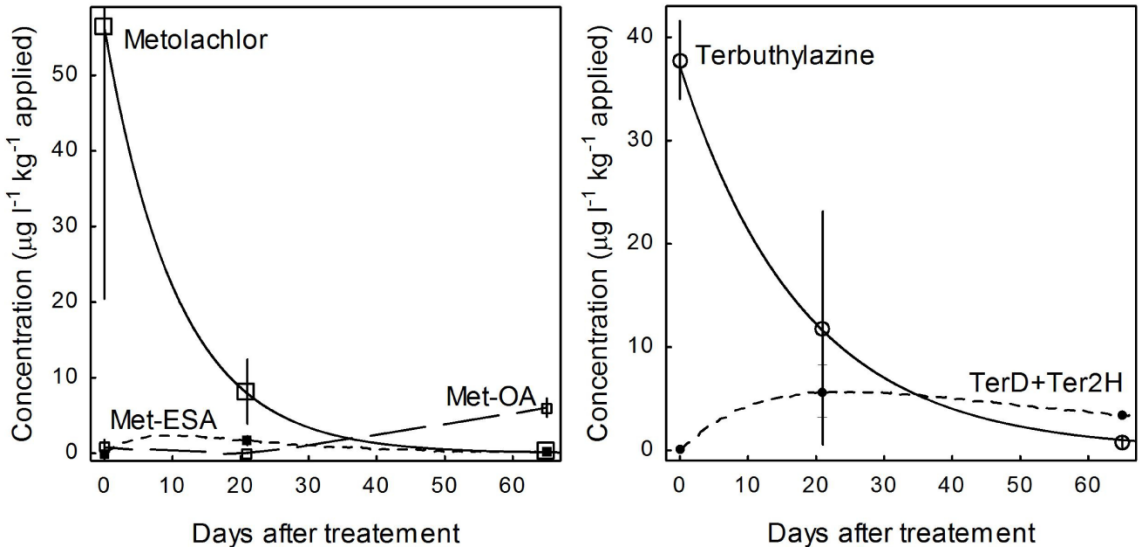


Figure 3 - Herbicides and metabolites concentration in the three floods at 0, 21 and 65 days after treatment (mean+SD) and fitted models (exponential for herbicides, two-exponential for metabolites). Most of the standard deviation bars are lower than the markers. Met-ESA: metolachlor ethane sulfonic acid; Met-OA: metolachlor oxanilic acid; TerD: terbuthylazine-desethyl; Ter2H: terbuthylazine-2-hydroxy. Parameters (st. err.) of Eq. 3 for TerD+Ter2H: P0=37.21, A=0.016 (0.009), B=0.030 (0.008), R^2=0.98

Discussion

Under extreme runoff events the saturation capacity of a CSFW of 3,200 m^2 is 353 m^3, and herbicides concentration is quite uniform in both flowing water and water table. This highlights that in these conditions the flow in a CSFW is mainly horizontal but also vertical.

Soon after application, mean concentrations of the two herbicides in surface water are similar, according to their similar lipophilia. A certain variability of concentration across the CSFW is likely as roughness and water speed vary along the flow path. The CSFW also has an immediate effectiveness under extreme runoff events, and reduces the concentration in runoff 45-80-fold, likely because adsorption by the plant-soil complex occurs promptly, in 3-4 hours, with a significant reduction of the amount that can by-pass the CSFW and potentially reach surface water. This is fast but, at least for terbuthylazine, consistent with other studies conducted with another triazine. Locke et al. (2011) observed a steady decrease in atrazine concentration over a 24 h period, and Hinman & Klaine (1992) observed a rapid plant-soil uptake of atrazine and a fast (2 h) equilibrium between shoots and water.

Adsorption of herbicides is likely superficial and quickly reversed by a subsequent flood. The amount mobilized is low but surface water quality can anyway be affected (Berghahn et al., 2012; Bjergager et al., 2011).

Considering the three floods, concentrations of metolachlor and terbuthylazine in the water were very similar and highly correlated (r=0.660, $p<0.001$). Trend in concentrations standardized by application rate show that terbuthylazine overtakes metolachlor 3-4 weeks after application due to its higher persistence.

Metabolites were also detected, showing that degradation is immediate and important and that the flood water from the CSFW contained a mixture of chemicals. Further research could assess accumulation of metabolites and explore the effect of physicochemical properties on adsorption over time.

Field trial results obtained on the Experimental Farm of Padova University show that metolachlor and terbuthylazine have a half-life in soil of 11.3 and 19.6 days respectively (Table 1). This suggests that 1) 3-4 months after application the residual amount in the

CSFW is so low that it makes further mobilization very unlikely even under a heavy flood, 2) there is no risk of accumulation over the years in the CSFW even after repeated spring applications.

In field conditions metolachlor and terbuthylazine are applied with the same timing in spring, mainly to maize. Agricultural runoff in north-eastern Italian plains are more likely in late spring and early summer (Otto el al., 2012), so the two herbicides are detected in similar concentration. Later events would have a higher terbuthylazine content, but this would probably remain unproved because of the scarcity of events and their very low expected concentration.

Conclusions

The CSFW is very effective in the reduction of herbicides runoff even when completely flooded, with a mitigation effectiveness of about 98% for metolachlor and terbuthylazine, two of the main herbicides applied to maize. This is in agreement with the conclusions of other recent European studies (Kay et al., 2009; Stehle et al., 2011; Maillard et al., 2011). Comparison with results from other research is possible only after a clear and simple definition of mitigation or removal, as proposed in this study.

It is difficult to single out exactly which processes cause the mitigation. The observed dynamic suggests that in the studied CSFW the mitigation is provided by a reversible adsorption to the superficial organic matter complex, i.e. by plants, plant residues and soil. In fact, following a successive severe flood, 15-30% of the herbicides detected in the first flood was mobilized after 25 days, and 40 days later another flood again mobilized a lower but detectable amount of herbicides. In both floods a mixture of herbicides and metabolites was present. It is worth noting that mobilization of terbuthylazine from the CSFW is correlated with the contact time with water, while that of metolachlor, slightly less adsorbed and more soluble, is not. Given that flooding speed is quite regular throughout the CSFW, mitigation can be linked either to the duration or residential time of the flood.

Results highlight that the CSFW is a dynamic system with a high buffer capacity. In ordinary conditions of the plain cropland in north-eastern Italy, where 3-4 runoff events of low volume occur (Cardinali et al., 2013), the mitigation capacity of a 0.3 ha CSFW

serving a 6 ha basin is likely complete, i.e. no herbicides will by-pass the CSFW and enter surface water outside the basin.

According to an iterative method for mitigation calculation, hypothesizing a final mitigation of 99.99% for a CSFW of 200 m, the mitigation capacity for a heavy runoff of 3.5 mm from a 10 ha basin is 90% for each 50 m in length for a 15 m wide wetland. This suggests that also smaller CFWS can be very useful at farm scale when other mitigation techniques are implemented, i.e. spray band applications, post-emergence only.

Chapter 3

Vegetated Ditches for the Mitigation of Pesticides Runoff in the Po Valley

Introduction

Risk mitigation measures for pesticides are increasingly important (European Commission. Directive, 2009). Previous research (Pappalardo et al., 2015) showed that a constructed surface flow wetland can reduce the pollution of watercourses from a watershed of hundreds of hectares in Northern Italy agro-systems. Indeed, in very fragmented landscapes such as in Po Valley there is also an urgent need for the mitigation of agricultural runoff from a large number of small farms in order to intercept pollutants before they enter a large watercourse, where mitigation is impossible.

Vegetated agricultural drainage ditches, hereafter ditches, are common in the Po Valley landscape, being a traditional part of field margins (Hackett et al., 2014), and even if they are mainly designed for drainage purposes, they can provide two important ecosystem services: 1) habitats and green corridors for wildlife and wild plants (Herzon et al., 2008), and 2) runoff mitigation for the protection of watercourses (Vymazal & Březinová, 2015).

According to accepted classification, the ditch is an "off-field mitigation measure" for runoff as it can reduce flow velocity, intercept and remove sediment, organic material, nutrients and chemicals carried in runoff water. This has been shown in general (Bennett et al., 2005), and for some studies the basic mitigation effectiveness is about 50% (Gregoire et al., 2009). Yet mitigation depends strictly on ditch characteristics, i.e. size, length, slope, vegetation cover (Bouldin et al,. 2004; Moore et al., 2008), macrophyte adsorption (Hand et al., 2001;Merlin et al., 2002), and a great variability exists in ditch types and effectiveness.

As reported by (Cardinali et al., 2013) 98% of herbicide loss by runoff in the Po Valley is caused by a few extreme events with an estimated return period of 25-27 years, while 3-4 runoffs of low intensity are expected each spring-summer. However, in emerging climate change scenarios in which frequency of extreme rainfall events is estimated to increase

locally (Zollo et al., 2015), heavy runoff from croplands could represent a massive and uncontrollable non-point source threat to surface water bodies. Therefore, for the Po Valley there is an urgent need to do specific field measurements and gain insights into the main mitigation processes.

The fugacity model is a multi-media model that has proved to be very accurate in predicting concentrations of organic pesticides, both at field and watershed scale (Di Guardo et al., 1994; Ghiradello et al., 2014). Its application could be very helpful to recognize and quantify the main pathway of environmental fate of pesticides in a little studied environment, so its application to a ditch is of interest.

The aim of the study was to assess in real field conditions the mitigation effect of a ditch for a simulated but realistic heavy runoff containing three of the main herbicides applied to maize in the Po Valley, and to highlight herbicides release after two subsequent floods with uncontaminated water. A simple fugacity model was applied to study the repartition of herbicides in the ditch, and predictions were compared to observations.

Materials and methods

Site information and experiment layout

The trial was conducted on the Exp. Farm of Padova University (North-eastern Italy).

The studied ditch was 500 m long, of trapezoidal section (1 m bed, 2 m top, 1.8 m height), with a low slope (0.3%) designed as an irrigation and main drainage channel from a network of smaller ditches on 20 hectares of cropland where maize herbicides were not used in the previous cropping season (Fig 1).

Figure 1 – The experimental site. Left: the drainage network, with indication of inlet (A) and outlet (B) of the ditch and the direction of the flow; this image is similar but not identical to the original, and is therefore for illustrative purposes only. The Centre: overview of the ditch next to inlet. Right: detail of the flooded bed after the simulated runoff event (Photos: S. Otto and S.E. Pappalardo).

The banks of the ditch were completely covered by vegetation 0.8-1.2 m tall, mainly perennial *Graminaceae*. Main species were *Dactylis glomerata*, *Convolvulus arvensis*, *Lolium multiflorum*, *Poa trivialis*, *Silene alba*, *Rumex crispus*, *Sonchus asper*, *Urtica dioica*, *Rubus* sp., *Bromus* sp., *Galium mollugo*, *Equisetum* sp., *Festuca arundinacea*, *Cynodon dactylon*. The bed part of the ditch was partially covered (10% of surface) by *Phragmites australis*, *Iris* sp., *Scirpus* sp., *Tipha* sp.

The estimated Manning's roughness coefficient of the ditch was 0.075, which is the median roughness coefficient for channels with dredged ditches covered by un-maintained weeds (Zhang & Zhang 2001).

In ordinary conditions the ditch is without free water, and only after a rainfall of at least 20 mm a depth of 2-7 cm of water flows slowly to the outlet (0.2 m min^{-1}).

In order to test the hydraulic performance of the ditch in an extreme runoff, a previous flood with uncontaminated water was conducted. About 50-55 m^3 were necessary for the flooding, velocity of the water during flooding ranged from 0.07 (inlet) to 0.01 m sec^{-1} (outlet); after about 3 hours the flux at inlet was very low, less than 0.003 m sec^{-1} and about 35-40 m^3 of water slowly passed the outlet in in the subsequent 10 hours. The ditch was therefore an open system that returns to its standard, dry, conditions in about 1 day.

On 24th April 2015 a heavy runoff simulation was performed, and the ditch was flooded in 20 min with 52 m^3 of water (corresponding to a flow of 156 m^3/hour, or 2.6 mm/hour from a 6 ha basin) containing 60 g of the herbicide Lumax®, a common product for weed control in maize containing 37.5, 212.5, 187.5 g L^{-1} of mesotrione (CAS 104206-82-8), S-metolachlor (CAS 87392-12-9) and terbuthylazine (CAS 5915-41-3), respectively. Herbicide was regularly added to flood water in order to prevent a concentration peak moving through the ditch, and given that about 8 m^3 of water were already in the ditch, the final concentration of the simulated runoff was 37, 213 and 188 μg L^{-1} of mesotrione, S-metolachlor and terbuthylazine, respectively.

These concentrations were about 100-fold higher than an ordinary runoff (Cardinali et al., 2013) to simulate an extreme runoff for both velocity and concentration of flow. The concentrations are similar to those observed for fungicides after exceptional rainfall in a study conducted in south-west Germany (7.0-83.4 μg L^{-1}) (Bereswill, 2012).

The flood increased the water level by about 10 cm (mean value for the entire ditch). After 3 hours, 50 samples of free water and 10 samples of the saturated layer on the bed (mean depth: 5 cm) were collected at regular intervals from inlet to outlet. The bed sample

included the suspended solids that precipitate within 3 hours, and hereafter called "sediment". After 27 and 82 days the flooding was repeated with uncontaminated water, and sampling repeated in order to detect herbicides release.

For water concentration, the distance (m) required to reduce initial herbicide concentration by 50% was estimated (half-distance or D50).

Calculation of runoff mitigation

The mitigation of runoff is calculated with the simple method suggested by Otto et al. (2015). For two values A and B of a quantitative parameter, with A greater than B, the percentage mitigation from A to B is:

$$M\% = 100*(A-B)/A \quad (1)$$

For example, if at the ditch inlet (A, reference scenario) the mean concentration of a chemical is 12 μg L^{-1}, and at the outlet (B, mitigated scenario) it is 3 μg L^{-1}, the percentage mitigation from A to B is:

$$M\% = 100*(12-3)/12 = 75\% \quad (2)$$

Analytical procedure

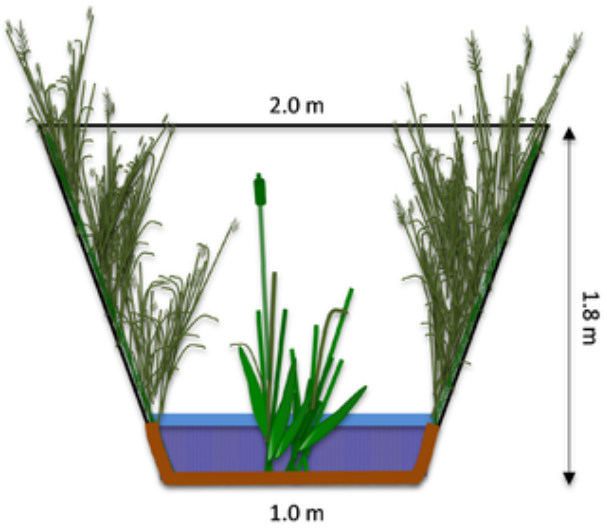
The procedures used for pesticide extraction and analysis derived from previous studies (Freitas et al., 2004; Barchanska et al., 2012). Details are in Supporting Information (S1 Text).

The fugacity model

The fugacity model is a multimedia model that calculates the concentration of organic pesticides applied to a suitably modelled multi-compartment environment (Mackay, 1982;; MacLeod et al., 2010). For chemicals used in agriculture a specific compartment for vegetation biomass was included by (Calamari et al, 1987). Repartition between compartments is based on partition coefficients of chemicals, fugacity capacity and volume of the compartments. The compartments are hypothesised as completely available, repartition is instantaneous, and the whole system in equilibrium. In field trials lasting hours, as in this study, this is the hardest condition to achieve. Nevertheless, differences between predicted and observed concentrations can highlight how far the system is from equilibrium and the main pathways and compartments involved in the repartition.

Ditch modelling and repartition calculation

The flooded ditch was modelled in 9 environmental compartments (Fig 2), and repartition of the herbicides calculated for the three floods.



Compartment	Volume (m^3)	%
Soil	0.025	0.94
Sediment	0.006	0.21
Susp. Solid	0.000	0.00
Air	2.514	93.10
Water	0.154	5.69
Biota	0.000	0.00
Root	0.001	0.02
Stem	0.0005	0.02
Leaves	0.000	0.01
Sum	**2.700**	**100.00**
Liquid/Solid	4.9	4.9

Figure 2 - Scheme of the ditch after the flood, and modelling of 1-m length.

Even if initial soil moisture content was slightly different between floods, for simplicity the model of the ditch was the same for all floods (Supporting Information, S2 Table). Therefore relative amount between compartments remained unchanged, and only concentration varied according to chemical load at flooding time. For the first contaminated flood the chemical load was the real amount applied, for the two subsequent uncontaminated floods the chemical load was calculated considering that after the flood the total amount of herbicides in the ditch decreased because: 1) part flowed out from outlet, 2) the rest degraded according to first-order kinetics.

Results

Water concentration after first flood (contaminated runoff)

After complete flooding, concentration of the three herbicides was decreasing almost throughout the ditch, from inlet to outlet 500 m apart (Fig 3, top).

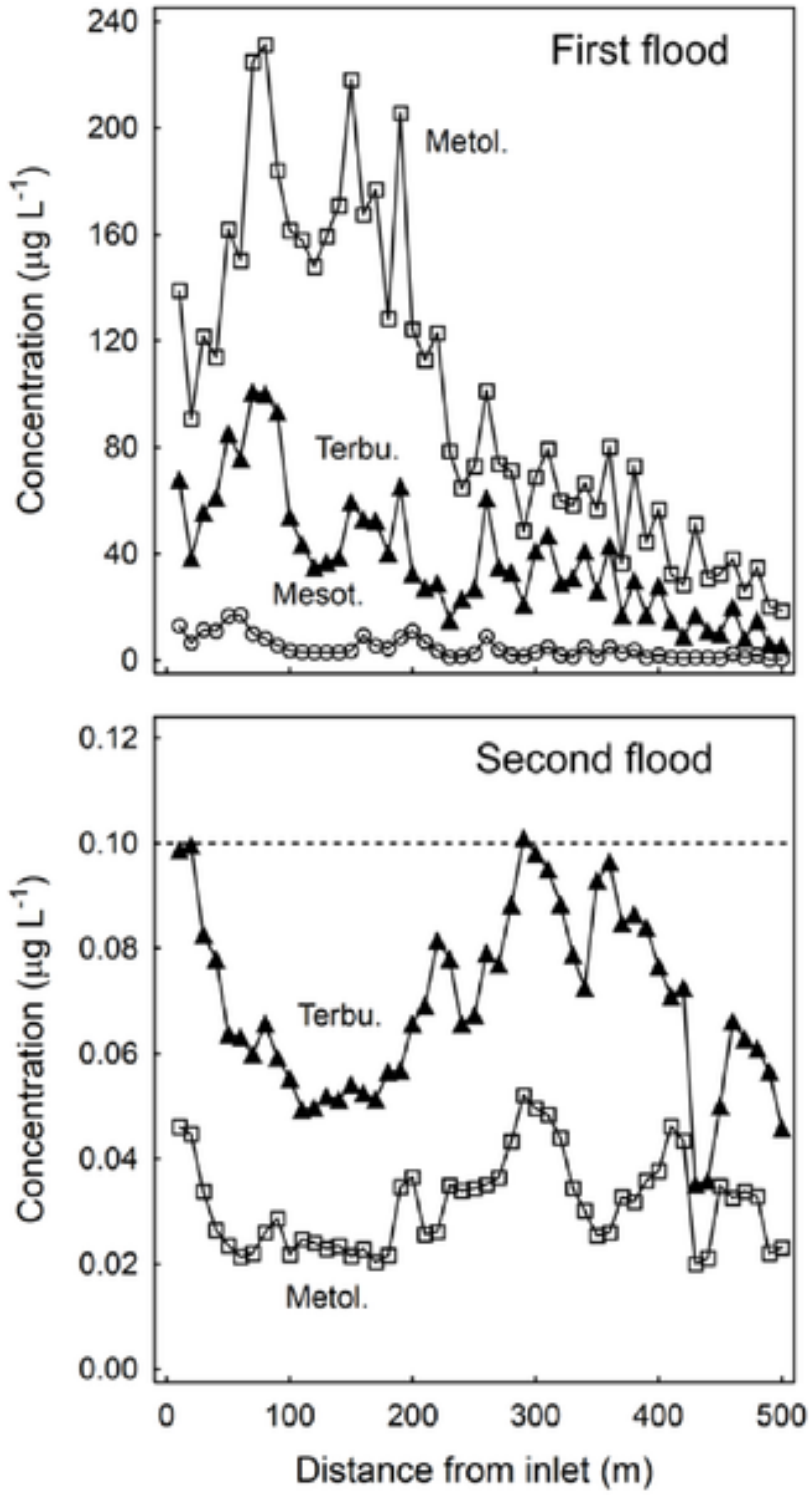


Figure 3 - Concentration of herbicides in water in the first and second flood; all values in the third flood were below the detection limits. Mesotrione: empty circles; metolachlor: empty squares; terbuthylazine: full triangles. The lower axis is the distance from the inlet (m). The drinking water limit (0.1 µg L^{-1}) is indicated. Detection limits: mesotrione=0.070 µg L^{-1}, S-metolachlor=0.020 µg L^{-1}, terbuthylazine=0.014 µg L^{-1}.

For the whole ditch, mean observed concentrations were 5, 99, 39 μg L^{-1} for mesotrione, S-metolachlor and terbuthylazine, respectively. The mean observed concentrations in water were lower than those applied, being about 12% for mesotrione, 47% for S-metolachlor and 19% for terbuthylazine. Sampling error was likely high because vegetation cover and water flow varied both along and across the ditch. Indeed, except for mesotrione, the observed values were very similar to that for atrazine (37%) obtained in a similar study by(Moore et al., 2001).

The highest concentrations of applied herbicides were found in the first 200 m of the ditch. The resistance to flow due to vegetation and the relevant length of the ditch, which is indeed a not rectilinear farm ditch with an open outlet (see Fig 1), hinder the achievement of a complete hydraulic equilibrium. At the outlet concentrations were lowest and the mitigation was 99%, 91% and 97% for mesotrione, S-metolachlor and terbuthylazine, respectively. These values are close to those obtained by (Cooper et al., 2012) in similar conditions.

For the three herbicides the concentration was about half of the maximum (i.e. D50) at about 250 m from the inlet.

Taking into account concentrations weighted by the application rate, S-metolachlor concentration was on average 2.3-fold that of terbuthylazine, in accordance with S-metolachlor lower lipophilia. The S-metolachlor concentration was also 4-fold that of mesotrione, likely because 1) mesotrione is much more soluble and was rapidly transferred to the outlet, 2) mesotrione was promptly transformed into some metabolites, according to its 2-5 days dissipation half-life in basic soils, as in this study. It is worth noting that using unweighted concentrations, the ratio S-metolachlor/mesotrione would have been about 21, i.e. very misleading.

Water concentration after second flood (first release)

The second flood 27 days after contamination caused a release of S-metolachlor and terbuthylazine from the ditch, while mesotrione was not detected (Fig 3, bottom). Concentrations of S-metolachlor and terbuthylazine were very low, close to the detection limit and almost uniform throughout the entire length of the ditch. Concentrations were below the drinking water limit (0.1 $\mu g\ L^{-1}$), in this study used as fixed and prudent reference value; an adequate ecotoxicological endpoint for agricultural ditches may also be the predicted no effect concentration (PNEC). For the three herbicides under study the sensitive target in aquatic environment are Algae [26], and PNEC ranges from 0.1 to 350 $\mu g\ L^{-1}$ so the risk is low. Average concentrations of S-metolachlor and terbuthylazine were 0.03 and 0.07 $\mu g\ L^{-1}$ respectively, 3,500-fold lower for S-metolachlor and 500-fold lower for terbuthylazine with respect to first flood, i.e. mitigation of both herbicides was about 99.9% from first to second flood. Applying these same reduction ratios to mesotrione would result in a concentration of less than 0.01 $\mu g\ L^{-1}$, well below the limit of detection (LOD) and in keeping with the lack of detections.

Concentration of S-metolachlor was regularly half or less that of terbuthylazine, and this is consistent with the physical-chemical characteristics: due to lower lipophilia, more S-metolachlor passed through the ditch in the first flood, and the rest almost dissipated before the second flood. This is in agreement with the relatively high persistence of terbuthylazine found in previous lab studies (Fava et al., 2007) and a field trial showing that about 30 days after application environmental load of terbuthylazine surpasses that of S-metolachlor (Otto et al., 2008).

Water concentration after third flood (second release)

Herbicides were not detected in the third flood performed 55 days after the second. This result is consistent with that of the previous flood, when concentrations were already close to the detection limit.

Sediment concentration

The content of the solid part in the saturated layer on the bed, i.e. the sediment in the ditch model, was on average 19% of the layer volume.

In the first flood, mean concentration in sediment was 10 and 7 $\mu g\ kg^{-1}$ for S-metolachlor and terbuthylazine respectively, i.e. 5-10-fold lower than in water, and length-dependent (Fig 4).

