Results of WEPAL-QUASIMEME/NORMANs first global interlaboratory study on microplastics reveal urgent need for harmonization

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HIGHLIGHTS

- Thirty-four laboratories participated in a microplastics interlaboratory study.
- Dissolvable tablets were developed to be used as test materials.
- Correct type of polymer was often reported indicating satisfactory performance.
- The large variation in reported particle numbers shows the need for harmonization.

GRAPHICAL ABSTRACT
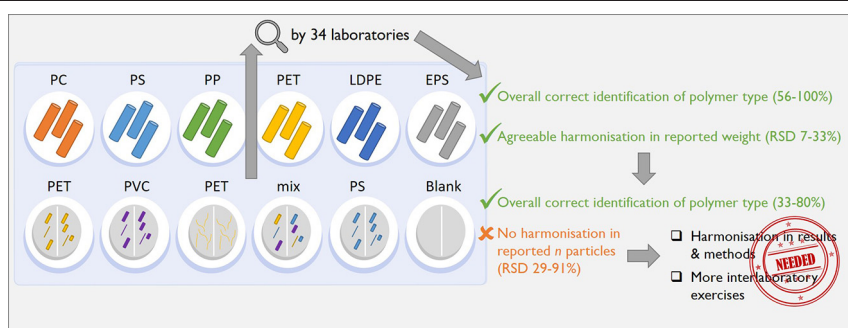
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ABSTRACT

To survey the conformity and quality of results among laboratories for microplastics determination worldwide, an international laboratory intercomparison and development exercise was organized. The 34 participants were requested to determine the polymer type and number or mass of polymer particles in 12 samples, i.e. six samples containing of pre-production pellets, five dissolvable soda tablets containing different (smaller) polymer particles and one blank soda tablet. A novel method for providing the test materials in aluminium strips was used. Thirty laboratories (88%) submitted data using their own method of choice, resulting in a variety of identification and quantification methods ($n = 7$). The majority of the labs (53–100%) correctly identified the type of polymer in all samples but one. The performance of the laboratories in quantifying and weighing the pellets was very good. The analysis of the number of the particles in the soda tablets varied considerably between laboratories (29–91%). The results of this study highlight the complexity of microplastics analysis and the need for harmonization of both reporting format and methods. Continued development and assessment of the comparability among analytical methods and laboratories are urgently needed to support monitoring programmes, research and decision-making.

1. Introduction

The extensive use of plastic materials in our human society has led to an unintentional ubiquitous presence of microplastics in the environment, including the atmosphere (Zhang et al., 2020b), soil (Möller et al., 2020), water (Zhang et al., 2020a) and biota (Wang et al., 2020). Microplastics have therefore gained interest as a major environmental pollutant, however their determination in the environment is extremely challenging.

The term 'microplastics' represents an analyte class of plastic particles spanning 6 orders of magnitude in particle size (few nm to 5 mm) with a large variety of chemical composition (GESAMP, 2015). These particles are mixtures of components such as (co)polymers, chemical

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additives, fillers, residual monomers, catalysts, non-intentionally added substances (NIAS), etc. Due to the diversity of this analyte class various methodologies are under consideration to support microplastic pollution monitoring, research and decision-making by state and non-state actors.

To date many different analytical protocols, methods and techniques have been developed and applied to samples containing multiple polymer types and certain fractions of particle size. However, validated standardized methods remain unavailable at this point (Liu et al., 2020; Zhang et al., 2020b). There is also still no consensus on the reporting format (EFSA, 2016). Microplastics are reported in different formats, such as number of particles per mass of sample, or total mass of particles (or total mass of polymers) within a given particle size range.

While Primpke et al. (2020), Hartmann et al. (2019) and Cowger et al. (2020) provide a path forward to harmonization, there is an urgent need for collaborative method development, (certified) reference materials and interlaboratory studies (ILS) to validate and harmonize (further) the various methods (including how to report results). These efforts and tools will enable a better assessment of data quality. Two previous ILSs organized on microplastic determination to assess the comparability between data showed indeed a discrepancy in results among laboratories (Isobe et al., 2019; Müller et al., 2020). However, as indicated by the authors there was room for improvement in conducting these pioneering ILSs. Firstly, both conducted only one round with a selected and small group of participants ($n = 12$–17) and a limited number of samples. Secondly, the analysis of microplastics particles in these testing schemes were limited to particle size ranges of 400–1000 µm (Isobe et al., 2019) or 8–140 µm (Müller et al., 2020). Thirdly, Isobe et al. (2019) focused only on determination of the number of particles and did not include polymer identification. Last but not least, the test material used study of Müller et al. (2020) showed large relative standard deviations (RSDs, 26–85%) to begin with, which would not have passed typical quality assurance and quality control (QA/QC) and ISO 13528 criteria (RSD <30%).

Wageningen Evaluating Programmes for Analytical Laboratories - Quality Assurance of Information for Marine Environmental Monitoring in Europe (WEPAL-QUASIMEME) and Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances (NORMAN), in collaboration with the Vrije Universiteit Amsterdam and the Norwegian Institute for Water Research (NIVA), have set up a worldwide and long-term development exercise scheme to assess and promote harmonization of laboratory results for microplastics analyses. It is designed in a step-wise way and includes different rounds of exercises with increasing complexity and difficulty, starting with the analysis of twelve 'standard' like test materials with plastic particles of 150–300 µm and 2000–4000 µm. The rounds are open for all laboratories involved in microplastics analysis and designed to enable a large number ($n > 20$) of participating laboratories and a wide variety of methods. This article presents the design of the ILS scheme as well as the results, conclusions and recommendations of the first round.

