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Agricultural Dairy Wastewaters

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1. Introduction

In Ireland, farming is an important national industry that involves approximately 270,000 people, 6.191 million cattle, 4.257 million sheep, 1.678 million pigs and 10.7 million poultry (CSO, 2006). Agriculture utilizes 64% of Ireland's land area (Fingleton and Cushion, 1999), of which 91% is devoted to grass, silage and hay, and rough grazing (DAFF, 2003). Grass-based rearing of cattle and sheep dominates the industry (EPA, 2004). Livestock production is associated with external inputs of nutrients. Phosphorus (P) surpluses accumulate in the soil (Culleton et al., 2000) and contribute to P loss to surface and groundwater (Tunney, 1990; Regan et al., 2010). Elevated soil P status has been identified as one of the dominant P pressures in Ireland (Tunney et al., 2000). Schulte et al. (2010) showed that it may take many years for elevated soil P concentrations to be reduced to agronomically and environmentally optimum levels. The extent of these delays was predominantly related to the relative annual P-balance (P balance relative to total P reserves). While the onset of reductions in excessive soil P levels may be observed within five years, this reduction is a slow process and may take years to decades to be completed.

Agricultural wastes and in particular dairy slurry and dirty water are discussed in this chapter. However, while the term 'waste' is commonly used for these materials, it is an unfortunate label, as it suggests that the materials have no further use and are merely a nuisance by-product of farming systems that must be managed. However, given the high nutrient contents of these materials, it is far more appropriate for them to be considered as organic fertilizers, and as such being a valuable commodity for the farmer. With higher and more volatile chemical fertilizer prices in recent years, the fertilizer replacement value in economic terms of these materials is increasing. Therefore, the management of agricultural 'wastes' in a manner that maximises the nutrient recovery and fertilizer value to crops should be a priority within any management plan for these materials.

Nutrient contents and various research areas regarding management, remediation and control of such nutrients to prevent losses to the environment are discussed. The Surface Water Directive, 75/440/EEC (EEC, 1975), the Groundwater Directive, 80/68/EEC (EEC, 1980), the Drinking Water Directive, 98/83/EC (EC, 1998), the Nitrates Directive, 91/676/EEC (EEC, 1991(a)) and the Urban Wastewater Directive, 91/271/EEC (EEC, 1991(b)), combined with recent proceedings taken against the Irish State by the EU Commission alleging non-implementation of some aspects of the directives, has focused considerable attention on the environmentally-safe disposal of agricultural wastewaters in Ireland. To address these directives, the WFD (2000/60/EC, 2000) came into force on 22nd December, 2000 and was transposed into Irish legislation by the European Communities (Water Policy) Regulations 2003 on the 22nd December, 2003. Eight "River Basin Districts" (RBD) were established in Ireland, north and south, with the aim of achieving "good status" in all surface and groundwater by 2015. The WFD will bring about major changes in the regulation and management of Europe's water resources. Major changes include:

- A requirement for the preparation of integrated catchment management plans, with remits extending over point and non-point pollution, water abstraction and land use;
- The introduction of an EU-wide target of "good ecological status" for all surface and groundwater, except where exemptions for "heavily-modified" water bodies are granted. Programmes of measures (POM) must be put in place to protect groundwater and surface water while being efficient and cost-effective. POM to achieve at least "good ecological status" must be implemented by the agricultural sector by 2012. In Ireland the Nitrates Directive is the main POM in place. At present, a strategy exists within Europe to restore the "good ecological status" of surface and groundwater. It focuses on reducing nutrient pressures to prevent further nutrient loss to surface and groundwater. However, intensification of agriculture poses a challenge to the sustainable management of soils, water resources, and biodiversity. N losses from agricultural areas can contribute to ground- and surface water pollution (Stark and Richards, 2008; Humphreys et al., 2008).

Results from a Water4all project suggest that regulation alone will not achieve sufficient reduction in water quality as nitrate builds up in soils and the long residence time of groundwater in aquifers needs a more immediate solution (Water4all, 2005; Hiscock et al., 2007). Therefore, remediation (nitrogen - N) and control (phosphorus – P) technologies must be an integral part of the process for point and diffuse pollution from historic or future incidental nutrient losses. Solutions developed must be integrated efforts within a catchment or river basin.

Good Agricultural Practice Regulations under The Nitrates Directive (European Council, 1991) is currently the main mitigation measure in place within the agricultural sector to achieve the goals of the WFD. These regulations came into effect in the Republic of Ireland in 2006 under Statutory Instrument (S.I) 788 of 2005, and subsequently under S.I 378 of 2006, S.I 101 of 2009 and S.I 610 of 2010. The Nitrates Directive sets limits on stocking rates on farms in terms of the quantity of N from livestock manure that can be applied mechanically or directly deposited by grazing livestock on agricultural land. A limit of 170 kg N ha^{-1} $year^{-1}$ from livestock manure was set. However, the EU Nitrates Committee approved Ireland's application for a derogation of this limit to allow grassland-based (mostly dairy) farmers to operate at up to 250 kg N ha^{-1} $year^{-1}$ from livestock manures, with the understanding that this derogation will not impinge on meeting the requirements of the Nitrates Directive. The current average stocking density on dairy farms is 1.81 livestock units (LU) ha^{-1}.

The "Good Agricultural Practice for the Protection of Waters" regulation, S.I 778 of 2005 (Anon, 2005), came into effect on February 1st 2006. The most recent revision of the regulation was published in 2010 (Anon, 2010). It constrains the use of P and N fertilizers, ploughing periods and supports derogation on livestock intensity. In particular it regulates farmyard and nutrient management, but also examines prevention of water pollution from fertilizers and certain activities. The linkage between source and pathway can be broken if pollutants remain within farm boundaries and are not discharging to drainage channels, subsurface drainage systems, or entering streams or open waterways within farm boundaries. These regulations also place restrictions on land spreading of agricultural wastes. This strategy looks at present loss and future loss prevention. There are no guidelines in place for the remediation or control of contaminated discharges to surface and/or groundwater or future discharges due to incidental losses. Traditionally, agricultural wastes are managed by land spreading. Following land spreading, the recharge rate, the time of year of application, the hydraulic conductivity of the soil, the depth of soil to the water table and/or bedrock, and the concentration of nutrients and suspended sediment in the wastewater (dirty water and any discharge containing nutrients) are some of the defining parameters that determine nitrate movement through the soil to the watertable. The maximum instantaneous rate of application is 5 mm per hour and the quantity applied should not exceed 50 m^3 per hectare per application (ADAS, 1985; 1994; DAFF, 1996) and these recommendations are present within best farm management practices. Infiltration depth of irrigated water and rainfall may be estimated when the annual effective drainage, number of effective drainage days, effective porosity, annual precipitation, and the hydraulic load of the irrigator are known (Fenton et al., 2009(b)). This data may then be combined with watertable data to examine if excess nutrients recharge to groundwater within a specific time frame.

