

# Some Observations on Chemical Water Quality Monitoring

Most chemical monitoring of rivers and effluents consists, almost exclusively, of taking individual, instantaneous, samples of water or effluent. This sampling method is referred to as spot sampling. Obviously, these samples can only be truly representative of the water quality at the time that the sample is taken.

When the scheme of spot sample monitoring was initiated, over 30 years ago, there was less information available on river water quality. Background quality of many rivers was uniformly poor, and was easy to detect by simplistic monitoring techniques. These times have changed, however, and it is now a more challenging task to obtain useful and relevant data. This is due to the fact that impacts on rivers caused by urban run-off, sewage overflows, diurnal variations in effluent quality and agricultural discharges were masked by the general overall poor quality of river water. As background quality has improved, the effects of general variability and intermittent events have become much more significant. This paper selects some of these examples to **demonstrate the need for a more sophisticated monitoring approach.**

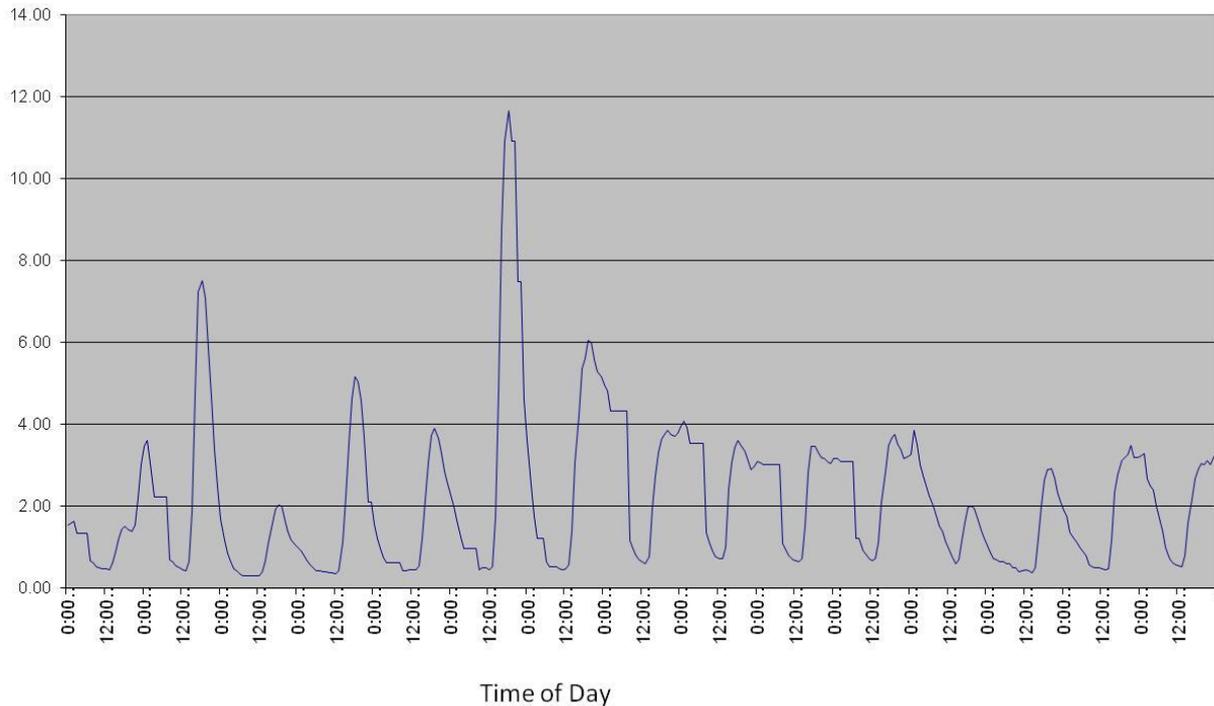
## Diurnal Variation of STW Effluent Quality

Most sewage treatment works exhibit a distinct flow pattern that varies according to time of day. Typically, flows increase during the morning, ease off during the afternoon, increase again during the early evening and then reduce through the night. This flow pattern can affect treatment works differently, but is likely to result in the sewage receiving different retention times in the different stages of treatment, according to the time of day. For example, sewage which enters the secondary treatment phase in the evening, will receive a much greater retention time – and hence better treatment – because there will be less flow during the late evening and overnight. Sewage which enters this phase of treatment during the morning will be propelled more rapidly through the treatment process, giving less retention time and less treatment. The treatment time can be critical, and if it drops below a certain level, the process becomes less stable, and variability in quality becomes much greater. For many works, the effluent that is discharged during the evening and overnight will be of inferior quality to that discharged during the daytime. Another factor that operates, together with the variation in flow at a treatment works, is the variability in strength of the raw sewage, which can, again, result in diurnal variability of the quality of the final effluent.

For many works, therefore, the final effluent is discharged at different flow rates and different quality throughout a 24 hour period. Figure 1 shows the variation of ammonia concentration in a sewage effluent discharge for a 16 day period. This variability is not random, but shows a consistent pattern according to time of day, **with lower concentrations always being during daytime, and peak concentrations occurring during the evening and overnight.** Any monitoring scheme must take account of this systematic variation if a true picture of sewage works performance is required, but sampling is normally restricted to a daytime ‘sampling window’,

the times of which vary, but are normally between about 08:00 and 15:00. Under these conditions, no amount of daytime sampling will ever provide a reasonable indication of effluent quality.

