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Galbally, P., Finnan, J., Ryan, D., Fagan, C. C. ORCID: https://orcid.org/0000-0002-2101-8694 and McDonnell, K. (2019) The fate of nutrients and heavy metals in energy crop plantations amended with organic by-products. Environmental Technology & Innovation, 15. 100434. ISSN 2352-1864 doi: https://doi.org/10.1016/j.eti.2019.100434 Available at https://centaur.reading.ac.uk/85174/

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To link to this article DOI: http://dx.doi.org/10.1016/j.eti.2019.100434

Publisher: Elsevier

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PII: S2352-1864(18)30421-8
DOI: https://doi.org/10.1016/j.eti.2019.100434
Article number: 100434
Reference: ETI 100434

To appear in: *Environmental Technology & Innovation*

Received date : 11 September 2018
Revised date : 11 July 2019
Accepted date : 17 July 2019

Please cite this article as: P. Galbally, J. Finnan, D. Ryan et al., The fate of nutrients and heavy metals in energy crop plantations amended with organic by-products. *Environmental Technology & Innovation* (2019), https://doi.org/10.1016/j.eti.2019.100434

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The fate of nutrients and heavy metals in energy crop plantations amended with organic by-products

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Keywords: Mass-balance; overland flow; groundwater quality; soil quality; biosolids; distillery effluent; *Miscanthus x giganteus*; short rotation coppiced willow.

Abstract

Organic by-products (OB) can provide nutrition to energy crops but there is a potential risk of pollution to soil, groundwater (GW) and surface water (SW). A mass-balance inventory for two energy crops spread with biosolids (BS) and distillery effluent (DE) was created in order to study the fate of nutrients. Biosolids and distillery effluent (DE) were spread on both *Miscanthus x giganteus* and short rotation coppice willow (SRCW). Applications were conducted at rates of 100%, 50% and 0% (control) of permissible P loads. Losses of nutrients (N,P) and heavy metals (Cd, Cu, Cr, Pb, Ni, and Zn) to groundwater and overland flow (OLF), and crop uptake were determined. Total inputs (from soil, OB amendment and atmospheric deposition) and losses were calculated and compared. The greatest input was from the soil, the smallest input was atmospheric deposition. The largest output was crop off-take; the smallest was loss to OLF. Elemental uptake by Miscanthus was lower than that of willow but losses to groundwater and overland flow was similar for both crops. This study has shown that organic byproducts can be used to enhance the nutrition of energy crops without deleterious environmental consequences.

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1. Introduction

Energy crops provide a fast growing supply of renewable energy which can replace fossil fuels and mitigate emissions of greenhouse gases (Finnan et al., 2012; Murphy et al., 2014). However, energy crop plantations can also offer other services to society such as the treatment of organic wastes and wastewaters (Dimitriou et al., 2006; Rosenqvist et al., 1997; Figala et al., 2015).

Willow (genus *Salix*, family *Salicaceae*) (Argus 1997) is a native plant in Ireland**.** The high transpiration and low nutrient requirements of willow (Hasselgren, 1998) facilitates disposal of large volumes of watery waste (Guidi et al., 2008)**.** Short rotation coppice willow (SRCW) exhibits good juvenile growth with yields of 7-12 t DM ha^{-1} yr^{-1} in Ireland when grown as short rotation coppice (Caslin et al., 2015b; Dieterich et al., 2008). It is also thought that the high transpiration rate and composition of willow allow it to phytoremediate soils receiving OBs (Hasselgren 1998; Dimitriou, 2005).

Miscanthus (*Miscanthus* × *giganteus* Greef J. M., Deuter ex Hodk. and Renvoize) is a perennial Southeast Asian C4-grass which is established by planting rhizomes from existing plants (Jones and Walsh, 2001). The crop can be used for bioremediation (Figala et al., 2015) and can produce yields of up to 12 t ha^{-1} in Irish conditions; the

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crop's useful lifetime is approximately 20 years (Caslin et al., 2015a). Both *Miscanthus* and SRCW are leading candidates for commercial energy in Ireland and elsewhere (Caslin 2015a; 2015b; Rosenqvist et al., 1997; Clifton-Brown et al., 2007).

Energy crops, as non-food crops offer a means of disposing of OB on farmland as the risk of direct contamination to the food chain is minimal (Dimitriou et al., 2006). Energy crops are usually resilient and can often remove heavy metals (HMs) and other toxins from soil with minimal effects on themselves (Britt and Garstang 2002; Figala et al., 2015). Tsadilas (2005) claims that OB amendment aids crop nutrition and improves soil quality via increased organic matter content, water retention, improved soil structure and better infiltration. Energy crops utilise nutrients to maximise yield although nutrient requirements are low compared to other crops (Caslin et al., 2015a; 2015b). The use of sewage sludge and wastewater to fertilize SRCW offers both environmental and economic benefits through decreased fertilization costs and increased biomass production (Dimitriou and Rosenqvist, 2011). Additionally, the use of SRCW for the bioremediation of effluent from rural waste water treatment plants offers an effective and practical treatment for wastewater management (McCracken and Johnston 2015).

However, there are concerns that applications of OBs may result in the leaching of pollutants to ground waters (GWs) or runoff to surface waters (SWs) (Merrington 2002). Build-up of both nutrients and HMs in soil receiving BS amendment is of particular concern (McBride, 1995; 2003). Incorrect application of fertilizer can result in excess nutrients in soil (Addiscott, 2005) which also applies to OBs (though nutrient content and release profiles differ). Links between OB-amendment and SW pollution have already been identified (Epstein 2003; Korboulewsky et al. 2002); however, studies with wastes such as distillery effluent are limited. Additionally, links between OB amendment to energy crops and GW pollution have also been established by Curley (2009) and Dimitriou and Aronsson (2004).

Increases in nutrients and HMs in soil have been noted following application of OBs in several studies (Haynes, 2009). Incorect amendment of OBs can therefore result in build-ups of HMs. Tian (2006) identified OB constituents that contaminate soil and result in loss of NO_3-, PO_4^{3}-, HMs and organic matter to SW. The presence of these constituents in DE and BS raises concerns regarding impacts from OB application (Haynes, 2009; Merrington 2002). However, build-up of HMs in soil after OB application may be mitigated by the bioremediation capacity of energy crops which have been reported to have good ability to absorb HMs from soil (Dimitriou et al., 2012; Figala et al., 2015).

In previous decades, untreated organic wastes were spread to Irish farmland used for food production; this practice was banned in the early 1990s (McGrath and McCormack, 1999). Following this, land filling and sea dumping were used before these routes were removed by European Commission (EC) directive (1999/31/EC) on land filling of waste and EC directive (91/271/EEC) on sea-dumping in the late 1990s. The regulations were introduced to improve treatment of OBs at source, and stimulate sustainable solutions to disposal (EPA, 2008). There is relatively limited information on the environmental impact of OB amendment to Irish SRCW and *Miscanthus*. Experiments were therefore conducted between 2007 and 2009 to assess such impacts and compare results obtained to those from other studies (Galbally et al., 2012; 2013;

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2014a; 2014b). The work was carried out with two energy crops (*Miscanthus* and willow) and involved two different waste products (distillery effluent and sewage sludge). The results showed that there was little risk to surface water from OB amendment on suitable sites (Galbally et al., 2014a&b) although it was found that amendment could lead to groundwater contamination in certain instances (Galbally et al., 2012;2013).

The objective of this present study was to study the fate of the nutrients and heavy metals applied to energy crops in OB amendments in the context of all inputs and outputs of nutrients and heavy metals to the soil-crop-water system. In order to achieve this objective, a mass-balance approach was used to create a complete inventory of nutrient and heavy metals entering and leaving the system.

2. Materials and Methods

2.1 Study Area

The experiments were conducted at Oak Park Research Centre, Carlow, Ireland. The facility (52º51'55" N lat 6º54'43" W long) occupies 350 ha and is situated 55.8 meters above mean sea level (AMSL).

All experiments were conducted on a soil type known as the Athy Complex (Conry and Ryan, 1968). The parent material of this soil are calcareous, fluvio-glacial gravels of Weichsel Age, composed mainly of limestone with small proportions of sandstone and granite. Three horizons are described; an upper horizon with a depth of approximately 25 cm described as a sandy loam, a second horizon with a depth of between 25 and 85

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cm described as a gravelly sandy loam and a third horizon below 85 cm consisting mainly of coarse sand.

2.2 Plot establishment

Twelve plots were laid out in total. In 2006, six plots were laid out in plantations of *Miscanthus* (established in 1993), three plots in the Barley Field (BF) (52°51'47.9" N lat 6°90'86.6" W long) for application of DE and three in the Near Avenue Meadow (NAM) (52°51'31.7" N lat 6°90'77" W long) for BS. All *Miscanthus* plots had an area of 0.1174 ha (42 m x 28 m). In 2007, a plantation of mixed *S. Viminalis* L. and *S. Schwerinii* L. willow hybrids was established in the Far Avenue Meadow (FAM). All SRCW plots were 0.0588 ha (14 m x 42 m) in dimension. Six plots were established in this plantation (arranged in two sets of three); three at 52º51'29.83" N lat 6º54'19.94" W long for DE and three at 52°51'31.7" N lat 6º54'14.15" W long for BS. The SRCW plots were spaced with 5 meters between their facing edges, to minimize interaction across plot surfaces.