2. Agricultural dairy wastes

2.1 Types of dairy wastes and nutrient content

In a grassland system, the N recovery rate of dairy slurry is highly variable due to variations in slurry composition, application methods, spreading rates, soil and climatic conditions and slurry N mineralisation rates (Schröder, 2005). In Ireland, approximately 80% of manures produced in winter are managed as slurries containing 70 g kg^{-1} dry matter, 3.6 g kg^{-1} total N (TN) and 0.6 g kg^{-1} total P (TP) (Lalor et al., 2010(a)). About 50% of the TN is in ammoniacal form and has the potential to be volatilised as ammonia during storage and following land spreading. Estimated organic managed waste generation for Ireland is presented in Table 1.

Waste Category	Waste Generation	
	Tonnes wet weight	%
Cattle manure and slurry	36,443,603	60.6
Water (dairy only)	18,377,550	30.5
Pig slurry	2,431,819	4.0
Silage effluent	1,139,231	1.9
Poultry litter	172,435	0.3
Sheep manure	1,336,336	2.2
Spent mushroom compost	274,050	0.5
Total	60,170,025	

Table 1. Estimated agricultural organic managed waste generation in 2001 (EPA, 2004a).

Great variation in the nutrient content of dairy slurry exists depending on feed type, age of sample when tested, age of the animal and how the effluent is stored and managed (Smith and Chambers, 1993). Seasonal differences in nutrient contents also exist (Demanet et al., 1999). Tables of published slurry nutrient contents in Europe exist (see MAFF, 2000). Such values are similar to South American dairy slurry concentrations found by Salazar et al. (2007). Some dairy slurry concentrations for undigested and digested samples are presented in Table 2. These tend to be similar to other nutrient contents across Europe found by Villar et al. (1979); Scotford et al. (1998(ab)) and Provolo and Martínez-Suller (2007). In Ireland, dirty water is generated from dairy parlour water and machine washings, precipitation and water from concreted holding yards (Photo 1). Average dirty water production per cow is 49 L^{-1} day^{-1}. Although dilute, dirty water has sufficient nutrients to give rise to eutrophication if lost to a waterbody through runoff or excess infiltration. Implementation of current legislation requires separation of faecal matter and water, thus diminishing the nutrient content of dirty water for land application (Photo 1). As the nutrient content is reduced and storage and water charges are high, an alternative solution to dirty water management is remediation and re-use for washing yards (Fenton et al., 2009). A number of papers have reported the chemical composition of dirty water from dairy farms (ADAS, 1994; Cumby, 1999; Ryan, 2006; Fenton et al., 2009(a);Minogue et al., 2010). Table 3 presents a range of nutrient contents available in dirty water from a number of studies. Minogue et al. (2010) and Cumby (1999) report higher mean TN nutrient figures for 20 farms in England and Wales of 580±487 mg TN L^{-1}. Martínez-Suller et al. (2010(b)) reviewed the composition of dirty water in the literature including others not mentioned in Table 3.

Photo 1. Dirty water generation: wash down high volume low pressure hose and drainage channel for speeding up washing after milking (Source: www.teagasc.ie)

Prediction of the nutrient content of agricultural waste waters would help farmers to more accurately calculate the nutrient fertiliser replacement value of the landspread materials and the additional fertiliser requirements for their crops. Martínez-Suller et al. (2010(a)) suggest that dry matter content or electrical conductivity are rapid, cheap methods to estimate the nutrient content of waste waters and manures.

2.2 Faecal microorganisms

Agricultural wastes not only pose a threat to waterbodies, a second major concern is the presence of pathogenic and/or antibiotic resistant bacteria in animal wastes (Sapkota et al., 2007) and the threat to human health. If properly handled and treated, manure is an effective and safe fertiliser. However, if untreated or improperly treated, manure may become a source of pathogens that may contaminate soil, food-stuffs, and water bodies (Vanotti et al., 2007). Animal manures are known to contain pathogenic bacteria, viruses and parasites (Pell, 1997). The contamination of surface waters with pathogenic micro-organisms transported from fields to which livestock slurries and manure have been applied is a serious environmental concern as it may lead to humans being exposed to such micro-organisms via drinking water (Skerrett and Holland, 2000); bathing waters (Baudart et al., 2000); and water used for the irrigation of ready to eat foods (Tyrel, 1999). A recent study

Table 2. Dairy slurry nutrient content from various studies.

Study	Manure Type	Digested/ Undigested	NH_4-N	Organic N
			mg L^{-1}	mg L^{-1}
Mulbry and Wilkie, 2001	Dairy	Undigested	306	904
		Digested (Maryland, USA)	1620	751
		Digested (Florida, USA)	178	47
Pizarro et al., 2002	Dairy	Digested	5 to 80	-
Wang et al., 2009	Dairy	Digested (Minnesota)	2232	
	Dairy	Undigested (Minnesota)	1782	
Kebede-Westhead et al., 2004	Dairy	Digested manure effluent (Florida, USA)	233	
Brennan et al., 2010(abc)	Dairy	Undigested (West Ireland) May	1759(123)	
	Dairy	Undigested (West Ireland) July		
	Dairy	Undigested (West Ireland) December		
Martínez -Suller et al., 2010	Dairy	Undigested (South East Ireland)		