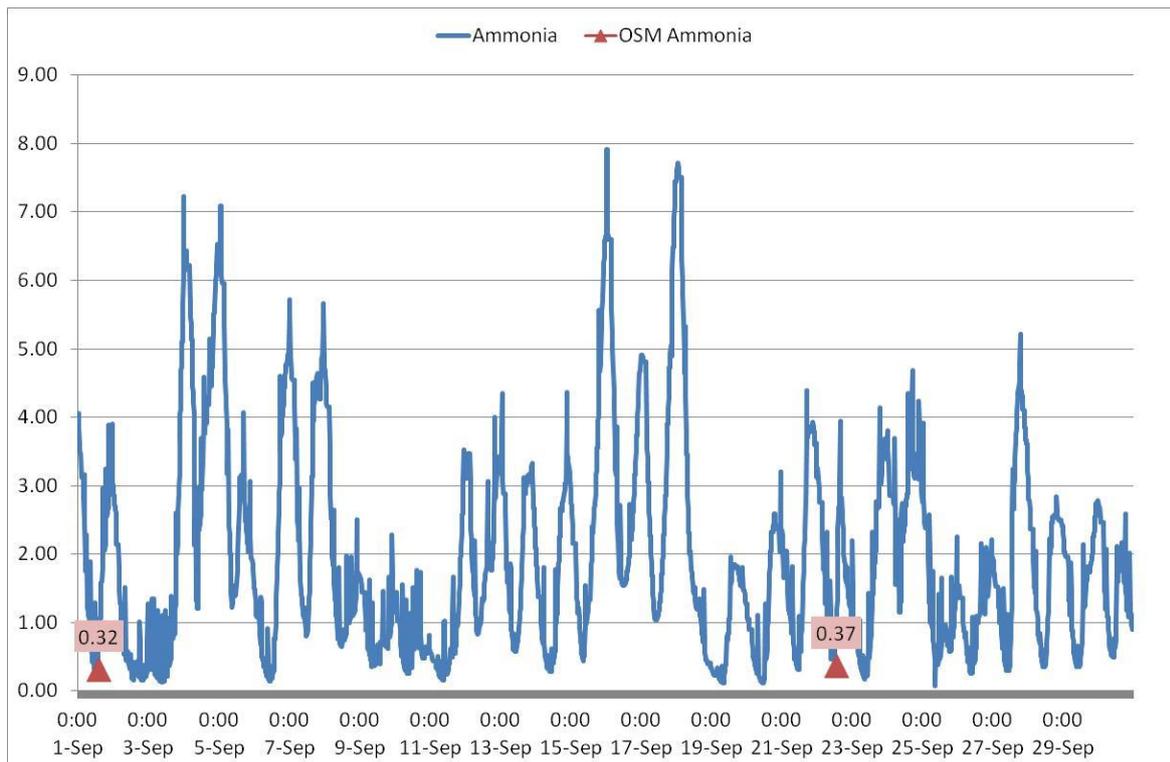
Figure 1. Diurnal Variation of Ammonia Concentration in Sewage Effluent



It is also relevant to note that the degree of diurnal variation at a sewage treatment works depends on the loading factor relative to the design load at the works. New works, because they initially have spare capacity, tend to exhibit very much lower diurnal variability, because sufficient retention time is provided, even for periods of peak flow. **As a works becomes increasingly overloaded, and plant starts to deteriorate, retention times become critical, and diurnal patterns will become more obvious. This makes it even more important to monitor night time quality, because it will be the first indication of impending problems,** and could feature as part of a risk based strategy to act as an early warning system for identifying STWs where performance is beginning to decline.

Figure 2 shows a similar effect for another STW, but with the routine compliance sample results superimposed (these samples are taken by the Water Company and are referred to as OPM – Operator Self Monitoring). It can be seen that these samples do not provide a valid indication of works performance.

Figure 2. Ammonia concentration of STW Effluent for One Month with Compliance Assessment Samples (OSM) Superimposed



In this particular example, the works is very close to failing the consent standard of a 95percentile of 5.0 mg/l ammonia, but the routine samples show it to be complying with ease. The frequency and magnitude of the elevated ammonia concentrations suggest that downstream ecology could be at risk

### Variation in River Water Quality as a Result of Upstream STW Effluent Discharges

Depending on the nature of the receiving watercourse, the effluent might receive different rates of dilution at different times of the day. This might, to a certain extent, reduce the effect of the variable effluent quality on the river. The net result, however, is still likely to be that different bodies of water flowing down the river will be of different quality throughout the day. Under these conditions, for any sampling point on the river, the quality will be dependent on time of day, and will depend on the time of travel from the STW to the river sampling point.

