Characterisation of Suspended Particles Collected from an Estuary in an Urban and Industrialised Centre using Magnets onboard an Autonomous Underwater Vehicle

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***Abstract*- An Autonomous Underwater Vehicle (AUV) equipped with rare-earth (Sm-Co) magnets was used to sample suspended particles during its transects of the Derwent estuary in Tasmania. Mineral characterization was then performed in the laboratory using ^{57}Fe Mössbauer spectroscopy (MB) and X-ray diffractometry (XRD). Results indicate the sources of the suspended particles to be both natural and industrial.**

I. INTRODUCTION

Traditional survey methods for estuarine and inshore marine suspended particles and sediments, involving sediment grabs or even diver-deployed probes, are proving inadequate for current environmental management needs [1]. They can also prove costly in both time and logistics, often demanding prolonged use of small boats with several field staff, can potentially place these staff in high-risk environments. In addition to these aspects, sampling is usually restricted to limited sites and as a result poor in spatial resolution. AUVs are being used as a new frontier technology for benthic mapping and water quality data recording [2]. Here, we propose the use of AUVs to sample suspended particles for later characterization in the laboratory. In a typical mission, distances between 4 and 20 km can be navigated. Provenance of sampled particles can be determined, since engineering data (e.g., position, depth) are recorded, and for the Derwent region, outputs from hydrodynamic and sedimentary resuspension models are available. The characterisation of suspended particles allows us to determine the origin of the material; and therefore, this information is in demand for environmental management of industrialized urban estuaries.

II. EXPERIMENTAL

A. Magnetic Sampling

Samples are collected during each deployment of the AUV using a pair of rare-earth magnets (Sm-Co) placed beside the autonomous underwater vehicle (Figure 1). Each magnet consists of a disk of 2 cm in diameter and 1 cm wide. The missions typically last for 4-6 hours and traverse 5-20 km.

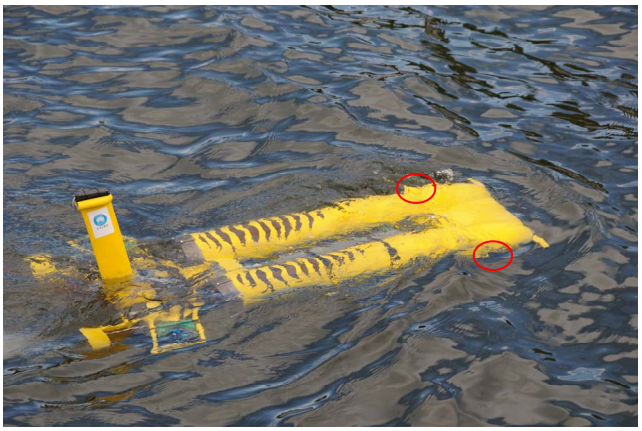

Figure 1. The AUV developed at CSIRO used to sample suspended particles in the Derwent Estuary. This AUV is 1.2m long and the magnets are placed where the red circles are indicated.

B. ^{57}Fe Mössbauer spectroscopy

Typical MB spectra recorded for a suspended particle sample are shown in Figure 2. The Mössbauer experiments, both at room temperature (298 K) and liquid nitrogen temperature (78 K), were performed in the standard transmission geometry with a ^{57}Co/Rh source of 100mCi of activity. The least-square fitted MB parameters were calculated using a linear combination of Lorentzians lines optimised using genetic algorithms [3]. The Mössbauer analysis is non-destructive, so all samples could be kept for other experiments. Relative concentrations of each Fe-bearing mineral phase is shown in Table I.

C. X-Ray Diffractometry

The powder XRD analysis was performed with a Siemens D500 powder diffractometer equipped with a CuK_α radiation source.

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TABLE I
TYPICAL MÖSSBAUER SPECTRAL AREAS OBTAINED FROM SUSPENDED PARTICLES COLLECTED USING OUR AUV IN THE DERWENT RIVER.

