

### TLS 14A1 BM – IR Microscopy

- SR-FTIR, FPA Mapping
- Bacteria-mineral Interaction, Arsenopyrite (FeAsS), Micro-colonization, Chemical Imaging

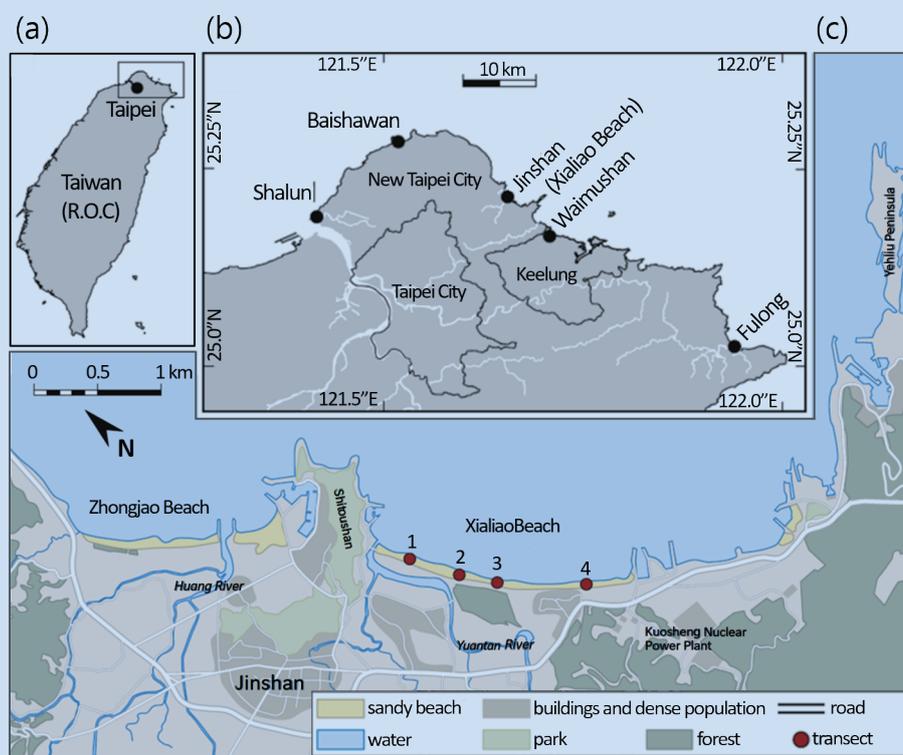
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## Microplastics at the Northern Coast of Taiwan

*Micro-colonization of arsenic-resistant Staphylococcus sp. As-3 on arsenopyrite (FeAsS) and Microplastic pollution is a global issue and greatly affects the environment in which we live. Synchrotron-based infrared microspectroscopy provides a precise identification of microplastic.*

The purpose of the invention of plastic bags in 1959 was to save the planet. Nowadays, it is ironic that plastic pollution is growing as a result of the plastic industrial development. According to a document of the World Health Organization (WHO), microplastics have been found in our living settings and even in food, of which the size of tiny plastic fragments less than five millimetres is defined as microplastics. If the size is larger than 150 micrometres it is unlikely to be absorbed in the human body, whereas the uptake of smaller particles is a small possibility according to WHO investigations.



**Fig. 1:** Maps of the study area and transects within Wanli Xialiao Beach near Jinshan, New Taipei City, and northern Taiwan. (a) Map of northern coast of Taiwan with a rectangle showing the study areas. (b) Map of northern Taiwan with the location of Jinshan, as well as locations of four beaches (Shalun, Baishawan, Waimushan, Fulong) that were sampled for microplastics. (c) Detailed map of the study area. The locations of the investigated transects on Xialiao beach are indicated with red dots. Numbers 1 to 4 represent transect 1 to transect 4. [Reproduced from Ref. 1]

