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CONTROL, TRATAMIENTO Y REDUCCIÓN DE MICROPLÁSTICOS Y CONTAMINANTES EMERGENTES EN AGUAS RESIDUALES URBANAS Y EN EL MEDIO COSTERO TRANSFRONTERIZO

workshop

21 de junho de 2024 | ETAR do Freixo, Porto | 12:30

Poluentes Emergentes e Microplásticos em Águas Residuais Urbanas e Água para Reutilização: *onde estamos e para onde vamos?**

Los Microplásticos en el Medio Ambiente: Importancia de Protocolos Estandarizados de Muestreo y Metodologías para su Determinación

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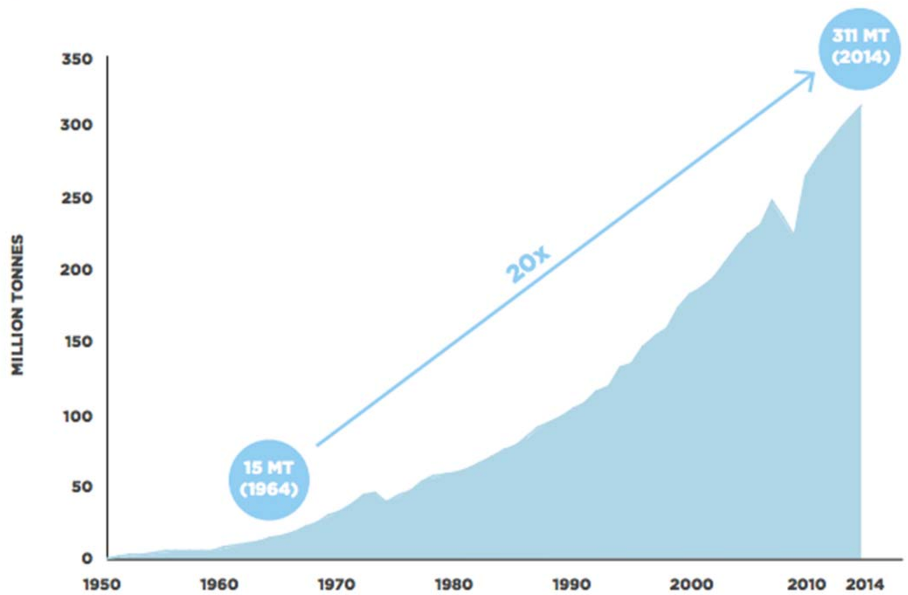
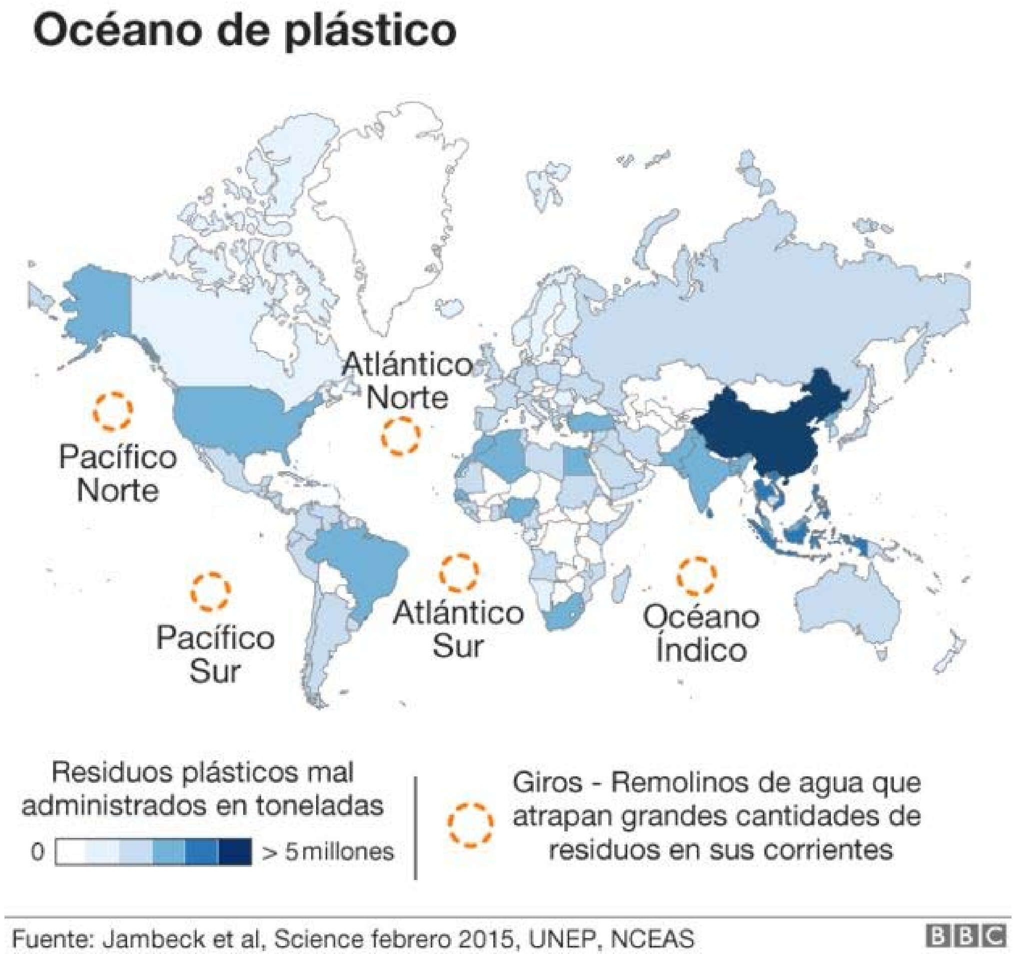
Porto. Águas e Energia do Porto

