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9 **Agricultural nutrient surpluses as potential input sources to grow**
10 **third generation biomass (microalgae): a review**

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12 **Owen Fenton^{a1}, Daire Ó hUallacháin^a**

13 ^aTeagasc, Johnstown Castle, Environmental Research Centre, Co. Wexford

14 ¹Corresponding author: owen.fenton@teagasc.ie

ABSTRACT

Biofuel consumption is increasing and in order to meet EU targets, alternatives to first and second generation biofuels are being examined. The use of micro-algal biomass in the production of biofuel is an area of research which has received attention in recent years. Traditionally, microalgae are commercially grown using synthetic fertilisers, the price of which is linked with rising oil prices. An alternative to the use of inorganic fertiliser is to use surplus agricultural manures in their raw state, bi-products of anaerobic digestion, or runoff and artificial drainage waters, all of which have variable nutrient contents within and across source types. Many studies showed that manures containing a high nutrient content e.g. pig and poultry manures, or bi-products from anaerobic digestion, are potentially viable sources of nutrients to grow algae. Feasibility issues prevail such as variable nutrient contents amongst and across source types, transparency issues and early and sustained nutrient losses during the storage phase. Agitation and efficient nutrient testing before use are important. In Ireland, pig and poultry manures, dairy dirty water, artificial drainage or runoff waters where coupled with agitation during storage to prevent P precipitation and a CO₂ source, all have potential to be used in the future.

Keywords: algae, biofuels, agricultural, manures

1. Introduction

An increase in energy demands, price volatility and concerns over climate change (as a result of greenhouse gas emissions) have resulted in increased interest in the development of alternative energy sources to fossil fuels [1]. The quest for sustainable and environmentally benign sources of energy has become urgent in recent years [2]. Biofuels, produced from biomass such as plants and organic waste, could help reduce the world's dependence on oil and could reduce CO₂ production [3]. The advantage of biofuels over traditional fuels, include greater energy security, reduced environmental impact, foreign exchange savings and socioeconomic benefits related to the rural sector [4].

Biofuels are divided into three categories; "first", "second" and "third" generation [5]. Such divisions are not universally accepted but for the purposes of this review the following definitions apply: first-generation biofuels are predominantly created from feedstocks that have traditionally been used as food. Second-generation biofuels are derived from non-food feedstocks and are deemed to be more sustainable and have a lower impact on food production. Third-generation biofuels, like second-generation biofuels, are made from non-food feedstocks, but the resulting fuel is indistinguishable from its petroleum counterparts. These fuels are also known as advanced biofuels or green hydrocarbons.

Questions regarding the sustainability of first-generation biofuels exist in relation to the impact on biodiversity, land-use and competition with food crops [3]. The transition from first and second-generation to third-generation biofuels offers a reduction in land requirement. This is due to higher energy yields per hectare as you move along this transition and to utilisation of non-agricultural land.

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61 Recently, there have been a number of reviews on micro-algae utilisation for third
62 generation biofuel production ([6]; [7]; [8]; [9]; [10]; [11]; [12]; [13]; [14]; [15]).
63 These studies focussed on the performance, special features, technical and economic
64 barriers of commercially growing algae. Furthermore, these studies also reviewed the
65 ability to isolate particular strains of algae and the economics associated with the
66 commercial production of algae. The above studies assumed inorganic (chemical)
67 fertiliser was utilised in commercial algal growing facilities. It is likely that chemical
68 fertilisers are selected over alternative sources of nutrients as they are based on known
69 quantities of nutrients, resulting in the ability to calculate rates of growth per kg of
70 fertiliser used.

71

72 With the expansion of the commercial micro-algae growing industry, competition
73 with the agricultural sector for inorganic fertilisers is expected to increase. Coupled
74 with the fact that fossil fuel prices are likely to increase, this could result in the fact
75 that inorganic fertilisers may be an economically unviable source of nutrients for
76 micro-algal production systems. Approximately 50% of all fossil energy input
77 required for the growth of algae for biofuel is linked to inorganic fertilisers [7].

78

79 A study by Pacheco-Ruiz [16] recommended the use of organic fertiliser as a source
80 of nutrients for algal production systems. A double-dividend may be achieved by
81 providing the commercial algae growing industry with a cheaper source of fertiliser,
82 whilst aiding agricultural industries in utilising surplus agricultural wastes. While the
83 term 'waste' is commonly used for these materials, it is however an unfortunate label,
84 as it suggests that the materials have no further use and are merely a nuisance by-

product of farming systems that must be managed [17]. Given the high nutrient contents of these materials, it is far more appropriate for them to be considered as organic fertilisers, and as such are a potential valuable commodity to the farmer. With higher and more volatile chemical fertiliser prices in recent years, the fertiliser replacement value of these materials (in economic terms) is increasing. Therefore, the management of agricultural ‘wastes’ in a manner that maximises the nutrient recovery and fertiliser value to crops should be a priority within any management plan for these materials. Utilising such nutrient sources to facilitate algal growth could be considered an alternative agricultural enterprise, especially where management practices are not currently in place.