Figure 3. Effect of Diurnal Variation from a STW at a Downstream Sampling Point

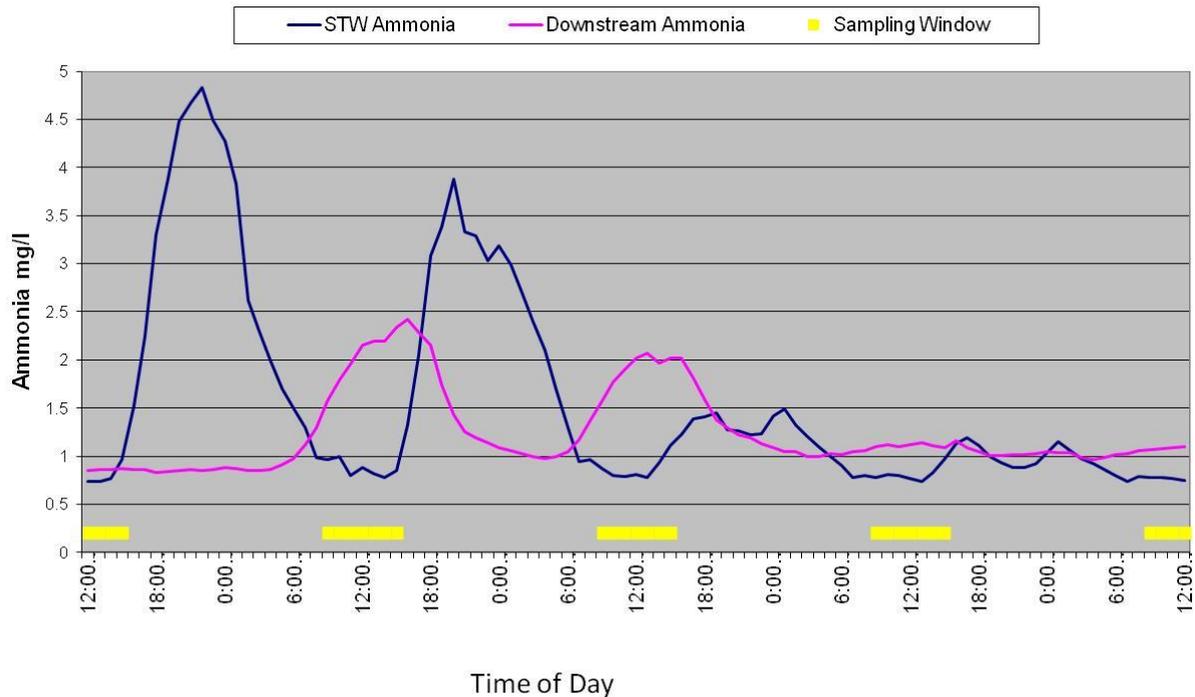


Figure 3 shows how the diurnal variation in ammonia concentration from a STW is observed at a downstream river sampling point. Dilution and attenuation have reduced the magnitude of the effluent variability, but the pattern and effect on the river is still apparent. This diurnal pattern will continue as the river flows downstream, and will be observed at other sampling points at different times, according to the time of travel from the STW discharge to the sampling point. The time of arrival at a sampling point may be outside the sampling window, in which case it will never be sampled, or within the sampling window, when it might be sampled according to chance. This can cause much confusion, because if the poor quality water is sampled during the day at one point, it will be assumed that the source could not be the STW, because the samples from the STW were taken during the day, when quality was good. The sampling window ensures that there is no knowledge of the poorer effluent quality that is discharged at night from the STW. Similarly, incorrect assumptions can be made when comparing the quality at other sampling points, depending on the time that the poor quality water flowed past the sample point and whether this was within the sample window. It is important to emphasise that the true picture of river quality on a day to day basis might be exactly the same, but the results of the spot samples might be showing differences according to the time when the samples were taken.

For the specific example shown in Figure 3, the diurnal ammonia peaks from the STW will never be sampled because they occur outside the “sampling window”, but the ammonia peaks at the downstream sample point occur within the “sample window”, so they may be sampled. In this situation, the STW is not being adequately regulated and downstream quality problems might be blamed on other sources.

## Variations in Dissolved Oxygen Concentration in Rivers

One of the most widely used indicators of river water quality is dissolved oxygen. In many rivers, the dissolved oxygen content varies significantly throughout the day, due to plant photosynthesis and respiration. Dissolved oxygen levels are normally lowest around dawn and highest at some time in the early afternoon. Levels will also change throughout the day according to oxygen demand, but normally the photosynthetic pattern will be the dominant factor. Figure 3 clearly shows that the variation in dissolved oxygen is not random, and the variations throughout the day are significant. Even within the sampling window there is a high level of variability, and a significant difference will be found between samples taken at different times. False trends can be apparent if no account is taken of sampling time. The plant photosynthetic effects are closely related to sunshine. On days with extensive cloud cover, photosynthesis decreases and the DO diurnal pattern in rivers is less pronounced. Samples taken around midday on a cloudy day will have much lower concentrations than on a sunny day. Figure 4 shows an example of this for August 7 and, to a lesser extent, August 3.

