Evaluation of Organic Matter Concentration in Winery Wastewater: A case study from Australia

Wendy C. Quayle*, Alison Fattore, Roy Zandona, Evan W. Christen, Michele Arienzo

CSIRO Land and Water, Griffith Laboratory, Research, Station Road, Griffith,

NSW 2680, Australia.

E-mail: Wendy.Quayle@csiro.au
Alison.Fattore@csiro.au
Roy.zandona@csiro.au
Evan.Christen@csiro.au
Michele.Arienzo@csiro.au

ABSTRACT

The 5-day biological oxygen demand (BOD_5) remains a key indicator for proof of compliance with environmental regulators in the monitoring and management of winery effluent. Inter-conversion factors from alternative tests that are more rapid, accurate and simpler to perform have been determined that allow prediction of BOD_5 in winery wastewaters, generally, and at different stages of production and treatment. Rule of thumb inter-conversion factors are: BOD_5 = 0.65 Chemical Oxygen Demand (COD), BOD_5 = 2.9 Total Organic Carbon (TOC) and BOD_5 = 3.0 Dissolved Organic Carbon (DOC). Out of the relationships between BOD_5 *vs* COD, TOC and DOC, in winery wastewater, irrespective of vintage or non-vintage production periods and stage of treatment, TOC offered the most reliable prediction of BOD_5. Ethanol, glucose and fructose were evaluated in untreated wastewater as predictors of BOD_5 due to their high specificity in winery effluent. A significant relationship was determined between BOD_5 and (ethanol+glucose+fructose; R^2 = 0.64, $n=19$; $p<0.05$), but relationships between BOD_5 and ethanol and BOD_5 *vs* (glucose+fructose) were weak (R^2 = 0.45 and 0.34; n = 19; $p<0.05$ respectively,). There was a very strong linear correlation (y=0.9767x+52.8; $R^2 = 0.97$; $n=23$; $p<0.05$) in COD data in winery effluents when using a commercially available mercury free test kit compared with using a traditional COD test kit that contained mercury. This suggests that mercury free COD test kits could be used by the wine industry for organic pollution assessment with associated reductions to user and environmental risk, as well as reducing the costs of kit waste disposal.

Key Words: BOD, effluent, COD, ethanol, water treatment

INTRODUCTION

Traditionally, organic pollution is measured by a standard biological oxygen demand five day test (BOD_5) test that was first published 90 years ago (Young and Clark, 1965). In spite of many problems with the application of the test, the meaning of results and its limitations, all of which have been extensively reviewed (Metcalf and Eddy, 1991), it remains the accepted environmental pollution indicator (Bourgeois *et al.* 2001). In the management and disposal of winery wastewater it is used as proof of compliance with environmental regulators (*e.g.* EPA SA, 2004).

An abundance of different techniques have been considered in the scientific literature as alternatives for the BOD_5 test for the assessment of organic pollution in municipal effluents (Fogelman *et al.* 2006; Puñal *et al*. 1999; Spanjers *et al.* 2002; Vanrolleghem and Lee, 2003). Reliable correlation factors have been established in some cases between chemical oxygen demand (COD) and BOD_5 in industrial effluents and equations presented *e.g.* domestic sewage and sewage/brandy stillage mixtures (Macmillan *et al.* 1959; Fadini *et al.* 2006), rubber and seafood industries (Chevakidagarn, 2007); winery wastewater (Chapman *et al.* 2001), pulp and paper mill wastewaters (Roppola *et al.* 2006) and slurry and effluents (Brookman *et al.* 1997). Ultra violet (UV) light absorption (Chevakidagarn, 2007; Carvallo *et al.* 2007; 1996; Muzio *et al.* 2001;) and fluorescence measurements are techniques that have been discussed (Hudson *et al*. 2008). Other tests use buffer capacity testing, respirometry (Carvallo *et al.* 2007, Roppola *et al.* 2006) and biosensors (Rastogi *et al.* 2003).