Herbicides were detected in both water and sediment in all samples. Since they were applied to the ditch with water, this suggests that adsorption to the solid part of sediment begins promptly, and is likely complete when the ditch returns to standard dry conditions.

In the second flood, mean concentration in sediment was similar to the previous, 3 and 6 $\mu g\ kg^{-1}$ for S-metolachlor and terbuthylazine respectively, but was 10-fold higher than in water. Concentration peak was shifted about 150 m nearer the outlet with respect to the first flood, according to the fact that in the first flood herbicides were added with water, in the second they were released from the bed by water.

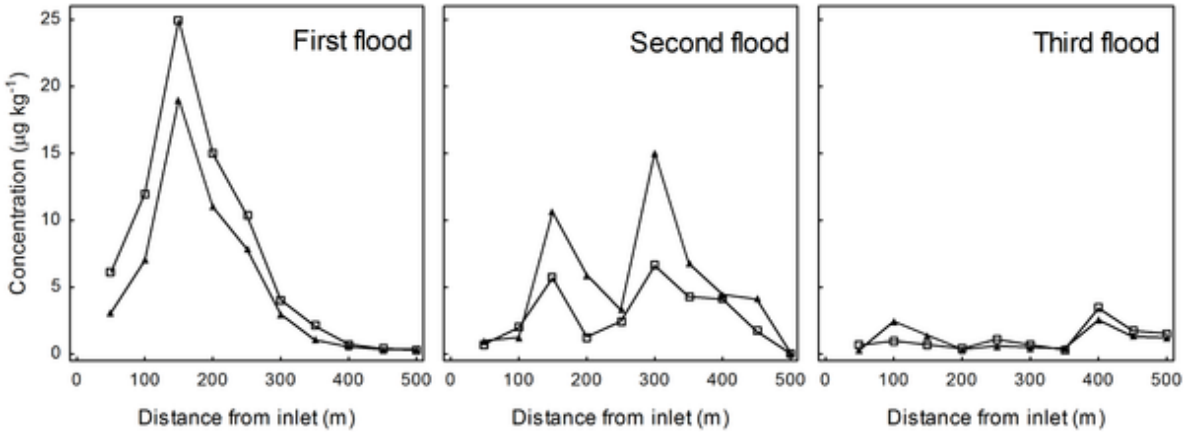


Figure 4 - Concentration of herbicides in the dry sediment in the three floods. Metolachlor: empty squares; terbuthylazine: full triangles. The lower axis is the distance from the inlet (m). For mesotrione all values were below the detection limit. Detection limits: mesotrione=0.070 µg kg^{-1}, S-metolachlor=0.020 µg kg^{-1}, terbuthylazine=0.014 µg kg^{-1}

This highlights, as for water, that environmental load of terbuthylazine surpasses S-metolachlor after 1 month, and confirms that the contamination source is the bed of the ditch.

In the third flood, the mean concentration in sediment was similar for both herbicides, about 1 µg kg^{-1}, while herbicides were not found in water. This shows that after 82 days the total environmental load is low for both S-metolachlor and terbuthylazine.

Mesotrione was not found in any flood, in accordance with the low concentrations observed in water, again highlighting the reduced environmental load of this herbicide after application.

Physical-chemical parameters selection

The main physical-chemical parameters of the applied herbicides were selected from the literature. Molecular weight, solubility, vapour pressure and K_{OW} were taken from

(MacBean et al., 2012), whereas, because several values of K_{OC} were reported, a selection was made (Supporting Information S3 Table).

For mesotrione a wide range of K_{OC} sorption coefficients is available because adsorption is directly correlated with soil organic carbon (MacBean, 2012; Tomlin, 2006; Chaabane et al., 2008); since organic matter in the ditch is estimated at about 2% (Supporting Information, S2 Table), the highest K_{OC} reported by (MacBean, 2012) (390 L kg^{-1}) was selected. For S-metolachlor the value of 118 L kg^{-1} reported by (Aslam et al., 2013) was selected since it was obtained with vegetation organic matter and is very similar to the value of 123 L kg^{-1} obtained by (Laabs et al,. 2000) in a topsoil with 2.6% of organic carbon. For terbuthylazine the average value in the literature was selected (259 L kg^{-1}).

Fugacity model results

93% of the ditch volume is air, but the studied herbicides have low vapour pressure, so concentration in air is negligible (Supporting Information, S4 Table). Even if the banks of the ditch were completely covered by vegetation, only the strip submerged by the flood is considered in the simulation, so the total vegetation biomass is only about 0.05% of total volume; repartition in this compartment occurs for 0.1% (mesotrione) to 4.0% (S-metolachlor and terbuthylazine) of applied amount, and accumulation is negligible. As a consequence, the solid (soil, sediments and suspended solids) and liquid compartments (free flowing water, water in the fluid layer on ditch bed, water in soil) were of most importance for repartition. Even if the liquid is about 4-fold the solid, the model calculates that 44-73% of applied herbicides is adsorbed onto the solid part and 26-51% dissolved in water. This highlights the magnitude of adsorption for these chemicals.

For the first flood, the concentrations calculated in water by the fugacity model were very close to those observed. For the first flood, predicted vs. observed values were 7 vs. 5, 86 vs. 99, 49 vs. 39 $\mu g\ L^{-1}$ for mesotrione, S-metolachlor and terbuthylazine respectively; the model was therefore very precise for water.

Considering that 37 m^3 of the contaminated flood passed the outlet, 10-22% of applied herbicides left the ditch with this. The remaining part degrades, and first order kinetics calculates that 4%, 32% and 51% of applied mesotrione, S-metolachlor and terbuthylazine respectively were in the ditch at the time of the second (uncontaminated) flood. This highlights the importance of degradation for these herbicides.

For the second flood, the concentration calculated in water by the fugacity model was 0.25 $\mu g\ L^{-1}$ for mesotrione, while observed concentrations were below the LOD of 0.070 $\mu g\ L^{-1}$. For S-metolachlor and terbuthylazine the fugacity model calculated concentrations of 24 and 21 $\mu g\ L^{-1}$, respectively, in accordance with the residual amount before flood. These values were 300-900-fold higher than those observed, so the model was very imprecise for water.

First order kinetics calculates that 65-99% of herbicides still in the ditch after the second flood are degraded before third. In particular, the residual amount of mesotrione is nearly zero (about 0.1 mg). The chemical load in the third flood was therefore low.

For the third flood, the concentrations calculated in water by the fugacity model were 0.0004, 3.0 and 6.3 $\mu g\ L^{-1}$ for mesotrione, S-metolachlor and terbuthylazine, respectively. Observed values were all below the LOD. Considering the LOD as “observed values” for comparison purposes, calculated values were 150-500-fold higher than observed, so the model was again very imprecise for water.

The fugacity model calculates in the first and second flood a concentration of S-metolachlor and terbuthylazine in sediment 2-70-fold higher than observed. This suggests that: 1) for the first flood full repartition is not achieved in the 3-hours sampling period; 2) for the second mobilisation (desorption) with flowing water is significant but incomplete, likely requiring days to finish.

It is possible that this steady overestimation in both water and sediments is caused by the absence of a specific "soil-sediment-plant" compartment in the model.

After the third flood, the fugacity model calculates an average concentration in the solid compartment of the ditch (soil and sediments) of about 0.005 $\mu g\ kg^{-1}$ for mesotrione, and 12-54 $\mu g\ kg^{-1}$ for S-metolachlor and terbuthylazine, corresponding to about 1.5 g of total herbicides in the whole ditch (500 m^2), a mass 1000-fold lower than a standard herbicide application on 1 ha of crop. This shows that herbicide accumulation is negligible, so debris from ditch maintenance is not toxic for crops.

Discussion

Even after one regular and intense input of herbicides, concentrations in water in the ditch were lower than input and quite regularly decreasing along the ditch, showing that repartition begins soon and is very effective, because the mean concentration detected in water was only 10-45% of that applied, and at the outlet the concentration was mitigated by 90-99% according to the calculation method suggested by (Otto et al., 2015). This highlights the importance of adsorption onto the sediment-soil-plant complex, and the ditch length or the residence time (hydraulic retention).

According to results from specific runoff studies, 3-4 ordinary runoff events are expected every year in the Po Valley, each with a load of about 0.2 g ha^{-1} of metolachlor and terbuthylazine (Cardinali et al., 2013).

In this study, the ditch was flooded with about 12 g of those herbicides, corresponding to the herbicide loss from 60-70 ha of treated cropland, and a 500 m long and 1 m bed wide ditch provided mitigation of 90-99%. In brief, for ordinary runoff, mitigation of at least 90% can be achieved with 10 m^2 of ditch/hectare of cropland. This highlights that ditches can be very effective for the mitigation of ordinary runoff, and that mitigation is similar to that obtained with vegetative filter strips (86–88% for S-metolachlor and terbuthylazine [33]).

It is of interest to compare mitigation effectiveness of a ditch and wetland for heavy or extreme runoff events.

According to Pappalardo et al. (2015) the mitigation effectiveness of a constructed surface flow wetland for a heavy runoff of 3.5 mm from a 10 ha basin is 90% for each 50 m in

length for a 15 m wide wetland, corresponding to the weighted value of 75 m^2 of wetland/hectare of cropland.

In the present study, taking into account concentrations at the outlet, 500 m of ditch 1 m bed wide provided mitigation of about 95% for a runoff of 52 m^3, corresponding to 3.5 mm runoff from 1.5 ha. For 90% mitigation (500/1.5)*90/95=318 m^2 of ditch/hectare of cropland are thus necessary. This weighted value is about 4-fold that of wetland, suggesting that a ditch is much less efficient, but it is reasonable because a runoff of 3.5 mm is extreme and the residence time in the ditch much shorter than in the wetland, where the laminar sheet flow enhances pesticide interception (Bereswill). It is worth noting that for a realistic runoff of 1 mm from 5.2 ha, 99% mitigation can be achieved with 100 m of ditch/hectare of cropland. This result can be summarized with the mitigation rule "1 mm from 5 ha is mitigated by 99% (M) in 100 m of vegetated ditch 1 m bed wide". For example, for a runoff containing 1 $\mu g\ L^{-1}$ of herbicide (A), application of this rule results in a concentration (B) at the outlet of:

$$B=-((M*A/100)-A)=-((99*1/100)-1)=0.01\ \mu g\ L^{-1} \quad (3)$$

For pesticides, mitigation effectiveness depends on many physical and chemical processes, degradation, sedimentation, infiltration and adsorption onto plant surfaces, the relative importance of which is not completely known. The role of adsorption coefficient and solubility of pesticides has still to be clarified, as also reported by (Vymazal, 2015), and in wetlands there are even cases of great mobility of pesticide with high K_{OC} [34]. Most information is still based on model simulations, i.e. with SWAT (Ghirardello), so there is a need for field trials.

Sampling error is likely high in field conditions, and a recent study show that changes in macrophyte biomass and particulate/dissolved organic carbon levels caused concentration

variations of several orders of magnitude in space, especially for highly hydrophobic chemicals (Morselli et al., 2015). Nevertheless, the results of the present study show that when a contaminated runoff is convoyed to a ditch covered by semi-natural vegetation, and the linear flow is about 3 m min^{-1}, a length of 250 m is enough for halving the initial concentration just by means of adsorption of the pesticide onto the sediment-soil-plant complex. For lower, and more realistic, flow velocity the half-length dissipation would be similarly lower.

When the ditch has an open outlet, in the case of heavy runoff events there is an immediate risk of transferring a runoff contaminated above the drinking water limit (0.1 μg L^{-1}) to surface waters. In the Po Valley this risk can be managed in two ways: 1) by insertion of a sediment pond after the outlet; 2) closing the outlet of the ditch, which practically becomes a linear constructed surface flow wetland. Implementation of this second option is anyway not easy and not often suggested because during heavy rainfall the primary role of ditches is to quickly remove water from fields to prevent flooding.

Adsorption onto the sediment-soil-plant complex is quickly reversible, and successive floods can mobilize herbicides according to their dissipation dynamics in soil and sediments. Observed concentrations were anyway very low, below the drinking water limit, showing that the ditch is an effective structure for trapping herbicides.

The lack of detection in the third flood 82 days after contamination highlights the low persistence of these chemicals in ditches, where dissipation half-lives can differ from those in agricultural soil. For example, (Barra Caracciolo, 2005) reported for S-metolachlor a half-life of 12 days for microbiologically active soils, while the mean generic value reported by (MacBean) is 28 days. The vegetation and the periphyton (Otto et al., 2012) could play a relevant role in stimulating biological degradation, and the inclusion of

experimental dissipation values for ditches would improve precision of dissipation dynamic modelling, but further research is needed for this.

The results of the fugacity model depend on some inevitable assumptions. Comparison of the model's outcome with observations for subsequent simulations can test the goodness of choices because the model should always succeed or fail, and provide information about relative magnitude of pathways. For a ditch the model highlights the importance of K_{OC} sorption coefficient and half-life of pesticides in flood concentration and mid-term release. When the calculation aims to estimate predicted environmental concentrations, there is a need for specific values of pesticides adsorption onto the sediment-soil-plant complex since 1) sorption depends on type and age of organic matter (Aslam et al., 2013), 2) the K_{OC} likely varies in time, as recently observed in studies conducted on a river (Boithias et al., 2014). When K_{OC} is about 200-400 L kg^{-1} the pesticide is mainly adsorbed and release from ditches is low. When the half-life is 3-5 weeks, accumulation is very unlikely. A runoff with 100-200 μg L^{-1} convoyed to a ditch can be practically decontaminated in 3-4 months. Furthermore, the model results suggest that when contaminated runoff enters a ditch, two subsequent stages occur: 1) solubilisation stage, when risk to surface water depends mainly on chemicals solubility and flow velocity; 2) repartition stage, when environmental load is driven by sorption and dissipation from the sediment-soil-plant complex. The inclusion of this compartment in the model would improve general precision of repartition calculation.

Debris from regular dredging and vegetation management of the ditch are calculated as non-toxic for crops, and can be spread on cropland before ploughing. The entire cycle of depuration with ditches is then of low impact and cost. Developing countries in particular could gain advantage from this low-cost and easily-implemented system (Mahabali, 2014).

Given that combinations of mitigation measures can be very effective (Otto et al., 2015), a sustainable scheme for the mitigation of pesticide runoff to surface water can be based on: 1) ditches for the immediate mitigation of direct runoff from fields; 2) wetlands, serving a watershed of hundreds of hectares; 3) linear buffer strips along water courses of high quality.

Vegetated ditches are already present on cropland, and their environmental and ecosystem services can be exploited by proper management and maintenance.

Conclusions

Vegetated ditches have a great herbicides runoff mitigation potential for the protection of watercourses and can be inserted in environmental schemes. Their effectiveness with shallow flooding is high and length-dependent. In typical ditches of North-eastern Italy, for the main pre-emergence herbicides applied in maize, the distance required to reduce initial concentration by 50% is about 250 m. As a general rule for herbicides with K_{OC} of 110-400 L kg^{-1}, a runoff of 1 mm from 5 ha is mitigated by 99% in 100 m of vegetated ditch 1 m bed wide.

The dissipation of herbicides in ditches is site-specific and mainly due to degradation and adsorption, while outflow with water discharge is low since the flood is shallow. Coverage of emergent plants and the hydraulic residence time is of great importance, and a better insight into herbicides adsorption onto the sediment-soil-plant complex is needed.

Supporting Information

S1 Table. Modelling of the vegetated ditch.

Parameter	Value	Note
Bed width (m)	1	
Top width (m)	2	
Height (m)	1.8	
Length (m)	500	
Volume of water in the flood (m^3)	52	(1)
Part of flood increasing the saturated layer on the bed (%)	20	(2)
Height of the saturated layer on the bed (cm)	3	(3)
Water in the saturated layer on the bed (%)	81	(4)
Vegetation biomass on the bank (kg/m^2)	2	(5)
Vegetation biomass density (kg/m^3)	0.8	(6)
Ratio (Veg. biom. in the bed)/(Veg. biom. in the bank)	0.6	(7)
Height of the saturated soil layer (cm)	4	(8)
Water in the saturated soil layer (%)	50	(9)
Slope of the ditch (%)	0,1	(10)
Suspended solids in the free water (m^3)	0.052	(11)
Volume of Biota in the whole ditch (m^3)	0	(12)
Part of the free water passing the outlet (%)	90	(13)
Organic carbon content in the soil (accessible part) (%)	2	(14)
Organic carbon content in suspended solid and sediment (%)	4	(14)

Notes

(1) Volume of water used in each of the three floods.

(2) Part of the flooding water increases the saturated layer of the bed, i.e. the fluid layer composed of sediment and water; the rest becomes free water flowing slowly to outlet and beyond.

(3) Height of the accessible part of the saturated layer, mean of the entire ditch length; height ranges from 1 cm (inlet) to 10 cm (outlet). The selected height of 3 cm is about half the observed, but is assumed to be the part completely accessible to chemicals during the 3 hours of sampling.

(4) Liquid part in the saturated layer, percentage of volume. This is an experimental value, average of 30 samples for the determination of herbicides in sediment.

(5) Green biomass of plants on the bank, kg m^{-2}. This is an experimental value, average of 10 sampling areas of 1 m^2 selected along the entire ditch length. In the fugacity model accumulation differs between root, stem and foliage. In the present simulation it has been assumed that aerial biomass is given 40% by leaves and 60% by stems, and that roots are 67% of total aerial biomass.

(6) Biomass density according to the European Commission. Directive 2009.

(7) Plant cover on the bed and on the banks was uniform along the ditch, the cover of the bank was regularly higher than on the bed; the relative cover was assessed visually.

(8) Height of the soil layer saturated by flooding water, on both the bed and the banks, assumed to be completely accessible by chemicals. Each flood increases the water level by about 10 cm (mean value for the entire ditch), then the full length of the saturated soil covering the ditch is given by:

Length=100 cm of bed width+2*3 cm height of the fluid layer+2*10 cm level free water=126 cm.

(9) Water-filled pore space in soil was set at 50% according to results in a specific study (Pappalardo et al., 2015).

(10) The slope of the ditch is low as is common in Po Valley, and free flowing water is only observed after heavy rainfall.

(11) The free flowing water had a variable content of suspended solids from inlet to outlet, being higher at about 200 m from inlet; the selected mean value was 1 L of suspended solids each 1,000 L of water.

(12) The original fugacity model includes the animal biomass (Biota), for example fish, because chemicals can accumulate in fat; in the present simulation this compartment is included with nil volume in order to retain the original structure and ease its inclusion when needed.

(13) According to field observation, about 90% of the flood passed the outlet and removed part of the chemicals; this advection reduced the chemical load in the vegetated ditch after each flood and consequently poses the highest potential risk for watercourses.

(14) On the Exp. Farm of Padova University the organic content in field soil is 0.92% (Hackett et al., 2014), but is estimated as higher in the soil under the ditch, sediments and suspended solids according to specific studies (Herzon).

S1 Text. Analytical procedure

The procedures used for pesticide extraction and analysis derived from previous studies. Herbicide standards: terbuthylazine (99.5% purity), metolachlor (98.0% purity) and mesotrione (99.5% purity) were purchased by Dr. Ehrenstorfer (Augsburg, Germany). Methanol (HPLC-grade), water (HPLC-grade) and all other chemicals (analytical-grade) were purchased from Sigma-Aldrich. All analytes with individual stock solutions were prepared in methanol with concentration of 0.1 mg mL^{-1}. Mixtures of standard solutions were prepared in concentration ranges from 0.1 to 2.5 μg mL^{-1}. They were used as spiked solutions for sample fortification and for calibration curves.

To determine herbicide concentration in water, 1 L field samples were filtered at room temperature with a vacuum equipment using cellulose nitrate membrane filters 0.45 μm pore size. After filtration an acetate buffer (2.5 M) was added (ca. 1%, v/v) and water samples were extracted using a TELOS *neo*^{TM} PRP polymeric SPE column (60 mg,

Kinesis) and a J.T. Baker SPE-12G glass column processor at a flow rate of 15 mL min^{-1}. After extraction the analytes were eluted with 5 mL of methanol without the vacuum and methanol aliquots were reduced to approximately 50 μL with the use of a nitrogen gas stream at 45 °C.

To determine herbicide concentration in sediment, 20 g of dry sediment were weighed in dark bottles and 50 mL of methanol-0.1 M HCl (9-1, v/v) was added. The bottles were shaken for an hour at 200 rpm at room temperature (about 18 °C). Mixtures were then centrifuged for 15 min at 3,200 rpm (Heraeus Christ Labofuge GL, Germany) and supernatant filtered at 0.45 μm pore size. The filtrate was then evaporated at 38 °C using an IKA® RV 8 rotary evaporator ((IKA®, Werke GmbH & C., Staufen, Germany) and the residue was dissolved in 50 mL of 0.1 M HCl. Subsequently, the extraction was conducted. The conditions of solid-phase extraction were the same as for water samples.

To define the analyte recoveries, water and sediment (without analytes) were spiked with herbicides at concentrations of 0.4, 1.0 and 2.2 μg mL^{-1}. Extraction was then the same as reported above. The recoveries in water were: mesotrione and metolachlor 95%, terbuthylazine 91%; the sediment recoveries were: mesotrione 81%, metolachlor 76%, terbuthylazine 79%.

The analyses were performed by LC-MS using a 1100 Series Agilent Technologies system (CA, US), equipped with binary pump, diode array detector, and MSD SL Trap mass spectrometer with ESI source. A Eurospher II (Knauer, Berlin, Germany) column C18 P with TMS endcapping, 150 × 4.6 mm i.d., 3 μm, 110 Å was used to analyze the samples, the mobile phase consisted of 0.6% formic acid in water (solvent A) and methanol (solvent B).

Gradient elution programme: from 0 to 4 min a linear increase of solvent B from 60% to 80% and flow rate from 0.4 to 0.6 mL min^{-1}, from 4 to 11 min a linear increase of solvent B from 80% to 100% at flow rate of 0.6 mL min^{-1}; initial conditions were re-established in 5 min and re-equilibration time was 2 min.

A 10 μL sample volume was manually injected each time. Retention times were 5.5 (±0.2), 10.1 (±0.3) and 9.0 (±0.2) min for mesotrione, metolachlor, and terbuthylazine respectively. The limit of detection (LOD), 3:1 signal-to-noise ratio, was 0.070 μg L^{-1} for mesotrione, 0.020 μg L^{-1} for S-metolachlor, and 0.014 μg L^{-1} for terbuthylazine.

