

Lab Journal: analysis of an Atlantic clay sediment sample near the Canary Islands

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I. INTRODUCTION

First, we shall discuss the points we are to research before starting our research plan. In literature, we shall attempt to find:

1. the sedimentation rate for this portion of the Atlantic, to determine the time resolution in our sample;
2. perturbation of the ocean floor through natural or human mechanisms;
3. concentration of microplastics, as an indication of the increase in nanoplastic concentration;
4. amounts of detritus, and whether this would contaminate the measurement;
5. protocols for extraction of the plastics from the clay.

From this, we shall construct a protocol for our measurements and from there, we shall find the tools we may need to acquire.

In general we split these into three categories: items 1 and 2 (to be researched by Joost) describe the context of the samples, items 3 and 4 (to be researched by Has) describe the contaminants, and item 5 (to be researched by Eva) describes the practical steps to be taken.

I.i. Question Answers

I.i.1. Sedimentation rate

We found numerous different values for the sedimentation rates, influenced by exact location, period, etc. The found values were however all in the range of several mm [12] to cm [16]

per thousand years. So either way, assuming the pollution of the environment started, say, a century ago [15], in theory only the upper millimeters of the ocean bottom should contain (traces of) plastic. Although that is unfortunately not the whole story. (There does perhaps seem to be more data, except we have not (yet?) figured out where exactly to find it or how to get it into a readable format, if we are even able to. Being this paper [17], but also the sites of several organisations, such as PLOCAN, BIOS and IODP)

I.i.2. Perturbation of the ocean floor

Something to take into consideration when analysing these samples, are possible perturbations caused by both human and natural causes. This could be for example anchors, strong water flows or (deep sea) animals mixing some of the upper layers. We found a source stating that the ocean floor in the area we're interested in is currently stable "Under static (gravitational) loading conditions" [14]. However, human influences can also cause mixing and other perturbations in the sedimentation. [11] [13]. Unfortunately there seems to be no way to deal with this, other than maybe changing our hypothesis on the (maximum) depth we expect to find significant amounts of (nano)plastics.

I.i.3. Microplastic concentration as proxy for nanoplastic concentration

It was found that microplastic concentration is not a valid approximation for nanoplastic concentration. Microplastics arrive at the sea floor with different mechanisms and therefore do not

have an exact relation to nanoplastics. [5] [6] Microplastics behave like particles and are capable of sinking. Nanoplastics behave like colloids and do not sink quickly, unless they (self)aggregate. [7] The aggregates are too big to pass through the less porous filters. This can lead to significant loss of nanoplastics in the sample. The aggregates can be destroyed using sonication. [4]

I.i.4. Significance of detritus in the sample

Detritus is present on the seafloor, as it is everywhere in the ocean. Detritus is also one of the things that the nanoplastics can aggregate on. As the aggregates are dispersed using sonication and afterwards the supernatant is filtered only very low mass organic compounds should remain in solution. These typically have a low boiling point so should not be detected at the same time as the nanoplastics (high boiling point). [8]p. 79 If they do somehow come along with the nanoplastics (if the nanoplastics aggregate to them again during the rise in temperature perhaps) then their MS footprints should be sufficiently different as to not warrant any concern.

I.i.5. Existing Protocols

There exists research on the filtration, dialysis, and ultrafiltration retention rates using polystyrene nanospheres between 1000 and 50 nm.[1]

From this research, we get several takeaways: Polymer membranes are not recommended, with retention rates far too high.

"there was always retention even if the porosity was up to 50 times larger than the beads diameter. This implies that for pre-filtration, in the view to NP quantification in a real sample, the recoveries would be insufficient and very difficult to rationalize because of the high particle heterogeneity."

Dialysis led to important losses of 50% after 48h and 70% after 72h.

Ultrafiltration had losses of 35-40%

Next, I found a publication which determined metal fractionation of a marine sediment core from Antarctica.[2]

Again, there were several takeaways:

Stainless steel was used to sample the core. It was subsampled using a Teflon blade. Only the inner part was analysed.

