Predicting the distribution of acid volatile sulfide in marine sediment from colour analysis of sediment-profile images

An example in situ sediment profile image and the sediment sulfide concentration profile and distribution derived from image analysis

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Predicting the distribution of acid volatile sulfide in marine sediment from colour analysis of sediment-profile images

Peter Wilson and Kay Vopel

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Auckland University of Technology
School of Applied Sciences
Mail No. C-43, Private Bag 92006
Auckland 1142
Phone +64 9 921 9999 ext 8185, Fax +64 9 921 9743
www.aut.ac.nz
1 Introduction

Organic enrichment of coastal sediments is a major concern worldwide. It is caused by an increase in the deposition of organic matter via terrestrial runoff (Gray et al. 2002) and aquaculture (Holmer & Kristensen 1994), or as a result of eutrophication driven by anthropogenic loading of coastal waters with phosphorus and nitrogen (Nixon 1995, Cloern 2001, Rosenberg et al. 2009). In coastal waters the majority of deposited organic carbon is mineralised by bacterial sulfate reduction because of the abundance of sulfate in the marine environment (Thode-Andersen & Jørgensen 1989, Bagarinao 1992). Hydrogen sulfide (H$_2$S), produced during sulfate reduction, reacts with dissolved iron or reactive iron minerals to form acid-extractable iron sulfides (termed acid volatile sulfide, AVS) that contribute to the distinct black colouration of organic-rich sediment.

Although there is a strong relationship between sedimentary sulfide content and organic matter input, its measurement has not been used in routine monitoring because of its laborious nature. Bull and Williamson (2001) tested a new approach to predict the sediment AVS concentration from sediment images. The authors used film photography in a laboratory and found a weak linear correlation ($R^2 = 0.67$) between sediment colour and AVS concentration.

The method used by Bull and Williamson (2001), however, is not without its flaws. The change in colour intensity in sediment cores is due predominantly to change in the concentration of one component of the sediment pool of AVS, the black iron sulfide (FeS). AVS has been heavily studied since it was conceptualised, and most researchers now accept that AVS is not equivalent to FeS (Rickard & Morse 2005). There are many other contributors to AVS including dissolved S$^{2-}$ species, and the sulfate-reducing organisms themselves (Rickard & Morse 2005). Even though a linear correlation between the concentration of AVS and colour intensity was achieved by Bull and Williamson for sediment from a particular location, such correlation may not exist in other sediments with different composition of the pool of reduced sulfur compounds.

As stated in our initial proposal, our goal is to further develop the above approach, with the help of new technology, into a rapid technique for monitoring the in situ distribution of AVS. Our aim is to develop a method which minimises errors arising from image processing and the loss of sulfur species via oxidation. Deploying a sediment imaging
device in situ to obtain digital sediment profile images allows us to avoid colour variation that arises during the development process of film photography. To minimise sulfur oxidation we use an H$_2$S microelectrode to rapidly measure AVS directly in the HCl extractant.

In the scholarship application we proposed four outcomes from this study:

1. A field protocol will be developed for the deployment of a novel sediment-profile imaging device and the acquisition of sediment-profile images.
2. A manuscript suitable for publication in an international peer-reviewed journal will be produced.
3. The results of the proposed research will be disseminated to professional colleagues at the New Zealand Marine Science Society Conference in 2011.
4. The results of the proposed research will be disseminated to end users (Auckland Regional Council, New Zealand Aquaculture Council Inc. etc.) by using popular articles.

This report describes the progress of this study, the preliminary results and their dissemination so far.

2 Study design

This study consisted of field and laboratory components. For the laboratory component, marine sediments were collected by SCUBA divers from the area surrounding a mussel farm in Man ‘O War Bay, Waiheke Island. The field component took place in the same location. We used cores of soft, subtidal sediment to test a new laboratory procedure to establish a correlation between sediment colour and AVS concentration. We then used the resulting correlation to predict the in situ AVS distribution from sediment profile images taken in situ with a novel sediment profile imaging device (SPI-Scan, Benthic Science Ltd., Figure 1).

2.1 Sediment collection

SCUBA divers collected seven sediment cores with clear acrylic tubes (64 cm$^2 \times 30$ cm) from arbitrary locations at 12 m water depth in Man O’War Bay off the eastern coast of Waiheke Island, New Zealand. The tubes were pushed vertically into the sediment until filled two-thirds with sediment, stoppered at both ends, and then transported in a
refrigerated box to a temperature-controlled laboratory. In the laboratory, we removed the upper lids and immersed the tubes gently in a plastic incubation container (1,444 cm² × 54 cm) containing 48 cm (78 L) aerated seawater.