Figure 4 Dissolved Oxygen Concentration at a River Sampling Point for a 10 Day Period

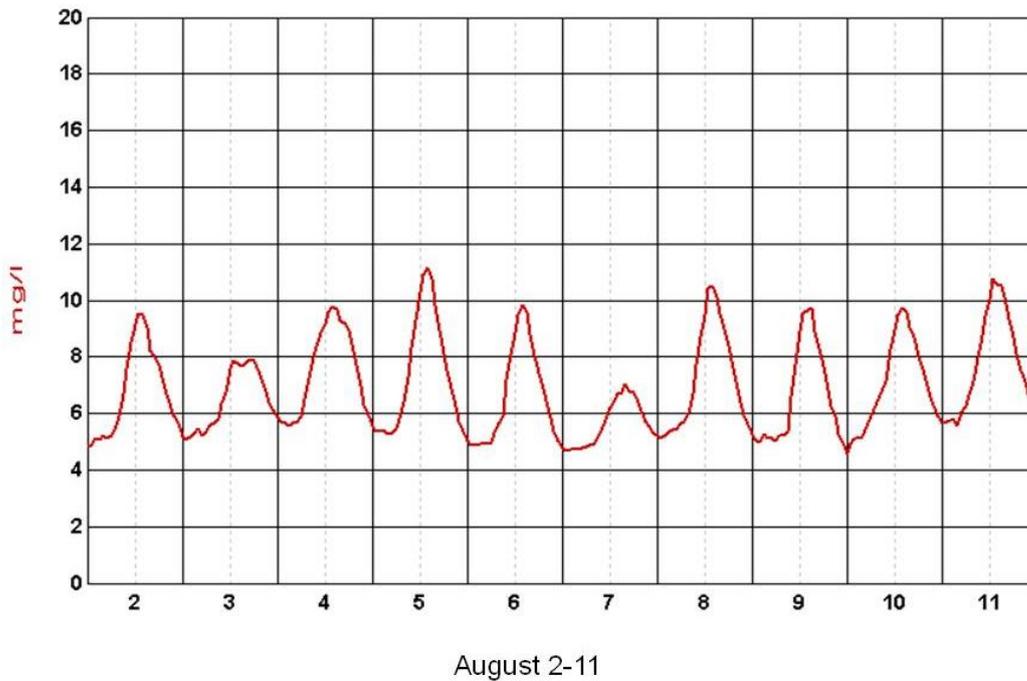
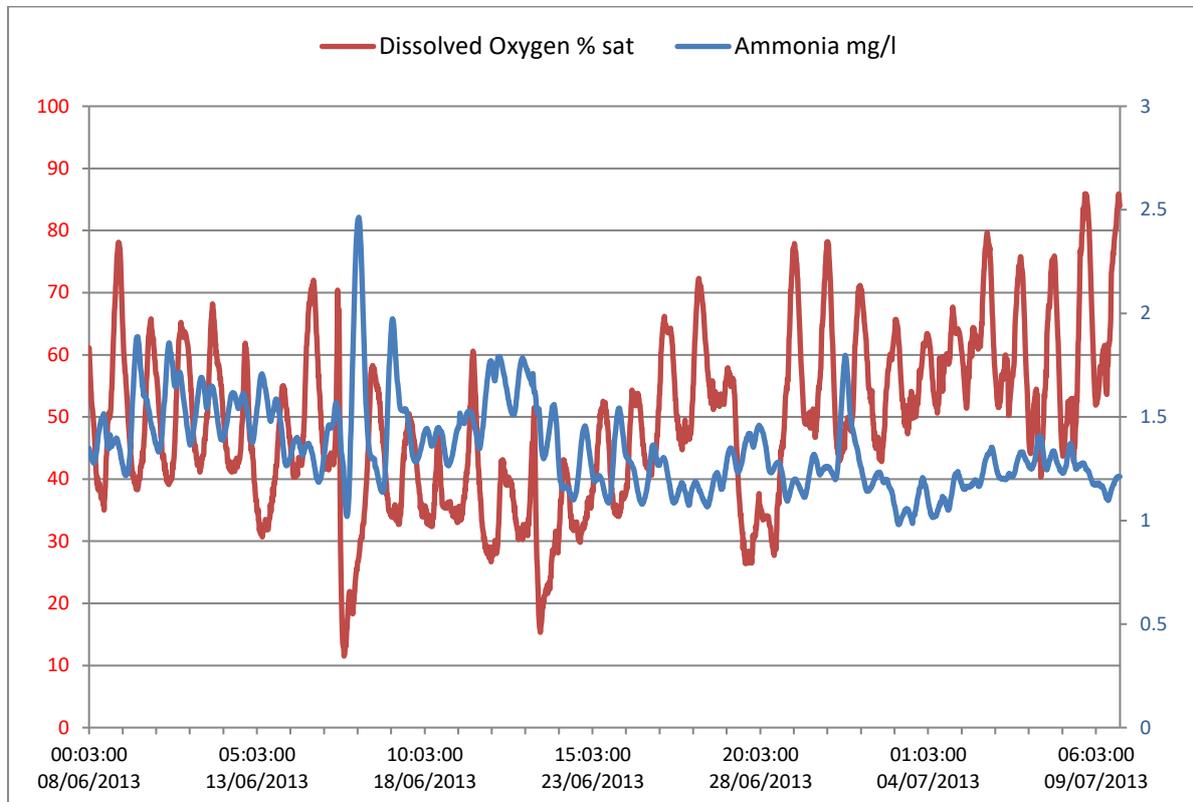


Figure 5 shows, for one month, the combined effects of the above points regarding diurnal variation of ammonia concentration in sewage effluent and dissolved oxygen in a river, at a river sampling point downstream of a sewage effluent discharge. It can be seen that it would

be very difficult to gain any useful information regarding water quality at this site by taking an occasional spot sample.

