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Dairy Factory Wastewaters, Their Use on Land and Possible Environmental Impacts – A Mini Review

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Abstract: Dairy factory wastewaters are increasingly being considered a valuable resource. However, these waters may also contain contaminants, natural or artificial, that may adversely affect the land to which they are applied. This review investigates dairy wastewaters, factors affecting their composition, some probable effects on land and compounds that may be used to trace the migration of pollutants.

Dairy factory wastewaters differ depending on the types of products made by the factory and the treatment afforded wastewaters. In addition to milk and milk by-products, dairy factory wastewaters contain cleaning chemicals that contribute to the salt load, and synthetic compounds.

From the limited studies where the effects on dairy processing wastewaters on land have been measured, the consensus of the literature results acknowledges the utility to agriculture can be highly variable and depends on the land to which it was applied and wastewater characteristics including concentrations of phosphorus, nitrogen, carbon and sodium. Excessive applications of nutrients such as nitrogen and phosphorus have resulted in runoff to nearby watercourses.

Even fewer studies have investigated the use of organic marker compounds in the dairy industry. Lipids, terpenes and sterols found in the plants consumed by livestock would be useful for identifying pollutants from the dairy industry. However, a library of biological marker compounds and their likely sources is needed before such a technology could be applied more widely.

INTRODUCTION

Australia is the world's driest inhabited continent with the world's fourth highest volume of water extraction from the environment per person [1]. The current drought and global climate change is likely to decrease rainfall by 2 to 5% by the year 2030 over much of temperate Australia [2]. This will place even greater pressure on the country's already limited water resources.

The latest account of water use in Australia (2004-05) found that the agricultural industry used approximately 65% of this resource [3]. The dairy industry is Australia's third largest rural industry supplying 11% of the world dairy trade and directly employing approximately 40, 000 people [4]. Australia's 1.7 million cows produce more than 9, 200 ML of milk annually that is processed into a range of value-added products including whole milk, milk powder, butter and cheese [4]. These processing facilities are commonly located in regional areas close to their suppliers, consuming on average 386 ML of potable water *per annum* (p.a.) and producing 452 ML p.a. of wastewater [5]. The variability in water use between processing facilities would suggest that improved in-factory water use efficiency may be one way to lessen the demand on domestic supplies [5]. However, wastewaters are themselves a resource that can be used to irrigate recreational reserves and agricultural land and thereby conserve potable water. Wastewater irrigation is not without risks; soil permeability, pathogens and other potential problems need to be considered before wastewaters can be used for this purpose [6].

In this review we examine the properties of dairy factory wastewaters, their potential effects on land to which they are applied and biological marker compounds that could be used to trace any contaminants that may be discharged off-site and potentially contribute to environmental degradation.

DAIRY FACTORY WASTEWATER

Dairy factory wastewaters commonly contain milk, byproducts of processing operations, cleaning products and various additives that may be used in the factory. Bovine milk typically contains water (87%), fat (4%), protein (3.5%), lactose (4.7%) and ash (0.8%) [7]. The fat content ranges from 3 - 5% with the major component being triglycerides (98%, Fig. **1**). Other fat components include phospholipids (0.5 - 1% of fat) and sterols (0.2 - 0.5% of fat) [8]. Depending on the diet of the cows, milk can also contain traces of other organic compounds, such as terpenes, that originate from plants [9].

The composition of dairy factory wastewaters depends on the type of products manufactured and whether wastewater streams within the factory are segregated. The typical characteristics of wastewaters from various types of dairy facilities are presented in Table **1**. Condensate collected from

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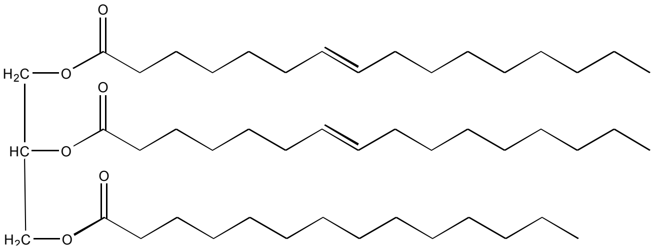

Fig. (1). An example of a triacylglycerol (triglycerides). Each of the long chains can be from any of the fatty acids occurring in milk.

the evaporation of milk or whey is one of the cleanest wastewaters although it may contain volatile organic components [10] and possibly liquid droplets of milk or whey entrained into the vapour stream from the evaporators. difficult to clean. Where wastewaters are ultimately applied to land, some factories use blends of sodium hydroxide and potassium hydroxide to minimise the concentration of sodium in the effluent. Considering that dairy factories produce a range of products and use a range of chemicals, it is not surprising that dairy processing wastewaters are highly variable in their composition.

