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THE DETECTION OF PHENOL IN UPLAND WATER SUPPLY CATCHMENTS USING ULTRA-VIOLET ABSORPTION SPECTROPHOTOMETRY

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Abstract

The need to protect drinking water against pollution is well recognised. This is especially true in the case of phenolic compounds. In recent years there have been a number of high profile water quality incidents involving these compounds. Phenolics are particularly problematic as they originate from a variety of sources and cause taste and odour problems at extremely low concentrations. i.e. at levels lower than routine monitoring practices detect.

This paper describes a series of experiments carried out to evaluate the utility of Ultra-Violet (UV) absorption technology for the routine detection of very low levels of phenolic compounds. This technology has been used for many years to detect changes in the quality of water at potable supply intakes and is known to detect certain phenolics at low concentrations. The objective of the trial was to evaluate the improved instrument specifications for the monitoring of raw water supplies in upland catchments. The potential of this approach for the screening of raw supplies for phenol was assessed.

The instrument was found to have an effective detection limit of 0.4mg/l of phenol in raw upland river water. This limit of detection, given the very low levels of phenolics experienced in upland supply streams, means that UV technology in this form is not suitable for the screening of phenol in upland streams. The poorer than expected limit of detection is probably due to the high absorption by the organic compounds present in upland waters. It may therefore be possible for lower limits of detection to be achieved in waters that contain lower concentrations of organics. Further research would be required to investigate this fully.

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N.B. *Phenolics*, *phenolic compounds* and *phenols* are used interchangeably throughout this paper to refer to any compound in the phenolic family. *Phenol* is used to describe the specific compound phenol (C_6H_5OH).

1. Introduction

The protection of drinking water supplies is fundamental to both human health and the satisfactory compliance with legislative and consumer requirements. Yorkshire Water Services (YWS) supplies 1500Mld (Megalitres per day) to their 4.5 million customers in Yorkshire and Humberside. Approximately 40% of this is collected from upland gathering grounds. The inherent quality of this water is determined by a number of processes impacting on its passage through the upland catchment.

Common problems affecting the quality of water from upland supply catchments include water discolouration by organic acids, low pH, protozoan contamination (including *Cryptosporidium* oocysts) from agriculture and high levels of manganese and suspended sediment. These can ultimately affect the efficiency and cost of treatment and the quality of the water available for distribution. An additional phenomenon known to exist in upland catchments, but which is poorly understood, is the release of phenolic compounds. These compounds can be particularly problematic to water supply companies and their early detection is therefore paramount.

1.1 Phenolic compounds:- a definition

The term "phenolic compound" refers to any organic compound whose molecules contain one or more hydroxyl (OH) group bound directly to a carbon atom of a benzene ring. In their simplest form, phenol, the molecular structure contains 6 Carbon and 5 Hydrogen atoms bound in a ring, with an OH group directly attached, as shown in Figure 1 below.

Any compound which contains this structure anywhere in its molecular form can be said to be a *phenolic*. The family of phenolic compounds, based around phenol itself, is therefore huge with a diverse range of properties and hence problems.

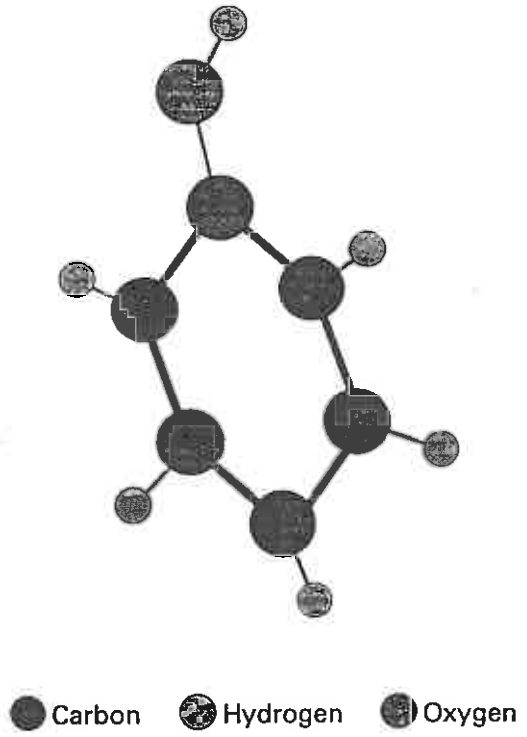


Figure 1 - Molecular structure of phenol (C_6H_5OH)

1.2 The significance of phenolic compounds to the water industry.

The primary significance of phenolics in drinking water is their ability to cause unsatisfactory tastes and odours at extremely low concentrations. Several phenolics have the ability to impart tastes and odours to drinking water supplies and edible aquatic life at parts per billion levels (µg/l). They have also been shown to be toxic to aquatic life at parts per million levels (mg/l). The organoleptic properties of phenolic compounds have been the primary reason for stipulating such low compliance levels in drinking waters (EC MAC for total phenols = 0.5 µg/l).

When drinking water is treated prior to distribution it usually undergoes chlorination. If phenolic compounds are present in the water, they may react with free chlorine atoms during treatment. Phenol itself has been found to be the most reactive aromatic towards chlorine incorporation (Buikema *et al*, 1979). Chlorophenols, which have taste and odour thresholds below levels at which potable water is normally tested, can therefore easily form if phenolic compounds are present in raw waters (Horth *et al*, 1992). These adverse taste and odours are often detected first by customers at the tap, resulting in complaints to the supply company.

Phenolic compounds are also known to affect public health, and in some cases can be highly toxic. In high concentrations they can also cause diarrhoea, nausea, vomiting, abdominal pains, mouth sores, dark urine and tissue burns in consumers (Jarvis *et al*, 1985). High concentrations of phenolic compounds in freshwater can be mutagenic to *Escherichia coli* and toxic to microbes, algae, plants and animals (Buikema *et al*, 1979). Milner & Goulder (1986) found that the activity of certain bacteria was inhibited by increased levels of phenolic compounds in a tributary of the River Calder.

In recent years there have been a number of high profile water quality incidents involving phenolic compounds. Perhaps the most widely publicised event was on the River Dee in Wales where a spillage of phenol caused the contamination of supplies to two million people in the north west of England. Smaller scale incidents have occurred in upland supply catchments in Scotland (River Dee) and Yorkshire (Harrogate / Harlow Hill taste complaints, April 1993). The incidents that have been traced to upland supplies are thought to of originated from diffuse sources, probably from naturally occurring phenolics.

The precise phenolic compound that causes the taste and odour complaints is thought to vary between occurrences (spatially at least) and is not accurately known (Horth *et al*, 1992). In the case of the incidents in Yorkshire, phenol and para-cresol (4-methylphenol) were detected in the upland waters at the time and thought to be the main precursors. The precise source and processes causing their mobilisation are as yet unknown.

Due to the extremely low concentrations of compounds thought to have caused the problems (i.e. parts per billion), precise sample analysis is currently considered to be the only accurate method to detect all of the (possible) problematic compounds. This involves the analysis of water samples in a gas chromatograph, a skilled and expensive process. However, in order to establish some indication of the sources and mobilisation processes of phenolic compounds in upland catchments a long-term intense sampling programme would be required. This, given the sporadic nature of the 'phenol flushing events', would produce a very large number of samples. As an appreciable amount of these may contain no phenolics, sophisticated laboratory analysis by GCMS (Gas Chromatography - Mass Spectrometry) would not be cost-effective.

The need for a screening tool capable of detecting 0.1µg/l of phenol in upland waters has therefore been identified (Foster, 1995). This report describes attempts to optimise the UV absorption technology currently used to protect supply intakes for this purpose. As phenol is the fundamental compound to the phenolic family, was present in raw water samples at the time of the incidents, and was readily available in the laboratory, efforts were focused on this compound.

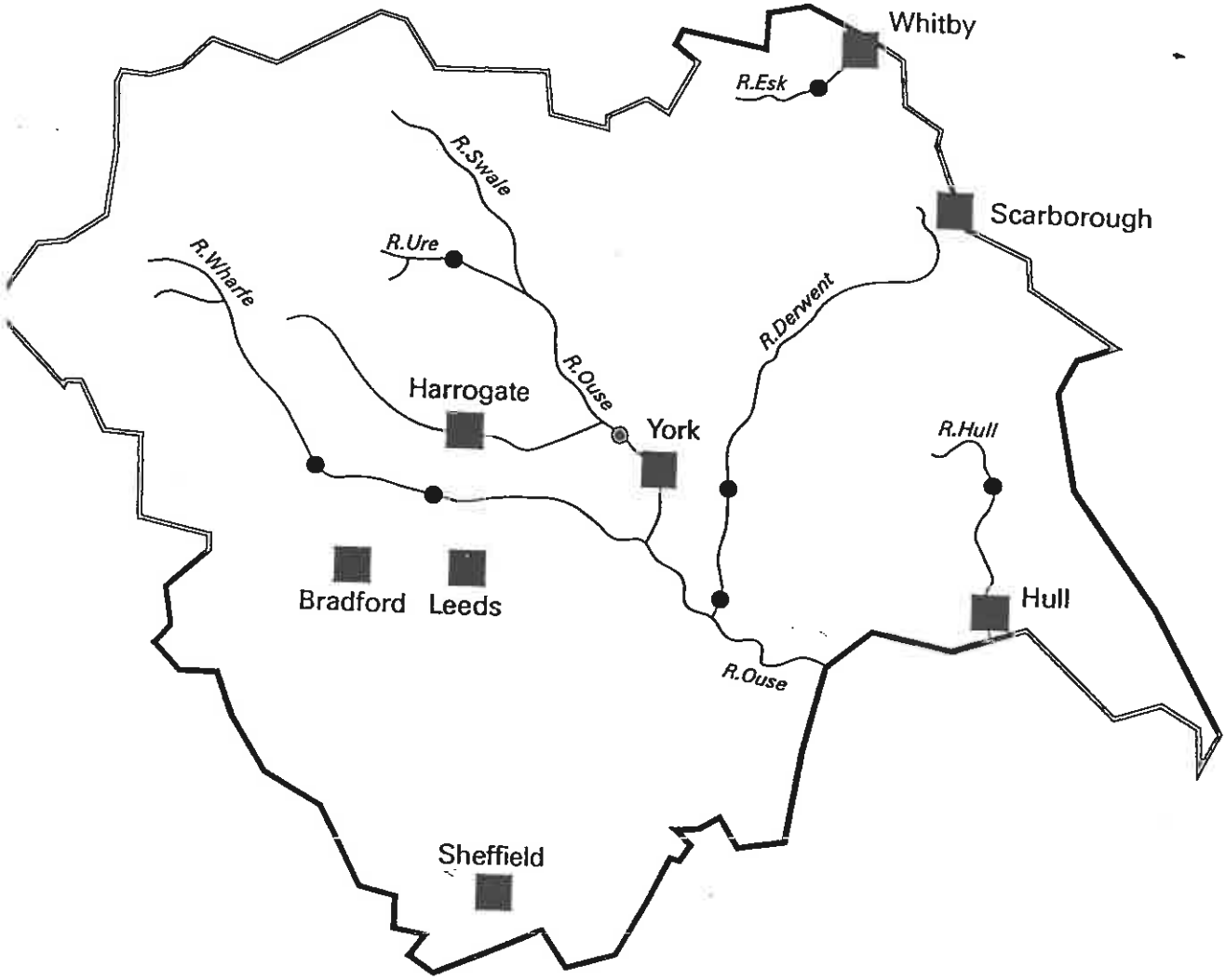
1.3 The Yorkshire Water intake monitoring system

The vulnerability of potable supply intakes to changes in raw water quality, especially incidents involving problematic substances such as phenols, has prompted Yorkshire Water Services to implement a number of non-specific intake protection monitors (Whitworth, 1994). All but one of these monitors employ ultra-violet (UV) absorption technology (the other being a fish monitor on the River Derwent).