() standard deviation

Study	Number of farms	Period of study		BOD_5	K	NH_4-N
Minogue et al., 2010	60-Ireland	Monthly for 1 year	Mean	2246	568	212
			Min	0	3	0
			Max	19085	7232	2933
			SD	2112	513	206
Martínez-Suller et al., 2010(b)	1-Ireland	13 weeks (January – May)	Mean	3084	415	32
			Min	1570	213	0
			Max	8400	977	106
			SD	1739	169	25
Serrenho et al., 2010	1-Ireland					
Fenton et al., 2009(a)	1-Ireland	3 months (August - October)	Mean	-	-	-
Singh et al., 2005				3000		
Dunne et al., 2005(ab)	1-Ireland	Winter		2828		42
		Spring		2703		53
		Summer		2682		36
		Autumn		2303		6
Ryan et al., 2005	1-Ireland		Min	-	-	-
			Max	-	-	-
Rodgers et al., 2003	1-Ireland			2208		
Cannon et al., 2000				1440		
Cumby et al., 1999	20- England and Wales	Summer		9670	150	58
		Autumn		7450	85	48
Richards, 1999	1-Ireland					84.4
Misselbrook et al., 1995	1-England				350	42
Ryan, 1991	1-Ireland			2077	210	92

Table 3. Dairy dirty water nutrient results from various studies in U.K. and Ireland. Based on new data and Martínez-Suller et al., 2010(b). All units in mg L^{-1}

(Venglovsky et al., 2009) has shown that animal manure contributes significantly to pathogen loading of soil and consequently runoff to waterways. Furthermore, a recent report by the EPA in Ireland (Lucey, 2009) highlighted land-spreading of manure or slurry as one of the main sources of microbial pathogens in groundwater. Additionally, a report by the Food Safety Authority of Ireland (FSAI, 2008) stated that 'there is potential for the transfer of pathogens to food and water as a result of land-spreading of organic agricultural material'.

Research from New Zealand, shows that dirty water contains faecal micro-organisms, which originate from dairy cattle excreta. Researchers such as Aislabie et al. (2001); McLeod et al. (2003) and Donnison and Ross (2003) have shown transfer of bacterial indicators, faecal coliforms and *Campylobacter jejuni* through soil. The Pathogen Transmission Routes Research Programme in New Zealand showed that significant faeces contamination arose through the deposition of faeces by grazing animals with access to waterways. Fencing and implementation of buffer strips were recommended as mitigation measures to prevent such losses (Collins et al., 2007). Presence of faecal indicator organisms is used to identify waters impacted by faecal matter from mammals. Indicators of faecal contamination such as *E. coli* are widely used as they are faecally specific and believed to not survive for more than 4 months post excretion (Jamieson et al., 2002). Recent research has shown that *E. coli* can survive for long periods of time in temperate soils (Brennan et al., 2010) and contribute to high detections in drainage waters from agricultural soils. *E. coli* were particularly associated with poorly drained soils due to the greater persistence of preferential flow channels and anaerobic micro-sites where they might survive. Thus the presence of *E. coli* in waters may not indicate recent contamination by faecal matter but could be due to historical pathogen deposition. Many treatment systems may be used to treat livestock waste and remove or decrease viral, bacterial and eukaryotic pathogens. Examples include bio-gas producing anaerobic digestion, composting, aeration, storage under a variety of redox conditions, and anoxic lagoons, all of which have been reviewed by Topp et al. (2009).

2.3 Current management practices for agricultural waste waters

The Nitrates Directive and rising costs are now forcing better use of nutrients in slurry. Research in the U.K. (Misselbrook et al., 1996; 2002; Smith and Chambers, 1993; Smith et al., 2000) includes improving N recovery from slurry by examining the effect of spreading method and timing, and reducing ammonia (NH_3) losses from slurry by evaluating splash-plate versus alternative techniques such as trailing shoe or trailing hose slurry application methods. The average abatement of these methods varies and differs when grassland or arable application are considered (Smith and Misselbrook, 2000; Misselbrook et al., 2002). Present research in Ireland follows similar patterns (Ryan, 2005). Ammonia emissions with respect to trailing shoe versus splash-plate and subsequent N uptake by the sward are being investigated in Irish grasslands (Lalor and Schulte, 2008). Farm management strategies aimed at prevention of nutrient loss to water have recently been reviewed by Schulte (2006).

The Nitrates Directive regulations impose limits to N and P inputs onto livestock and tillage farms. Cattle and dairy farming systems are required to make more efficient use of nutrients. International experience suggests that significant gains in nutrient efficiency can be made by increasing the utilisation of N in slurry. Lalor (2010(b)) suggested N-utilisation efficiencies from slurry as low as 5% under existing practices, whereas international literature suggests that there is scope to raise efficiencies to 40-80%. Despite the relatively low utilisation in practice, the Nitrates regulations set a nitrogen fertilizer replacement value

(NFRV) target of 40%, presenting a considerable challenge for the grassland sector. In addition, the ceiling to nutrient inputs imposed under the Nitrates Directives made it difficult for many livestock farmers to continue to accept pig slurry as a fertilizer onto their farm. In Ireland, as a result, the potential for the traditional practice of spreading slurry on grasslands has been reduced significantly. Returning pig slurry to arable land allows a more closed nutrient cycle to operate, since cereal grains constitute a significant proportion of the diet of pigs. However, this creates a major logistic challenge where arable land and pig farms are not closely located (Lalor et al., 2010(b)).

In an Irish study, cattle slurry application on grassland shows that the NFRV in the year of application is affected by application method and timing. Cattle slurry applied (using traditional methods) with splashplate had an NFRV of 21% in April and 12 % in June. Application using trailing shoe (a modern alternative which places slurry in thin bands along the soil surface) increased the NFRV to 30% in April and 22% in June. Changing application timing from summer to spring with existing splashplate machinery is the most cost effective strategy for improving NFRV. Approximately 4% of the total slurry N applied was recovered in the second year after application. For repeated applications over a number of years, models indicate that the maximum cumulative residual recovery would be 12-14% of the annual slurry N application rate. It would take approximately 10 years of repeated slurry applications for the residual N release to reach this maximum level (Lalor et al., 2010(b)). In Ireland, research by Lalor et al. (2010(b)) showed that the NFRV target of 40% set in the Nitrates regulations can only be achieved when the residual N release is included, and when best practice strategy of trailing shoe application in April was adopted. Spring application of slurry is often restricted by soil trafficability, particularly on poorly drained soils. The trailing shoe application method can provide more flexibility for spring application as grass contamination is reduced compared to splashplate.