1. Introducción: Problemática Ambiental

Figure 1: Growth in Global Plastics Production 1950–2014



Note: Production from virgin petroleum-based feedstock only (does not include bio-based, greenhouse gas-based or recycled feedstock)
Source: PlasticsEurope, Plastics – the Facts 2013 (2013); PlasticsEurope, Plastics – the Facts 2015 (2015).



1. Introducción: Problemática Ambiental

Objetos

Polímeros

Persistencia

1. Introducción: Problemática Ambiental

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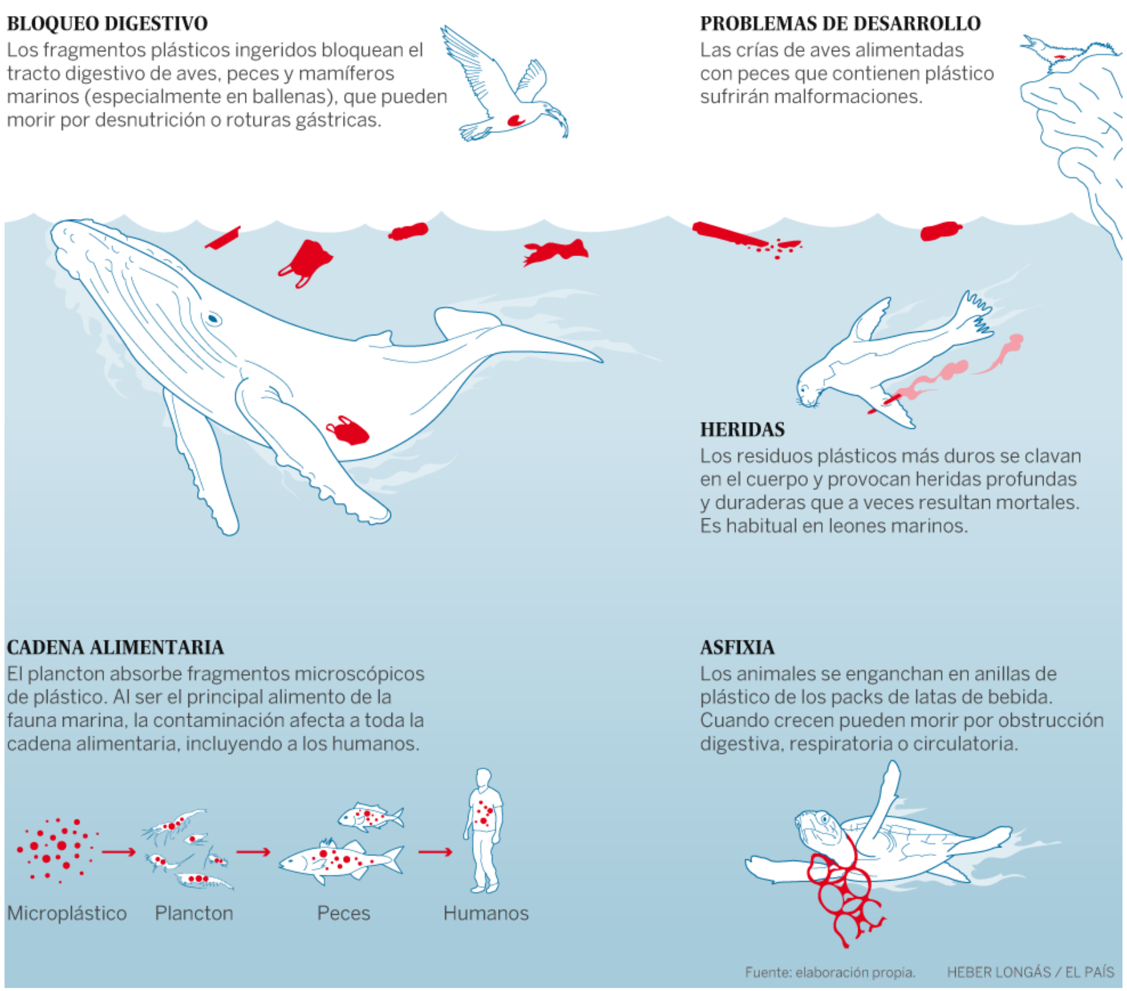
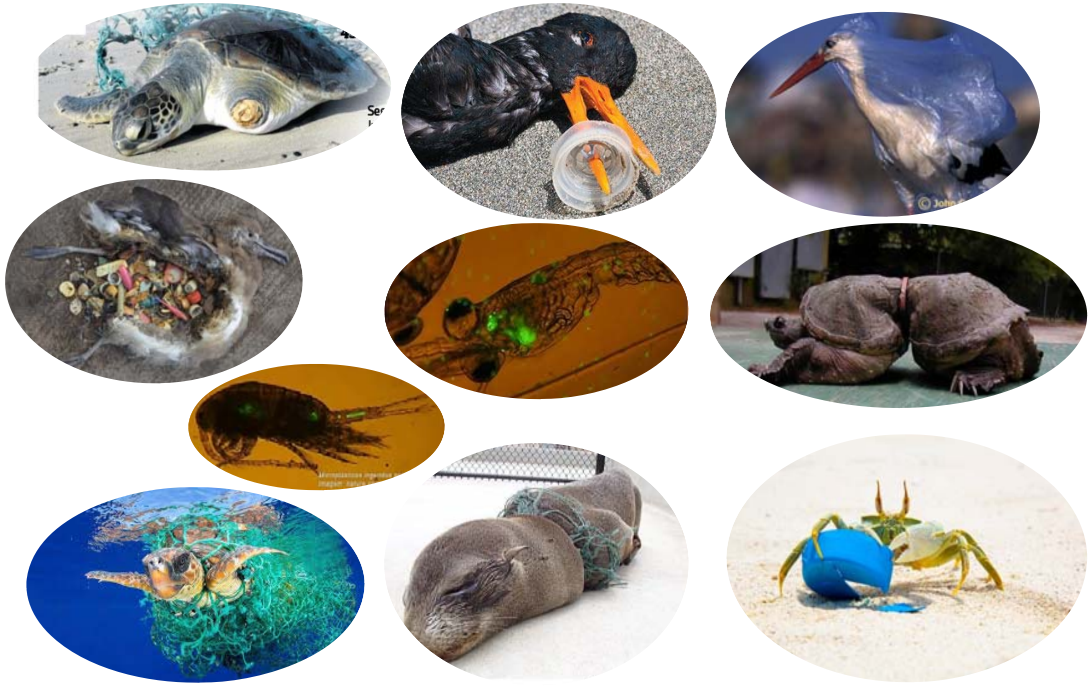
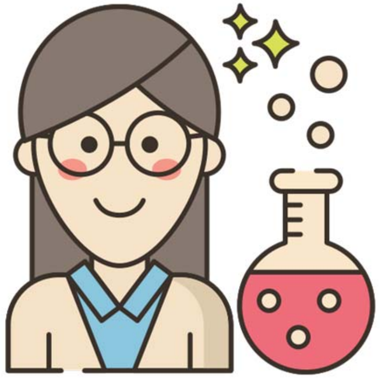




