Analysis of trace organic compounds from a dairy factory milk processing plant "wastewater" used to irrigate soils

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Abstract
Clean wastewater streams from a milk processing dairy factory are reused for irrigation of a nearby recreation oval in South-Eastern Australia. The wastewaters and drainage from both irrigation and rainfall events were analysed for general wastewater constituents and trace level, semi-volatile organic compounds. Samples were pre-concentrated using SPE cartridges, derivatised and analysed using GC-MS. Initially, phenol and nitrogen containing compounds that may adversely affect receiving waters were investigated. These compounds could originate from the wastewaters, irrigation infrastructure or the soil itself. The results tentatively suggest that there are few compounds in either the wastewaters or drainage that are of concern for receiving waters. Importantly there appear to be a range of compounds that originate from the soil.

Key Words
Gas chromatography-mass spectrometry, recycling, nutrients, phenols.

Introduction
Potable water is an essential and major input into processing our food supplies and the continued growth in food manufacturing is placing increased pressure on this limited resource (Watterson *et al.* 2007). Recycling and reuse of factory wastewater can lessen potable water use but requires a detailed understanding of wastewater properties (Verheyen *et al.* 2009). Burra Foods Pty. Ltd. (38º 25' 37" S, 145º 49' 16" E; Figure 1) produces customized fresh and frozen dairy ingredients for the food manufacturing sector with over 60% going to export markets. Using milk from farms in the Gippsland region of South-Eastern Australia, the factory at Korumburra processes greater than 10,000 kilotonnes of milk solids annually. Over the last three years, Burra Foods has reduced potable water use from 28 kL per tonne of milk solids to 13 kL per tonne of milk solids, a water saving of over 150 ML a year. These savings have been achieved in part by the separation of evaporator condensate and other clean water streams from the milk waste stream. This has provided opportunities to substitute potable water with wastewater both within the factory and for irrigation applications in the wider community. Burra Foods wastewater has been used to irrigate a nearby recreation oval. An irrigation system comprising a pipeline from the factory, holding tank (90 kL), pumps and a water cannon, was built for this purpose. While through the Environment Improvement Plan major contaminants such as nitrogen and phosphorus are managed, trace organic compounds (e.g. endocrine disruptors) in drainage are a potential threat to receiving waters. These organics may originate from the wastewater itself, transformations occurring during wastewater storage and irrigation, or the soil-plant system to which the wastewaters are applied. This research investigates trace, semi-volatile compounds in the wastewaters applied to and draining from the Korumburra Recreation Reserve. The study focussed on compounds with phenolic and heterocyclic nitrogen functional groups which due to their toxicity and persistence pose a major threat to the environment.

Methods
Location and water sampling
The origins of the wastewaters used in this study and their relationships to the processing that occurs at Burra Foods Pty. Ltd. are illustrated in Figure 2. Factory wastewaters included "condensate" from the dryers and a combined "clean" water stream which was largely condensate.

Wastewater and drainage were collected after rainfall on November 23, 2008 and a single irrigation event on January 14, 2009 (Table 1). For the irrigation sampling an initial sample of water from the Burra Foods pipeline was collected from the sprinkler used to irrigate the oval (5.35 pm). As normal irrigation in summer results in no drainage, the sprinkler system was then fixed in place (Spray Angle: 110°; Radius of spray: 29 m) and operated at 315 L/min for 175 minutes. Collection of the initial runoff into the drains occurred at 7.16 pm and collection of 20 L samples occurred at approximately 30 minute intervals until flow from the subsurface drains ceased (9.22 pm). All samples were collected from inside the polyethylene collector drains away from the sumps to ensure the samples reflected the water passing through the soil. A final sample of water was taken after the sprinkler had been turned off (approximately 16 minutes after the previous sample). Water samples (20 L) were kept at <4 ºC until analysed. All materials (e.g. hosing and valves) in contact with the samples were pre-rinsed with 1% Extran MA03, 10% HCl and deionised water prior to use.

Physicochemical analysis
Water samples were analysed for Total Solids (TS), Electrical Conductivity (EC), Dissolved Reactive Phosphorus (DRP), Total Dissolved Phosphorus (TDP), Total Phosphorus (TP), Total Dissolved Nitrogen (TDN), Nitrate/Nitrite (NO_2/NO_3) and Ammonia (NH_3) using standard methods (Eaton *et al.* 2005).

Gas Chromatography-Mass Spectrometry (GC-MS) workup
Extractions were completed within one week of sample collection. The waters were pre-filtered and passed *via* a siphon arrangement onto pre-conditioned Solid Phase Extraction (SPE) cartridges. No more than 5 L was processed on any individual cartridge. Acid-base extraction techniques were used to collect the compounds for analysis (Munch 2000).

GC-MS analysis
The GC-MS column oven was programmed to hold at 75 ºC for 2 min, increased to 320 ºC at 8 ºC/min and held for a further 14 min. The transfer line to the mass spectrometer was heated to 170 ºC and the trap was operated at 150 ºC. In MS mode, the scan range was 35 – 450 amu with 0.61 sec/scan. Tentative identities were assigned to compounds based on their retention time and mass spectral data. Mass spectra were compared to the NIST/EPA/NIH 2005 library with all computer spectral matches checked manually. Peak structural assignments were further validated by comparing their retention time and mass spectra with methylated and methylsilylated samples.