Plots were labelled according to treatment; i.e. plots subject to DE applications are denoted DE_x and BS are denoted BS_x, the subscript *x* denotes treatment application level (0, 50, 100%). Codes are preceded by an "M" or "W" to indicate *Miscanthus* or SRCW, respectively (e.g. M-BS_x).

2.3 Climate Conditions

Ireland has a temperate climate dominated by Atlantic weather systems and typified by mild, year-round precipitation. This results in soils that rarely dry out and are saturated where drainage is poor (Keane and Collins 2004). Precipitation is low intensity; most

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agricultural soils drain well and do not become waterlogged. A summary of conditions during experiments is presented in Table 1. Climate conditions were slightly different for the crops because of start times and durations of experiments; however prevailing conditions were the same. Data was obtained from Met Eireann's synoptic meteorological station in Oak Park. Temperature and rainfall were above 30-year averages (1960-1990) during the 30 month experimental period. Atmospheric deposition rates were obtained from the literature (Aherne and Farrell, 2002; Jennings et al., 2003; Nicholson et al., 2003). Average deposition rates are presented in Table 2.

2.4 Organic waste application

The OBs were obtained from a commercial waste-management company, Ormonde Organics (Co. Kilkenny, Ireland). All BS were sourced from municipal waste-water treatment plants in Ireland. Distillery effluent was sourced from First Spirits Ireland Ltd (Co. Laois, Ireland). All OBs applied underwent analysis for nutrient- and HM-concentrations at FBA Laboratories, Co. Waterford, Ireland, prior to spreading; to ensure that all OBs complied with Irish Regulation SI. No.148/1998. The OBs were applied at treatment rates of 100% (W-BS$_{100}$, W-DE$_{100}$), 50% (W-BS$_{50}$, W-DE$_{50}$) and 0% (W-BS$_{0}$, W-DE$_{0}$) on the basis on permissible P application (Caslin et al. 2015a and 2015b).

Biosolids (Tables 4&6) were spread by a disc-spreader during the experimental-period. Annual treatment-rates varied due to variation in P-content and dry matter content of each batch. The spreading duration differed between *Miscanthus* (30 months) and willow plantations, the duration being lower for willow plantations (20 months).

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The DE was spread during the September-October period (DE materials was not available prior to this period) using an irrigation system. The total DE-amended (and a breakdown of constituents) are provided in Tables 3&5. Further details are available in Galbally et al. (2012, 2013, 2014 a&b).

2.5 Monitoring of Losses

The quantities of nutrients (N&P) and HMs (Cu, Cr, Pb, Ni and Zn) lost to GW (Galbally et al., 2012 and 2013) and SW via OLF (Galbally et al., 2014a and 2014b) was quantified. Concurrent with monitoring GW and SW, crop and soil samples were obtained from each treatment prior to (and following) OB applications.

2.5.1 Groundwater Sampling

A series of three wells were drilled in each plot to obtain groundwater samples, samples were extracted once per month and were bulked, further details are provided in Galbally et al., (2012).

Volumes of water ingressing to groundwater were calculated by first calculating effective rainfall by subtracting overland flow and evaporation from precipitation. In the case of treatments amended with distillery effluent, volumes of DE added were added to precipitation amounts. Curneen and Gill (2016) reported that evapotranspiration from willow systems in Ireland substantially exceeded reference evapotranspiration during summer months. On the basis of their figures, it was conservatively assumed that reference evapotranspiration values for both crops doubled during the months of August, September and October but were equal to reference evapotranspiration figures

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for the remaining months of the year. Effective rainfall was then multiplied by a recharge coefficient which reflects the permeability of the subsoil. It was assumed that the subsoils under the study area had a high permeability corresponding to Irish soils with a recharge coefficient of 0.81-0.85.

2.5.2. Over Land Flow (OLF) Samples and Data

The occurrence and duration of overland flow events were collected to data loggers fitted to sensors designs to record OLF events. Both basic 'grab' samples and samples which were proportionally accurate representations of OLF were obtained. Further details are provided in Galbally et al., 2014a; 2014b).

2.5.3. Soil and Crop Sampling

Topsoil samples were taken from each plot to a depth of 10 cm; each topsoil sample was a bulked-composite of 6 sub-samples. To obtain four complete bulk-samples per plot, 24 sub-samples were taken using a "W" pattern; this sampling-scheme was used for all plots.

Crop samples were obtained annually at the end of each growing season by sampling the above ground parts of at least five plants per plot. Plants were cut into small pieces and mixed to ensure a representative bulk samples before being weighed and dried. Dried samples were sent for elemental analysis.

2.6 Mass Balance

To assess all inputs and outputs (and compare treatment effects), all results were compiled into a useful whole value and therefore, a mass-balance budget was created.

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Analysis involved creating an inventory of the available mass of each nutrient (kg) or HM (g) (different units were used for reasons of utility) and determining availability loss during the course of the experiment. A mass balance of nutrient and heavy metal inputs and losses was constructed for each plot. The mass balance of nutrient and heavy metal availability included deposition by atmosphere, nutrient and heavy metals added by OB amendment together with quantities of HMs and nutrients in soil. The mass balance of nutrient and heavy metal loss included losses to GW and SW (via OLF) together with crop uptake. Mass in crop was determined by consideration of concentration in crop samples by yield. Volatilization of nutrients and HMs was not considered. Comparison of all plots was equalized in terms of duration and plot areas.

3. Results

3.1 Introduction

Mass balance results are presented in several sections. The first section deals with available nutrients and HMs; values for nutrients are in kilos and HMs in grams (as values for nutrients were an order of magnitude greater than HMs). The second section looks at individual element losses to GW, OLF and crop uptake. Loss via volatilization was not considered and total losses will be greater for volatilizable species (such as N). Results for nutrients and HMs are presented in separate figures (for clarity).

3.2 Available nutrients and total metals present on plots

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Tables 3 to 6 show total available (and unavailable) nutrients and HMs for all plots, including existing soil nutrient pools, the amount applied in OB and deposited material from the atmosphere. Distillery effluent application (Table 3 and 5) made a considerable contribution to available nutrients. Atmospheric deposition of P was minimal but N deposition was significant compared to N application. The contribution of DE to total nutrients was important; increasing DE amendment increased the quantity of nutrients available. Background levels of P in soil were high (see Tables 3 to 6).

Table 3 shows HMs in *Miscanthus* plots treated with distillery effluent; the largest pool of HMs was in soil, HMs from OB application were small; the exception was Zn and Cu. Atmospheric deposition provided highly solubised metals to *Miscanthus* plots. In general, quantities of metals from atmospheric deposition were considerably smaller than the quantities of metal applied through DE amendment although concentrations of Zn deposited through atmospheric deposition were significant and comparable with DE amendment.

Table 4 shows sources of nutrients and heavy metals in *Miscanthus* plots treated with biosolids, as with the *Miscanthus* plots treated with distillery effluent, OB application made a large contribution to the available nutrients (particularly P). Atmospheric deposition of P was minimal. Deposition of N was significant in relation to BS application (5% of all OB amendment N). Variability in soil HM was observed between individual plots (and between *Miscanthus* sites receiving either biosolids or distillery effluent). Metals deposited through atmospheric deposition were considerably smaller than the quantities of metal applied through BS amendment

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although concentrations of Zn deposited through atmospheric deposition were significant and comparable with BS amendment. Atmospheric deposition of Zn was 12% of that supplied by BS amendment (at the 50 % treatment rate).

Table 5 shows sources of nutrients and heavy metals on SRCW plots treated with distillery effluent; it can be seen that P added to the soil-plant system through DE amendment was comparable to the P concentrations in soil whereas P deposition was low. The quantity of nutrients supplied by DE to SRCW plots was lower than supplied to *Miscanthus* plots receiving distillery effluent (Table 3).Rates of deposition were lower (due to slight scale differences). Background soil nutrients varied between sites (Tables 3-6) demonstrating variability in soil conditions at field scales.

Soil HMs in SRCW plots receiving distillery effluent were a much greater potential source of metals than amendment or deposition (Table 5). Ratios of individual HMs in willow soils was approximately equivalent to *Miscanthus* plots.

Table 6 shows available nutrients and heavy metals for SRCW plots receiving BS; quantities of P in soil were similar to quantities of P added through BS amendment but much higher than quantities added through atmospheric deposition. In terms of OB application, rates of N were higher for SRCW plots receiving BS compared to SRCW plots receiving DE due to greater concentrations of these nutrients in BS; P-applications were approximately equivalent. The largest source of potentially available heavy metals was from the soil. In comparison, the quantities of potentially available heavy metals in BS amendment were small.

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Table 6 also shows sources of input metals to SRCW plots receiving BS; and the large pool of HMs bound in the soil organic matter is again evident. The concentrations of metals in these plots were smaller than in the corresponding *Miscanthus* plots or in SRCW plots receiving DE (despite the latter's proximity) again demonstrating variability in soil HMs over very short ranges. However, the amount of HMs introduced to these plots via BS was greater than HMs introduced to SRCW plots receiving DE via DE application.

3.3 Nutrient and heavy metal losses

In this section, losses of nutrients and HMs from plots are broken down by fractions lost to crop uptake, leaching to GW and loss to OLF. Figure 1(a) shows fractions (loss to GW, OLF and crop uptake) of nutrient loss from *Miscanthus* plots receiving DE. The role of crop uptake and positive correlations between DE treatment rate and loss of P and N are evident. Crop uptake increased with DE amendment rates. High rates of N were lost to drainage relative to P and losses of N to drainage were influenced by DE application rate. Crop uptake of P was lower than that of N but P losses to drainage were lower than those of N but increased with application rates. Losses of N and P through OLF were very small but there was a relation between application rate and loss.

