

REAL TIME MONITORING FOR WATER QUALITY EFFECTS ALONG RIVERS AND ACROSS RESERVOIRS.

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ABSTRACT

Rivers and reservoirs contain a vast array of compounds in an almost constantly changing matrix. Drivers to understand the compositional changes in this matrix in real time have always existed however cost and technology availability will always limit what we can know. Drivers such as 9/11 have seen a recognition that significant risk is present for contamination of water sources and produced a driver to explore new technology to mitigate some of this risk. This has seen the installation of full spectrum field version UV/Vis spectrophotometers connected to field computers running special software on a number of river/reservoir drinking water source intakes. The target here being to detect "anomalies" in water composition in real time. This work has had the spin off of making large amounts of spectral data available to others, such as researchers wanting to understand naturally driven changes in these waterways. The unexpected gains in these areas has seen uptake of the technology and processing methods by the water research industry. This paper uses data from a number of such systems as case studies to highlight specific outcomes achieved.

INTRODUCTION

Terms.

Absorption/metre (Abs/m=(labAbs/cm) x100). Wavelength Derivative Spectrum (WDS= mathematical derivative of the spectrum with respect to wavelength)

Difference from average spectrum (DFA= subtraction of a spectrum from a mathematically determined average spectrum)

A254. Absorption at 254 (solids corrected)

Historically a limited range of parameters such as pH, temperature, Electrical Conductivity (EC) have been measured in situ and sometimes continuously in key locations on waterways and in reservoirs. Grab or composite samples were collected and tested in the laboratory for a wider range of nutrients and contaminants such as pesticides and heavy metals.

The cost of laboratory testing is high, in part due to the range of parameters needing testing. This prevents many tests which would be nice to have from being financially justifiable. In many cases, unless the variable was present at reasonably elevated concentrations, or a dramatic change in concentration occurred, events may have passed undetected. In addition, there was a small chance of collecting a grab sample during a shorter term "event". While pH, EC and temperature data may be useful for many applications, it is inadequate for detecting many of the issues facing water resource managers..

This paper looks at the potential to obtain a more comprehensive data set with event based sampling for lab verification using on line field mounted UV/Vis spectrophotometers couple with advanced mathematical techniques. The challenge is then to find the limits of what can be extracted from this new data form. Note that trend plots of parameters such as DOC, Nitrate, Colour, Turbidity etc are based on calculations of "equivalents" from the UV/Vis spectrum.

Methods

All results were obtained using scanning spectrolyser UV/vis spectrophotometers from Austria in either permanently mounted and powered locations or in portable configurations running off battery packs.

Data trends were obtained using scanning algorithms supplied with the instruments and validated by DCM Process Control to provide nitrate, DOC, TOC, Turbidity equivalents, calculated from the spectral data. The spectral data plots were produced using custom Matlab software developed by DCM Process Control.

Spectral Data and Spectral Data Images

Note: all unmarked vertical axis are in Abs/m

Spectral data plots 2,3,4,5 and 9a and 9b need some clarification to make them more easily understood. The images are 3 dimensional data plots with the Y axis the Abs/m which is a function of concentration of various components present. The X axis is the wavelength in nm with the UV part of the spectrum represented by the area from 200 to 380nm and the visible part of the spectrum being represented by the region from 380 to 730nm. The Z axis is time.

Different solutes will be represented by absorptions in appropriate areas of the UV spectrum. For example nitrate, which has its maximum absorption around 210nm. The intensity of the absorption is a quantitative measure of the concentration of the compound. The absorption spectrum obtained in the field will be the sum of all compounds that have some absorption at that frequency. For this reason, the majority of spectral images presented here have had additional math processes applied so as to recalculate the spectra as a difference from average or as a wavelength differentiated spectrum. These forms allow specific components of the raw spectrum to be extracted via mathematics rather than physically as would normally be done via a separation column in a laboratory situation. Spectral images that are seen as 2D images are 3D images rotated into 2D to clarify some aspect. (see plots 9a and 9b.) Various other forms of the spectra the mathematical wavelength derivative of the entire spectrum.