2. Materials and methods

2.1. Experimental design and development exercise scheme

Following a well-attended WEPAL-QUASIMEME/NORMAN workshop ($n > 110$) on the analysis of microplastics and the participants' ILS needs in Amsterdam, the Netherlands in November 2018, an interlaboratory development exercise scheme was designed for the determination of microplastics. The set-up of the development exercise scheme was designed to start with the analysis of test samples resembling analytical standards. This round will be followed by further exercises including the standard test samples as well as more complex sample materials such as spiked and naturally contaminated environmental samples. Three of such developmental exercises are envisioned.

Because of the many different analytical protocols, methods and techniques available at the moment, materials for the first round were prepared to enable analysis by a broad variety of analytical methods and techniques. These included microscopy (Wang et al., 2017), mass spectrometry (Dierkes et al., 2019; Duemichen et al., 2019), Fourier transform infrared spectroscopy (FTIR) (Primpke et al., 2018), and Raman spectroscopy (Araujo et al., 2018). The identification of the participating laboratories is primarily encoded and data is therefore submitted anonymously.

In the first round of the study, participants were asked to identify polymer types and quantify, i.e. count particles (integer) and/or determine the mass of particles (mg or µg), in twelve samples using an identification and quantification method of their choice. Participants chose from a dropdown list of 40 polymer types and could add other polymer types manually. They were also requested to provide a short description on the methodologies used for sample preparation (when applied), identification and quantification.

2.2. Test material

Participants received an aluminium strip (Fig. S1) with twelve sample 'pockets' prepared by NIVA. In six pockets three preproduction pellets of a single polymer type were added: polycarbonate (PC), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), low-density polyethylene (LDPE) and expanded polystyrene (EPS) (samples 1–6, Table 1). Five pockets contained one dissolvable soda tablet with a known number of added microplastic fragments or fibres, (samples 7–11, Table 2). The twelfth pocket contained a dissolvable tablet without added microplastics and was referred to as the blank (sample 12, Table 2).

Test materials were prepared in a clean environment in which contamination was continuously monitored and reduced to a minimum (especially in the case of fibres). Preproduction pellets with a size range of 2.4–4.3 mm were used for samples 1–6. The pellets were added and sealed in the aluminium strip as they were received. To simplify the exercise, no distinction was made between EPS and PS in sample 6, and participants could only select PS (not EPS) as option in the dropdown list. The dissolvable soda tablets (Table 2) were made manually to avoid the use of lubricant which could interfere with the analysis. For the production of the tablets different microplastic fragments were acquired from Goodfellow (Cambridge Ltd., England) and different fractions (150–250 µm, 250–300 µm and 250–350 µm) were obtained by filtration of PET, PVC and PS (samples 7–8 and 10–11) using different glass fibre filters (500 µm, 355 µm, 250 µm, 150 µm and 50 µm). The fibres in sample 9 were obtained by washing polyester blankets ('Skogsklocka', IKEA, Norway) in a clean domestic-like washing machine system (Candy CS 1272D3/1-S, Italy) on a 15-min cycle at 40 °C and centrifuging at 1200 rpm. No detergents or softeners were used. The effluent was then collected in a stainless-steel pressure vessel and vacuum filtered through a 10 µm nylon membrane, which yielded fibres of 101–2194 µm in length and 29 µm wide. The fraction of 300–400 µm was manually selected and subsequently these fibres were added

Table 1
Characteristics of the preproduction pellets.

Sample	Polymer	Total weight[a] ($n = 3$)	Average size (mm)[a]
1	Polycarbonate (PC)	46.2	2.40 × 1.94 × 3.33
2	Polystyrene (PS)	64.8	2.27 × 3.08 × 3.58
3	Polypropylene (PP)	88.2	4.31 × 4.67 × 2.43
4	Polyethylene terephthalate (PET)	55.8	3.33 × 2.18 × 2.44
5	Low-density polyethylene (LDPE)	78.6	2.83 × 4.00 × 4.19
6	Expanded polystyrene (EPS)[b]	1.80	NA

NA not analysed.
[a] Unknown to participants.
[b] Identifiable only as PS for participants.

Table 2
Characteristics for samples 7–12[a].

Sample	Polymer	Average tablet weight (g ± RSD)[b]	Polymer added (mg)	Average number of other particles measured by reference analysis[b,c] (n ± RSD)
7	PET	0.50 ± 0.7%	0.556[d]	3.3 ± 38%
8	PVC	0.49 ± 0.9%	0.0556[e]	2.0 ± 52%
9	PET fibres	_[f]	_[f]	19 ± 22%
10	PET	0.50 ± 4.0%	0.0900[d]	5.0 ± 37%
	PVC		0.0900[e]	
	PS		0.0900[g]	
11	PS	0.50 ± 0.4%	0.0739[g]	3.4 ± 48%
12	Blank	0.50 ± 1.3%	–	

AVG average; NA not applicable; RSD relative standard deviation; PET Polyethylene terephthalate; PVC Polyvinylchloride; PS Polystyrene.
[a] Information on number of particles added per sample can be found in Table 4.
[b] Reference analysis performed by Norwegian Institute for Water Research.
[c] Other particles than the particles added, also referred to as background.
[d] Particle size of 250–300 μm.
[e] Particle size of 150–250 μm.
[f] Fibres were added individually by hand to each tablet.
[g] Particle size of 250–350 μm.

manually to each individual tablet. The fragments of samples 6–8 and 10–11, were added to a mixture of sodium hydrogen carbonate (NaHCO$_3$), citric acid (C$_6$H$_8$O$_7$) and a binder (lactose) and the tablets were produced from this batch. The ingredients of the tablets do not interfere with the analysis as the tablets completely dissolve in water. All tablets were produced using a metal cast in which the tablets were moulded under pressure.

