PROTECTION OF WWTP BY REAL-TIME DETECTION OF TRADE WASTE

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ABSTRACT

Industrial and trade waste discharged to sewer has the potential to cause process problems in receiving biological waste water treatment plants (WWTP) and advanced water reuse plants (AWP). Detection and quantification of intermittent and short lived industrial discharges by random discrete sampling is costly and unreliable because a large number of samples must be analysed for a range of possible contaminants with no guarantee of detection. Composite sampling is also problematic as averaging over a day or week makes it difficult to identify discrete discharges. Online monitoring for trade waste discharges is an efficient alternative.

In this work describes experiences in real-time monitoring for industrial waste effluents at a WWTP inlet location with a UV/Vis spectrometer. A number of trade waste discharges were detected and characterised by the equipment. A fraction of these correlated with process problems at the WWTP. Investigation upstream led to identification of a non-compliant industry. Resulting enforcement action resulted in cessation of the trade waste discharge and improvement in WWTP operation.

A brief review of similar data available from permanent monitoring locations at NZ WWTP is also presented and comments on potential for similar risks here are made.

KEYWORDS

Trade waste, UV/Vis, influent monitoring, process protection

1 INTRODUCTION

The effective operation of primary, secondary and tertiary treatment processes depend to a large extent on the presentation of treatable wastewater at the plant inlet. Arrival of either untreatable wastewater or unusually high quantities of treatable wastewater may result in costly process failure, for example by disrupting the biological processes in the plant.

A wide variety of industrial chemicals are known to be inhibitory to biomass (Johnson 1983; Manusadzianas et al. 2003; Chen 2008). Detection and quantification of intermittent and short lived discharges within the bulk wastewater matrix is complicated and traditional grab or composite sampling techniques, while widely used, may not properly quantify the variability in wastewater pollutant loading (Ort et. al. 2010) which can lead to uncertainty around the causes of treatment process upsets.

A variety of online techniques are available to continuously detect changes in wastewater treatability. Online bio-monitors allow for non-specific detection of toxic contaminants by automatically monitoring stress indicators or mortality of test organism (e.g. Inui et al. 2001; Melidis et al. 2005; Vanrolleghem et. al. 1993). Such devices have shown promise for detection of discrete toxic discharges. De Hoogh et. al. (2006) performed targeted sampling and laboratory analysis of river water to investigate non-specific toxicity alarms from a cabinet analyser monitoring swimming behaviour of *Daphnia magna*. Detailed laboratory analysis of the suspect samples resulted in identification of four unusual industrial chemicals in the river water which was suggestive of dumping. A comparable case is described by van der Schalie et al. (2001), who used a system monitoring the ventilatory system of fish to monitor the effluent of a groundwater treatment facility and identified several occasions of elevated metal concentrations (Al, As) in the effluent. Geenens and Thoeye (1998) used an online activated sludge respirometer to investigate incidences of total nitrification inhibition at a WWTP and identified the cause to be slugs of toxic influent from industry within the catchment.

Notwithstanding these notable successes, the use of continuous online screening for influent toxicity remains limited. For example, to the authors' knowledge, online screening is not carried out in any WWTP in New Zealand or Australia. This may be partly because maintenance requirements for biological detection systems in unscreened wastewater applications are high due to sample pre-filtration requirements (Inui et. al. 2001) and biomass mortality issues.

Non-biological monitoring techniques may address some of the operational barriers to wider screening for influent treatability. For example, Hoes et. al. (2009) have made use of fibre optic cables deployed within stretches of sewers to detect localised variations in temperature, some of which were found to be associated with illicit discharges. UV/Vis absorption derivative spectroscopy (Langergraber et al., 2004) can provide indications of trade wastes which absorb ultra violet or visible light, some of which may be damaging to receiving plant biomass. The use of UV/Vis methods can be advantageous in unscreened sewage applications as the systems are essentially solid state, more robust and memory-less.