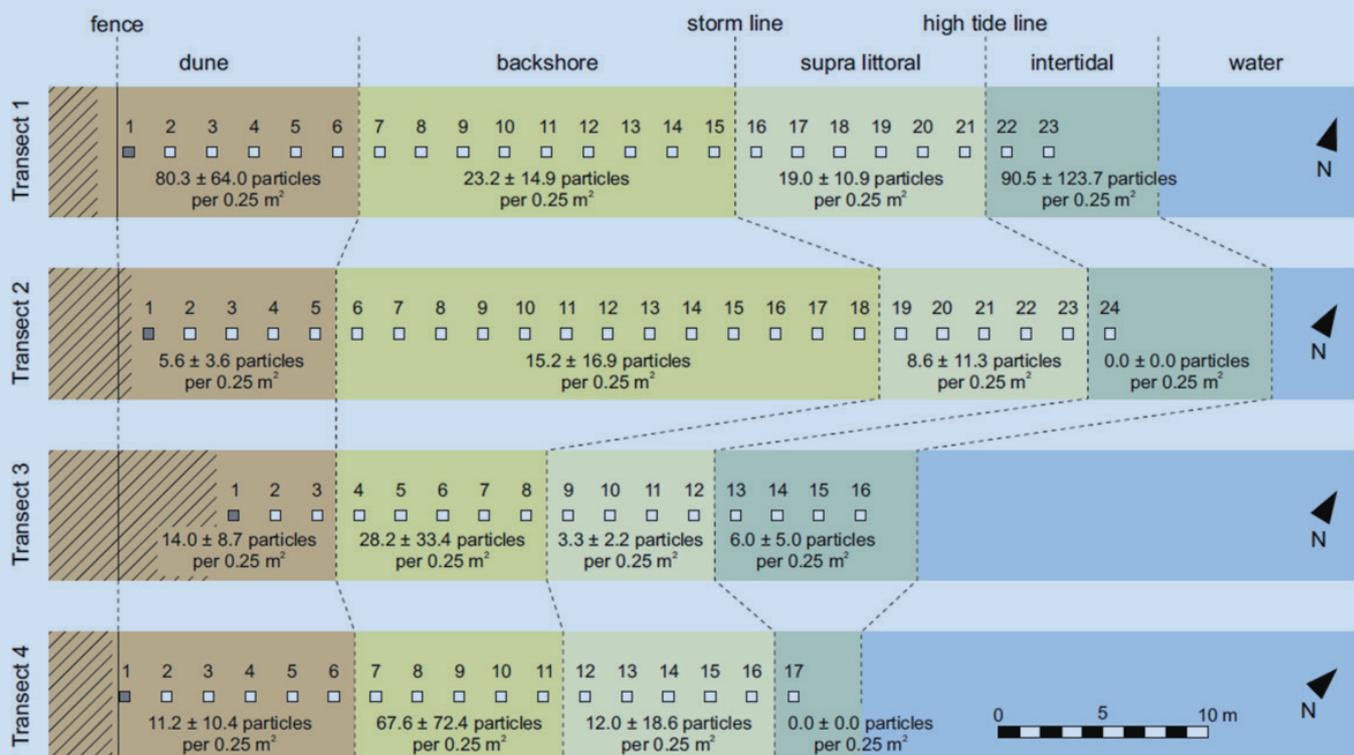
Based on the growing microplastic problem, a research team of Taipei Medical University, National Taiwan University and National Sun Yat-sen University investigated since early 2015 the microplastic and mesoplastic pollution of an area of Wanli Xialiao Beach near Jinshan in northern Taiwan using SR-FTIR microspectroscopy and ATR-FTIR microspectroscopy. The research team studied a sand sample of depth under 1 cm from the surface that was collected in a systematic manner. In total 80 samples were collected along four transects; the plastic particles ( $\geq 1$  mm) were extracted and quantified. In total, 1939 microplastic particles were recovered, with an average 96.8 particles per square metre. Statistical analysis showed that the backshore had significantly more microplastic particles than the supra littoral or intertidal. Approximately 6.8 million plastic particles ( $\geq 1$  mm) weighing about 250.4 kg were estimated in the surface layer of Wanli Xialiao Beach on extrapolating the num-

bers of plastic particles found. Resampling curves were created from the data set, which showed that 20 samples as a minimum should be taken to estimate adequately the mean particle abundance.