This review does not comment on potential algae growth rates from specific nutrient input sources. Such a review is outside the remit of the current study and would need to examine lipid/carbohydrate contents or lipid/carbohydrate productivities of algae grown on wastewaters. Instead the current study:

1. Reviews the nutrient content of a) agriculturally derived organic fertilizers and b) runoff and drainage water; both of which could be potentially used to facilitate biomass growth.
2. Reviews nutrient type and contents of agricultural wastes used in algal growth studies and investigates the feasibility of using such nutrient sources.
3. Presents Ireland as a case study and investigates which potential nutrient sources would be the most feasible alternative to inorganic fertilizer inputs to facilitate algal growth.

2. Agricultural nutrient sources

Nutrients support the primary production of all terrestrial and aquatic flora and fauna. However, over-enrichment of nutrients in freshwater, particularly phosphorus (P) and nitrogen (N), can cause a shift in the species structure of an aquatic ecosystem, which can lead to excessive growth of algae. Nutrient losses from agricultural systems can result in algal blooms with subsequent eutrophication of rivers and estuaries after cell death and microbial decay ([18]; [19]). The transport of P and N from agricultural land to aquatic systems occurs through 1) critical losses from the soil (nutrients build up quickly in soils and such accumulations can take many years to decline in concentration, even when no further inputs occur in the system) and 2) incidental losses where fertilization is followed by a storm [20] or baseflow [21] event. Other sources of P and N include sub-surface drainage systems [22], or where contaminated groundwater interacts with a surface waterbody [23] e.g. migration pathways in limestone aquifers. The speciation of nutrients (e.g. nitrate, nitrite, ammonium for nitrogen) within these pathways is complex and important for the bioavailability of such nutrients e.g. inorganic forms of P are not taken up by plants and are generally lost in runoff, organic forms on the other hand are generally lost in sub-surface drainage systems. A detailed account of P speciation in manures was carried out by He et al. [24].

Nitrates, although commonly present in runoff, are typically lost through leaching from the rooting zone and are then transferred to groundwater and in turn (after a certain time lag) are discharged to a surface waterbody [25]. In Ireland, as effective rainfall is high (e.g. mean of 700 mm per year [26]), catchment losses would require to be as low as 0.21 kg Total Phosphorus ha⁻¹ yr⁻¹ to conform with current EU maximum admissible concentrations (30 µg L⁻¹). The onset of eutrophication (20 µg

L⁻¹ [27]), may be lower than this threshold, with equivalent catchment losses of 0.14 kg Total Phosphorus ha⁻¹ yr⁻¹. In other countries this threshold may vary e.g. Australia has average trigger values for the onset of eutrophication of 37 µg TP L⁻¹ and 1.60 mg TN L⁻¹, which were derived for lowland rivers and 50 µg TP L⁻¹ and 0.44 mg TN L⁻¹ for freshwater lakes.

The nutrient concentrations in organic and inorganic fertilisers far exceed such eutrophication trigger values. When flow data are coupled with concentration data, a load can be calculated. In the long term, total nutrient loads (kg m² yr) lost from grassland can be considered a better indicator of the risk of algal blooms in waterways than the concentrations in runoff or in stream concentrations. This is because the total amount of P available determines the final biomass, rather than the growth rate, of aquatic plants and algae [28].

Microalgae typically depend on sufficient supplies of carbon (in the form of CO₂), light (although some species do not require CO₂ or light [29]) and nutrients [11] to undertake photosynthesis and biomass growth. The nutrient requirements for the majority of microalgae include N, P and potassium (K), with the amounts required being species specific. These requirements could be catered for by dilute agricultural manure, dirty water, runoff or drainage water. In general, the nutrient requirements of algae are low - at concentrations <0.2 µmol P L⁻¹, phosphate availability in the growth medium is a growth-limiting factor [30]. Nitrate availability must remain >0.2 µmol N L⁻¹ to ensure growth [31]. Such low nutrient requirements infer that the majority of agricultural wastes would be suitable substitutes for inorganic fertiliser for commercial algae production [8]. Establishing critical thresholds for concentrations of

N and P is important for algal growth [32], but as stated previously, these thresholds are species specific. The N: P ratio of 7:1 (Redfield ratio) is the range for balanced nutrients in algae [33], higher ratios result in P limitations and a reduction in algal growth [28].