In this work we first report on our experiences using online UV/Vis methods to identify the source of contamination impacting a 7.5 ML/day advanced water reuse plant that has recently been commissioned in Victoria, Australia. The plant receives sewage from the "Oyster Cove" domestic catchment (2.4 ML/d) and the "Corio West" industrial subdivision (3.3 ML/d) along with wastewater from the adjacent Shell Refinery (1.8 ML/d). The advanced water reuse plant is comprised of;

- screening and grit removal;
- a secondary activated sludge biological treatment process (35% anoxic volume, 20 day sludge age) with conventional circular clarifiers and associated solids handling systems;
- an Advanced Water Treatment Plant (AWTP). Wastewater is treated to Class A standard for non-potable re-use in the refinery and Class C for local irrigation.

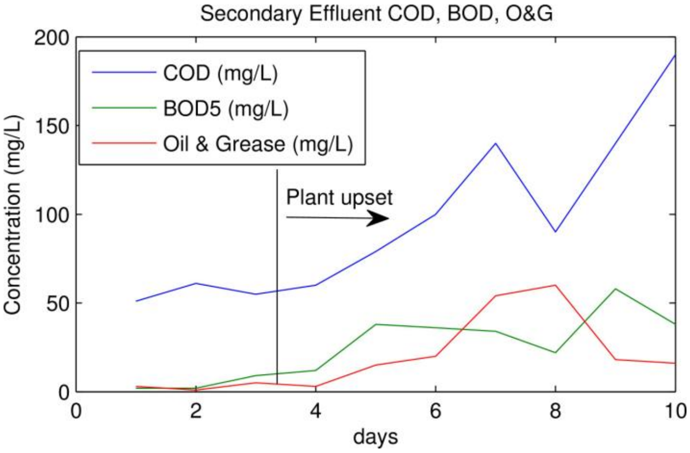
The plant is unique in Australia in terms of the proportion of industrial influent being co-treated with domestic wastewater to Class A standard (up to 50% allowing for the Corio West industrial contributions). The advanced tertiary process is vulnerable to secondary process upsets and breakthrough of organic carbon compounds and relies on stable performance of the WWTP. The absence of primary sedimentation upstream of the secondary biological process means that rapid changes in influent load can impact the secondary process within a very short timeframe, with limited time to detect and respond.

If the secondary process does not perform well then large amounts of untreated organics may be present in the secondary effluent. High contaminant concentration in the secondary effluent can influence the downstream UV transmissivity which may reduce the efficacy of UV-disinfection, increase the necessary chlorine dose, affect pH stability and potentially lead to RO membrane fouling. This means that good performance of the biological process is essential for providing good enough quality effluent to supply the AWTP.

During commissioning it became apparent that the WWTP was failing to consistently meet the target concentrations for feed to the AWTP. On occasions effluent concentrations from the secondary treatment process would increase, indicating some form of process upset placing the AWTP process at risk (Figure 1).

On-site investigations of these process failures lead to the hypothesis that untreatable industrial waste was being discharged from the Corio industrial subdivision and there was the possibility of occasional excessive loadings originating from the refinery.

Figure 1: Secondary effluent quality measured by 24h composite sample during high trade waste loading event, time in days.



2 MONITORING METHODOLOGY

Little information about the nature of industrial material originating in the catchment of the WWTP/AWTP was available. The major industry in the Corio West catchment is a slaughterhouse. Composite sampling during earlier pilot testing had not identified any unusual loading patterns in the subdivision nor had the slaughterhouse wastewater been identified as a process risk.

An alternative to composite sampling is online instrumentation. In this work an automated monitoring station was deployed to a pump station (PS) at the outflow point of the Corio West industrial subdivision, and immediately upstream of the WWTP/AWTP.

The station included a submersible online UV/Vis spectrometer (spectro::lyser, s::can Messtechnik GmbH), ancillary logging hardware and a 3G modem for real-time telemetry. The spectrometer measures the absorption of ultra-violet and visible light at 2.5 nm increments between 200 and 700 nm and may be programmed to sample as frequently as every 20 seconds. The spectrometer function has been described in detail by Langergraber et al. (2003).