The *Watersure* intake protection system is based around the Uvikon 860 and 940 scanning spectrophotometers and is in use at eight major river intake sites throughout the YWS region (Figure 2). It was developed by YWS staff to detect a broad range of organic pollutants at parts per million levels. The system is designed to collect a sample of river water every 5-10 minutes. This allows continuous unattended monitoring of intake water quality even where alterations in background absorbance are experienced due to changes in flow conditions.

The system operates by passing ultra-violet light through a sample of river water. The transmission of light through water is affected by substances carried within the water (suspended and dissolved materials), as well as the water itself. Projecting a beam of light of known intensity through a water sample and measuring the light that passes through gives a measure of the sample absorbance. The amount of energy that is retained by the sample will be a function of the distance of travel from source to measurement (the path length) and the contents of the water sample. Organic compounds are known to absorb light in various wavebands, however there is a 'window' between 250 and 290nm (nanometers) which is largely unaffected by variations in absorbance caused by natural changes in water quality. An absorbance scan between 250 and 290nm through a 4cm cell is therefore used routinely to monitor intake quality for the presence of pollutants.

Figure 2 - Major river intakes in the Yorkshire Water region utilising the *Watersure* intake monitoring system



Key

● = River intake using the *Watersure* intake monitors ■ = Urban area

▬ = Boundary of Yorkshire Water's supply area —— = River

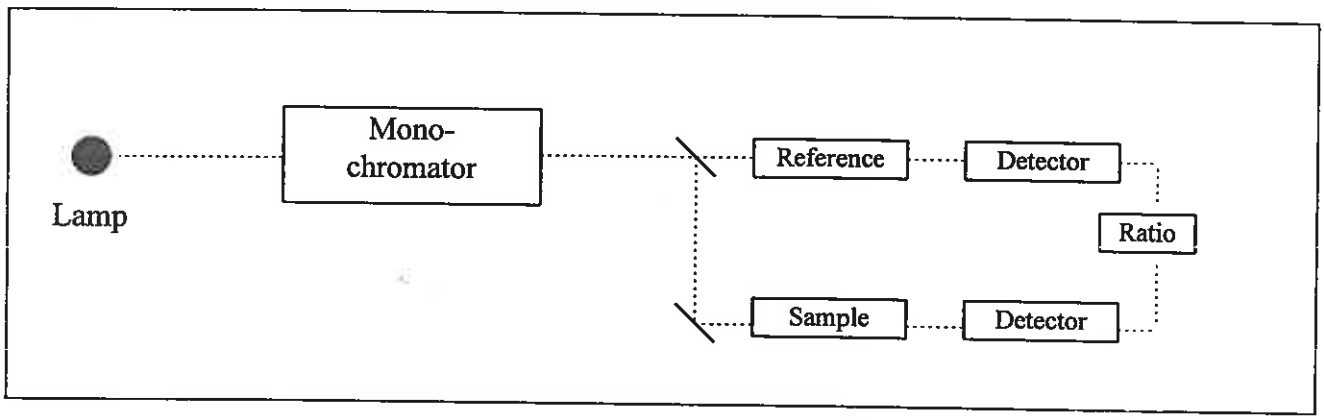
By analysing the difference between the first order derivatives of the most recent river scans with previous UV scans, the existence of pollutants can be distinguished from natural quality variations. Experimentation has shown that the technology, operated in this format can reliably detect 1.0mg/l of phenol in raw river water.

It was therefore suggested that the use of an updated instrument could significantly improve sensitivity. If detection limits of 0.1µg/l could be reached then the system may have applications for the screening of upland supplies. In order to establish the feasibility of UV absorption technology for use as a screening tool in the study of phenolic compounds in upland catchments a Uvikon 922 spectrophotometer was obtained on loan from Kontron Instruments of Watford.

2. The Uvikon 922 Spectrophotometer

The Uvikon 922 is a double beam scanning spectrophotometer that allows the measurement, analysis, display and storage of absorbance data. The manufacturers claim the instrument to be capable of measuring the absorbance of samples at wavelengths of between 180nm and 900nm at intervals as small as 0.1nm (Kontron Instruments, 1994). The instrument can be operated in a number of modes but the *Watersure* investigations have shown that a wavelength scan from 250 - 290nm is the optimum for its proposed use as an intake monitor as this waveband detects a large number of organic compounds but is not influenced by colour causing organics (these are most apparent at 400nm). A schematic diagram showing the nature of a double beam spectrophotometer is shown below.

Figure 3 - Schematic diagram of a double beam spectrophotometer



The main advantages of this newer model over the Uvikon 860 used at the Lobwood intake on the River Wharfe are improved data capture facilities, better data presentation and manipulation capabilities, and a more user-friendly operating interface. The ease of use is made possible by the inclusion of an internal 486 processor, providing DOS capabilities and storage facilities on the hard disk as well as direct to a 3.5inch floppy drive. This removes the need for a connection to an external PC as has been routinely done before. The instrument can be easily connected to accessories such as sippers and cell changers, the operation of which can also be controlled from the internal processor.

3. Experimental methodology

3.1 The field site:- Carlesmoor Beck, North Yorkshire

The Carlesmoor Beck, a tributary of the River Laver, lies approximately 13km west of Ripon (Figure 4) and is part of a large network of upland gathering grounds operated by Yorkshire Water. Raw water is abstracted from the stream and fed directly to the Harlow Hill water treatment works. From here it is distributed throughout Harrogate and the surrounding area. The beck and its tributary Wandley Gill were cited as the source of a chlorophenolic taste incident in April of 1993 (Short, 1993). An investigation following customer complaints found unusually high levels of phenol and para-cresol in the beck during this time and in the following months, as illustrated by Figure 5.

The Carlesmoor Beck was chosen to assess the feasibility of the spectrophotometer as it was known to produce phenolic events in the past. The spiking of samples from this watercourse could therefore be considered representative of an event that may occur.

Ten litre samples were taken from each of the two sample sites indicated in Figure 4, three times a week during the month long trial. The first sample site was approximately ten metres upstream of the supply intake and the second on open moorland five metres downstream of the confluence with Wandley Gill. The sheep dip by this site (Figure 4) was ruled out as a pollution source in the original investigation as it not been used for some time. This was also considered to be the case during this study.

Measurements of temperature, pH and specific conductance were measured each time a sample was collected. Discharge was estimated by measuring the depth of water flowing out of the culverted section of stream by sample point 2. In order to minimise the impacts of compound decay the samples were returned to the laboratory and analysed on the spectrophotometer on the day of collection. Further tests on the stability of stored samples did however show that their UV absorbance varied very little over a 48 hour period (see Appendix).

Some of the samples were then spiked with a phenol solution to simulate the conditions seen during the 1993 incident. These samples were then re-analysed and compared to the original raw water samples.

Figure 4 - Location of the Carlesmoor Beck sampling points

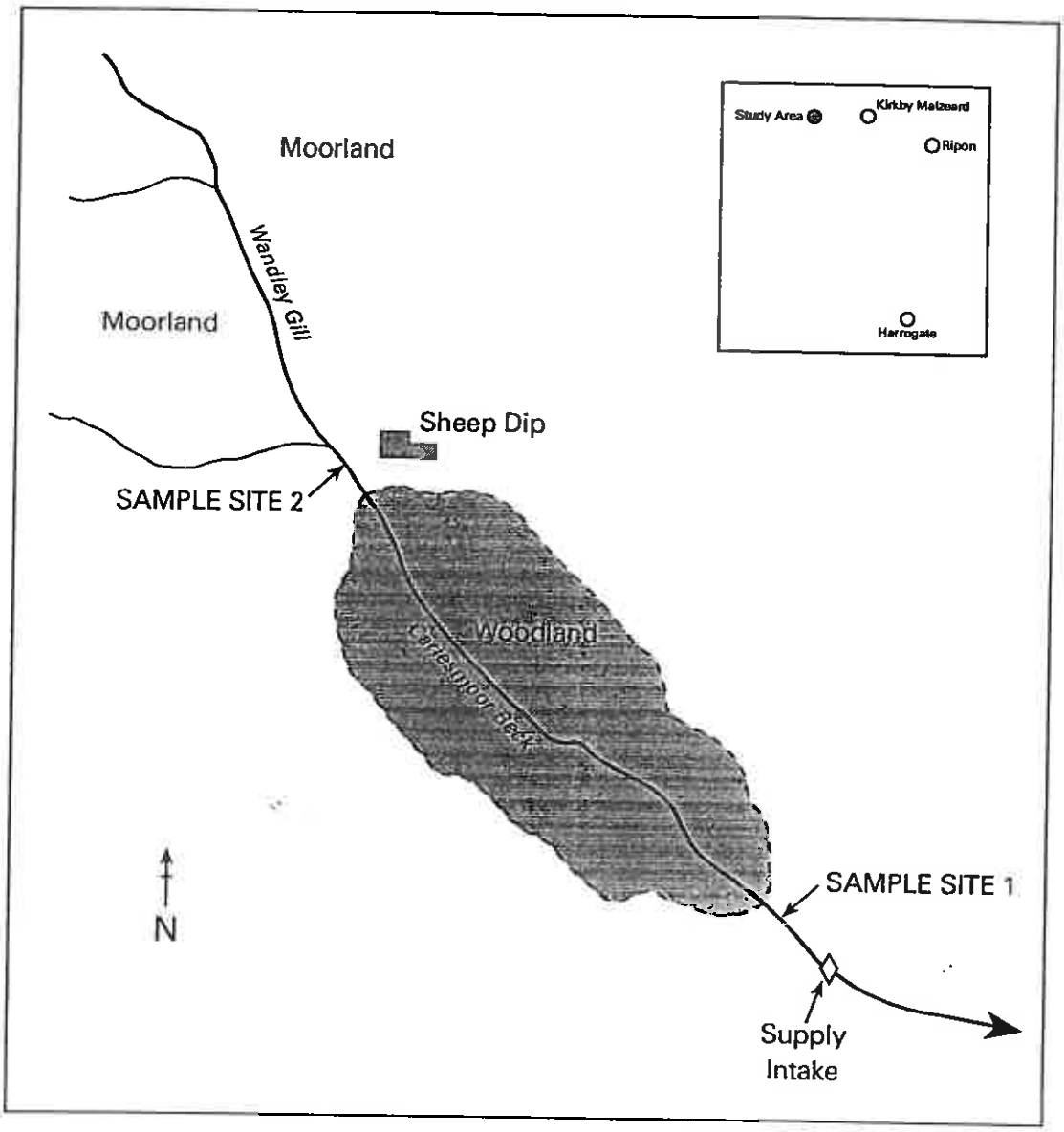
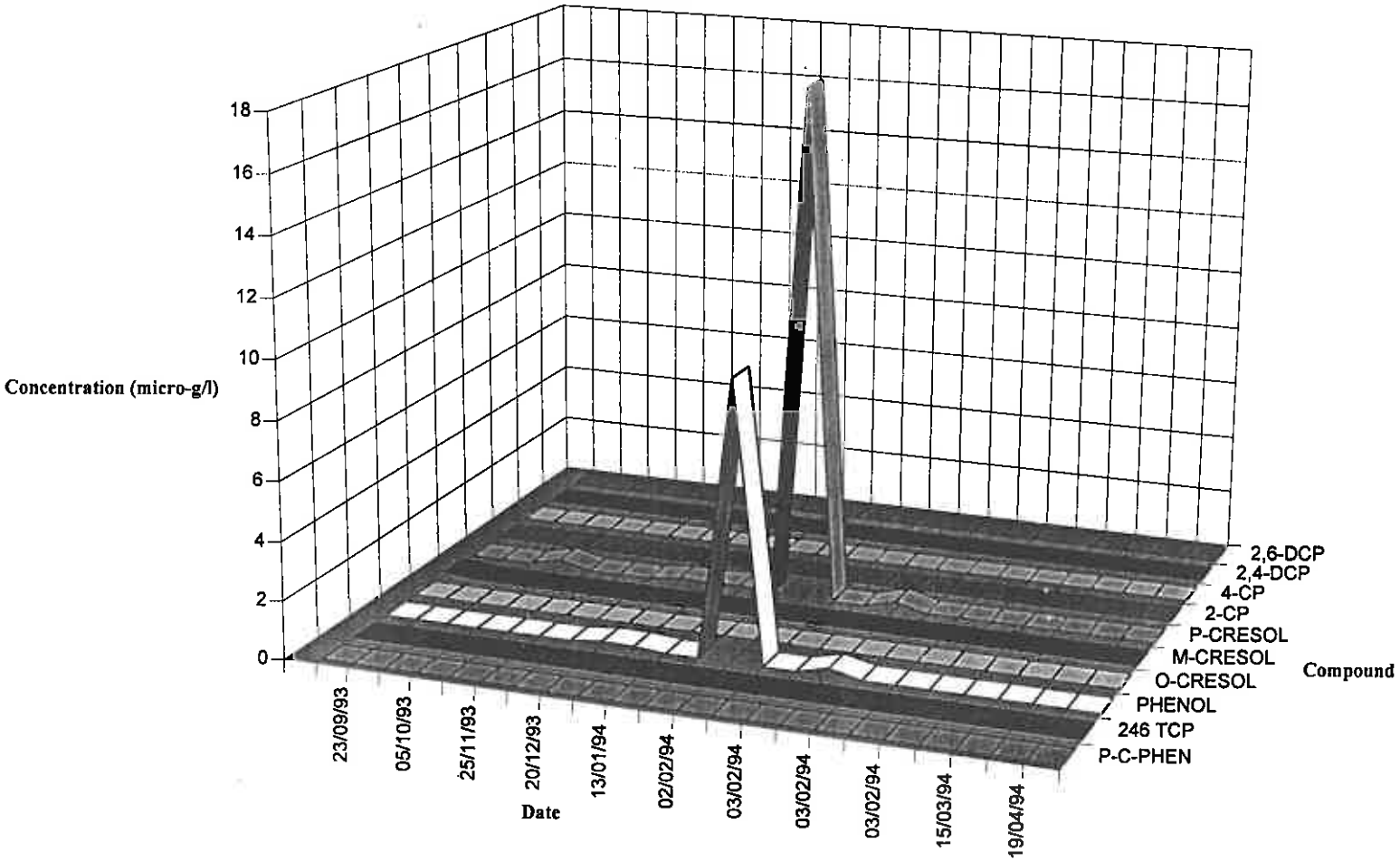