The spectral data plots in Excel –Plot 6 and 7- are simple subtraction spectra in the same way that a lab UV/Vis spectrophotometer essentially subtracts the spectrum measured from a zero reference spectrum. All that changes in these plots is the “zero” we have chosen to subtract the spectrum from to provide the detail required.

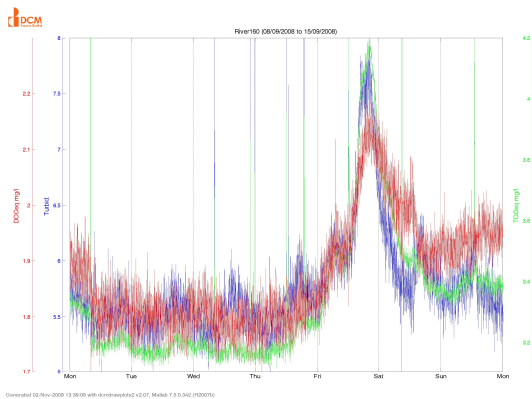
CASE STUDIES

Three case studies covering a range of applications where data from such systems is available from NZ and Australian waters is presented. Confidentiality issues prevent some sites being identified.

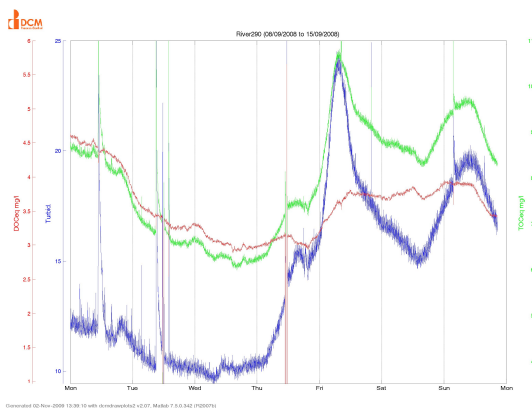
Case Study 1 - Understanding River Dynamics.

Two locations on a large river with a lake source have been monitored over a significant period using full spectrum UV/Vis spectrophotometers running on a 2 minute measurement interval. The locations are about 100 km apart, with numerous tributary streams entering the river along this distance. These tributaries drain intensively farmed areas. In addition, some discharges from dairy and meat processing facilities are also present.

The data in plot 1a and b shows the general trend in absorption values at these two points. The Upriver point has far lower concentrations of components that absorb in the UV/Vis spectrum which includes many organics and nitrate. This is reflected in the scales used in the plots.



Plot 1a. Calculated equivalents for DOC, Turbidity and TOC from upstream site collected over a one week period.



Plot 1b Downriver for same week

The event noted as a peak in all trends on the Friday/Saturday in the upriver data relates to the event noted on the Sunday midday peak in the downriver data as the river has a speed of greater than 1m/s over much of its length. This time difference had already been determined by a large number of events seen in the data over a period of more than 2 years.

The event noted as a sharp peak downriver on the Friday was caused by the same significant rain event that produced the one in the upriver data

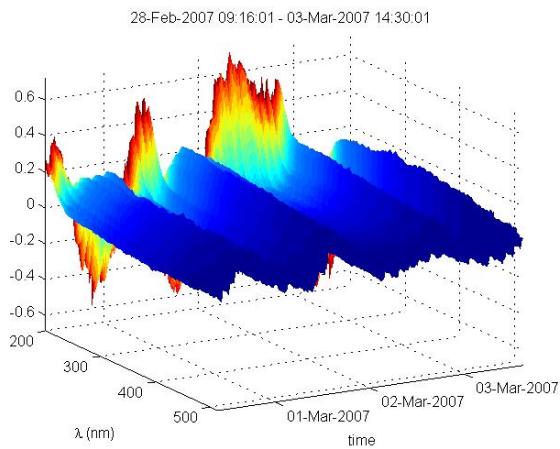
Short term sudden shifts in solids as seen on the Monday and Tuesday in Plot 1b indicate events very close to the measuring point and are unlikely to represent whole of river events.