In the configuration used in this work the spectrometer is not deployed directly into the waste stream. This is because the (unscreened) wastewater in the PS sump would quickly rag the instrument and make reliable measurements impossible without regular manual de-ragging. Access to the PS sump represents an occupational health and safety risk so frequent maintenance is not desirable. Instead, a sample of wastewater was reticulated to the spectrometer every 2 minutes using a specialised wastewater sampling pump (SDU, DCM Process Control Pty.). The pump head self-cleans with an aggressive air purge after every delivery to minimise maintenance requirements. Only the intake head (ø76 mm x 485 mm, 4.6 kg) is deployed in the hazardous environment and for maintenance it may be easily winched to surface level through a small portal cut in the PS cover plate, leaving the majority of the monitoring station on the surface.

UV/Vis absorption measurement quantifies the attenuation of light by a sample at different wavelengths. The measured reduction in light intensity at different wavelengths is related to all of the dissolved chemicals which absorb light according to the Beer-Lambert Law *and* scattering of light by particulate material (Huber and Frost, 1998). UV/Vis methods have been used to estimate standard municipal wastewater quality parameters such as chemical oxygen demand (COD), suspended solids (TSS), nitrate (NO_3) (Langergraber et al., 2003; Torres and Bertrand-Krajewski, 2008) and hydrogen sulphide (Sutherland-Stacey et al., 2008).

The wastewater passing through the Corio West PS is a mixture of domestic wastewater, slaughterhouse effluent and smaller discharges from a number of trade waste customers. Times of high loading from the slaughterhouse were easily identified from the UV/Vis signal of haemoglobin (Sutherland-Stacey et al., 2009) originating from kill and carcass handling. In the Corio West PS location slaughterhouse discharges occur daily, usually during the afternoon.

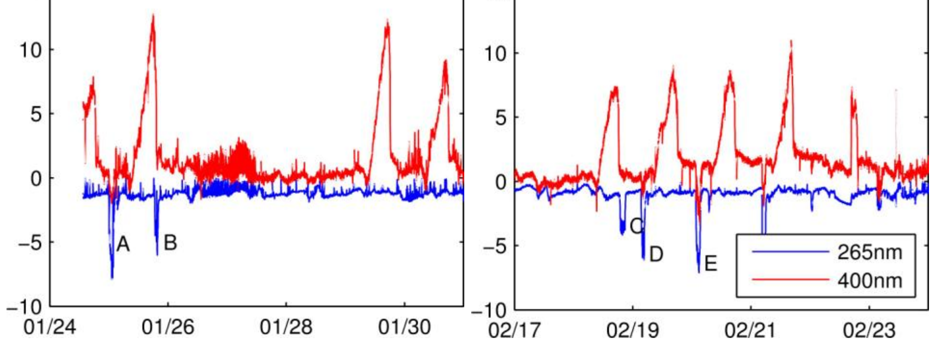
Intermittent discharges from industrial or trade waste customers may be detected from unusual changes in the characteristics of the time resolved derivative UV/Vis measurements (Langergraber et al., 2004). After an initial data collection period, the recorded UV/Vis spectra were automatically processed to calculate 1^{st} derivatives of the absorbance spectrum for predefined wavelength bands. Derivative spectra provide information about the slope of the spectrum and give better insight into its component parts, e.g. showing a subtle deformation due to the presence of a foreign compound. The derivative spectrum is also largely insensitive to changes in solids concentration- in comparison to single wavelength devices. These resulting time series were automatically treated to flag outlier deviations from their respective means which might indicate industrial discharge activity. A quality control step was used to discard measurements affected by air ingress into the pump or temporary blockages- both of which also generate outlier derivative spectra.

This methodology flagged not only the expected deviations related to daytime slaughterhouse activity (for example, distinct positive upwards trending in the derivative signal at 400 nm in Figure 2) but also a second distinct, but intermittent, signal related to a suspected non-municipal early morning discharge (sudden downwards spikes in derivative UV/Vis signal over a range of wavelengths including 265 nm, same figure).

The raw UV/Vis measurements which corresponded to the early-morning signal were then manually examined in an attempt to gain insight into the cause of this sudden change in influent character. The difference between UV/Vis readings before and during the outlier events were calculated to obtain an estimate of the pure absorption spectra of the contaminant.