In industrial settings, it is becoming more common for wastewater managers to use alternative tests to BOD_5 to assess water quality, that are simpler to perform, more reliable and rapid, allowing for better management of effluents. However, relationships between many of the parameters are complicated and often empirical. Precise values depend on test conditions employed, molecular structure and ease of chemical oxidation of wastewater components. Definitive relationships between BOD_5 and COD, for use with many effluents including winery wastewater is difficult, as the quality and biodegradability is so variable over an annual cycle (Chapman *et al.,* 2001). The only reliable way to inter-convert BOD_5, COD, TOC and theoretical oxygen demand is by testing and calculation over time. Nevertheless, COD, in particular which is sold commercially as a kit test (*e.g.* supplied by CHEMetrics®) and provides results after two hours is being widely used for the assessment of organic load within effluent monitoring programmes (USEPA, 1993). It is unaffected by toxic substances and a linear relationship between BOD_5 and COD can be established in easily biodegradable domestic effluent streams. Some rules of thumb do exist to permit the inter-conversion with a reasonable degree of confidence (BOD_5 = 0.68COD) in readily biodegradable waste streams (ICI, UK, 1996).

This study focuses on appraising some of the methods used for organic load determination, that were originally intended for municipal wastewater treatment, such as COD, total organic carbon (TOC), dissolved organic carbon (DOC), against BOD_5, in winery effluents at different stages of treatment. The work also employed some rapid, simple tests for ethanol, the sugars; fructose and glucose, and citric acid and correlates them to BOD_5 in winery wastewater. These tests were chosen as it has been previously found that ethanol and, at certain times during wine processing, the sugars contribute as much as 90% of the COD of winery effluent (Colin *et al.,* 2005). Citric acid is also used regularly in winery sanitation processes for tank and bottle cleaning and a slug of a 5% solution of citric acid with a BOD_5 of 17599 mg O_2 L^{-1} (Chapman *et al.,* 2001), could enter the wastewater receiving system undiluted. It was considered therefore, that the ethanol, sugar and citric acid tests, may act as simple surrogates for organic pollution appraisal and would be easy to conduct in an in-house winery laboratory where sugar and ethanol and organic acids are routinely measured to assess wine quality. A comparison of COD data using conventional commercially available COD kits that contain mercury (USEPA approved method 410.4) with those that are mercury free is also presented for untreated winery wastewater.

METHODS

Sample Collection

Winery wastewater samples were collected weekly from a large winery (annual crush ~80,000 tonnes) near Griffith, NSW in the Riverina wine growing region of Australia from 28th July, 2006 – 16th July, 2007. The sample set provided representation of an annual cycle of production, including the 2007 Australian vintage (13th January, 2007 – 4th April, 2007). Wastewaters (1 L in amber glass bottles) were grab sampled at different stages of treatment: the inlet and outlet points of a primary treatment process consisting of a baffled serpentine arrangement designed to settle out solids, and the outlet of a more rigorous treatment process designed to remove high organic load consisting of an active aerated lagoon. Part way through the monitoring period, the winery changed the aerobic treatment system from a lagoon that was aerated by four large mechanical aerators to a lower energy system involving microbubble aspiration (Ecosafe™) of only the surface waters of the lagoon. The removal of organic matter by these two treatment systems was quite different and so the data from each system have been recorded here separately.

Sample Analysis

Organic load measurements included: chemical oxygen demand (COD; 107 samples), biological oxygen demand (BOD_5; 107 samples), total organic carbon (TOC; 72 samples), dissolved organic carbon (DOC; 72 samples) ethanol, glucose, fructose and citric acid (19 samples). A breakdown of the number of corresponding samples analysed at different stages of production and treatment of winery effluent are included in Table 1. Commercially available COD kits (CHEMmetrics Inc) were used for additional sample testing from January, 2007 (n = 23 samples; n = 14 non-vintage and n = 9 vintage) which included the use of a USEPA approved method containing mercuric sulphate in the reagents and a less commonly known mercury free method. All of these data were derived from untreated effluent samples. Specific details of the test procedure are as follows:

500 ml of sample were homogenized for 2 minutes in a vortex mixer. A digestion block was heated to 150ºC. The cap from a COD vial provided in the kit was removed and 2 ml of sample (for samples in the range 0-1,500 mg/L COD, or 0.2 ml for samples in the range 0-15,000 mg/L) were micro-pipetted into the vial. The cap was secured tightly and the vial inverted several times to mix the contents. The vial was placed in the preheated digester block and allowed to digest for 2 hours. The block was turned off and allowed to cool for 15-20 minutes. The digested samples and reagent blanks were measured in a pre-programmed CHEMmetrics photometer.