The data indicates a diurnal fluctuation which had been noted previously in many years of grab samples. These grab samples were taken from different times of the day allowing a rough diurnal shape to be determined. It had been thought that the prime driver here was biological activity in the river. The data were inconclusive as to the cause and the cost to clarify it and its causes was relatively high.

The spectral data indicates that the variation is primarily driven by dilution with the probable cause being the changing volume of cleaner lake water passing through upstream hydro stations (to match power requirements) with some smaller concentration changes caused by the river ecology.

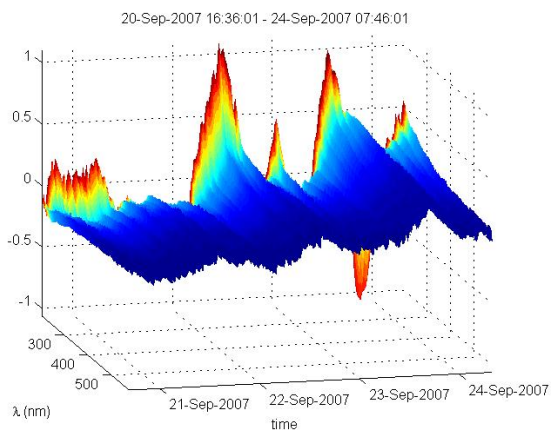
This can be seen in the data by looking at diurnal shifts in spectra. A dilution driven change from a clean source would affect almost all components in the spectrum while a biological change will see an increase in the nitrate spectral absorption during the day as the river biology reacts to sunlight and oxidises ammonia, with a small corresponding reduction in some organics and a rise in others as they are consumed or released by the biomass. In Plots 2 to 5, the nitrate, which absorbs directly in the UV spectrum, can be considered to be the major contributor to the red/orange coloured components. The data in Plots 2 to 5 below show summer and winter spectral images for the two river locations in Plots 1a and b. They show that the degree of dilution and biologically driven change varies over the year. There is more biological activity during the warmer summer

months however the main driver of the visible change, especially in winter is dilution. In winter the temperature is lower and sunlight hours reduced which slows biological changes. Higher winter power use results in more flow and more flow variation through hydro stations creating a larger dilution factor in the diurnal variation.



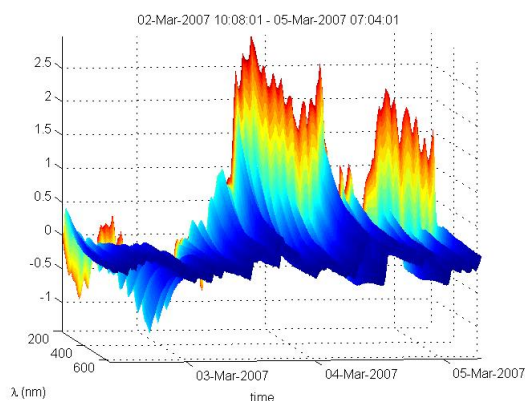
Plot 2. Summer Period Upriver. DFA spectrum

Plot 2 shows a distinct offset between the deep UV components and the rest of the spectrum as seen by the rise in the blue components while the red yellow components fall. I.e partly dilution and partly biological. Note the variation overall is 0.6 to -0.6 Abs/m



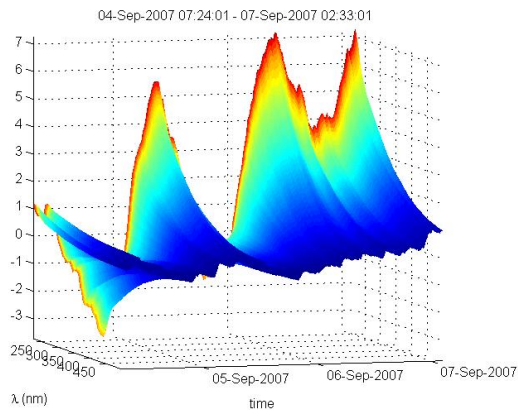
Plot 3. Winter Period Upriver. DFA spectrum

The plot shows a greatly reduced offset between changing concentrations of components indicating reduced biological activity. The overall shift in absorptions is approx 60% greater than during summer which fits a higher flowrate change from hydropower production.