1. Introducción: Problemática Ambiental

Preocupación y alarma social

Ayuda científica



1. Introducción: Problemática Ambiental

Ausencia de protocolos consensuados de muestreo y análisis

Resultados difícilmente comparables

Las metodologías eran diferentes en tres aspectos:

1. Muestreo
2. Pretratamiento de muestra
3. Análisis

2. Protocolos de muestreo

Sobre las cantidades y tipos de microplásticos encontrados en diferentes ambientes y comparativas entre diferentes metodologías de muestreo y análisis.

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Comparative study of three sampling methods for microplastics analysis in seawater

Yifan Zheng[a,d], Jingxi Li[a], Chengjun Sun[a,b,*], Wei Cao[a], Menghui Wang[c], Fenghua Jiang[a], Pen…

sustainability

Review

A Practical Overview of Methodologies for Sampling and Analysis of Microplastics in Riverine Environments

Claudia Campanale [1,*], Ilaria Savino [1], Iulian Pojar [2], Carmine Massarelli [1] and Vito Felice Uricchio [1]

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

On the representativeness of pump water samples versus manta sampling in microplastic analysis

Matthias Tamminga*, Sarah-Christin Stoewer, Elke K. Fischer

Contents lists available at ScienceDirect

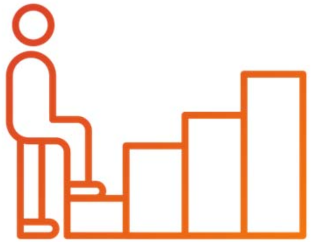
Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Overview of analytical methods for the determination of microplastics: Current status and trends

Huike Dong[a,b], Xiaoping Wang[a,b,c,*], Xuerui Niu[a,c], Jiamin Zeng[a,c], Yunqiao Zhou[a,b], Zhuoga Suona[d], Yuefu Yuan[d], Xu Chen[d]

Esto supuso un primer paso a la hora de establecer protocolos estandarizados de muestreo y análisis.



3. Protocolos de muestreo

Toma de muestras para microplásticos en aguas costeras marinas:

1. Red de muestreo

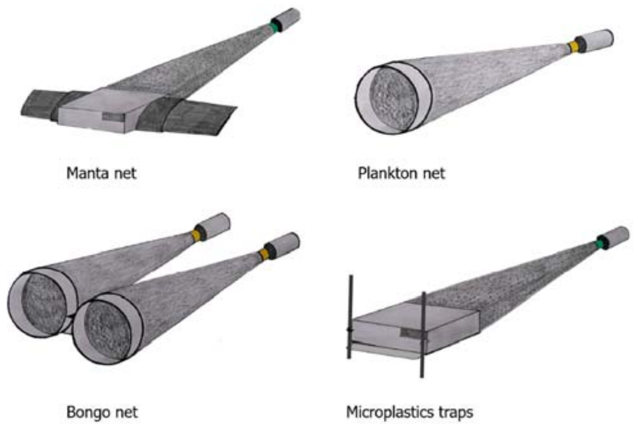
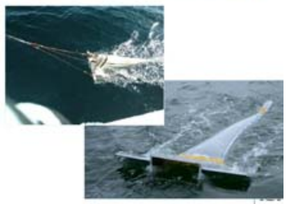


Figure 2. Examples of nets used for microplastics (MPs) sampling.