Reference analyses and homogeneity studies were carried out by analysing a batch of ten replicates of preproduction pellets and tablets using visual analysis followed when needed by FTIR (Tables 1 and 2), as described in previous work (Lusher et al., 2020). For samples 7–12, the number of the added particles for each batch are given (for easier comparison presented alongside the results in Table 4), as well as the number of other particles detected (in most cases fibres, referred to as background, Table 2). With every batch, 10 blank tablets were analysed as a control for background. Particles smaller than 20 μm were not measured in either the samples or the blanks due to instrumental limitations (>20 μm). On average 2–5 microplastics (mostly fibres) were found in samples 7–8 and 10–12, which contained the particles. The production of the PET fibres sample included several manual steps resulting in larger exposure and on average 20 fibres (no PET) were present in these samples.

2.3. Evaluation of the results

Criteria for successful participation of laboratories were based on the evaluation of three types of parameters: polymer type identification, the number of particles (total and per polymer type) and/or the mass of particles (either gravimetrically or by MS, total and per polymer type). The evaluation of the data reported for the preproduction pellets (samples 1–6) focused rather on the correct identification of the polymers than on the number and weight. The evaluation of tablet samples (samples 7–11) focused on all three results parameters.

The Normal Distribution Approximation (NDA) method (Cofino et al., 2000; Molenaar et al., 2018), a robust method used routinely in the WEPAL-QUASIMEME proficiency testing schemes, was used for the statistical evaluation of the data. The NDA approach is based on a model using observations represented by probability density functions as input. It determines the "average probability density" of the set of observations. This average probability density function is used to calculate the population mean and standard deviation. In proficiency tests, usually only single data (i.e. no replicates) are reported by laboratories without information on the uncertainty of this datapoint. The NDA is an implementation of the model that is used when uncertainty information is unavailable. The NDA approach has a breakdown point of 50% and is more robust than the methods described in ISO 13528 (Molenaar et al., 2018).

Youden statistics were applied to explore the characteristics of within- and between-laboratory errors using the approach outlined in Lischer (1996). The total reported number of particles includes the polymer type added plus other particles present in the samples, also known as background. Background includes particles introduced through contamination by the participating laboratories as well as particles that have been incorrectly identified by the laboratories as plastic (false positives). Given the method for preparation of the test material (avoidance of airborne plastic contamination) and consequently the low average number of other particles detected by the reference analysis for samples 7–8 and 10–11 (2–5 particles, Table 2), a close correspondence between the total number of individual polymer types added and the total number of polymer types reported by laboratories can be expected. The polymers PET in tablets 7 and 10, PVC in tablets 8 and 10, and PS in tablets 11 and 10 are considered Youden pairs as the composition is similar although the values of the measurands may differ significantly. The approach described by Lischer (1996) is followed with a small modification. The values reported for a measurand are {x_i, i = 1,2,…,n} for tablet k and {y_i, i = 1, 2, …, n} for tablet 10. The sums $\mathbf{v} = \{(x_i + y_i)/2)\}$ and differences $\mathbf{w} = \{(x_i - y_i)/2)\}$ were calculated. The variances of these terms are $Var[v_i] = \frac{1}{2}\sigma_r^2 + \sigma_L^2$ respectively $Var[w_i] = \frac{1}{2}\sigma_r^2$ (Lischer, 1996). The term σ_r reflects the average within-laboratory errors, the term σ_L the average between-laboratory errors. The variances $Var[v_i]$ and $Var[w_i]$ were calculated with the NDA method.

3. Results and discussion

A flow-diagram of number of participants and submitted results is presented in Fig. 1. In total, 34 laboratories participated from 13 different countries (Fig. S2), of which 30 laboratories submitted data (completion rate 88%).

3.1. Sample preparation methods and instruments applied

Table S1 describes the sample preparation methods reported by the participating laboratories. As samples 1–6 consisted of clean preproduction pellets, most participants ($n = 26$) did not use any sample pretreatment (i.e. extraction, clean-up, purification and/or modification of the sample prior analysis). Four participants reported filtration as sample pretreatment. Of the four, one participant reported filtration before staining using Nile Red, while one other washed the pellets after filtration with analytical grade water prior to pyrolysis combined with GC–MS analysis (Py-GC–MS).