Figure 1(b) shows loss of nutrients from *Miscanthus* plots receiving BS; loss of nutrient from *Miscanthus* plots spread with BS were greater than from plots to which DE had been applied. This correlates with the greater quantities of nutrients supplied by BS compared to DE (Tables 3 and 4). Losses of N to GW increased with BS application rate. However, losses of P to GW were lower than those of N and were unrelated to BS

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application rate. However, nutrient loss in OLF, although very small, was significant but unrelated to application rate.

Figure 1(c) shows loss of HMs from *Miscanthus* plots receiving DE, Zn had the greatest loss rate of all metals and losses of Zn were dominated by crop uptake. Losses of all metals generally increased with DE application. For most metals, losses to groundwater were greater than losses to crop uptake. The Zn pool in soil (Table 3) was considerably smaller than the Ni pool although quantities of Ni in DE were smaller than quantities of Zn. However, loss of Ni was low compared to Zn. The patterns of loss for Zn, Ni and Cu corresponded with OB amendment rates rather than soil pools (Table 3). Results suggested that this was also the case with Cu and Pb. Losses to OLF were very small, with the exception of Cu and Zn where losses to OLF increased with application rate. The results showed that almost all HM losses occur through leaching or crop uptake up, OLF was not a major loss pathway for metals. indicating OLF is not a major issue for metals (even for more mobile species such as Zn).

Figure 1(d) shows the loss of HMs to crop, GW and OLF from *Miscanthus* plots amended with biosolids. A high uptake of Zn and Cu is evident (as with *Miscanthus* DE plots plots) which was related to the level of BS amendment. Results from Figures 1c and 1d show commonalities in how HMs are mobilized, regardless of OB type. Losses of Zn and Cu tended to be dominated by crop uptake. Losses of Cd, Cr, Pb and Ni tended to be dominated by drainage losses. Losses to OLF were very small in comparison to losses to drainage and crop uptake.

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Figure 2(a) shows nutrient losses from SRCW plots amended with DE by crop uptake , leaching to GW and surface OLF loss. Comparison with Figure 1 shows take up of nutrients by SRCW was greater than take up by *Miscanthus.* Nutrient losses were dominated by crop uptake although there were drainage losses in the case of N but not P. In contrast, losses to OLF were very small. Figure 2(b) shows the loss of nutrients from willow plots amended with BS and their breakdown into crop uptake, leaching through profile and loss to OLF. Again, crop uptake was greater than loss to either GW or OLF. Losses via the OLF pathway were very small. The uptake of nutrients by SRCW on BS plots was comparable to DE plots, Figure 2 (a), though rates do not correlate with rates of BS applied. Nutrient loss to OLF was similar for DE and BS plots, Leaching of nutrients to GW were comparable between both types of waste.

Figure 2(c) shows loss of HMs from W-DE plots; when compared to Figure 1, results show the higher uptake up of Zn by SRCW compared to *Miscanthus* for both DE and BS. Crop uptake of Ni and Cr was comparable but low, possibly because of the smaller levels of these metals in DE. Surface loss of HMs via OLF from SRCW DE plots was low. Differences in HM losses in OLF (between *Miscanthus* and SRCW plots) were similar to patterns of nutrient loss. Leaching of HMs to GW from SRCW DE plots (Figure 2) was lower than leaching from *Miscanthus* DE plots (Figure 1). Figure 2(d) shows total HM losses from SRCW BS plots. Metal uptake by crop, leaching to GW and loss to OLF were similar to patterns of loss for SRCW DE treatments, with significant take up of Zn. Soil HM pools and HMs derived from OB application were higher for SRCW BS plots (deposition from the atmosphere was equivalent); however, HM losses were lower (or equivalent) for SRCW BS plots compared to SRCW DE plots , indicating lower HM mobility in BS. Based on these results, greater

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concentrations of HMs in BS did not automatically equate to greater HM losses from plots spread with BS materials.

4. Discussion

By far the largest pool of (potentially available) nutrients and metals is from the soil which far exceeds the quantities of nutrients and heavy metals in OB amendment and atmospheric deposition pools. However, the vast majority of soil HMs will be bound in the soil (Haynes et al. 2009) and only a very small percentage becomes bioavailable (Alloway & Jackson 1991; McGrath et al. 2008). Some OB borne nutrients and HMs will also be immobile; however, a substantial quantity of elements in OB will be available immediately while more becomes available over time (Haynes et al. 2009). This is particularly true of HMs, organic byproducts contain a very high percentage of bioavailable metals (Pacyna and Ottar, 1989). Although the availability of soil HMs is lower than from OB or deposition (Alloway & Jackson 1991), the size of this (soil) pool will result in large losses if a small fraction becomes available. Metals introduced via amendment were greater from BS applications than DE agreeing with previous reports of the composition of these materials (Carton, 2007) although concentrations of Zn in both materials were approximately equivalent.

Nutrients and HMs from atmospheric deposition will be very bioavailable as solutes within rainfall (Pacyna & Ottar, 1989). Deposition also occurs directly on plot surfaces giving this vector a disproportionately important impact on OLF. The relatively large quantities of HMs deposited on plots by the atmosphere over the experimental period,

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puts the potential impact of BS and DE amendments into perspective. That said, the quantities of HMs derived from OB amendments (even DE) were larger than from atmospheric deposition (despite increases in atmospheric metals such as Pb in recent years) (EPA 2008). Most metals had low deposition rates compared to DE or BS amendments; however, this was not true of all metals, particularly those present in small concentrations (such as Cd). Deposition of some HMs was comparable (or even greater) than from DE amendment (Zn supplied by DE to W DE was a tenth of the Zn introduced via the atmosphere). For Cu, this was more pronounced (with Cu from DE being 5% of deposition to SRCW DE plots) implying DE application would not contribute significantly to risks of quality degradation from HM losses (at these amendment rates).

Due to HM immobility in soil (Alloway and Jackson, 1991), soil pools do not significantly influence short-term metal losses, although long-term impact on crop uptake and GW is important. Surface flows of HMs are strongly affected by atmospheric deposition and OB applications relative to soil pools. This is less true of nutrients, as nutrient pools in healthy soil usually provide significant amounts of N and P in bioavailable forms (Merrington 2002). In terms of the nutrient mass balance, the total input of available N in this work does not include available soil-N (as there is no reliable Irish test): the soil-N status of the soils was typical for Irish grasslands (based on the Index-scale system) (Coulter and Lawlor 2008). Existing soil-N is likely to contribute to total-N budgets for each crop. In terms of deposition of nutrients, there is a small though important contribution (given almost all deposited nutrients will be bioavailable and remain on the surface) (Aherne and Farrell 2001); they will therefore have a disproportionate impact on OLF and uptake (relative to the other sources).

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Previous results show that OB applications can result in nutrient loss (Galbally et al. 2012; 2013; 2014a; 2014b). It is likely that deposition of nutrients is also a factor in losses to OLF; however, this is equivalent across plots and difficult to detect. The greater uptake of nutrients by SRCW was noticeable, though leaching to GW was low (and similar for both crops). Additionally, there was not always a clear relationship between OB application and nutrient drainage loss suggesting that nutrient losses were influenced as much by background soil nutrient levels as by nutrients in OB applications as reported previously by Galbally et al (2012). Losses of nutrients to drainage differed between the two crops as *Miscanthus* had greater losses of N compared to willow. Dimitriou et al., (2012) previously reported high P losses to leaching under willow crops. Nutrient losses via the OLF pathway were influenced by OB application but losses were very small in comparison to losses to drainage and crop uptake as reported previously by Galbally et al. 2014a &b. Losses of HMs to OLF were influenced by OB application and were small in relation to drainage losses. For willow, HM losses were dominated by crop uptake. Cadmium, considered the most hazardous element in the food chain, is readily taken up by SRCW (Dimitriou et al., 2006; 2012) and this research found that losses to drainage and OLF were miniscule in relation to crop uptake. In contrast offtakes of Cd by *Miscanthus* were much lower, comparable to drainage losses, possibly attributable to greater concentrations of Cd in roots and rhizomes compared to shoots (Fernando & Oliveira, 2004). Zn was the element which was most readily taken up by both crops, crop uptake increasing with OB application. Dos Santos Utmazian and Wenzel (2004) previously reported much higher concentrations of Zn compared to Cd in willow grown on contaminated soils. Similarly, Kocon and Matyka (2012) reported much higher concentrations of Zn compared to Pb

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in *Miscanthus* grown on contaminated soils even though the concentrations of both these elements in soil were equivalent.

