Analytical considerations following accidental discharge of material into a river

Dr Alison Crossley, Dr Kerstin Jurkschat, Chris Salter and Dr Colin Johnston

Oxford Materials Characterisation Service Department of Materials Oxford University OX5 1PF

Jan ’17: HGV crash spills 12,000 litres paint on M606

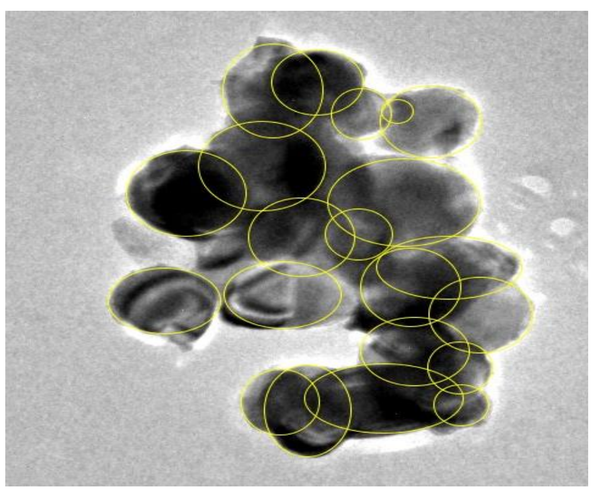
River flows white for several miles

INTRODUCTION

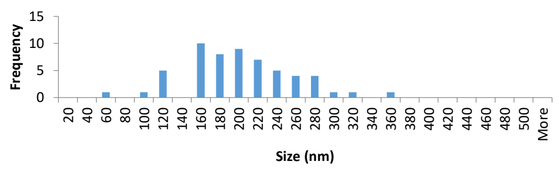
An opportunity to study the fate and potential transformation of small particles in the natural environment. The possible transfer of spilled material to the bed sediments and uptake by the benthic invertebrates is being investigated.

Such information will be required to take into account any specific considerations needed for risk assessment of engineered nanomaterial. The debate on what should be categorised as nanomaterial continues[2] with the aim of providing clear and unambiguous criteria to identify materials for which special considerations apply. It is vital that standards, instrumentation and validated procedures for metrology progress at the same rate as nanotechnological innovation.

Stone recovered from river bed



TiO2 particles

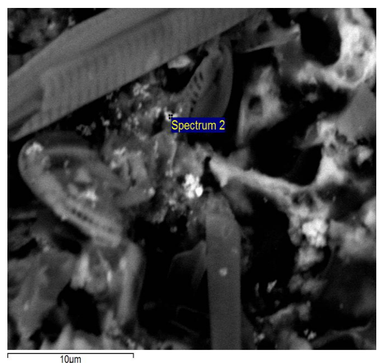


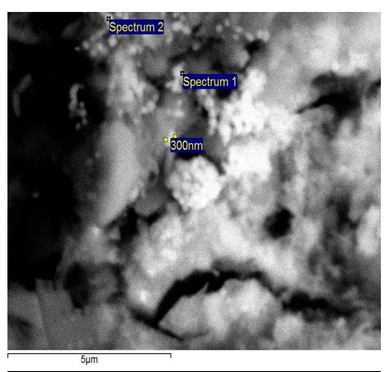
TiO_2 particle size distribution was estimated by fitting ellipses to the projected images of the particles where at least 20% of the circumference could be identified. The average size was 193 nm (Standard deviation 61nm)

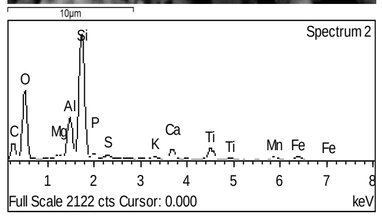
EXPERIMENTAL METHOD

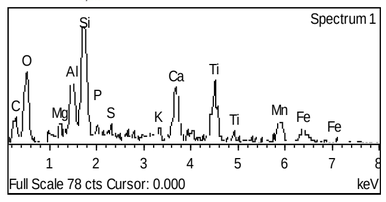
Following an initial UK Environment Agency investigation of river water quality CEH (Centre for Ecology and Hydrology) Lancaster sampled (January and July 2017) parts of the stream system where residual chemical signatures from the spill were anticipated. These included the bottom sediments and the benthic invertebrates. Stones from the river bed with white surface deposits were also collected and analysed and the results are shown here. Further experiments are planned which will involve the analysis of the sediments and the invertebrates.

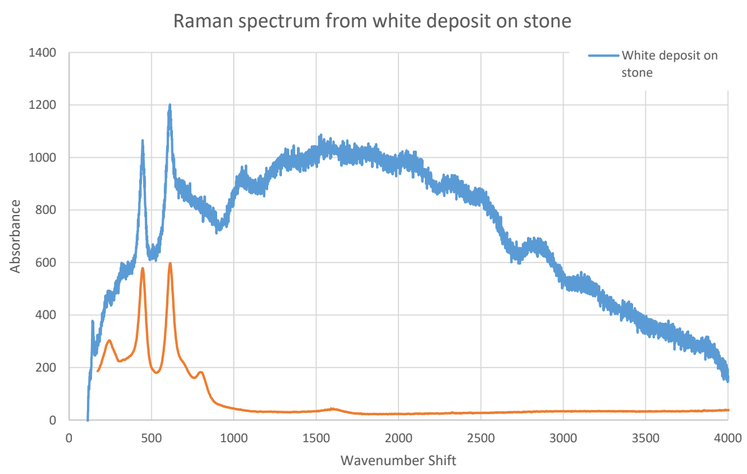
Established analytical, imaging and metrology methods such as Raman spectroscopy (JY Horiba LabRAM Aramis using a 532 nm laser), a JEOL 6480 LVSEM (low voltage scanning electron microscopy) equipped with EDX (energy dispersive X-ray analysis) and a JEOL ARM-200F TEM (transmission electron microscope) were applied and compared with methods designed specifically to determine number concentration, particle size and size distribution of nano-particles in complex media such as sp-ICPMS[3] (single particle inductively coupled mass spectrometry).











RESULTS

SEM/EDX analysis of the deposit remaining on the stone was performed. These images show the stone surface is covered with epilithic diatom flora as expected from a pebble recovered from a river bed. Clusters of TiO_2 particles are also observed. The spectra are dominated by the presence of silicon resulting from the diatom silicatious composition. More detailed analysis of the deposit shows it consists of TiO_2 particles with a primary particle size around 200 nm confirmed by TEM.

Raman analysis of the deposit on the stone identified rutile TiO_2 .

Sp-ICMPS used by CEH to measure the number and size of particles associated with the spill material positively identified titanium in a sample taken from the stone. Preliminary results gave a particle size distribution centred around 80 nm.

CONCLUSION

The analysis performed on the white deposit observed on the stone recovered from the proximity of a paint spill shows that it is composed of rutile TiO_2 with a particle size distribution around 200 nm. These are as expected from pigment grade TiO_2. The particulate deposit is confirmed as engineered material however no nano-sized particles were confirmed and no nano-specific effects are anticipated.

The results obtained highlight discrepancies between results from established imaging methods and emerging methods. The sp-ICPMS results showed a significant bias towards smaller particles. This could be due to sample preparation methods, poor calibration or preferential selection of smaller particles. This illustrates the importance of method validation against other techniques such as those used in this study and has implications for accurately measuring material from unplanned release of engineered nano-materials into complex media where quantification as well as detection are considered important as a regulatory issue.

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