For the soda tablets containing the smaller microplastics (sample 7–12), nearly all 26 laboratories reported use of sample pretreatment, of which the majority ($n = 25$) reported filtration. After filtration, five laboratories reported additional pretreatment steps.
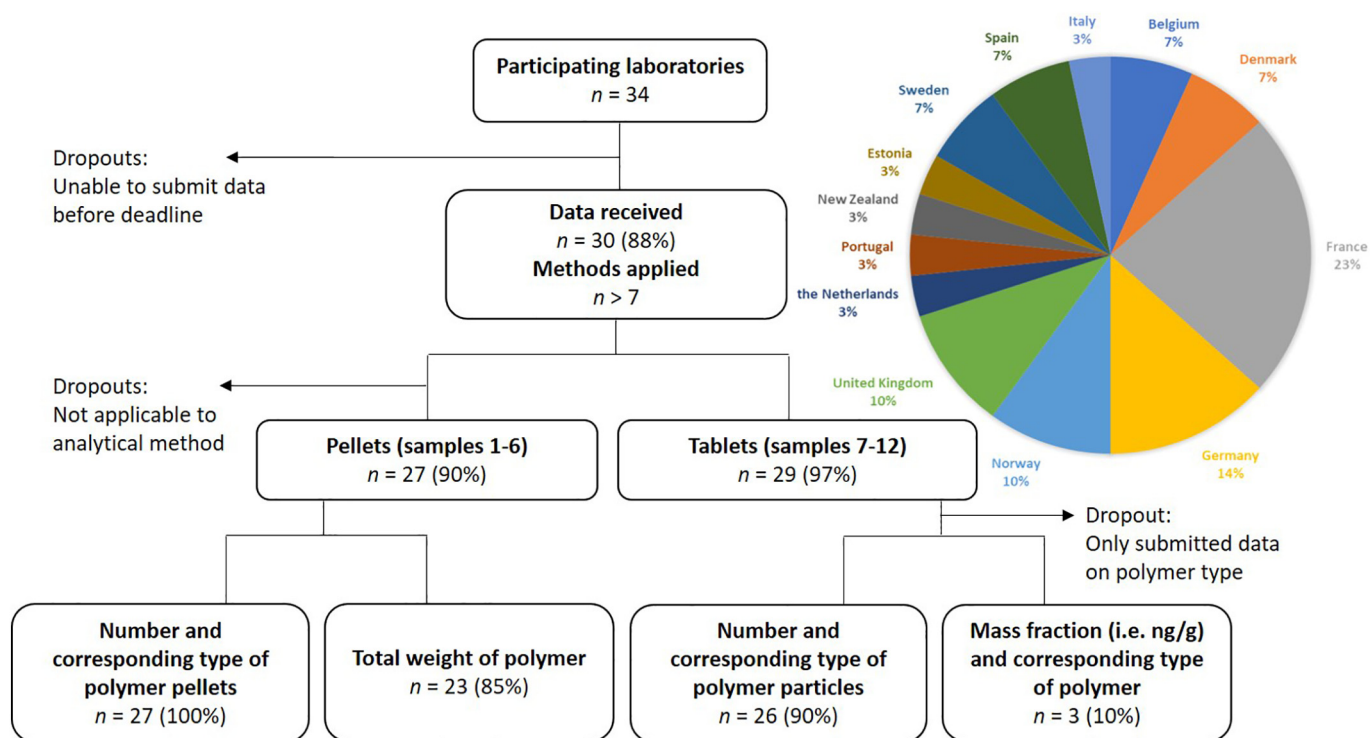
Fig. 1. Flow diagram showing the number of participants and number of submitted results (left) and a pie chart representing participating laboratories categorized per country (right).
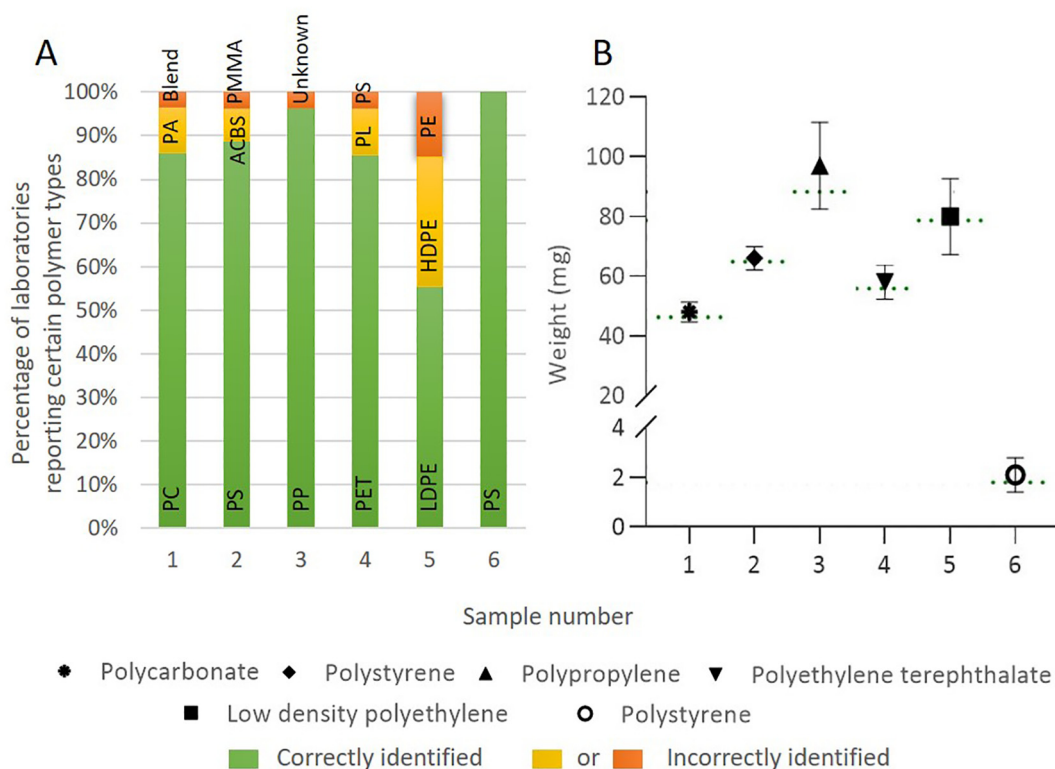

Fig. 2. Reported data for preproduction pellets (samples 1–6): reported polymer type, expressed as percentage of the number of laboratories reporting the polymer type by the total number of laboratories (n = 27) that reported data (Graph A); and average reported total weight of the preproduction pellets (Graph B). The green bar in graph A represents the correct polymer type. The green dotted lines in graph B represents the value obtained by the reference analysis, while error bars represent the standard deviations. ACBS acrylonitrile butadiene styrene LDPE low-density polyethylene, HDPE high-density polyethylene, PA polyamide PC polycarbonate, PE polyethylene, PET polyethylene terephthalate; PL polyester, PMMA poly (methyl methacrylate), PP polypropylene, PS polystyrene.