S2 Table. Physical-chemical parameters of applied herbicides

Parameter	Unit	Mesotrione	Reference	S-metolach.	Reference	Terbuthylaz.	Reference
CAS	#	104206-82-8	[1]	87392-12-9	[1]	5915-41-3	[1]
Applied rate	kg/ha	0.15	Rec. rate in maize	1.25	Rec. rate in maize	0.75	Rec. rate in maize
Mol. weight	g/M	339.30	[1]	283.80	[1]	229.70	[1]
Solub. in water	g/L	15	[1]	0.480	[1]	0.009	[1]
Vapor press.	Pa	0.00569	[1]	0.004	[1]	0.00009	[1]
$LogK_{OW}$	L/kg	0.11	[1]	3.05	[1]	3.40	[1]
				3.13	[2]	3.04	[3]
				3.00	[4]	3.20	[4]
		0.11	**Selected value**	**3.05**	**Selected value**	**3.40**	**Selected value**
K_{OC}	L/kg	19-141	[4]	121-309	[4]	162-378	[4]
		80	Mean [4]	215	Mean [4]	270	Mean [4]
		19-390	[1]	61-369	[1]	162-333	[1]
		210	Mean [1]	215	Mean [1]	248	Mean [1]
				83-118	[5]		
				101	Mean [5]		
				123	[6]		
		145	General Mean	163	General Mean	259	General Mean
		390	**Selected value**	**118**	**Selected value**	**259**	**Selected value**
t50 in field	days	3-7	[4]	11-30	[4]	30-60	[4]
		5	Mean [4]	21	Mean [4]	45	Mean [4]
		2-14	[1]	6-49	[1]	6.5-149.8	[1]
			Mean [1]	28	Mean [1]	78	Mean [1]
			Median [1]	30	Median [1]	17	Median [1]
			[7]	12	[7]	20	[7]
				12	[8]	35	[9]
				23	[3]	45	[3]
				14	[10]	27	[10]
		5	General Mean	21	General Mean	38	General Mean
		5	**Selected value**	**21**	**Selected value**	**38**	**Selected value**

S3 Table. Calculation of herbicides repartition in the vegetated ditch using the fugacity model

Chemical	**Mesotrione**	**S-Metolach.**	**Terbuthyl.**
Molecular weight	339.30	283.80	229.70
Solubility in water (g/l)	15.000	0.480	0.009
Solubility in water (M/m^3)	44.209	1.691	0.039
Vapor pressure (Pa)	5.69E-03	3.70E-03	9.00E-05
Lipophilia: logKow (L/kg)	0.11	3.05	3.21
T (°C)	25	25	25
R (gas constant) ($Pa*m^3$)/(M*°K)	8.3136	8.3136	8.3136
Half-life (t50) (days)	5	21	38
Density of compartments (Di) (kg/m^3)			
Soil: Ds		1500	
Sediment: Dsed		1500	
Suspended solid: Dss		1500	
Air: Da		1.19	
Water: Dw		1000	
Biota: Db		1000	
Root: Dro		800	
Stem: Dst		800	
Foliage: Dfo		800	
Moles introduced (n)	0.007	0.045	0.049
Mass introduced (g)	2.25	12.75	11.25
Volumes of compartments (Vi) (m^3)			
Soil: Vs		12.680	
Sediment: Vsed		2.850	
Susp. Solid: Vss		0.052	
Air: Va		1256.893	
Water: Vw		76.830	
Biota: Vb		0.000	
Roots: Vro		0.279	
Stems: Vst		0.250	
Leaves: Vle		0.166	
Sum(Vi)		1350.000	
Partition coefficients			
Soil			

Soil: Koc (L/kg)	390.00	118.00	259.00
Soil: Koc (m^3/kg)	3.900E-01	1.180E-01	2.590E-01
%OCsoil=%OMsoil	2.00		
Kp=Koc*%OC/100 (L/kg) (=Cs/Cw)	7.805E+00	2.361E+00	5.183E+00
Soil (Cs/Cw): Kp (m^3/kg)	**7.805E-03**	**2.361E-03**	**5.183E-03**
Sediment			
%OCsed	4.00		
Ksed=Koc*%OCsed/100 (L/kg) (=Csed/Cw)	15.60	4.72	10.36
Sediment (Csed/Cw): Ksed (m^3/kg)	**1.560E-02**	**8.600E-03**	**1.036E-02**
Susp. Solid			
%OCss	4.00		
Kss=Koc*%OCss/100 (L/kg) (=Css/Cw)	15.60	4.72	10.36
Susp. solid (Css/Cw): Kss (m^3/kg)	**1.560E-02**	**8.600E-03**	**1.036E-02**
Air			
Air: Ka (M/pa*mc) (=1/RT)	**4.0342E-04**	**4.0342E-04**	**4.0342E-04**

Water			
Water: Kw=H=VP/S (Pa*m^3/M)	**1.287E-04**	**2.188E-03**	**2.297E-03**
Air/Water (Ca/Cw): Kaw=H' adim.=(H/RT)	**5.192E-08**	**8.825E-07**	**9.267E-07**
Biota (Aquatic biom.)			
LogBCF (0.85*logKow-0.7)	-0.61	1.89	2.03
BCF (dmc/kg) (=L/kg) (=Cb/Cw)	2.475E-01	7.807E+01	1.068E+02
Biota (Cd/Cw): BCF (m^3/kg)	**2.475E-04**	**7.807E-02**	**1.068E-01**
Root			
RCF (dmc/kg)=10^(0.77*logKow-1.52)+0.82	8.567E-01	7.558E+00	9.767E+00
Root: RCF (m^3/kg)	**8.567E-04**	**7.558E-03**	**9.767E-03**
Stem			
SCF (dmc/kg)=(10^(0.95*logKow-2.05)+0.82)*0.784*EXP(-((logKow-1.78)^2)/2.44)	2.078E-01	3.181E+00	3.665E+00
Stem: SCF (m^3/kg)	**2.078E-04**	**3.181E-03**	**3.665E-03**
Foliage			
Zw=1/H (M/pa*mc)	**7769.537**	**457.117**	**435.350**
Kaw=H' adim.=(H/RT) (=Ca/Cw)	5.192E-08	8.825E-07	9.267E-07
LogKaw	-7.28	-6.05	-6.03
Foliage: FCF (m^3/kg)=10^(-1.61+logKow-logKaw))/Da	**5.118E+05**	**2.623E+07**	**3.610E+07**

Coefficients summary			
Solubility in water (g/l)	1.500E+01	4.800E-01	9.000E-03
Vapor pressure (Pa)	5.690E-03	3.700E-03	9.000E-05
Lipophilia: Kow (m^3/kg)	1.288E-03	1.122E+00	1.622E+00
Soil: Koc (m^3/kg)	3.900E-01	1.180E-01	2.590E-01
Soil (Cs/Cw): Kp (m3/kg)	7.805E-03	2.361E-03	5.183E-03
Sediment (Csed/Cw): Ksed (m^3/kg)	1.560E-02	4.720E-03	1.036E-02
Susp. solid (Css/Cw): Kss (m^3/kg)	1.560E-02	4.720E-03	1.036E-02
Air: Ka (M/pa*mc) (=1/RT)	4.034E-04	4.034E-04	4.034E-04
Air/Water (Ca/Cw): Kaw=H' adim.=(H/RT)	5.192E-08	8.825E-07	9.267E-07
Water: Kw=H=VP/S (Pa*m^3/M)	1.287E-04	2.188E-03	2.297E-03
Biota (Cd/Cw): BCF (m^3/kg)	2.475E-04	7.807E-02	1.068E-01
Root: RCF (m^3/kg)	8.567E-04	7.558E-03	9.767E-03
Stem: SCF (m3/kg)	2.078E-04	3.181E-03	3.665E-03
Foliage: FCF (m^3/kg)	5.118E+05	2.623E+07	3.610E+07
Calculation of Zi [M/(m^3*Pa)]			
Soil: Zs=Kp*Ds*Zw	9.096E+04	1.619E+03	3.385E+03
Sediment: Zsed=Ksed*Dsed*Zw	1.818E+05	3.236E+03	6.765E+03
Susp. solid: Zss=Kss*Dss*Zw	1.818E+05	3.236E+03	6.765E+03
Air: Za=Ka=1/RT	4.034E-04	4.034E-04	4.034E-04
Water: Zw=1/Kw=1/H	7.770E+03	4.571E+02	4.354E+02
Biota: Zb=BCF*Db*Zw	1.923E+03	3.569E+04	4.649E+04
Root: Zro=RCF*Dro*Zw	5.325E+03	2.764E+03	3.402E+03
Stem: Zst=SCF*Dst*Zw	1.292E+03	1.163E+03	1.277E+03
Foliage: Zfo=FCF*Za	2.065E+02	1.058E+04	1.456E+04
Sum(Zi)	4.711E+05	5.874E+04	8.308E+04

Calculation of Zi*Vi (M/Pa)			
Soil	1.153E+06	2.053E+04	4.292E+04
Sediment	5.182E+05	9.224E+03	1.928E+04
Susp. Solid	9.454E+03	1.683E+02	3.518E+02
Air	5.071E-01	5.071E-01	5.071E-01
Water	5.969E+05	3.512E+04	3.345E+04
Biota	0.000E+00	0.000E+00	0.000E+00
Root	1.484E+03	7.703E+02	9.482E+02
Stem	3.224E+02	2.904E+02	3.186E+02
Foliage	3.436E+01	1.760E+03	2.424E+03
Sum(Zi*Vi)	2.280E+06	6.787E+04	9.969E+04
Calculation of Fugacity (Pa): f=n/Sum(Zi*Vi)	2.909E-09	6.620E-07	4.913E-07
Concentration (μg/L)=f*Zi*PM*1000			
Soil	8.98E+01	3.04E+02	3.82E+02
Sediment	1.79E+02	6.08E+02	7.63E+02
Susp. Solid	1.79E+02	6.08E+02	7.63E+02
Air	3.98E-07	7.58E-05	4.55E-05
Water	7.67E+00	8.59E+01	4.91E+01
Biota	-	-	-
Root	5.26E+00	5.19E+02	3.84E+02
Stem	1.27E+00	2.19E+02	1.44E+02
Foliage	2.04E-01	1.99E+03	1.64E+03

Chapter 4

Assessing water purification service in an integrated agricultural wetland within the Venice lagoon drainage system

Introduction

Wetland systems represent an important cornerstone for beneficial ecosystem services, especially in intensive agricultural landscapes. They provide a crucial suite of regulating, supporting, provisioning and cultural ecosystem services to regulate water flows and nutrient cycling, remove and detoxify excess fertilizers and pesticides, sequester carbon, enhance biodiversity and provide cultural and educational benefits to local communities (MEA, 2005; Swinton 2007; Power 2010; Borin and Malagoli, 2015). Wetlands can also play an important role in nutrient and sediment retention and water purification services, especially in the presence of shallow and surface water (Tanner *et al*., 2013; Tournebize *et al.,* 2013; Pappalardo *et al*., 2015). The water purification service is mainly performed by the complex physical, chemical and biological processes established within the "plant-soil-microorganism" system, so that wetlands can trap and retain 80 to 90% of sediment from runoff and eliminate 70 to 90% of entering nitrogen (N) (Borin *et al*., 2001; Jordan *et al*., 2011). Water purification is basically provided by different biogeochemical processes such as degradation of organic compounds under anaerobic conditions, suspended solids retention by filtration and sedimentation, nitrogen removal by uptake and denitrification (Vymazal, 2010). (Mthembu *et al*., 2013). The ability of natural wetlands to trap nutrients is well mimed by constructed or semi-natural wetlands that can assume even more importance in treating agricultural drainage water (Borin and Tocchetto, 2007; Otto *et al.,* 2016) by reducing N and P load and protecting surface and ground water. Indeed, "agricultural wetlands" efficiency in water purification is widely recognized, even if local conditions such as vegetation, climate and hydrology strongly affects performances (Gottschall *et al*., 2007). Depending on hydrology conditions and system management, different Constructed Wetlands (CWs) have been engineered and classified. They are generally divided into horizontal and vertical CWs, according to the flow direction; the former are further classified as Free Water Surface (FWS) and Sub-Surface CWs (Vymazal, 2010). Different combinations of hybrid designs of CWs are implemented in order to achieve greater treatment effect for pollution removal. In fact, FWS CWs resemble natural wetlands in appearance and are very effective in removal of organic compounds by microbial degradation and suspended solids by settling and filtration through the dense vegetation, plus abatement in biological oxygen demand (BOD), total nitrogen (TN) and

total phosphorus (TP) (Borin *et al.,* 2001). Generally, FWS CWs are set up in a shallow isolated basin or a sequence of sub-basins, with a water depth of 20-40 cm (Vymazal, 2010).

The selection of plant species for CWs plays a pivotal role in water purification performances. According to numerous studies the suitable species are emergent macrophytes, mainly due to the physical effects of the plant biomass such as reduction of wind speed facilitating sedimentation, provision of surface for attached microorganisms, oxygen release from roots and, finally, plant metabolism (Brix, 1994; Vymazal *et al.*, 2006; Gottschall *et al.,* 2007).

The macrophyte most used in CWs world-wide is *Phragmites australis*, both for horizontal subsurface flow and FWS CWs (Vymazal, 2011); its performance in nutrient uptake can reach up to 134 g N m^{-2} for TN and 13.6 g P m^{-2} for TP (Hernández-Crespo *et al*., 2015). Other typical macrophytes often planted in FWS CWs are *Typha angustifolia* L., *Canna indica* L., *Cyperus papyrus* L., *Juncus effusus* L., *Schoenoplectus lacustris* (L.) Palla, *Schoenoplectus californicus* (C.A. Meyer), *Phalaris arundinacea* L. (Vymazal, 2011). Even if CWs with one dominant botanical species showed individual differences in N removal (e.g. a *Typha* spp. CW showed removal of 565 mg N m^{-2} d^{-1} compared to 261 mg N m^{-2} d^{-1} by a *Scirpus* spp. CW), density of vegetation, rainfall regime and local ecological conditions may significantly affect water purification efficiency (Jaddhav and Buchberger, 1995; Bachand and Horne, 2001). Moreover, Floating Treatment Wetlands (FTW) have also been engineered to integrate CW systems due to their flexibility to apply to the local hydrological system and the particular design of the phytoremediation system (De Stefani *et al.*, 2011; Mietto *et al*., 2013). FTWs are innovative phytoremediation technologies that basically emulate a natural floating wetland "as a marsh of vascular vegetation having a significant mat of live and dead roots, peat and detritus, that floats over a layer of free water" (Sasser *et al*., 1991). Macrophytes installed on self-buoyancy mats cannot move out of the FTW, so they are potentially able to colonize the water body space required, and can extend the root system in a greater water column compared to conventional wetlands. The most common species tested in FTW are *P. australis*, *T. latifolia*, *J. effusus*, *P. arundinacea, Iris pseudacorus* L., *Carex spp*. L., *Glyceria maxima* (Hartman) Holmb., *C. indica*, and *Chrysopogon zizanioides* (De Stefani *et al*., 2011). Performances in pollutant

removal are also relevant as they can reduce important parameters such as 33-68% of chemical oxygen demand (COD), 66-95% of suspended solids (Van Acker *et al*., 2005; Mietto et *al*., 2013). FTWs are also highly efficient in the removal of some nutrients, showing abatement of almost 50% for TN and 22% for NO_3^- in five days of detention time (Lianpeng *et al.,* 2009). However, the choice of botanical species is crucial in terms of survival rate and therefore water purification performances. Previous studies suggested selecting local species or well-adapted plants that exhibit vigorous growth in polluted water under the local climate regime (Headly and Tanner, 2006; De Stefani *et al.,* 2011; Pavan *et al*., 2015).

The general aim of this study is to assess the water purification service of a 3.2 ha integrated wetland system to control diffused nutrient pollution from a conventional cropping system; the specific aims are focused on two different phytoremediation systems, a FWS CW and a FTW system, to estimate performance in reduction of NO_3^- and TN in water flow, quantify the survival rate of FTW species, and screen survival, biometrics and biomass production of seven macrophytes adapted for FTW.

Material and Methods

Geographical framework and the integrated agricultural wetland

The study area is located within the Venice lagoon drainage system (NE of Italy), a dense minor hydrographic network directly managed by the *Adige Euganeo Land Reclamation Authority*. This hydrographic network is crucial for two important roles: draining water from wide "lowlands" lying below the mean sea level into the Venice Lagoon system and providing a water supply to the farms (Pappalardo *et al*., 2015). The experiment is conducted on the "Tenuta Civrana" farm (365 ha) at 45.166° N and 12.066 E, in the Province of Venice (Cona, VE). It is land obtained from the drainage of the "Cavarzerano" marshes performed in the 1930s and contains natural environments such as lowland forests and wet environments (Fig. 1).

The climate is sub-humid (Köppen climate classification), with mean annual rainfall of 850 mm, fairly uniformly distributed throughout the year. The temperature increases from January (average minimum value: -1.5 °C) to July (average maximum 27.2 °C).

The integrated agricultural wetland covers 3.3 ha and was created in 2014 by restoring a semi-natural wetland and implementing five sub-basins in a FWS CW. At the outlet, the water flows through a subsurface pipe into a vegetated channel 470 m long that has been used to create a second phytoremediation system, the FTW (Fig. 1). The farm and integrated agricultural wetland are fed by a water diversion from the “Canale dei Cuori”, one of the main channels draining water from the surrounding territory.

Figure 1 - A. Map of the Free Water Surface Constructed Wetland (FWS CW): white dots are sampling points and white narrows represent the flow direction (High-resolution imagery, Digital Globe, winter 2015); B. Unmanned Aerial Vehicle image during spring; C. The Floating Treatment Wetland system, flow direction and sampling points; D. *L. Salicaria* flowering in the floating system (F2)

GIS analyses and weather data

Due to the peculiar geomorphology of the territory, a preliminary dGPS survey was performed in 2013 to investigate the microtopography and drainage system of the area. By analysing aerial images (satellite and UAV images) and processing Digital Terrain Models (DTM) in GIS environment, the experimental site has been set up for agro-environmental monitoring. 16 geo-referenced spots were identified for sampling and measuring physical parameters of water. Sampling points follow the water flow from the inlet to the outlet in both CWs. Moreover, qualitative and quantitative information from fieldwork activities, such as pictures of the basins and riparian zones, the floating barriers and the agglomeration of plants, have been georeferenced to analyse the spatial evolution of the system and its components. In order to have access to the most reliable climate dataset, the nearest official weather station at 4.2 km from the experimental site was used (Cesia, ARPAV station, Veneto Region). Validated weather data such as the daily cumulative precipitation and temperature were collected during 2014 and 2015, in order to analyse rainfall events and thermic trends (Fig. 2).

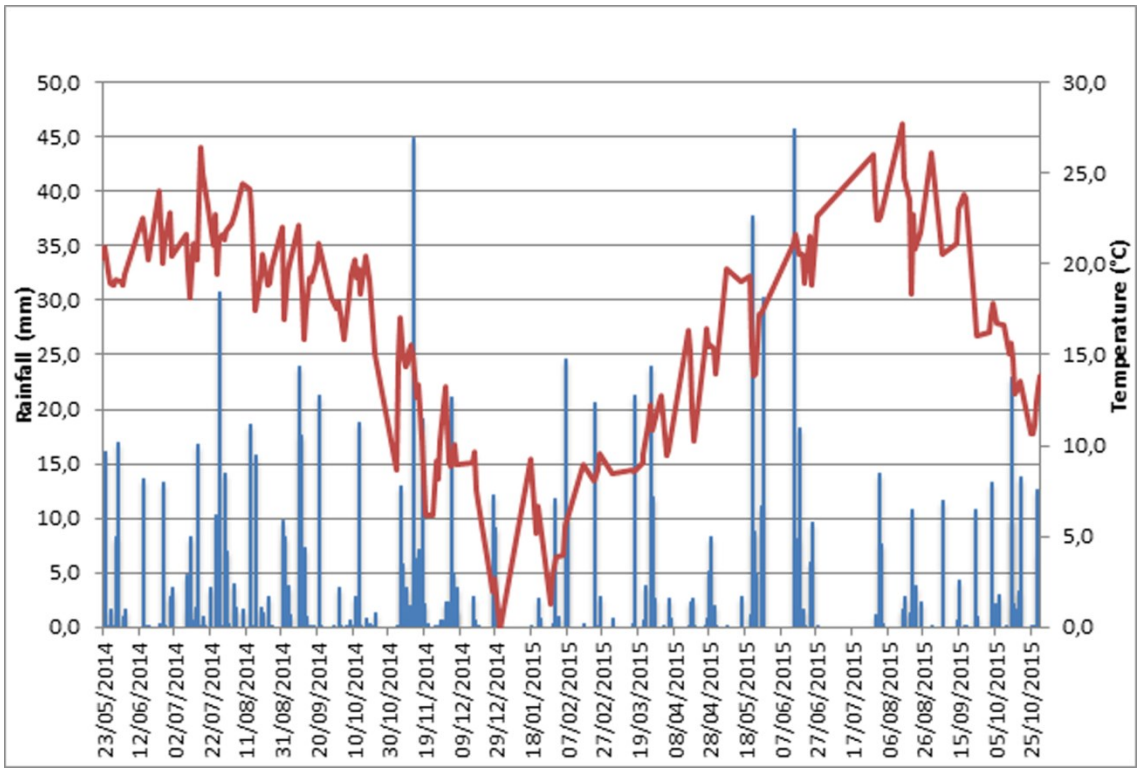


Figure 2 - Daily cumulative precipitation and temperature (°C) in 2014-2015

The Free Water Surface Constructed Wetland

The FWS CW system covers 2.4 ha and the hydraulic system is managed to feed, by gravity, five sub-basins during the crop season (March-November). Water flow passes through a set of sequential basins connected by sub-surface pipe (Fig. 1). The mean detention time is about 8-10 days. Due to the climate regime and geomorphology of the area, in winter the water flow from the canal is intentionally interrupted at the inlet, leading to the partial drying out of the basins. In spring (mid-March) the main canal restarts to feed the downstream basins, filling the FWS CW system. It is structured in two main sub-trapezoidal basins (B1 and B2) derived from restoring a semi-natural wetland, with 0.5 and 1 ha of surface area respectively; water depth is around 0.6 m in B1 and 0.4 m in B2. Hence, three other sequential downstream basins (B3, B4, and B5) with a shallower depth (0.3-0.4 m) have been created to complete the water purification treatment. Wetland vegetation has been restored and integrated with several local macrophytes that have established along riparian zones and inside the basins: *P. australis, T. latifolia, I. pseudacorus, P. arundinacea, Menta aquatica* L*., Carex* spp., *Juncus* spp. Through the creation of four islands vegetated with *P. australis, Juncus* spp. *and Carex* spp., B1 and B2 basically have the task of slowing down the water flow, allowing a first stabilization of suspended solids. B2 is the most vegetated, with *P. australis* fully colonizing the banks (Fig. 1). The last three basins (B3, B4 and B5) have been planted with *M. aquatica, Carex* spp., *P. arundinacea and P. australis* in 2014; however, vegetation is still in the process of establishment. Instead, two years after implementation, the vegetation in B1 and B2 is showing a gradual naturalization, especially *P. australis.*

The Floating Treatment Wetland

After a first stage of purification, water flow from the FWS CW basins enters the FTW system, set up along the canal (Fig. 1). It is worth noting that the FTW is an open system, probably receiving drainage water from croplands bordering the northern side. The FTW system is based on a set of self-buoyant mats, rectangular (50 x 90 cm), with eight windows that have grids to sustain plants. The combined morpho-functional floating system is the

"TECH-IA®", a technology of Padua University spin-off PAN Ltd.; it is a floating structure, support for aquatic macrophytes, made in a recyclable material, ethylene vinyl acetate (EVA), rectangular in shape and weighing about 2 kg (De Stefani *et al*., 2011; Mietto *et al*., 2013; Pavan *et al*., 2015). Single units were assembled to compose three vegetated floating barriers of 120 units each (F1, F2 and F3), divided into 6 modules (20 units per module). The floating units were tied using plastic strips and maintained in situ by means of ropes firmly anchored to the shore with stakes (Fig. 1). Flexibility of the barriers' movement was ensured so that they can follow the water level in the main downstream channel and not incur damage to root systems. Two plants were transplanted into each unit, for a total of 40 plants per module and 240 per floating barrier.

The first upstream floating barrier (F1), the first to meet the water from FWS CW, was vegetated in May 2014 with 240 plants of *Carex* spp. The F2 barrier was vegetated in May 2014 with six different macrophytes: *Sparganium erectum* L*., S. lacustris*, *M. aquatica, Caltha palustris* L*., P. arundinacea, J. effusus* for a total of 240 plants. This barrier was re-vegetated in April 2015 with 240 plants of *Lythrum salicaria* L. The F3 barrier is composed of 240 plants of *I. pseudacorus,* vegetated in 2014 and re-vegetated in 2015. The three barriers are about 30 meters apart and are kept at a certain distance from the shore so that the selected macrophytes do not compete with wild plants on the banks. The outlet is at the end of the canal, with a sub-surface pipe discharging into agricultural ditches. The water is used for irrigation in the summer.

Fieldwork activities: water sampling, physical parameters and plant survey.

170 representative water samples were collected periodically during the crop season in 2014 and 2015; generally twice per month and after important rainfall events for a total of 17 dates in spring, summer and autumn of the two years in 10 different points at the inlets and outlets of FWS CW and FTW (Fig. 1). Each representative sample is a bulk of 3 replicates obtained at the same point separated by an interval of 30 minutes.

Some chemical parameters of water were measured to determine water quality and efficiency of depurative systems. Electric conductivity (µS/cm), dissolved oxygen (mg/L), pH and temperature (°C) were measured at inlets and outlets of wetland sub-basins as well as in the main channel containing the floating systems using HQD (HACH Lange HQ 40d), a portable multitasking device used to assess some of the physical and chemical properties of water. Water turbidity was measured in means of Nephlometric Turbidity Units (NTU) using a portable turbidimeter (HACH 2100P Turbidimeter).

The survival rate of plants in the FTW system (F1, F2, and F3) was assessed periodically during the two vegetative seasons counting the number of living plants in each of the three barriers monthly from May to August 2014 and from April to October 2015. The total survival percentage of each species was calculated at the end of the season.

Plant height and root system length and width were used as parameters to monitor the performance of plants in the floating systems and test their capacity for adaptation and establishment. No plant measurements were taken in 2014 due to the newly set out floating systems not allowing enough time for establishment and sufficient growth of plant species. In 2015, plant height (above mat) and root length (below mat) were measured twice in June and October, while root system width was measured in October. Results were analysed and presented as means of Medians, 1st and 3rd quartiles.

Laboratory activities: biomass production and chemical analyses for N and P determination

A biomass production survey was done on plants established in the FTW system. In October 2015, 12 random plant samples were each taken for *Carex* spp., *L. salicaria* and *I.*

pseudacorus and divided into aerial and root system. Total fresh weight was quantified on site; fresh matter samples were dried in a force draught oven at 65 °C for 35 h, milled at 2 mm (Cutting Mill SM 100 Comfort, Retsch, Germany); in addition, 10 g ground sub-samples were then dried at 130 °C to measure the residual moisture content. Biomass production data has been expressed in terms of grams per meter square ($g\ m^{-2}$).

Above and below ground dry matter of each plant sample was tested using the standard Kjeldahl method to determine Total Kjeldahl Nitrogen (TKN) and spectroscopic methods (ICP-OES, SPECTRO ARCOS) to determine TP concentrations (AOAC, 2000; Arduino and Barberis, 2000). Nitrogen and phosphorus uptakes by plants were calculated in terms of dry matter per square meter of floating mats (above and below mats separately).