Figure 5 - Levels of phenolic compounds in the Carlesmoor Beck (08/09/93 - 04/05/93)



3.2 Instrument configuration

The spectrophotometer was used in conjunction with two 4cm quartz glass cuvette cells and the data produced exported to an external computer for analysis in Microsoft Excel.

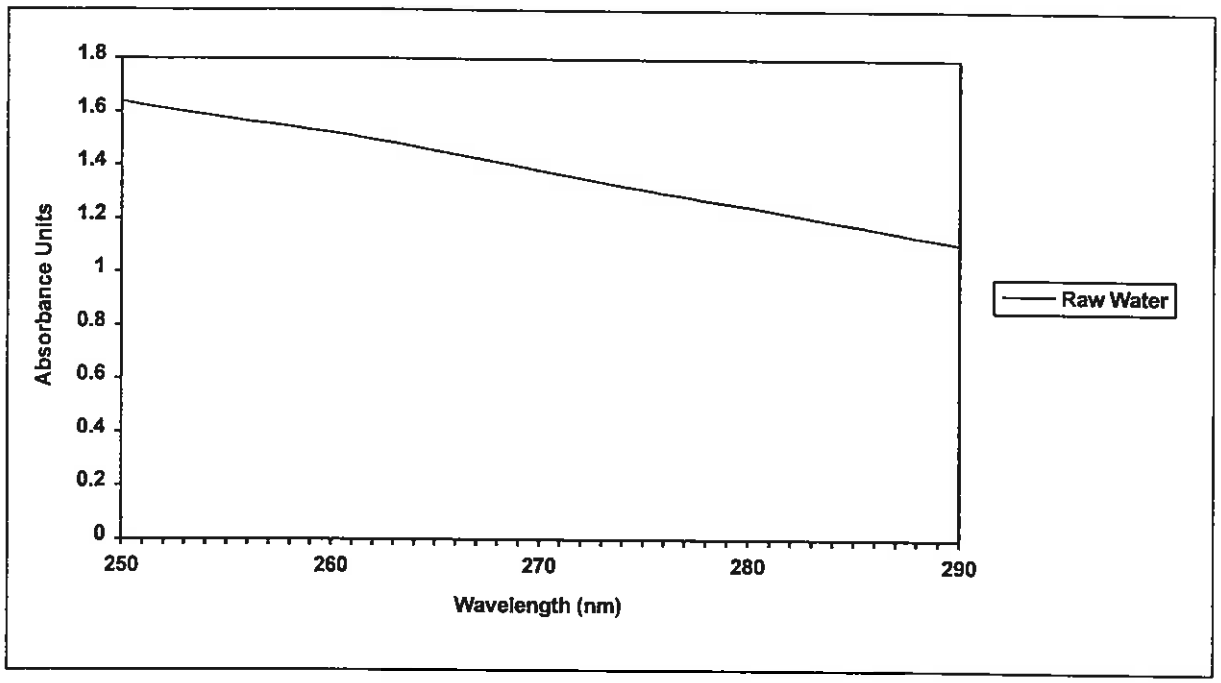
Initial trials with upland waters in a 10cm cell analysed by a Uvikon 860 machine suggested that, due to the high organic content of the water samples, performance was inhibited by the use of long cell paths. To begin with therefore the two 4cm cells were used separately, i.e. one was used in the reference position and the second contained the sample. This gave a sample path length of 4cm as used on the Lobwood intake monitor. The resultant UV scans were analysed, as were the first, second and third order derivatives of the scans. The first order derivatives were expected to prove the most useful (as was the case with the Watersure monitors). Due to the method of mathematical calculation (differentiation) these will amplify the difference between data sets to a greater extent than higher order derivatives.

3.3 Experiment A (4cm path length)

The first tests carried out on the raw beck samples were conducted with the same system set-up as recommended for earlier trials using the Uvikon 860, i.e. a wavelength scan from 250-290nm, at a scan speed of 200nm/min and an interval of 1nm.

Raw beck water was first scanned by direct comparison to a distilled water reference sample. This produced an absorbance scan similar to that shown in Figure 6 below.

Figure 6 - Typical UV absorbance scan for Carlesmoor Beck water

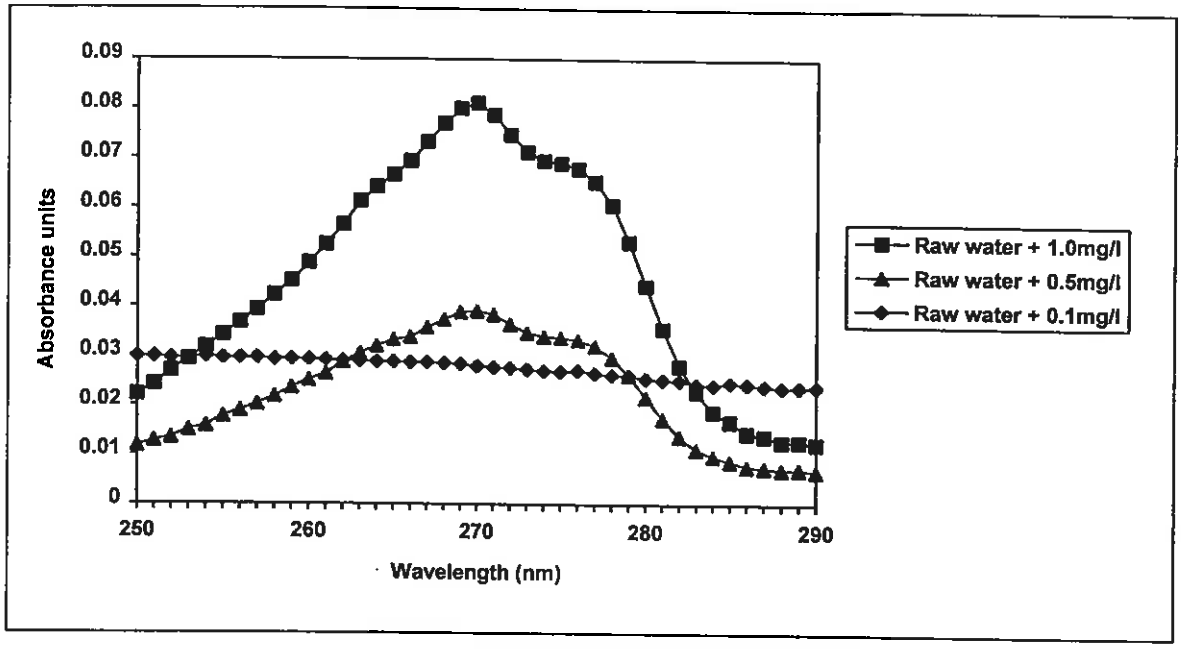


The absolute values of the scan traces varied slightly between samples due to variations in flow conditions over the one month trial period, but the general shape (of a straight line with negative gradient) was consistent throughout the study. This was true for samples from both sites, although absorbance was generally higher throughout the waveband for the moorland samples.

Samples of raw beck water were then spiked with 1.0mg/l, 0.5mg/l and 0.1mg/l of phenol and their absorbance measured against a reference of raw beck water, i.e. optically subtracting the raw sample from the spiked sample to illustrate any effect caused by the presence of phenol. Some typical scans produced by this approach are shown in Figure 7 below.