Table 3
Identification method performance for samples 1–6.

Identification method	Method applied (n)	Percentage that identified correct polymer					
		Sample 1 PC	Sample 2 PS	Sample 3 PP	Sample 4 PET	Sample 5 LDPE	Sample 6 PS
μFTIR	6	83%	67%	83%	83%	83%	100%
ATR-FTIR	15	100%	100%	100%	87%	53%	100%
Raman	3	100%	100%	100%	67%	67%	100%
μRaman	1	100%	100%	100%	100%	100%	100%
Py-GC-MS	2	50%	50%	100%	100%	50%	100%

PC, Polycarbonate; PS, Polystyrene; PP, Polypropylene; PET, Polyethylene terephthalate; LDPE, Low-density polyethylene.

Participants applied various analytical methods to determine microplastics (Fig. S3), and within the same analytical method, different instruments. Analytical methods reported included microscopy, gravimetric, attenuated total reflectance FTIR (ATR-FTIR), FTIR spectroscopy (μFTIR), Py-GC-MS and Raman spectroscopy. ATR-FTIR was the most commonly applied technique polymer identification for samples 1–6 (46%), followed by μFTIR (23%). μFTIR was most commonly applied for the polymer identification of samples 7–12 (63%). Microscopy was the most commonly applied method for quantification (36%), followed by μFTIR (23%).

3.2. General performance

The majority of the laboratories (56 to 100%, Fig. 2) reported the correct polymer type for the pellets (samples 1–6). The polymer type that was most problematic for identification was LDPE (sample 5). Fifteen out of the 27 laboratories reported LDPE, eight HDPE, while four did not distinguish between LDPE and HDPE and reported just PE. In future ILSs, it is important to address the difficulties that arise when identifying and reporting PE. One participant reported for sample 4 besides PET also PS.

PS (sample 6) was correctly identified by all participants (Fig. 2), regardless of the method applied (Table 3). The participant that applied μRaman identified the correct polymer type for all other pellets also (sample 1–5, Table 3). All participants that applied Raman (n = 3) identified correctly PC, PS and PP (samples 1–3), while one participant identified PET as polyester (sample 4) and one LDPE as HDPE (sample 5). Participants who applied ATR-FTIR (n = 15) also identified the right polymer type in case of PC, PS and PP. For PET one reported polyester. For LDPE five reported HDPE while three just PE. When μFTIR was used (n = 6), 1–2 (different for each sample) participant(s) identified the wrong polymer type. For example, poly(methyl methacrylate) (PMMA)/PVC blend was reported in case of PC, PPMA or acrylonitrile butadiene styrene for PS, 'unknown' for PP, polyester for PET and HDPE for LDPE. In the case of LDPE, a relatively high percentage (83%, Table 3) identified LDPE correctly, while methods such as ATR-FTIR and Raman scored less (53–67%). Only two participants applied Py-

GC–MS for identification. One identified polyimide for PC, acrylonitrile butadiene styrene for PS and HDPE for LDPE.

With the exception of sample 6, all participants correctly reported the number of the rather large (2–4 mm) preproduction pellets added to sample pockets 1–6 (n = 3, Table 1). For sample 6, four participants reported a number of four pellets. The average reported weights for samples 1 to 5 agreed well among laboratories (Fig. 2b), with relative standard deviation (RSD) between 7 and 16%. This is low especially considering the heterogeneous nature of the weight of the pellets. The highest variation in reported weight (33%) was found in sample 6, containing the expanded PS sample (also the lowest reported average weight).The polymer identification and determination of number and weight of particles of the relatively large preproduction pellets is considered a relatively straight forward analysis. Nevertheless, not all participants were able to correctly identify all polymer types of, and count and weigh the six preproduction pellet samples.

In case of the tablet samples (samples 7–11), the majority of laboratories (53–80%) reported the correct polymer type (i.e. most abundant polymer type) in the tablets that contained only one added polymer type (samples 7–8, 10–11, Table 4). The identification of the polymer type in sample 9 was complicated by unintended contamination of small fragments during production; only 33% reported the correct polymer type (PET fibres) as the dominating polymer type, while the majority of laboratories (66%) reported large amounts of small PS fragments (<20 μm). Sample 9 was only supposed to contain PET fibres (Table 2) and we suspect that the textile that was used to produce PET fibres contained also very fine (<20 μm) PS fragments that remained undetected by FTIR used in the reference analysis. The results of sample 10 indicate that the laboratories experienced more difficulties in identifying the correct polymer type when the number of different polymer types in a sample was high. For example, while 70% of the laboratories correctly identified PET in sample 7 (containing PET only), only 53% did so in sample 10 (containing not only PET but also PVC and PS, Table 4).

While the difference in the reported number of particles for the added PET particles (sample 7) among laboratories was acceptable (RSD <30%, Table 4), the results of the other added polymers varied

Table 4
Summary of reported data for samples 7–11.