Organic Load Assessment Technique Ratio	Vintage untreated effluent	Non-Vintage untreated effluent	Vintage Serpentine	Non-Vintage Serpentine	Vintage Fully Aerated Lagoon	Non-Vintage Fully Aerated Lagoon	Vintage Facultative Lagoon micro-bubble surface aspiration	Non-vintage Facultative micro-bubble surface aspiration
BOD/COD	0.8	0.8	0.9	0.7	0.2	0.2	0.7	0.7
n	10	24	10	27	3	14	6	13
Range	0.5-1.1	0.4-1.3	0.5-1.3	0.5-1.3		0.1-0.8	0.6-0.9	0.6-0.9
SD	0.2	0.2	0.3	0.2	0	0.2	0.1	0.1
BOD/TOC	2.9	2.8	2.8	2.9	0.3	0.5	2.9	3.0
n	9	14	8	15	3	15	3	5
Range	2.1-2.7	1.7-6.0	1.8-3.9	1.8-3.9	0.2-0.3	0.2-0.7	2.0-3.7	2.8-3.1
SD	0.6	1.0	0.3	0.6	0.1	0.6	0.7	0.2
BOD/DOC	3.0	3.2	3.0	3.3	0.4	1.0	3.8	4.0
n	9	17	10	17	3	15	5	3
Range	1.9-4.0	1.8-5	1.9-4	2.2-5.4	0.3-0.6	0.3-2.8	2.8-4.7	3.5-4.3
SD	0.7	0.9	0.7	0.8	0.2	0.7	0.7	0.4
BOD/Ethanol	3.8	3.2					5.5	4.0
n	5	14					4	14
Range	2.7-6.2	1.1-4.9					4.1-8.1	1.9-11.1
SD	1.4	1.6					1.8	2.8
BOD/ (glucose + fructose)	3.0	17.8					2394	5723
n	5	14					5	14
Range	1.0-5.4	2.8-134					203-5121	600-14316
SD	1.2	49.5					2149	4288

Table 1. Mean Ratios of BOD (mg O_2 L^{-1}) to other parameters that may be used to assess organic load in winery wastewater at different stages of treatment. Number of samples (*n*) used to determine the mean values and the range of ratios that were determined are also provided.

Samples for BOD_5 were adjusted to pH 6.5-7.5 and stored at 4ºC immediately after collection. Analysis was carried out according to standard methods using unseeded dilution water (Standard Methods for the Examination of Water and Wastewater, 1995). A range of dilutions was carried out in duplicate and when more than one sample dilution met the criteria of a residual dissolved oxygen (DO) concentration of at least 1 mg L^{-1} and a DO depletion of at least 2 mg L^{-1}, mean results were reported. Control limits were set at mean glucose-glutamic acid checks being 200 ± 40 mg L^{-1} and blank DO uptake being < 2 mg L^{-1}. Dissolved organic carbon samples were prepared by filtering a sample aliquot through 47 mm GF/F filters (Whatman). Unfiltered and filtered samples were stored at -20ºC prior to analysis by a high temperature combustion analyzer for TOC and DOC resepctively. Ethanol, glucose, fructose and iso-citric acid were analysed using commercially available assay kits (Megazyme International).