Figure 7 - UV scans for samples spiked with phenol

(against a river water reference)

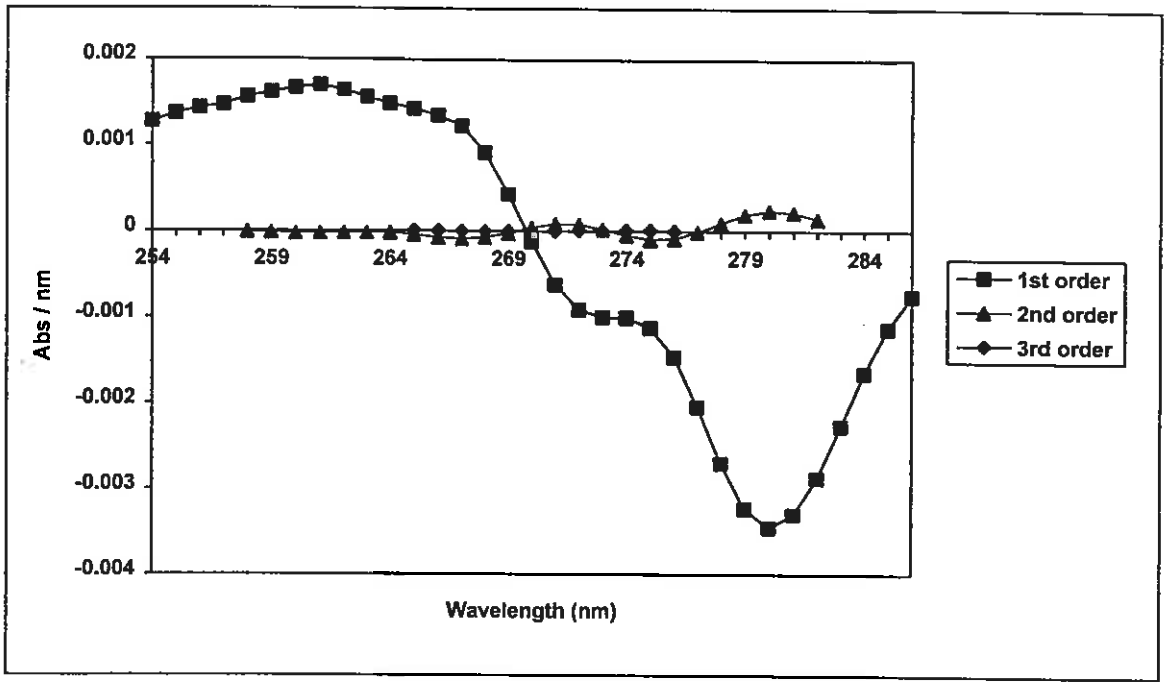


Taking the x-axis as normal river absorbance, it can be seen that 0.1mg/l of phenol only causes a small, linear increase in the absorbance scan. From the above scan traces it would therefore be difficult to distinguish between the UV scans of raw samples and spiked samples for spiked concentrations of less than about 0.5mg/l given any significant background variation in the absorbance of the river. The scans of 0.5mg/l and 1.0mg/l do however produce a different shaped curve making them easily distinguishable from the background river conditions. Given that 0.5mg/l is approximately 5000 times the ideal detection limit required, further optimisation of the system was necessary. The derivatives of these scans were therefore investigated in an attempt to clarify the effect of the presence of phenol in the samples.

In the evolution of the *Watersure* monitoring systems it was found that differences in the first order derivatives produced more useful results due to the method of calculation. Differences caused by variations in the natural river quality produced different scans. However, if the first order derivative was calculated, the same shaped curve appeared. In contrast to this, differences caused by pollutants produced different shaped derivative curves. The pollutants could therefore be detected against a background of natural variation.

The graph below (Figure 8) shows how successive derivations affect the identification of the phenol pollution.

Figure 8 - Derivative curves for raw water sample spiked with 0.5mg/l phenol (relative to a raw water reference)



From Figure 8 it is evident that the derivatives of the UV scans for the spiked samples show a distinct difference from the raw water reference samples. Comparison between Figures 7 and 8 suggests that the existence of 0.5mg/l of phenol is more clearly shown by looking at the derivatives of the basic scans (the shape of these curves were seen to be characteristic of spiked samples throughout the experiment) rather than the raw UV data. However, it can be seen from Figure 8 that the first order derivative shows the greatest response to the addition of phenol. As expected, when subsequent orders of derivation are carried out the difference between the absorbance of raw and spiked samples becomes less evident.

Experiment A has shown that 0.5 mg/l of phenol is detectable in upland stream water using a 4cm cell. It has also been shown how the first order derivative of the UV scan can be more useful than the UV scan itself in detecting differences caused by pollution. Given the findings of the initial *Watersure* experiments and the results seen above, first order derivatives obviously have the greatest potential for the detection of phenol in subsequent experiments.

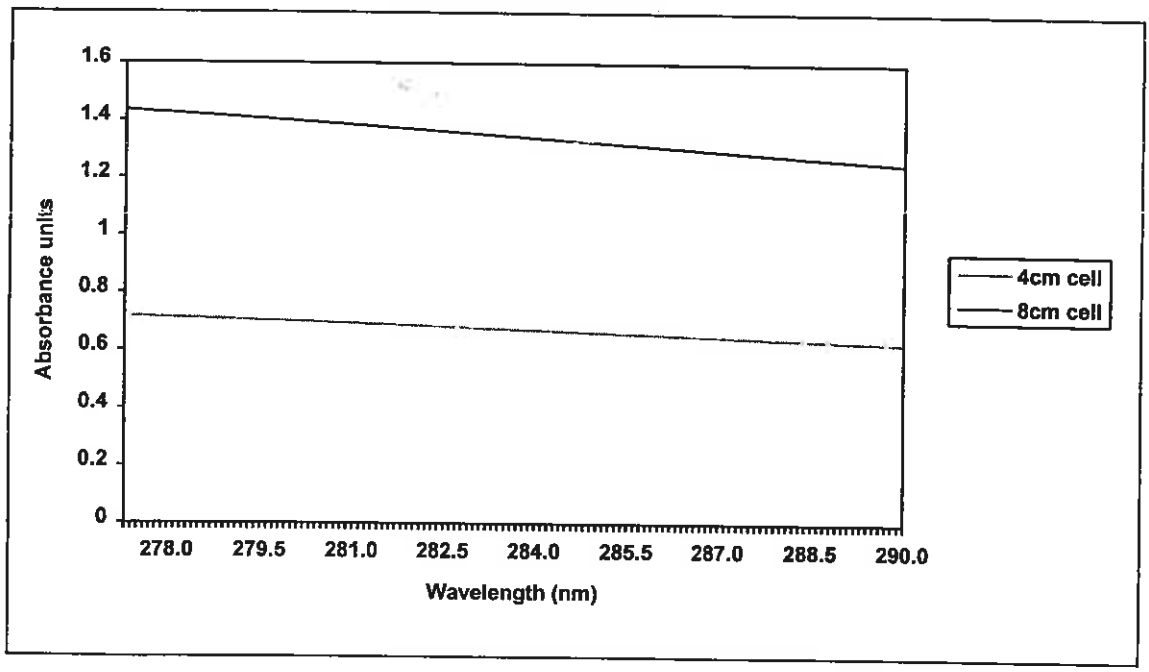
As 0.5mg/l appeared to be the approximate limit of detection at this stage, experimentation with longer cell paths was necessary to detect lower levels of phenol that would be useful in the monitoring of upland catchments.

3.3 Experiment B - (8cm path length)

For experiment B the system configuration was altered slightly. In order to free one of the 4cm cells all determinations were carried out using an air blank as the reference sample. This allowed the second cell to be placed in the sample holder to form an 8cm sample path length. A longer path length would be expected to give greater accuracy as this provides more opportunity for the light to be absorbed by the pollutants. This does however mean that the naturally occurring organic compounds (present in day-to-day variations in river quality) will also absorb a greater proportion of the light, as shown by the trials on the Uvikon 860 using a 10cm sample cell. It was hoped that 8cm would provide an optimal response to this problem. As was expected a doubling of the direct absorbance was seen (Figure 9).

Figure 9 - Impact of a longer sample cell path length

(Zero order UV scans)



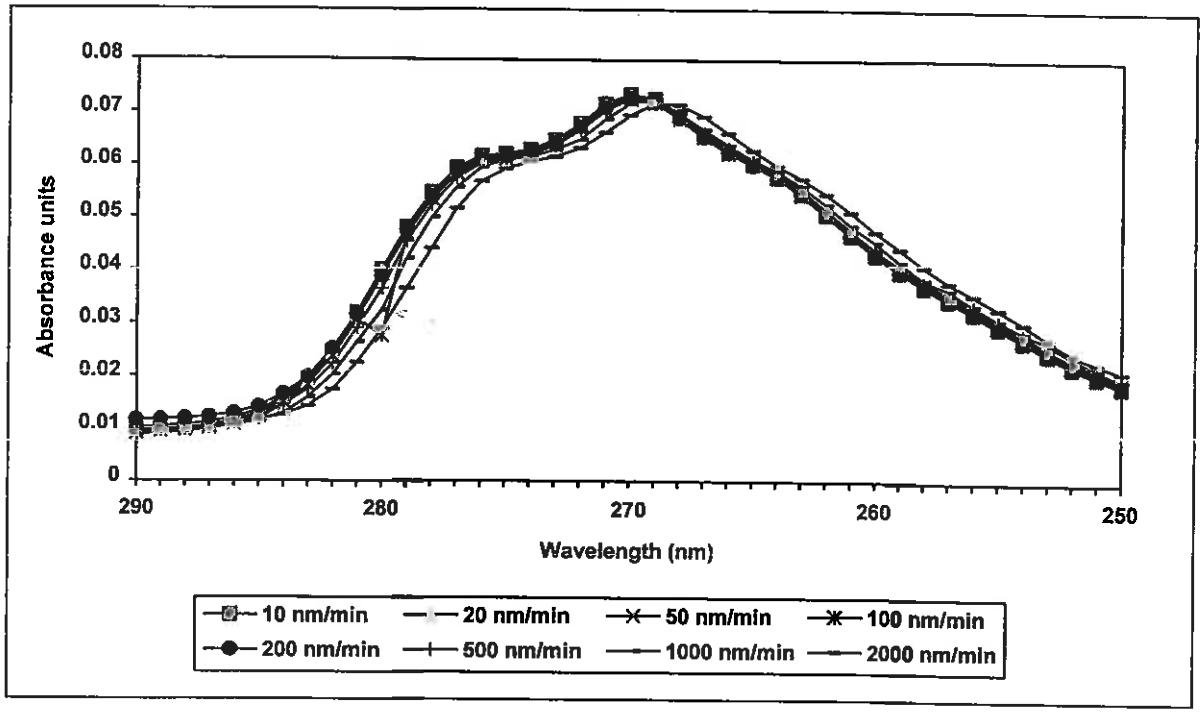
At this stage the concentration of the phenol spiking was changed in an attempt to show any increase in the detection ability of the system. Concentrations of 1000µg/l (1mg/l), 100µg/l, 10µg/l, 1.0µg/l and 0.1µg/l of phenol were created in the raw beck water before analysis in the spectrophotometer.

The results of the analyses of the spiked samples were then subtracted from those of the raw samples manually (rather than optically as had be done previously).

Attempts were also made at this stage to optimise the scan performance. The wavelength scan mode on the 922 has a number of settings. The scan speed can be varied between 10nm/min and 2000nm/min, and the scan interval can be set at intervals from 0.1nm to 2.0nm . It was expected that a slow scan speed and small scan interval would optimise the collection of absorption data. Figure 10 shows that altering the scan speed has little effect on the response. However, the faster scan speeds appear to result in slightly less absorption then the lower ones, and the minimum scan speed (10nm/min) and minimum sample interval (0.1nm) were therefore selected for all subsequent analyses.

Figure 10 - Effect of changing the scan speed

(Sample In4 + 1.0mg/l Phenol)



The following graphs show the results of the analyses of the spiked samples using the instrument configuration described above. Again the traces are relative to raw water samples and therefore indicative of the effect of the phenol on absorption.