Sample	Added polymer	Laboratories reporting correct polymer type[a] (n (%))	Average reported number of particles of the added polymer[b] (n ± RSD)	Average reported total number of all particles[b] (n ± RSD)	Average number of particles of the polymer type that was added by reference analysis[c] (n ± RSD)
7	PET	21 (70%)	42 ± 29%	37 ± 57%	50 ± 15%
8	PVC	22 (73%)	14 ± 66%	19 ± 78%	27 ± 14%
9	PET fibres	10 (33%)	13 ± 46%	20 ± 91%	22 ± 21%
10	PET	16 (53%)	5.5 ± 73%	42 ± 58%	8.0 ± 38%
	PS	22 (73%)	17 ± 78%		25 ± 16%
	PVC	17 (57%)	20 ± 46%		27 ± 25%
11	PS	24 (80%)	12 ± 75%	16 ± 81%	24 ± 11%

PET Polyethylene terephthalate; PVC Polyvinylchloride; PS Polystyrene; RSD relative standard deviation.
[a] Polymer type that was reported most frequently, with percentage of laboratories that reported the polymer type of the total number of laboratories (n = 30) that reported data.
[b] Reported by participants.
[c] Reference analysis performed by the Norwegian Institute for Water Research.

greatly (46–78%). The reported average number of total particles also varied greatly (57–91%), indicating an urgent need towards harmonization and more assessments of harmonization, for example by ILSs. In general, the reported number of the added polymer type or total particles was lower than that of the reference analysis (Table 4 and Fig. 3, black lines versus coloured lines). This could be due to loss of particles during sample preparations, for example while dissolving of the tablets and/or collection by filters.

One would expect the reported number of polymer particles added to be the same as the reported total number of particles, i.e. that any laboratories that incorrectly identified the polymer type still counted the number of particles correctly. However, the difference between the reported number of added polymer particles and the reported total number for samples 7–11 was between 0.5 (mixture sample 10) and 7 (PET fibres sample 9). Interestingly, the lowest difference (0.5 particle) was found in the sample that had multiple polymers added (sample 10). In sample 7, the average reported number of total particles was lower that than the average reported number of PET particles (Table 4). This was because the six laboratories that reported no PET particles reported a low total number of other particles (3 up to max 42). Overall, the difference between the number of added polymer particles and total number of particles indicates that the situation is more complicated.

Fig. 3 shows the reported number of total particles (grey dots) in the tablets (samples 7–11) as well as particles per polymer type of polymers that were added to the tablets (coloured as presented by legend) and other polymer types that were reported by more than five laboratories (for example propylene (PP), grey squares), sorted by method applied. For tablet 10 the three added polymers are presented separately in three graphs (Fig. 3D–F). Fig. 3D and E show that in particular ATR-FTIR and μFTIR have difficulties identifying PET and PVC respectively when other polymers are added to the tablet too. Overall, the difference in reported particles (either per polymer type or as total) varied greatly between and within the methods applied.

Only two participants used py-GC–MS for samples 7–11, while one laboratory determined the mass of the tablets gravimetrically. The reported weight of one of the participants who used py-GC–MS agreed well with the theoretical amount added to the samples 7–8 and 10–11 (Table 1), with values of 0.05 mg PET for sample 7, 0.079 mg PVC for sample 8 and 0.073 mg PET, 0.012 mg PS and 0.131 mg PVC for sample 10. The reported weight for lighter expanded PS in sample 11 differed with a factor of 5 (0.103 mg PS versus 0.556 mg added). As the fibres in sample 9 were added individually, a theoretical amount added is unavailable for comparison.

Youden plots are provided to explore the relative importance of within and between-laboratory errors. In Fig. 4, these plots are given for PET, PVC and PS particles. Given the amounts of polymers added to the tablets, the ratio of PET in test sample 7 relative to the PET amount in sample 10 is expected to be 0.16 (Fig. 4A, dotted line). A robust linear regression carried out on the data of laboratories reporting PET in both samples and using a bisquare algorithm forcing the intercept through zero yields a slope equal to 0.14 ± 0.070 (df = 14, $R^2 = 0.55$), which agrees well with the ratio expected on the basis of the production of the pellets. The within-laboratory standard deviation $\widehat{\sigma_r}$ is calculated to be 11.7, the between-laboratory standard deviation $\widehat{\sigma_L}$ is estimated to be 5.15.

Fig. 4B depicts the two-sample plot for PVC in samples 8 and 10. Given the amounts of PVC added to the tablets, the expected ratio of PVC in sample 8 relative to 10 is expected to be 1.62 (dotted line in figure). The robust linear regression provided a negative coefficient of determination, R^2, implying that the model with a zero intercept is not appropriate. The coefficient of determination R^2 for robust and regular linear regressions without constraints for the intercept were 0.06 and 0.16, respectively. The regression line is not given in Fig. 4B in view of this poor correlation. The within- and between-laboratory standard deviations $\widehat{\sigma_r}$ and $\widehat{\sigma_L}$ are estimated to be 5.67 respectively 5.58.