RESULTS AND DISCUSSION

Using all of the data obtained for BOD_5, COD, TOC and DOC on corresponding samples, inclusive of vintage, non-vintage and all the different treatment stages provided conservative correlations, that provide rule of thumb figures of BOD_5 = 0.65COD, BOD_5 = 2.9TOC and BOD_5 = 3.0DOC. The BOD_5 to COD estimate is similar to previous estimations (Chapman *et al.,* 2001; Tofflemire, 1972).
Quantitative analysis of winery wastewater by Chapman *et al.,* (2001) and Tofflemire (1972), indicated that BOD_5 is around 66% of COD (0.2-0.8). It was postulated by these workers that this ratio may be a result of the dominance of sugars and ethanol which have a BOD/COD ratio of approximately 0.7. However, the BOD_5 ratio of approximately three times TOC determined here is higher than that estimated by Chapman *et al.* (2001), whose limited quantitative data suggested BOD_5 was only twice that of TOC.

The specific equations for the linear correlations determined here are shown below. All R^2 values were significant (P<0.05).

$$BOD_5 = 0.65\ COD + 457.8;\ R^2 = 0.70$$
$$BOD_5 = 2.9\ TOC - 222.3;\ R^2 = 0.85$$
$$BOD_5 = 3.0\ DOC + 206.0;\ R^2 = 0.83$$

The relationships enable reasonably good estimation of BOD_5 using quicker, easier, and quantitatively more reliable methods than the classical BOD_5 test for this particular effluent.
Table 1 presents mean and ranges of ratios of BOD_5 (mg O_2 L^{-1}) to the other parameters that may be used to assess organic load in winery wastewater when the data is separated into different stages of production and treatment. Linear relationships between BOD_5 *vs.* COD and BOD_5 *vs.* TOC tended to get progressively weaker, as the effluent progressed through the treatment process, probably due to the treated samples having been collected at variable stages of primary and secondary treatment rather than as 'finished' samples that may be more consistent in their organic load status. This suggests that wastewater managers should exert some caution when applying conversion factors, taking into account when and at what stage and type of treatment they sample.

In untreated effluent, produced during vintage and non-vintage, ratios of BOD_5/COD ranged from 0.5 - 1.1 and from 0.4 - 1.3 respectively (Table 1). The untreated effluent BOD_5/COD ratio was generally higher than that of the treated effluent. There was little difference in all of the ratios between untreated effluent and those sampled at the outlet of the serpentine settling system. Although we have determined that the majority of the organic load is dissolved (discussed below), it should also be noted that the serpentine settling system was not always being adequately maintained. A large build up of sludge had occurred in the serpentine during our sampling period. It was only being removed very occasionally and for much of the time it appeared that input wastewater was not being retained for sufficient time to allow significant settling to occur. The lowest BOD_5/COD ratios (0.2) were observed in fully aerobically treated wastewater. In these samples, oxidation of the easily degradable components had occurred during the treatment process resulting in a larger proportion of more recalcitrant compounds being detected in COD testing but to a lesser extent, in the BOD_5 test.

Previous detailed determinations of the composition of winery wastewater have indicated that 50-80% of COD is made up of ethanol and about 30% consists of fructose and glucose. The remainder is in the form of glycerol, organic acids such as tartaric, and citric acid and a variety of other organic compounds in trace levels such as volatile fatty acids, phenols and tannins (Bories *et al.,* 2005, 2007). Colin *et al.,* (2005) claim that ethanol (2500-8000 mg L^{-1}), and to a smaller extent, and on a temporary basis, sugars (fructose, glucose reached a total of 6000 mg L^{-1}) represent more than 90% of the organic load of winery effluent. In this study, ethanol concentrations in untreated wastewater ranged from 472 mg L^{-1} – 4727 mg L^{-1}. Mean ethanol concentrations did not appear to be connected strongly to vintage
(1550 mg L^{-1}) and non-vintage (1840 mg L^{-1}) periods (Table 2).

Wastewater Component	Vintage Untreated	Non-vintage Untreated	Vintage (facultative lagoon)	Non-vintage (facultative lagoon)
Ethanol mgL^{-1}	1550 (772)	1840 (1325)	1541 (395)	1168 (375)
Glucose mgL^{-1}	897 (459)	384 (394)	2.2 (0.9)	1.4 (1.8)
Fructose mgL^{-1}	1277 (687)	428 (459)	11 (19)	0.2 (0.2)
Citric Acid mgL^{-1}	0.75 (0.48)	1.03 (0.93)	0.0	0.4 (1.0)
Ethanol-C/TOC	0.4 (0.2)	0.56 (0.25)		
Glucose-C/TOC	0.24 (0.11)	0.08 (0.05)		
Fructose-C/TOC	0.19 (0.10)	0.08 (0.10)		

Table 2. Organic composition of winery wastewater at different stages of production and treatment. Mean values with standard deviation in parentheses, vintage*:* *n*=5, non-vintage *n*=14.