For water samples, TKN was determined using the standard Kjeldahl method (AOAC, 2000; Arduino and Barberis, 2000), nitric nitrogen (NO_3^-) was determined according to Cataldo *et al.* (1975), TN content for each sample was calculated by summation of TKN and NO_3^-. TP was negligible as it did not reach the instrumental detectable threshold; orthophosphate (PO_4^{-3}) was determined for each of the samples in parts per million (ppm) using the standard colorimetric ascorbic acid method (Murphy and Riley, 1962; Edwards *et al.*, 1965). Results were analysed and represented by box and whiskers plots. Data of chemical and physical parameters of water did not show normal distribution so they were statistically analyzed using the Kruskal–Wallis nonparametric test (accepted at the level of $p<0.05$).

Results and discussion

Water purification assessment

During the 2014 and 2015 crop seasons, median concentrations of TN at the inlet (B1) and outlet (B5) of the FSW CW were 2.43 and 1.79 ppm respectively; median values were 1.65 ppm at the inlet (F1 IN) and 1.39 ppm at the outlet (F3 OUT) of the FTW system set up along the canal (Fig. 3). However, the Kruskal–Wallis test did not show any statistical differences in concentration decrease through the two phytoremediation systems. These results are probably due to the short life of the experimental site and phytoremediation macrophytes established along banks and vegetated barriers, in both the FSW CW and

FTW system. Decreases in $N\text{-}NO_3^-$ concentrations are also not notable because the concentration in the drainage water that feeds the integrated wetland system in B1 and F1 is generally low (always below 10 ppm). However, it is worth noting that, after three days of rainfall (25-27 of March 2015) with a cumulative value of 42.4 mm, TN concentration notably increased at B1 IN and B2 IN to median values of 6.34 and 6.04 ppm respectively; therefore, it decreased throughout the basins to reach 1.29 ppm at B5 OUT (Fig. 3).

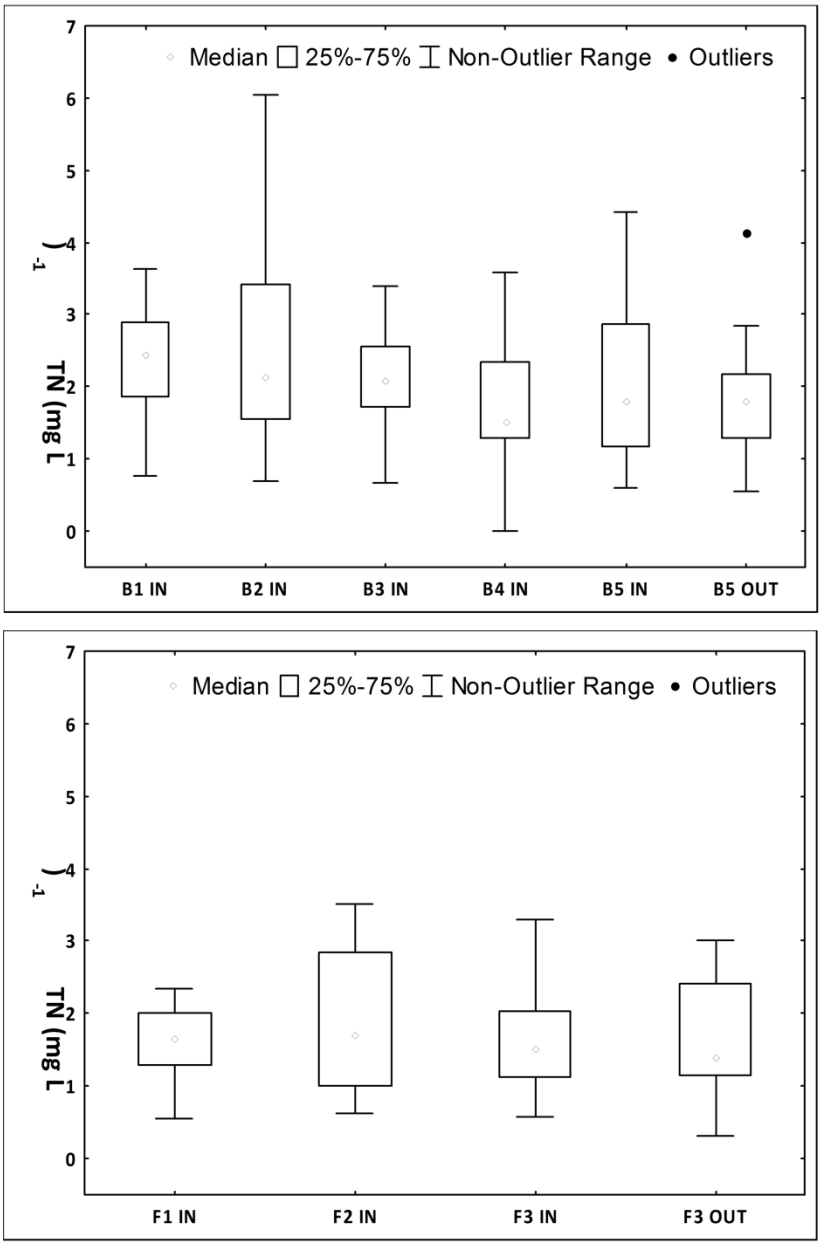


Figure 3 - Box and plots with total N concentration in the integrated wetland system: FWS CW System (sub-basins) and Floating Treatment Wetland system (FTW) during two successive seasons, 2014 and 2015.

NO_3^- contributed most to this increase recording 5.23 and 4.96 ppm at B1 IN and B2 IN respectively and decrease to 0.09 at B5 OUT. In the same manner, TN decreased from 1.77 ppm at F1 IN to 1.31 ppm at F3 OUT and NO_3^- decreased from 0.91 to almost zero ppm (F1 IN to F3 OUT). The high TN and NO_3^- contents at inlets may be related to the rain that fell during the period of fertilization (March-April) for maize and other crops in the area. A possible diffused contamination by nutrient run-off from the agricultural basin could therefore be identified as the direct source (Fig. 4).

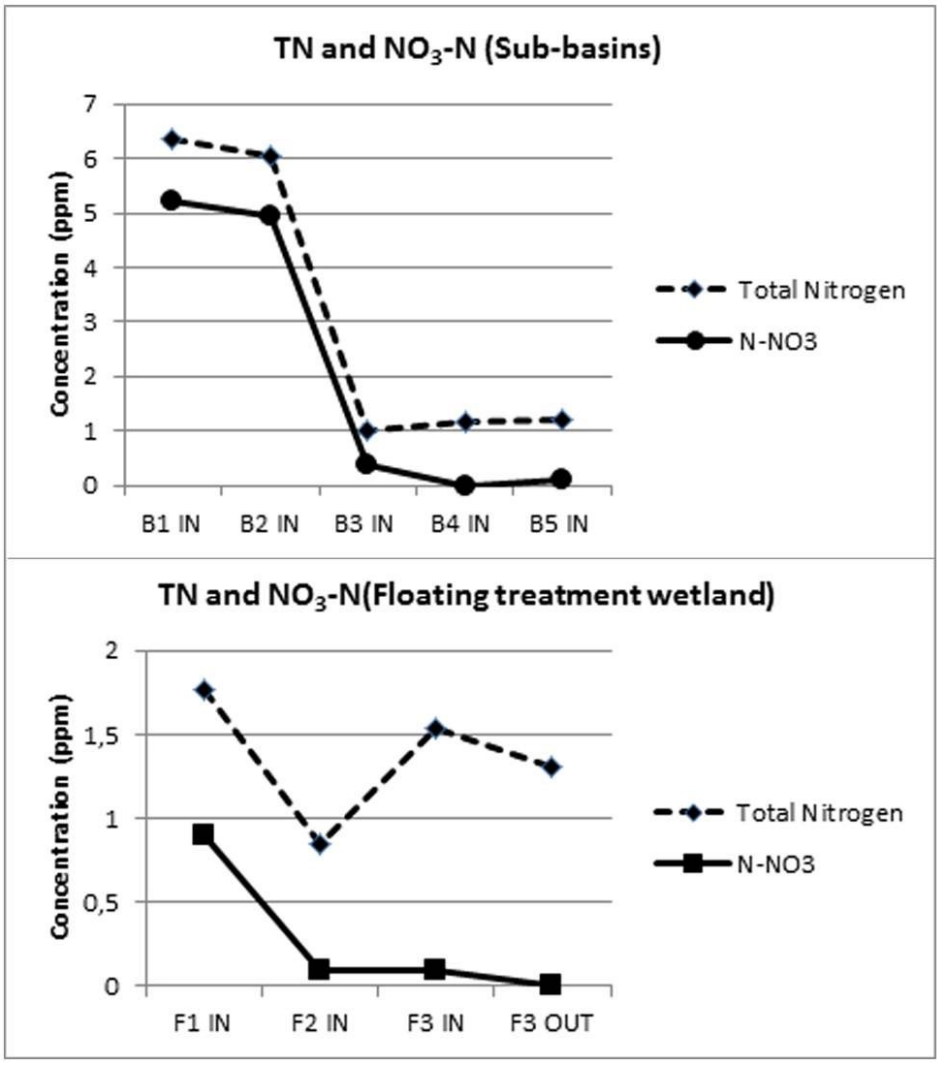


Figure 4 - Line chart with total N and nitrate concentration in FWS CW system (sub-basins) and Floating Treatment Wetland system (FTW) on 30 March 2015.

Decrease in TN and NO_3^- through the wetland sub-basins (FTW CW) and main channel (FTW) can be attributed to nitrification and denitrification processes (Kadlec and Knight, 1996; Kadlec and Wallace, 2009; Maltais-Landry *et al*., 2009; Vymazal, 2007 and 2010;

Mthembu *et al*., 2013). Other mechanisms that can lead to this decrease include assimilation by plants and reduction into ammonia (Kadlec and Wallace, 2009; Vymazal, 2007 and 2010). Such a decrease in TN and NO_3^- concentrations may suggest an interesting depurative effect of the wetland integrated system, at least during a combined event of persistent rainfall after an intensive fertilization in the surrounding cropland. Total P was not detectable in any samples obtained during the early stages of the study. Conversely, determination of orthophosphates (PO_4^{-3}) was used as a tool to determine available traces of phosphorus forms. Concentrations of PO_4^{-3} were very low in water with median value always lower than 0.03 ppm. According to Vymazal (2010), "phosphorus retention is low in all types of constructed wetlands and CWs are seldom built with phosphorus being the primary target of the treatment".

Concerning water turbidity, median values in the FWS sub-basin system fluctuated between high values of 152 NTU in B4 IN and 148 NTU in B3 IN and values as low as 78 and 68.5 NTU for B5 OUT and B1 IN during the 2014 season. Although they did not show significant variation among the sampling points, these fluctuations may indicate instability of soil particles in the newly established wetland system. In the FTW system, values were lower downstream in the canal (56.6 and 55.7 NTU in F1 IN and F3 OUT) which may indicate more soil stability in this area. On the contrary, during 2015, turbidity considerably decreased in FWS sub-basin systems with median values as low as 43.4 NTU in B1 IN and 45.3 in B5 OUT (Fig. 5). This decrease may suggest a better establishment and consolidation of the wetland system that leads to the precipitation of sediments (low re-suspension of particles) (Petticrew and Kalff, 1992) and improvement of water quality (O'Geen *et al.*, 2010). At the same time, turbidity in the FTW system decreased along the canal from 55.4 NTU at F1 IN to 28.6 NTU at F3 OUT, highlighting a better stability of soil and better establishment of root systems of floating plants preventing the re-suspension of sediments (Horppila and Nurminen, 2001, 2003 and 2005). Turbidity of water may be used as a physical parameter to evaluate changes in stability of total soluble solids in both sub-basins (FWS CW) and main downstream channel (FTW) (Fig. 5).

In addition, low water velocity in the FWS sub-basin system promotes the sedimentation of TSS (Kadlec and Wallace, 2009). Median values of other physical parameters like electric conductivity, pH and dissolved oxygen are given in Table 1 as supporting data.

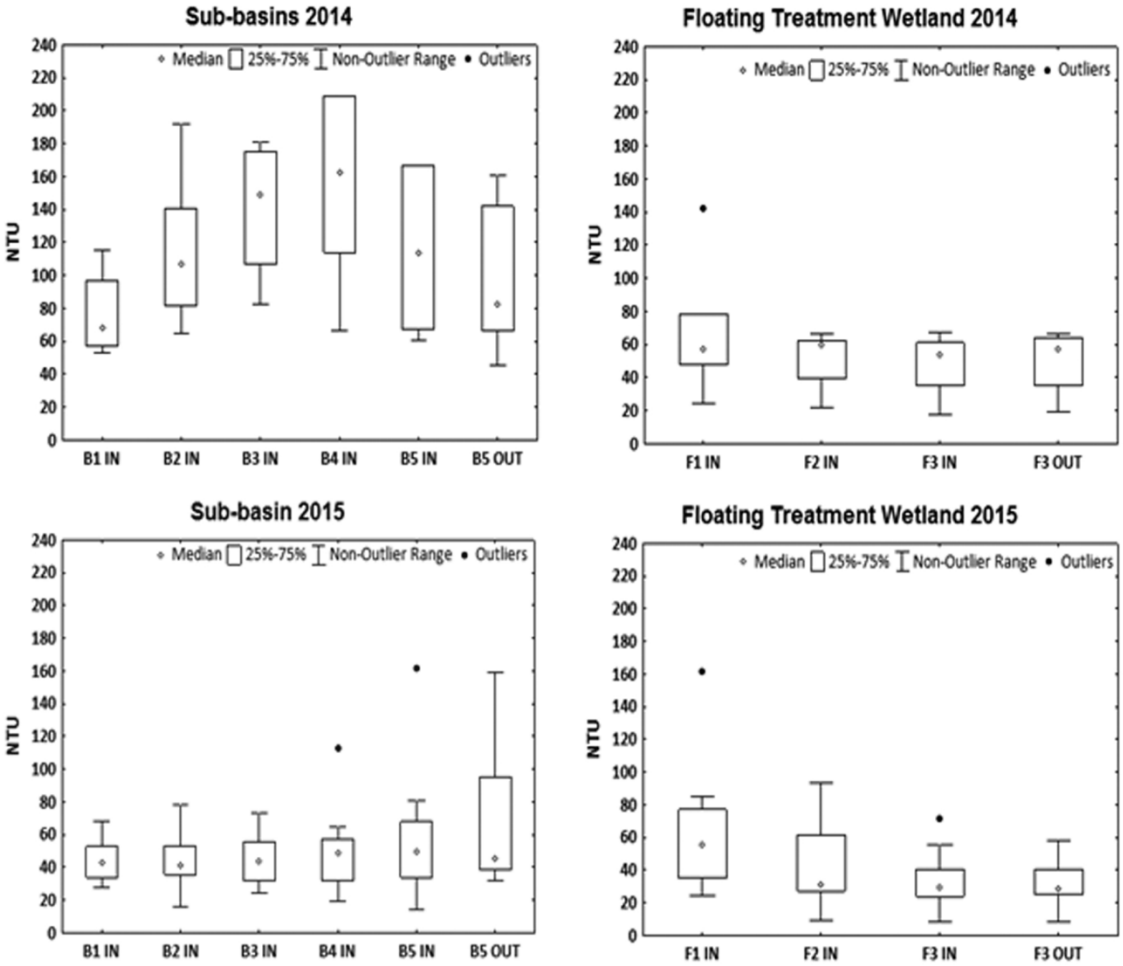


Figure 5 - Box and plots representing turbidity (NTU) in wetland sub-basins (FWS CW) and mainstream channel (FTW) during the seasons 2014, 2015.

	Median									
Parameter	B1 IN	B2 IN	B3 IN	B4 IN	B5 IN	B5 OUT	F1 IN	F2 IN	F3 IN	F3 OUT
pH	7.72	8.16	8.28	8.08	8.18	8.19	8.04	8.08	8.00	8.11
EC	721	746	720	682	730	762	1069	1140	1195.5	1203.5
O2 (mg/l)	10.14	11.17	8.81	9.79	9.61	8.75	8.24	8.93	9.39	8.80

Table 1 - Physical parameters of water represented as supportive data

Plant survival in the Floating Treatment Wetland system

Plant species in FTW system showed different survival rates between the two vegetative seasons 2014 and 2015 (Fig. 6). In the first season, survival rate varied between 3-100%; *P. arundinacea* and *M. aquatica* exhibited the highest survival rate during August 2014 with 100% survival, followed by *Carex* spp. (98%), *J. effusus* (88%), *C. palustris* (73%) and *I. pseudacorus* (48%). *S. lacustris* and *S. erectum* showed the lowest rates, 8 and 3% respectively. However, all plant species reached the end of the season, according to their natural cycle. In the second season (2015), only *Carex* spp. survived the winter and completely regrew during spring; other species did not and had to be replaced with new plants. *L. salicaria* expressed the highest survival rate (95%) followed by *Carex spp.* (82%) and *I. pseudacorus* (48%). In autumn-winter, all three species went into senescence. *Carex* spp. proved great adaptability and a high tendency to establish in FTW, surviving two successive seasons with a high rate (82%) and large number of living plants (33 out of 40 plants per 10 m^2). *L. salicaria* showed great stability and a steady growth habit throughout the season with the highest survival rate (95%) and largest number of living plants (38 out of 40 plants per 10 m^2). *I. pseudacorus* did not show much tendency to establish and grow in the second season in comparison with other species, with the lowest survival rate (48%) and fewest living plants per 10 m^2 (16 out of 40 plants). Low survival rate of *I. pseudacorus* can also be related to some alien animal species such as *Myocastor coypus* feeding on plants.

L. salicaria, a depurative and competitive macrophyte (Jacobs, 2008), selected as a native species commonly growing along riparian zones, is a promising plant for use in FTW systems.

Plant growth in the Floating Treatment Wetland system

In 2015, plant height (above mat) and root length (below mat) were measured twice in June and in October while root system width was measured in October (Table 2). *L. salicaria* showed the maximum increase, with median value 59.5 cm in October versus 33.5 cm in June; *I. pseudacorus* showed median values of 24 cm in June and 37.5 cm in October, which were very low in comparison with similar studies. De Stefani (2012) reported median plant height values for *I. pseudacorus* of 136 and 116 cm at the end of the season in

two different experiments. On the other hand, *Carex* spp. did not show much increase in plant height with median values of 59.5 and 60 cm in June and October (92 cm was recorded for *Carex elata* Gooden. by Salvato and Borin, 2010). *Carex* spp. most probably attain an increase in density and bulkiness of leaves, contributing to plant width, rather than an increase in plant height. Regarding root depth, *I. pseudacorus* exhibited the maximum increase with median values 16 and 76 cm in June and October (median values of 46 and 55.5 cm for root length were recorded by De Stefani (2012) at the end of the season in two different experiments, while root length reported by Pavan (2014) was 16cm at the end of the season). *Carex* spp. showed moderate increase in root length (median value of 36 and 49 cm in June and October). *L. salicaria* did not show any increase in root length with median values of 48.5 cm in June and 42.5 cm in October. Increases in root length for the three species can be related to the growth habit of each species as well as nutrient translocation, with *Carex* spp. and *L. salicaria* showing increase in bulkiness and width while *I. pseudacorus* showed more increase in root length, exceeding the maximum length (30 cm) described by Jacobs *et al.* (2011). This increase may be attributed to nutrients contributing to root length rather than aerial part height. Root system width was measured in October 2015 only where maximum width attained by representative samples for each species was recorded. Median values for maximum root system width for *Carex* spp. and *L. salicaria* were similar at 16.5 and 15.5 cm respectively while *I. pseudacorus* showed a median value of 7.5 cm.

		Carex* L. *spp.			***Lythrum salicaria* L.**			***Iris pseudocorus* L.**		
Plant character	**Date**	**Median**	**25%**	**75%**	**Median**	**25%**	**75%**	**Median**	**25%**	**75%**
Plant Height	Jun-15	59.5	40	69	33.5	22	38.25	24	15.15	32.75
	Oct-15	60	60	77.25	59.5	37.5	83.75	37.5	34.25	42.75
Root Depth	Jun-15	36	28	42.25	48.5	38.75	53.25	16	11.25	21.75
	Oct-15	49	45	61.5	42.5	40	47	76	63.5	89
Root system width	Oct-15	16.5	14.25	20	15.5	13.25	20.75	7.5	6.25	9

Table 2 - Plant growth dimensions for the three species during June and October 2015

Observations showed bulkier and stouter root systems for *Carex* spp. and *L. salicaria* than *I. pseudacorus*, which tended to increase in length rather than width. According to Mthembu *et al.* (2013), the potential rate of nutrient uptake by plants is determined by plant growth rate and the concentration of nutrients in the plant tissues, thus nutrient storage in the plant is dependent on plant tissue nutrient concentrations and plant biomass accumulation. Based on this, the ideal characteristics for plants to be used as macrophytes in wetland systems are fast growth rate, high tissue nutrient content and the ability to attain a high standing crop (plant sustainability).

Plant biomass production and nutrient uptake

Carex spp. ranked first regarding dry biomass production with a total average of 433.13 g m^{-2}, followed by *L. salicaria* with a total average of 210.32 g m^{-2}. *I. pseudacorus* scored least biomass production with a total average of 106.95 g m^{-2}. For the three species, the below ground mat (root system) biomass production was higher than the above mat (aerial parts); biomass production of *Carex* spp., the highest, averaged 266.94 g m^{-2} (62%) for below mat biomass versus 166.19 g m^{-2} (38%) for above mat biomass which is almost half of the above mat biomass production reported by Salvato and Borin (2010) for *C. elata* (349 g m^{-2}). *L. salicaria* came in second place with average below mat biomass 174.61 g m^{-2} (83%) and above mat biomass 35.71 g m^{-2} (17%), with *I. pseudacorus* ranking last (average below mat biomass 86.73 g m^{-2} (81%) and above mat biomass 20.22 g m^{-2} or 19% of total biomass) (Table 3). *Carex* spp. exhibited the best performance in terms of above, below mat and total biomass production, proving great stability and establishment in the second season. *L. salicaria* showed good performance and high stability ranking in second place for above, below mat and total biomass production, though it was only introduced during this season and was already in senescence stage during sampling. *I. pseudacorus* did not seem to adapt well in the second season with the least above, below mat and total biomass production. Results of biomass production for *I. pseudacorus* are in contrast with those given by De Stefani (2012) and Pavan *et al.* (2015), which otherwise confirm the suitability and increased productivity of this species in similar FTWs; De Stefani (2012) reported median values of 3693 and 1516 g m^{-2} for above mat dry biomass in two different experiments, while the below mat dry biomass reached 3346 and 801 g m^{-2} in the same

experiments. Median values for above mat dry biomass of *I. pseudacorus* recorded by Pavan (2015) reached 180 and 500 g m^{-2} in two successive seasons. However, it is worth noting that this experiment was set up on an open wetland in an agricultural landscape; during agro-environmental monitoring activities *M. coypus* were observed feeding on *I. pseudacorus*.