Wanli Xialiao Beach in Jinshan is located on the northern coast of Taiwan (Fig. 1) and is part of a beach system developed along the floodplain of the Huang River and Yuantan River. Zhongjiao Beach and Xialiao Beach are separated by the Shitoushan Hills. Xialiao Beach has length 2.33 km; the width, measured from the dune to the high tide line, varies from approximately 70 m in the northwestern part to approximately 30 m in the south-eastern part. The total area of the beach is estimated about approximately 70130 m<sup>2</sup> based on satellite images provided by Google Earth. The northwestern part of the beach is bordered by the mouth of the Yuantan River. With length 6.2 km and catchment area 22.33 km<sup>2</sup>, which is mostly in unpopulated mountainous areas, the river is relatively small.

The sampling scheme was based on the Marine Strategy Framework Directive (MSFD) Technical Subgroup on Marine Litter report,<sup>2</sup> Kunz<sup>3</sup> and Besley.<sup>4</sup> Samples were collected from a square with each side of length 0.5 meter. Keeping the sampled area and depth as constant as possible at 1 cm using a Polyvinyl chloride (PVC) tube frame, sand was collected from the surface with a metal scoop. The sampling depth varied from 1 to 2 cm in some sampling places. Each sample therefore represents an area 0.25 m<sup>2</sup>, or an estimated average volume 0.0025 m<sup>3</sup> but with some variation. The starting point for sampling plastic of each transect was at the fence on the top of the dune; a constant distance frame 2 m was moved towards the water line until the wet part of the intertidal zone was reached. For transect number 3, the starting point was, however, on the slope of the dune and not at the fence because of the dense vegetation in that area of the beach (Fig. 2).

268 potential microplastic particles were recovered from transect 2 (Fig. 1); 249 particles of these particles were analyzed at the endstation for SR-FTIR microspectroscopy at TLS 14A1. Potential microplastic particles were further analyzed with the attenuated-total-reflection Fourier-transform infrared (ATR-FTIR) microspectroscopy, which includes a FTIR spectrometer equipped with an IR microscope coupled with a dedicated 20x ATR objective, which is an anvil-shaped Ge crystal with contact area 80 μm<sup>2</sup>. Functional groups of chemical components were identified based on the characteristic IR absorption lines of plastics. The FTIR spectra of each plastic particle