Figure 5 Dissolved Oxygen and Ammonia for One Month at a River Sample Point

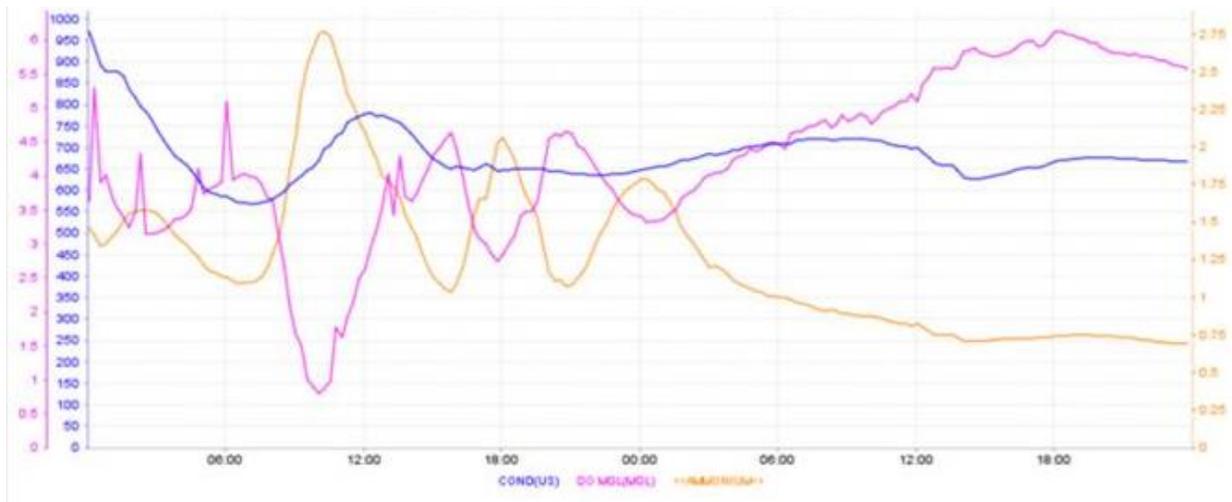


### Variability Due to Rainfall and River Flow

Weather related events, particularly rainfall, can have a strong influence on river and effluent quality. Wet weather discharges occur from STW storm tanks, CSOs, and run-off from agricultural and urban areas (sometimes referred to as diffuse sources). Many of these discharges are not normally included in the spot sample programme, so there is little information to link poor water quality with these events.

Figure 6 shows the effect of a discharge from storm tanks at an upstream STW. This is highly significant in terms of the likely ecological effect, but is very unlikely to be detected by occasional spot sampling.

Figure 6 Effects of a Storm Tank Discharge on a Downstream River Monitoring Point



Rainfall will also cause an increase in flow to STWs, which is likely to exert extra pressure on treatment processes and result in variable effluent quality throughout the rainfall event. Normally, quality will deteriorate initially and then recover later in the event. The quality deterioration at some works may contribute to significant downstream problems. The chance of a spot sample of the effluent being taken during the critical stages of a rainfall event is very small. It should be emphasised that in many cases, depending on the individual catchment and the nature of the STW, it does not follow that poor quality wet weather discharges will be adequately diluted by increased river flows.

River flow is obviously affected by rainfall, and will have a dominant influence on most aspects of water quality in many different ways. Probably the 3 most important effects of river flow are:

- An increased volume of water will dilute some substances that are normally present in river water.
- Wet weather discharges and run-off to the river will increase the level of certain substances that are associated with run-off or sewage overflows.
- Increase in river velocity will resuspend river sediment and increase concentrations of substances contained in the sediment.

It is therefore not normally appropriate to compare samples that have been taken under different flow conditions, and it will be a matter of chance as to how many samples in a data set have been taken at times of high flow. This makes it extremely difficult to assess the significance of any changes that might be shown by the data if no account is taken of river flow.

River water quality is likely to vary throughout periods of change in flow rate and will depend on the intensity and duration of the rainfall event. Increased flows will also be maintained after rainfall has ceased, depending on the nature of the catchment. Conversely, for some catchments there might be little effect on river flow during the initial stages of rainfall. It is

most unlikely that, overall, there will be a good correlation between quality and river flow in all rivers because of the complexity of the above factors.

The following Figures 7-9 show how water quality at a river site can be affected by rainfall and river flow. The charts were prepared from the *Catchment Sensitive Farming Project* data sets, consisting of auto-samples and manual spot samples. The manual spot samples were individual instantaneous samples taken at approximately weekly intervals, whereas the auto-samples were taken by automatic samplers, which were remotely activated when river flows reached a certain level. These took either one hourly or two hourly samples until flows subsided.