The frequency and stages of the cleaning process depend on the product runs, but occur at least daily. A typical 'cleaning in place' (CIP) cycle begins with a water flush, followed by a sodium hydroxide wash, a water rinse, then an acid wash, followed by a second water rinse. A sanitiser may then be used. For example, Burra Foods (located in Korumburra, Victoria and producing evaporated milks, cheeses, yoghurts and specialty products) performs sodium hydroxide washes after each product run and performs acid washes at least daily as well as before runs if the plant has been idle for more than twelve hours; sanitiser is used after the plant has been shutdown for more than four days[1]. Murray Goulburn's Koroit factory (with products including milk powders, butter and milk protein concentrate) uses neutral cleaners on all cold processing surfaces, and a recent upgrade to their CIP chemical recovery system has decreased sodium hydroxide usage by 45% [12] with the result that the quantities of sodium discharged in the wastewater has been decreased.

Table 1. Characteristics of Untreated Wastewater from Dairy Plants

	pH	Biological Oxygen Demand (BOD_5, g/m^3)	Sodium Adsorption Ratio (SAR)	Nitrogen (g/m^3)	Phosphorus (g/m^3)	Electrical Conductivity (µS/cm)
[a]Whey	4.6	35000	3	1400	640	N/A
[b]Condensate	8.3	N/A	N/A	0.6	0.1	7700
[b]Cheese/evaporated milk manufacturing, clean effluent stream	N/A	12	N/A	N/A	N/A	880
[b]Cheese/evaporated milk manufacturing, dirty effluent stream	8-12	700-1700	N/A	50-70	10	2600
[c]Cheese/milk powder manufacturing, effluent	10.6	1500	N/A	0.01	35	2600
[d]Cheese manufacture effluent	6.9	2800	21	150	42	3500

[a][11]; [b]this laboratory; [c]D. Kleinert [Murray Goulburn] pers. comm., December 2008; [d]R. Knight [Murray Goulburn] pers. comm., January 2009; N/A: Not Available.

Microbial contamination and cross contamination of products is a major issue for all dairy processing facilities and cleansing chemicals commonly contaminate wastewater. Sodium hydroxide is often used for removal of fats and proteins from milk lines and other surfaces. It contributes sodium to wastewater and increases wastewater pH. Nitric, phosphoric, hydrochloric, acetic and citric acids may also be used to remove remaining deposits, especially mineral scale. These acids can decrease the wastewater pH significantly which can necessitate neutralisation of the excess acid before treatment. Nitric and phosphoric acids contribute to the nutrient load of the wastewater and, as these nutrients can be difficult to remove from the wastewater, it can lead to accelerated eutrophication when discharged to the environment. From an environmental standpoint, phosphoric acid is the least desirable acid to be used for cleaning so factories have moved away from using phosphoric acid to minimise discharge concentrations of phosphorus. Strong oxidants or bleaches such as peroxyacetic acid, sodium hypochlorite and chlorine dioxide are used for sanitising equipment and chlorine bleaches may produce toxic organochlorine compounds that contaminate the wastewater. Other chemicals that are used for specific applications include enzymes and detergents that are particularly useful for cleaning cool surfaces and have less adverse downstream consequences. In most plants caustic chemicals are generally preferred for higher temperature surfaces which are more

Various processes have been developed to minimise water use during cleaning. For example, 'burst rinsing' [12] is a technique that uses less water than regular rinsing, and is suitable to pre-clean tanks and tankers. The rinse water is pulsed in bursts rather than as a continuous stream. Burst rinsing has been introduced at Peters and Brownes (now Fonterra) in Balcatta, Perth where they produce flavoured milk and ice cream. The burst rinsing technique takes longer to achieve the same level of cleanliness as conventional rinsing, but water consumption has been decreased by 15 ML p.a.

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[1] K. Wild [Burra Foods] pers. comm., Sept. 2008.

Water recycling is an alternative strategy for achieving water savings. Cleaning in place systems normally drain rinse waters and spent solutions to waste unless the systems have been designed to reuse or recover these streams. Chemical solutions can be reused and topped up with fresh chemicals until no longer effective, but a full recovery system typically uses membrane technology to recover cleaning chemicals and water [12]. The result is a decrease in water and chemicals used and discharged into the effluent.