### 2.2 Laboratory sediment analysis

We sectioned sediment cores at 5 mm intervals using a plastic scraper while the core was held stationary in a wooden frame. Each sediment slice was thoroughly homogenised before removing ~1 g for AVS determination. We divided the remainder evenly for sediment characterisation by water content, organic content, and particle size distribution, and sediment colour intensity.

We determined sediment AVS content using the reagents of ACS grade or equivalent and deoxygenated them by purging with nitrogen for ≥20 minutes. We performed all extractions in quadruplicate using the following procedure: We added approximately 1 g of sediment into a 40 mL glass vial filled with 30 mL HCl (1 mol L⁻¹). The vial was closed with an air-tight lid and shaken thoroughly. We weighed each HCl filled vial before and after adding sediment to determine the mass of sediment used in the extraction. We left the vials to stand while we sectioned the remainder of the core. Sectioning of one core was completed within one hour. We used an amperometric hydrogen sulfide microsensor (Unisense A/S, 500 μm tip diameter, response time ~1 second) to measure the concentration of H₂S in the HCl extractant.

We determined the water content of the sediment by drying at 90°C for 24 h and the organic content as loss on ignition (LOI) by combusting in a furnace for 6 h at 400°C. The sediment particle size distribution (% volume) of the upper 9 cm was measured using a laser-based particle analyser (Malvern Mastersizer 2000).

We scanned a portion of each 5-mm sediment section, including a colour calibration strip, with a flatbed scanner (Canon CanoScan LiDE 100) at a resolution of 600 dpi (0.04 mm pixel⁻¹). The colour of the resulting images were analysed with the software analySIS FIVE LS Research 3.3 (Olympus Soft Imaging Solutions) using the following procedure. First, we extracted the colour intensity channel of the image as defined by the hue, saturation, and intensity (HSI) colour model. We then calibrated the image so that the black and white squares on the calibration had the values 0 and 255 respectively. We then averaged the intensity values over the entire sample, approximately 50 cm², excluding anomalies such as air bubbles, to obtain an average grey value.
2.3 Sediment profile image acquisition

To obtain high-resolution in situ sediment profile images, we used a novel SPI-Scan instrument (Benthic Science Ltd., New Zealand, Figure 1). This instrument consists of a consumer flatbed scanner housed inside a polycarbonate cylinder. The electrical components are contained in a larger body attached to the top of the cylinder. The device is connected to a computer on the boat by means of an electrical tether.

To obtain in situ images, we lowered the SPI-Scan over the side of the boat to the seafloor at a water depth of 10 m, approximately 2 m from the seafloor. We then released the tether allowing the momentum of the SPI-Scan to push the scan head far enough into the sediment so that two thirds of the image showed sediment and the remaining third showed the water column. The area captured using the SPI-Scan in this study was $117 \times 216$ mm, including the water column, at a resolution of 300 dpi ($0.08 \text{ mm pixel}^{-1}$). The resulting images were ready for analysis.

2.4 Image analysis

With the image analysis software (see above) we wrote a macro that created a two dimensional AVS distribution plot (Figure 3B and D) from an in situ sediment profile image. This macro automates four steps in the image analysis process. Firstly, the intensity channel of the sediment profile image is extracted as defined by the hue, saturation, and intensity (HSI) colour space, creating a grey scale image. The macro then applies a $4 \times 4$ pixel averaging filter to minimise noise and anomalies caused by small shell fragments before calibrating the image. The calibration step ignores 2% of the brightest and 2% of the darkest pixels and spreads the intensity range of the remaining pixels linearly to cover the maximum available value range, that is, it adjusts the image so the black and white calibration squares on the right of the image (Fig. 3A and C) have values of 0 and 255 respectively. If 2% of the brightest and darkest of pixels are not ignored, some cases resulted in other parts of the image being brighter or darker than the calibration strip voiding the image calibration. The final step associates the grey value of each pixel to its corresponding AVS concentration, based on the previously established correlation,
generating a heat map. We grouped AVS concentrations into 5 μmol g⁻¹ ranges and assigned colours from blue through to red for low to high concentrations respectively.

To generate a vertical AVS concentration profile we used a macro similar to the one described above that extracts the intensity channel of the in situ sediment profile image, applies an averaging filter, and calibrates the image. We defined a rectangular area and the software calculated the average horizontal grey value for every row of pixels within this area. We took the average of 50 rows, approximately 4.2 mm, to produce one data point. Finally, we converted the grey value to AVS concentration using the previously derived correlation equation.