Waste-waters, with low levels of nutrients (such as carpet mill effluents), have been used as nutrient inputs to support algal growth [34]. Ruiz-Marin et al. [35] found that the biomass production potential and lipid content of algae cultivated in treated wastewater were 9.2–17.8 Mt ha⁻¹ yr⁻¹ and 6.82%, respectively [35]. Although these results appear quite promising, Mulbry et al. [36] found that the utilisation of agricultural nutrient products was more feasible than up-grading existing water treatment plants in sensitive catchments. As the nutrient needs of algae are low, the large quantities of animal manures, produced from concentrated feeding operations, present economic opportunities [37]. A detailed review of the all agricultural manure types used in the U.S.A (with particular emphasis on the Mid-West) was carried out [38], which included nutrient contents, volumes produced, sampling techniques, and nutrient losses during the storage period.

2.1 Algal grown from dairy manure and dirty water nutrient sources

A number of studies have investigated commercial algal biomass growth using agricultural manures from dairy systems ([36]; [39]; [40]; [41]; [42]) (Table 1). Where no slurry management system is in place, or where surpluses occur, one alternative to land application could be to use this nutrient-source to commercially grow algae. Algae utilise the N and P present, converting nutrients into biomass [43]. This biomass may then be exported for commercial uses or recycled on the farm as feed, compost or fertiliser. Pizarro et al. [44] presented a nutrient-flow chart, using a 1000

dairy cow unit as an example, showing both off-farm (outlined in reviews stated above) and on-farm uses (land application from composted algae and surplus biomass from raceways fed by digested manures) of algal biomass. From an N perspective, inputs to the system were 1.5×10^5 kg N in feed, outputs were 4.2×10^4 kg N in milk (meat was not mentioned), with 1.1×10^5 kg N remaining in the manure. Manure was divided during the solid separation phase with the first portion as manure effluent 7.3×10^4 kg N (anaerobically digested) and the second portion as 3.7×10^4 kg N composted. Algal biomass from the anaerobic digested manure amounted to 5.9×10^5 kg DW and 4.5×10^4 kg N. Pizarro et al. [44] used a similar approach for P, with 3.0×10^4 kg P in the input feed and 5.9×10^3 kg P in the algal biomass. Mulbry et al. [43] evaluated the nutrient content of algal biomass, grown from anaerobically digested dairy manure derived nutrients, and found comparable growth results with algal biomass grown with inorganic fertilisers.

Adey and Hackney [45] treated algal turf scrubbers with five different loading rates of anaerobically digested dairy manure (from 5 to 80 mg $\text{NH}_4\text{-N L}^{-1}$ and 1 to 20 mg $\text{PO}_4\text{-P L}^{-1}$) over 2-h incubation periods. Turf scrubbers may be used for diffuse or point source nutrient capture, and have been implemented in lake restoration and CO_2 sequestration studies in the U.S. The algal nutrient removal rates from the manure in this study were very high: $3.68 \pm 2.55 \mu\text{mol min}^{-1} \text{ g}^{-1}$ DW for $\text{NH}_4\text{-N}$ and $0.40 \pm 0.08 \mu\text{mol min}^{-1} \text{ g}^{-1}$ DW for $\text{PO}_4\text{-P}$ for a 4% manure dilution. The study highlighted the importance of maintaining pH during the incubation phase between 7 and 7.5, as pH greater than 8.5 (caused by photosynthesis) resulted in ammonia volatilisation and precipitation of P with reduced algal growth. Using a typical dairy manure input containing 0.6 -0.96 g TN day^{-1} , the dried algal yield was approximately $5 \text{ g m}^{-2} \text{ day}^{-1}$.

The dried algae contained approximately 1.5-2% P and 5-7% N. Algal N and P accounted for 42-100% of input $\text{NH}_4\text{-N}$ (33-42% of TN) and 58-100% of input TP respectively [46].

Using dairy manure, Mulbry and Wilkie [46] studied the production of benthic freshwater algae. Using TN loading rates of 0.64 to $1.03 \text{ g m}^{-2} \text{ d}^{-1}$, the dried algal yields were 5.3 to $5.5 \text{ g m}^{-2} \text{ d}^{-1}$. The dried algae contained 1.5 to 2.1% P and 4.9 to 7.1% N. At a DM yield of $5.5 \text{ g m}^{-2} \text{ d}^{-1}$, this is the equivalent to an annual N uptake of $1430 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

It is important to note that the process of methanogenic or psychrophilic anaerobic digestion of agricultural manures, using sequencing batch reactors, is effective at pathogen removal ([47]; [48]; [49]; [50]). If a multi-stage digester or a pasteurisation step is introduced, pathogen obliteration rates are higher [51]. The bi-products of slurry anaerobic digestion may still be used for crop fertilisation as they still contain valuable nutrients ([52]; [53]). Both these facts make them a safer option than raw slurry for the commercial growth of algae .