Condensate from the milk evaporation process is a relatively clean wastewater stream and has been reused for decades [13]. The recycled water is not suitable for all uses without further treatment but it is typically used for boiler feed water and membrane plant washing. Murray Goulburn Koroit pumps its excess condensate to local farms for irrigation [12], while Burra Foods sends excess clean wastewater to a local recreation ground for irrigation thereby reducing demand for potable water.

Other water streams that are relatively clean that can be recycled include defrost water, boiler blowdown, flushing water and pump sealing water [12]. Further purification of water streams may be achieved in different ways, but reverse osmosis allows Burra Foods to reuse water (from milk washings) throughout the factory for processes such as cleaning flushes during the CIP cycles.

Finally, effluent treatment creates sludge, and the sludge may be used as animal feed or for compost [12]. Murray Goulburn Kiewa compost the sludge from their dissolved air floatation (DAF) process and it is then distributed to regional end users by a contractor [13].

Where possible, waste streams can be treated to recover high-value products or bulk components to increase profits or offset disposal costs. Where this occurs the concentration of these products will often be low in the effluent stream. Whey, previously considered a waste product, is now sold in various forms and components such as protein concentrates and lactose, as well as some speciality ingredients including lactoperoxidase (an anti-microbial enzyme) and lactoferrin (anti-microbial protein) [12]. Murray Goulburn market a mineral product that is extracted from cheese whey [13].

DAIRY FACTORY WASTEWATER TREATMENT

Wastewater treatments used by dairy factories include various arrangements of standard technologies for treating wastewater. Fats and other solid materials are often removed using DAF or induced air floatation, and skimming. In the DAF process compressed air is fed into a portion of the clarified effluent and the effluent is returned to the float tank where the air comes out of solution as tiny bubbles. The bubbles attach to fat and other suspended materials and they float to the top to be removed by skimming. Induced air floatation is similar but the air is introduced by an eductor or impeller and results in larger bubbles which are less efficient in bringing fat and suspended particles to the surface.

Following fat removal, dairy wastewaters are commonly treated biologically to lessen the load of organics compounds that are usually measured as the biochemical oxygen demand (BOD). During anoxic periods organic nitrogen is converted to ammonia (ammonification) while under oxic conditions ammonia is converted to nitrate (nitrification). Nitrate can be subsequently denitrified (through intermediates of NO_2, NO, and N_2O) to gaseous nitrogen under anoxic conditions. Nitrogen is also removed from the effluent in microbial biomass which is most prevalent at high carbon to nitrogen ratios (C:N > 15 - 20). At lower C:N ratios (C:N < 10) nitrification/denitrification predominates [14]. Phosphorus is also removed in microbial biomass especially by polyphosphate-accumulating organisms which are able take up significantly more phosphorus than is required by the organism [15]. The sludge produced in the biological reactors is therefore enriched with phosphorus.

There are many biological treatment systems. A system in common use is the Sequencing Batch Reactor (SBR) where a single tank that operates in batch mode runs a sequence of operations. Stages of the sequence can include periods with or without aeration to control the type of biological processes (anaerobic and aerobic) occurring in the reactor. In these systems supernatant water is decanted for disposal or potentially reused, while some of the remaining biomass is reused for the next batch of wastewater to be treated [16].

Burra Foods uses two SBR's and another digester that processes excess sludge. Only twice a year does the treated sludge need to be removed for disposal[2] [13]. Murray Goulburn Leongatha employs a similar system where DAF is used to remove protein and fats followed by anaerobic digestion in a Bulk Volume Fermenter (BVF). Aerobic digestion follows in two SBR's and sludge from the SBR is returned to the BVF. About twice a year sludge is removed from the BVF for disposal to farms as a fertiliser [13]. Fonterra Darnum uses an alternative system. Their system begins with a fat skimmer followed by two aerated lagoons with final disposal by irrigation.

The typical composition of dairy factory effluent after treatment is presented in Table **2**. The cheese/evaporated milk factory wastewater was treated by SBR, the cheese factory wastewater was treated with a low-rate anaerobic digester, while the cheese/milk powder factory used an aerated lagoon system.

Table 2. Typical Composition of Treated Dairy Factory Effluent

	pH	BOD (g/m^3)	N (g/m^3)	P (g/m^3)	EC (µS/cm)
cheese/milk powder[a]	8.7	13 - 75	0.004	16	3500
cheese/evaporated milk[b]	8.8	N/A	10	3	1800
cheese[c]	7.1	110	120	50	3500

[a]D. Kleinert [Murray Goulburn] pers. comm., Dec. 2008; [b]K. Wild [Burra Foods] pers. comm., Oct. 2008; [c]R. Knight [Murray Goulburn] pers. comm., Jan. 2009.