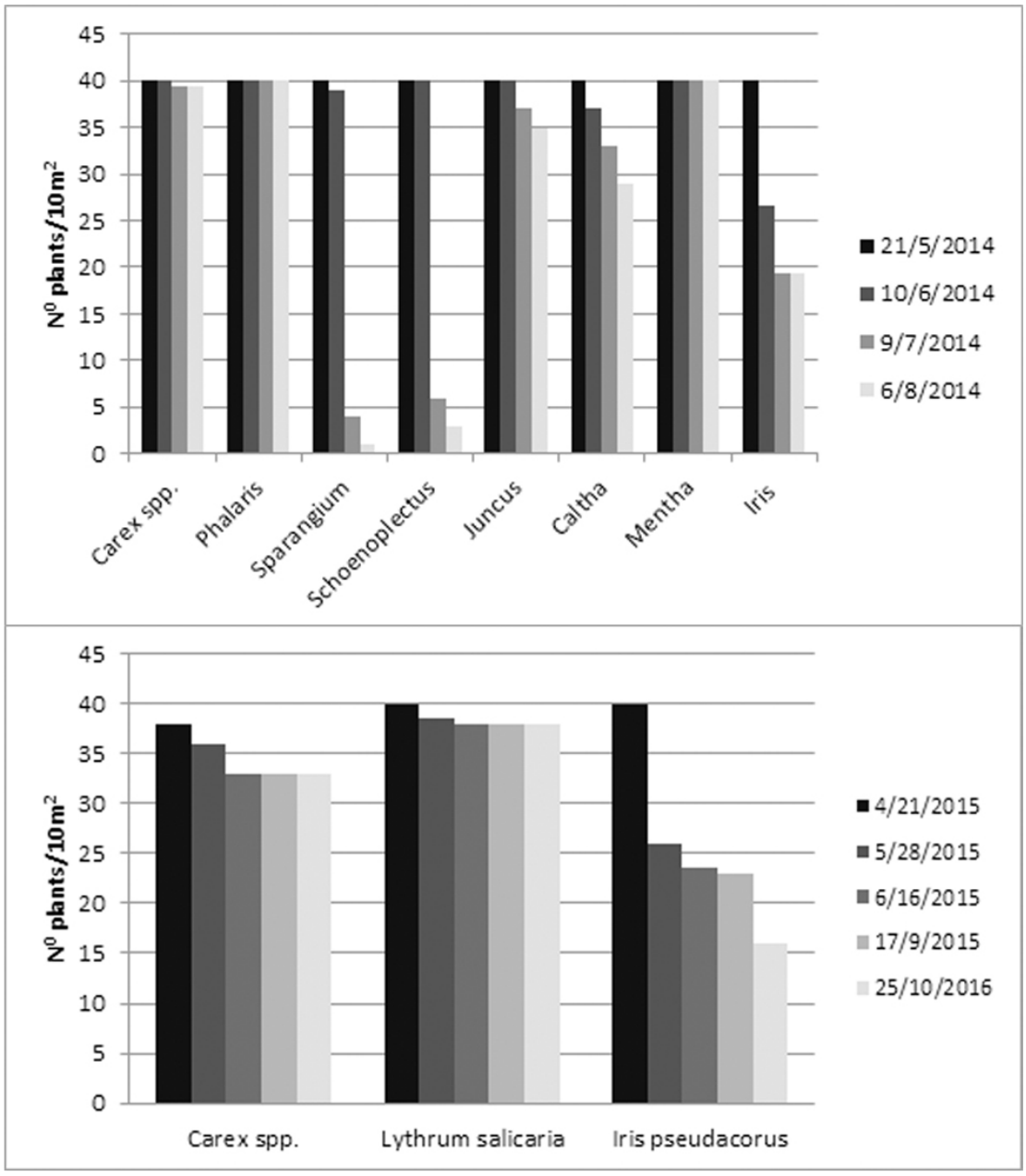


Figure 6 - Floating Treatment Wetland system (FTW): number of surviving plants per 10 m^2 for each species during two successive seasons (2014 and 2015)

Total nitrogen concentration in total dry biomass was closely related in the three species (1.12% in *Carex* spp. and *L. salicaria*, 1.02% for *I. pseudacorus)* but varied between above and below mat plant parts with higher nitrogen concentration in below mat parts averaging 1.21, 1.19 and 1.04% for *Carex* spp., *L. salicaria* and *I. pseudacorus* respectively. Average above mat nitrogen concentration for *Carex* was 1.02% (1% was reported by Salvato and Borin, 2010) followed by *I. pseudacorus* (0.91%) and *L. salicaria* (0.64%). *Carex* spp. showed the highest nitrogen concentration in above and below mat dry biomass, indicating efficient performance. Although *L. salicaria* showed high nitrogen concentration in below mat biomass it had the least concentration among the three species in above mat biomass, which could be related to senescence of aerial parts and relocation of nitrogen to the root system (Vymazal, 2007). Nitrogen concentrations for *I. pseudacorus* were lower than those reported by De Stefani (2012) and Pavan (2015), which reached up to 4.62% for below mat and 2.77% for above mat dry biomass. In terms of nitrogen uptake, *Carex* spp. showed a total uptake of 4.84 g m^{-2} with higher uptake through roots (3.19 g m^{-2}, 66% of total uptake) followed by *L. salicaria* with total uptake of 2.35 g m^{-2} (2.11 g m^{-2} (90%) though roots). *I. pseudacorus* showed the least uptake (total 1.09 g m^{-2}, below mat 0.92 g m^{-2} or 84% of total uptake). Nitrogen uptake by *I. Pseudacorus* was also very low in comparison to results found by De Stefani (2012) and Pavan (2015), with values up to 115 g m^{-2} for below mat and 70 g m^{-2} for above mat uptake.

Total phosphorus concentration was not very high in relation to nitrogen concentration, being highest in *L. salicaria* (0.09%) followed by *Carex* spp. and *I. pseudacorus* (0.07% for both). Like nitrogen concentration, phosphorus content was higher in below mat than above mat biomass. *L. salicaria* had the highest phosphorus concentration in roots (0.1%), *Carex* spp. and *I. pseudacorus* had nearly same concentration (0.08 and 0.07%). Phosphorus concentration for *I. pseudacorus* was low in comparison with that indicated by Pavan (2015), which reached 0.33%. Total phosphorus uptake was highest for *Carex* spp. (0.31 g m^{-2}), with maximum uptake through the root system (0.24 g m^{-2}, approx. 78% of total uptake). *L. salicaria* ranked second with total uptake 0.2 g m^{-2} (0.185 g m^{-2} (93%) in roots) with the least uptake by *I. pseudacorus* (total 0.074 g m^{-2}, 0.066 g m^{-2} (89%) in roots). For the three species, phosphorus uptake was just in traces through aerial parts, with least for *L. salicaria* due to senescence and translocation to roots.

According to Hernández-Crespo *et al*. (2015), the nutrient concentration is inversely correlated with the quantity of aboveground biomass *i.e.*, as above ground biomass increases, nutrient concentration decreases as most of the nutrients are already used by the plant for growth and performance during the peak of the season (Mthembu *et al.*, 2013). In this study, a higher concentration of nutrients was located in the root system due to the translocation of most nutrients nearing the senescence period (Bonaiti and Borin, 2000; Vymazal, 2007).

	Above mat Dry			Below mat Dry			Total		
Parameter	*Carex* L.	*Lythrum salicaria* L.	*Iris pseudacorus L.*	*Carex* L.	*Lythrum salicaria* L.	*Iris pseudacorus L.*	*Carex* L.	*Lythrum salicaria* L.	*Iris pseudacorus L.*
DM (g/m^2)	166.1 ± 29.40	35.71 ± 6.06	20.22 ± 3.11	266.94± 57.36	174.61 ± 24.25	86.73 ±12.56	433.13	210.32	106.95
N% (plant DM)	1.02 ± 0.09	0.64 ± 0.12	0.91 ± 0.19	1.21 ± 0.07	1.19 ± 0.11	1.04 ± 0.11	1.12	1.12	1.02
N uptake (g/m^2)	1.65 ± 0.28	0.24 ± 0.043	0.18 ± 0.02	3.19 ± 0.66	2.11 ± 0.312	0.92 ± 0.14	4.84	2.35	1.09
P% (Plant DM)	0.04 ± 0.008	0.03 ± 0.008	0.04 ± 0.018	0.08 ± 0.018	0.10 ± 0.015	0.07 ± 0.015	0.07	0.09	0.07
P uptake (g/m^2)	0.068 ± 0.013	0.013 ± 0.002	0.008 ±0.001	0.240± 0.057	0.185 ± 0.029	0.066 ±0.013	0.308	0.198	0.074

Table 3 - Average biomass production, nutrient concentrations and uptake for the three species

Conclusion

Although abatement percentage has not yet been calculated through the integrated wetland system and decreases in the concentrations of nitrogen through the system were not significant (mainly related to the low concentration of nitrogen in the initial inlet point (B1 IN) as well as the newness of the experimental site), a generally promising depurative effect appears from the concentration trend throughout the system. This effect is notable during March 2015 as emphasized by the major decrease in TN and NO_3^- concentrations throughout the wetland sub-basins (FWS CW) and downstream channel (FTW) after a combined event of intensive rainfall and crop fertilization run-off. Phosphorus concentrations were almost negligible. Monitoring the vegetation in the floating treatment wetland system, *Carex* spp. showed the best adaptability through high survival rate, hardiness and continuity over two successive seasons, highest plant parameters, especially biomass production, as well as highest nitrogen and phosphorus uptakes. *L. salicaria* showed great stability, excellent growth performance during the season and good potential for establishment in the floating system while *I. pseudacorus* lagged behind in the second season with the lowest survival rate, plant growth parameters and nutrient uptake. Free water surface constructed wetland and floating treatment wetlands can thus be considered in an integrated agro-environmental management to control nutrient runoff from intensive cropping systems.

Chapter 5

Assessment of energy potential from wetland plants along the minor channel network on an agricultural floodplain

Introduction

Renewable Energy Sources (RES) embody, at present, one of the most important challenges to preserve, in the future, security of energy supply and reduction of Greenhouse Gases (GHG), by the progressive substitution of fossil fuels. In 2009, the European Union established a goal of 20% of RES in the energy supply and 10% of energy in the transport sector, in order to replace roughly 50 billion litres of fossil transportation fuels (European Commission 2006, 2008). Moreover, a long-term target has been included in the Strategy Plan 2020, to cut GHG from 80% to 95% by 2050. To develop RES, a cornerstone for the EU "20-20-20" triple goal[1] is currently represented by energy derived from biomass, which is expected to account for 56% of RES supply by 2020 (Bentsen and Felby 2012). Bioenergy is mainly derived from cultivated crops (Rahmam et al. 2014). The International Energy Agency (IEA) reported a large increase in energy crop production, leaping from an estimated 14 Mha in 2004 (about 1% of global crop production) to 36 Mha in 2008, out of the 1,545 Mha of total land area available worldwide (Rahmam et al. 2014). According to IEA, FAO and UNEP reports, this share could further increase to 3 to 4 times by 2030 (IEA 2006; FAO 2008; UNEP 2009). Similarly in the EU (EU27), about 5.5 Mha (3.2% of the total agricultural land) is presently growing energy crops. Most of this land is used for biofuel production, which covers 82% of energy crops; the remainder is used for the production of first-generation bioethanol (11%), biogas (7%), and perennial species mostly go into electricity and heat generation (1%) (Dworak et al. 2009; Elbersen et al. 2012). Biomasses are typically diversified into forest biomass (woody species in short rotation forestry), agricultural residues, post-processing biomass wastes (i.e. sewage sludge, manure) and energy crops of annual herbaceous species. The latter mainly include traditional food crops such as rapeseed, sugarbeet, sorghum, wheat, sunflower and silage maize (Betsen and Felby 2012; Elbersen et al. 2012). In Italy bioenergy is mainly derived from traditional widespread food crops such as wheat, barley, maize, rapeseed, soybean, sunflower, grain sorghum and sugarbeet (Cosentino et al. 2008). Recently, there has been increasing interest in high productivity perennial herbaceous species such as *Arundo donax*,

[1] The main target of the EU Energy 2020: a strategy for competitive, sustainable and secure energy. The strategy is oriented to increase energy efficiency, by saving 20% of the EU's primary energy consumption and GHG emissions, as well as the inclusion of 20% of renewable energies in energy consumption (European Commission, 2010).

Miscanthus spp. and *Phalaris Arundinacea*; however, such species still show constraints related to propagation techniques and harvest and storage systems (Cosentino et al. 2009; 2012)

To produce bioenergy, different conversion engineering techniques, combined with biotechnologies, are continuously under development, for both small- and large-scale applications: combined heat and power (CHP) for electrical (E_{el}) and thermal energy (E_t), and combustion for domestic and industrial heat supply by biomass pellets and briquettes; second generation biomass integrated gasification combined cycle system (biogas, BG); and, by physical, biochemical conversion of the main biomass components (carbohydrates, cellulose, hemicelluloses and lignin), first- and second-generation biofuels such as biodiesel and bioethanol (Naik et al. 2010; Chiaramonti et al. 2012).

Despite the initial emphasis on the key role of bioenergy in mitigating GHG emissions, it is widely acknowledged that important parameters are necessary to assess the sustainability of the whole energy process. In fact, serious constraints of energy crops are mirroring business-as-usual, environmental impacts from intensification processes of agricultural systems for food production. Crutzen et al. (2008) and Bouwman et al. (2010) stress energy crops are speeding up the N cycle by the increasing application of N fertilizer, leading to emission of reactive N, including NO_3 leaching, NH_3 volatilization, and emission of N_2O and NO. The low energy density of biomass, implying large volumes to be stocked, transported and processed in the energy plant, is another limiting factor for bioenergy production (Elbersen et al. 2012).

On the contrary, bioenergy from spontaneous perennial grasses growing in natural or semi-natural habitats, such as wetlands, give immediate and consistent advantages in terms of cost reduction (Fazio and Monti, 2011; Kallioinen et al. 2012).

Recently, biomass of perennial herbaceous species of wetland areas has aroused interest as an energy crop for the production of electricity and heat by CHP, BG and second-generation bioethanol. Some species, such as reed canary grass (*Phalaris arundinacea* L.) and common reed (*Phragmites australis* (Cav.) Trin. ex Steud) revealed notable bioenergy performances (Fazio and Monti 2011; Kallioinen et al. 2012). At present, one of the promising energy conversion technologies is oriented to the production of lignocellulosic

ethanol, giving a larger role to wetland plants and marginal lands in a future supply scenario (Fazio and Monti 2011; Kallioinen et al. 2012).

The general aim of this paper is to assess the energy potential of wetland vegetation associated to the minor hydrographic network of a reclamation area in North-East Italy, by identifying possible pathways towards a better sustainability in the use of local renewable energy sources.

The specific objective is to perform a GIS-based analysis on beds of common reed at territory scale, combining experimental survey analyses on biomasses in the field with spatial simulations. By categorizing the geographical context of the area based on Land Use Land Cover (LULC), three different energy scenarios have been performed-for combustion, biogas and second-generation ethanol.

Materials and methods

Geographical framework and study area

The study area is located within the reclamation territory of the "Consorzio di Bonifica Adige Euganeo", which covers 119,207 hectares in the North East of Italy, including 46,000 hectares of the Venice Lagoon drainage system. The reclamation territory encompasses about 1,800 km of a minor hydrographic network, most of which is essential to drain water from lowland areas below the mean sea level to the Venice Lagoon (Consorzio Adige Euganeo, 2013). The eastern sector is characterized by a dense network of collector channels and ditches mainly vegetated by continuous beds of common reed (Fig. 1).

A preliminary geographical analysis was done to categorize the typical landscape matrix within the reclamation territory, and to identify suitable study sites to perform spatial simulations on energy potential at local scale. Remote sensing analyses were performed by interpreting aerial images such as orthophotos (Veneto Region, 2006), high resolution satellite imagery (Spot Image, 2013), LiDAR DTM (2006) and official cartography at different scales (1:50,000 IGM; 1:5,000 Regional Technical Map). A specific territorial dataset on the minor channel network and vegetation was also acquired from the

"Consorzio di Bonifica Adige Euganeo" to support the geographical framework and field survey.

Geomorphological and ecosystem characteristics are heterogeneous within the reclamation territory: a range of hills, the Euganean Hills, is located in the north-west sector; elevation range decreases from west to east. Therefore, due to the highly complex territory, the analysis focused on the floodplain in the eastern sector, where riparian vegetation and the hydraulic system are more homogenous (Fig. 1).

According to the different landscape matrices, three specific study sites of 100 hectares each were identified and categorized with the Corine Land Cover map (CLC, 2006).

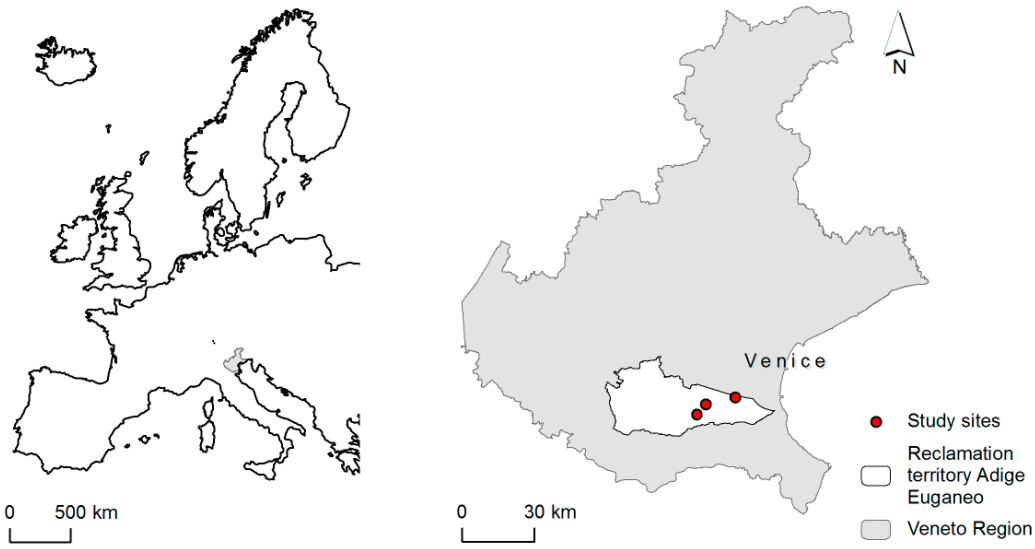


Figure 1 - Geographical framework: Veneto Region and the reclamation territory of Consorzio di Bonifica Adige

Remote sensing technologies and spatial analysis

Geographical Information Systems (GIS) were chosen as the main tool to process spatially explicit data, and to perform spatial analyses and simulations of the energy potential of riparian vegetation. Therefore, all the biophysical, ecological, anthropic data acquired by both a literature search and fieldwork activities were processed and integrated into the Database Management System (DBMS), in order have a powerful geographically and temporally referenced and thematically differentiated data storage.

Spatial analyses were carried out thanks to the availability of aerial images and a LiDAR DTM at 1 m resolution dated back to 2006, with a horizontal accuracy of about 0.3 m, and a vertical accuracy of ±0.15 m (RMSE estimated using DGPS ground truth control points), provided by the Ministry for Environment, Land and Sea (*Ministero dell'Ambiente e della Tutela del Territorio e del Mare*, MATTM).

In order to evaluate energy potential from biomass of beds of common reed associated to the minor channel network, it was first necessary to characterize the network conformation. A semi-automatic approach developed by Cazorzi et al. (2013) was applied for this purpose. From a LiDAR DTM, it was possible to automatically detect the network and compute its length, density and average channel widths. The procedure does not consider a hydrological characterization: neither the connectivity of the network nor the flow directions are accounted for (Cazorzi et al. 2013). The feature extraction relies on a thresholding approach based on the standard deviation of a morphological parameter called Relative Elevation Attribute (REA) (Carturan et al. 2009), automatically derived from the DTM. As the network identification is based on relief control, prior to local relief evaluation, it was necessary to identify and mask the man-made terrain features on the original DTM because they might greatly increase false detections and peak values on the relief index (Cazorzi et al. 2013). In addition, urban areas do not have a minor network system and considering them would only increase computational time, without any meaningful results. For the three study sites, urban, residential and industrial areas were therefore masked according to the 2006 CLC map and a comparative analysis of aerial images, official cartography and ground truthing. These have been shown to be crucial especially in study area n. 2 because most recent satellite imagery highlighted the presence of a roundabout that could not be identified in the previously-mentioned data.

The semi-automatic approach was applied in order to characterize the whole minor drainage network system, including small ditches within agricultural fields. This method was used in order to only extract the channels representing surfaces potentially vegetated by common reed. For this reason, it was also necessary to mask the internal portions of the fields in order to improve the detection of the bigger channels that are usually located along their boundaries. For the purpose of this work, each study area was divided into sub-areas of 0.0025 km^2 to speed up the elaborations and spatially distribute the measures (Fig. 2).

The thresholding approach applied to label REA peak values is based on the fact that different processes leave their signature on the statistical properties of landform geometry, and by quantifying and labelling these signatures in detail, it is possible to identify a threshold to label where a process starts (Lashermes et al. 2007; Tarolli and Dalla Fontana 2009; Passalacqua et al. 2010a, 2010b; Tarolli et al. 2010; Pirotti and Tarolli 2010; Sofia et al. 2013). The result is represented by a Boolean map with features taking only binary values, 1 or 0 for network pixels and landscape pixels respectively (Fig. 2).

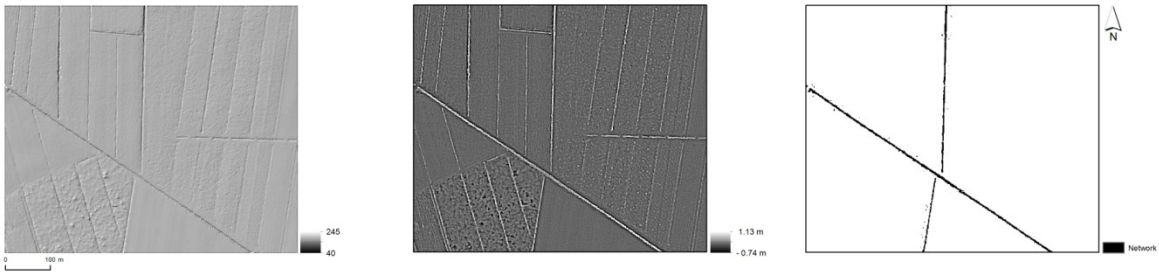


Figure 2- The three main steps of the semi-automatic approach: input DTM (a), derived REA map (b), and the Boolean map (c) detecting the drainage network after masking procedure and thresholding approach

Once the network had been extracted, it was possible to focus on its geometrical characterization and, thus, on the computation of its total length and average width for each sub-area of analysis. By summing up channel lengths and by averaging channel widths of all the sub-areas, we ended up, for each of the three study sites, with a total channel length and an average channel width.

Field survey

The first step was to spatially validate, adopting the ground truthing methodology (Desai and Potter 2006), the LULC distribution within the three study sites previously identified by remote sensing and GIS analyses on the reclamation territory scale. Ground truthing was performed by GPS technology. Secondly, with a specific territorial dataset provided by the Consorzio di Bonifica Adige Euganeo, representative spots for biomass sampling were

identified along the minor channel network within the three study sites. Sampling areas of 50 m^2 (site 1), 110 m^2 (site 2) and 50 m^2 (site 3) for biomass production were measured and geo-referenced. Common reed has been confirmed as the predominant species (about 90% of vegetation) growing on the riparian surfaces of the minor channel network. Vegetation was cut by mechanical mowing at 5 cm height and harvested in order to calculate the dry matter weight. Total fresh weight of the collected aboveground biomass was quantified on site; samples of 1,000 g were dried in a force draught oven at 65 °C for 35 hours, milled at 2 mm (Cutting Mill SM 100 Comfort, Retsch, Germany); in addition, 10 g powered sub-samples were dried at 130 °C to measure the residual moisture content. Biomass sampling was carried out in the summer (2013), during the ordinary channel maintenance operations of the drainage network by the Reclaimaing Authority Consorzio di Bonifica Adige Euganeo. Such operations are carried out annually to protect the territory from hydrogeological risk. Finally, fieldwork data on biomass sampling (DM, t/ha) were multiplied by the total useful area, in order to assess the potential production on the minor channel network. Maintenance operations such as cutting vegetation and cleaning channel beds are necessary to protect the territory from hydrogeological risk. Sample areas were georeferenced and processed in GIS environment.

To assess the bioenergy potential of riparian surfaces several surveys were performed in the field by a Differential Global Positioning System (DGPS) to gather data about the bank-to-bank channel widths. By using a laser rangefinder telemeter (Bushnell YardagePROtm 800) for the wider channel sections (6-25 m) and a surveyor tape for the small ones (3-6 m), the total width of ditches was measured. Lastly, 65 bank-to-bank channel sections were measured in the three study areas: 19 in the first, 21 in the second and 25 in the third (Fig. 3). By averaging the values gathered, we ended up with a mean bank-to-bank channel width for each study site. Since common reed mainly grows at the water edges and spreads along the banks, we subtracted the average channel width obtained with the semi-automatic approach from the average bank-to-bank channel derived in the field surveys, ending up with an average bank width for each study area. The total channel length was then multiplied by the average bank width in order to estimate the potential surface with the presence of common reed.

Common reed energy values

To perform the energy potential assessment the literature data on common reed was reviewed and selected.

For combustion, common reed showed energy contents similar to reed canary grass, Miscanthus (*Miscanthus x giganteus*, Greef et Deu) and wood chips, providing ca. 18.5-20 MJ/kg (Komulaien et al. 2008; Cubars and Noviks 2012; Kask et al. 2013). Other experimental measurements give values such as 18-19 MJ/kg (Komulaien et al. 2008) and 16.187 MJ/kg (Kitzler et al. 2012). However, for the purpose of this work, the Low Heating Value (LHV) of 10.41 (±3.18) MJ/kg (Politeo et al. 2011) for common reed cultivated in a constructed wetland in the Veneto Region was selected (Table 1).

Biogas energy potential is determined by content in Total Solid (TS) and Volatile Solids (VS); Biochemical Methane Potential (BMP) expresses the CH_4 potentially achievable by degradation of organic matter. According to Amon et al. (2007a; 2007b), yield in biogas ranges from 315 $Nm^3\ t^{-1}$ VS for fresh reed to 421 $Nm^3\ t^{-1}$ VS for reed silage treated with enzymes. Ensiling increases BG and CH_4 yield compared to fresh material; enzyme pre-treatment significantly increases the yield of both (Helbig 2009). Differences in energy performances from variation of harvest date are not significant; on the contrary biochemical pre-treatment processes using enzymes significantly increases energy values from 350 to 421 $Nm^3\ t^{-1}$ (Amon 2007b). CH_4 content in BG production varies from 44.8% (silage) to 48.3% (silage and enzymes) (Amon 2005). Hansson and Fredriksson (2004) confirm such a range in CH_4 energy values. Therefore, assuming mean composition in VS of common reed DM is about 91% (Amon et al. 2007a, 2007b; Helbig 2009) and the total CH_4 yield in accordance with VDI 4630 (2006) is about 200 $Nm^3\ t^{-1}$of VS (Hansson & Fredriksson 2004; Risèn et al. 2013; Nkemka and Murto 2013), the energy value for BMP assessed for the purpose of this paper is 182 $Nm^3\ t^{-1}$ (Table 1).