Crop uptake was the largest nutrient output pathway for both crops although willow took up approximately three times the quantity of nutrients and heavy metals taken up by *Miscanthus,* thus the superior phytoextraction performance of willow is evident. Dimitriou (2005) previously reported that willow could be used in phytoremediation systems. Lower uptake of nutrients, and perhaps heavy metals, by *Miscanthus* is possibly related to the greater nutrient use efficiency of *Miscanthus* which is attributable to its C4 photosynthetic system (Naidu and Long, 2004) whereas willow has a C3 photosynthetic system with lower nutrient use efficiency. Willow, typically, has higher nutrient requirements compared to *Miscanthus* (Caslin et al., 2015 a&b) while N fertilization experiments which were conducted close to the experimental sites in this study have demonstrated that willow crops have higher N requirements compared to *Miscanthus* (Finnan and Burke, 2014; Finnan et al., 2014). Crop uptake involves absorption through roots and requires soluble elemental forms being accessible to root systems. The depth of both crops' roots was >1.5 m (Finch et al. 2004); however the topsoil in which HMs tend to be present does not extend below 25 cm. This mass balance does not account for nutrients and heavy metals which are absorbed by and remain concentrated in the root and rhizomes systems of both energy crops. For example, Kocon and Matyka (2012) found that Zn was concentrated in the aerial parts of Miscanthus whereas Pb was concentrated in the roots. *Miscanthus* and willow have extensive rooting systems (Finnan and Burke, 2014; Matthews and Grogan, 2001; Cunniff et al., 2015) which can potentially store significant quantities of nutrients and heavy metals. *Miscanthus* has an extensive rhizome system just under the surface of the

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soil, the weight of the underground part of the crop can exceed that of the aerial parts of the crop (Finnan and Burke, 2014). Willow plants also have an extensive shallow rooting system which is concentrated in the 0-25 cm depth, the proportion of underground biomass is lower for willow than *Miscanthus* although underground biomass under willow plantations can still be significant (~10 t DM/ha; Cunniff et al., 2015). However, given that underground biomass is greater for *Miscanthus* than for willow, it is possible that the *Miscanthus* rhizomes system may store greater quantities of nutrients and heavy metals than for willow. For both species, nutrients and heavy metals retained by roots remain on the soil-plant system, at least temporarily, and are not lost from the system unless translocated to aerial parts of the plant. This study quantified losses from the system, including losses from harvesting but harvest offtakes underestimate the quantity of nutrients and heavy metals absorbed by the crop.

The greatest source component are the soil pools (demonstrating the influence of background soil conditions); and the largest output is crop uptake. The smallest input is (often) atmospheric deposition, and the smallest losses are from OLF. Atmospheric deposition has a disproportionate impact on OLF loss due to mobility of species introduced by this pathway. Input from OB application is considerable for nutrients and less so for metals (though Zn and Cu are supplied in large quantities by both OBs). In some instances, HMs applied via amendment are lower than deposition, suggesting low risks of quality degradation from OB-derived metals.

Leaching of nutrient and HMs to GW make up a substantial fraction of the total losses, greater than comparative loss to OLF (though risk profiles for GW and OLF are different and needs to be considered). Loss of individual species to GW are relatively

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large for nutrients but much less so for metals (with exception of Zn). There is some correlation between the loss of (some) nutrients and HMs and the rate and application of BS and DE, implying both forms of OB application can impact losses. This relationship is most evident for loss to OLF and the most serious potential risk from such losses arises from loss of P to OLF (there was also evidence of loss of N to GW). The uptake of nutrient and HMs by both types of crop was strongly influenced by existing levels in soil and the soil conditions; this was particularly the case for all the HMs.

In this study, nutrient removal at harvest (crop uptake) was the largest loss pathway. Loss of nutrients at harvest, unless replaced will lead to a reduction in soil fertility and ultimately in yield and nutrient off-takes are the basis for calculating the fertilizer requirements of both *Miscanthus* and willow (Caslin et al., 2015a, 2015b). Thus, the replacement of nutrient off-takes is the primary reason for the application of organic by-products to energy crops. Energy crop fertilization may be accompanied by increases in growth and productivity, nitrogen fertilization of willow crops grown on this site increased yield by 35% (Finnan et al., 2014) while nitrogen fertilization of recently sown Miscanthus crops increased yield by 35 – 43% (Finnan and Burke 2016).. However, on the same site, nitrogen fertilization of a mature *Miscanthus* crop did not stimulate spring harvested yields (Finnan and Burke, 2014). Similarly, Adegbidi et al., (2003) found that the application of organic amendments increased yield of willow crops by 30-38% whereas other studies have not found any yield benefit from the application of organic wastes to willow (Quaye et al., 2011; Quaye and Volk, 2013). Irrespective of whether willow yields are stimulated by the application of organic amendments, the primary purpose of organic fertilization is the replacement of nutrient offtakes and the prevention of any loss of soil fertility and subsequent yield reduction. Secondary advantages of organic amendment to energy crops, however, arise from the disposal of potentially difficult wastes in a manner which does not contaminate the food chain and in this study we have demonstrated that organic byproducts can be used to enhance the nutrition of energy crops without deleterious environmental consequences.

Conclusions

The quantities of nutrients and heavy metals supplied to soil/plant systems in OB amendments are often substantially smaller than the quantities of such elements in soil or even the quantities supplied to the system by atmospheric deposition, this is particularly the case for heavy metals. Losses of nutrients and heavy metals to groundwater and surface water can increase with OB amendment but the principal component of such loss pathways is often made up of elements lost from soil or atmospheric deposition. Losses to groundwater and surface water are often substantially lower than crop uptake, the main loss pathway. Willow had much greater phytoremediation potential compared to *Miscanthus* although nutrient losses to groundwater and surface water did not increase as a result of reduced uptake by *Miscanthus*.

Organic wastes can be applied to energy crops without causing significant increases in the quantities of nutrients and heavy metals entering groundwater and surface water bodies. The quantities of environmentally sensitive elements supplied in organic wastes are typically smaller than corresponding elemental pools in soil, particularly for heavy metals. Thus, the dominant influence on the quantities of elements entering groundwater and surface waters are the concentrations of such elements in soil, elements deposited from the atmosphere can also have an important influence on elemental flows to surface waters. Crop offtake is the principal output pathway from

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the system although elemental removal varies with crop type. This study has shown that organic byproducts can be used to enhance the nutrition of energy crops without deleterious environmental consequences.

Acknowledgements

The authors would gratefully like to acknowledge the help of Teagasc (The Irish Agricultural Research Authority) and University College Dublin as well as the financial assistance provided by the Irish Department of Agriculture through the Research Stimulus fund.

Researchers Paul Galbally and Declan Ryan sadly passed away during 2017. Their contribution to this work was highly significant and their presence is very much missed. May they rest in peace.

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Figure Captions:

Figure 1: Pathways of loss of nutrients and heavy metals from *Miscanthus* plots applied with distillery effluent (graphs a and c) and biosolid (graphs b and d), loss of nutrients given in kilograms and metals in grams for convenience. 20 months.

Figure 2: Pathways of loss of nutrients and heavy metals from short rotation coppice willow plots applied with distillery effluent (graphs a and c) and biosolid (graphs b and d), loss of nutrients given in kilograms and metals in grams for convenience. 20 months.

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Table 1: Climate conditions† during the experimental period

Start Date	17/03/2007
End Date	31/12/2009
Total days, d.	1019
Total Rain, mm	2657
Rainfall during experiment (as % of 30 year mean)	115%
Total evaporation, mm	1724
Net rain (total for 1019 d.)	1638
Mean daily evaporation (1019 days), mm	1.69
Mean daily rainfall (1019 days), mm	2.61
Mean net rainfall, mm	0.92
Evaporation (mean for January), mm	11.3
Evaporation (Mean for June), mm	108.7
Rainfall, mean (January), mm	109.4
Rainfall, mean (June), mm	87.3
Net rain (Jan), mm	98.0
Net rain (Jun), mm	-21.5

†: Climate figures are for 25 month period of the experiment.

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Table 2: Atmospheric deposition during the experimental period

Type	Species	Units	Values
Nutrients	N	kg ha^{-1} yr^{-1}	12
	P	kg ha^{-1} yr^{-1}	0.4
Heavy Metals	Cd	g ha^{-1} yr^{-1}	0.6
	Cr	g ha^{-1} yr^{-1}	0.7
	Cu	g ha^{-1} yr^{-1}	13
	Pb	g ha^{-1} yr^{-1}	13.3
	Ni	g ha^{-1} yr^{-1}	1.6
	Zn	g ha^{-1} yr^{-1}	235

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Table 3: Sources of nutrients and heavy metals in *Miscanthus* plots treated with distillery effluent (DE), all figures per ha

Plot	Nutrient	Background nutrients in topsoil	Nutrients in DE amendment	Nutrients in atmospheric deposition	Heavy metal	Background metals in topsoil	Metals in DE amendment	Metals in atmospheric deposition
M-DE100	N kg ha^{-1}	n/a	82.6	30.0	Cd, g ha^{-1}	593	2.7	1.5
M-DE50	N kg ha^{-1}	n/a	40.0	30.0	Cd, g ha^{-1}	445	1.3	1.5
Control	N kg ha^{-1}	n/a	0.0	30.0	Cd, g ha^{-1}	371	0	1.5
M-DE100	P kg ha^{-1}	64.2	[illegible]	1.0	Cu, g ha^{-1}	41510	5894	32.4
M-DE50	P kg ha^{-1}	88.7	46.0	1.0	Cu, g ha^{-1}	37063	2939	32.4
Control	P kg ha^{-1}	79.6	[illegible]	1.0	Cu, g ha^{-1}	38545	0.0	32.4
M-DE100					Cr, g ha^{-1}	25203	138.0	1.79
M-DE50					Cr, g ha^{-1}	22238	69.0	1.79
Control					Cr, g ha^{-1}	22238	0.0	1.79
M-DE100					Pb, g ha^{-1}	29650	235.9	33.2
M-DE50					Pb, g ha^{-1}	26685	118.4	33.2
Control					Pb, g ha^{-1}	[illegible]	0.0	33.2
M-DE100					Ni, g ha^{-1}	[illegible]	128.6	4.0
M-DE50					Ni g ha^{-1}	[illegible]	[illegible]	4.0
Control					Ni, g ha^{-1}	93398	0.0	4.0
M-DE100					Zn, g ha^{-1}	40028	[illegible]	[illegible]
M-DE50					Zn, g ha^{-1}	34098	2399	[illegible]
Control					Zn, g ha^{-1}	34098	0.0	587.7