Figure 11 - Effect of 1mg/l of phenol on the UV absorbance of river water

(First order derivatives; 8cm sample cell)

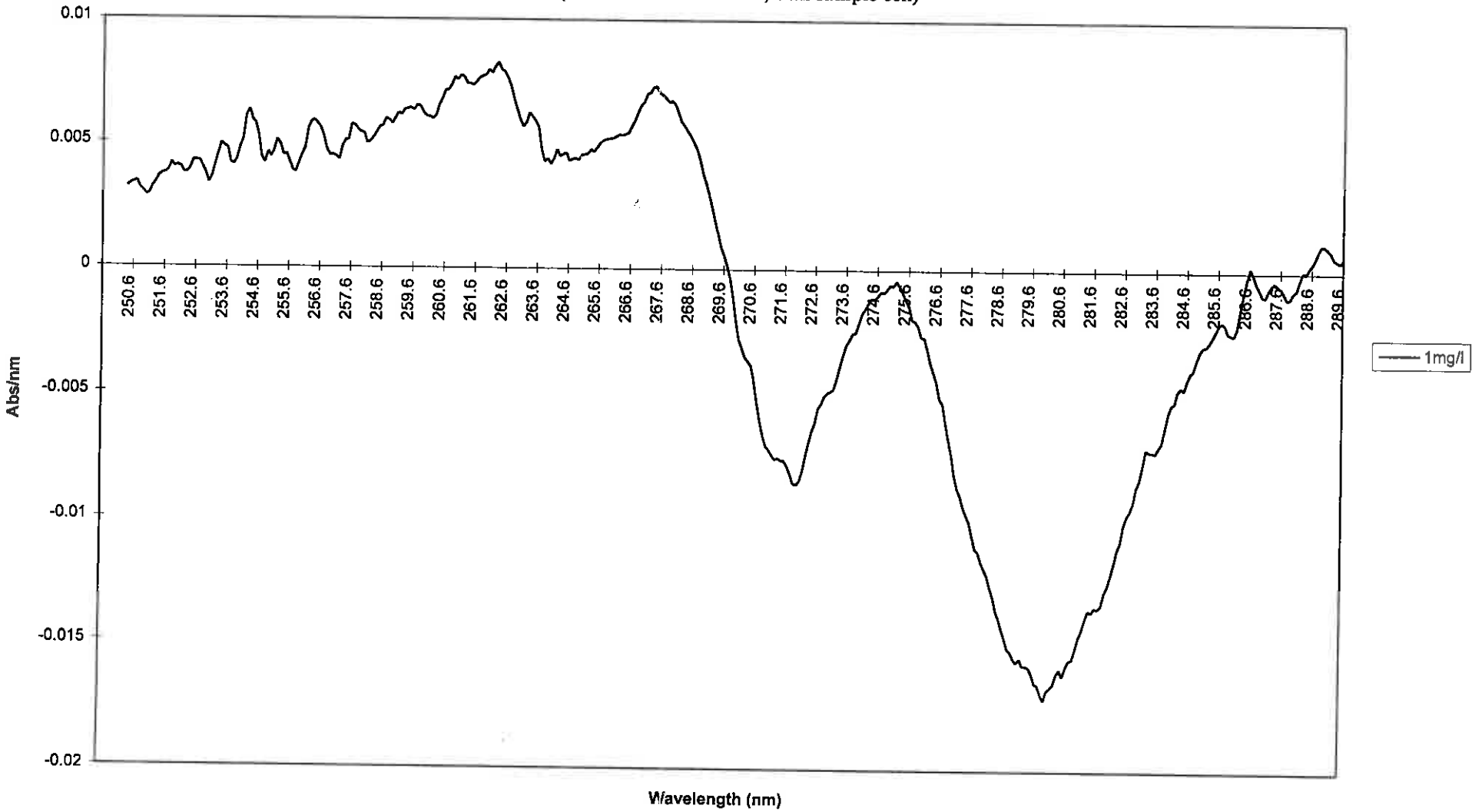


Figure 12 - Effect of 0.1mg/l of phenol on the UV absorbance of river water

(First order derivatives; 8cm sample cell)

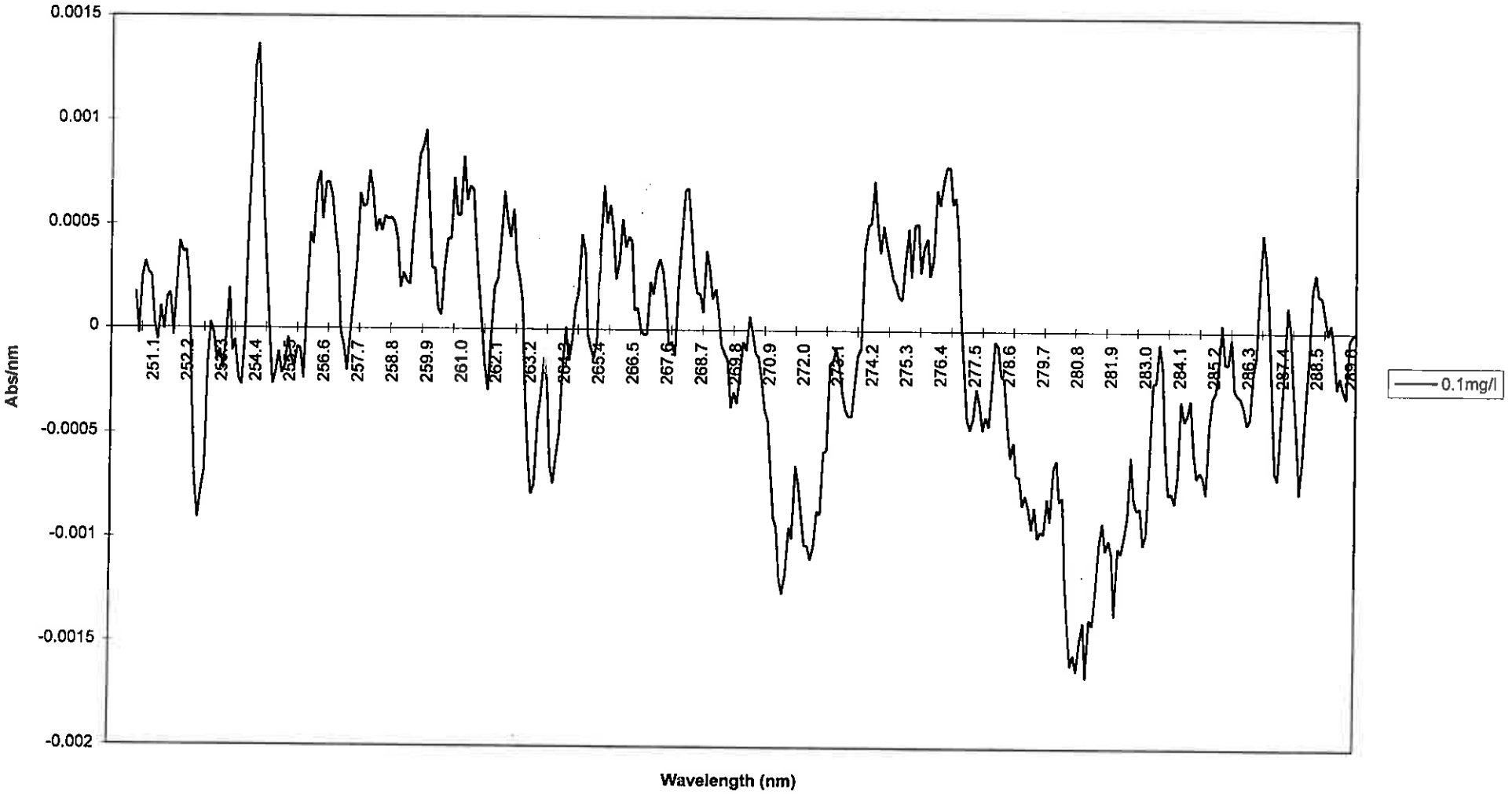


Figure 13 - Effect of 0.01mg/l of phenol on the UV absorbance of river water

(First order derivatives; 8cm sample cell)

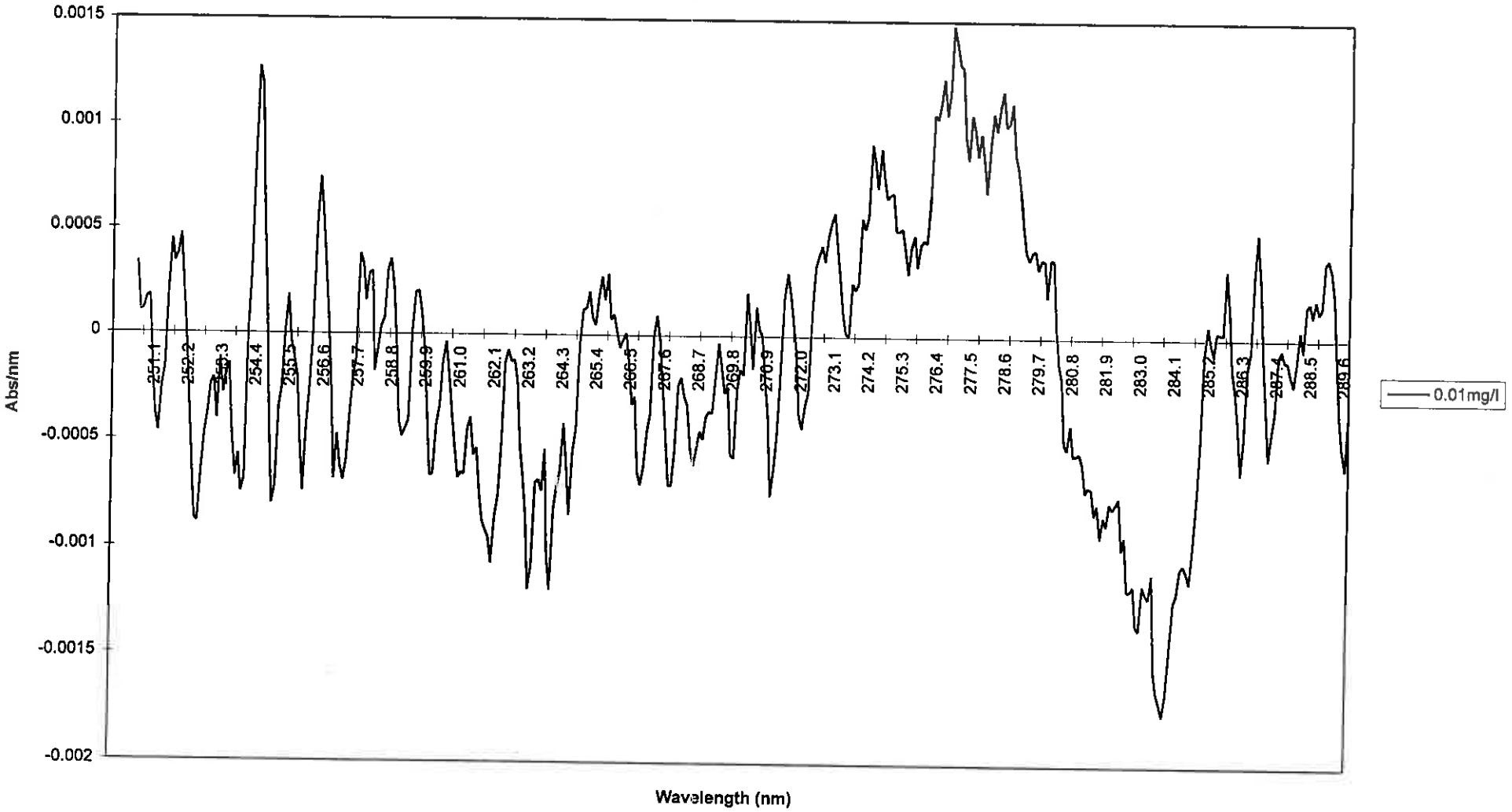


Figure 14 - Effect of 0.001mg/l of phenol on the UV absorbance of river water

(First order derivatives; 8cm sample cell)