Results and Discussion
For the irrigation sampling, phosphorus from the wastewaters measured at the sprinkler (DRP, 4.0 mg/L; TDP, 4.0 mg/L; TP, 4.1 mg/L) was lower than measured at the drains (Mean DRP, 2.8 mg/L; TDP, 2.9 mg/L; TP, 3.0 mg/L, Table 1) indicating adsorption of phosphorus by the soil. These concentrations are not dissimilar to those measured in runoff from dairy pastures in the Korumburra region (Nash *et al.* 2000). Nitrogen levels in the recreation oval soil appeared to be low. Nitrogen concentrations were similar in irrigation water (TDN, 38 mg/L; TN, 39 mg/L) and drainage (mean TDN, 38 mg/L; mean TN, 39 mg/L). Nitrate and Ammonium concentrations were much lower than TDN suggesting most of the nitrogen in these waters was in an organic form.

On passage through the soil, EC increased by 11-25% (mean EC in drainage, 679 µS/cm; mean EC in irrigation water, 564 µS/cm). Typically, irrigation at this site does not produce runoff so some accumulation of salts in the soil would be expected over the dry summer months. Interestingly, TS was higher in the irrigation water than in the water supplied by the factory (irrigation water TS, 323 mg/L vs. factory water TS, 284 mg/L) indicating some accumulation of solids in the irrigation infrastructure (Verheyen *et al.* 2009). The concentrations of all analytes were higher where the drainage was derived from irrigation, rather than rainfall. For instance, drainage from irrigation had a higher EC than that from rainfall (rainfall drainage EC, 45 µS/cm; irrigation drainage EC 679 µS/cm). Clearly a large component of the EC in irrigation drainage can be attributed to salts added with the irrigation water.

No phenols or nitrogen containing compounds as listed as Priority Pollutants by the USEPA were found (USEPA 2007) and those compounds that were found were generally benign. Classes of compounds found included fatty acid methyl esters, sugars (e.g. 2,5-methylene-d,l-rhamnitol), herbicides (e.g. dicamba), purines (e.g. 1,7-dihydro-1-methyl-6H-purine-6-thione), and other natural products (e.g. vanillin). The synthetic endocrine disruptor bisphenol A was found but its presence is most likely due to its ubiquitous presence in the environment with previous studies of the wastewaters from the factory finding no detectable levels of this compound in the “clean” wastewater stream used for irrigation.

Table 1. Physicochemical results of wastewaters used for irrigation along with results from the drainage after rainfall.

Sample Type	Time	DRP (mg/L)	TDP (mg/L)	TP (mg/L)	TDN (mg/L)	TN (mg/L)	TS (mg/L)	EC (□S/cm)	NH3 (mg N/L)	NO3 (mg N/L)
Sprinkler System	5:35 pm	4.0	4.0	4.1	38.5	39.1	323	564	0.2	3.5
Drain	7:16 pm	2.4	2.5	2.5	39.0	39.2	554	747	0.1	6.9
Drain	7:50 pm	2.9	2.8	2.9	40.8	41.3	506	698	0.1	6.9
Drain	7:19 pm	2.9	2.9	3.0	37.3	38.7	427	670	0.1	6.8
Drain	8:49 pm	2.9	3.3	3.3	39.2	40.6	458	639	0.1	6.8
Drain	9:05 pm	2.7	3.0	3.1	36.1	38.4	457	642	0.2	9.8
22-23/11/08 rainfall (Drain)	overnight	0.1	0.1	0.1	0.4	0.4	11	45	0.1	8.3

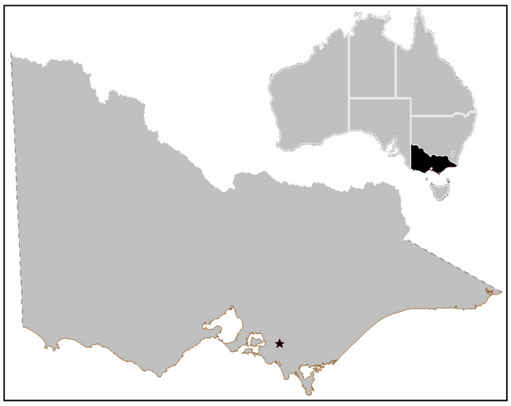

Figure 1. Location of the Burra Foods milk processing factory in Korumburra (38º 25' 37" S, 145º 49' 16" E), Victoria, Australia.

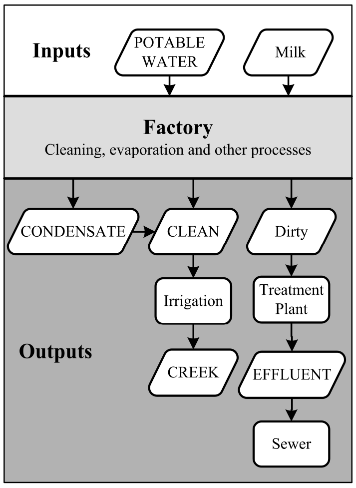

Figure 2. Schematic of water flows at Burra Foods Pty. Ltd. milk processing factory. Sampling points was taken from the Irrigation Output, both before irrigation onto the recreation oval and after irrigation but before entry into the creek.

Conclusion

Physiochemical and GC-MS analyses on wastewaters used for irrigation of soils in Korumburra suggest that they to pose little risk to the environment. Similarly, it would appear that the nutrients in drainage from the Korumburra recreation reserve poses no greater risk to the environment than might be expected to have occurred had the drainage been from grazed pastures. Trace organic compounds found after passage through the soil are either ubiquitous or benign to both the environment and human health.

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