In Ireland, besides land application methods (splashplate or trailing shoe (Photo 3)), dirty water irrigation using centre pivotal irrigation systems is common (Photo 2). The recommended irrigation rates should not exceed 5 mm hr^{-1}. Strict guidelines for their safe use are in place. Application timing of dirty water should take soil moisture status and soil physical properties into account (Houlbrooke et al., 2004). Two pond systems are used in many countries reducing the biological oxygen demand and suspended solids contents. A limitation here is that the nutrients remain unchanged and need to be landspread with potential environmental consequences. An upgraded “advanced pond system” has been

Photo 2. Rotational centre pivot sprinkler system used for dairy dirty water irrigation (Source: www.teagasc.ie)

Photo 3. Slurry tanker with trailing shoe application system (Source: Teagasc)

designed by Craggs et al. (2004) and could be an alternative on dairy farms. Houlbrooke et al. (2006) showed that individual irrigation systems with low intermittent irrigation rates (0.4 to 4 mm hr^{-1}) could be used without nutrient losses. To facilitate this low irrigation rate, increased storage is needed on a farm. Adapted low irrigation lines have now also been investigated, the position of which may be changed through use of a quad-bike system.

Bolan and Swain (2004) reviewed issues and innovations in land application of farm wastes in New Zealand and showed that research must focus on improved systems to convert manure based wastes into a valuable but also environmentally benign product.

An alternative manure management system in some countries is anaerobic digestion. Manures are an excellent source of organic material for anaerobic digestion and the production of bio-gas. Co-digestion of agricultural wastes with sewage sludges can further improve the methane production in anaerobic digesters (Ward et al., 2008).

2.4 Environmental Impact of agricultural waste waters

Agricultural waste waters can contain N, P, K, S, C, pathogenic micro-organisms and a range of other micro nutrients. Nutrients returned to agricultural soils through land-spreading are important for nutrient efficiency on farms and for reducing reliance on inorganic fertilisers. Land application should be at rates that supply nutrients for crop growth and at the time when these nutrients are required. Addition of excessive nutrients at times of reduced crop demand can increase the potential for losses of nutrients such as N and P, which contribute to surface water eutrophication and can lead to pollution of drinking waters. In addition, land application to wet soils can lead to increased emissions of greenhouse gases such as nitrous oxide (N_2O).

Landspreading of dairy slurry and wastewaters has been associated with ammonia volatilisation to the atmosphere. Application of ammoniacal nitrogen (NH_4^+) to soils in wastewater increases the soil solution NH_4^+ concentrations, which is in equilibrium with free ammonia (NH_3) which is also in equilibrium with the concentrations in the atmosphere (See Equation 1).

$$\begin{array}{lcc} \text{Atmosphere:} & & NH_3 \\ & & \updownarrow \\ \text{Soil Solution: } NH_4^+ + OH^- & \longleftrightarrow & NH_3 + H_2O \end{array}$$

Ammonia volatilisation from soil lowers the pH of soil directly under the waste water. Further soil pH reduction can also occur when the volatilised NH_3 is re-deposited and nitrified. Agriculture is the main emitter of NH_3 to the atmosphere accounting for ~80% of total global emissions (Stark and Richards, 2008) and is expected to reach 109 Tg N yr^{-1} by 2050. Once in the atmosphere, NH_3 can readily combine with NO_3 and SO_4^{2-} in acid cloud droplets to form particulates and can be transported over long distances before being deposited again to soil or water. Atmospheric N deposition has increased over recent decades and ranges from 5 to 80 kg ha^{-1} yr^{-1} with a global average of 17 kg ha^{-1} yr^{-1} have been observed. Deposited NH_3 can then lead to acidification of soil and eutrophication of waters, which led to the UN establishing the Convention on Long-range Transboundary Air Pollution including NH_3 and the EU set limits for NH_3 from European countries. Emissions of NH_3 from agricultural slurry and waste waters can be reduced through utilisation of low emission storage facilities where stores are covered to reduce contact with the atmosphere. Emissions can also be reduced from the field through the use of low emissions spreading methods such as band spreading and injection (See section 2.3). Land application of dilute waste wasters has lower NH_3 emissions compared to more solid waste due to a reduction in the NH_4^+ content and the infiltration of the liquid waste into soil, reducing atmospheric contact. Thus dilute effluents have lower NH_3 emissions, but potentially greater N_2O and NO_3^- emissions.

Application of animal slurries and wastewaters to soils promotes denitrification through the supply of readily available N and C for microbial respiration and also by promoting anaerobic conditions in the soil through partial sealing of soil pores and the consumption of oxygen through C oxidation. Storage of manures leads to the build up of volatile fatty acids which are readily degradable forms of C. Microbial denitrification associated with landspreading of organic wastes can be an important source of the potent greenhouse gas, N_2O. Emissions of N_2O from slurry spreading are mainly related to the application method, and the soil temperature combined with soil moisture at the time of application. Methods for reducing N_2O emissions associated with waste waters include limiting the hydraulic loading to ensure soils remain aerobic; adjusting application timing to when soils are not anaerobic; adjusting application method/rate; inclusion of nitrification inhibitors to slow the rate of NO_3^- formation; manipulation of the C/N ratio; digestion or storage to reduce labile C content and inclusion of materials with high cation exchange capacity e.g. zeolite. A schematic of soil N transformations is presented in Figure 1.

There have been numerous reports of water pollution occurring after landspreading of wastewaters to soils. Richards et al. (2004) reported nitrate leaching losses ranging from 95 to 323 kg N ha^{-1} when wastewaters were over-applied to free draining soils. Houlbrouke et al (2004) reported between 2 and 20% of N and P applied in agricultural wastewaters leached through soils and the concentrations leaching were above ecological limits for good water quality.