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Table 4: Sources of nutrients and heavy metals in *Miscanthus* plots treated with biosolid (BS), all figures per ha

Plot	Nutrient	Nutrients in topsoil	Nutrients in BS amendment	Nutrients in atmospheric deposition	Heavy Metal	Background metals in topsoil	Metals in BS amendment	Metals in atmospheric deposition
M-BS_{100}	N, kg ha^{-1}	n/a	336.5	30.0	Cd, g ha^{-1}	2162	0.5	1.5
M-BS_{50}	N, kg ha^{-1}	n/a	184.0	30.0	Cd, g ha^{-1}	2328	0.3	1.5
Control	N, kg ha^{-1}	n/a	0	30.0	Cd, g ha^{-1}	2162	0	1.5
M-BS_{100}	P, kg ha^{-1}	79.5	155.0	1.0	Cu, g ha^{-1}	51547	1405	32.4
M-BS_{50}	P, kg ha^{-1}	26.3	83.5	1.0	Cu, g ha^{-1}	44896	767	32.4
Control	P, kg ha^{-1}	10.6	[illegible]	1.0	Cu, g ha^{-1}	56536	0	32
M-BS_{100}					Cr, g ha^{-1}	34919	250	1.79
M-BS_{50}					Cr, g ha^{-1}	36582	136	1.79
Control					Cr, g ha^{-1}	33256	0	1.79
M-BS_{100}					Pb, g ha^{-1}	49884	544	33.2
M-BS_{50}					Pb, g ha^{-1}	58198	324	33.2
Control					Pb, g ha^{-1}	58198	0	33.2
M-BS_{100}					Ni, g ha^{-1}	191723	135	4.0
M-BS_{50}					Ni g ha^{-1}	199537	74	4.0
Control					Ni, g ha^{-1}	207851	0	4.0
M-BS_{100}					Zn, g ha^{-1}	66512	2378	588
M-BS_{50}					Zn, g ha^{-1}	69838	1268	588
Control					Zn, g ha^{-1}	59861	0	588

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1 **Table 5:** Sources of nutrients and heavy metals in short rotation coppice willow plots treated with distillery effluent (DE), all figures per ha

Plot	Nutrient	Background nutrients in topsoil	Nutrients in DE amendment	Nutrients in atmospheric deposition	Heavy Metal	Background metals in topsoil	Metals in DE amendment	Metals in atmospheric deposition
W-DE$_{100}$	N kg ha^{-1}	n/a	45.4	19.0	Cd, g ha^{-1}	1876	1.2	1.0
W-DE$_{50}$	N kg ha^{-1}	n/a	22.8	19.0	Cd, g ha^{-1}	3248	0.5	1.0
Control	N kg ha^{-1}	n/a	0	19.0	Cd, g ha^{-1}	2156	0	1.0
W-DE$_{100}$	P kg ha^{-1}	84.0	[illegible]	0.68	Cu, g ha^{-1}	14725	1.19	20.6
W-DE$_{50}$	P kg ha^{-1}	84.0	17.0	0.68	Cu, g ha^{-1}	26505	0.51	20.6
Control	P kg ha^{-1}	84.0	0.0	0.68	Cu, g ha^{-1}	21877	0.0	20.6
W-DE$_{100}$					Cr, g ha^{-1}	8975	13.6	1.19
W-DE$_{50}$					Cr, g ha^{-1}	11920	5.10	1.19
Control					Cr, g ha^{-1}	10378	0.0	1.19
W-DE$_{100}$					Pb, g ha^{-1}	17670	3.40	21.09
W-DE$_{50}$					Pb, g ha^{-1}	[illegible]	1.70	21.09
Control					Pb, g ha^{-1}	[illegible]	0.0	21.09
W-DE$_{100}$					Ni, g ha^{-1}	[illegible]	3.40	2.55
W-DE$_{50}$					Ni g ha^{-1}	122006	1.70	2.55
Control					Ni, g ha^{-1}	85825	0.0	2.55
W-DE$_{100}$					Zn, g ha^{-1}	16127	95.2	[illegible]
W-DE$_{50}$					Zn, g ha^{-1}	25523	40.8	[illegible]
Control					Zn, g ha^{-1}	19773	0.0	[illegible]

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Table 6: Sources of nutrients and heavy metals in short rotation coppice willow plots treated with biosolid (BS), all figures per ha

Plot	Nutrient	Background nutrients in topsoil	Nutrients in BS amendment	Nutrients in atmospheric deposition	Heavy Metal	Background metals in topsoil	Metals in BS amendment	Metals in atmospheric deposition
W-BS100	N kg ha^{-1}	n/a	221.1	19.0	Cd, g ha^{-1}	1260	2.0	1.0
W-BS50	N kg ha^{-1}	n/a	71.4	19.0	Cd, g ha^{-1}	1848	0.7	1.0
Control	N kg ha^{-1}	n/a	0	19.0	Cd, g ha^{-1}	1176	0.0	1.0
W-BS100	P kg ha^{-1}	4.2	28.9	0.7	Cu, g ha^{-1}	17639.8	66.3	20.6
W-BS50	P kg ha^{-1}	26.0	[illegible]	0.7	Cu, g ha^{-1}	26599.7	20.4	20.6
Control	P kg ha^{-1}	5.0	0.0	0.7	Cu, g ha^{-1}	17919.8	0.0	20.6
W-BS100					Cr, g ha^{-1}	10919.8	377.6	1.19
W-BS50					Cr, g ha^{-1}	10919.9	129.3	1.19
Control					Cr, g ha^{-1}	13719.8	0.0	1.19
W-BS100					Pb, g ha^{-1}	[illegible]	389.5	21.1
W-BS50					Pb, g ha^{-1}	[illegible]	183.7	21.1
Control					Pb, g ha^{-1}	[illegible]	0.0	21.1
W-BS100					Ni, g ha^{-1}	[illegible]	[illegible]	2.55
W-BS50					Ni g ha^{-1}	108918.7	11.9	2.55
Control					Ni, g ha^{-1}	86518.9	0.0	2.55
W-BS100					Zn, g ha^{-1}	20439.8	716.0	372.4
W-BS50					Zn, g ha^{-1}	29959.6	226.2	372.4
Control					Zn, g ha^{-1}	23799.7	0.0	372.4

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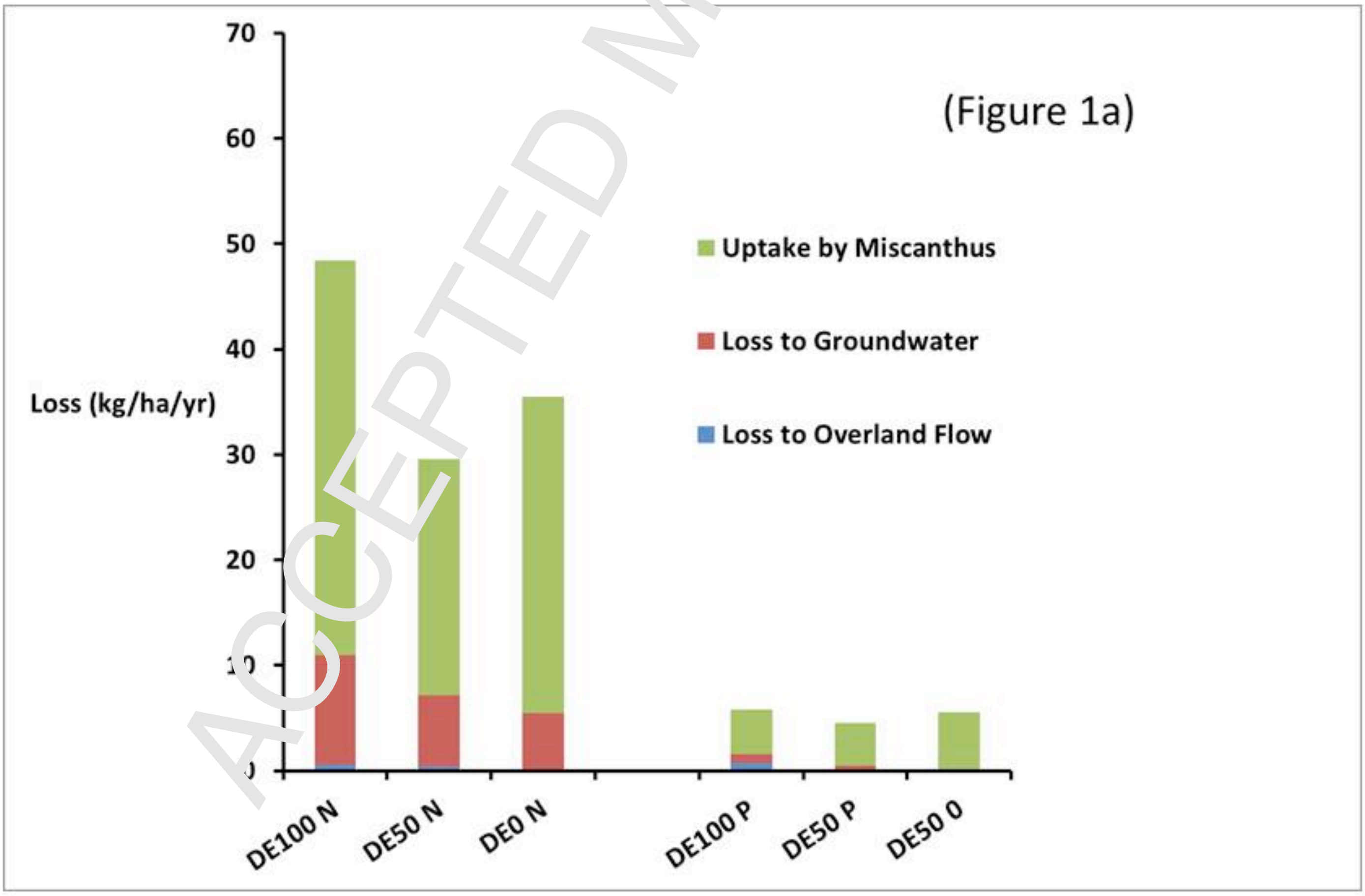