The two sample plots for PS are given in Fig. 4C. On the basis of the amounts of polymer added, the expected ratio of PS in sample 11
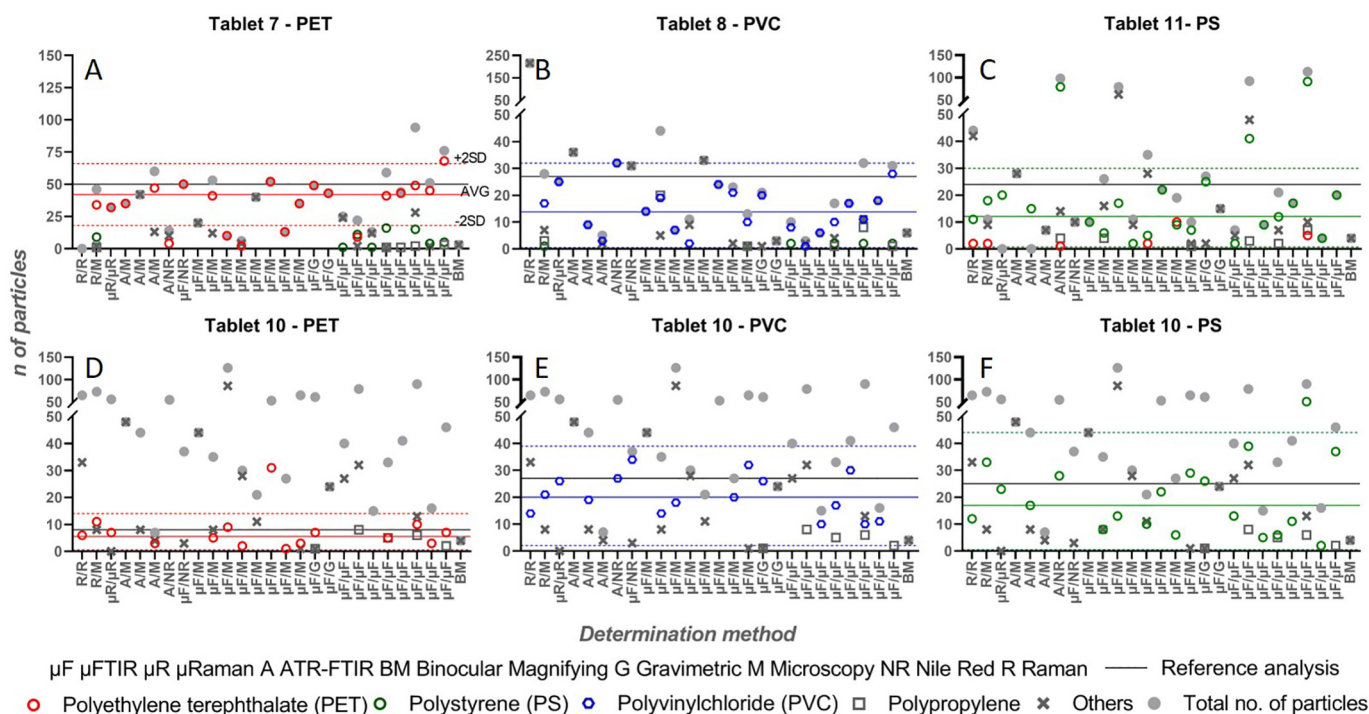

Fig. 3. Reported data for tablets (samples 7–8 and 10–11): reported polymer type and number of particles (total and per polymer type, see legend). Only showing polymer types that were either added to the tablet and/or were reported by ≥5 laboratories (i.e. polypropylene). If a polymer type was reported that was not added and reported by <5 laboratories it is classified as 'Others'. Lower graphs show the results for the added PET, PVC and PS in tablet 10 separately. Black lines represent the results of the reference analysis for the added polymer type. Coloured lines are the average reported number of particles for the polymer type that was added to the tablet, while the coloured dotted lines represent 2*standard deviation (SD), indicated on the right in graph A Tablet 7 – PET. Results for samples 9 and 12 are shown in Fig. S4.
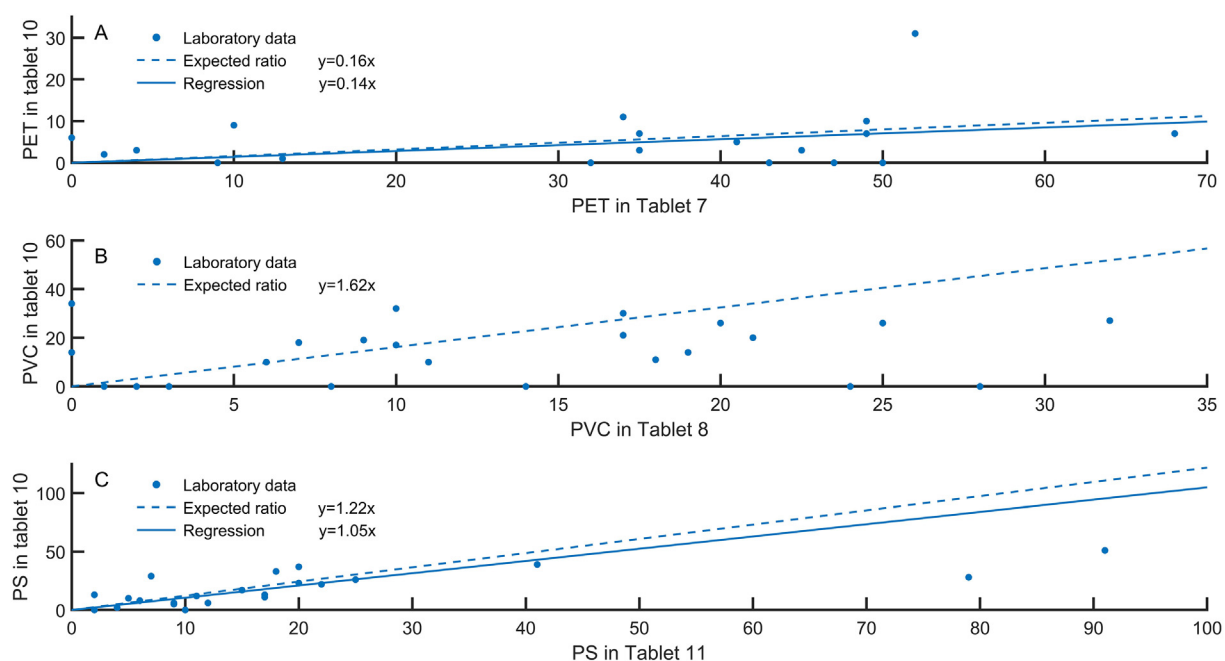
Fig. 4. Youden biplot for polyethylene terephthalate (PET, A) polyvinylchloride (PVC, B) and polystyrene (PS, C) showing the relationship between the reported number of particles in samples (e.g. tablets) 10 and 7 (A), 8 (B) and 11 (C). The dotted line represents the number of particles expected for sample 10 (y-axis) given the concentrations in samples 7,8 or 10 (x-axis) using the expected ratio listed in text.