A number of papers have reported the chemical composition of dirty water from dairy farms ([54]; [55]; [56]; [57]; [58]). Table 2 shows the range of nutrient contents available in dirty water [57]. Cumby et al. [55] reported that the mean TN nutrient concentration for dirty water from 20 farms in England and Wales was $580 (\pm 487) \text{ mg L}^{-1}$. These studies and others have been reviewed elsewhere [59]. Year round supplies of such nutrients would be guaranteed in North Atlantic areas of Europe as the climate and farming practices (animals outside for long periods of the year) are sufficient to

produce large volumes of dirty water. In farming systems where animals are kept indoors for longer periods or at all times, dirty water waste volumes would be even greater.

2.2 Algal growth from swine manure

Recovery of nutrients from swine manure wastewaters by microalgae has been researched by a number of authors ([60]; [61]; [62]; [63]; [64]; [65]). Algal productivity in these studies ranged from 7 to 33 g m² day. To avoid algal growth collapse, algae cultures must receive air enriched with 1 % CO₂ (this of course is specific to the studies cited and not a general constant. Algae can also thrive on much higher amounts of CO₂ (> 1%). Slight agitation and light exposure is also needed. Cultures must maintain a significant biomass, greater than 300 mg DM L⁻¹ in summer and 250 mg DM L⁻¹ in winter. Removal of ammonia-N was 0.5 mg L⁻¹ d⁻¹ in winter and 4-8 mg L⁻¹ d⁻¹ in summer and the swine manure (nutrient content is presented in Table 1) was diluted 40 to 50 times before use.

Aerobically digested pig manure, mixed with sea water (nutrient content Table 1), has been successfully used to grow *Spirulina sp.* in bench raceways in Mexico [66]. Two algal species, *Scenedesmus intermedius* Chod and *Nannochloris sp.* were grown using swine manure, with P uptake rates of 0.014 (free cells), 0.022 (immobilized cells) mg P h⁻¹ and 0.006 (free cells), 0.009 mg P h⁻¹ and 0.011, 0.006 mg P h⁻¹ (immobilised cells) respectively [67]. These rates are higher than those of other published studies i.e. *Chorella vulgaris* of 1.23 -8.07 mg N⁻¹ d⁻¹ and 0.42 mg P L¹ d⁻¹ for free cells and 0.41 mg P L⁻¹ d⁻¹ for immobilised cells [57]. Mulbry et al. [36] cultivated algae (*Rhizoclonium sp.*) using raw and anaerobically digested dairy and

pig manure in the U.S. Algae growth was due to loading rates of 0.2 to 1.3 g TN m⁻² day⁻¹ for swine manure and 0.3 to 2.3 g TN m⁻² day⁻¹ for dairy manure.

2.3 Algal growth from poultry manure

Poultry manure contains significant amounts of inorganic and organic P. Most of the P in manures and composts is inorganic (60-90% of TP), with smaller amounts of organic and residual forms. Early work on algae growth using poultry manure was undertaken in India and China ([68]; [69]; [70]). These studies showed high growth yields of algae using poultry manure with TN content at approximately 2% and available phosphate content of 261.3 ±54 mg L⁻¹ [69].

2.4. Algal growth using runoff and drainage water from agricultural lands

As N and P cycle through the farm system, unavoidable losses from agricultural systems occur [71] through runoff or leaching pathways. Nutrients can find their way to a waterbody (groundwater or surface water) and lead to algal blooms in surface waters [19]. The concentrations of such nutrient losses are presented here, which are indicative nutrient values at the point of export within each of the studies. Further buffering or dilution of such nutrients may occur if they were collected as a nutrient input source to grow algae. Incidental losses occur where a rainfall event follows a fertilization event. Chronic losses occur from the soils nutrient reserves during rainfall. The nutrient loads from runoff and drainage, particularly during storm events after fertiliser application, and in some cases during baseflow conditions, can be high and negatively affect waterbody status. In addition, nutrients in runoff from soils with a high P Index (soil test P > 8 mg Morgan's P L⁻¹) can be high. Such losses are enough to support eutrophication of surface water.

Regan et al. [72] found that tillage soil with a soil test P (STP) in excess of 8 mg Morgan's P (P_m) L^{-1} produced a mean weighted dissolved reactive P (DRP) in excess of 30 $\mu g L^{-1}$ (the concentration above which eutrophication may occur). This is similar to the findings of other studies ([73]; [74]; [20]; [75]).