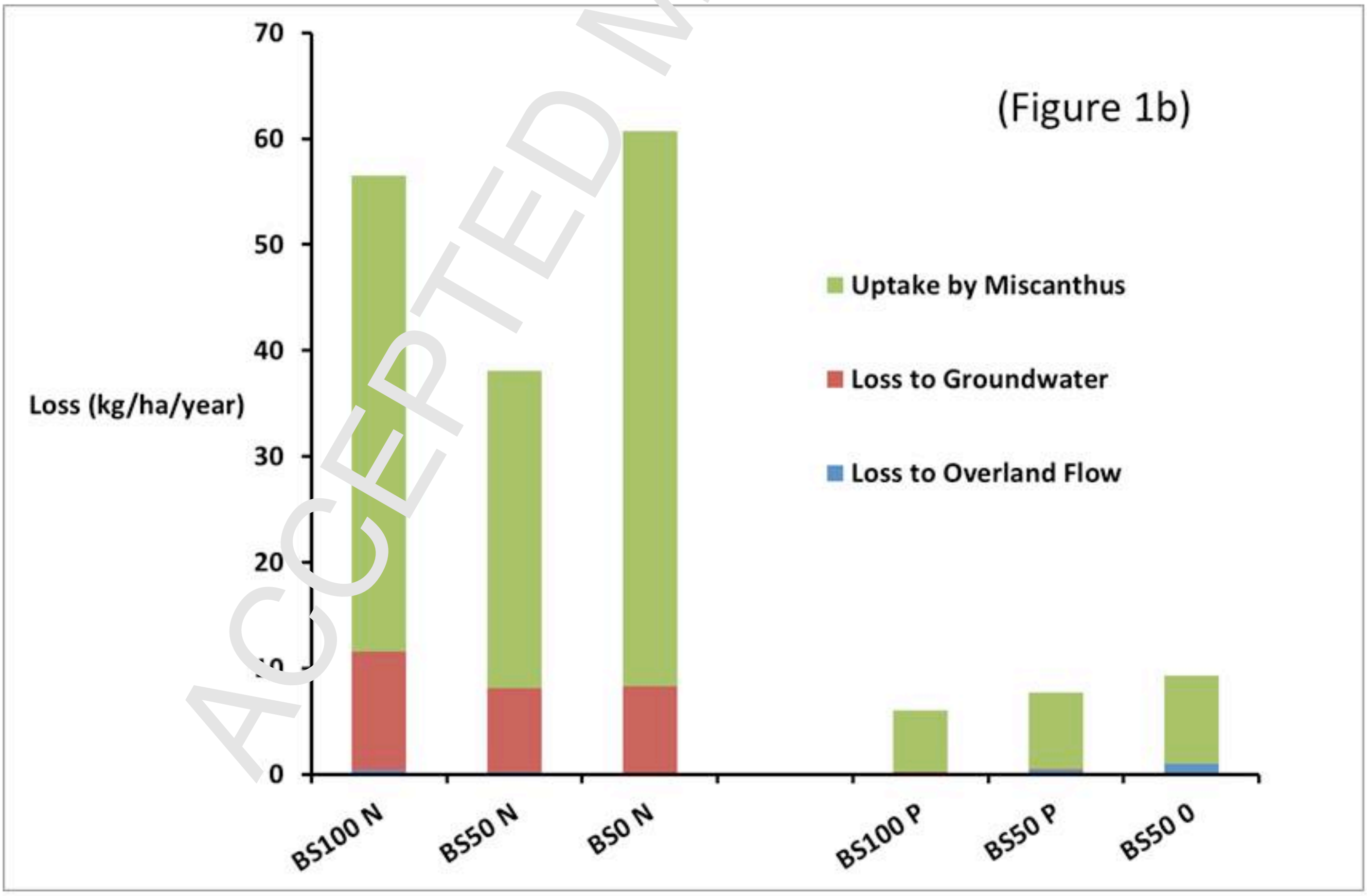

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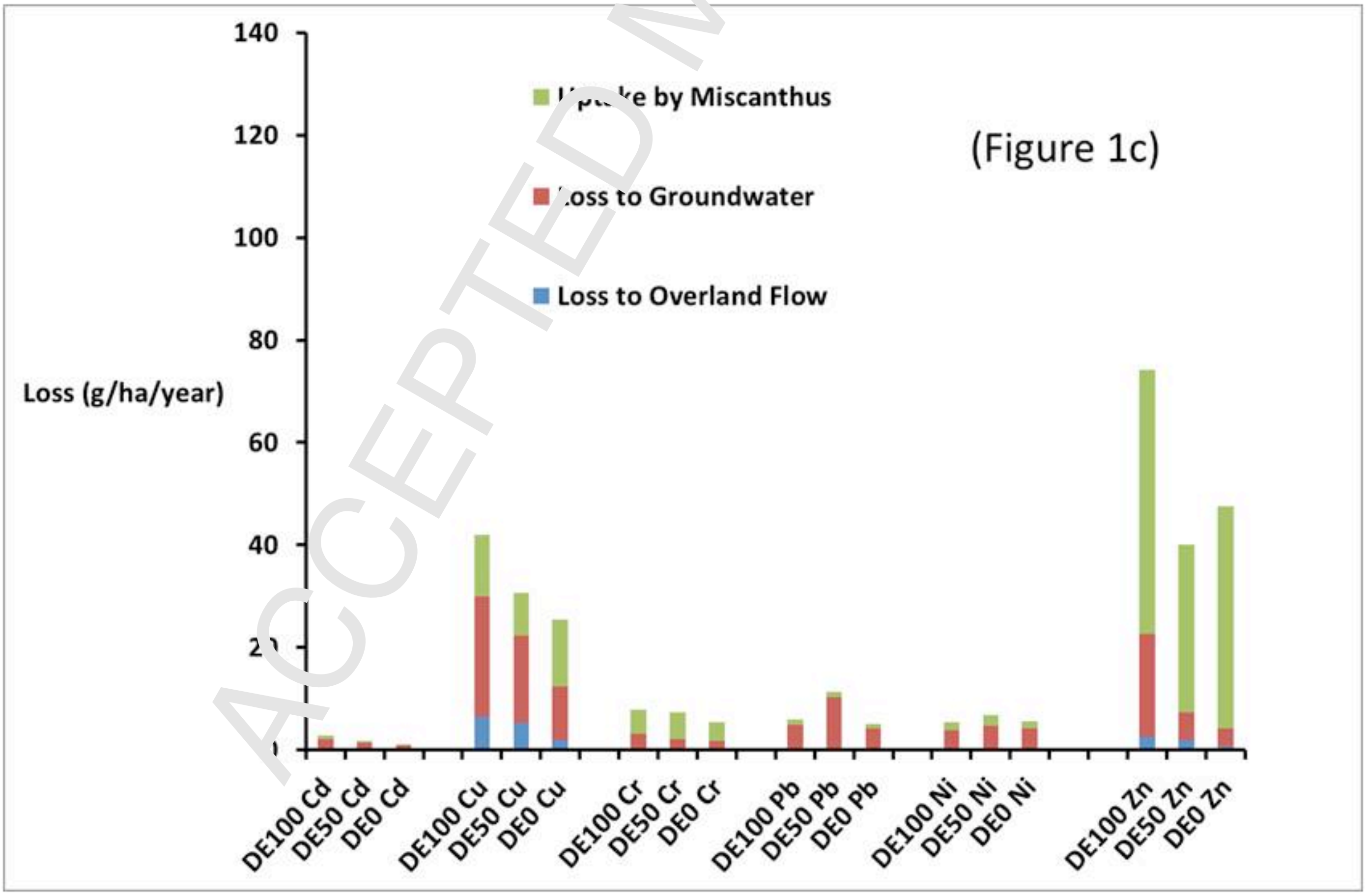