relative to 10 is expected to be 1.218 (dotted line in Fig. 4C). This is in reasonable agreement with slope obtained with robust regression that is equal to 1.05 ± 0.14 (df $= 19$, $R^2 = 0.53$). The within and between-laboratory standard deviations $\widehat{\sigma_r}$ and $\widehat{\sigma_L}$ are estimated to be 4.48 respectively 10.67. The results suggest that between-laboratory errors dominate for PS.

The systematic differences observed for PS and PET may result from the application of different methodologies, different practices in the application of methods based on similar principles, or systematic errors. No correlation could be found between methodology and accuracy of results reported. The random errors observed for PVC might be due to small variations in applying the methodology, environmental factors and the uncertainty in the procedure to identify the polymer type as well as to quantify the number of particles (for example due to the extrapolation).

The results of this study give unique insight into the state-of-the-art of microplastic analysis by using both larger preproduction pellets and the innovative use of soda tablets containing well characterized amounts of microplastic particles or fibres. To our knowledge fibres have never been used in laboratory comparison studies and only two other interlaboratory comparisons on microplastics have been reported in the peer reviewed literature; one study of Isobe et al. (2019) with 12 participating laboratories, two seawater samples with added polymer in a size range of 400–1000 μm and without polymer identification, and the study of Müller et al. (2020) with 17 laboratories, two water samples with added polymer in a size range of 68–112 μm and 9–26 μm. The RSDs of the reported results between the laboratories for the smaller fraction (<1 mm) of Isobe et al. (2019) was similar to our results (50%) and just as our study FTIR was predominantly used. The results in the study of Müller et al. (2020) showed larger variance between and within the methods (RSDs were not reported) than our study. Notably, 50% of deviation was assigned as a successful z-score in Müller et al. (2020).

The RSDs of the reported number of added polymers in the tablets (29–78%, Table 4) are quite similar to those of ILSs on other compound classes conducted in periods when analytical methods were still in the early stage of development. For example, the RSDs of results in the

first ILS on polybrominated diphenyl ethers in standard solutions were 11–52% while in environmental samples they were up to 237% (de Boer and Cofino, 2002). Likewise, the RSDs of short-chain chlorinated paraffins (Tomy, 2010), was 23–56% in standard solutions, while in environmental samples 47–137% (van Mourik et al., 2018), and showed to improve over time. Although some progress in harmonization of results among laboratories was made in our study, there is still a long way ahead to achieve acceptable results, especially for a larger number of laboratories worldwide to start systematic monitoring of microplastic in different samples including e.g. drinking water.

4. Conclusions and outlook

The first round of the QUASIMEME/NORMAN development exercise scheme on microplastics analysis has resulted in a detailed assessment of the state-of-the-art of this analysis. The dissolvable tablets developed for this study were found suitable with acceptable homogeneity study results and can be used as standard like materials in future ILSs. The wide variety of different identification and quantification methods ($n > 7$) highlights that a standardized method is currently unavailable. The type of polymer was correctly reported in most cases, both in the pellets and in the tablets. The average reported weights for all pellets but one (PS) agreed also well among laboratories. However, not all laboratories were able to correctly identify the polymer type and quantify (number) of the relatively large preproduction pellets, easily visible to the naked eye. This confirms the importance of designing a proficiency testing scheme in a step-wise way and continuing to include simple standard test materials in future rounds. The large RSDs of reported numbers of particles in the tablets highlight both the difficulties of analysis of small microplastics and the need for harmonization and comparability in terms of reporting and applied analytical methods. The next steps of this development exercise scheme will include simple standard test materials and more complex sample matrices, such as biota and sediment. Initially these will be spiked samples, though in a future exercise we will explore the possibilities of using naturally contaminated samples (if they pass tests for homogeneity and stability during the preparation phase of test samples for the exercise).

CRediT authorship contribution statement

Louise van Mourik: Conceptualization, Writing - Original Draft, visualization, supervision, project administration, formal analysis. **Steven Crum:** Conceptualization, Project administration, Resources, Methodology, Formal analysis, Writing - review & editing. **Elena Martinez-Frances:** Development of analysis, Resources, validation and investigation, Writing -review & editing. **Bert van Bavel:** Conceptualization, Methodology, Resources, Investigation and Writing - review & editing. **Heather Leslie:** Conceptualization, Writing -Review & editing. **Jacob de Boer:** Conceptualization, Methodology, Writing -review & editing. **Wim Cofino:** Conceptualization, Methodology, Software, Formal analysis, Statistics and Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145071.

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