Relative Spectral Area [%]	Possible Fe-bearing minerals
81%	Magnetite
4%	Schwetmannite
3%	Goethite
12%	Silicates

The spectral area corresponds to an approximate concentration of Fe, as a given mineral. For example, a spectral area of 81% of magnetite corresponds to say 81% of the Fe in the form of magnetite. Both ferric and ferrous sites in magnetite (i.e., from the inverse spinel structure) are counted here. Deviations from this are usually caused by f-recoil factor, usually smaller for Fe^{2+} phases. This means that ferrous concentration might be a fraction higher than detected by Mössbauer spectroscopy. To determine the total concentration of Fe-bearing minerals it is necessary to measure the concentration of iron in the sample using a chemical analysis method. This was not performed at this stage.

III. RESULTS AND DISCUSSION

The spectra are combinations of sextets and doublets associated with magnetite (Fe_3O_4), schwertmannite ($Fe_{16}O_{16}(OH)_{12}(SO_4)_2$), goethite (α-FeOOH) and Fe-bearing silicate phases (probably staurolite and dolerite). Schwertmannite [4] is formed under acidic conditions that are likely to be found only within in-plant processes or in industrial effluents around the sampling area.

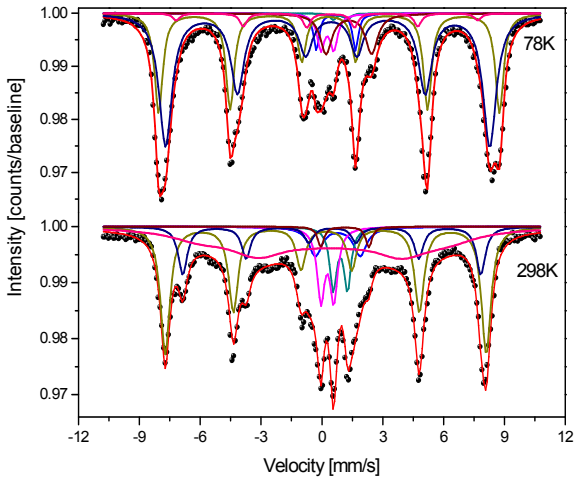

Figure 2. Least-square fitted 57Fe Mössbauer Spectra recorded at room temperature (298K) and at liquid nitrogen temperature (78K). Each color represents a Fe-bearing mineral site. The broader line appearing in the 298K spectrum is associated with goethite (α-FeOOH) which orders magnetically with temperature, becoming a well-defined set of six peaks (sextet) at 78K.

The XRD measurements confirm the presence of magnetite and quartz. Quartz cannot be seen by MB, but Fe-containing minerals can. Natural phases are the silicates and quartz. Magnetite can be formed in industrial or anthropogenic processes. Schwertmannite has not been found occurring in natural soils or sediments in Tasmania. Schwertmannite is then associated with anthropogenic emissions. The transformation of Schwertmannite to goethite is well-known [5]. So, it is possible that part of the goethite found could be a secondary product of anthropogenic emissions.

IV. CONCLUSIONS

Sampling suspended particles using an AUV increases the efficiency and ease of collecting particles for further characterisation in the laboratory. Magnets are relatively cheap devices and easily attachable to the AUV structure. The sampling procedure is inexpensive and has the advantage of sampling suspended particles at locations where additional information is being collected (e.g., water temperature, conductivity, pH, turbidity, dissolved oxygen). Taking advantage of the MB to identify Fe containing minerals and the mobility of the AUV, we were able to characterise key phases sampled by the magnets.

The AUV is a very convenient vehicle to use for this purpose because it documents the path navigated during the mission.

The use of Mössbauer spectroscopy and X-ray diffractometry is very valuable, because both techniques are non-destructive. Therefore, samples can be retained for further analysis using destructive techniques, such as LIBS (Laser Induced Breakdown Spectroscopy), ICP-AES or thermogravimetric analysis. Both techniques used in the characterisation were also complementary: Mössbauer spectroscopy provides qualitative information on Fe-bearing minerals and XRD on both these and non-ferrous materials.

The potential source of the suspended materials could also be assessed. Considering that paramagnetic materials were collected, it is possible to assume that, for example, silicates and magnetic phases form aggregates. Magnets are not expected to sample silicates, unless they are physically attached to magnetite or other strong magnetic material.

Further work is underway to use different magnets, with different strengths to sample strong magnetic samples (ferromagnetic material) and weak magnetic oriented materials (e.g., antiferromagnetic or ferromagnetic).

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