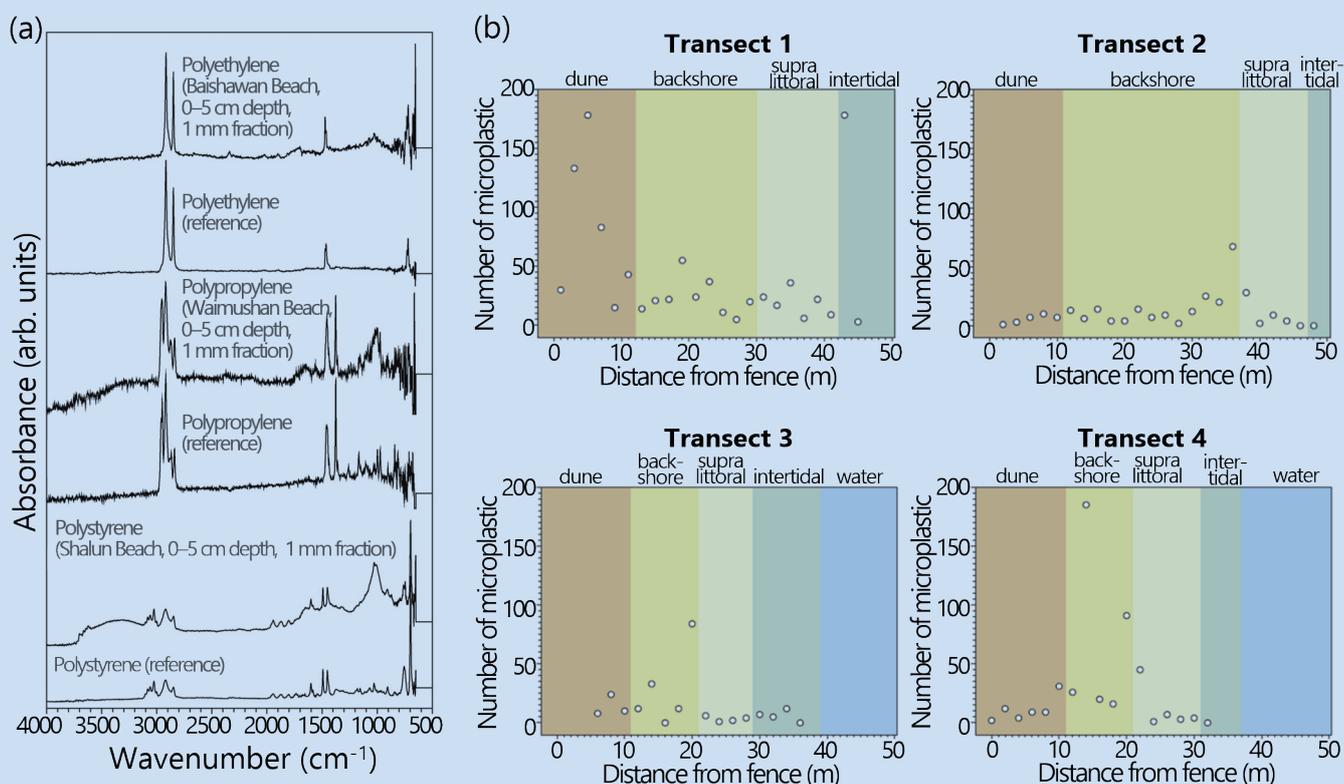


**Fig. 2:** Sampling points along the four transects for each beach zone and each transect (the mean and standard deviation of potential microplastic particles per 0.25 m<sup>2</sup> are also given). The grey square marks the starting point for each transect. Beach zones were assigned during field work by visual interpretation of the beach morphology. Please note that each transect was rotated and aligned along the fence for illustrative purpose. All transects have the same scale. [Reproduced from Ref. 1]

adhering on the filter paper sheet were acquired with 512 scans at spectral resolution  $4\text{ cm}^{-1}$  in spectral range  $4000\text{--}400\text{ cm}^{-1}$ . The FTIR spectra of each microplastic particle were compared with a database of standard spectra (OMNIC 9.2, 2012; Thermo-Fisher Scientific Inc., Waltham, MA, USA), which the research team collected from various plastic objects made of varied plastic types: acrylonitrile butadiene styrene (ABS), polyamide (PA), high-density polyethylene (PE-HD), low-density polyethylene (PE-LD), polyethylene terephthalate (PET), polylactic acid (PLA), polypropylene (PP), polystyrene (PS), polyurethane (PUR) and PVC; at least five specimens of each plastic type were measured with the FTIR spectrometer as described above to obtain representative spectra for each plastic type (Fig. 3).<sup>3</sup>

For the microplastic pollution of Xialiao Beach in northern Taiwan, there were on average 96.8 particles per square meter on this particular beach because microplastics were found in 75 out of 80 samples (94%). Based on these findings, the research team deduced that the entire beach was polluted with microplastics – approximately 6.8 million plastic particles with estimated mass 250.4 kg at the surface of the entire beach, which should be present in the surface layer of Xialiao Beach. Most microplastics, identified with synchrotron-based infrared microspectroscopy and ATR-FTIR microspectroscopy, accumulated at the backshore with a high level of variation between samples, transects and beach zones (Fig. 3). Reporting a complete and unbiased picture of microplastic pollution, either randomly or systematically with several transects and a sufficient number of samples on each transect, were strongly suggested for sampling. Furthermore, the representative large number of overall microplastic pollution is necessary for sampling microplastic samples from a target area. The investigation results from other studies were possibly greater than that of the result of this research team in East Asia. The research team suggested reporting an average for the entire beach, but the number of locations at which plastic samples were obtained was too small, so as to cause an unexpectedly large extent of microplastic pollution. Based on the results of the resampling curves, we believe that our results represent the true average pollution of Xialiao Beach rather closely. (Reported by Yao-Chang Lee)

*This report features the work of Alexander Kunzd and his collaborators published in Mar. Pollut. Bull. 140, 75 (2019).*