Wastewater from Australian dairy factories is commonly disposed of by irrigation (58%) or directly to the sewer (37%). Only 2% is sent to ocean outfall, leaving 3% disposed by other methods [17]. For example, Murray Goulburn factories discharge 2, 700 ML p.a. to local dairy

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[2] K. Wild [Burra Foods] pers. comm., Oct. 2008.

farms in Victoria for irrigation [13]. Burra Foods sends clean wastewater for irrigation of a local football field (4 ML p.a.) when they have surplus to their factory's needs.

EFFECTS OF DAIRY WASTES ON SOIL

The application of dairy wastes to land has been an accepted disposal method for many years but there are few studies investigating the long-term effects of dairy effluent irrigation on soils.

The effect of casein wastewater applied to pasture for 15 years was studied by McAuliffe *et al*. in New Zealand [18]. The studies found marked increases in inorganic and organic forms of nitrogen and phosphorus in the soil, soil bulk density had decreased, and the soil had higher rates of respiration and more earthworms. Irrigation occurred, on average, eight hours per day once every 17 to 18 days. The irrigation is estimated to have provided 100 times more total nitrogen and phosphorus than would be applied when using normal fertiliser application for the maintenance of pasture. Therefore nitrogen and phosphorus either accumulated in the soil or was lost to groundwater (soil infiltration rate was measured to be approximately 3, 000 mm/day). Nitrate was found to be low in the topsoil water but increased with depth to a maximum of 20 mg/L just above the water table. The concentration of dissolved inorganic phosphorus in soil water increased from 10 - 20 mg/L in the control to 220 - 660 mg/L in the top 300 mm of soil, with the higher figures found in the upper 100 mm. This represents a significant accumulation of nutrients and it would therefore be beneficial to irrigate over a much larger area of land. Soil pH was found to increase less than one pH unit after effluent application, even though the effluent was acidic with a pH of about 4.5. The reason for the increase in pH was probably due to calcium and ammonium ions being liberated from the decomposing whey. The disposal of effluent had a beneficial effect on the farms as milk production increased with up to twice the amount of butter fat produced per cow per day than did the control farms. The effluent farms suffered pugging and pasture-pulling problems, both of which were expected to be improved by providing better drainage. However, improved drainage will also increase nutrient exports from the site. The authors concluded that a multitude of factors must be taken into account when considering the use of effluent; while the benefits to the land were immediately obvious with increased production, these very factors and the peak season they occur in resulted in both increased concentrations of effluent solids while spraying liquids onto a surface with a high water table.

Sparling *et al*. [19] reported on two sites used for the treatment of dairy factory effluent in the Waikato region of New Zealand to determine changes in key soil properties. One site, Hautapu, had received effluent (from a factory producing cheese and casein) for 22 years while the other, Lichfield, had received effluent (from a factory producing cheeses) for two years. The Hautapu irrigation site consisted of silt loam soils (Te Kowhai silt loam and Horotiu silt loam) that were irrigated with up to 25 mm per day of effluent for up to three consecutive days, and repeated with at least a 14 day gap between irrigation cycles. The Lichfield site consisted of Taupo shallow fine sandy loam soil that was irrigated with a maximum of 50 mm during an irrigation cycle, with no more than 25 mm per day; time between irrigations was typically at least 20 days. Nitrification potential, respiration and unsaturated hydraulic conductivity were greatly increased on the Hautapu soil whereas the Lichfield site had few changes compared to an equivalent non-irrigated site. However, overall the only significant differences were in irrigated *vs* non-irrigated soils, the trends in most parameters measured being the same despite differences in soil and time irrigated. This improvement in the irrigated soils was postulated as being the result of two possible reasons. It was noted that the microbial biomass (i.e. worms) had increased in comparison to the non-irrigated soils and that this has been seen previously to increase both infiltration and fine pores. Another reason for the improvement in the pastures is that while effluent is well known to increase pH with application and so decrease plant productivity, the concentration of nutrients from the effluent compensated for this. Finally the authors attribute the lack of detectable differences in nitrogen loading or respiration by the current management practices at the Taupo property to minimise such issues as nitrate leaching.

Cameron *et al*. [20] studied the fate of nitrogen in pasture irrigated with untreated dairy factory effluent. The study was conducted on Templeton fine sandy loam (Typic Haplustept) from the Lincoln University dairy farm in Canterbury, New Zealand, using large 500 mm diameter lysimeters, as well as field plots. The effluent was applied at two rates (300 and 600 kg of N per ha per year) both with and without urine. The tests without urine represented pasture usage for silage and hay, whereas the added urine represented grazing pasture. Controls were also set up and irrigated with an equivalent volume of water instead of effluent. The urine was applied at a rate of 1, 000 kg of N per ha in the autumn (to represent the worst case scenario for leaching).