3 Preliminary findings

Our preliminary results show that the relationship between sediment colour intensity and sediment AVS concentration does have the predictive power to be used in an analytical application. Many of the difficulties and errors involved with sectioning sediment cores in a laboratory and exposing them to air, as required by laboratory based AVS measurements, are avoided using in situ sediment profile imagery. We have aimed to minimise any variation in assigning colours grey values by using similar models of scanning hardware in the flatbed scanner used in the laboratory and the SPI-Scan instrument, and using identical colour calibration strips in both environments. This in situ approach speeds up the image acquisition process and ensures the highest accuracy and reproducibility when representing sediment colour digitally, a step that the authors had noted as a point of concern.

Our correlation between sediment colour intensity and sediment AVS concentration using data obtained from seven cores so far can be seen in Figure 2. The data suggests a quadratic relationship rather than a linear one as first published by Bull and Williamson (2001). A linear fit through all data points had a strong correlation ($R^2 = 0.93$), however, it overestimated the measured AVS concentrations over the 4–8 μmol g⁻¹ range and underestimated at both ends of the linear fit.

Analysis of the sediment profile image in Figure 3A to produce an AVS concentration profile resulted in predicted concentrations ranging from 4.7 μmol g⁻¹ dw in the top 4 mm of sediment to 12.9 μmol g⁻¹ dw at a depth of 27 mm. The AVS concentration gradually decreases after this peak down to 129 mm, the bottom of the sediment image.
Figure 2. A scatter plot showing the correlation between AVS concentration and colour intensity measured in seven marine sediment cores. The solid line is a quadratic fit through all points ([AVS] = 0.006 × colour intensity² – 1.554 × colour intensity + 101.820, $R^2 = 0.95$) and the 95% confidence interval is shown by the dashed lines on either side.

Figure 3. An example in situ sediment profile image acquired with the SPI-Scan (A). Small black and white bars on the scale to the right of the image are 1 mm; the larger bars are 10 mm. The image is overlaid with the AVS concentration, [AVS], profile as predicted by image analysis. (B) The two dimensional AVS distribution plot derived from the A.
The predicted AVS concentration profile reaches a maximum concentration at a depth of 26 mm whereas analysis of sediment core in the laboratory using acid extraction techniques revealed peaks at a lower depth of 60 mm. The shape of the analysed image profile does however retain the similar features; once the rapid increase in AVS concentration stops, the concentration remains relatively constant up to a depth of 90 mm which was the greatest depth measured in the laboratory.

The AVS distribution plot, Figure 3B, shows 36% of the image correlates to an AVS concentration between 5 and 10 μmol g⁻¹ dw and another 36% of the image between 10 and 15 μmol g⁻¹ dw. 61% of Figure 3D correlates to an AVS concentration between 5 and 10 μmol g⁻¹ dw and 25% between 10 and 15 μmol g⁻¹ dw.

Extracting marine sediments using cold 1 M HCl is a widely used method. It extracts many sulfides species present in the sediment in both dissolved and solid phases. In addition to the iron sulfides, which are black and abundant in the iron rich sediments used in this experiment, minerals such as greenockite (CdS) and sphalerite (ZnS) are extracted when present and their colours range from yellow to brown unlike their iron counterparts [Cooper & Morse 1998]. It is likely the colour contribution of these species is negligible as their concentrations will be much lower than those of the iron sulfides. The dissolved fraction of AVS is largely colourless and although the inclusion of these species is accounted for during the calibration stage, it may not be adequate if their relative concentrations change dramatically. This is of particular concern at depths >10 cm in marine sediments where H₂S concentrations are known to substantially increase [Jørgensen & Kasten 2006]. When using cold, 1 M HCl, we know that the predominant iron sulfides are not extracted quantitatively, only 92% of mackinawite (FeS) and 40–67% of greigite (Fe₃S₄), and it has been suggested that this method may significantly underestimate the concentration of AVS [Rickard & Morse 2005]. Using this extraction method however, enables us to compare our data to the many other published studies that have used the same parameters. The sediment acid extraction process used to establish the correlation between sediment colour and AVS concentration is easily modified to accommodate specific requirements. Essentially in this study, we are predicting the sediment AVS concentration obtained during a sediment AVS extraction using 1 mol L⁻¹ HCl. Despite measuring some colourless and ignoring some coloured sulfur compounds, the results so far show an excellent ability to predict the otherwise time consuming
sediment AVS distribution. This issue is the major focus of our upcoming experimental work.

4 Dissemination of results

1. A draft manuscript titled “Predicting the in situ distribution of acid volatile sulfides from sediment profile images” is being prepared for submission to the journal “Oceanography and Limnology: Methods” before December 2011.