**Fig. 3:** (a) FTIR spectra of the three most common plastic types found in the collected samples. The reference spectra and one representative spectrum from a sample are shown. [Reproduced from Ref. 2] (b) Number of potential microplastic particles found in each transect in relation to the distance from the fence on the dune at 0 m. The scales of the x and y-axes were kept constant in each figure to allow for visual comparison between each transect. [Reproduced from Ref. 1]

### TLS 14A1 BM – IR Microscopy

- FTIR Microspectroscopy
- Environmental Science, Biological Science, Medical Science, Materials Science, Chemistry

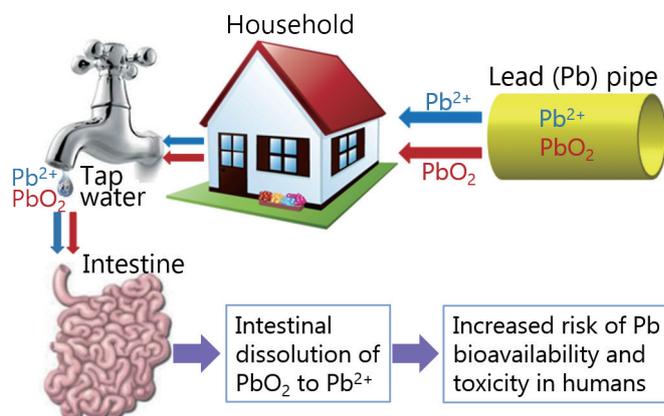
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## Lead (Pb) Poison in Drinking-Water Systems

*Nanoscale lead dioxide particles ( $n\text{PbO}_2$ ) in the corrosion product formed inside lead-bearing pipes or lead-containing faucets in systems for the distribution of drinking water can release toxic lead ions ( $\text{Pb}^{2+}$ ), which cause lead poisoning in human beings, especially children.*

Many countries, including USA, UK, Canada, Australia and Taiwan, still have Pb service pipes in their distribution systems for drinking water. Pb-contaminated drinking water was reported to cause blood lead poisoning in human beings, especially children. Nanoscale Pb dioxide ( $n\text{PbO}_2$ ) is a solid particulate of tetravalent Pb oxides known to form on the inner surface of lead pipes with drinking water of high oxidation-reduction potential, such as chlorinated water.  $n\text{PbO}_2$  can be reduced to lead ions ( $\text{Pb}^{2+}$ ) when free chlorine is switched to monochloramine, which causes the lead water crisis. The water matrices that affect aqueous redox conditions also alter the stability of  $n\text{PbO}_2$  contributing to this Pb contamination problem. The dissolution of  $n\text{PbO}_2$  increases with increasing concentration of dissolved inorganic carbon and natural organic matter and with decreasing pH. Furthermore,  $n\text{PbO}_2$  can be dislodged from a pipe surface under large flow rates, so to enter the water supply and become released into the environment. Although the replacement of lead pipes with copper and stainless-steel pipes has been attempted in various countries to remove lead sources from their distribution systems, small segments of lead pipes typically remain because of the high cost and poor accessibility in private premises; this partial replacement can induce galvanic corrosion, releasing more lead into the water supply. The major sources of lead in the distribution system are hence the remaining lead service pipes and lead-containing plumbing materials such as solder, faucets and valves, particularly those made from brass that contains about 2% Pb to en-



hance its machinability. Many authors have reported various toxic effects induced by metallic or metal-oxide nanoparticles *in vitro* and *in vivo*. These authors suggested that some observed toxicity symptoms of nanoparticles are similar to those of their respective metal ions. Further information on the toxic mechanism of  $n\text{PbO}_2$  is essential to understand the Pb bioavailability and toxicity in humans.

Pei-Jen Chen (National Taiwan University) and her collaborators recently used adult medaka fish (*Oryzias latipes*) as an animal model to investigate the uptake, lead dissolution, bioaccumulation and toxic effects of  $n\text{PbO}_2$ , microscale bulk Pb dioxide ( $b\text{PbO}_2$ ) and  $\text{Pb}^{2+}$  *in vivo* upon acute to sub-chronic aqueous exposure.<sup>1</sup> Utilizing X-ray absorption near-edge structure (XANES) spectra at **TLS 07A1** the team found that both  $n\text{PbO}_2$  and  $b\text{PbO}_2$  could be reductively dissolved