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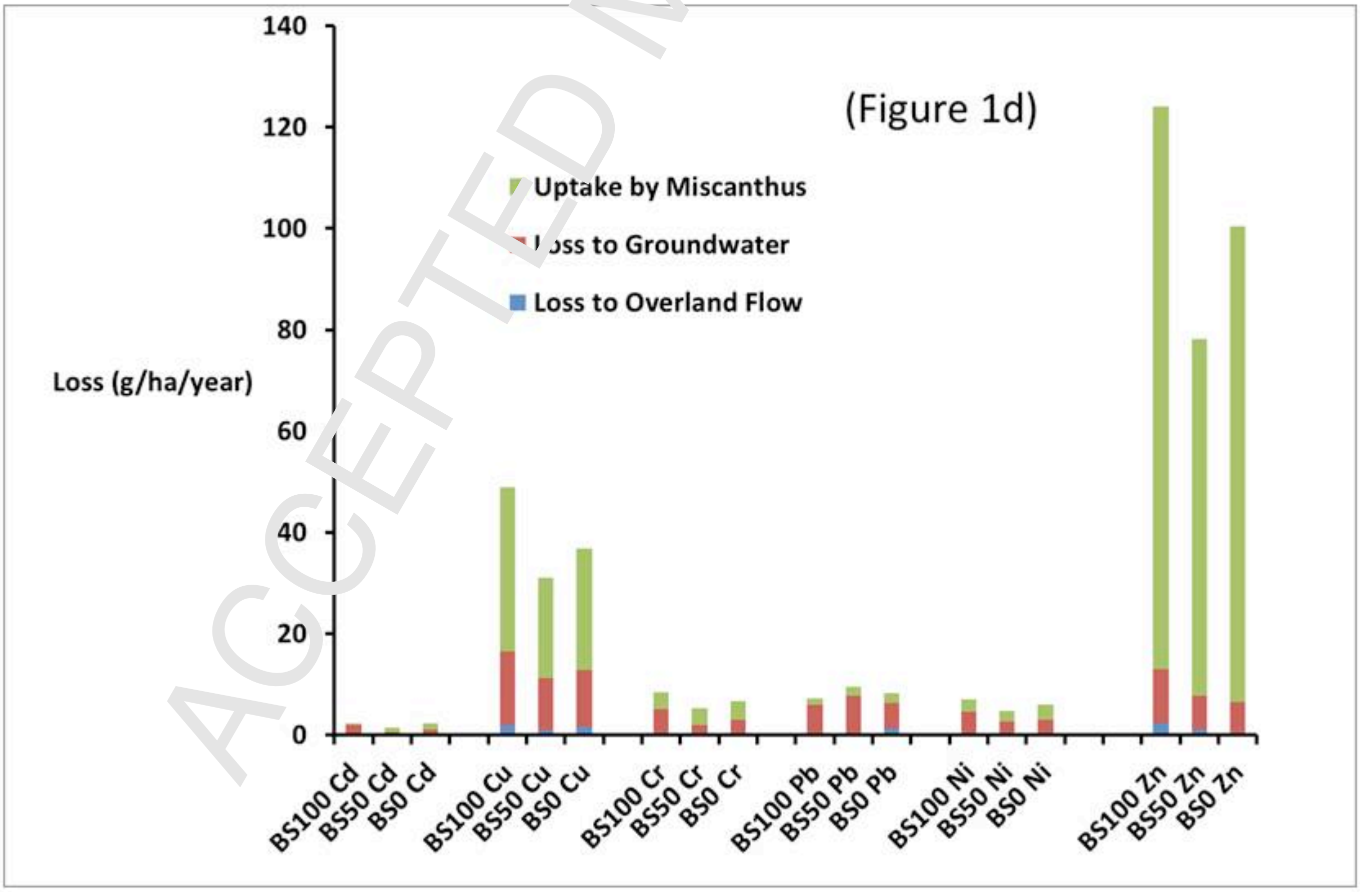

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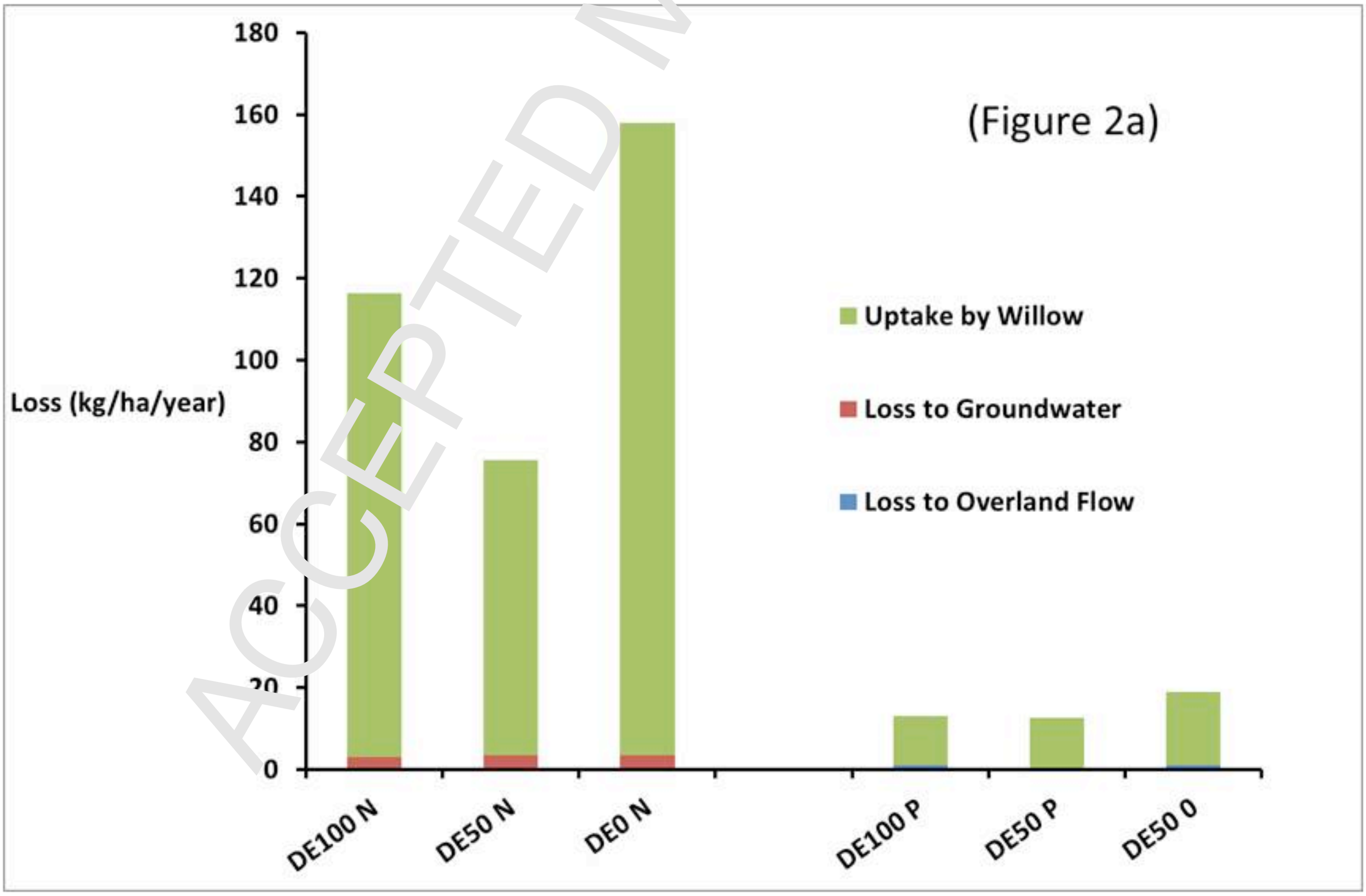

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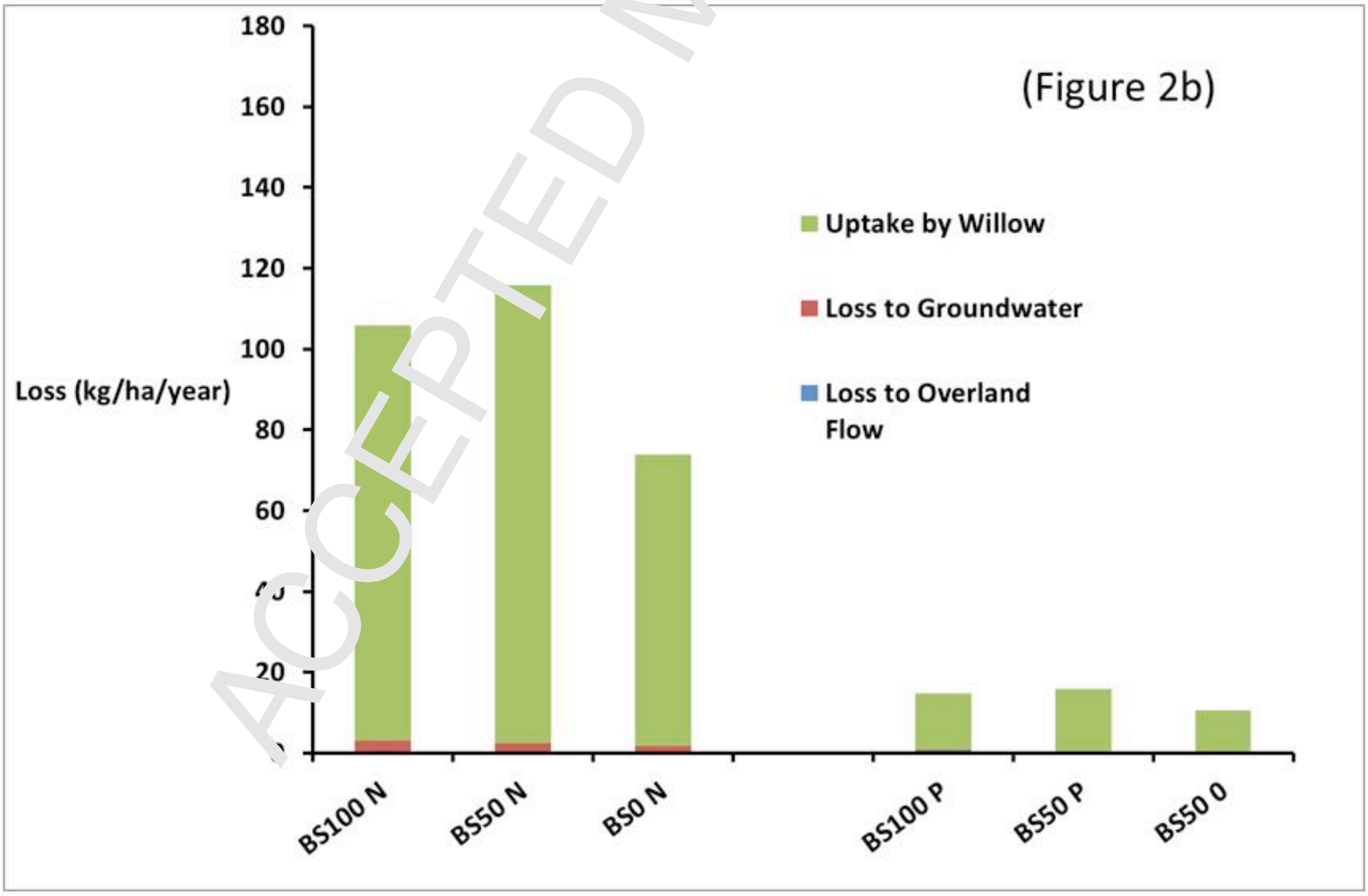