The average annual pasture production (dry weight) for the low rate application without urine increased by 63% (to 13,752 kg per ha) over the control (equivalent applied water), which can be attributed to the nutrients contained in the dairy factory effluent. With added urine the production increased further to 236% (to 19,977 kg per ha) of the control which suggests that nitrogen availability was a limiting factor when irrigating with dairy factory effluent alone. In the case of the higher rate application without urine, pasture production only increased by 8% (to 12, 913 kg per ha) over the control. This presumably occurred as a result of water logging (and the associated anoxic soil conditions) as effluent ponded on the soil surface with the pasture occasionally becoming yellow and wilted. When urine was also applied the plant yellowing was eliminated, suggesting that the extra nitrogen assisted, and pasture production improved to 203% (to 24, 217 kg per ha) of the control.

The annual average nitrogen uptake by the pasture followed a similar pattern to the pasture production. The low rate application achieved a nitrogen uptake that was 203% (304 kg N per ha per yr) of the control, and with added urine it was 326% (489 kg N per ha per yr) of the control. For the high rate application rate the corresponding figures were 108% (285 kg N per ha per yr), and 245% (644 kg N per ha per yr) respectively. Losses due to denitrification (N_2 & N_2O) may have important environmental impacts as N_2O is an important contributor to the greenhouse effect. In this study, losses by denitrification were about 5 - 20% of nitrogen applied, while the loss of N_2O represented 0.4 - 6.6% of the applied nitrogen.

Nitrate leaching ranged from 5.5 to 25.2 kg N per ha per yr for the low application rate and 4.6 - 7.4 kg N per ha per yr for the high application rate. When urine was present, the leaching losses were much higher being 65 - 123 kg N per ha per yr and 48 - 76 kg N per ha per yr for low and high rate treatments respectively. In summary the research presented suggests that the use of high soluble carbon such as lactose it is possible to immobilise nitrogen in the soil rather than to lose it to leaching. It was with caution that the authors suggested that further long term studies need to be performed to see further effects of the use of untreated effluent.

Untreated dairy factory wastewater is nutrient-rich and can provide beneficial nitrogen and phosphorus for pastures under irrigation. However, adverse changes to soil structural properties (such as porosity) and infiltration rate, downstream contamination of streams and groundwater, and depressed plant growth can all result from wastewater irrigation. In considering irrigation, wastewater sodium, calcium, magnesium, phosphorus, nitrogen, carbon and the area of land under irrigation are all worthy of consideration [21]. In poorly managed systems excess nutrients, especially nitrate, may leach through the soil profile and contaminate groundwater. Both nitrogen and phosphorus may be exported off site in surface runoff and accelerate eutrophication of receiving streams or lakes. Treated wastewater, on the other hand, contains fewer nutrients resulting in a lower risk of ground and surface water contamination, but still has a risk associated with the relatively high content of sodium, even after treatment of wastewater.

WASTEWATER CHARACTERISTICS

Sodium

Sodium in irrigation water can affect the structure of the soil to which it is applied. High concentrations of sodium compared to calcium and magnesium in irrigation water can induce clays to swell and disperse, lowering soil infiltration rates and hydraulic conductivity. These changes affect gas permeability which in turn can decrease the viability of the soil for pasture and crop production. A compounding problem is that soil with increased sodium concentrations can appear to be in good condition but may subsequently degrade when lower conductivity water is applied, either from irrigation or from rainwater [22].

An important characteristic of soil is the exchangeable sodium percentage (ESP) which is defined as the percentage of the soil's cation exchange sites that are occupied by sodium. If the ESP of a particular soil increases due to irrigation there is an increased risk of degrading the soil texture [23]. The sodium adsorption ratio (SAR; Equation 1) of irrigation water is used to estimate this effect [24]. As the concentration of sodium increases relative to calcium and magnesium, the SAR also increases and hence the water becomes more likely to degrade soil structure. It should be noted that the effect of evapotranspiration is to increase the SAR in the soil. The definition of the SAR is described in the equation below where cation concentrations are in meq/L.

$$SAR = [Na^+]/[Ca^{2+} + Mg^{2+}]^{0.5} \tag{1}$$

The SAR value can be higher than calculated if the activity of calcium and magnesium is decreased by chelation with organics or precipitated from solution by reaction with carbonates in the soil [25].