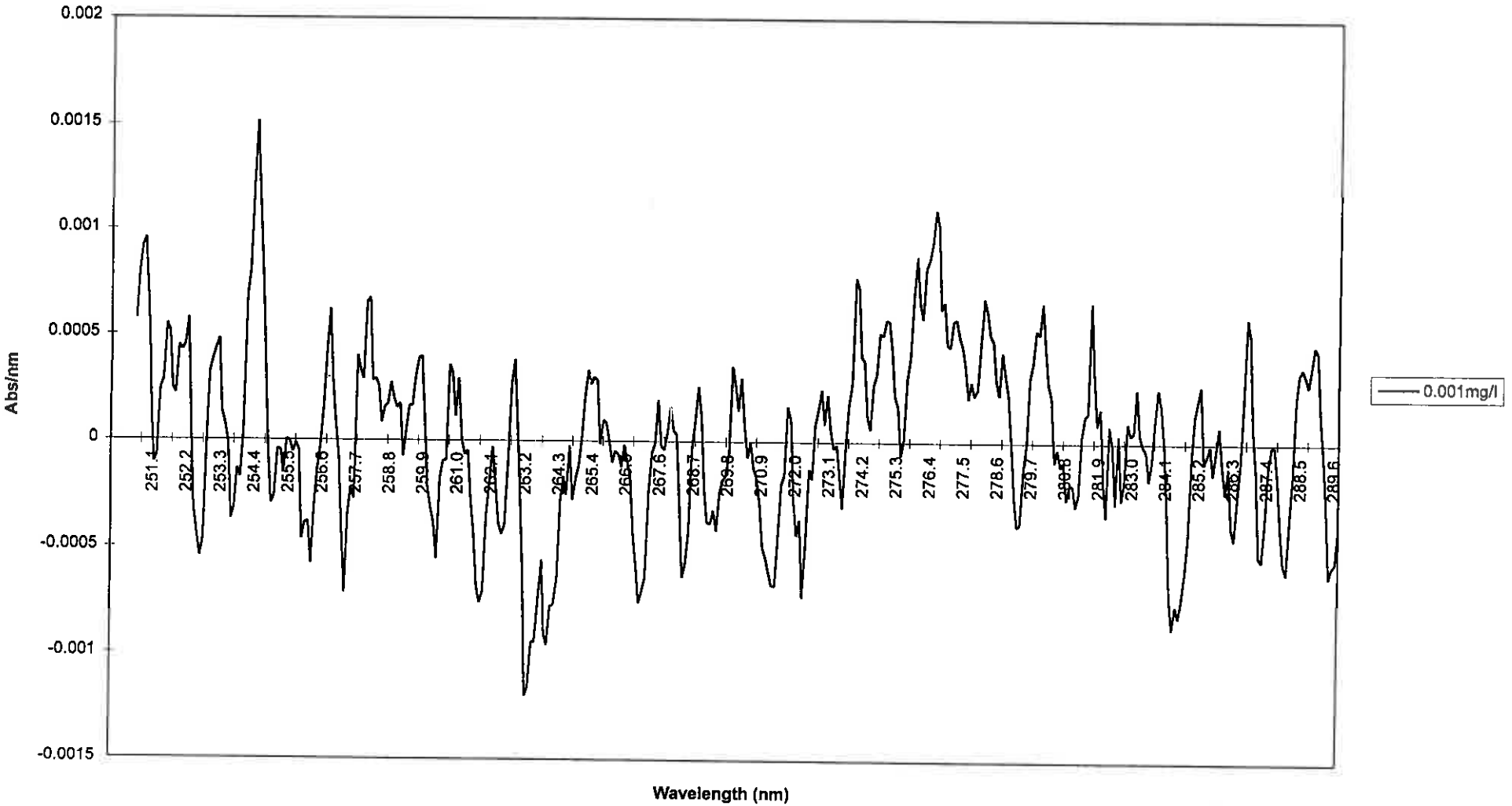


Figure 15 - Effect of 0.0001mg/l of phenol on the UV absorbance of river water

(First order derivatives; 8cm sample cell)

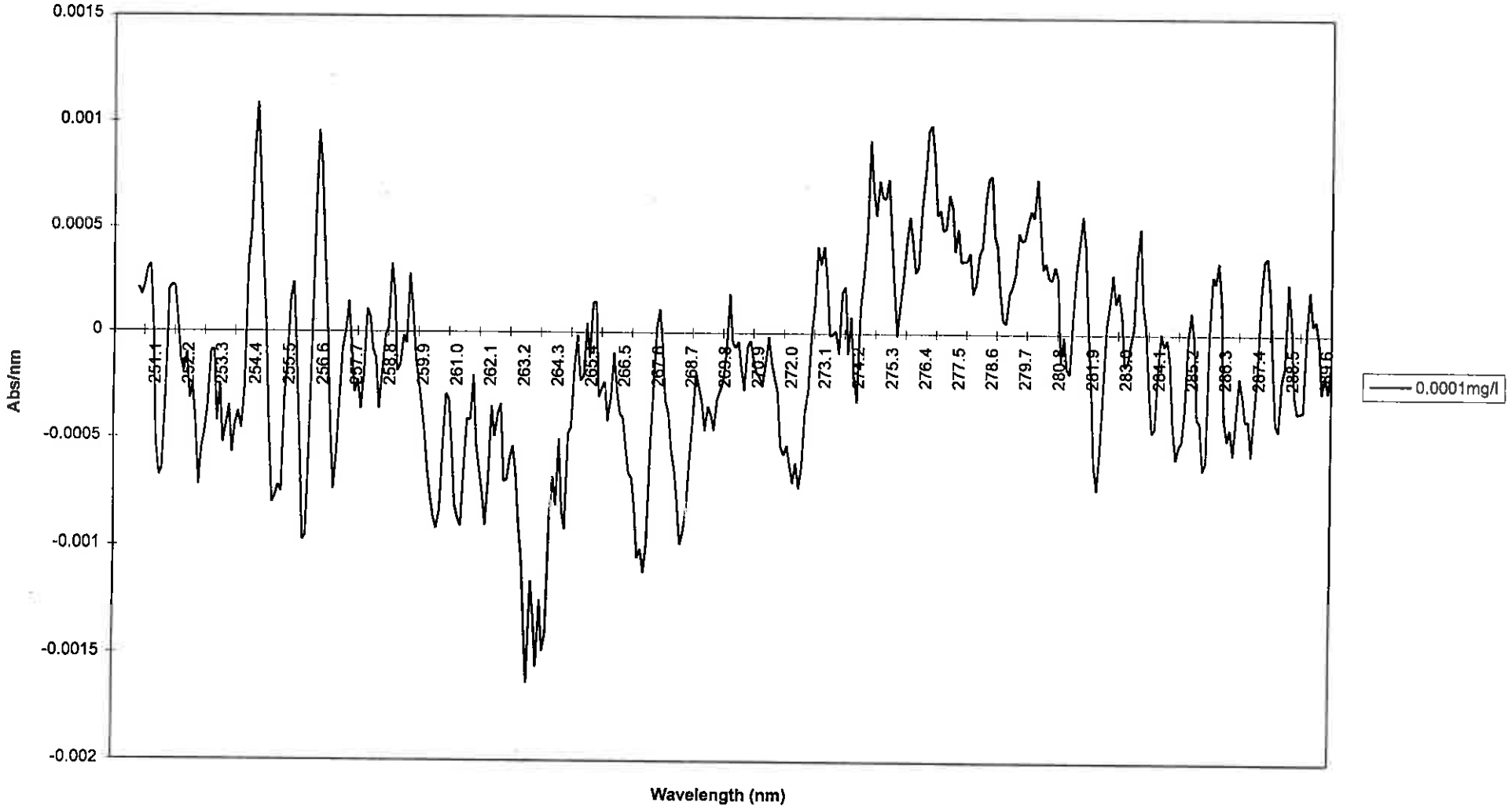


Figure 11 shows that for higher concentrations (1mg/l), there is a distinctive change in the trace caused by the existence of phenol in the samples. Below this concentration however (Figures 12 - 15), the variations from zero (implying a difference from the blank samples) are extremely small (±0.0015 absorbance units per nanometer) and very erratic. It is unlikely that these changes would show up against a background of variations in river quality.

In order to assess the significance of the variations caused by the spiking of samples with phenol, the responses of spiked samples were superimposed on the absorbance graphs of all the raw water samples taken throughout the study period. This enables an effective limit of detection for phenol in upland waters to be determined.

As can be seen from Figures 16 and 17, 1mg/l of phenol shows up well against a background of natural river variations. However, 0.1mg/l shows no significant difference from the background scans seen over the period of a few weeks.

Figure 16 - Effect of 1mg/l of phenol on the UV absorbance of river water (against the background variation seen during the trials)