Figure 3 gives an example of the extracted contaminant spectra for the first six outlier events observed during the monitoring period. The changes in the UV/Vis absorption spectra vary between events with only some commonalities for all events. The trigger point for defining detection of this outlier was an increasingly negative gradient at 265 nm, so it is not surprising that all events (A - F) exhibit a substantial increase in UV absorption in the UV range 200 - 270 nm. Events A - D also involve a general increase in absorption against the background measurements immediately before and after the event. Such an increased absorption across the entire spectrum is typical for the presence of elevated levels of particulate matter (Huber and Frost, 1998). Events A & B appear to have an additional shoulder around 280 nm suggesting the presence of an additional compound or functional group. Meanwhile events E & F exhibit no change in background visible light absorption at all suggesting a the presence of water soluble material only. An additional weak but distinct absorption peak at 360 nm differentiates these two discharges from the previous four events.

Figure 2: time resolved derivative UV/Vis absorption at selected wavelengths for two 1 week monitoring periods at the PS location.

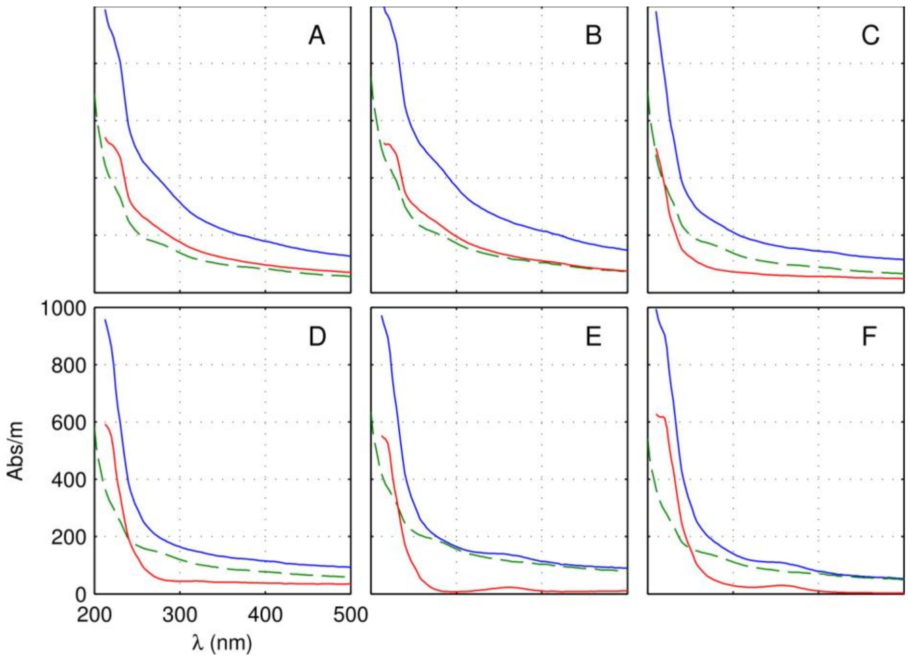


After events A & B were observed it was decided that there was sufficient evidence of illicit activity within the Corio industrial catchment to justify a grab sampling campaign. The monitoring station control computer was connected to a standard glass bottle refrigerated discrete auto sampler and programmed to trigger sample collection in the event a non-standard industrial discharge was detected by the spectrometer. A trigger point was set to drive the auto sampler if the derivative at 265 nm was less than -7 Abs/m/nm. This work was completed in time to obtain discrete samples of events E & F. The auto-sampler was also triggered at pre-determined times to sample the baseline diurnal and weekly variability.

All samples were tested in the first instance for standard wastewater parameters: COD, CODf and TSS (APHA 2005). The event E & F triggered samples exhibited a distinct "petrochemical" odour, therefore they were also tested for volatile organic compounds (VOC) and for semi volatile organic compounds (USEPA 8260 and 8270).

Figure 4 gives an alternative visualisation of the UV/Vis derivative spectra alarm signal. The chart can be read in the same way as a seismogram: Each line (left to right) represents one day and subsequent days are plotted top to bottom. A flat thin grey line represents no events but a valid measurement. Solid shading indicate detection of a suspected trade waste discharge. Both the 265 nm outlier events (solid black) and slaughterhouse haemoglobin signal (solid grey) are plotted for comparison.