An example of sodium accumulation following wastewater application was conducted at a tree plantation site at Forest Hill, Australia, that had been irrigated for five seasons with treated sewage [23]. The soil was a mix of Red Chromosols and Red Kandosols [26] with a sandy or loamy surface horizon overlaying a light to medium clay subsoil horizon. The ESP increased from <2% throughout the soil profile to >25% at some depths and was larger than predicted from the SAR of the irrigation water alone (SAR average of 5.0). The authors concluded that the sodicity of the soil would increase in time at greater depths due to irrigation; however, this was not likely to affect the plantation's current use. Also, the sodicity may affect future uses of the land, especially if utilised for agriculture and cultivation where mechanical disturbance of the soil will disperse the clay soil and reduce permeability of the sodic soils.

Nitrogen and Carbon

Carbon can play a valuable role in improving the soil structure and microbial activity of the soil while nitrogen is one of the three main nutrients required by plants. Most of the nitrogen held in soil is contained in the organic matter, and the nitrogen content in effluent serves as a valuable nutrient source for soils and decreases the need for added nitrogen fertiliser. Some nitrogen will be available for use directly by plants, but organic nitrogen must be mineralised by microbes to inorganic ammonium (ammonification) or nitrate (nitrification) before plants can use it. Excess nitrogen in the effluent that is above the needs of the plants may be exported *via* surface runoff or leaching.

Nitrogen leaching is enhanced when nitrification occurring in the soil creates nitrate, a nitrogen form which is highly soluble in water and does not bind to clays or organic matter [27]. Losses are influenced by soil characteristics, cropping practices (e.g. tillage, rotation), and fertiliser practice. Stocking rates of grazing animals also influence nitrogen losses [20]. Losses of nitrogen to the atmosphere occur through ammonia volatilisation, and through denitrification from nitrate [28]. Factors that increase nitrification/denitrification rates include high moisture level, high temperature, limited oxygen availability and a source of soluble carbon for the microbes [29].

The availability of nitrogen to plants depends on a number of factors. The carbon to nitrogen (C:N) ratio is an important characteristic of dairy factory effluent when used for irrigation. Increased concentrations of easily degradable carbon cause an increase in microbial activity. With the increased microbial activity comes increased competition between plants to consume nitrogen and therefore the amount of nitrogen available to plants will decrease. This effect has been observed as a suppression of plant growth after application of untreated dairy wastes to pasture [30]. Typically material with a C:N ratio of 20 to 30:1 [28] produces a balance of mineralisation and immobilisation that promotes rather than suppresses plant growth. In the project by Ghani *et al*. [30] the mineralisation and immobilisation of nutrients were studied using untreated dairy factory effluent onto a sandy loam soil in the Edgecumbe region of New Zealand. Laboratory leaching column tests were performed at various temperatures and application rates of effluent with the effluent applied fortnightly. It was found that the effluent, with its high soluble carbon content, produced an increase in microbial activity that caused immobilisation of nitrogen. Consequently, in the short-term, fewer nutrients would be available to plants due to competition with microbes. This may help explain the poor performance of dairy factory effluent irrigated pastures [30]. Higher temperatures favoured increased conversion of effluent by microbial biomass.

The presence of organics can also lead to odour problems and needs to be considered when applying dairy waste to agricultural land. Typically, there should be a sufficient buffer zone to mitigate any smell reaching populated areas. Runoff must be minimised, as high levels of organics can support microbial growth and result in a decrease in stream quality due to depletion of dissolved oxygen which can contribute to accelerated eutrophication.

Phosphorus

Phosphorus is "one of the scarcest nutrients in terms of its demand" [31] and very small quantities can have a severe impact on receiving waters where it causes accelerated eutrophication. It is therefore important to consider phosphorus concentration in water runoff (including rain) from land irrigated with dairy factory effluent. In a properly designed and sized system the dairy factory effluent would provide a means of beneficially using the phosphorus without causing adverse environmental effects, and as such, decrease or eliminate the need for added phosphorus fertiliser. Phosphorus can be lost from irrigation areas due to erosion as well as leaching of particles through soil pores [31]. In addition, dissolved phosphorus can be exported from wastewater application sites primarily in overland flow, and also *via* interflow, macropore flow and to a lesser extent matrix flow [25], particularly during high run off events [32]. Because phosphorus takes time to diffuse into the soil and become fixed, the application of wastewater may need to be withheld if rainfall is likely, so as to minimise the load of phosphorus exported. Phosphorus is also exported from farms in the form of sold livestock and crops.