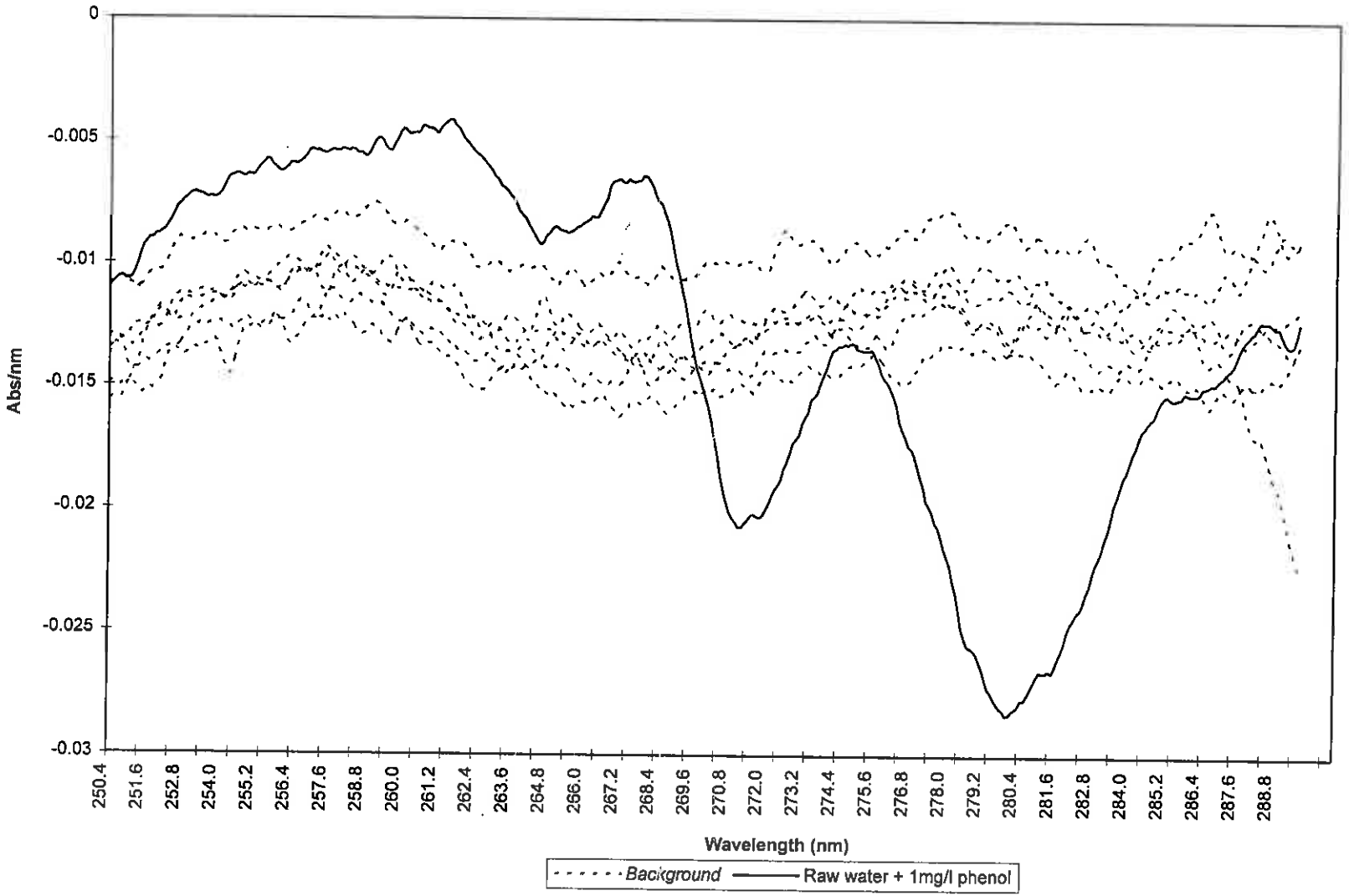
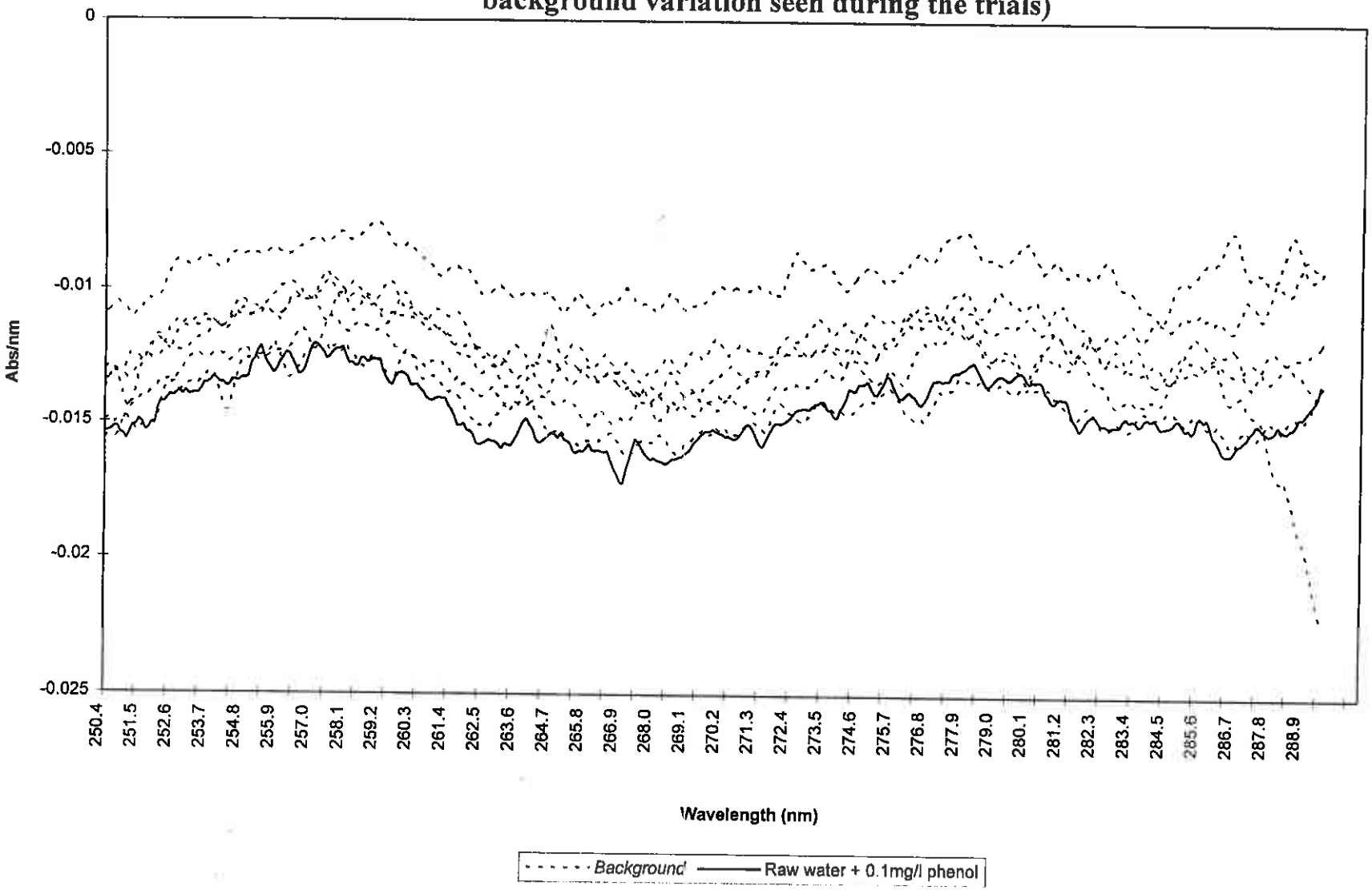


Figure 17 - Effect of 0.1mg/l of phenol on the UV absorbance of river water (against the background variation seen during the trials)



In order to determine accurately the detection limit of this method (which is now known to lie between 1.0mg/l and 0.1mg/l of phenol) further analysis was carried out on samples containing 0.9mg/l, 0.8mg/l, 0.7mg/l etc. of phenol.

The response of these concentrations can be summarised in the table below. A positive (✓) response indicates that the response of this sample was clearly apparent against a background of normal river variations. A negative (X) response indicates that it is not obviously different from the 'normal' variation.

Concentration of Phenol (µg/l)	*Response (apparent in river water)*
900	✓
800	✓
700	✓
600	✓
500	✓
400	✓
300	X
200	X

The experiments showed that concentrations of phenol between 1.0mg/l and 0.4mg/l could be routinely detected in upland river water. As can be seen from Figures 15 to 17 the response of the spectrophotometer is reduced as the concentration of phenol approaches 0.4mg/l. At concentrations below this (i.e. 0.3mg/l) the absorbance scan of the spiked sample is not significantly different from background variations in the response of the river (Figure 21). Further concentration steps between 0.3mg/l and 0.4mg/l failed to produce any significant response below 0.4mg/l.

Figure 18 - Effect of 0.6mg/l of phenol on the UV absorbance of river water (against the background variation seen during the trials)

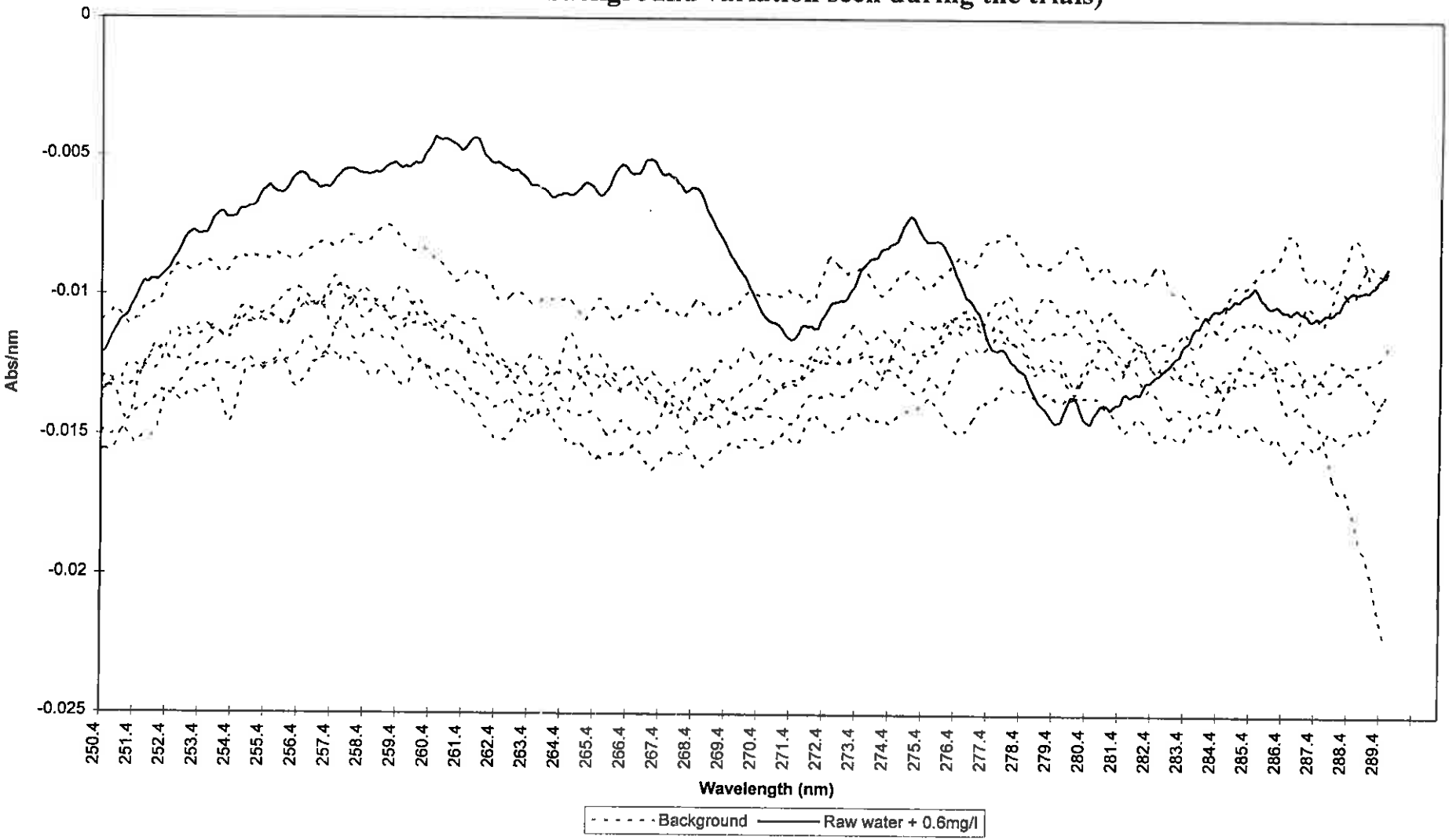


Figure 19 - Effect of 0.5mg/l of phenol on the UV absorbance of river water (against the background variation seen during the trials)