To determine moisture content, a subsample was dried at 105° C until the mass was constant. The storage containers were cleaned extensively. They used a clean room (Class-100.000 / ISO 8, the "dirtiest" clean room[3]).

Next, I analysed section 2 ('Materials and method') of a publication in which a core sample was analysed from the Indian Ocean.[9] In this, they used acetic acid to remove inorganic carbon contents of the sediment, and hydrogen peroxide to remove organic carbon contents. After this, they were washed with deionized water to remove remaining acids, peroxide, and salt.

Finally, I read a paper of the PASADO core processing strategy, which appeared to have been made to allow several disciplines to perform research on the same core. Still, I extracted some points that I thought might be useful.

Namely, the idea of leaving one half of the core (if split lengthways) for archiving purposes, if we have enough of the core to do that. Secondly, the idea to use a cutting tool with the right shape to not take the sides of the core, as those might be contaminated.

In summary:

We should try to avoid any filtering with porosity less than two orders of magnitude above 1 μm . If needed, stainless steel grids with cut off at 5 or 10 μm are preferred, with 15-20% retention.

We should use steel and glass tools wherever possible, as to not contaminate the sample. We clean the bottles using temperature. Verify if we can get a glovebox.

Peroxide can be used to remove organic carbon contents, acetic acid can be used to remove inorganic carbon contents.

A D-shaped cutter is useful as not to incorporate plastics from the storage medium.

Furthermore, to use only one half of the sample may be a good idea for insurance's sake.

II. PRACTICAL

II.i. Day 1 (May 22nd 2025)

. *Research preparation* Before starting the practical, 4 beakers, which had been labeled from A to D (for 4 subsamples) and a stanley knife with some extra blades (to cut the sample into subsamples) were heated in an oven for a sufficient time. The soil sample had in turn been frozen. The sonicator was cleaned by wiping it with moist (just regular tap water) paper towels and then rinsing it with demineralized water. Also all the beakers were weighed. See Table 1 for the found masses.

. *Blanks* To start, some blanks were prepared. To do so, first about 15-20 mL HPLC water was brought into beaker B, 10-15 mL of which was immediately brought into a syringe, which was in turn put in the freezer. This was the syringe blank, SB for short. Then a little bit of the HPLC water in beaker B was transferred into a vial (the same ones which will be used throughout the rest of the practical). This was the beaker blank, BB for short. Some HPLC water was poured directly from the bottle in another vial. This was the HPLC blank, HB for short. Lastly, an "empty" vial (meaning filled with air) was labelled our system blank, SB for short.

. *Subsample preparation* First, the sample was taken out of the freezer, in order for it to melt a bit. There was about 9 cm of soil left

in the syringe. As the outside of the syringe was dirty, it was scraped using a stanley knife. In order to prevent contamination, the bottom of the sample was scraped off. The sample was then slowly pushed out the syringe, and cut with the aforementioned heated stanley knives into 4 subsamples. They were, starting at the bottom, 3, 2, 2 and 2 cm thick and were transferred into beakers B, C, D and A respectively (also see Table 1). The top layer of the soil was left in the syringe, in order to prevent any contamination. For each subsample, a new stanley blade was used. The plan was to also scrape of the outer layer of each sample, as the contact with the syringe might have caused contamination and mixing. This was forgotten at first, but as nothing had been done to the subsamples when this mistake was realised, it was still done. All the subsamples were then weighed in their respective beakers, in order to determine the weight of all the subsamples (see Table 1). In order to dissolve all the subsamples, 25 mL of HPLC water was added to all the beakers, using a graduated cylinder and a pipette. As beaker C was a 150 mL beaker, contrary to the other beakers, which were all 100 mL beakers, that subsample was not fully dissolved in the HPLC water. So, 25 mL more was added to all the beakers, bringing the total to 50 mL HPLC water per subsample. Some of the HPLC water was also transferred into a vial, as a cylinder blank (CB). To prepare the beakers for the upcoming sonication, they were covered with aluminum foil, which was kept in place with some binding wire. They were then attached to the sonicator, which was then turned on for several hours.

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