Plot 4. Summer Period Downriver. DFA spectrum

A range of changes can be seen to occur in Plot 4 during the summer over a time relating approximately to that seen upriver in Plot 2. Greater overall variation occurs as many more sidestreams enter between the two measurement locations.



Plot 5. Winter Period Downriver. DFA spectrum

The data from winter clearly shows a substantial change in concentration of various components with an almost exclusively dilution driven change in concentrations.

Extensive further studies will be possible in the future with data from both of these measurement locations and hopefully with more monitoring stations along the river. Data can be automatically downloaded and processed to include spectral subtractions. The output is then the difference in components between the two locations without the confusion of the background material present at the upper measuring station. The ongoing cost for a substantial increase in output will be minimal compared to historic techniques. The intent is to be able to rapidly detect spills into the river by the huge variety of users of this water source in addition to detection of inputs from sources such as a recent incident with a truck tipping over on a river bridge and losing its load into the water.

Case Study 2.

River Monitoring for Point Pollution Ingress.

A Pulp Mill discharging treated waste into a waterway has a river boundary bordering the mill operation. Monitoring by regulators is based on several standard parameters including black spot visibility testing and comprehensive laboratory testing of water quality. The regular river survey of a number of upstream, mid mill and downstream water testing points was augmented by use of an on line UV/Vis spectrophotometer run off a battery pack for a period during the 20 minutes or so spent at each location undertaking other tests. The unit was directly submerged in the waterway by cable tying to a pointed metal pole pushed into the streambed out from the bank.

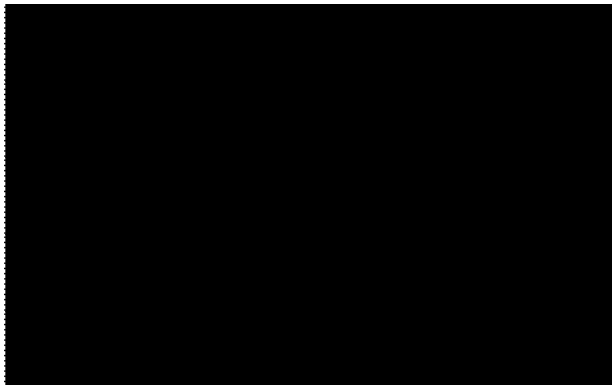
The key in this study was to find out what difference there was between the water quality at various points along the river from the lake source to the ocean outfall beyond the mill intake/discharge points. A normal study involving parameters such as DOC may or may not show the ingress of a new dissolved organic component clearly as the stream river itself is actively removing organics of various types while others are being added. Here we have the opportunity to essentially compare full spectra between each test point which in this case gives us 256 discrete measurements to determine changes in composition not just concentration

The spectral data from the UV/Vis spectrophotometer is shown in several forms. The spectra in Plot 6 are subtraction spectra with the reference being the lake water. This means that the spectra shown are the material that has come into the river since the water left the lake only, with no "background" of the lake water components.



Plot 6 Solids Compensated Spectra- Lake Reference.

The spectra show a clear increase in the organic levels in the river with a shift in components noted particularly in the 280nm band. Interestingly, some components appear to be removed between the downstream measurement point and the ocean outfall. This is likely to be biological in nature and a further study as with Case 1 would confirm this.



Plot 7. Solids Compensated Raw Spectra related to next upstream point.

In this plot the same raw spectra have been treated differently. Rather than using the Lake outlet spectrum as a reference the measuring point above the current point is used as a reference. The changes occurring only between those two points is not visible spectrally. This approach is totally valid as the spectrum is a primary standard and an absolute measure of the sum of the components absorbing in this spectral region. There are 4 spectra which are visibly well away from zero (zero indicating no change between points). A substantial shift is seen between the upstream measurement point and the mill intake. This may be a function of the small industrial area upstream which provides services to the mill. Another shift is seen caused by compounds entering between sampling point 2 and 3 along the mill river boundary. Neither of these shifts were previously known or recognised. There is by far the largest shift after the mill waste enters the river however this also includes some river boundary with dairying operations. The composition is seen to shift here in many areas of the spectrum including into the lower end of the visible spectrum above 380nm although this is small compared to the organic shifts. A fourth negative change is seen in the final point between the downriver and ocean outfall points. It is clear that certain compounds entering via the mill discharge are being removed by the river between these points which are a number of Km apart.