In, contrast, concentrations of glucose and fructose were both significantly higher during vintage (Figure 1; Table 2).

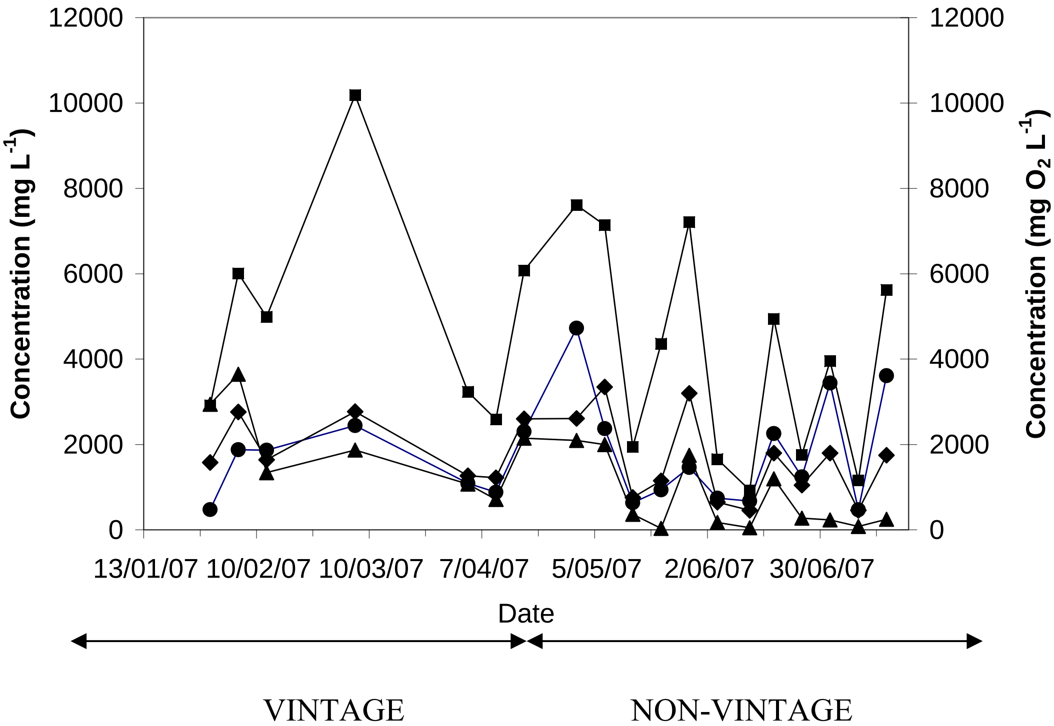

Figure 1. Production of ethanol (●mg L^{-1}), glucose +fructose (▲ mg L^{-1}), TOC (♦ mg L^{-1}), and BOD (■mg O_2 L^{-1}) during vintage and non-vintage periods in untreated winery effluent.

The microbubble surface aspiration treatment employed by the winery, that essentially created an aerobic cap, over an anaerobic hypolimnion, in a lagoon that was approximately 3 m deep, had minimal effect on diminishing ethanol concentrations. However, both glucose and fructose were almost completely removed (>99%) by this treatment. As a proportion of TOC, ethanol-C ranged between 15 - >100% (mean; 55%) in untreated wastewater. Total sugars (glucose + fructose) concentrations ranged from 32-3646 mg L^{-1} with a dominance in the vintage (2174 mg L^{-1}) compared with non-vintage period (811 mg L^{-1}). As a proportion of wastewater TOC, the sugars ranged between 1-75% (mean 24%). Citric acid was determined at relatively low concentrations, ranging from 0.05-2.9 mg L^{-1} , it tended to be more abundant during non-vintage and accounted for <0.1% of TOC. Summing the ethanol, sugars and citric acid components accounted for on average, 79% of the organic load of winery wastewater.