Figure 3: estimate of the pure UV/Vis spectra of the unknown contaminant (red) obtained by differencing measurements made during (blue) and immediately after (dashed green) an outlier event.

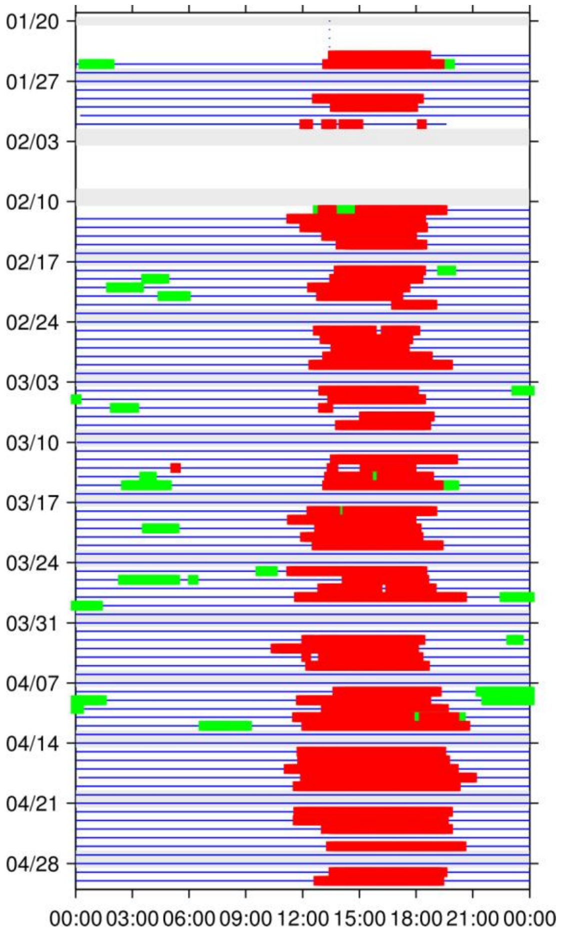


3 RESULTS AND DISCUSSION

Standard methods COD testing of events E & F returned results of up to 9,000 mg/L, most of which was stored in the soluble form. This is significantly higher than the usual wastewater COD in the Corio West PS suggested by grab sampling (Table 1).

Numbers of these magnitudes indicate a large amount of oxygen would be required to completely oxidise the variety of chemicals in the samples. However, it was not clear that the plant biomass will suitably adapt to be able to assimilate the unusual and possibly non-polar materials. Therefore, more detailed analysis of the samples was performed in order to identify the substances present and evaluate their impact on plant biology and if they could be responsible for reported increase air usage or poor quality effluent.

Figure 4: Time distribution of flagged outlier conditions at 265 nm (green) and 400 nm (red). Weekends are shaded with a lighter grey.



An initial assessment of the UV spectra recorded during the alarm periods (Figure 3) showed increased absorption in the UV part of the spectrum, with characteristic features visible at 350 nm and 270 nm. A review of UV/Vis spectra available in literature (Perkampus (1992), Thomas and Burgess (2007)) revealed that the absorption peaks of the material contained in the sample were characteristic of compounds of low molecular aromatic nature. Based on this evaluation, the analytical methods for VOC and semi volatile organics were chosen for detailed chemical analysis of the samples.

The VOC analysis of the same samples revealed the presence of ethylbenzene (1 mg/L), xylenes (10 mg/L), methylphenols (2 mg/L), acetone (50 mg/L) and bis(2-ethylhexyl) phthalate (also known as DEHP) (5 mg/L) as well as smaller amounts of other benzenes (dichlorobenzene, toluene and naphthalene). The UV/Vis spectra of the different compounds are consistent with the GC observations. The total sum concentration of the substances identified with the VOC method was high enough and so explain the absolute absorption of the spectra. These chemicals are neither standard components of municipal wastewater nor slaughterhouse effluent. They are more readily identifiable as industrial chemical precursors for manufacturing of more complex organic chemicals.