In interpreting these spectra it is important to note that the first point upstream of the mill has already been exposed to extensive logging operations. This will include all aspects of pine tree growth and management including clear felling. The sources of the inputs noted here need to be located and identified to ensure that the mill is not disadvantaged in compliance work where inputs affecting the river actually come from other sources. It is also important that it does accept responsibility for inputs which

may be coming from sources such as leaching from open chemical/wood storage or possibly from it's geothermal power system as seen between points 2 and 3. Since the spectra here effectively represent the spectra of the components we are looking for, testing and identification can be inexpensive and rapid as a simple UV spectrum of suspected sources is all that is needed. It is hoped that such data is used as an effective monitoring and management tool in the future.

Case Study 3.

Protecting Drinking Water Sources and Comparing Components.

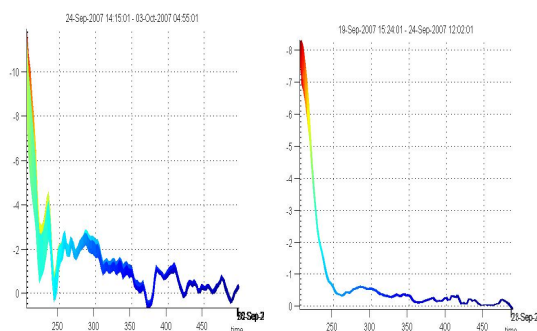
Drinking water or other use of river sources creates a myriad of potential issues where many stakeholders have access to river for intake and discharge. A large and long inland river acting as a water source for a large city based near it's mouth has to deal with many such issues. Extensive agriculture along it's length, extensive public recreational use, plus the presence of many upstream municipal and industrial sources discharging into it's waters results in significant potential for chemical spills and low level residues to be present. The use of such water therefore relies on sufficient timely testing.

The rivers trend plot, Plot 8, shows relatively little variation in key parameters over the one week period with the exception of the event seen on Wednesday 26th September.

Note that the sharp rise of the event and tapered fall off is typical of plug flow events in waterways. The further from the source the less clearly defined the rise and more tapered the fall in values is likely to be. A rain event on the river, which has a huge catchment would produce a clear shift over a long time period which is not seen here. The Turbidity, Nitrate, Colour and DOC trends indicate that it is a short term event from a close by source. It is likely to have come from a discharge from a source in the small town a 0.5 Km upriver. Apart from stormwater there are other legal and suspected illegal discharge points which are generally unmonitored.



Plot 8 . Data Trends for 1 week



Plot 9a and b . WDS spectral data from two separate sites.

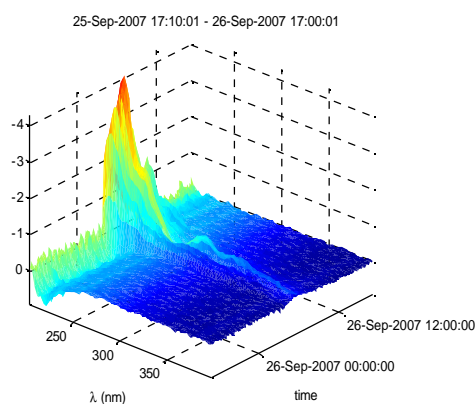
The spectral data from this river is seen to be quite different from other lowland rivers studied. Plot 9b which is from a forested catchment with stock operations for a relatively short length of river upstream, also exhibits significant changes from it's source waters,

however such rivers rarely exhibit the complexity seen in Plot 9a. Plots 9a and 9b are both wavelength derivative spectra which have been inverted for ease of viewing.