Figure 7 shows the ammonia concentration for both sets of samples at the River Eden, taken in 2014. Even though the spot samples were taken at a higher frequency than normal (weekly rather than monthly), it can be seen that they completely failed to detect the higher ammonia values that occurred during wet weather. The ammonia was probably indicative of a storm sewage discharge in the close vicinity to the sampling point, and might be of significance to the overall quality of the river downstream of this location, but it is unlikely that it would ever have been detected by routine spot samples.

Figure 7 River Eden at Sheepmount

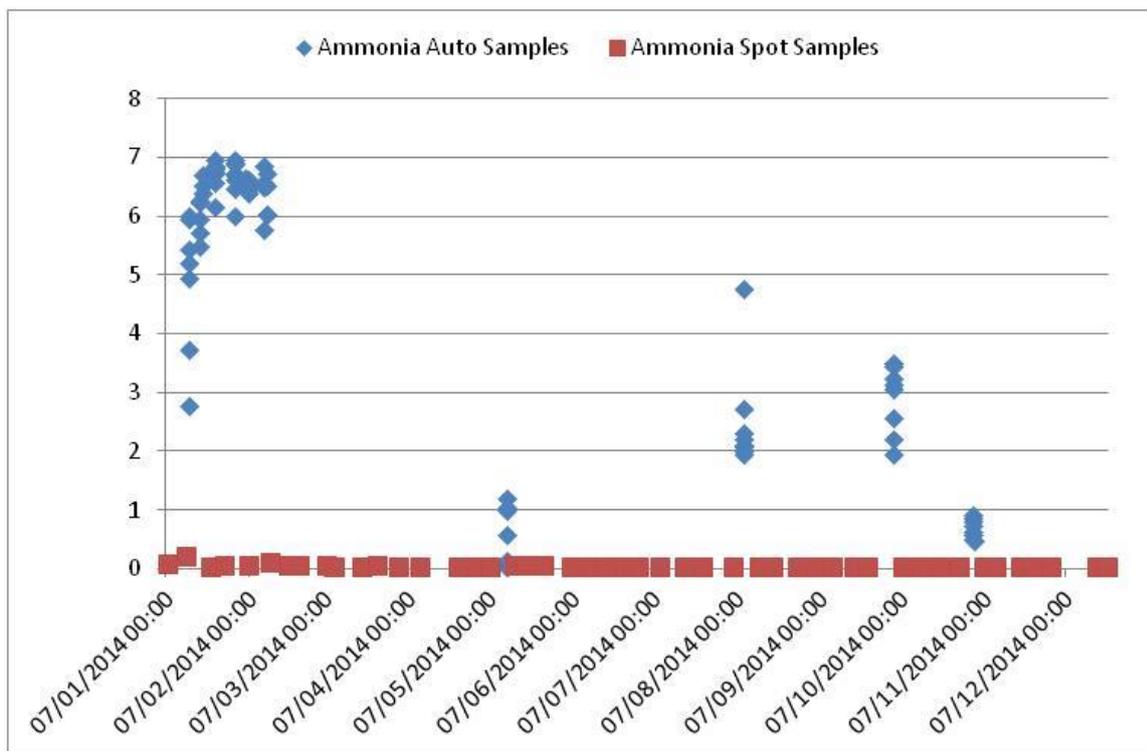


Figure 8 shows the concentration of suspended solids for spot samples and auto-samples taken at a sampling point on the River Wyre. It can be clearly seen that all of the spot samples contain low concentrations of solids because they were taken at times of low river flow. This has implications, not just for the monitoring of solids, but for monitoring any

other substance that is associated with solids or run-off. This demonstrates the difficulty of attempting to characterise river quality by taking random spot samples. **There are many substances, including pesticides, heavy metals and harmful organic compounds that will be present in the river at different concentrations under different river flows. Random spot sampling will provide a very confusing picture of the various pathways of these substances, their sources and the likely environmental impacts.**