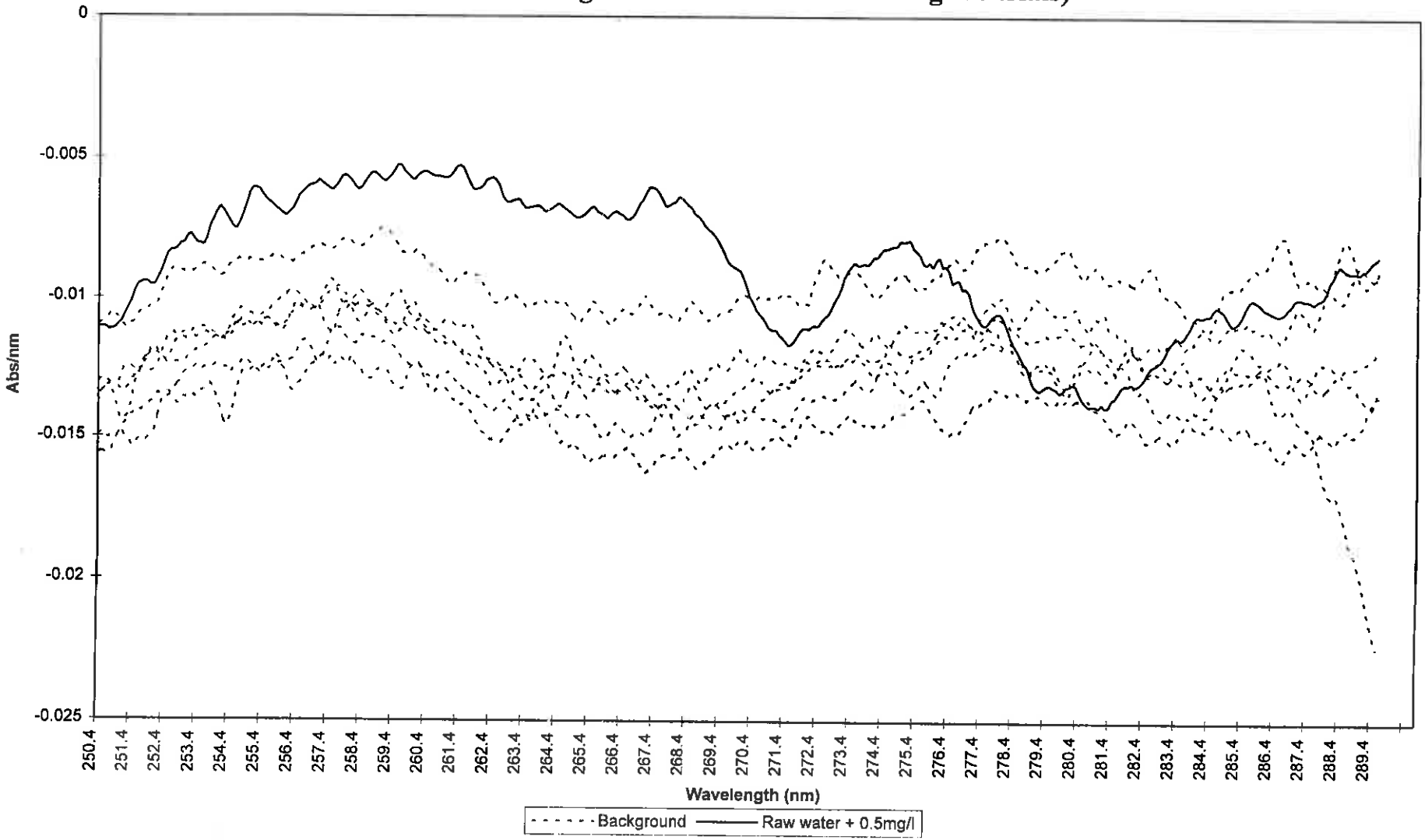


Figure 20 - Effect of 0.4mg/l of phenol on the UV absorbance of river water (against the background variation seen during the trials)

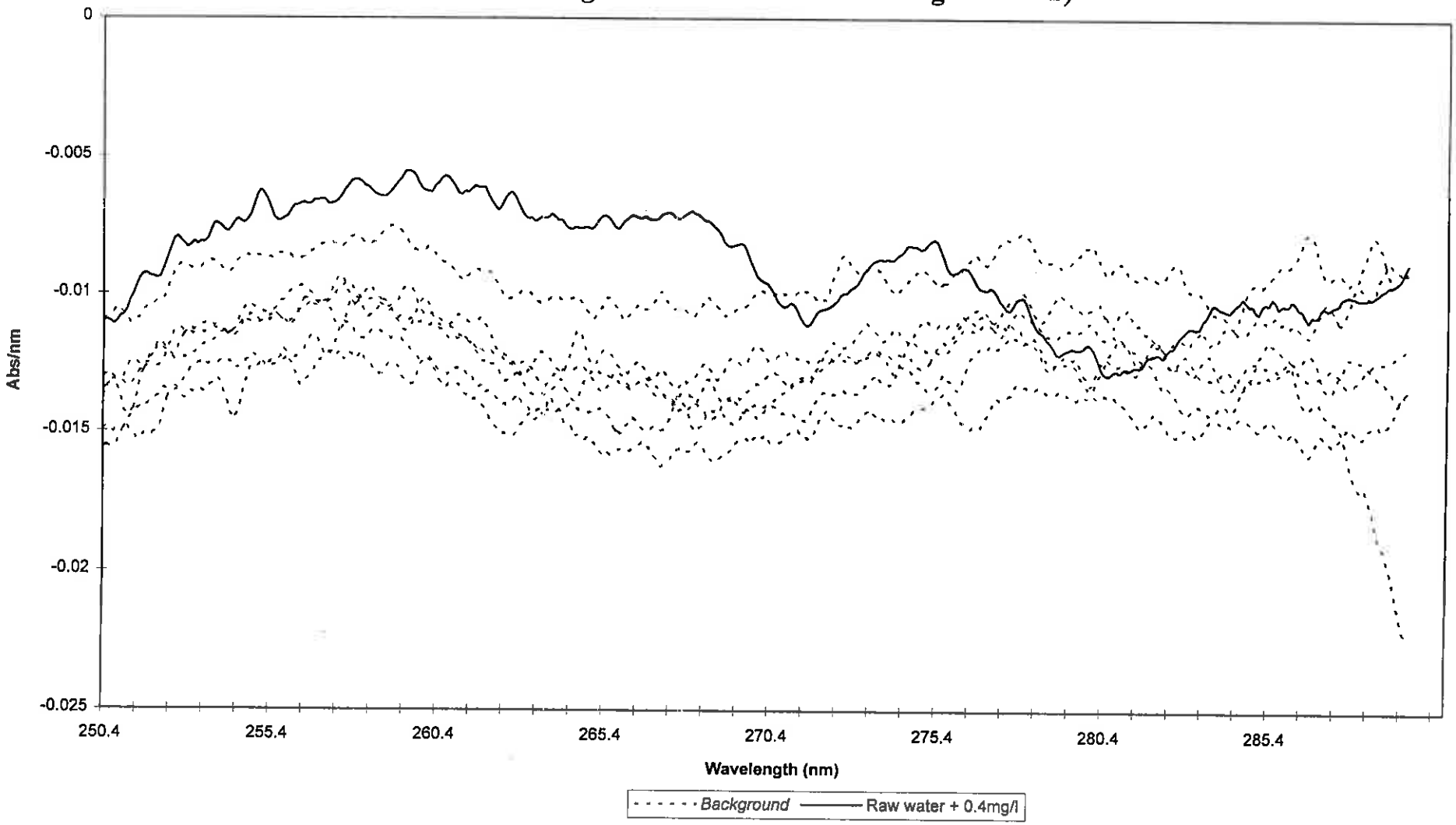
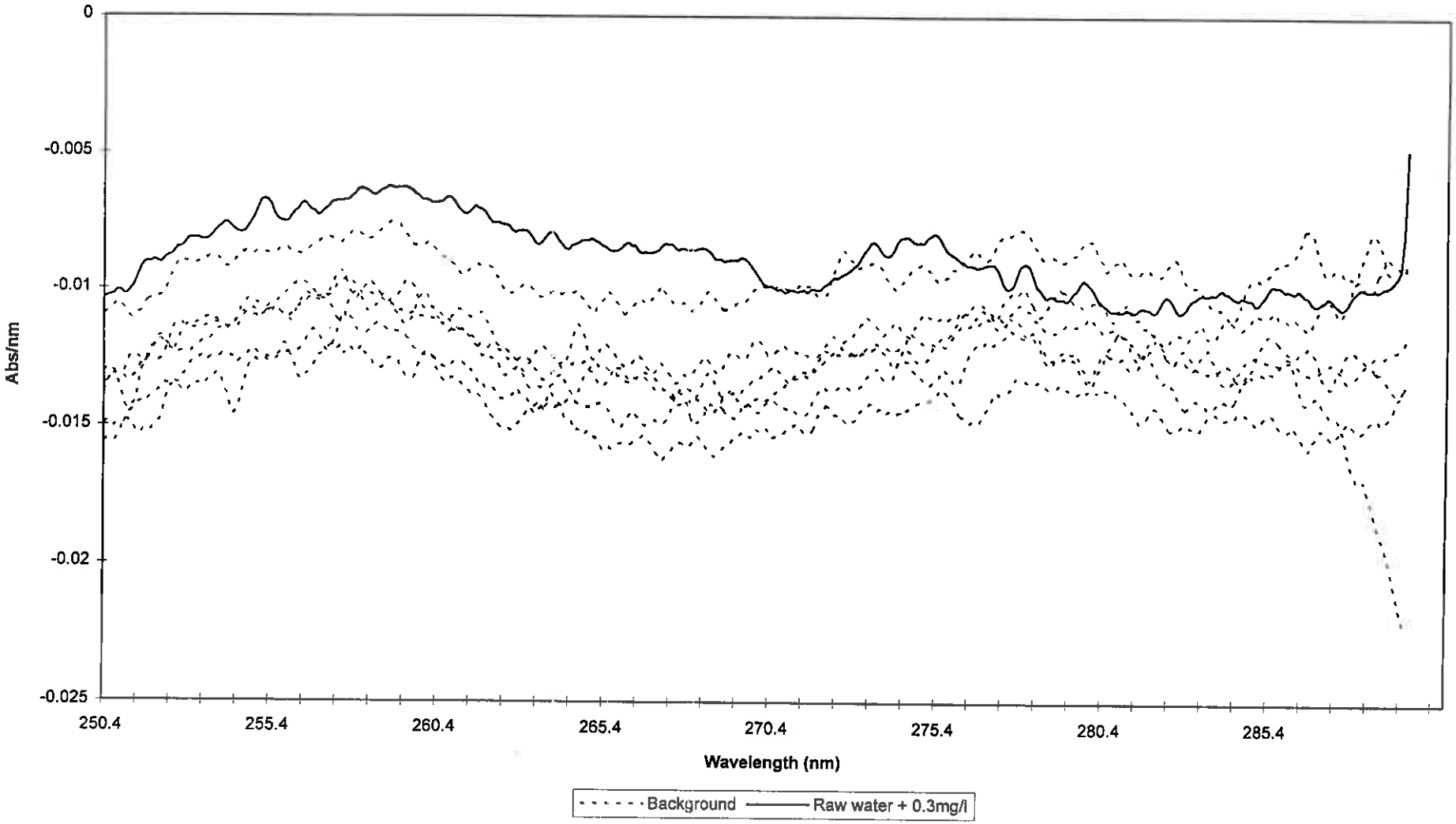


Figure 21 - Effect of 0.3mg/l of phenol on the UV absorbance of river water (against the background variation seen during the trials)



4. Conclusions

The effective detection limit of this analytical approach for phenol in upland river water would therefore appear to be 0.4mg/l. This value has been obtained by comparison of spiked samples against the variation of raw river samples over a period of four weeks. The limit of detection may well be different if a longer sampling period were considered as long-term variations in river water absorbance are likely to be considerably higher than those seen during the trial period (where very little rainfall or variation in flow conditions were seen). The poorer than expected limit of detection is probably due to the high absorbance by organic compounds in upland waters.

Very little variation in any of the other water quality parameters measured (temperature, pH, specific conductance) was seen throughout the trial period. It is not apparent therefore whether different physiochemical conditions would influence the results of the experiments. It may be possible for lower limits of detection to be achieved in waters that contain lower concentrations of organics but further research would be required to investigate this fully.

This limit of detection, given the very low levels of phenolics experienced in upland supply streams, means that UV absorption technology is not suitable for the screening of phenolics in upland streams in its current format. It would seem therefore, that for any study of phenolic compounds where the concentrations experienced are below 0.4mg/l, expensive laboratory analysis is the only realistic method of measurement and may result in severe financial constraints on the sampling regime chosen.

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Appendix:

Raw Sample Stability Experiments