On the other hand, 2nd generation bioethanol derived from cellulose, hemicellulose and lignin ranges widely in energy values, according to factors such as harvesting period, the different pre-treatment and fermentation processes to separate and provide easier access to the main biomass components (Chiaramonti et al. 2012; Kallioinen et al. 2012). However, experimental results on common reed grown in Veneto Region have been used, showing a yield of 88 kg (EtOH) t^{-1} (Florio 2014).

Energy transformation	*Values MJ/kg*	*Sources*	*Selected*
Combustion	18.5-20	Cubars & Noviks	10.4
(Low Heating Value)	18-19	2012	
	16.1	Komulaien et al.	
	10.4	2008	
		Kitzler et al. 2012	
		Politeo et al. 2011	
BMP (VS)	12.5-16.7	Amon et al. 2007a	7.2
	13.9-15.7	Hansson &	
		Fredrikson 2004	
Second-generation ethanol	2.3	Florio 2014	2.3

Table 1 Energy values for combustion, methane and 2nd generation bioethanol

To equalize methane and bioethanol values to the same measurement units (MJ), conversion factors of 39.79 and 26.8 were used to compare different energy scenarios (Beitz and Kuttner, 1987; Bauer et al. 2009).

Results

Land Use Land Cover classification

Preliminary results, obtained by a quantitative analysis to spatially categorize the LULC distribution per study site, show that every study site presents different areas for artificial surfaces (AS), agricultural lands (AL) and water bodies (WB). Although agricultural areas are the dominant LULC, results highlight different patterns of LULC matrix: study site n. 1 is characterized by 2% of AS, 96% of AL and 2% of WB; study site n. 2 presents 38% of AS, 60% of AL and 2% of WB; study site n. 3 has 26% of AS, 70% of AL and 4% of WB (Figure 3; Table 2). Considering the actual LULC scenario of the whole reclamation territory, the selected sample sites represent three typical territorial matrices of the region: a dominant rural landscape, mainly characterized by cropland (study site n. 1); a mixed rural/anthropic landscape (study site n. 2), and prevalently rural (70%) with relevant presence of artificial surfaces (26%) (study site n. 3).

Study sites	*AF (ha)*	*AL (ha)*	*WB (ha)*	*TDN (km)*	*UDN (km)*	*Total area (ha)*
area 1	2	96	2	27.6	5.5	100
area 2	38	60	2	21.6	9.1	100
area 3	26	70	4	25.2	8.9	100

Table 2 GIS analysis of the Land Use Land Cover surfaces and drainage network of the three study sites: Artificial Surfaces (AF), Agricultural Lands (AL), Water Bodies (WB), Total Drainage Network (TDN) and Useful Drainage Network (UDN)

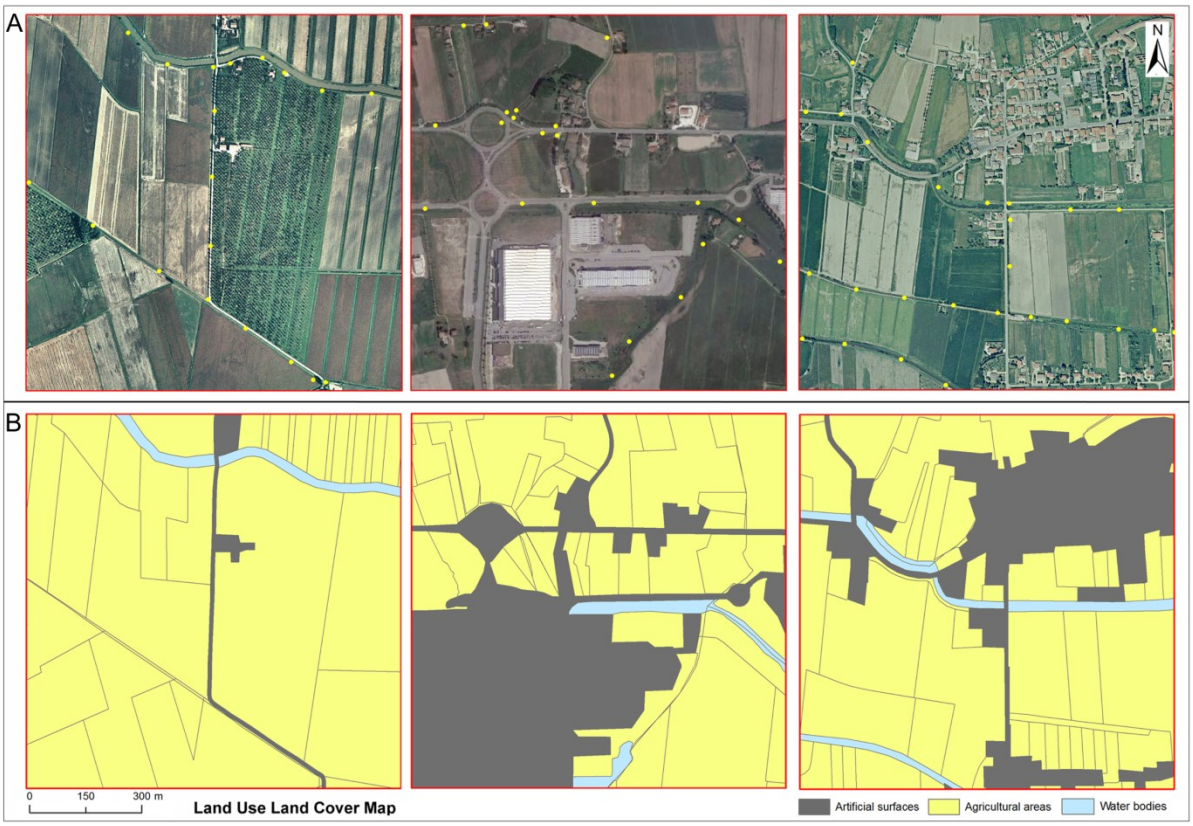


Figure 3 A) Field surveying campaign over the three study sites: ground truthing and bank-to-bank channel section measurements; B) Land Use Land Cover analysis of the three study sites: Artificial Surfaces, Agricultural Land and Water Bodies

From the total to the productive drainage network

According to spatial analysis of the minor hydrographic system, the useful drainage density network for biomass production was quantified within the three study sites. Results obtained by semi-automatic extraction from LiDAR DTM firstly showed that the total drainage system is 27.6 km for study site n. 1, 21.6 km for study site n. 2, 25.2 km for study site n. 3; performing masking technique, the useful drainage network for common reed biomass production was calculated, of 5.5 km, 9.1 km and 8.9 km respectively (Table 2). Moreover, GIS analysis of drainage systems highlights two different drainage network scenarios calculated on 100 ha study sites: total drainage density and the useful drainage density for biomass production. Therefore, the useful minor channel network for harvestable common reed on riparian surfaces was quantified by comparative analysis of both drainage systems calculated for each study site.

By overlay of Boolean maps (Figure 4) which show linear values of the hydrographic network, significant differences in drainage lengths, and therefore in density, were detected in all three study sites. The average drainage density based on 0.0025 km^2 cells was then calculated for each study site by a comparative analysis: study site n. 1 has 11 km/km^2, while useful drainage density is 2.2 km/km^2; in study site n. 2, total drainage density is 8.7 km/km^2, useful drainage density is 3.6; in study site n. 3, total drainage density is 10 km/km^2, while useful drainage density is 3.6 km/km^2 (Figure 4). Such a relevant deviation in drainage density values is mainly related to the presence of agricultural ditches within productive farmland. This pattern is very visible on the map of study site n. 1 (Figure 4a), characterized by 96% of agricultural land, 27.6 km of drainage network but just 5.5 km of productive riverbanks (Table 2,3).

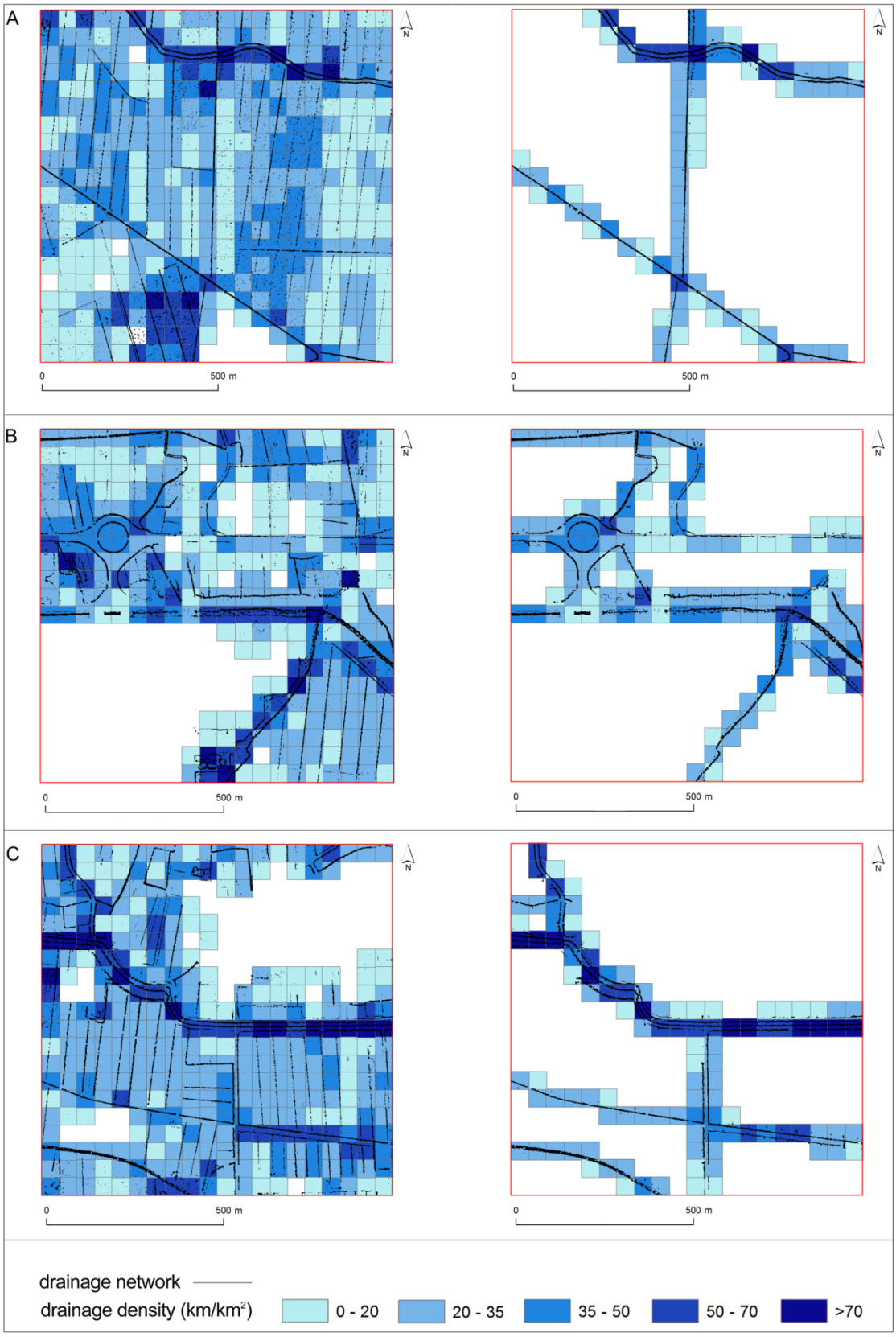


Figure 4 Drainage network analysis and overlay of Boolean maps in the three study sites (A, B, C): in the left column the total drainage network, in the right one the productive drainage network

Common reed biomass production

GIS analysis of riparian surfaces allowed vegetated areas along the drainage systems to be calculated. The three study sites present 8.5, 13 and 11.2 ha of vegetated surfaces for biomass production respectively. Fieldwork data on the aboveground biomass (DM) has been spatially processed to quantify potential productivity of each study site, calculated on the useful drainage network. Results on total biomass production reveal 30 t for study site n. 1, 222 t for study site n. 2 and 159 t for study site n. 3. Consequently, the three study sites show different values of average production per unit area: 1.5 t/ha for study site n.1, 6.7 t/ha for study site n. 2 and 6 t/ha for study site n. 3 (Table 3).

	Site 1	***Site 2***	***Site 3***
Vegetated surfaces (ha)	8.5	13.0	11.2
Total biomass production DM (t)	30	222	159
Average Production DM (t /ha)	1.5	6.7	6

Table 3 - Vegetated surfaces and biomass production on the useful drainage network within the three study sites

Results seem to confirm the average production recorded within the same geographical context, with a constructed wetland, vegetated by *Phragmites australis*, showing an aboveground biomass production of 8.8 t/ha (Maucieri et al. 2014).

Cartographic outputs in figure 5 show the total production distribution on the useful drainage network, calculated for each 0.0025 km^2 cell. GIS analysis displays a general low production for study site n. 1, in which the highest range values are 0.75-1 t just in five cells; the most diffuse biomass production is in the range 0.25-0.50 t. On the contrary, study site n. 2 shows a higher production value, mainly clustered in a range of 1.5-3 t along the two banks of a major channel, running in a west-east direction (Figure 5b). Spatial analysis on study site n. 3 displays less clusters in the range 1.5-3 t, but a higher concentration of cells with values >3 t of biomass production, mainly localized along the two banks of the major channel in the area. Overlay of Boolean maps allows the total channel network to be visualized and biomass production localized on the productive riparian surfaces (Figure 5). Finally, by a relative frequency calculation, it emerges that

both study sites 2 and 3 have areas with a greater biomass production: the most frequent biomass classes are those from 1.0 to 1.5 and from 1.5 to 3.0 t. Instead, study site 1 is clearly less productive with biomass values mostly ranging from 0.25 to 0.50 t (Figure 6)

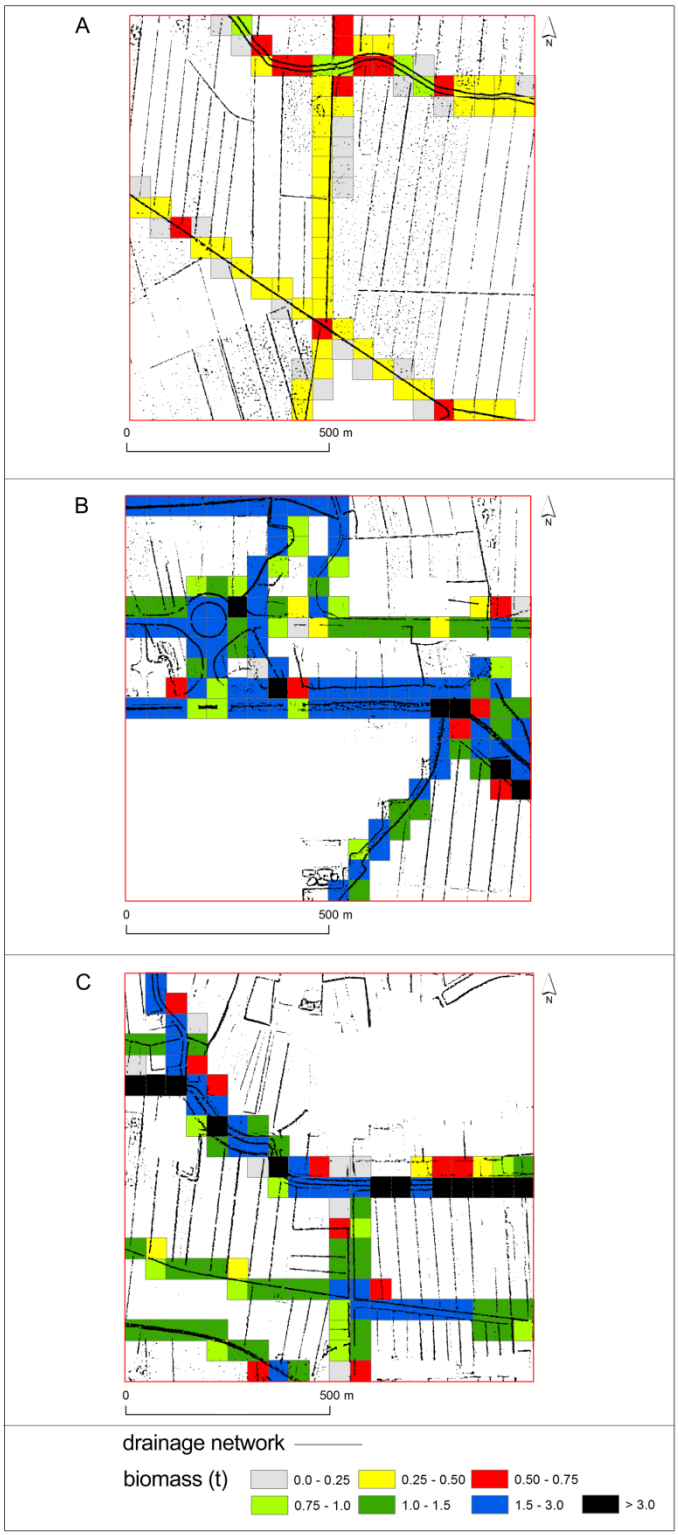


Figure 5 - GIS analysis of total biomass production within the three study sites. Production values (t) are performed on 0.0025 km^2 cells. Boolean map overlays display the total drainage network length

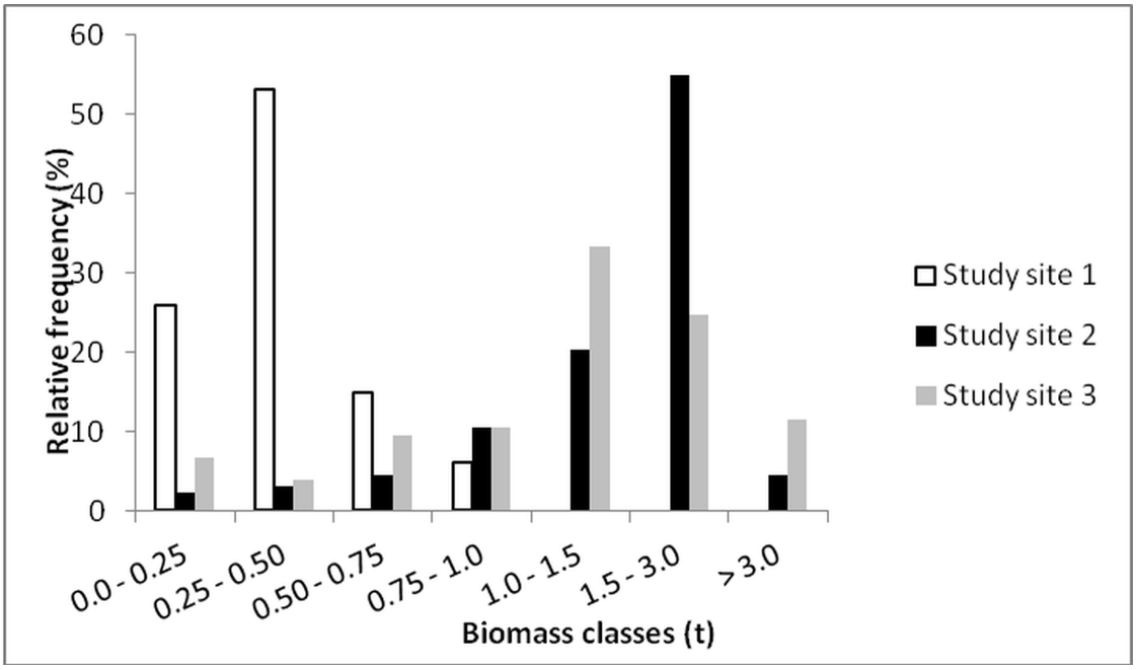


Figure 6 - Relative frequency (%) for biomass production classes within the three study sites

GIS analysis of energy potential

Results for combustion conversion, based on a conservative assessment of heating values, reveal study site n. 1 as the lowest energy scenario, with cell values of LHV between 0.43 to 48.37 GJ ha^{-1}, an overall average value of cells of 15.55 GJ ha^{-1} and a median value of 13.21 GJ ha^{-1}. On the contrary, study sites n.2 and 3 show similar yields with average values of 69.4 GJ ha^{-1} and 63.1 GJ ha^{-1} respectively (Table 4)

Biomass conversion for methane production presents lower performances compared to combustion: the highest average energy values are obtained in study site n. 2, with an average of 48.32 GJ ha^{-1}; the lowest methane yield is in study site n. 1, with 10.81 GJ ha^{-1}.

The second-generation bioethanol scenario displays the lowest values: average values of 3.53 GJ ha^{-1} for study site n. 1, 15. 73 GJ ha^{-1} for study site n. 2, and 14.28 GJ ha^{-1} for study site n. 3 (Table 4).

In general, results showed different possible scenarios for bioenergy production from common reed in three dissimilar LULC matrices (Figure 3). Among the three energy

options, the highest performances are represented by combustion technologies, followed by methane and second-generation bioethanol production.

GIS analysis on bioenergy displays energy values for three different technology scenarios with spatially explicit data for each study site (Figure 7).

Energy scenarios	*Study site 1*	*Study site 2*	*Study site 3*
Combustion	*(GJ ha^{-1})*	*(GJ ha^{-1})*	*(GJ ha^{-1})*
Min-max	0.43-48.37	1.94-168.7	2.84-183.65
Average	15.55	69.4	63.1
Median	13.21	68.8	48.56
Methane (BMP)			
Min-max	0.3-33.64	1.35-117.37	1.98-127.74
Average	10.81	48.32	43.87
Median	9.19	47.86	33.78
2nd generation bioethanol			
Min-max	0.09-10.97	0.44-38.22	0.64-41.59
Average	3.53	15.73	14.28
Median	2.99	15.58	11

Table 4 - Bioenergy potential for three different technology scenarios: combustion, methane and 2nd generation bioethanol

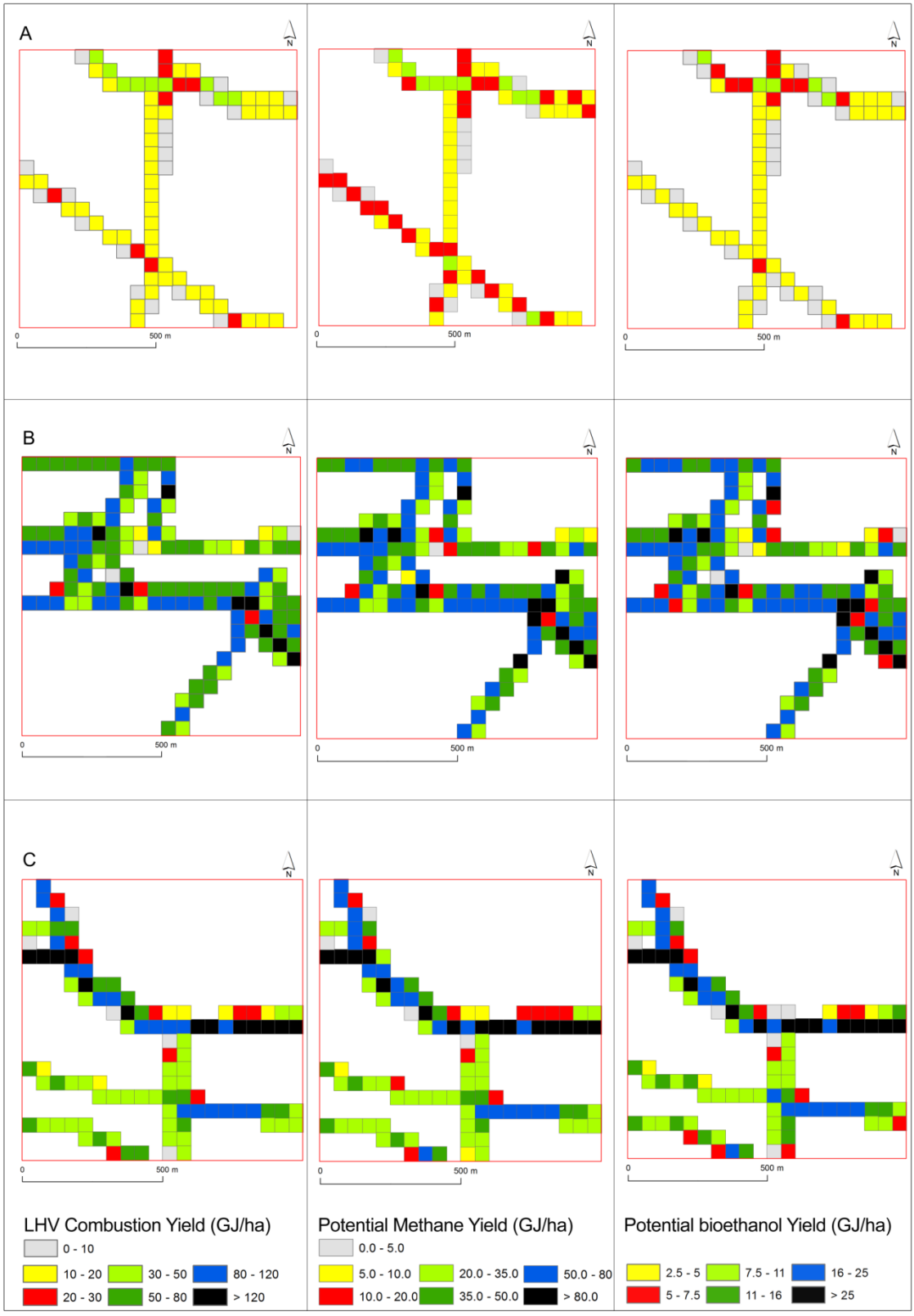


Figure 7 GIS analysis of the three conversion technology scenarios for each study site

Discussion and conclusions

The developed cross-cut methodology aimed to assess energy potential from natural riparian vegetation of the minor channel network. It introduces an integrated GIS-based approach to evaluate at local scale possible energy scenarios from three dissimilar LULC matrices. The highest performances are clearly represented by combustion technologies, followed by methane and 2nd-generation bioethanol production.