Repeated application of wastewaters to soil can lead to an increase in the organic fractions of N, P, K and organic carbon due to changes in soil organic matter. In New Zealand, Barkle et al. (2000) reported significant increases in soil total N and organic C. At low temperatures increasing soil C content due to dirty water application can lead to greater N immobilisation due to changes in the soil C/N ratio (Ghani et al., 2005). Increasing soil nutrient status above the agronomic optimum has been shown to increase the risk of nutrient loss to water (Sharpley and Tunney, 2000). Other soil properties can be influenced by land application such as increasing soil pH, changes in soil hydraulic conductivity due to clogging, plugging and macropore/aggregate collapse. Often the actual effect of landspreading on soil physical properties is difficult to quantify due to variability in soil physical properties, short term observation and experimental approaches within a background of seasonal variation in properties (Hawke and Summers, 2006) Agricultural waste waters can contain high concentrations of pathogen micro-organisms such as Campylobacter, Listeria, Cryptosporidium and Salmonella spp. Loss of high concentrations of faecal pathogens to water can result in the waters being unfit for human consumption and failing to meet water quality standards for bathing water quality. Pathogen transfer to water can occur when waste waters are applied to water-logged soils where water flow over soil leads to high pathogen losses to rivers and associated bathing waters (Kay et al., 2007). Reducing the volume and area contaminated by waste waters on farms can reduce emission of pathogens to water by 10% (Kay et al., 2007).

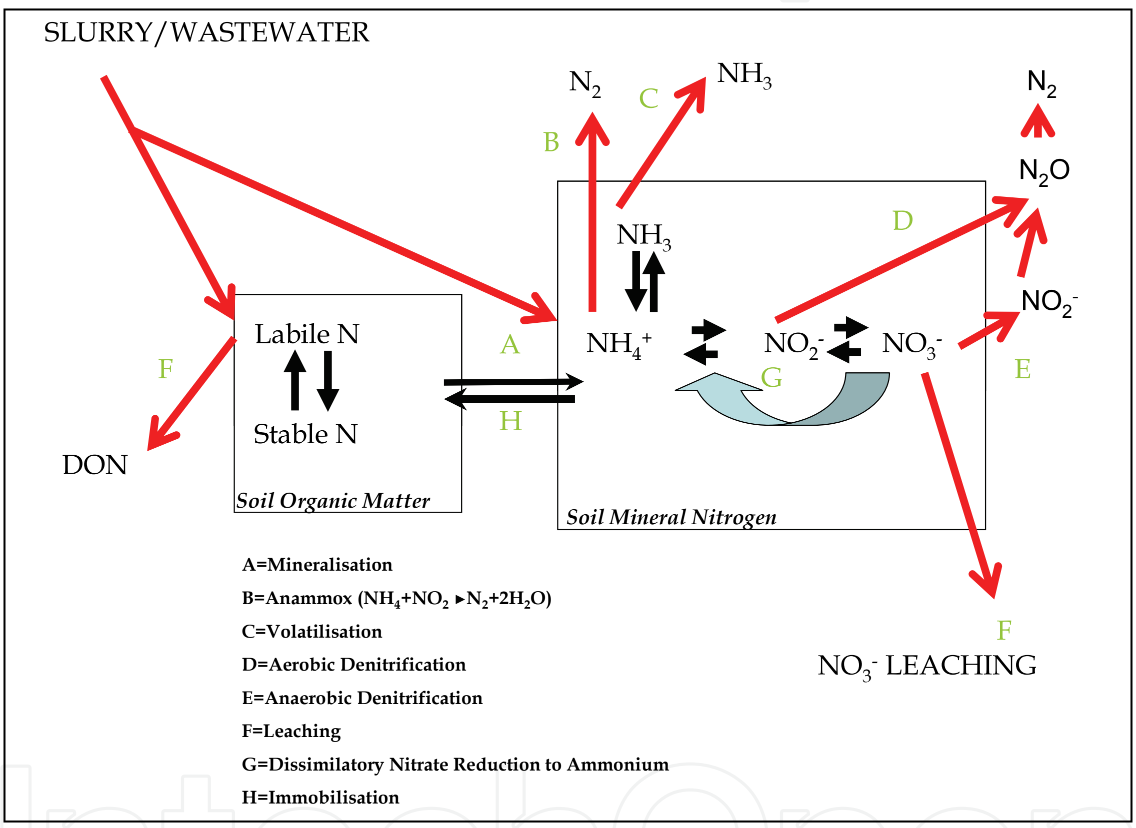

Fig. 1. Soil N transformations of slurry/wastewater derived nitrogen inputs.

3. Novel remediation techniques currently being researched

Fenton et al. (2008) reviewed agricultural wastewater remediation and control technologies suitable for Ireland. Several options such as use of chemical amendments, subsurface carbon emplacement and wetlands were some of the options proposed for further research.

3.1 Amendments to dairy slurry and dirty water

Dairy dirty water is a bio-product of dairy farming. The usual method for disposal of this product is land-spreading (Healy et al., 2007). This can increase the P concentration on the soil surface and the pollution related with the natural run-off during rain events. Not many studies have been made regarding this subject.

Due to the properties of the dairy dirty water, the potential for leaching should also be considered. Usually, P leaching is not considered to be a significant problem in groundwater because it is not very mobile in soils or sediments, and should therefore be retained in the soil zone. However, in extremely vulnerable areas, where the soil and subsoil are shallow and where P enters groundwater in significant quantities, groundwater may act as an additional nutrient enrichment pathway for receptors such as lakes, rivers and wetlands (EPA, 2008). Phosphorus leaching may occur in sandy soils (Carlyle et al., 1998) or where there are preferential flow paths in the soil.

In the past, the primary objective of chemical amendment of manure was to reduce NH_3 losses from manure as this increased N availability to plants. In recent years environmental concerns have shifted this focus to amendments, which mitigate P loss from soils and manure. In Ireland, the focus of recent research has been to find amendments which reduce solubility of P in dairy cattle slurry in particular. The use of such amendments must be practical and cost effective for the farmer. The effect of reducing P solubility on reducing subsequent P fertilizer replacement value of the material should also be considered.

Alum (aluminium sulphate) has been used extensively to treat poultry litter in the U.S for over 30 years with great success to reduce NH_3 in poultry houses and reduce soluble P in poultry litter (Moore and Edwards, 2007). These authors also found that alum addition to poultry litter reduced P loss, ammonia volatilisation and had negligible effect on metal release from amended soil. Work involving amendments of swine and dairy cattle slurries for the control of P have been limited to laboratory batch studies with little emphasis on cost or feasibility of treatments (Dao, 1999; Dou et al., 2003; Kalbasi and Karthikeyan, 2004; Smith et al., 2001; Moore et al., 1998).