Flow weighted DRP losses, measured during ten rainfall events on a permanent grassland site in south east Ireland [75] was from 0.01 to 1.0 $mg L^{-1}$ (low Morgan P soil) and from 0.1 to 5.1 $mg L^{-1}$ (high Morgan's P soil). Total organic nitrogen ranged from <0.3 to 9.1 $mg L^{-1}$ and <0.3 to 49.3 $mg L^{-1}$, for low and high Morgan's P soil conditions. Edwards and Withers [76] investigated the TP concentration range in different runoff sources (farmyard runoff, pig slurry, road runoff, septic effluent, sewage treatment works effluent, track runoff and rivers). Total P in runoff within an agricultural setting ranged from 0.02 to 247 $mg L^{-1}$. Hart et al. [77] reviewed event-specific P losses in runoff following fertiliser application (incidental mobilisation). DRP ranges included: 131 to 1296 $\mu g L^{-1}$ (1 ha grazed lysimeter plots, fertiliser rate-16 kg P ha, rainfall-50 mm) [78], 1.2 $mg L^{-1}$ to 26 $mg L^{-1}$ (0.4 ha grazed plots, fertiliser rate 51 kg P ha⁻¹) [79], 0.06 to 6.4 $mg L^{-1}$ and 0.46 to 31.5 $mg L^{-1}$ (simulated rainfall on micro plots) [80]. Concentrations in excess of 50 $mg L^{-1}$ have been observed within 24 hr of fertiliser application [81]. In general, the peak duration, consisting of high DRP concentrations, is quite short but the effects of the fertiliser application on DRP lasts a period of 30 to 50 d.

Nitrogen and P losses may also occur in drainage systems. In many agricultural catchments in the U.S, approximately 80% of the land area may be drained by ditches and subsurface drainage systems. This leads to decreased surface storage and

increased migration of nutrients to a waterbody [82]. A complete review of the water quality impacts of agricultural drainage has been carried out by Skaggs et al. [83]. While P losses through soils are generally low with regard to economic losses to the farmer, they still may trigger eutrophication (as low as 0.02 to 0.035 mg P L⁻¹). In the literature, drainage water contains negligible to a few mg P L⁻¹ in tillage and grassland soils, with higher concentrations in organic soils [84]. Kladivko et al. [85] reported that annual NO₃-N losses to subsurface drainage, ranged from 18 to 70 kg ha⁻¹ and averaged 41.7 kg ha⁻¹ from silty loam textured soils. Annual average ammonium-N, soluble P, and K losses were 0.5, 0.04, and 2.6 kg ha⁻¹, respectively. Particulate matter (PM), particulate P (PP), and DRP in drainage ranged from 63 to 334 mg PM L⁻¹, from 0.177 to 0.876 mg PP L⁻¹, and from 0.042 to 0.103 mg DRP L⁻¹, respectively. In rapid drainage between the plots and a tile-drained catchment (13.3 ha) over nine rainfall events, losses were 171 to 630 g PM ha⁻¹ mm⁻¹ vs. 141 to 892 g PM ha⁻¹ mm⁻¹, and 0.57 to 1.75 g PP ha⁻¹ mm⁻¹ vs. 0.71 to 5.92 g PP ha⁻¹ mm⁻¹, respectively [86]. Therefore, runoff and drainage water collected before discharge to a groundwater or surface waterbody has the capacity to support algal growth.

2.4.1 Capture of nutrients from runoff or artificial drainage systems

Runoff may be a result of infiltration or saturation excess, driven from variable source areas (VSAs), which expand and contract seasonally, as well as during storm events [87]. A further extension of the VSA is the critical source area (CSA), where only P sources, in that particular part of the landscape generating runoff, actually influences the P concentration [88]. P losses from CSAs are generally in particulate form and account for 75-90% of TP losses to surface water [89]. Applying P-immobilizing materials (alum, water treatment residuals, fly ash, gypsum) in VSAs or CSA's, to

edge-of-stream soils is one possible means of intercepting soluble P from aquatic systems ([90];[91]). This intercepted P could then be used as a source of nutrients for algae production. Iron (Fe)-rich materials, which have high P adsorption capacities, have been used to sequester P from wastewaters ([92];[93]; [94]; [95]; [96]). The P sorption capacity of ochre from coal mining and metal mining areas has been investigated to sequester P from agricultural and municipal wastewater ([97]; [98]; [99]; [100]; [101]). Sequestered materials can then be removed dried and used as a slow release fertiliser for algal production. Other ways to collect runoff or artificial drainage from the landscape is through topographical management [102], directing runoff to a collection point, or installation of buffer pools or wetlands at the outlet of a CSA or drainage systems. The settled sediment can be re-used on the farm or as a source of nutrients for algal production.