Since BOD_5 and COD measure mg O_2 L^{-1} required to oxidize a certain amount of organic matter rather than organic carbon directly, DOC or TOC have been considered by some to be more rational parameters to express the amount of organic material present in an effluent sample. They can provide a quicker indication of irregularities in a wastewater treatment system and both are easier to conduct and more precise than the standard BOD_5 test. Bories *et al.* (2005) calculated the contribution to organic load of individually determined components in wastewater by multiplying the concentration of each component (ethanol, sugars, organic acids *etc.*) by their theoretical yield of total oxidation and expressing as a proportion of dissolved COD. This is a reasonable approach on the basis that the COD of these compounds is approximately the same as the theoretical oxygen demand. We found no statistical difference when comparing results by a t-test ($p\leq 0.05$) between using this method and determining the concentration of carbon contributed by the individual components as a proportion of TOC.

Corresponding data for 19 samples of untreated wastewater during vintage and non-vintage enabled a direct comparison of different correlations (Table 3).

Ratio	EQUATION	R^2
BOD_5/COD	BOD_5=0.58COD+322	0.83
BOD_5/TOC	BOD_5=2.5TOC+95	0.81
BOD_5/(ethanol+glucose+fructose)	BOD_5=1.1(eth+gluc+fruc) +1062	0.64
BOD_5/ethanol	BOD_5=1.4ethanol+1914	0.45
BOD_5/(glucose+fructose)	BOD_5=1.4(gluc+fruc)+2809	0.34
COD/ethanol	COD=2.5ethanol+2696	0.55
COD/(glucose +fructose)	COD=2.2(gluc+fruc)+4571	0.33
COD/(ethanol+glucose+fructose)	COD=1.9(eth+gluc+fruc)+1496	0.72

Table 3. Correlations between different parameters in untreated winery wastewater effluent inclusive of vintage and non-vintage. eth =ethanol, gluc = glucose, fruc= fructose; $P=<0.05$).

Of all the relationships, BOD_5 *vs.* COD offered the highest linear correlation in untreated winery wastewater, closely followed by BOD_5 *vs.* TOC using data that was sourced from the same vintage and non-vintage samples.
Strong linearity between dissolved COD and ethanol concentrations was determined by Colin *et al.* (2005), but in this study BOD_5 and COD relationships with ethanol alone or with the summed concentrations of glucose and fructose were weaker (R^2 ~≤0.5), than the other parameters discussed (Table 3).

Some studies have claimed that much of the oxygen demand in winery effluent is sourced from settled material such as grape pulp, yeast, bacteria, pectins, tannins and proteints (lees). However, our studies here confirmed that much of the organic matter is dissolved. DOC/TOC values ranged from 47-100% (mean 83%, n = 50). For a selection of samples (n=19) COD was determined on raw effluent and corresponding sub-samples that had been filtered through GF/F (Whatman) filters. Chemical oxygen demand in the filtered samples (dissolved COD) ranged between 64 -100% (mean; 84%) of unfiltered samples.

The traditional COD test uses chemicals such as acid, chromium, silver and mercury, producing liquid hazardous waste that requires specialized disposal. Mercuric sulphate is used in the USEPA approved COD method (Method 410.4, USEPA, 1993) to complex chlorides which can produce a positive interference. A mercury free COD test is commercially available, that may reduce the hazard of test waste, for effluents such as winery wastewater, where there is unlikely to be chloride interference. This offers the potential to reduce environmental risk and costs of disposal. However, the mercury free COD test has not yet been properly validated so that it may be interpreted in terms of the mercury containing test, or BOD_5 results.

A highly significant linear correlation was determined between the mercury containing and mercury free commercially available COD kits (Figure 2), suggesting that the mercury free COD test kit could be successfully used for winery effluent testing.