Aluminium chloride has been recommended as the most suitable amendment for controlling P solubility in swine and cattle slurry (Smith et al., 2001). In an incubation study Dou et al. (2003) found that technical grade alum added at 0.1 kg/kg (kg alum per kg slurry) and 0.25 kg/kg reduced Water Extractible P in dairy and swine slurry by 99% and 80%, respectively. Dao (1999) amended farm yard manure with calcium carbonate, alum and fly ash in an incubation experiment and reported WEP reductions in amended manure compared to the control of 21, 60 and 85%. Penn et al. (2009) examined the sorption and retention mechanisms of several P sorbing materials (PSMs) including acid mine drainage treatment residuals, water treatment residuals, fly ash, bauxite mining residual and FGD in lab experiments and found the degree of sorption of P to be strongly influenced by the solution pH, buffer capacity of manure, and ionic strength of amendments. These amendments are attractive as they are free. However, they are more variable than chemicals and commercial coagulants used by other workers and much more research is required before there could be used in practice. Internationally, P sorbing amendments have been used to control P losses after manure application. P sorbing amendments can either be added directly to the manure before land application (Moore et al., 1998), spread on the ground before manure application (McFarland et al., 2003), or incorporated into the topsoil at (Novak and Watts, 2005).

Ochre from coal mining origins in the U.K. is a low value waste product from acid mine drainage and has been used as an amendment to sequester P in filters or drainage ditches, or in wetlands receiving sewage or agricultural waste. In Ireland, metal release from metal mining Avoca ochre has made it unsuitable for environmental purpose (Fenton et al., 2008; Fenton et al., 2009(a)). Ochre has a high P sequestration capacity with 97% of sequestration occurring within 5 minutes of contact with an agricultural waste.

3.2 PRB and reactive media for enhanced denitrification

Low-cost, in situ treatment systems, called permeable reactive barriers (PRB), may be used to treat groundwater. In these systems, N-rich wastewater flows through a carbon (C)-rich mixture to reduce nitrate concentrations to acceptable levels. Organic C amendments offer low-cost surface and subsurface treatment alternatives for wastewater treatment. C availability is an important factor that affects denitrifying activity in soils. The presence of C provides an energy source, thereby enhancing the potential for denitrification. Denitrification may be increased in soils by the addition of an external C amendment. This amendment may be natural C such as woodchip, wheat straw, corn, vegetable oil, sawdust mulch, or other materials, such as treated newspaper or unprocessed cotton (Volokita, 1996). A PRB or denitrification wall is only one of many denitrifying bioreactor types, i.e. denitrification beds, up-flow bioreactors, stream bed bioreactor or denitrification layers. The limitations of a denitrification wall are that they require site specific analyses of hydraulic gradient, the depth and extent of the nitrate plume/s, removal of nitrate is confined to up-gradient pollution sources and within the upper 2 m of groundwater. Problems may arise if the denitrification wall has a lower saturated hydraulic conductivity than the surrounding sub-soil. If this occurs, nitrate plumes tend to flow around the wall and not through it. However, in cases where nitrate contamination occurs below 2 m, the diameter (parallel to flow path of contaminant) of the trench may be widened. This causes up-welling into the more permeable trench. Flow through these denitrification bioreactor systems may be either horizontal or vertical. In laboratory studies, vertical flow systems, wherein influent water is pumped from the base of a column, tend to be preferred, as anaerobic conditions are easy to maintain and constant flow rates can be maintained.

3.2.1 Vertical flow systems

Different types of filter media have been examined in PRBs. Gilbert et al. (2008) studied seven types of materials (softwood, hardwood, coniferous, mulch, willow, compost and leaves) to select a suitable natural organic substrate to use in a PBR. Subsequent to a batch test, the material used in the laboratory-scale study was softwood. The columns were 0.09 m in diameter and 0.9 m long, and received an influent concentration of 50 mg NO_3-N dm^{-3} loaded from the column base at two HLRs: 0.3 cm^3 min^{-1} and 1.1 cm^3 min^{-1}. At the lower HLR, removals of more than 96% were measured, whereas removals of 66% were measured for the higher HLR. The impact of residence times was also studied by Claus and Kutzner (1985), who studied N removal in an up-flow packed bed reactor, with lava stones as support for the microbial growth. Using nitrate solution of different concentrations (1.8; 3.0; 4.3; 6.1 g NO^3 L^{-1}) and 5 different residence times (5; 3.3; 2.5; 2.0; 1.7 h), 95% denitrification was measured at the longest residence time.

Other types of filter media, such as shredded newspaper, have also been examined. Volokita et al. (1996) treated water in 0.55 m-high x 0.1 m-diameter laboratory columns using shredded newspaper (0.4 cm width). Complete nitrate removal of the inlet solution (100 mg L^{-1}) was achieved at an ambient temperature of 32°C. Sawdust has high denitrification rates due to its large surface area, but it is prone to clogging. Bedessem et al. (2005) used a mixture of sawdust and native soil in a 4.6 m-long, 7.6 cm-diameter laboratory column to treat synthetic wastewater. The total nitrogen (TN) removal was 31% in the control column (comprising only native soil) and 67% in columns with an organic layer (soil and sawdust). Saliling et al. (2007) evaluated woodchips and wheat straw using an up-flow bioreactor. The influent concentration was 200 mg NO_3-N L^{-1} and a 99% removal was obtained. Vrtovšek and Roš (2006) examined the effectiveness of a 1 m long x 0.12 m diameter fixed-bed biofilm reactor, comprising a mixture of PVC plastic and powdered activated carbon (PAC) as packing material. The reactor was inoculated with municipal wastewater before operation. Influent water with a concentration of 45 mg NO_3-N L^{-1} and sodium acetate ($CH_3COONa.3H_2O$) was loaded from the base of the column. Different loading rates were applied to the column, with drinking water quality being achieved at nitrogen loading rates (NLR) of lower than 1.9 g NO_3-N m^{-2} d^{-1}. Phillips and Love (2002) investigated a denitrifying bio-filter to remove nitrate from re-circulating aquaculture system waters using an up-flow fixed film column and two fermentation columns. Two nitrate concentrations (1.13 kg NO_3-N m^{-3} d^{-1} and 2.52 kg NO_3-N m^{-3} d^{-1}) were loaded at a HLR of 3.0 m hr^{-1}. The column was packed with polystyrene media with a specific surface area of 1000 m^2 m^{-3} and was seeded with activated sludge prior to operation. Commercial fish food was used as a fermentation source. Nitrate removal of greater than 99% was achieved. Rocca et al. (2007) used a coupling heterotrophic-autotrophic denitrification processes (HAD) supported by cotton and zero-valent iron (ZVI) to measure nitrate reduction. Two sets of columns filled with cotton and 150 g or 300 g of ZVI were used in this experiment. This had an up-flow inlet concentration of 100 and 220 mg NO_3 L^{-1}, and 3 and 6 mg L^{-1} of phosphate. The HAD had a higher volumetric nitrate removal ratio (VNR) than cotton-supported denitrification alone.