Table 1 Selected accredited laboratory standard quality parameter results obtained from the Corio West pump station.

Date/Time	ID #	TSS (mg/L)	COD (mg/L O_2)	CODf (mg/L O_2)	Type
2013/02/20 02:16	2	390	8000	4900	E triggered
2013/02/21 05:00	3	160	8900	9000	F triggered
2013/03/04 00:18	12	280	560	210	random

2013/02/26 17:10	4	360	1200	520	Random

Identification of any direct correspondence between air usage and the industrial contaminant is confounded during working hours by the already high slaughterhouse loadings and intermittent gating of influent from the Corio subdivision. This interference is not present at night time when all wastewater from Corio is accepted by the plant and little slaughterhouse wastewater is present. Events which occurred overnight (A & D-F) caused no noticeable increase in blower demand, suggesting that the industrial contaminant is not an attractive food source to the plant biomass. It is therefore possible that this material passes through the biological process without modification and results in poor effluent quality. Therefore, identification of the source to preclude further discharges was deemed critical.

No significant progress in identifying the source of the material could be made from chemical analysis alone. Instead it was decided to make use of the detailed time distribution of the outlier events (e.g. Figure 4, solid black) to assist with backtracking to source up the sewer network. The suspected organic contaminant (indicated from the derivative spectral measurement at 265nm) was only ever detected overnight on weekdays and then at most once per day. This pattern is consistent with a small volume point source discharge. It was speculated that the contaminant was for the most part detected overnight for one of both of two reasons. It might be that during the day the discharge is diluted by the much larger flow from the slaughterhouse and is not detected. Alternatively the industry may only discharge over night or the wet-well into which the discharge occurs might receive only a small flow and pump out only intermittently.

Inspection of the PS sump and collected samples immediately following outlier events (after event F) indicated a white oily material (or at least a soluble fraction of material accompanied by an oily discharge) adhering to the sides of the wet-well. It appeared to be responsible for the elevated readings and operations staff continued to report the material was characterised by a "hydrocarbon" odour suggesting a commonality with previously obtained grab samples. In one case the auto-sampler suction tube was completely blocked with this material after an outlier trigger.

Following subsequent outlier events, compliance officers from the local water authority performed immediate inspections of wet wells upstream of the monitoring location. By following traces of the white material a suspected point source was identified. A composite auto-sampler was installed at the suspect location and checked when the downstream monitoring station issued alarm warnings. This extra monitoring was undertaken at the start of April 2013 and an undiluted sample consistent with downstream observations was captured after an alarm event. The pure sample was sent for laboratory analysis and COD reading in excess of 80,000 mg/L-O_2 were returned, along with breach conditions for various organic chemical constituents.

The non-compliant discharge was found to relate to manufacture of chemicals for use in the mining industry. The majority of production at the discharge site was petrochemical polymers (reported to be ethyl-hexanoic acid) that are used in the manufacture of explosives. The factory attributed the non-compliance to a three way valve being opened to the incorrect position. This caused a discharge of waste product at unpredictable times.

After enforcement action the customer made several changes to waste management procedures and installed additional storage and treatment tanks. The site has reverted to a batch discharge system and are now performing on-site analysis at their internal (NATA accredited) laboratory, as well as notifying the receiving authority prior to discharging.

Monitoring of the Corio West PS continued after enforcement action (from 2013/04/15) and no further outlier events at 265nm were detected (as indicated by the absence of early morning events in the lowest area of Figure 5). Anecdotal reports from plant operations suggested no further breakthrough events occurred after the compliance action.