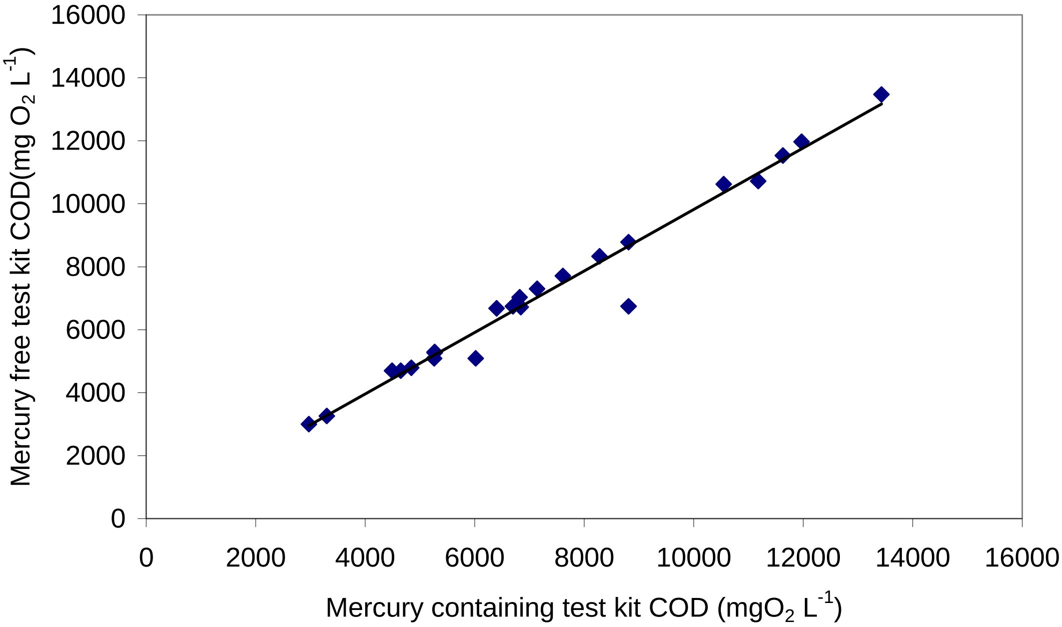

Figure 2. Relationship between COD (mg O_2 L^{-1}) in untreated winery wastewater effluent measured using conventional mercury containing COD test kits and kits that contain no mercury (y=0.9767x+52.8; $R^2 = 0.97; n=23; p<0.05$).

This method minimizes health and safety risks to users of the kits, the environment and reduces the economic costs for test waste disposal compared with the mercury containing test kit.

CONCLUSIONS

Rules of thumb factors for the inter-conversion of COD, TOC and DOC with BOD_5 measurements of winery effluent were determined. These are: $BOD_5 = 0.65COD$, $BOD_5 = 2.9TOC$ and $BOD_5 = 2.9DOC$.

Ethanol and the sugars (glucose and fructose) were dominant constituents of winery effluent at mean proportions of 55% and 24 %, albeit with high variability. Ethanol did not seem to be connected with vintage and non-vintage periods, which was in contrast to the sugars which were most dominant over vintage.
Overall, the sum of ethanol, glucose, fructose and citric acid accounted for approximately 75% of winery wastewater organic load.

Although not compared directly with conventional chromatography methods, the rapid enzyme based test kits for ethanol, glucose and fructose seemed to perform well with winery effluents, providing data that appeared reasonable compared with standards, previous studies and in comparison with the TOC determinations.

Out of all the relationships between BOD_5 *vs* COD, TOC, DOC, ethanol, (glucose+fructose) and (ethanol+glucose+fructose), BOD/COD offered the linear relationship with the highest correlation factor. In contrast to previous studies (Colin, *et al.* 2005), the correlation determined here between COD and ethanol, was less significant.

Most of the organic load was in dissolved form. Mean DOC/TOC values were 84% and dissolved COD accounted for 84% of total COD.

A highly significant linear correlation (R^2 = 0.97; $p<0.05$) was determined between values obtained from mercury containing and mercury free commercially available COD kits. This suggests that the mercury free COD test kit could be successfully used for winery effluent testing with the associated environmental and economic benefits for test waste disposal compared with traditional mercury containing COD test kits.

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