Concerning combustion potential, study site n. 2 presents an average value of 69.4 GJ t^{-1}, showing an interesting energy yield. However, it has been performed the LHV of 10.41 (±3.18) GJ t^{-1} for a conservative yield assessment; on the contrary, by using the High Heating Values of 16.69 (±0.53) GJ t^{-1} (Politeo et al. 2011), combustion yield would increase about 62.37%, highlighting a more promising energy scenario. Concerning methane and 2nd generation bioethanol production yields are lower than common bioenergy crops. In the best case values in BMP (48.3 GJ ha^{-1}) and 2nd generation bioethanol (15.7 GJ $^{-1}$) are at present not competitive with bioenergy crops such as sugarbeet, silage maize and silage sunflower, which show CH_4 yields from 60 to 131 GJ ha^{-1} (Amon et al. 2007a; 2007b) and 74.7 GJ ha^{-1} respectively (European Biofuels Technology Platform, 2013; Goldember and Guardabassi 2010). The latter is almost 4.5 times higher than the best energy performance in study site n. 2.

Riparian zones of the minor channel network could generally represent a significant source of bioenergy, mainly for combustion transformation; however, such bioenergy production implies some important limitations. Firstly, not all the territory displays homogeneous potential bioenergy values: in study site n.1, characterized by a dominant rural landscape (95% of LULC is Agricultural Land) and by the longest total drainage network (27.6 km), biomass production and, therefore, energy yield, are the lowest. As a matter of a fact biomass is available only along 5.5 km of riverbanks. Many agricultural ditches and small channels make common reed not easily harvestable in this area (Figure 3, 4a). On the contrary, study site n. 2, despite the shortest total drainage network of 21.6 km, presents the highest bioenergy potential with 9.16 km of vegetated riparian zones, which provide 221.9 t of biomass production.

Further spatial analysis are definitely required to assess an efficient and sustainable energy system, identifying suitable spots for biomass storage, transformation and energy utilization. Such assessments are necessary to minimize transport and energy infrastructure costs.

It is important to mention that such biomass production required no energy inputs in terms of soil management (tillage, fertilization) or water supply. Biomass is produced naturally on marginal lands associated to the minor channel network and it is usually cut and directly stocked *in situ* by the Reclamation Authority. Such biomass management implies the potential physical dispersion of biogenic agents which strongly contribute to water bodies eutrophication and other ecological impacts.

Finally, the results of this study highlight some workable alternatives for increasing the energy supply, turning the ecological problem of the waste disposal of common reed biomass into an opportunity to produce a sustainable and delocalized bioenergy at local scale.

Chapter 6

Conclusions

Conclusions

The present thesis showed different agricultural uses of vegetated systems which were tested mainly to provide water purification services and other ancillary ecosystem services. The choice of adopting wetlands and vegetated ditches as experimental trial was basically related to the ecological and climatic condition of the Po floodplain: seasonal shallow groundwater, sub-humid climate (about 850 mm fairly uniformly distributed throughout the year), a dense and often vegetated minor hydrographic network, and the wide presence of high performance phytoremediation plants such as *P. australis, T. latifolia, P. arundinacea, I. pseudacorus*, *L. salicaria* and *Carex* spp. (Borin and Malagoli 2015; Gregoire *et al*., 2011; Vymazal, 2011; Vymazal, 2013; Vymazal and Brezinovà, 2015). Moreover, the presence of a dense minor hydrographic network within the agricultural territory, realized both for irrigation and for draining out water from the depressed areas (below M.S.L.), makes more feasible the use of constructed wetlands and controlled vegetated ditches for phytoremediation purposes (Pappalardo *et al*, 2014).

The first study (Chapter 2) showed that a constructed surface flow wetland is very effective in the reduction of herbicides runoff, with a mitigation effectiveness of about 98% for two of the main herbicides applied to maize: metolachlor and terbuthylazine. This is in agreement with the conclusions of other recent European studies (Kay et al., 2009; Stehle et al., 2011; Maillard et al., 2011). Comparison with results from other research is possible only after a clear and simple definition of mitigation or removal, as proposed in the study. It is difficult to single out exactly which processes cause the mitigation. The observed dynamic suggests the mitigation is provided by a reversible adsorption to the superficial organic matter complex, i.e. by plants, plant residues and soil. In fact, following a successive severe flood, 15-30% of the herbicides detected in the first flood was mobilized after 25 days, and 40 days later another flood again mobilized a lower but detectable amount of herbicides. In both floods a mixture of herbicides and metabolites was present. It is worth noting that mobilization of terbuthylazine from the constructed surface flow wetland is correlated with the contact time with water, while that of metolachlor, slightly less adsorbed and more soluble, is not. Given that flooding speed is quite regular throughout the constructed surface flow wetland, mitigation can be linked either to the duration or residential time of the flood. Results highlight that the constructed surface flow

wetland is a dynamic system with a high buffer capacity. In ordinary conditions of the plain cropland in north-eastern Italy, where 3-4 runoff events of low volume occur (Cardinali et al., 2013), the mitigation capacity of a 0.3 ha constructed surface flow wetland serving a 6 ha basin is likely complete, i.e. no herbicides will by-pass the constructed surface flow wetland and enter surface water outside the basin. According to an iterative method for mitigation calculation, hypothesizing a final mitigation of 99.99% for a constructed surface flow wetland of 200 m, the mitigation capacity for a heavy runoff of 3.5 mm from a 10 ha basin is 90% for each 50 m in length for a 15 m wide wetland. This suggests that also smaller constructed surface flow wetland can be very useful at farm scale when other mitigation techniques are implemented, i.e. spray band applications, post-emergence only.

The second study (Chapter 3) showed how the management of vegetated ditches may have a great herbicides runoff mitigation potential for the protection of watercourses and can be inserted in environmental schemes. Their effectiveness with shallow flooding is high and length-dependent. In typical ditches of north-eastern Italy, for the main pre-emergence herbicides applied in maize, the distance required to reduce initial concentration by 50% is about 250 m. As a general rule for herbicides with KOC of 110-400 L kg^{-1}, a runoff of 1 mm from 5 ha is mitigated by 99% in 100 m of vegetated ditch 1 m bed wide. The dissipation of herbicides in ditches is site-specific and mainly due to degradation and adsorption, while outflow with water discharge is low since the flood is shallow. Coverage of emergent plants and the hydraulic residence time is of great importance, and a better insight into herbicides adsorption onto the sediment-soil-plant complex is needed.

The third study (Chapter 4) highlighted the use of an integrated agricultural wetland system of 2.4 ha in abating nutrients load from an agricultural basin and the adaptability of seven macrophyte species in a floating treatment wetland system, located downstream along an agricultural canal. Although wetland performance in water purification were not so high and decreases in the concentrations of nitrogen through the system were not significant - mainly related to the low concentration of nitrogen in the initial inlet point as well as the newness of the experimental site - a generally promising depurative effect appears from the concentration trend throughout the system. This effect is notable during March 2015 as emphasized by the major decrease in TN and NO^{3-} concentrations throughout the wetland sub-basins and downstream channel after a combined event of intensive rainfall and crop

fertilization run-off. Phosphorus concentrations were almost negligible. Monitoring the vegetation in the floating treatment wetland system, *Carex* spp. showed the best adaptability through high survival rate, hardiness and continuity over two successive seasons, highest plant parameters, especially biomass production, as well as highest nitrogen and phosphorus uptakes. *L. salicaria* showed great stability, excellent growth performance during the season and good potential for establishment in the floating system while *I. pseudacorus* lagged behind in the second season with the lowest survival rate, plant growth parameters and nutrient uptake. Free water surface constructed wetland and floating treatment wetlands can thus be considered in an integrated agro-environmental management to control nutrient runoff from intensive cropping systems.

The fourth study (Chapter 5) would highlight the potential use of "wetland plants" growing along the riparian zones of the minor channel network as source of sustainable bioenergy, mainly for combustion transformation. However, the study showed such bioenergy production implies some important limitations: firstly, not all the territory displays homogeneous potential bioenergy values: in study site n.1, characterized by a dominant rural landscape (95% of LULC is Agricultural Land) and by the longest total drainage network (27.6 km), biomass production and, therefore, energy yield, are the lowest. As a matter of a fact biomass is available only along 5.5 km of riverbanks. Many agricultural ditches and small channels make common reed not easily harvestable in this area. On the contrary, study site n. 2, despite the shortest total drainage network of 21.6 km, presents the highest bioenergy potential with 9.16 km of vegetated riparian zones, which provide 221.9 t of biomass production. Further spatial analyses are definitely required to assess an efficient and sustainable energy system, identifying suitable spots for biomass storage, transformation and energy utilization. Such assessments are necessary to minimize transport and energy infrastructure costs. It is important to mention that such biomass production required no energy inputs in terms of soil management (tillage, fertilization) or water supply. Biomass is produced naturally on marginal lands associated to the minor channel network and it is usually cut and directly stocked *in situ* by the Reclamation Authority. Such biomass management implies the potential physical dispersion of biogenic agents which strongly contribute to water bodies' eutrophication and other ecological impacts. Finally, the results of this study highlight some workable alternatives for

increasing the energy supply, turning the ecological problem of the waste disposal of common reed biomass into an opportunity to produce a sustainable and delocalized bioenergy at local scale.

In general, wetlands and vegetated ditches may represent an important opportunity to manage, both at field and territory scale, water purification services such as nutrient and sediment retention, and mitigation from pesticide runoff by the implementation of in-site and off-site mitigation devices.

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References

Amon, T., Amon, B., Kryvoruchko, V., Machmuller, A., Hopfner-Sixt, K., Bodiroza, V., Hrbek, R., Friedel, J., Potsch, E., Wagentristl, H., Schreiner, M., Zollisch, W. (2007b). Methane production through anaerobic digestion of various energy crops grown in sustainable crop rotation. *Bioresource Technology* 98, 3204–3212.

Amon, T., Bodiroza, V., Kryvoruchko, V., Machmüller, A., Bauer, A. (2007a). Energetische Nutzung von Schilfgras von extensiven Naturschutzflächen des Nationalparks Neusiedler See und Makrophyten des Neusiedler Sees (Energy use of common reed from extensive conservation grassland in the Neusiedler See National Park and of macrophytes in the Neusiedler See lake). *Research Report*, Vienna.

Amon, T., Kryvoruchko, V., Amon, B., Bodiroza, V., Zollitsch, W., Boxberger, J., Potsch, E. (2005). Biogas production from grassland biomass in the alpine region. *Agric. Eng.* (Landtechnik) 60, 336–337.

Anderson, B.S., Phillips, B.M., Hunt, J.W., Largay, B., Shihadeh, R., Tjeerdema, R.S. (2011). Pesticide and toxicity reduction using an integrated vegetated treatment system. *Environmental Toxicology and Chemistry* 30, 1036–1043.

AOAC International (2000). Official methods of Analysis of AOAC International, 17th ED. http://www.eoma.aoac.org/.

Arduino, E., and Barberis, E. (2000). In: Violante, P. (Ed.), Metodi di Analisi Chimica del Suolo. Ministero delle Politiche Agricole e Forestali, Osservatorio Nazionale Pedologico e per la Qualità del Suolo. Franco Angeli, Milano (sec. XV), Italia.

Aslam, S., Garnier, P., Rumpel, C., Parent, SE., Benoit, P. (2013). Adsorption and desorption behavior of selected pesticides as influenced by decomposition of maize mulch. *Chemosphere* 91, 1447–1455. DOI: 10.1016/j.chemosphere.2012.12.005.

Bachand, P.A.M., and Horne, A.J. (2000). Denitrification in constructed free-water surfacewetland: II. Effects of vegetation and temperature. *Ecological Engineering* 14, 17–32.

Balvanera, P., Daily, G.C., Ehrlich, P.R., Ricketts, T.H., Bailey, S., Kark, S., Kremen, C., Pereira, H. (2001). Conserving biodiversity and ecosystem services. *Science* 291, 2047.

Barchanska, H., Rusek, M., Szatkowska, A. (2012). New procedures for simultaneous determination of mesotrione and atrazine in water and soil. Comparison of the

degradation processes of mesotrione and atrazine. *Environ. Monit. Assess.* 184, 321–334. DOI: 10.1007/s10661-011-1970-5.

Barra Caracciolo, A., Giuliano, G., Grenni, P., Guzzella, L., Pozzoni, F., Bottoni, P., Fava, L., Crobe, A., Orrù, M., Funari, E. (2005). Degradation and leaching of the herbicides metolachlor and diuron: a case study in an area of Northern Italy. *Environ. Poll.* 134, 525–534. DOI: 10.1016/j.envpol.2004.08.014.

Bauer, A., Leonhartsberger, C., Bosch, P., Amon, B., Friedl, A., Amon, T. (2009). Analysis of methane yields from energy crops and agricultural by-products and estimation of energy potential from sustainable crop rotation systems in EU-27. *Clean Techn Environ Policy* 12, 153–161. DOI: 10.1007/s10098-009-0236-1.

Beitz, W., Kuttner, KH. (1987). Dubbel pocket-book for engineering. (Dubbel Taschenbuch fur den Maschinenbau). *Springer*, Berlin.

Bennett, ER., Moore, MT., Cooper, CM., Smith, S., Shields, FD., Drouillard, KG., Schulz, R. (2005). Vegetated agricultural drainage ditches for the mitigation of pyrethroid-associated runoff. *Environ. Toxicol. Chem.* 24, 2121–2127. DOI: 10.1897/04.357R.1.

Bentsen, NS., Felby, C. (2012). Biomass for energy in the European Union - a review of bioenergy resource assessments. Biotechnology for Biofuels. 5, 25. DOI: 10.1186/1754-6834-5-25.

Bereswill, R., Burkhard, G., Streloke, M., Schulz, R. (2012). Entry and toxicity of organic pesticides and copper in vineyard streams: Erosion rills jeopardise the efficiency of riparian buffer strips. *Agr. Ecosyst. Environ*. 146, 81–92. DOI: 10.1016/j.agee.2011.10.010.

Berghahn, R., Mohr, S., Hübner, V., Schmiediche, R., Schmiedling, I., Svetich-Will, E. & Schmidt, R. (2012). Effects of repeated insecticide pulses on macroinvertebrate drift in indoor stream mesocosms. *Aquatic Toxicology* 122–123, 56–66.

Bjergager, M.-B.A, Hanson, M.L., Lissemore, L., Henriquez, N., Solomon, K.R., Cedergreen, N. (2011). Synergy in microcosms with environmentally realistic concentrations of prochloraz and esfenvalerate. *Aquatic Toxicology* 101, 412–422.

Boithias, L., Sauvage, S., Merlin, G., Jean, S., Probst, J-L., Sánchez Pérez, JM. (2014). New insight into pesticide partition coefficient K_d for modelling pesticide fluvial

transport: Application to an agricultural catchment in south-western France. *Chemosphere* 99, 134–142. DOI: 10.1016/j.chemosphere.2013.10.050.

Bonaiti, G., and Borin, M. (2000). Agronomic observations of *Phragmites australis* (Cav.) Trin. and *Typha latifolia* L.: biomass and nitrogen seasonal dynamics. *IWA Specialist Group on The Use of Macrophytes in Water Pollution Control Newsletter* 22, 20–4.

Borin, M., and Malagoli, M. (2015). Ecology, functioning and management of wetland systems. *Environmental Science and Pollution Research* 22, 2357–2359.

Borin, M., and Tocchetto, D. (2007). Five year water and nitrogen balance for a constructed surface flow wetland treating agricultural drainage waters. *Science of the Total Environment* 380, 38–47.

Borin, M., Bonaiti, G. (1997). Versatilità dei sistemi *wetland* per la fitodepurazione delle acque inquinate. Alcuni esempi applicativi in Texas. *Inquinamento* 10, 56–59.

Borin, M., Bonaiti, G., Santamaria, G., and Giardini, L. (2001). A constructed surface flow wetland for treating agricultural waste waters. *Water Science Technology* 44, 523–530.

Borin, M., Tocchetto, D. (2007). Five year water and nitrogen balance for a constructed surface flow wetland treating agricultural waters. *Science of the Total Environment* 380, 38–47.

Bouldin, JL., Farris, JL., Moore, MT., Cooper, C.M. (2004). Vegetative and structural characteristics of agricultural drainages in the Mississippi Delta landscapes. *Environ. Poll.* 132, 403–411. DOI: 10.1016/j.envpol.2004.05.026.

Bouwman, AF., van Grinsven, JM., Eickhout, B. (2010). Consequences of the cultivation of energy crops for the global nitrogen cycle. *Ecological Applications* 20(1), 101–109.

Brinson, M. M. & Eckles, D.S. (2011). U.S. Department of Agriculture conservation program and practice effects on wetland ecosystem services: a synthesis. *Ecological Applications* 21, S116–S127.

Brix, H. (1994). Functions of macrophytes in constructed wetlands. *Water Science Technology* 29, 71–78.

Calamari, D., Vighi, M., Bacci, E. (1987). The use of terrestrial plants biomass as a parameter in the fugacity model. *Chemosphere* 16, 2359–2364. DOI: 10.1016/0045-6535(87)90293-1.

Cardinali, A., Otto, S., Zanin, G. (2013). Herbicides runoff in vegetative filter strips: evaluation and validation of a recent rainfall return period model. *Int. J. Environ. Analyt. Chem.* 1, 1–10. DOI: 10.1080/03067319.2013.841151.

Carturan, L., Cazorzi, F., Dalla Fontana, G. (2009). Enhanced estimation of glacier mass balance in unsampled areas by means of topographic data. *Annals of Glaciology* 50, 37– 56.

Cataldo, D.A., Haroon, L.E., Schrader, L.E., and Youngs, V.L. (1975). Rapid colorimetric determination of nitrate in plant tissue by nitration of salicylic acid. *Communications in Soil Science and Plant Analysis* 6, 71–80.

Cazorzi, F., Dalla Fontana, G., De Luca, A., Sofia, G., Tarolli, P. (2013). Drainage network detection and assessment of network storage capacity in agrarian landscape. *Hydrological Processes* 27(4), 541–553. ISSN: 0885-6087, DOI: 10.1002/hyp.9224.

Chaabane, H., Vulliet, E., Calvayrac, C., Coste, C-M., Cooper, J-F. (2008). Behaviour of sulcotrione and mesotrione in two soils. *Pest Manage. Sci.* 64, 86–93. DOI: 10.1002/ps.1456.

Chiaramonti, D., Prussi, M., Ferrero, S., Oriani, L., Ottonello, P., Torre, P., Cherchi, F. (2012), Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method. *Biomass and Bioenergy* 46, 25–35.

Cooper, CM., Moore, MT., Bennet, ER., Smith, S., Farris, JL., Milam, CD., Shields, FD (2004). Innovative use of vegetated drainage ditches for reducing agricultural runoff. *Water Sci. Technol.* 49, 117–123.

Cosentino, SL., Copani, V., Patanè, C., Mantineo, M., D'Agosta, GM. (2009). Agronomic, energetic and environmental aspects of biomass energy crops suitable for Italian environments. *Italian Journal of Agronomy* 2, 81–95.

Cosentino, SL., Testa, G., Scordia, D., Alexopoulou, E. (2012). Future yields assessment of bioenergy crops in relation to climate change and technological development in Europe. *Italian Journal of Agronomy* 7, 22.

Costanza, R., Costanza, F., (2002). Introduction to the special issue on the dynamics and value of ecosystem services: integrating economic and ecological perspectives. *Ecological Economics*, 41(3), 367–73.

Costanza, R., Fisher, B., Mulder, K., Liu,S., Christopher, T. (2007). Biodiversity and ecosystem services: A multi-scale empirical study of the relationship between species richness and net primary production. *Ecological Economics* 61, 478– 491.

Crutzen, PJ., Mosier, AR., Smith, KA., Winiwarter, WW. (2008). N2O release from agro-fuels production negates global warming reduction by replacing fossil fuels. *Atmospheric Chemistry and Physics* 8, 389–395.

Cubars, E. and Noviks, G. (2012). Evaluation of reed resources in Latvia and analysis of its use for energy production. *Journal of Environmental Biology* 33, 387–392.

Dabrowski, M., Peall, S.K.C., Reinecke, A. J., Liess, M., Schulz, R. (2002). Runoff-related pesticide input into the Lourens River, South Africa: basic data for exposure assessment and risk mitigation at the catchment scale. *Water, Air, Soil Pollution* 135, 265–283.

Daily, GC. and Matson, A. (2008). Ecosystem services: From theory to implementation. *PNAS* 105, 9455–9456.

De Groot, R., Stuip, M., Finlayson, M., Davidson, N. (2006). Wetlands: guidance for valuing the benefits derived from wetland ecosystem services. Ramsar Technical Report No. 3 CBD Technical Series 27. Gland, Switzerland.

De Stefani, G. (2012). Performance of floating treatment wetlands (FTW) with the innovative Tech-IA® system. PhD thesis. Università degli Studi di Padova, Padova, Italy.

De Stefani, G., Tocchetto, D., Salvato, M., and Borin, M. (2011). Performance of a floating treatment wetland for in-stream water amelioration in NE Italy. *Hydrobiologia* 674, 157–167.

Desai, V., Potter, RB. (2006). Remote Sensing, GIS and Ground Truthing. *SAGE*. http://dx.doi.org/10.4135/9781849208925.

Di Guardo, A., Calamari, D., Zanin, G., Consalter, A., Mackay, D. (1994). A fugacity model of pesticide runoff to surface water: Development and validation *Chemosphere* 28, 511–531. DOI: 101016/0045-6535(94)90295-X.

Durel, L., Estrada-Peña, A., Franc, M., Mehlhorn, H., Bouyer, J. (2015). Integrated fly management in European ruminant operations from the perspective of directive 2009/128/EC on sustainable use of pesticide. *Parasitology Research* 114, 379–89.

Dworak, T., Elbersen, B., Van Diepen, K., Staritsky, I., Van Kraalingen, I., Suppit, I., Berglund, M., Kaphengst, T., Laaser, C., Ribeiro, M. (2009). Assessment of inter-linkages between bioenergy development and water availability. Ecologic – Institute for International and European Environmental Policy Berlin/Vienna.

Dyson, J.S., Beulke, S., Brown, C. D., Lane, M.C.G. (2002). Adsorption and degradation of the weak acid mesotrione in soil and environmental fate implications. Organic compounds in the environment. *Journal of Environmental Quality* 31, 613–618.

Edwards, G.P., Molof, A.H., and Schneeman, R.W. (1965). Determination of orthophosphate in fresh and saline waters. *Journal of American Water Works Association.* 57, 917.

Elbersen, B., Startisky, I., Hengeveld, I., Schelhaas, MJ., Naeff, H. (2012). Atlas of EU biomass potentials. Spatially detailed and quantified overview of EU biomass potential taking into account the main criteria determining biomass availability from different sources. Biomass Future, European Commission: Intelligent Energy Europe.

European Biofuels Technology Platform (2013) Report bioenergy report, http://physicsweb.org/articles/news/11/6/16/1. Accessed 26 June 2007.

European Commission (2006). Communication from the Commission to the Council and the European Parliament. Renewable energies in the 21st century: building a more sustainable future. COM/2006/0848.

European Commission (2008). Proposal for a Directive of the European Parliament and of the Council on the promotion of the use of energy from renewable resources. COM/2008/0019.

European Commission, (2011a). Our life insurance, our natural capital: an EU biodiversity strategy to 2020, COM/2011/244, Brusells.

European Commission, (2011b). Proposal for a regulation of the European parliament and of the council on support for rural development by the European Agricultural Fund for Rural Development (EAFRD). COM/2011/627, Brussels.

European Commission. Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides.

FAO, (2008) The State of Food and Agriculture. Biofuels: prospects risks and opportunities. ISSN 0081-4539.

FAO, (2009). Statistics from www.faostat.fao.org, updated April 2009, Rome, Italy: FAO.

Fava, L., Orrù, MA., Scardala, S., Funari, E. (2007). Leaching potential of carbamates and their metabolites and comparison with triazines. *Microchem. J.* 86, 204–208. DOI: 10.1016/j.microc.2007.03.003.

Fazio, S., Monti, A. (2011). Life cycle assessment of different bioenergy production systems including perennial and annual crops. *Biomass and Bioenergy.* 35, 4868–4878.

Florio, G. (2014). Agronomic and environmental evaluation of perennial herbaceous plants fertilized with slurry to obtain biomass for bioenergy. PhD thesis, Università degli Studi di Padova, Padova, Italy.