Figure 8 River Wyre at St Michaels

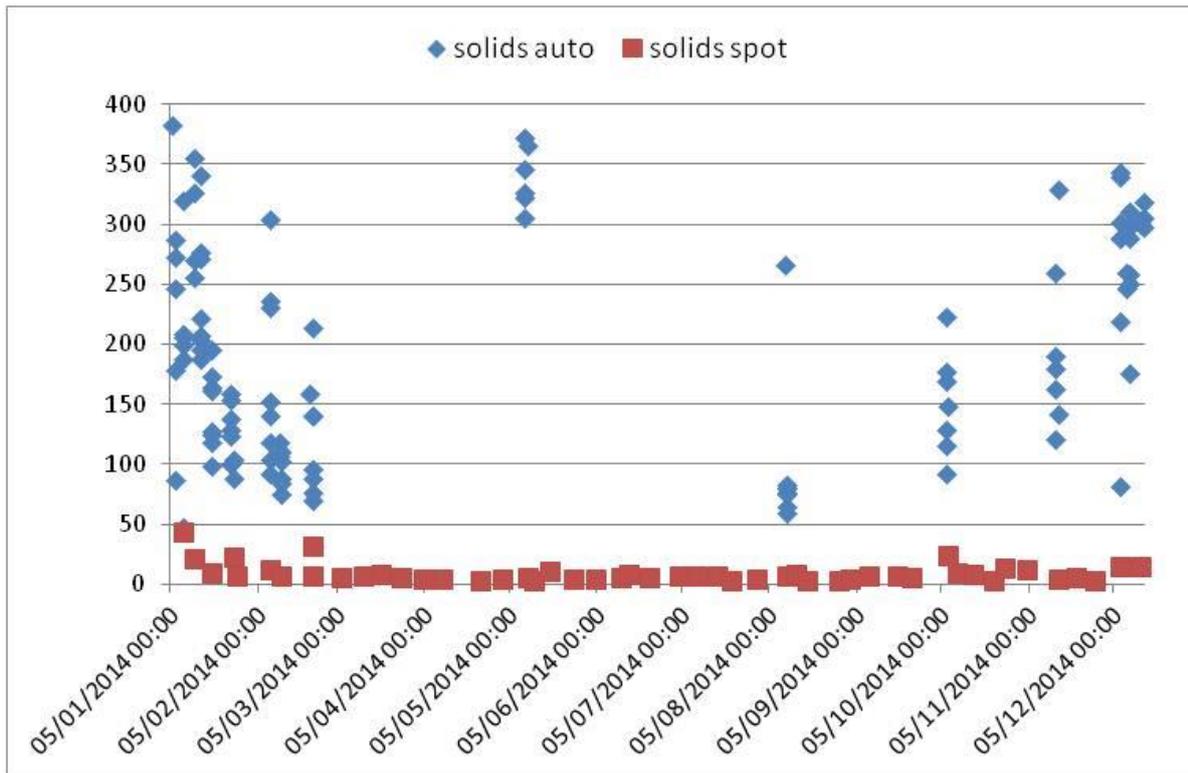
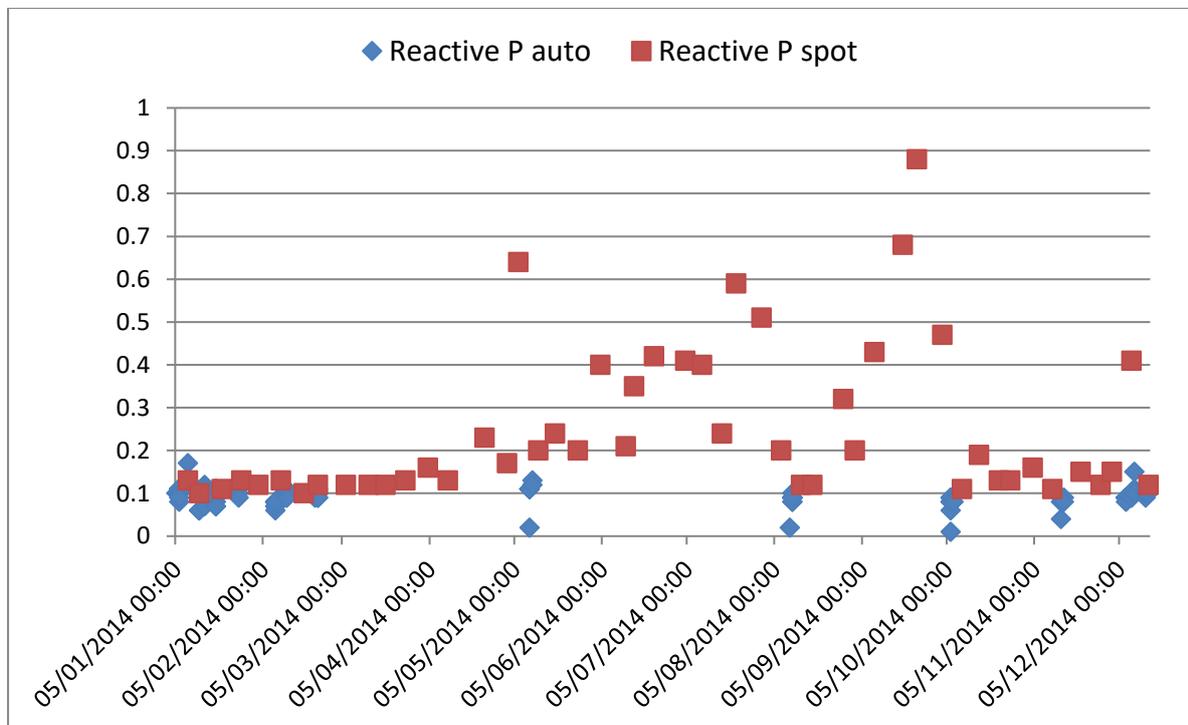


Figure 9 shows the concentration of reactive phosphorus for both sets of samples taken from the River Wyre. In this case, it can be seen that the higher river flows provide dilution, and the **reactive phosphorus is lower in the auto-samples that were taken under high flow conditions.** There are other rivers where the reverse would apply because rainfall run-off from agricultural land or sewage overflows might increase the concentration of phosphorus in

wet weather. There are also situations where the concentration of phosphorus would fluctuate according to the intensity and duration of the rainfall event. Whatever the case, it would be very difficult to gain an understanding of the true picture simply by using random spot sampling.