In Plot 9a there are 9 days of spectra at 2 minute intervals from the time period from the 24th Sept to the 3rd Oct overlaid on top of each other. Plot 9b has about half that number in the plot from 19th to 24th Sept. The consistency in the composition of both rivers is easy to see.

The event seen in the data trend in Plot 8 on the 26th Sept is visible as a broadening of the 2D spectrum in Plot 9a in several areas of the spectrum below 240nm and between 270nm and 350nm. In contrast 9b shows almost no variation other than a minor one in the very deep UV where no event occurred. The greatly reduced complexity of 9b is related to the upstream catchment.

As an example of how such data can be mathematically processed to enhance the visibility of changes noted in 9b, plot 10 shows the spectral data over the preceding and following 12 hours or so in a difference from average spectrum format. There is no doubt of the change in composition here using this technique. This can be related to the data in Plot 7 with the difference being that Plot 7 relates to different points along the river while Plot 10 relates to differences over time at one point.



Plot 10. DFA plot of event in graph 8

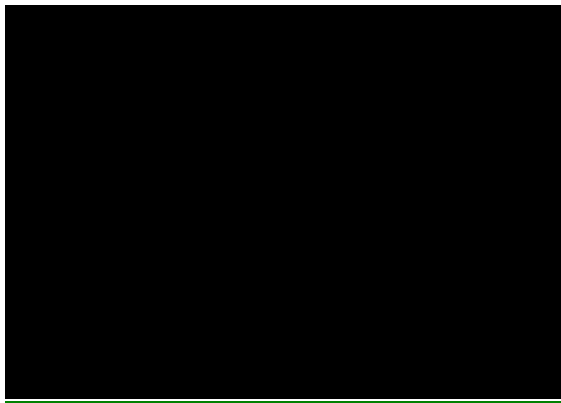
The measuring point on the river is set up to utilise not only alarms based on individual specific parameters but on spectral deviation from normal. This is a very sensitive yet simple solution. Programming to add all possible new contaminants would simply not be feasible due to the number of possibilities. Contaminants can come from spills of diesel or petrol from river craft or from filling stations on the river, from pesticides and herbicides used in agriculture along the rivers path (ref the recent Tasmanian event with the herbicide hexazinone used in forestry operations) or from disasters that may result in any combination of chemicals being present (ref the Sandoz fire affecting the Rhine in Germany).

Case Study 4.

Reservoir Compositional Changes

Reservoirs and Lakes by their nature tend to have long retention times. Depth, temperature, sunlight hours along with surface area and nutrients tend to determine what biological and physical changes occur within them.

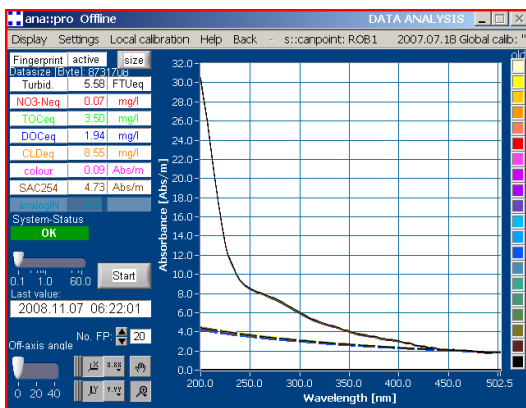
Plot 11 shows inlet and outlet UV/Vis spectra from Lake Waahi in the North Island of New Zealand during an early summer low rain period.



Plot 11. Lake Waahi inlet, outlet and difference spectra

The yellow spectrum is a simple subtraction of the outlet spectrum from the inlet spectrum to provide a spectrum representing only what has been removed from the lake during the water residence time in it. The fact that absorptions by specific compounds in the UV/Vis spectrum are very stable over the range of temperatures and pH's likely to be seen in the field makes it a good indicator of composition. Interpretation of this spectral data is required to relate it to the standard parameters we are used to seeing however it is clear that significant changes are visible.

Plot 12 shows a typical screen on the computer unit and includes the spectral data and interpretation based on algorithms developed for this work.