Freitas, LG., Götz, CW., Ruff, M., Singer, HP., Müller, SR. (2004). Quantification of the new triketone herbicides, sulcotrione and mesotrione, and other important herbicides and metabolites, at the ng/l level in surface waters using liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* 1028, 277–286. DOI: 10.1016/j.chroma.2003.11.094.

Ghirardello, D., Morselli, M., Otto, S., Zanin, G., Di Guardo, A. (2014). Investigating the need of complex vs. simple scenarios to improve predictions of aquatic ecosystem exposure with the SoilPlus model. *Environ. Poll.* 184, 502–510. DOI: 10.1016/j.envpol.2013.10.002.

Goldemberg, J., Guardabassi, P. (2010). The potential for first-generation ethanol production from sugarcane. *Biofuels, Bioproducts and Biorefining.* 4(1), 17–24.

Gómez-Baggethun, E., de Groot, R., Lomas, P.L., Montes, C. (2010). The history of ecosystem services in economic theory and practice: From early notions to markets and payment schemes. *Ecological Economics* 69(6), 1209–1218.

Gottschall, N., Boutin, C., Crolla, A., Kinsley, C., and Champagne, P. (2007). The role of plants in the removal of nutrients at a constructed wetland treating agricultural (dairy) wastewater, Ontario, Canada. *Ecological Engineering* 29, 154–163.

Greenaway, M. (2007). The role of macrophytes in nutrient removal using constructed wetlands. *Environmental Bioremediation Technologies*, 331–351, Springer. ISBN: 978-3-540-34790-3.

Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R., Passeport, E., Payraudeau, S., Schütz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J., Trevisan, M., Wanko, A. (2009). Mitigation of agricultural nonpoint-source pesticide pollution in artificial wetland ecosystems. *Environ. Chem. Lett.* 7, 205–231. DOI: 10.1007/s10311-008-0167-9.

Hackett, M., Lawrence, A. (2104). Multifunctional role of field margins in arable farming. CEA report. *Cambridge Environmental Assessments*, ADAS UK Ltd., Battlegate Road, Boxworth, Cambridge, CB23 4NN, UK.

Hand, L.H., Kuet, S.F., Lane, M.C.G., Maund, S.J., Warinton, J.S., Hill, I.R. (2001). Influences of aquatic plants on the fate of the pyrethroid insecticide lambda-cyhalothrin in aquatic environments. *Environ. Toxicol. Chem.* 20, 1740–1745. DOI: 10.1002/etc.5620200817.

Hansson and Fredriksson, (2004). Use of summer harvested common reed (*Phragmites australis*) as nutrient source for organic crop production in Sweden. *Agriculture, Ecosystems and Environment.* 102, 365–375.

Headley, T.R., and Tanner, C.C. (2006). Applications of floating wetlands for enhanced stormwater treatment: a review. Auckland Regional Council, Technical Publication, Auckland.

Helbig, S. (2009). Biogas Production from Common Reed in Mariental. Renewable Energy and Ecological Development Solution. REEDS Project. http://www.drfn.info/docs/reeds/Biogas_production_from_REEDS.pdf. Accessed 14 September 2013.

Hernández-Crespo, C., Bixquert, J., Gargallo, S., Oliver, N., and Martín, M. (2015). Comparison of three plants in a surface-flow constructed wetland 1 treating eutrophic water in Mediterranean climate. *Hydrobiologia.* DOI: 10.1007/s10750-015-2493-9.

Herzon, I., Helenius, J. (2008). Agricultural drainage ditches, their biological importance and functioning. *Biol. Cons.* 141, 1171–1183. DOI: 10.1016/j.biocon.2008.03.005.

Hinman, M.L., Klaine, S.J. (1992). Uptake and translocation of selected organic pesticides by rooted aquatic plant Hydrilla verticillata Royle. Environmental Science & Technology 26, 609–613.

Horppila, J., and Nurminen, L. (2001). The effect of an emergent macrophyte (Typha angustifolia) on sediment resuspension in a shallow north temperate lake. *Freshwater Biology* 46, 1447–1455.

Horppila, J., and Nurminen, L. (2003). Effects of submerged macrophytes on sediment resuspension and internal phosphorus loading in Lake Hiidenvesi (southern Finland). *Water Research* 37, 4468–4474.

Horppila, J., and Nurminen, L. (2005). Effects of different macrophyte growth forms on sediment and P resuspension in a shallow lake. *Hydrobiologia* 545, 167–175. DOI: 10.1007/s10750-005-2677-9.

IEA (2006). World Energy Outlook 2006. International Energy Agency, Paris.

Istituto Geografico Militare (1976). Carta geografica "Regione", scala 1:250000, Firenze.

Jacobs, J. (2008). Ecology and Management of Purple Loosestrife (*Lythrum salicaria* L.). United States Department of Agriculture, Natural Resources Conservation Service (NRCS), Invasive Species Technical Note No. MT-21.

Jacobs, J., Pokorny, M., Mangold, J., and Graves-Medley, M. (2011). Biology, Ecology and Management of Yellow flag Iris (*Iris pseudacorus* L.). Montana State University Extension.

Jaddhav, R.S., and Buchberger, S.G. (1995). Effects of vegetation on flow through free watersurface wetlands. *Ecological Engineering* 5, 481–496.

Jordan, S., Stoffer, J., and Nestlerode, J. (2011). Wetlands as sinks for reactive nitrogen at continental and global scales: A meta-analysis. *Ecosystems* 14(1), 144–155.

Kadlec, R.H., and Knight, R.L. (1996). Treatment Wetlands. CRC Lewis Publishers, Boca Raton, FL, USA.

Kadlec, R.H., and Wallace, S.D. (2009). Treatment Wetlands, Second Edition. CRC Press, Taylor and Francis Group, NY, USA. p. 1016.

Kallioinen, A., Uusitalo, J., Pahkala, K., Kontturi, M., Viikari, L., von Weymarn, N., Siika-aho, M. (2012). Reed canary grass as a feedstock for 2nd generation bioethanol production. *Bioresource Technology* 123, 669–672.

Kask, U., Kask, L., Link, S. (2013). Combustion characteristics of reed and its suitability as a boiler fuel. *Mires and Peat* 13(05), 1–10.

Kay, P., Edwards, A. C., Foulger, M. (2009). A review of the efficacy of contemporary agricultural stewardship measures for ameliorating water pollution problems of key concern to the UK water industry. *Agricultural Systems* 99, 67–75.

Kitzler, H., Pfeifer, C., Hofbauer, H. (2012). Combustion of reeds in a 3MW district heating plant. *International Journal of Environmental Science and Development* 3(4).

Komulaien, M., Simi, P., Hagelberg, E., Ikonen, I., Lyytinen, S. (2008). Reed Energy. Possibilities of using Common Reed for energy generation in Southern Finland. *Reports from Turku University of Applied Science*. ISBN: 978-952-216-035-5.

KTBL (2005). Key data for agriculture. (Faustzahalen fur die Land-wirtschaft). Kuratorium fur Bauwesen in der Landwirtschaft e. V, Darmstadt.

Laabs, V., Amelung, W., Pinto, A., Altstaedt, A., Zech, W. (2000). Leaching and degradation of corn and soybean pesticides in an Oxisol of the Brazilian Cerrados. *Chemosphere* 41, 1441–1449.

Lashermes, B., Foufoula-Georgiou, E., Dietrich, WE. (2007). Channel network extraction from high resolution topography using wavelets. *Geophysical Research Letters* 34, L23S04. DOI: 10.1029/2007GL031140.

Lazzaro, L., Otto, S., Zanin, G. (2008). Role of hedgerows in intercepting spray drift: Evaluation and modelling of the effects. *Agriculture Ecosystems and Environment* 123, 317–327.

Lianpeng, S., Yang, L., and Hui, J. (2009). Nitrogen removal from polluted river by enhanced floating bed grown canna. *Ecological Engineering* 35, 135–140.

MacBean, C. (2012). The Pesticide Manual, 16th Edition. British Crop Protection Council Publications. Alton, Hampshire, UK.

Mackay, D., Paterson, S. (1982). Fugacity revisited. Environ. *Sci. Technol.* 16, 654A–660A. DOI: 10.1021/es00106a724.

Mackay, D., Shiu, W.Y., Ma, K.C. (1997). Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. *Volume V: Pesticide Chemicals*. Lewis Publisher, Boca Raton, USA.

MacLeod, M., Scheringer, M., McKone, TE., Hungerbuhler, K. (2010). The state of multimedia mass-balance modeling in environmental science and decision-making. *Environ. Sci. Technol.* 44, 8360–8364. DOI: 10.1021/es100968w.

Maes, J., Egoh, B., Willemen, L., Liquete, C., Vihervaara, P., Schagner, J.P., Grizzetti, B., Drakou, E.G., La Notte, A., Zulian, G., Bouraoui, F., Parachini, M.L., Braat, L., Bidoglio, G. (2012). Mapping ecosystem services for policy support and decision making in the European Union, *Ecosystem Services* 1, 31–39.

Mahabali, S., Spanoghe, P. (2014). Mitigation of two insecticides by wetland plants: feasibility study for the treatment of agricultural runoff in Suriname (South America). *Water Air Soil Pollut* 225, 1771. DOI: 10.1007/s11270-013-1771-2.

Maillard, E., Payraudeau, S., Faivre, E., Gregoire, C., Gangloff, S., Imfeld, G. (2011). Removal of pesticide mixtures in a storm water wetland collecting runoff from a vineyard catchment. *Science of Total Environment* 409, 2317–2324.

Maltais-Landry, G., Maranger, R., Brisson, J., and Chazarenc, F. (2009). Nitrogen transformations and retention in planted and artificially aerated constructed wetlands. *Water Research* 43, 535–545.

Maucieri, M., Salvato, M., Tamiazzo, J., Borin, M. (2014). Biomass production and soil organic carbon accumulation in a free water surface constructed wetland treating agricultural wastewater in North Eastern Italy. *Ecological Engineering* 70, 422–428.

Mayo, A.W., and Bigambo, T. (2005). Nitrogen transformation in horizontal subsurface flow constructed wetlands I: Model development. *Physics and Chemistry of the Earth* 30, 658–667. http://dx.doi.org/10.1016/j.pce.2005.08.005.

MEA, Millennium Ecosystem Assessment, (2005a), *Ecosystems and human well–being: Synthesis*, Washington, DC: Island Press.

MEA, Millennium Ecosystem Assessment, (2005), *Ecosystems and human well–being: wetlands and water,* Washington, DC: Island Press.

MEA, Millennium Ecosystem Assessment. (2005). Ecosystems and human well–being: wetlands and water. Island Press, Washington DC.

Meng, P., Pei, H., Hu, W., Shao, Y., and Li, Z. (2014). How to increase microbial degradation in constructed wetlands: Influencing factors and improvement measures. *Bioresource Technology*, 157, 316-326.

Merlin, G., Vuillod, M., Lissolo, T., Clement, B. (2002). Fate and bioaccumulation of isoproturon in outdoor aquatic microcosms. *Environ. Toxicol. Chem.* 21, 1236–1242.

Mietto, A., Borin, M., Salvato, M., Ronco, P., and Tadiello, N. (2013). TECH-IA floating system introduced in urban wastewater treatment plants in Veneto Region – Italy. *Water Science Technology* 68(5), 1144–1150. DOI: 10.2166/wst.2013.357.

Moore, MT., Bennet, ER., Cooper, CM., Smith, Jr S., Shields, Jr FD., Milam, CD., Farris, JL. (2001). Transport and fate of atrazine and lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi Delta, USA. *Agr. Ecosyst. Environ.* 87, 309–314.

Moore, MT., Denton, DL., Cooper, C.M, Wrysinski, J., Miller, JL., Reece, K., Crane, D., Robins, P. (2008). Mitigation assessment of vegetated drainage ditches for collecting irrigation runoff in California. *J. Environ. Qual.* 37, 486–493. DOI: 10.2134/jeq2007.0172.

Morselli, M., Semplice, M., De Laender, F., Van den Brink, PJ., Di Guardo, A. (2015). Importance of environmental and biomass dynamics in predicting chemical exposure in ecological risk assessment. *Sci. Total Environ.* 526, 338–345. DOI: 10.1016/j.scitotenv.2015.04.072.

Mthembu, M.S., Odinga, C.A., Swalaha, F.M., and Bux F. (2013). Constructed wetlands: A future alternative wastewater treatment technology. *African Journal of Biotechnology* 12(29), 4542–4553. DOI: 10.5897/AJB2013.12978.

Murphy, J., and Riley J. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica. Chimica Acta* 27, 31.

Naik, SN., Goud Vaibhav, V., Rout Prasant, K., Dalai Ajay, K. (2010). Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews* 14, 578–597.

Nkemka, VN., Murto, M. (2013). Two-stage anaerobic dry digestion of blue mussel and reed. *Renewable Energy* 50, 359–364.

O'Geen, A.T., Budd, R., Gan, J., Maynard, J.J., Parikh, S.J., and Dahlgren, R.A. (2010). Chapter one - Mitigating nonpoint source pollution in agriculture with constructed and restored wetlands. *Advances in Agronomy* 108, 1–76.

Otto, S., Cardinali, A., Marotta, E., Paradisi, C., Zanin, G. (2012). Effect of vegetative filter strips on herbicide runoff under various types of rainfall. *Chemosphere* 88, 113–119. DOI: 10.1016/j.chemosphere.2012.02.081.

Otto, S., Cardinali, A., Marotta, E., Paradisi, C., Zanin, G. (2012). Effect of vegetative filter strips on herbicide runoff under various types of rainfall. *Chemosphere* 88, 113–119.

Otto, S., Loddo, D., Baldoin, C., Zanin, G. (2015). Spray drift reduction techniques for vineyards in fragmented landscapes. *J. Environ. Manage.* 162, 290–298. DOI: 10.1016/j.jenvman.2015.07.060.

Otto, S., Pappalardo, S.E., Cardinali, A., Masin, R., Zanin, G., Borin, M. (2016). Vegetated ditches for the mitigation of pesticides runoff in the Po Valley. *PLoS ONE* 11(4): e0153287. DOI: 10.1371/journal.pone.0153287.

Otto, S., Riello, L., Düring, R-A., Hummel, H. E., Zanin, G. (1997). Herbicide dissipation and dynamics modelling in three different tillage systems. *Chemosphere* 4, 163–178.

Otto, S., Vianello, M., Infantino, A., Zanin, G., Di Guardo, A. (2008). Effect of a full-grown vegetative filter strip on herbicide runoff. Maintaining of filter capacity over time. *Chemosphere* 71, 74–82. DOI: 10.1016/j.chemosphere.2007.10.029.

Pappalardo, S.E., Otto, S., Gasparini, V., Zanin, G., and Borin, M. (2015). Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland. *Hydrobiologia.* DOI: 10.1007/s10750-015-2375-1.

Pappalardo, S.E., Prosdocimi, M., Tarolli, P., and Borin, M. (2015). Assessment of energy potential from wetland plants along the minor channel network on an agricultural floodplain. *Environmental Science Pollution Research* 22(4), 2479–2490. DOI: 10. 1007/s11356-014-3105-3.

Pappalardo, SE., Otto, S., Gasparini, V., Zanin, G., Borin, M. (2015). Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland. *Hydrobiologia*. DOI: 10.1007/s10750-015-2375-1.

Passalacqua, P., Do Trung, T., Foufoula-Georgiou, E.; Sapiro, GDWE. (2010a). A geometric framework for channel network extraction from LiDAR: Nonlinear diffusion and geodesic paths. *Journal of Geophysical Research* 115, F01002. DOI: 10.1029/2009JF001254.

Passalacqua, P., Tarolli, P., Foufoula-Georgiou, E. (2010b). Testing space-scale methodologies for automatic geomorphic feature extraction from LiDAR in a complex mountainous landscape. *Water Resources Research* 46, W11535. DOI: 10.1029/2009WR008812.

Pavan, F., Breschigliaro, S., and Borin, M. (2015) Screening of eighteen species for digestate phytodepuration. *Environmental Science Pollution Research*. 22(4), 2455–2466. DOI: 10.1007/s11356-014-3247-3.

Petticrew, E. L., and Kalff, J. (1992). Water flow and clay retention in submerged macrophyte bed. *Canadian Journal of Fisheries and Aquatic Sciences* 49, 2483–2489.

Pirotti, F., Tarolli, P. (2010). Suitability of LiDAR point density and derived landform curvature maps for channel network extraction. *Hydrological Processes* 24, 1187–1197. DOI: 10.1002/hyp.758.

Politeo, M., Borin, M., Milani, M., Toscano, A., Molari, G. (2011). Production and energy value of Phragmites australis obtained from two constructed wetlands. 19th European Biomass Conference and Exhibition. Berlin, Germany.

Porter, J., Costanza, R., Sandhu, H., Sigsgaard, L., Wratten, S. (2009). The Value of Producing Food, Energy, and Ecosystem Services within an Agro-Ecosystem. Royal Swedish Academy of Sciences Ambio Vol. 38, No. 4.

Power, A.J. (2010). Ecosystem services and agriculture: tradeoffs and synergies. *Philosophical Transactions of the Royal Society*, *Biological Sciences* 365, 2959–2971.

Power, A.J. (2010). Ecosystem services and agriculture: tradeoffs and synergies. *Philosophical Transactions of the Royal Society*, *Biological Sciences* 365(1554), 2959–2971.

Power, A.J., (2010). Ecosystem services and agriculture: tradeoffs and synergies. *Philosophical Transactions of the Royal Society, Biological Sciences* 365, 2959–2971.

Rahman, MD., Mostafiz, SB., Paatero, JV., Lahdelma, R. (2014). Extension of energy crops on surplus agricultural lands: A potentially viable option in developing countries while fossil fuel reserves are diminishing. *Renewable and Sustainable Energy Reviews* 29, 108–119. DOI: http://dx.doi.org/10.1016/j.rser.2013.08.092.

Ramsar Technical Report No. 3, CBD Technical Series No. 27, De Groot R., Stuip M., Finlayson M., Davidson N., (2006), *wetlands: guidance for valuing the benefits derived from wetland ecosystem services,* Gland, Switzerland.

Rawlings, J.O., Pantula, S.G., Dickey, D.A. (1998). Applied regression analysis: a research tool. 2nd ed. Springer-Verlag Inc., New York.

Reichenberger, S., Bach, M., Skitschak, A., Frede, H.G. (2007). Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; A review. *Science of the Total Environment* 384, 1–35.

Risen, E., Gregeby, E., Tatarchenko, O., Blidberg, E., Malmstrom, ME., Welander, U., Grondahl, F. (2013). Assessment of biomethane production from maritime common reed. *Journal of Clearer Production* 53, 186–194.

Robertson, G.P., Swinton, S.M. (2005). Reconcilling agricultural productivity and environmental integrity: a grand challenge for agriculture. *Frontiers in Ecology and the Environment* 3, 38–46.

Ruhl, J.B., Kraft, S.E., Lant, C.L. (2007). *The law and policy of ecosystem services*, Washington DC, Island Press.

Salvato, M., and Borin, M. (2010). Effect of different macrophytes in abating nitrogen from a synthetic wastewater. *Ecological Engineering* 36(10), 1222–1231.

Sasser, C. E., Gosselink, J.G., and Shaffer, G. P. (1991). Distribution of nitrogen and phosphorus in a Louisiana freshwater floating marsh. *Aquatic Botany* 41, 317–331.

Scott, M., Swinton, Frank, L., Philip Robertson, G., Douglas A. Landis, (2006). Ecosystem Services from Agriculture: looking beyond the usual suspects. *American of Agricultural Economics*, 5, 1160–1166.

Seppelt, R., Dormann, C.F., Eppink, F.V., Lautenbach, S., Schmidt, S. (2011). A quantitative review of ecosystem service studies: approaches, shortcomings and the road ahead. *Journal of Applied Ecology* 48(3), 630–636.

Sofia, G., Pirotti, F., Tarolli, P. (2013). Variations in multiscale curvature distribution and signatures of LiDAR DTMs errors. *Earth Surface Processes and Landforms* 38, 1116–1134. DOI: 10.1002/esp.3363.

StatSoft Inc. (2011). Statistica (data analysis software system), version 10.http://www.statsoft.com StatSoft, Inc. Tulsa, OK, 74,104, USA.

Stehle, S., Elsaesser, D., Gregoire, C., Imfeld, G., Niehaus, E., Passeport, E., Payraudeau, S., Schäfer, R. B., Tournebize, J., Schulz, R. (2011). Pesticide risk mitigation by vegetated treatment systems: A meta-analysis. *Journal of Environmental Quality* 40, 1068–1080.

Swinton, S. M., Lupi F., Robertson, G. P., and Hamilton, S. K. (2007). Ecosystem services and agriculture: cultivating agricultural ecosystems for diverse benefits. *Ecological Economics* (64), 245–252.

Swinton, S.M., Lupi, F., Robertson, G. P., Hamilton, S.K. (2007). Ecosystem services and agriculture: cultivating agricultural ecosystems for diverse benefits. *Ecological Economics* 64, 245–252.

Tanner, C.C., Howard-Williams, C., Tomer, M.D., Lowrance, R. (2013). Bringing together science and policy to protect and enhance wetland ecosystem services in agricultural landscapes. *Ecological Engineering* 56, 1–4.

Tarolli, P., Dalla Fontana, G. (2009). Hillslope to valley transition morphology: new opportunities from high resolution DTMs. *Geomorphology* 113, 47–56. DOI: 10.1016/j.geomorph.2009.02.006.

Tilman, D., Socolow, R., Foley, JA., Hill, J., Larson, E., Lynd, L., Pacala, S., Reilly, J., Searchinger, T., Somerville, C., Williams, R. (2009). Beneficial biofuels—the food, energy, and environment trilemma. *Science* 325(5938), 270–271. DOI: 10.1126/science.117797.

Tomlin, C.D.S. (2006). The Pesticide Manual, 14th Edition, British Crop Protection Council Publications, Alton, Hampshire, UK.

Tournebize, J., Passeport, E., Chaumont, C., Fesneau, C., Guenne, A., and Vincent, B. (2013). Pesticide de-contamination of surface waters as a wetland ecosystem service in agricultural landscapes. *Ecological Engineering* 56, 51–59.

Tournebize, J., Passeport, E., Chaumont, C., Fesneau, C., Guenne, A., Vincent, B. (2013). Pesticide de-contamination of surface waters as a wetland ecosystem service in agricultural landscapes. *Ecol. Eng.* 56, 51–59. DOI: 10.1016/j.ecoleng.2012.06.00.

UNEP (2009). Towards Sustainable Production and Use of Resources - Assessing Biofuels. ISBN No: 978-92-807-3052-4.

Van Acker, J., Buts, L., Thoeye C., and De Gueldre, G. (2005). Floating plant beds: BAT for CSO treatment? Book of abstracts from international symposium on wetland pollutant dynamics and control, September 4–8, 2005, Ghent, Belgium: 186–187.

VDI (2006). VDI standard 4630: fermentation of Organic Materials. Characterisation of the Substrates, Sampling, Collection of Material Data, Fermentation Tests. VDI-Handbuch Energietechnik.

Vianello, M., Vischetti, C., Scarponi, L., Zanin, G. (2005). Herbicide losses in runoff events from a field with a low slope: role of a vegetative filter strip. *Chemosphere* 61, 717–725.

Vymazal, J. (2007). Removal of nutrients in various types of constructed wetlands. *Science of the Total Environment* 380, 48–65.

Vymazal, J. (2010). Constructed wetlands for wastewater treatment. *Water* 2010, 2, 530–549. DOI: 10.3390/w2030530.

Vymazal, J. (2011). Plants used in constructed wetlands with horizontal subsurface flow: a review. *Hydrobiologia* 674, 133–156.

Vymazal, J. (2013). Emergent plants used in free water surface constructed wetlands: A review. *Ecological Engineering* 61P, 582– 592.

Vymazal, J., Březinová, T. (2015). The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: a review. *Environ. Int.* 75, 11–20. DOI: 10.1016/j.envint.2014.10.026.

Vymazal, J., Greenway, M., Tonderski, K., Brix, H., and Mander, Ü. (2006). Constructed wetlands for wastewater treatment. In *Wetlands and Natural Resource Management*; Ecological Studies. Verhoeven, J.T.A., Beltman, B., Bobbink, R., Whigham, D.F., Eds.; Springer Verlag: Berlin, Germany, 190, 69–94.

Wichtmann, W., Joosten, H. (2007). Paludiculture: peat formation and renewable resources from rewetted peatlands. *IMCG-Newsletter* 3, 24–28.

Wichtmann, W., Wichmann, S. (2011). Environmental, social and economic aspects of sustainable biomass production. *Journal of Sustainable Energy & Environment Special Issue*, 77–81.

Zhang, X., Zhang, M. (2001). Modeling effectiveness of agricultural BMPs to reduce sediment load and organophosphate pesticides in surface runoff. *Sci. Total Environ.* 409, 1949–1958. DOI: 10.1016/j.scitotenv.2011.02.012.

Zollo, LA., Rillo, V., Bucchignani, E., Montesarchio, M., Mercogliano, P. (2015). Extreme temperature and precipitation events over Italy: assessment of high resolution

simulations with COSMO-CLM and future scenarios. *Int. J. Climatol.*, in press. DOI: 10.1002/joc.441.