A laboratory sulphur-based reactive barrier system was evaluated by Moon et al. (2008) and was able to transform 60 mg N L^{-1} in di-nitrogen (N_2) in the presence of phosphate. The denitrification rate was higher than 95%. Cameron and Schipper (2010) compared nitrate removal, hydraulic and nutrient leaching characteristics of nine different carbon substrates. Mean nitrate removal rates for the period 10–23 months were 19.8 and 15 g N m^{-3} d^{-1} (maize cobs), 7.8 and 10.5 g N $m^{-3}d^{-1}$ (green waste), 5.8 and 7.8 g N m^{-3} d^{-1} (wheat straw), 3.0 and 4.9 g N m^{-3} d^{-1} (softwood), and 3.3 and 4.4 g N m^{-3} d^{-1} (hardwood) for the 14 and 23.5 C treatments, respectively.

3.2.2 Horizontal flow systems

Horizontal flow systems have also been used in studies. Healy et al. (2006) examined the use of various wood materials as a carbon source in laboratory horizontal flow filters to denitrify nitrate from a synthetic wastewater. The filter materials were: sawdust (*Pinus radiata*), sawdust and soil, sawdust and sand, and medium-chip woodchips and sand. Two influent NO_3-N concentrations, 200 mg L^{-1} and 60 mg L^{-1}, loaded at 2.9 to 19.4 mg NO_3-N kg^{-1} mixture d^{-1}, were used. The horizontal flow filter with a woodchip/sand mixture, loaded at 2.9 mg NO_3-N kg^{-1} d^{-1}, performed best, yielding a 97% reduction in NO_3-N at steady-state conditions. Using a sand tank containing a denitrifying zone in the centre (sand coated with soybean oil), Hunter (2001) measured a 39% nitrate removal of the initial concentration of 20 mg NO_3-N L^{-1} at a flow rate of 1112 L $week^{-1}$.

3.3 Wetlands

Dairy dirty water (DDW), defined in Section 2.3, can have a significant adverse effect on the environment. In Ireland, management of DDW is explained in Section 3.3, but in recent years, the use of constructed wetlands (CWs) for the treatment of DDW, as well as domestic and municipal wastewaters, has being gaining in popularity. This is due to their relatively low capital costs and maintenance requirements.

3.3.1 Wetland types

There are two types of CW: free water surface constructed wetlands (FWS CWs) and subsurface CWs. In FWS CWs, wastewater flows in a shallow water layer over a soil substrate. Subsurface CWs may be either subsurface horizontal flow CWs (SSHF CWs) or subsurface vertical flow CWs (SSVF CWs). In SSHF CWs, wastewater flows horizontally through the substrate. In SSVF CWs, wastewater is dosed intermittently onto the surface of sand and gravel filters and gradually drains through the filter media before collecting in a drain at the base. CWs may be planted with a mixture of submerged, emergent and, in the case of FWS CWs, floating vegetation. However, the ability of vegetation to capture nutrients, particularly in a cool temperate climate, is limited (Healy et al., 2007).
The large surface area of CWs provides an environment for the physical/physico-chemical retention and biological reduction of organic matter and nutrients (Knight et al., 2000; Lu et al., 2009). Depending on the type of CW used, its design, organic loading rate (OLR) and hydraulic retention time (HRT) (Karpiscak et al., 1999); a CW can have a significant nutrient removal capability. However, due to the effect of changing temperatures, the treatment efficiency of these systems tends to vary throughout the year (Bachand and Horne, 2000).

3.3.2 Design guidelines for dairy dirty water treatment

American guidelines for the design loading of SSHF CWs treating agricultural wastewater (NRCS, 1991) recommend an areal OLR of 7.3 g 5-day biochemical oxygen demand (BOD_5) $m^{-2}d^{-1}$; similar rates are used in wetland design for cool temperate climates (Cooper et al., 1996; Dunne et al., 2005ab). New Zealand guidelines for the disposal of DDW (Tanner and Kloosterman, 1997) recommended that an FWS CW should only succeed two waste stabilization ponds (an anaerobic and an aerobic pond, respectively) before entering the wetland with an OLR not exceeding 3 g BOD_5 m^{-2} d^{-1}. Generally, FWS CWs are used for the treatment of DDW as issues such as blockage of the filter media – normally associated with the operation of SSHF CWs – do not arise.

3.3.3 Treatment efficacy

Results from CWs have been variable. Table 4 tabulates the performance of FWS CWs in the treatment of DDW in a range of countries. In a study of planted and unplanted SSHF CWs, where the unplanted SSHF CWs acted as an experimental control, Tanner (1995ab) found that under 5-day carbonaceous biochemical oxygen demand ($CBOD_5$) OLRs ranging from 0.9 to 3.4 g $CBOD_5$ m^{-2} d^{-1} (unplanted) and 0.9 to 4.1 g $CBOD_5$ m^{-2} d^{-1} (planted), maximum $CBOD_5$ removals of 85% and 92%, respectively, were measured. Ammonification was more pronounced with increasing HRT, and total nitrogen (Tot-N) removal varied between 48 and 80% for planted CWs. Similar OLRs were used in a study on a 3-cell integrated FWS CW in Co. Wexford, Ireland (Dunne et al., 2005ab) where, under OLRs varying from 2.7 to 3.5 g BOD_5 m^{-2} d^{-1}, good organic removal was measured, but nitrification was not complete during winter.
Cronk et al. (1994) also found that under reduced retention times (with OLRs of 60 g BOD_5 m^{-2} d^{-1}) BOD_5 and suspended solids (SS) concentrations were not reduced to acceptable levels after treatment in a 1-cell FWS CW, and that no significant reduction of total kjeldahl nitrogen (TKN) occurred. In a study on a dairy farm in Drointon in the U.K (Cooper et al., 1996), a SSHF CW was used to treat influent with an average BOD_5 concentration of 1192 mg L^{-1}. The system initially utilized only the wetland alone and performed poorly under an OLR of approximately 26 g BOD_5 m^{-2} d^{-1}. However, when two SSVF CWs and a lagoon were