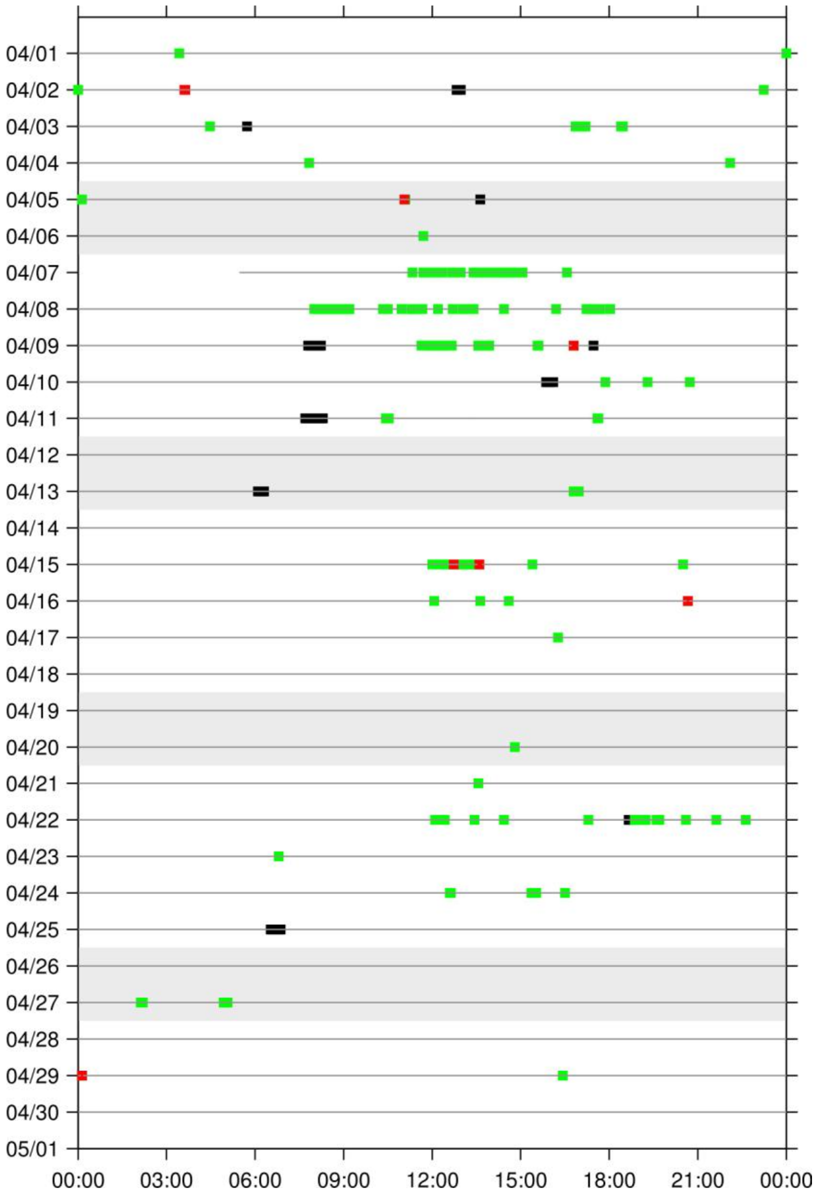
4 SIMILAR PATTERNS AT OTHER WWTP SITES

The derivative spectra analysis used in this work may be applied retrospectively to archived UV/Vis absorption measurements obtained from other WWTP. Analysis was performed on 16 additional sites in New Zealand to test if UV/Vis measurements might be useful for detection of possible trade waste activity at existing monitoring locations.

On average 4 distinct UV/Vis signals consistent with trade waste activity were detected at these WWTP inlet locations. There was some commonality between sites, for example a variety of smaller regional WWTP exhibited prolonged loadings consistent with slaughterhouse activity. This result was not particularly surprising as in all cases the slaughterhouse was known to be a major contributor.

A more surprising result was the variety of short lived (5-30 minute) but highly concentrated abnormalities identified in many of the datasets. Palmerston North WWTP is one such plant and receives a variety of domestic and trade waste loadings. A visualisation of the influent abnormality analysis for May and June is present in Figure 5.

Figure 5: Time distribution of flagged outlier conditions at characteristic of three different abnormal influent conditions at PNCC WWTP. Weekends are shaded with a lighter grey.