2. A poster titled “Predicting the in situ distribution of AVS from sediment profile images” has been presented at the NZ Marine Sciences Society’s annual conference in Stewart Island, July 2011 (Appendix 8.1).

3. An oral presentation titled “Monitoring organic enrichment of coastal sediment with sediment profile imagery” was given at the NZ Marine Sciences Society’s annual conference in Stewart Island, July 2011 — this presentation was awarded “runner up best student talk”.


5 Summary

The results of this project so far provide a rapid method for investigating the AVS chemistry of marine sediments. This is an area which has had much interest in the past, but because of the time intensive analysis, has been neglected in coastal monitoring. Measuring AVS involved treating sediment in a laboratory with deoxygenated acid to extract H₂S, which is then quantified electrochemically.

The aim of this study is to develop a rapid approach to monitoring the functioning of seafloor ecosystems affected by organic enrichment. There is a need for monitoring techniques that are robust, cost effective, encourage frequent monitoring, and importantly, do not compromise the profitability of commercial operations. The method we are developing is able to be incorporated into current monitoring schemes, providing greater insight into the sediment chemistry. Analysis of sediment profile images can produce an
AVS concentration profile as well as a 2D sulfide distribution. As a standalone technique, sediment profile image analysis could assess the footprint of a mussel farm or fish farm.

Taking advantage of new technologies, an in situ sediment-profile scanning device (SPI-Scan) and amperometric H₂S microelectrodes, it is hoped that further developments of this research will make AVS an accessible parameter for rapid assessment of the effects of organic enrichment in marine sedimentary environments.
6 References


8.1 Poster presented at the New Zealand Marine Sciences Society conference, July 2011

Organic enrichment of coastal sediments is a major concern worldwide. In estuaries, up to 90% of the deposited organic carbon is mineralised by bacterial sulfate reduction (Jorgensen 1982). Hydrogen sulfide (H$_2$S), produced during sulfate reduction, reacts with dissolved iron or reactive iron minerals to form acid-extractable iron sulfides (ferrihydrite) and AVS that contribute to the distinct black colouration of organic-rich sediment. AVS measurements have not been used in routine monitoring because they are time consuming; the sediment is treated in a laboratory with deoxygenated acid to extract H$_2$S, which is then quantified photometrically or electrochemically. Bull and Williamson (2001) tested a new approach to predict the sediment AVS concentration, hereafter (AIVS) from sediment images. The authors used film photography in a laboratory and found a weak linear correlation ($R^2 = 0.67$) between sediment colour intensity and (AIVS) as measured by a microfusions technique. With the help of new technology, our goal was to further develop the above approach into a rapid technique for monitoring the in situ distribution of AVS.

### Methods

- **Sediment sampling**
  - 7 subtidal sediment cores collected at 15 m water depth off the coast of Waheke Island, New Zealand

- **Image acquisition**
  - In situ deployment of sediment profile imaging device (SPI-Scan, Benthic Science Ltd.) (Fig. 1)

- **Image and AVS analysis**
  - Each core sectioned in 5 mm increments and each slice homogenised
  - 1 g of each slice extracted in deoxygenated 1 M HCl (AIVS) in the form of H$_2$S under acidic conditions, measured directly with an amperometric H$_2$S microelectrode
  - Image of the remaining slice obtained using a flatbed scanner
  - Colour intensity of each slice correlated to the measured (AIVS) (Fig. 2)

### Findings

We established a strong correlation (Fig. 2) between sediment colour intensity and (AIVS) allowing for the accurate prediction of the in situ distribution of AVS from a sediment profile image.

Two types of AVS predictions can be made: (1) the colour intensities of horizontally aligned slices are averaged to obtain a vertical (AIVS) profile (Fig. 3A), or (2) individual pixel colour intensities are mapped to create a two dimensional distribution plot of (AIVS) (Fig. 3B).

### Conclusion

Using in situ sediment profile imagery and amperometric H$_2$S microelectrodes, we have vastly improved the predictive power of the Bull and Williamson (2001) approach. Our new technique makes AVS an accessible parameter for rapid assessment of the effects of organic enrichment in marine sedimentary environments.
8.2 Popular article published in the Costal Society’s “Coastal News”, April 2011

Monitoring Organic Enrichment of Coastal Sediment

Peter Wilson and Kay Vople, Auckland University of Technology

Organic enrichment of coastal sediment is of interest to coastal managers worldwide. It results from excess supply of organic carbon to coastal waters from both natural and anthropogenic sources such as, terrestrial runoff, eutrophication, and aquaculture.