Parameter	Wetland Type	Loading rate	Influent ± SD	Effluent ± SD	Removal efficiency	Reference
BOD						
Ireland	FWS		998±1034	16±5	98	[1]
USA	FWS	~60	7130	2730	62	[2]
	FWS	~12	242	246	-2	[3]
	FWS	NP	1914	59	97	[4]
	FWS	18	2680	611	77	[5]
Australia	FWS	5.6	220	90	59	[6]
Italy	FWS	~1.9	451	28	94	[7]
N. Zealand	FWS	~4.1	113	27	76	[8]
	FWS	~1	337	11	92	[8]
COD						
Ireland	FWS		1718±2008	162±83	91	[1]
SS						
Ireland	FWS		535±434	34±31	94	[1]
USA	FWS	NP	5540	990	82	[2]
	FWS	NP	911	641	30	[3]
	FWS	NP	1645	65	96	[4]
	FWS	9	1284	130	90	[5]
N. Zealand	FWS	~8.5	150	33	78	[8]
	FWS	~1.9	142	34	76	[8]
Tot-N						
USA	FWS	0.7	103	74	28	[5]
	FWS	NP	170	13	92	[4]
N. Zealand	FWS	2.7	~38	20	48	[9]
	FWS	0.6	~38	10	75	[9]
NH_4-N						
Ireland	FWS		48±25	6±5	88	[1]
USA	FWS	0.05	8	52	0	[5]
	FWS	NP	72	32	56	[4]
Israel	FWS	NP	51	44	14	[10]
N. Zealand	FWS	NP	33	22	34	[9]
	FWS	NP	38	11	71	[9]
NO_3-N						
USA	FWS	NP	5.5	10	0	[4]
	FWS	$2x10^{-3}$	0.3	0.1	67	[5]
Tot-P						
USA	FWS	NP	53	2.2	96	[4]
	FWS	0.2	26	14	46	[5]
N. Zealand	FWS	0.8	~11	6.9	37	[9]
	FWS	0.2	~11	2.9	74	[9]
PO_4-P						
Ireland	FWS		15±7	3±2	80	[1]

Avg±SD; FWS = free-water surface constructed wetland; NP = not published
[1] Healy and O' Flynn (pers. comm.); [2] Cronk et al., 1994; [3] Karpiscak et al., 1999; [4] Schaafsma et al., 2000; [5] Newman et al., 2000; [6] Geary and Moore, 1999; [7] Mantovi et al., 2003; [8] Tanner et al., 1995(a); [9] Tanner et al., 1995 (b); [10] Ran et al., 2004.

Table 4. Average influent and effluent concentration (mg L^{-1}), loading rates (g m^{-2} d^{-1}), and removal efficiencies of wetlands treating dairy dirty water (DDW).

installed in front of the SSHF CW, the system had an OLR of approximately 4 g BOD_5 m^{-2} d^{-1} and had good organic and SS removal rates, but had limited nitrification due to large fluctuations in the inlet wastewater strength. Even under significantly reduced OLRs, SSHF and FWS CWs have under-performed. In Italy, a study on a 2 cell FWS CW operated in series and monitored over a 26 month period, treating a mixture of domestic and DDW at an average influent OLR under 2 g BOD_5 m^{-2} d^{-1}, showed that anoxic zones which developed in the wetland inlet meant that nitrification was inhibited, producing an effluent Tot-N which was mainly composed of ammonium-N (NH_4-N) (Mantovi et al., 2003).

Present agricultural practice in Ireland is governed by The European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2009 (S.I. No. 101 of 2009), which places a responsibility on the individual farmer and the public authority to adhere to the conditions set out within the Nitrates Directive (EEC, 1991(a)) and other water quality directives to ensure good wastewater management practices. On account of this, CWs are becoming popular for the treatment of DDW. Healy and O' Flynn (*pers. comm.*) evaluated the performance of seven CWs treating DDW in Ireland. They found that average removals of chemical oxygen demand (COD) from DDW were 91%. However, average effluent concentrations were 162 mg L^{-1}, which was much higher than the maximum allowable concentration (MAC). The performance of the CWs in the reduction of NH_4-N and ortho-phosphorus (PO_4-P) was also highly variable.

4. Conclusion

Much research focuses on the nutrient content of agricultural wastewaters and their inorganic fertilizer replacement potential. Many options for dairy slurry and dirty water are in place including land application, irrigation and treatment using a variety of on farm or off farm options. Nutrient, gaseous and microbial losses can result from land application of agricultural wastes. Much research focuses on matching crop requirements with organic fertilizer applications. In addition, the control of P within such wastes can prevent incidental losses to the environment e.g. chemical amendments. Once nutrients are lost, other forms of remediation such as PRB's or wetlands may be applicable to protect a waterbody.

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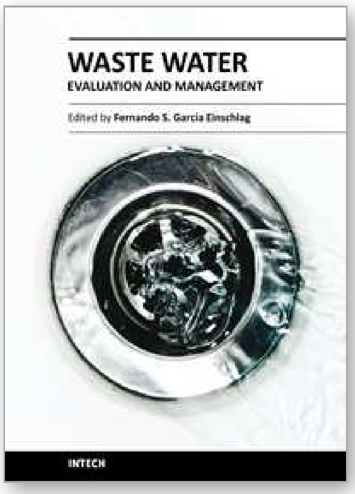

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Fresh water resources are under serious stress throughout the globe. Water supply and water quality degradation are global concerns. Many natural water bodies receive a varied range of waste water from point and/or non point sources. Hence, there is an increasing need for better tools to asses the effects of pollution sources and prevent the contamination of aquatic ecosystems. The book covers a wide spectrum of issues related to waste water monitoring, the evaluation of waste water effect on different natural environments and the management of water resources.

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