Three different abnormal influent conditions are flagged. The most frequent unusual influent type (green) appears to be associated with food processing wastes. Palmerston North hosts a number of major customers which could be the origin of these high solid / BOD discharges. Discharge levels are higher during the working week, reflecting the shift patterns typical of these industries. The most infrequent abnormal influent type (red) is likely an industrial quantity of cleaning chemical. A variety of possible trade waste sources are known in the network, including major research institutes, food processing sites, and commercial laundry operations. Incidences of high hydrogen sulphide concentration (black) have also been identified. Arrival of dissolved hydrogen sulphide at the inlet monitoring location may be indicative of highly septic conditions developing in the sewer network, a potential risk to infrastructure life. At Palmerston North WWTP operations staff are investigating the origin of each distinct abnormality and potential for process problems by building a library of trade waste UV/Vis spectra by testing upstream samples from industry drains.

Similar weekday skewed time distributions of abnormality patterns are obtained at other WWTPs with combined domestic/industrial catchments, supporting the idea that industrial sites are responsible for the majority of abnormalities. Some trade wastes are readily identifiable from their UV/Vis spectra, for example caffeine has a very distinct UV/Vis spectra and intermittent highly caffeine discharges are detected at the receiving works of a WWTP with a coffee processing plant in its catchment. In other cases more concerning chemicals have potentially been detected- analysis of long term monitoring at a major metropolitan plant has identified infrequent UV/Vis measurements matching Cr(VI), which presumably indicates poor trade waste management strategies in heavy industry within the catchment.

There is also some indication of a variety of substituted aromatic compounds in archived UV/Vis spectra logged at the major metropolitan plants. These chemicals have no plausible domestic source so must be present in effluents from chemical manufacturing processes. A variety of aromatic chemicals were present in the problematic waste at NWP, so their presence in New Zealand influents should be of concern. In one case a specific aromatic compound has been detected only a few times per year, and immediately following every occurrence the receiving WWTP experienced nitrification problems.

5 CONCLUSIONS

The front-gate monitoring approach used in this work gives operations a small warning (about 1 hour at NWP) that trade waste is about to arrive at the plant. Before a monitoring system was available at NWP, operators may not have been aware that the plant has received difficult to treat industrial wastewater until indicators from the biological process (such as increased or reduced air demand, variations in dissolved oxygen concentrations) or compliance testing indicated problems.

The industrial waste detected in this work appears to have been untreatable and the biological process may not be able assimilate the industrial contaminant at all, or may be inhibited by the unusual material. This may have resulted in untreated industrial chemicals presenting at the inlet to the AWTP. Fortunately effluent monitoring prevented this water being taken up into the AWTP, however if such breaches are not detected there is a real risk of damage to RO membranes.

Two permanent spectrometers have now been installed at the Northern Water Plant on the combined and refinery influent streams to provide continuous protection. Potential actions in response to an alarm include;

- Temporarily shutting down the intake from the Corio West pump station and diverting the flow to Black Rock WWTP, which has much greater capacity (approximately 15 times the Corio West flow). The significantly increased dilution from the baseline wastewater flows to that plant minimises the impact of the trade waste load;
- increasing aeration air in advance of the load increase to improve removal of soluble biodegradable components; and
- diverting the secondary effluent to protect the AWTP.

Comparative analysis of archived UV/Vis measurements obtained from <N> WWTP in NZ has been undertaken to test if this is likely to be an isolated problem. Analysis of the data revealed almost all WWTP surveyed received short lived abnormal influents, with the majority of events being relatively short lived. Such events are unlikely to be well characterised by averaging sampling techniques (e.g. composite sampling) suggesting use of online time-resolved measurements will be necessary to make progress with unravelling trade waste contributions to sewer catchments.

This work clearly demonstrates the power of real-time non-specific UV/Vis monitoring to protect advanced WWTP processes. However, more investigation is required to establish a methodology to link variability in UV/Vis absorption measurements to non-biodegradable, toxic or inhibitory substances. For example, many food processing wastewaters exhibit distinct UV/Vis absorption patterns but are not toxic to biological wastewater treatment processes. Therefore at present site-specific experience and time is required to train a UV/Vis alarm system, potentially resulting in false alarms. This limitation could be reduced by compilation of a database of UV/Vis absorption spectra of trade waste discharges. UV/Vis absorption spectroscopy can also only detect compounds which absorb light, so could not, for example, detect many types of heavy metals. A side-by-side comparison of UV/Vis and biological alarming systems could better quantify the importance of this limitation.

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