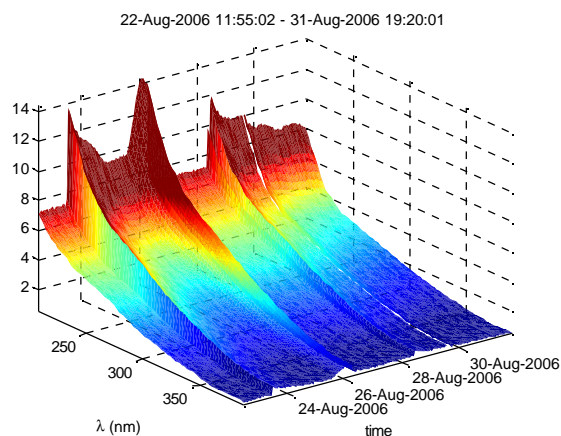


Plot 12. Typical spectra and calculated lab equivalents (eq is short for lab equivalent)

Lab equivalents are based on derivations calculated using algorithms linking spectral data and lab data obtained from lab testing of the field samples. These should always be checked for validity using the on line system to advise when compositional and concentration variation is at a maximum to ensure correlations indicated are likely to be worst case values.

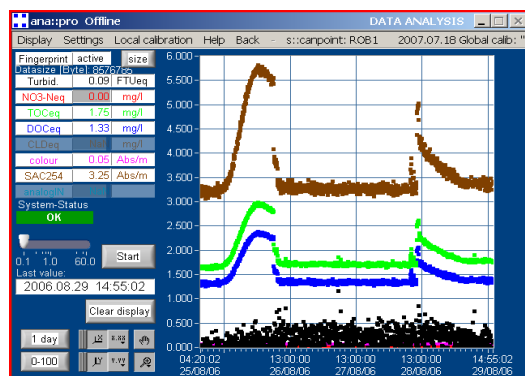
In the case of Lake Waahi, it can be seen that substantial reduction of absorption through the traditional "organics" range which some regulators determine by measuring the 0.45nm filtered absorption value at 254nm. Solids which blocks light at all frequencies is also seen to be reduced, which would be expected with settling processes.

Interpretation of individual spectra, as with any grab sample, tends to rely heavily on assumption of stability of conditions. Image 13 shows the reality of a reservoir inlet and outlet multiplexed by a water plant which switches between the river feeding the reservoir and the reservoir outlet depending on the river water quality. The reservoir outlet is very stable in comparison to the inlet however considerable overall change is found during hotter periods.



Plot 13. Spectral step changes between inlet and outlet of the reservoir.

When interpreted by the software the following trend is obtained for the period from 25th to 29th August 2006



Plot 14. Trend data showing river and reservoir quality.

At 4.20 am on the 25th august the river has the same water quality in terms of calculated parameter equivalents as the reservoir outlet but as a fresh develops the water quality degrades until at around midday the plant operator switched to the reservoir outlet. Two days later when the weather events subsided and the river water quality improved the feed source was switched back to the river.

This process is now automated as an additional unit has been put in place to allow simultaneous measurement.

The availability of systems capable of supplying such huge amounts of data and the ability to make sense of the data provided has the potential to radically rethink the way we currently regulate and sample.

If such systems become an integral part of the monitoring network of our rivers and reservoirs, there is likely to be a shift from traditional sampling to event based sampling, with investigate studies to find specific causes being far more common and cost effective.

CONCLUSIONS

The ability to utilise full spectrum UV/Vis field mounted devices coupled to modern computing and mathematics clearly allows a far greater inherent understanding of water composition and the changes in composition that occur over time.

Measurement of the full UV/Vis spectrum at any one point on a waterway has the potential to vastly increase our understanding of water composition dynamics and to detect previously unrecognised compositional events.

The use of full spectrum UV/Vis spectrophotometers at multiple points along a waterway provides not only a wider data window of aspects monitored at any single point, it enables subtraction spectra to be calculated to identify minute compositional changes unlikely to be detectable in a single system.

Such devices provide a pathway to greatly reduce the amount of routine lab sampling and replace it with specific investigative testing capable of rapidly producing required outcomes.

ACKNOWLEDGEMENTS

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