The pH of the soil affects the availability of phosphorus as a result of the competing phosphorus-fixing reactions with iron, aluminium and calcium. In alkaline soils phosphorus is fixed by calcium, whereas in acidic soils fixation is due to the formation of aluminium and iron phosphates. The result is that phosphorus has its highest availability when the pH is neutral. Certain soils, such as Ferrosols, have higher contents of free iron oxide and aluminium and therefore fix more phosphorus.

BIOLOGICAL MARKER COMPOUNDS AND THE RE-USE OF DAIRY FACTORY WASTEWATERS

Biological marker compounds (biomarkers) can indicate the fate of dairy factory wastewaters and their constituents, both within plants and where wastewaters are discharged to another receiving environment. The use of biomarkers is common in geochemistry and marine science [33-35], but relatively little work has been done to authenticate a food product's origin or identify the source of pollutants in agricultural runoff [36, 37].

Extremely sensitive analytical techniques can be used for detecting biomarkers. For example, gas chromatography coupled with mass spectroscopy (GC-MS) is commonly used with detection limits in the order of nanograms (ng = 10^{-9}g) to femtograms (fg = 10^{-15}g). When investigating polar and high molecular weight compounds, liquid chromatography coupled with mass spectroscopy (LC-MS) can be used. Both of these techniques can suggest molecular structures and resolve structural isomers. However, Compound Specific Isotope Analysis (CSIA) [38] distinguishes between marker compounds, and therefore marker sources, on the basis of the isotopic composition of carbon, nitrogen or hydrogen atoms contained in the molecule. For example, a compound of interest may be enriched with a particular isotope due to differing reaction rates for the different isotopes of an element when the compound was being formed, often in a biological context (e.g. degradation of aromatic compounds). This enrichment with a particular isotope can then be useful as a "signature" for a particular reaction or marker source.

Possible biomarkers in dairy wastewater are likely to vary depending on the forage species that cattle supplying the milk are consuming, the microbial transformations of forage in the rumen (and this is likely to vary seasonally and possibly even diurnally), industrial chemicals entering the waste stream, the waste treatment processing and the microbes present in that system. In the context of a land application system, marker compounds may also be affected by any chemical or biological processes occurring in the soil after irrigation.

When applied to the land, water constituents (including marker compounds) are subject to processes such as sorption, degradation and leaching that are in turn are affected by nutrient concentrations, soil temperature, soil pH, microbial biomass and the concentrations of enzymes, colloids and cations. Sorption refers to the binding of compounds to solid materials *via* electrostatic attraction (i.e. adsorption or ion exchange). Degradation can occur physically (e.g. *via* ultra-violet light), or through microbial decomposition. Organic matter in wastewater can stimulate the microbial activity in the soil, increasing biodegradation of organic compounds. Leaching or vertical matrix flow, on the other hand, is one of a number of physical processes that can transport water-borne wastewater constituents from the site where they were applied [39]. In addition, some forms of organic matter in wastewaters may chelate with ionic contaminants or block adsorption sites and thereby facilitate the transport of otherwise relatively harmless moieties offsite [25].

Useful marker compounds for dairy factory wastewaters could well include unsaturated lipid compounds and biopolymers that are common to all biota [40] but have structural attributes that help indicate their origin. For example, the strong odd or even numbered carbon composition that occurs in lipids present in epicuticular waxes of higher plants (as a result of acetate as a building block) is a useful attribute. Compounds, such as n-alkanes, n-alkanols, and n-alkanoic acids (Fig. **2**), are representative of plant origin when they have strong even or odd numbered carbon composition. Similarly, the distribution of the homologous series, usually characterised with the carbon number of the most dominant component (C_{max}), can be useful in attributing biomarkers to source materials [41].

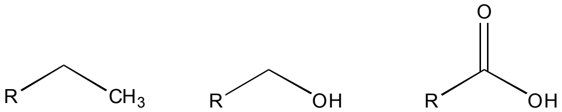

Fig. (2). Functional groups representative of biomarkers of plant origin include n-alkanes, n-alkanols and n-alkanoic acids (R = alkyl chain, saturated or unsaturated).

For dairy factory wastewaters, another group of potential biomarkers are terpenes, a diverse range of compounds synthesised by plants which can, depending on the cow's diet, be present in milk in low concentrations. The basic terpene building block is isoprene (Fig. **3**). The terpenes are classified according to the number of isoprene elements in the molecule: mono-terpene has two isoprene units, sesqui- has three, di- has four, sester- has five and tri- has six. When the terpenes are chemically modified with functional groups such as alcohols and ketones they are referred to as terpenoids. Steroids (Fig. **4**) and hopanoids (Fig. **5**) are derivatives of triterpenoids. De Noni & Battelli [9] investigated the effect of fodder consumed by cattle on the content of terpenes and fatty acids in the resultant milk and cheese manufactured from that same milk. The terpenes and fatty acids present in the fodder were found to influence the milk and cheese composition. Analysis of the monoterpene profiles of pastures using radar plots revealed some resemblance to those of milk samples, but the sesquiterpenes, although present in the pasture, were negligible in the milk. The monoterpene content of the cheese was essentially unchanged from that of the milk used.