2.5 Feasibility of using agricultural wastes to grow algae

Tables 1 & 2 highlight a potential problem with respect to using organic agricultural wastewaters as a source of nutrients to grow algae i.e. the variations in nutrient content and P availability within and across agricultural waste types. During the manure storage phase, P precipitates quite easily. Agitation, which is a standard procedure to enable suction of slurry into a vacuum tanker, would alleviate such a problem. Phosphorus content of manures is more stable than N and is correlated more closely to dry matter. The storage period for N is an important factor, as volatilisation will diminish nutrient contents (up to 30% in some cases). Ammonia emission factors, used for slatted and loose bedded cattle housing, range from approximately 10 to 42 g N LU⁻¹ day⁻¹ [103]; [104]. These emissions factors are altered for Irish conditions and are within the range of other European research findings ([105]; [106]; [107]) and at

the lower end of the range from research on naturally ventilated slatted sheds by [108].

Sampling and nutrient analysis of manure should be carried out as close as possible to utilisation. Other changes can occur due to dilution by rainwater, but this can be overcome by alterations to storage facilities. One challenge for the use of manures as nutrient inputs would be their transparency, as they prevent light penetration for algal growth, particularly with respect to the use of slurry. Further dilution would be needed to create dirty water out of slurry and this could be carried out during the storage period and pre-utilisation phase.

One of the main concerns over the use of slurry is the variability in its nutrient content within or amongst a particular slurry type (e.g. dairy, poultry or swine). There will always be high variability around the average nutrient content reflective of animal types and management of the slurry. Use of on-farm equipment such as hydrometers or nutrient sensors may help in quantifying the exact nutrient content of slurry. For dairy dirty water, dry matter and specific gravity provide the best indicator of biochemical oxygen demand, TN and TP, and micro and macro nutrients [109]. For dairy slurry, correlations between physico-chemical properties (pH, EC, DM) and nutrient concentration highlight that DM and electrical conductivity (EC) could be used to estimate nutrient concentration. Generally, DM is the best estimator of N (R^2 0.75) and P (R^2 0.82), while EC is the best estimator of K (R^2 0.73). EC is also highly correlated with N concentration (R^2 0.67) [110]. Other studies have also attempted to elucidate nutrient contents of slurries based on readily available parameters ([111]; [112]; [113]; [114]). Martínez-Suller [115] characterised nutrient values of pig and

cattle slurry and dairy dirty water in Spain, Italy and Ireland. Strong single property relationships between NPK and EC and DM content were found. These parameters are best when attempting to estimate total Kjeldalh N, total ammoniacal N, P and K.

Ideally, a source of fertiliser that is currently surplus to the requirements of the agricultural sector would be most suitable as a source of nutrients for algal growth e.g. excess manure from intensive pig and poultry production units. Several factors are vital when locating an enterprise for the production of algal biomass. These include: a water supply, suitable land topography, geology, favourable climatic conditions and easy access to nutrients and a carbon supply. A critical resource required for the cultivation of many microalgae, is carbon in the form of CO₂. This can be provided easily to algal production plants directly, or from exhaust emissions from fuel combustion. Microalgae have high CO₂ tapping and fixation ability therefore they can be used to reduce carbon dioxide emission from power plants and other industries with high carbon dioxide emissions [116]. In Ireland, emission plants that utilise coal or peat (of which there are 120 sites nationwide) [30] may be suitable locations for algae growing facilities.

3. Case study - Ireland

In Ireland the main focus within the dairy sector is a targeted 50% expansion by 2020 [117]. This planned growth will require efficient utilisation of grassland, as extra production must primarily come from low-cost, grass-based production systems requiring higher stocking rates, longer grazing seasons, and more intensive use of land with some level of wetness limitations. Total dairy slurry production in Ireland is estimated at 39.3 Mt per annum (Hyde, pers comm.) and is dominated by cattle slurry

(Table 3). Singh et al. [118] predict that Irish animal populations will increase to 5.5 M cattle, 1.49 pigs M and 3.28 M sheep by 2020 (current figures have already exceeded such predictions [119]). Using Singh's estimations, Ireland has the potential to produce in excess of 15.53 PJ of energy in 2020 from anaerobic digestion of agricultural slurry. Similarly, Brown and Zeiler [116] estimates that by 2020, 5% of cattle and pig slurry and 75% of poultry slurry will be anaerobically digested. This digested product may subsequently be used as a nutrient source to grow algae. In Ireland, centralised anaerobic digestion, with grass and slurry feed-stocks, has been recommended by Singh et al. [118]. The nutrient contents of manure (digested and undigested) utilised to grow algae in a number of studies are presented in Table 1. As can be seen from this table, the nutrient value of the manure is maintained following anaerobic digestion, which has also been demonstrated by Dahlberg et al. [120].