Figure 9 River Wyre at St Michaels



The above examples show that small numbers of randomly taken spot samples are unlikely to show the true picture of river quality, because of wet weather effects and variations in river flow. Under these conditions, it is inevitable that false assumptions will be made and false trends detected, according to the chance of occasional spot samples coinciding with rainfall events. **It would be very unwise to draw any conclusions from a data base that does not take account of river flow at the time of sampling.** This clearly demonstrates the need to be absolutely clear with regard to the objectives of any monitoring programme and to ensure that the monitoring is appropriately targeted to meet the objectives.

### Use of Spot Sample Data

There are many large spot sample data bases available that are used for numerous purposes, but great care needs to be exercised when using such data. It is important to consider the specific objective and what data is required in order to achieve this, rather than to just use data

that is readily available. Some of the areas where there may be potential problems in using data derived from spot samples are summarised below:

- Assessment of STW compliance with consent conditions
- Identifying the impact of a discharge on a river
- Detecting trends in river and effluent quality
- Identifying sources of pollution
- Comparing water quality at a number of different sites
- Calculating loads for source apportionment studies
- Developing water quality models

The use of spot samples is sometimes justified on the basis that they can form part of a multi-layered system of monitoring for detecting possible problems and trends, which can then be followed up with more intensive monitoring. The difficulty with this concept is that, in order to detect trends, a fairly sophisticated approach is required, and for the examples given in this paper, any method of utilising small numbers of random samples is unlikely to achieve a reliable level of trend detection.

### Overall Summary of Problems Associated with the Use of Spot Samples

The basic problem is that, in situations where quality varies significantly with time of day and/or with weather conditions, it is not possible to obtain reliable information by taking small numbers of random spot samples. This should not be of any surprise, because it is well understood that many everyday situations change according to time of day and the weather.

The existing form of monitoring allows chance to play a major role in the data that is obtained. Small numbers of random spot samples are unlikely to detect intermittent deterioration in water quality, but if by chance, some samples are taken on these occasions, the results are likely to be misinterpreted, leading to false assumptions regarding trends and sources of pollution. Although the sensible use of statistical processes can sometimes be of help in the understanding of data that is acquired under such conditions, there is a limit to the value that can be obtained from a method of monitoring that allows chance to play such a big role.

It is accepted that some of the points covered in this paper do not affect all rivers and all STWs, but it is likely that it is the areas where there are known to be problems which are the areas being affected by wet weather discharges, effluent variability and DO fluctuations. This makes it all the more necessary to recognise and understand these problems. It is also of interest to note, that the existing practice of using random spot sampling probably only performs well in situations where there are no problems caused by poorly treated sewage, wet weather discharges from STWs, urban run-off, CSOs or contaminated agricultural drainage. In these situations, conditions are stable and monitoring is largely unnecessary. There is, therefore, a very strong case to develop strategies based on risk, which will allow resources to be diverted to those areas where more effective forms of monitoring are required.

### Ways Forward

Although the above examples have serious implications on almost all components of water quality management, there are some fairly simple ways forward. Many of the problems outlined in this paper can be avoided by giving greater priority to the interpretation and understanding of data, rather than just accepting statistical outputs at face value. **The solution to many monitoring problems is to make better use of continuous monitoring, and to target monitoring to the time or situation which is most relevant.** The most cost-effective option for many situations is likely to be to **monitor continuously for a short period of time**, and to analyse this data to select the most appropriate method of targeting for future monitoring, according to risk.

For over 20 years, the Environment Agency has been developing different forms of continuous monitoring, which have been successfully deployed at a large number of river, estuary and discharge sites. This equipment can generate comprehensive and reliable data, which could become an important component of a modern and sophisticated monitoring strategy.

It is important to stress that, although this type of monitoring is referred to as *continuous*, this does not imply that it needs to be continuous for long periods of time. **The equipment used is highly versatile and can be quickly and easily deployed for just a few days, weeks, or whatever timescale is necessary.** It is most effectively used in a targeted manner to cover vulnerable areas, using knowledge and understanding of the information that is required. **Even short periods of continuous monitoring can provide much needed information on patterns of variability**, which can then be used to ensure that monitoring is targeted to the needs and risks of a particular situation rather than to employ methods which are vulnerable to chance. In terms of cost benefit, it is important to recognise that, if a low cost form of monitoring cannot produce the required information, it has no benefit whatsoever, and might even have harmful consequences if it supplies misleading information.

There will always be a range of substances that cannot be monitored remotely or continuously, and that will require spot samples to be taken for laboratory analysis. In this case, it is essential that the sampling is targeted to those times and situations that are most relevant for supplying the required information.

**Targeted monitoring is likely to be more demanding than the simple pre-programming of samples, but the concept of Citizen Science and Volunteer Monitoring will make this considerably easier to achieve, particularly with regard to the likely availability of local people to carry out monitoring at short notice, such as during rainfall events.**

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