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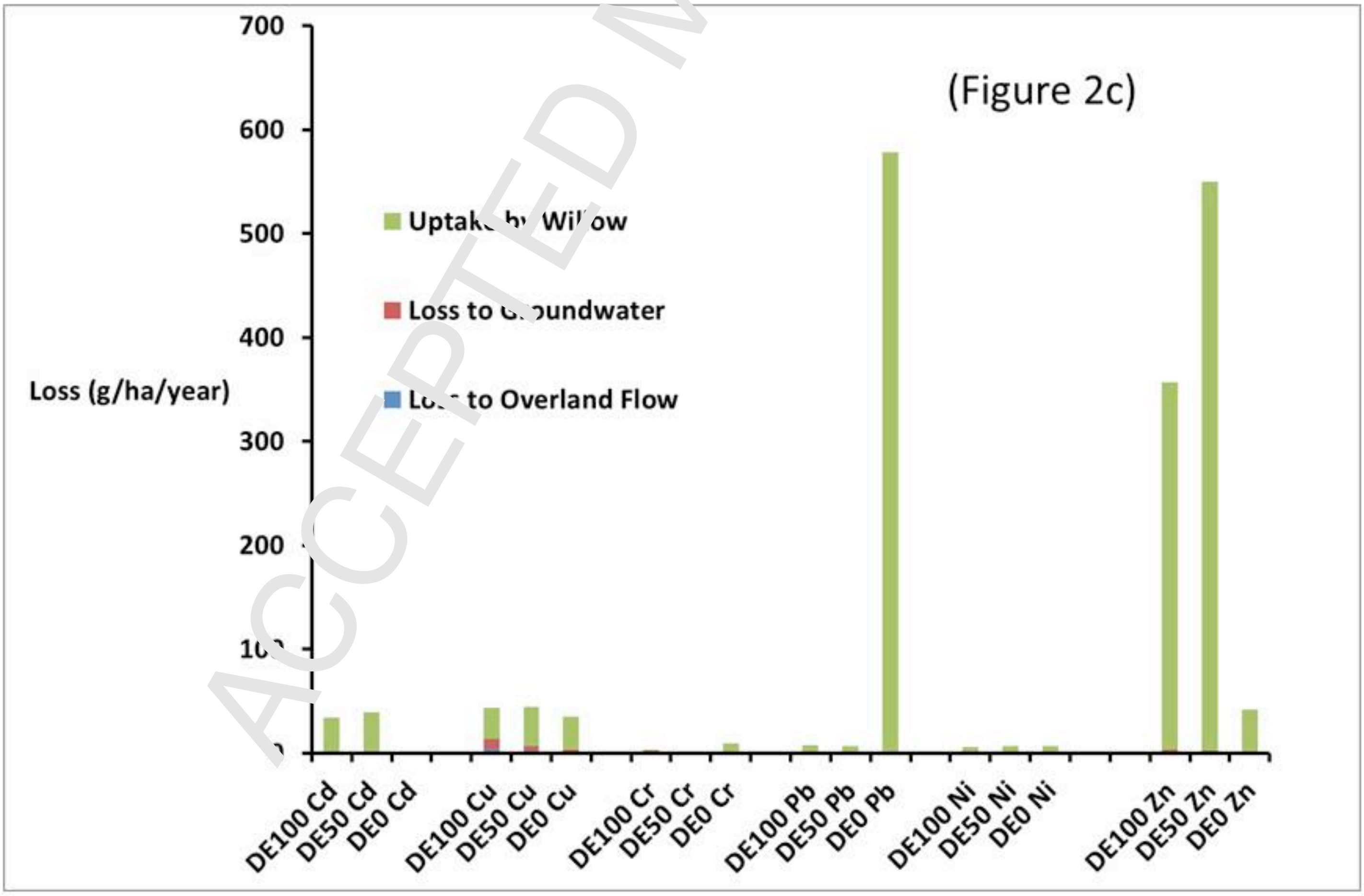

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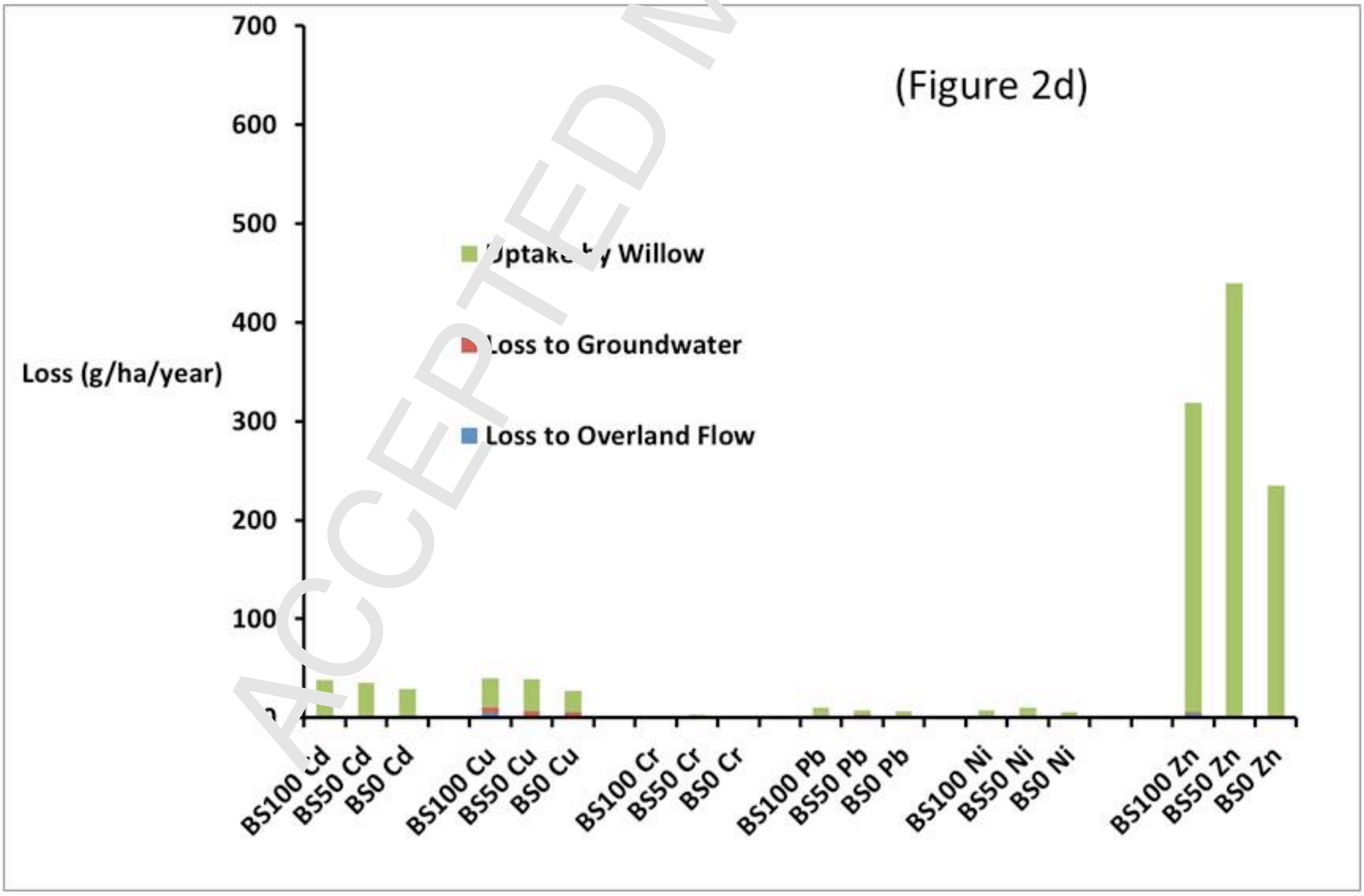

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The fate of nutrients and heavy metals in energy crop plantations amended with organic by-products

Highlights:

- The greatest inputs to the system came from the soil, the smallest input was from atmospheric deposition.
- The largest output from the system was crop take up; the smallest was loss to OLF.
- Organic byproducts can enhance energy crop nutrition without deleterious environmental consequences.