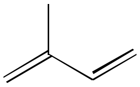

Fig. (3). Isoprene, the basic building block of terpenes.

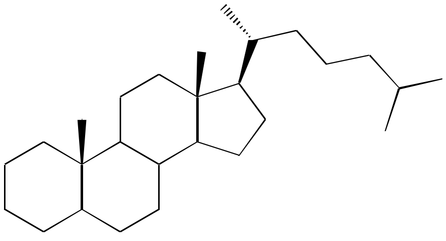

Fig. (4). The skeletal backbone of a steroid.

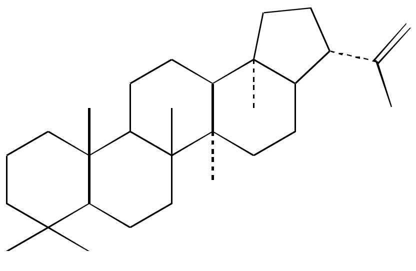

Fig. (5). The skeletal backbone of a hopanoid.

Sterols are another group of marker compounds that have been applied, also in an agricultural context, to track faecal pollution although there are no studies where they have been used in association with dairy factory wastewaters (Fig. **6**) [36, 42, 43]. Coprostanol, in particular, has been proposed as an alternative to *Escherichia coli* as a measure of faecal pollution [43] and calculating the ratios of certain faecal sterols has been shown to provide a better attribution of contamination sources (Fig. **7**) [42].

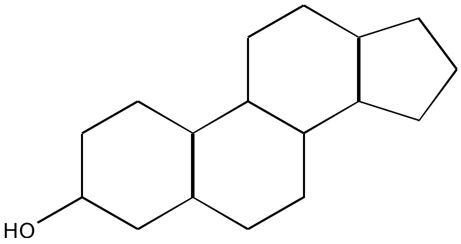

Fig. (6). The skeletal backbone of sterols.

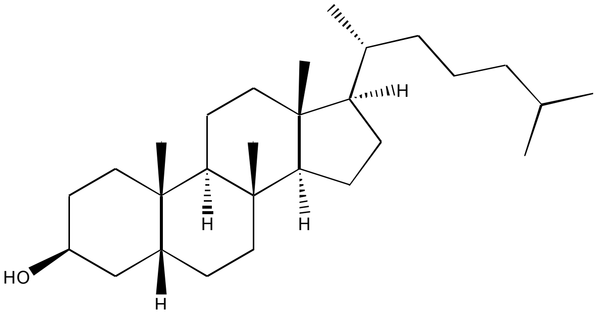

Fig. (7). A possible biomarker of faecal pollution, coprostanol.

A combination of isotopic and molecular biomarkers have been used in the dairy industry for purposes such as identifying the geographical origin of milk and the effect of food source on milk composition [44, 45]. The study by Engel *et al.* [44] found that the ratio of fatty acids in bovine milk had the strongest discriminative potential as biomarkers for distinguishing between upland and lowland sources of milk.

CONCLUSION

Potable water is a precious resource. The composition of dairy factory wastewaters depend on the products being manufactured, cleaning processes and the recycling protocols deployed in the plant, as well as the wastewater treatment methods and the diet of the cows. These all affect the concentrations of nutrients, inorganic salts, organics, and BOD in the various wastewater streams. Increased recycling of these wastewaters is in everybody's interests.

In addition to in-plant recycling, dairy factory wastewaters can be used to irrigate pasture or public grounds, thereby conserving potable water and reusing the nutrients they contain. However, there are potential risks. Irrigation needs to be carefully managed to prevent salinisation or nutrient export in leachate and surface runoff so that the production of the land remains viable, even after cessation of irrigation. Biological marker compounds are one possible technology that can assist in that regard.

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ABBREVIATIONS

BOD = Biochemical Oxygen Demand
BVF = Bulk Volume Fermenter
CIP = Cleaning In Place
DAF = Dissolved Air Flotation
ESP = Exchangeable Sodium Percentage
SAR = Sodium Adsorption Ratio
SBR = Sequencing Batch Reactor
N_2O = Nitrous Oxide

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