Campanale et al., 2020.

1. MANTA DE FONDO

2. MANTA DE SUPERFICIE



2. Bomba de muestreo

Fig 2. Sampling device diagram. The pump underway system of the RV Ángeles Alvariño had a tap connection at the wet lab to which the filtering device was connected with a ¾" hose. This figure shows real pictures of the sampling device used in this study, with the stacked sieves that it contains shown on the right.

https://doi.org/10.1371/journal.pone.0232744.g002

Montoto-Martínez et al., 2020.

3. Toma discreta de muestras

Superficie

Fondo

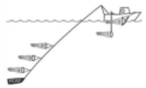
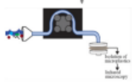
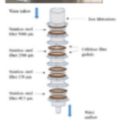
3. Protocolos de muestreo

Table 1. Sampling devices used for the collection of MPs in surface waters.

	Sampling Device	Advantages	Disadvantages	Costs $	Time (Minutes)	References
Nondiscrete sampling devices	Manta net	Sampling of large volumes of water; The lateral wings allow the floating of the device and the sampling of the water surface.	Expensive equipment; Requires boat; The lower limit of detection is 333 µm; Clogging problems; Risk of sample contamination; Underestimation of the total buoyant microplastic amounts.	~3500	15–240	[34,41,42,46–51]
	Neuston net	Sampling of large volumes of water; Widely used (useful for compare positions).	Expensive equipment; Requires a boat; The lower limit of detection is 333 µm; Clogging problems; Risk of sample contamination; Underestimation of the total buoyant microplastic amounts.	~2300	30	[34,52–55]
	Plankton net	The lower limit of detection is 100 µm; Sampling of medium volumes of water; Possibility to sample the water column.	Expensive equipment; Requires a boat; Clogging problems; Sampling of lower volumes of water compared to Manta trawl; Risk of sample contamination; Underestimation of the total buoyant microplastic amounts.	~2400	30	[26,34,56–58]
	MP traps	Possibility to sample in several points of the water stream; Possibility to choose mesh dimensions from 100 µm to 333 µm.	Expensive equipment; May involve difficulty in anchoring to the riverbed; In the presence of a low flow rate, samples the first 15 cm of water; Risk of contamination.	~1200	30	[35]
	Autosampler	Well-known and precise volume of filtered water; Minimises the risk of contamination; Allows a dimensional separation of the particles directly in the field.	Costly equipment; Difficult and heavy to transport and deploy; May be very fragile; Requires electric energy; Requires a large amount of instrumentation.	10,000–70,000	-	[45,59]
Nondiscrete sampling devices	Pumping systems	Allows the user to sample smaller MPs and fibre loss is limited; Well-known and precise volume of filtered water; Allows standardisation of sampling.	Requires energy to work; Requires boat; It can be challenging to transport and apply. Allows the sampling of a single point; Requires the transport of bulky samples to the lab; Sampling is less representative; -Risk of sample contamination.	300–1000	15–180	[30,34,43,44,51,60]
Discrete sampling devices	Niskin bottles/Jars/Bottles/Buckets/Rosette/Integrated water sampler (IWS)/Ruttner bottles/Friedinger bottles/Bernatowicz bottles	Relatively quick and straightforward to use; Rosette provides multi-point measurements; Allows sampling at different depths; Allows the user to sample smaller MPs and fibre loss is limited; Well-known and precise volume of filtered water; Allows standardisation of sampling.	Requires boat; Rosette can be challenging to transport; Sampling of a small volume of water; May be very fragile; Requires the transport of bulky samples to the lab; Sampling is less representative; Risk of sample contamination.	Very variable (300–50,000)	15–30	[34,35,58,61–66]
Devices for surface microlayer	Stainless-steel sieves/Rotating Drum Sampler	Does not require specialised equipment; Quick and straightforward to use; Well-known and precise volume of filtered water; Allows choice of mesh size; Allows a dimensional separation of the particles directly in the field.	Sampling of medium/low volumes of water; Requires the transport of significant volume of water to the lab; Manual transfer of water with buckets; Potential contamination by the apparatus.	From 50	Depending on mesh size	[34,60,67]

Campanale et al., 2020.