A large fraction of this carbon is mineralised by sulfate reduction, a bacterially mediated reaction that leads to the production of hydrogen sulfide (H₂S). This is the culprit for the ‘rotten egg’ smell you encounter when digging up estuarine sediments. H₂S readily reacts with sedimentary iron compounds to form iron sulfides that contribute to the distinct black colouration of organic-rich sediment.

In the laboratory, we can convert the majority of these iron sulfides back into H₂S by adding acid to the sediment and so indirectly measure the concentration of the acid volatile sulfides (AVS). Although this concentration is well suited as an indicator of organic enrichment, its measurement has not been used in routine monitoring because of its laboursome nature.

Almost 10 years ago, Bull and Williamson (2001) tested an easier approach to predict the sediment AVS concentration from sediment images taken in the laboratory. The authors analysed photographs of sediment sections and found a weak linear correlation (r² = 0.67) between sediment colour and AVS concentration. During the past 12 months, with the help of new technology, we improved and further developed this approach into a rapid technique for monitoring the in situ distribution of AVS.

Using H₂S microelectrodes, we established a strong linear correlation (r² = 0.93) between sediment colour and the concentration of AVS. This allows for the accurate prediction of the distribution of AVS from a sediment profile image. We also tested the suitability of a novel sediment profile imaging device (SPI-Scan, Benthic Science) Figure 1 to obtain high-resolution sediment profile images readily in the field. Our new image analysis procedure allows us to make two types of predictions from the acquired images with a simple mouse click. Firstly, the colour intensities of horizontally aligned pixels are averaged to obtain a vertical AVS concentration profile.
profile (Figure 2a). Secondly, individual pixel colour intensities are mapped to create a two-dimensional distribution plot of AVS concentration (Figure 2b).

Both types of predictions provide parameters well suited to environmental monitoring, for example, an assessment of the environmental impact of marine farms. The maximum AVS concentration and the depth at which this occurs are readily visible on the vertical AVS concentration profile. The two-dimensional AVS distribution plot can be used to assess spatial heterogeneity in this distribution and how this variability is affected by macrobenthic fauna. Most importantly, rapid surveys of the seafloor underneath marine farms with our sediment profile imaging device can now reveal the depth and the size of the farm AVS footprint and how these change over time.

Our new technique makes AVS an accessible parameter for rapid assessment of the effects of organic enrichment in marine sedimentary environments. To assess these effects, marine consultants have been using a number of techniques that deal with selected functions of the marine ecosystem.

We believe that the inclusion of AVS measurements into current monitoring practices will be an important step towards a more holistic and integrated approach to routine monitoring.

Reference


Upcoming Conferences

EDS Coastlines Conference

The Environmental Defence Society Conference Coastlines (Auckland, 1 to 2 June 2011) will examine spatial planning of New Zealand’s coasts, lakesides and oceans.

Marine spatial planning is becoming a key mechanism for the implementation of oceans policy in many other developed countries. The conference will explore this international thinking and experience along with recent scientific developments and professional practice in New Zealand.

Sessions planned for the first day of the conference include international experiences in coastal and oceans management, the case for oceans reform in New Zealand, implementation of the New Zealand Coastal Policy Statement, and a Leaders’ dialogue.

Sessions on the second day will focus more closely on the practical application of spatial planning to coasts, lakesides and oceans. There will be a field trip, which will consist of a cruise around the inner Hauraki Gulf viewing coastal management issues, on the afternoon of Tuesday 31 May.

The programme is currently under development and regular updates will be posted on the conference website.

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Visit www.coastalsociety.org.nz and follow the “Publications” link on the front page.

For further details, programme information, and registrations see www.edsconference.com.

Coasts and Ports 2011

Mark your calendars now for Coasts and Ports 2011 which will be held 28 to 30 September 2011 in Perth, Western Australia. The conference is an amalgamation of the 20th Australasian Coastal and Ocean Engineering conference and the 37th Australian Port and Harbour Conference. Hosted by the National Committee for Coastal and Ocean Engineering (Engineers Australia), IPANCAustralia and the Institute of Professional Engineers New Zealand (IPENZ), the conference is also supported by the New Zealand Coastal Society.

The Coasts and Ports Conference series is the pre-eminent forum in the Australasian region for professionals to meet and discuss issues extending across all disciplines related to coasts and ports. Coasts and Ports 2011 will bring together engineers, planners, scientists and researchers to focus on the technological, scientific, policy, planning and design issues related to our diverse and developing coasts.

For further details, programme information, pre-conference short courses and registrations, see www.coastsandports2011.com.au.