Manure production per agri-sector in Ireland is summarised in Table 3. In recent years, agricultural manure has been seen as a source of valuable nutrients as opposed to a waste product. From December 2006 to August 2008 the price of fertiliser N, P and K increased due to rising oil prices. This increase raised the value of nutrients within slurry e.g. 1,000 gallons of slurry (4.5 m³) increased in value by 168% during this period [121]. This rise renewed interest in the efficient use of slurry on dairy farms. On-farm fertiliser replacement calculations in Ireland clearly show the typical dry matter, N, P and K levels in animal manures and the average N, P and K levels available in manures applied in spring or summer [122]. This emphasises the clear variation in nutrient concentrations, which is not the case with chemical fertiliser. The value of nutrients in slurry is related to its nutrient content, which is highly variable. Such variability is due to differences in animal diet, animal type, and slurry dilution

with water. A dairy manure management strategy is already in place in Ireland (under the Nitrates Directive) and research now aims to maximise the nutrient utilisation of slurry. This means that dairy slurry is unlikely to be a viable source of nutrients for algal growth in Ireland. However dairy slurry may be a viable option in international agricultural systems e.g. intensive farms with surplus dairy manure (digested or undigested).

The Nitrates Directive [123] enacted in Ireland in 2006 (under Statutory Instrument (SI) 101, 2009) is currently the main mitigation legislative measure in place to achieve the goals of the European Unions Water Framework Directive. In Ireland, dirty water is generated from dairy parlour water and machine washings, precipitation and water from concreted holding yards. It has a biological oxygen demand of $< 2500 \text{ mg L}^{-1}$, DM content of $< 1\%$ and does not contain any faecal matter (S.I. No. 101 of 2009). Average dirty water production per cow is $49 \text{ L}^{-1} \text{ day}^{-1}$ [58]. Current dirty water management is typically either land application or irrigation using a centre pivot roto-rainer system. Dirty water (under the Nitrates Directive) requires the separation of faecal matter and water, thereby reducing the nutrient content. Any material containing faecal matter is slurry. As the nutrient content of dirty water is low and volumes are high (a 100 cow unit, milked twice daily in the SE of Ireland produces 9500 L of dirty water daily), storage costs and water charges become higher and ultimately unfeasible for algal production systems. Such sources are likely to be available for other enterprises but would prove un-economical if transported off the farm. Nutrient concentrations of soluble wastes i.e. dirty water, runoff or drainage are lower than slurry or anaerobic digestion by products. Transportation costs would therefore quickly become prohibitive. Co-locating algae production with animal waste

treatment could be made environmentally effective as well as financially viable in the future [124]. As previously stated, a source of CO₂ is required for commercial algal production. CO₂ distribution is common-place in large scale commercial operations therefore availability of CO₂ would not greatly influence the location of an algal growing facility.

The intensive agricultural poultry and pigs sector in Ireland have surplus manures to land application possibilities (due to the high nutrient content of their manures). Management often involves on-site treatment or off-site transport of waste. The introduction of regulations regarding the use of organic manures as part of the Nitrates Directive restricts the amount of grassland available to intensive pig producers for land application of manure and therefore tillage land is often utilised [125]. An estimate of annual N and P outputs from the pig industry in Ireland amounts to 13,500 Mt of N and 2,600 Mt of P. Typical manure nutrient content value offer only a guideline to the actual nutrient value, as manure composition can vary considerably depending on crusting or settling during storage and dilution by rainwater.

An economic assessment of pig manure transport from an intensive pig farm to spreading lands was undertaken in Ireland by McCutcheon and Lynch [126]. This analysis showed that at distances over 50 km, the cost of transport of un-separated pig slurry exceeded the value of nutrients in the slurry (at 2008 prices). As stated previously, the Nitrates Directive restricts the grassland available for the application of pig slurry due to soil test phosphorus restrictions. There has been renewed interest in the disposal of excess pig manure, particularly in relation to landspreading on tillage land. The majority of intensive pig production units are located in the north-

east of Ireland, whereas the majority of the tillage growing areas are located at distances greater than 50 km from intensive pig production units (in the east and south-east of the country). As pig manure has a high N, P and K status, and nutrient requirements of algae are low, the manure could be used in commercial algal production plants. It would be most economical if algal growing plants were located in relatively close proximity to the major pig production areas to reduce transportation costs. A CO₂ source and a dilution facility could be located offsite or all three elements merged together at the nutrient source or within the transport boundary. Alternatively pig slurry could be transported to a bio-reactor facility and subsequently the bi-products from this facility could be used to grow algae (see Table 1 for nutrient contents).

Future research should focus on a financial assessment of using pig and poultry waste surpluses to act as nutrient inputs for algal growth for the production of algal biomass in Ireland. In addition, negative considerations should be examined when using manure to grow algae such as: the presence of non biodegradable components of manure such as heavy metals, micro-pollutants e.g. antibiotics and hormones, bacteria and pathogens.