Table 1
New sampling techniques of microplastics in different environmental matrixes.

Matrix	Technique	Actual photographic	Advantages	Disadvantages	Reference
Water	Vertical trawl		Can collect sub-surface water samples in different depths (≤15 m)	Unable to sample at specific water depths; Can not differentiate the vertical variation	[44]
	CTD sampler		Continuous sampling in different depths; Can collect very deep samples	Limited sampling volume at each depth; Needs power supply and control system	[39]
	PLEX sampler		Can sample large volumes; Combined with filtration	Unable to sample from the surface water layer; Needs power supply and control system	[45]
	Peristaltic pump filtration		Easy to transport; Supports a range of sampling volumes; Reduce sample handing; Supports a variety of filter types	Sampling volume can be small; Only fits for small waterbody	[43]
	Portable stainless steel multi-layered filtering system		Can detect small-sized microplastics (≥1 µm); *In situ* sample purification from interferents; Reduce clogging and pressure	Can not get the characteristic information of MPs	[48]
	Cascade filtration assembly		Fits for stormwater sampling; Easy filtration and separation of microplastics; minimize clogging	One assembly can only use for one sample	[46]
	Cascadic filtration plant		Fits for WWTPs wastewater; Can filtrate large volumes of water	Needs power; High pressure might cause loss of microplastics	[47]

Dong et al., 2023.

3. Protocolos de muestreo

Pero…¿Qué estamos muestreando exactamente?

Table 1
Classes of plastics that are commonly encountered in the marine environment.

Plastic Class		Specific Gravity	Percentage production[#]	Products and typical origin
Low-density polyethylene	LDPE LLDPE	0.91–0.93	21%	Plastic bags, six-pack rings, bottles, netting, drinking straws
High-density polyethylene	HDPE	0.94	17%	Milk and juice jugs
Polypropylene	PP	0.85–0.83	24%	Rope, bottle caps, netting
Polystyrene	PS	1.05	6%	Plastic utensils, food containers
Foamed Polystyrene				Floats, bait boxes, foam cups
Nylon	PA		<3%	Netting and traps
Thermoplastic Polyester	PET	1.37	7%	Plastic beverage bottles
Poly(vinyl chloride)	PVC	1.38	19%	Plastic film, bottles, cups
Cellulose Acetate	CA			Cigarette filters

[#] Fraction of the global plastics production in 2007 after (Brien, 2007).

Andrady, 2011.

A lo que se suma el hundimiento de microplásticos una vez envejecen y adquieren fouling