This case study focuses on Ireland, however, similar agricultural systems in other countries e.g. Atlantic Europe [127] could also learn from this study.

4. Conclusion

This review has demonstrated that the nutrient content of agriculturally derived organic fertilizers, runoff and drainage waters has the potential to facilitate algal biomass growth. In particular, the review has shown that surplus manures that require alternative management strategy for their effective utilisation (e.g. pig and poultry manures), or bi-products from anaerobic digestion, are potentially the most viable sources of nutrients to grow algae. However, prior to their use as a source of nutrients for algal growth, feasibility issues such as variable nutrient contents amongst and across source types, transparency issues and early and sustained nutrient loss during the storage phase (N volatilisation and P precipitation) must be addressed. Agitation and efficient nutrient testing before use may be a means of addressing some of these feasibility issues. Further practical investigation regarding the growth of algal biomass from surplus agricultural nutrient sources is required.

Captions for Figures

Fig.1 - Agricultural nutrient sources as alternatives to chemical fertiliser to grow algal biomass.

Captions for Tables

Table 1 - Selection of studies used to create algal biomass utilising nutrients from manures.

Table 2 - Manure figures for Rep of. Ireland (Hyde, pers comm)

Table 3 - Dairy dirty water nutrient results from various studies in U.K. and Ireland.

Fig. 1 - Agricultural nutrient sources to grow algal biomass.

Table 1 - Selection of studies used to create algal biomass utilising nutrients from manures. ($\pm$ standard deviation)

Study	Manure Type	Digested/ Undigested	Nh ₄ -N	Organic N	NO ₃ -N	TN	TP
			mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹
Mulbry and Wilkie, (2001) [46]	Dairy	Undigested	306	904	<1	1210	303
		Digested (Maryland, USA)	1620	751	<1	2371	240
		Digested (Florida, USA)	178	47	<1	225	24.7
Pizarro et al. (2002) [44]	Dairy	Digested	5 to 80	-	-	-	1 to 20
Sevrin-Reyssac, (1998) [65]	Swine		14000				2000-2300
Olguin et al. (2001) [66]	Swine	Digested	1700			2330	
Natarajan and Varghese, (1980) [68]	Poultry	Undigested (India)				3.5%	5.64%
Cheung and Wong, (1981) [69]	Poultry	Undigested (Hong Kong)				2.056 $\pm$ 0.08	261.3 $\pm$ 54.2
	Swine	Undigested (Hong Kong)				2.524 $\pm$ 0.04	344.2 $\pm$ 46.9
Wang et al. (2009) [124]	Dairy	Digested (Minnesota)	2232			3456	249.7
	Dairy	Undigested (Minnesota)	1782			3305	266
Kebede-Westhead, et al. (2004) [40]	Dairy	Digested manure effluent (Florida, USA)	233		<1	412	64.5

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Table 2 - Dairy dirty water nutrient results from various studies in U.K. and Ireland.

Study	Number of farms	Period of study		Kjeldahl N	BOD	K	NH ₄	P	SUS	TN	TON	TP	Org N
Minogue et al., 2010 [57]	60	Monthly for 1 year											
Ireland			Mean		2246	568	212	37	5120	587	1	80	381
			Min		0	3	0	0	48	0	0	2	0
			Max		19085	7232	2933	1240	79400	6030	240	795	4251
			SD		2112	513	206	53	5865	536	10	68	413
									mg L ⁻¹				
Fenton et al., 2009a [101]	1	3 months (August, September, October)	Mean		-	-	-	14.0	-	170	30.4	20.1	-
Ireland			SD		-	-	-	9.2	-	33.2	9.2	6.9	-
Ryan et al., 2005 [128]			Min		-	-	-	-	-	43	88	-	-
Ireland			Max		-	-	-	-	-	126	225	-	-
Cumby et al., 1999 [55]	20	3 months (Feb, June, September)	Mean (Feb)		2.66	-	0.31	-	0.34	-	-	-	-
England and Wales			SD		1.8	-	0.32	-	0.34	-	-	-	-
			Mean (June)	0.95	9.67	1.50	0.58	0.49	0.83	-	-	-	-
			SD	0.76	9.67	1.05	0.48	0.34	0.66	-	-	-	-
			Mean (Sep)	0.70	7.45	0.85	0.48	0.34	0.52	-	-	-	--
			SD	0.60	6.55	0.40	0.41	0.22	0.37	-	-	-	-

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Table 3 - Manure figures for Rep of. Ireland (Hyde, pers comm)

Manure Type	Mt	%
Cattle	36,005,848.06	91.4
Pigs	2,219,407.01	5.6
Poultry	135,385.08	0.3
Sheep	1,014,876.85	2.6
Total	39,375,517.01	
Mt = metric tonne		

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