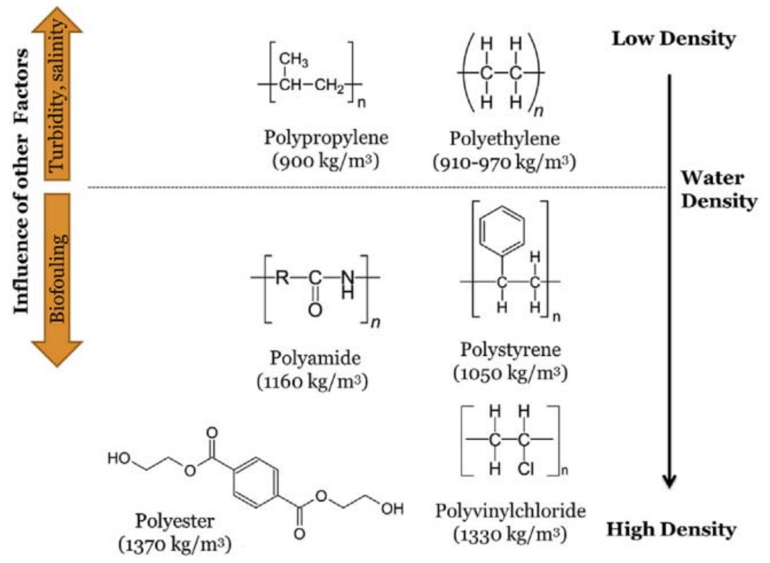
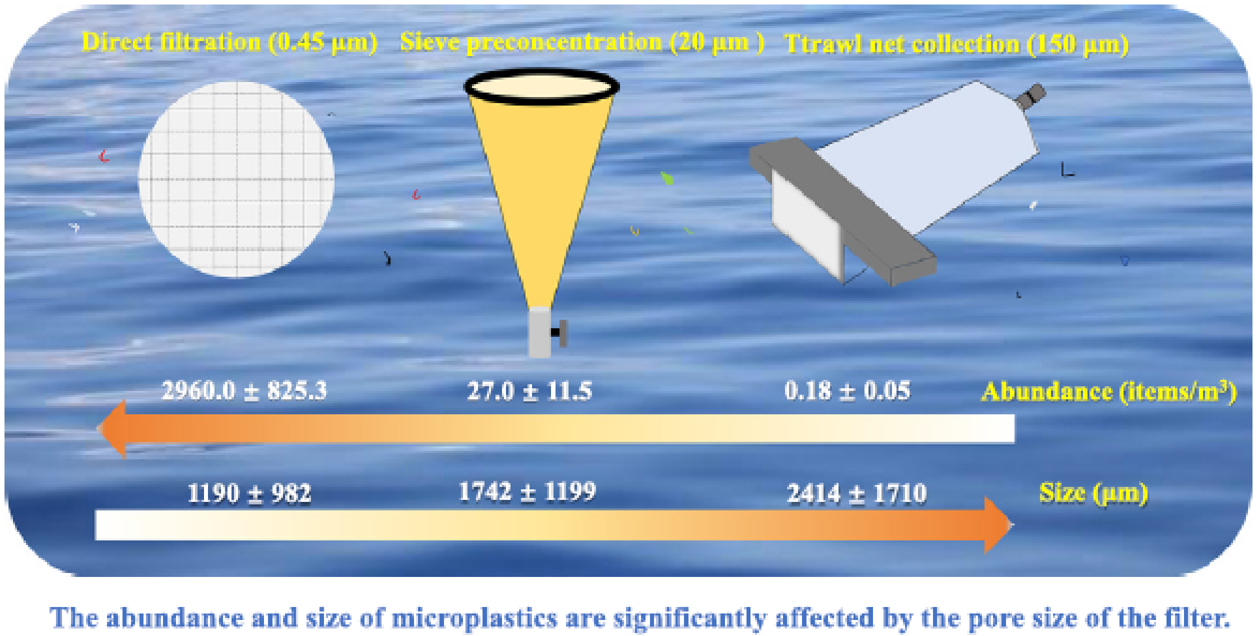


Fig. 1. Densities, structures, and expected distributions of different plastic polymers in the water column. Factors affecting buoyancy, and the direction of the change, are indicated with the arrows on the left.

Anderson et al, 2016.

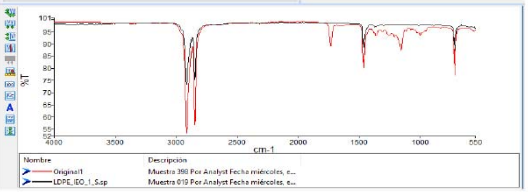
Proceso filtración:



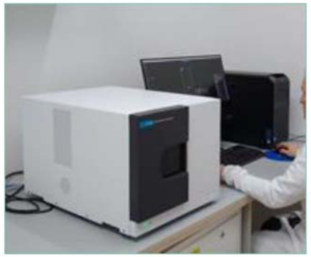
Zheng et al., 2021

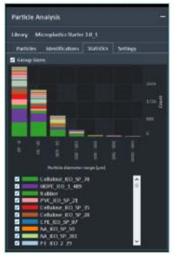
5. Métodos de análisis

FTIR-ATR

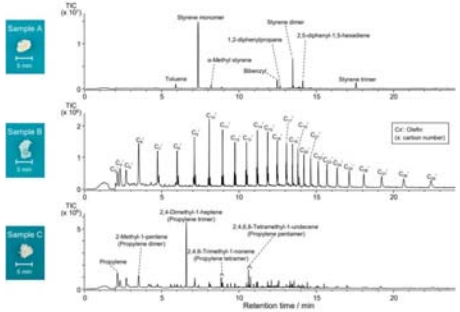


LDIR





GCMS-pyrolysis



Dong et al., 2023.

Table 4
Comparisons among different detection methods.

Method	Size limit	Features	advantages	disadvantages
Optical microscopy	50 µm	Quantification; Non-destructive	Can easily get the characteristics of microplastics and other particles	Time consuming; Bears big human errors; Usually acts as a supplement to other spectrometric methods
Fluorescence microscopy	3 µm	Quantification & semi-qualification; Non-destructive	Time saving; Easy to operate; Fits for bulk samples	Needs staining treatment
µ-FTIR	10 µm	Qualification; Non-destructive	Has standard spectral libraries; FPA-FTIR can automatic scan and positioning	ATR-FTIR could destroy the samples
LDIR	10 µm	Quantification & qualification; Non-destructive	Fast detection of single particle; Labor saving; Can get detailed statistical information of particles by computer	High requirements for pretreatment; Interferes with other non-polymeric particles
µ-Raman	1 µm	Qualification; Non-destructive	Has standard spectral libraries; Can scan the filter directly	Time consuming; May burn the sample
Pyr-GC/MS	–	Quantification (mass) & qualification; Destructive	Needs no sample pretreatment; Can measure additives; Small inletting sample amount	Can not analyze fiber and light weight particles; Only suits for homogeneous samples
Depolymerization-LC/MS	–	Quantification (mass) & qualification; Destructive	Can get accurate mass concentrations of certain microplastics	Needs pretreatment; Demands enough sample weight
TOF-SIMS	<20 µm	Quantification (mass) & qualification; Destructive	Small sample amount; Small reagents consuming; Time saving and easy to pretreat	Needs standard samples of polymers; Needs clean sample pretreatments
ASAP-MS	5 µm	Qualification; Destructive	Fast detection for single particle; Can get MS-based chemical characterization; Supports multimodal characterization of microplastics	Requires relative clean sample matrices; Needs to pick out the single particle first
EIS-based graphene electrode	1 µm	Quantification (mass); Destructive	Low detection size range; Specially made electrode	Can only measure one certain microplastic polymer type at a time
SERS	100 nm	Quantification (mass) & qualification; Non-destructive	Can detect certain polymers of nanoplatics; Small sample volume	Needs to prepare metal nanoparticles; Only fits for clean matrixes; Can not categorize the size ranges
µ-Raman coupled with optical tweezers	50 nm	Quantification & qualification; Non-destructive	Can detect both the size and polymer type of single nanoplastic particle; Can detect the liquid samples directly	Disturbs the Brownian movement thus limits the volume of optical trapping

6. Control de la contaminación

Como en muchos otros caso cuando se están analizando contaminantes, existe el riesgo de contaminación de la muestra. Para ello, es necesario el uso de protocolos limpios que en los primeros estudios sobre microplásticos, no se tenían en cuenta.

-Blancos de muestreo
-Blancos de pretratamiento de muestra
- Blancos analíticos

Necesidad de trabajar en ambientes limpios:
- Salas blancas
- Cabinas de flujo laminar

6. Conclusiones

Existen muchas combinaciones de metodologías para la determinación de **microplásticos** desde el muestreo hasta el análisis.

Necesidad de realizar **protocolos estandarizados** tanto de muestreo como de pretratamiento de muestra y análisis para que los resultados entre diferentes estudios sean comparables.

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