Quantitative detection of microplastics in water through fluorescence signal analysis

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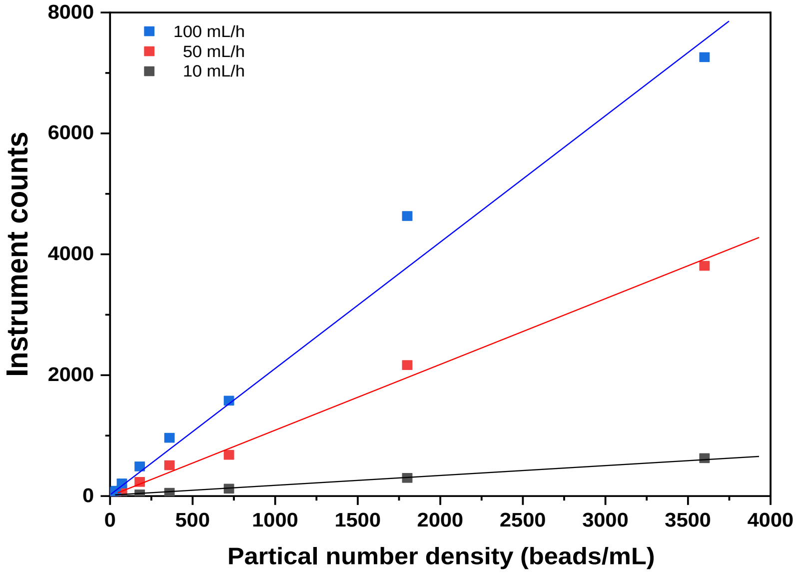
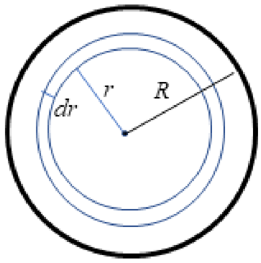


Figure S1. Experimental counts as a function of particle number density for different values of flow rate.

Model for the pulse duration distribution



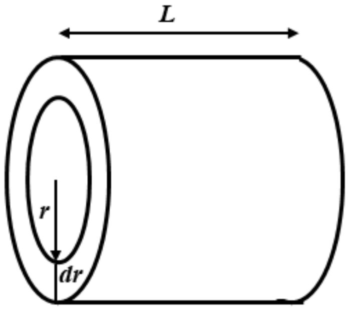
We assume the parabolic velocity profile with circular symmetry inside a circular tube/capillary given by:

$$\mathrm{v}(r) = \mathrm{v}_M \left[1 - \left(\frac{r}{R}\right)^2\right] \qquad (1)$$

where:

$$\mathrm{v}_M = 2 < \mathrm{v} > = 2\ \frac{Q}{\pi R^2}$$

with Q as the liquid flow rate.



Eq. 1 gives:

$$\frac{d\mathrm{v}}{dr} = -2\mathrm{v}_M \frac{r}{R^2}$$

Let us consider the particle concentration ***n*** uniform inside the liquid and, thus, a uniform particle number density per unit volume. Therefore, the number of particles within a certain cylindrical annulus of ray *r*, thickness *dr*, and length *L* in the tube section will be:

$$N(r)dr = 2\pi n r dr L \qquad (2)$$

From Eq. 1, we have:

$$r = R\sqrt{1 - \frac{\mathrm{v}}{\mathrm{v}_M}} \quad , \qquad dr = -\frac{R^2}{2\mathrm{v}_M r} dv$$

which can be substituted in Eq. 2 (neglecting the sign) to obtain the velocity distribution:

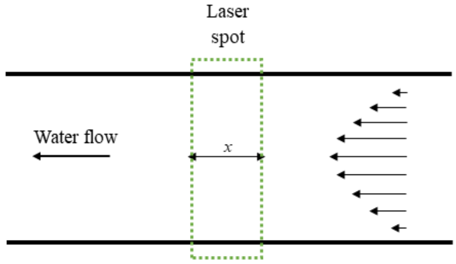
$$N(\mathrm{v})d\mathrm{v} = 2\pi n L R\sqrt{1 - \frac{\mathrm{v}}{\mathrm{v}_M}} \times \frac{R^2}{2R\mathrm{v}_M\sqrt{1 - \frac{\mathrm{v}}{\mathrm{v}_M}}} dv = \frac{\pi n R^2}{\mathrm{v}_M} L d\mathrm{v} \qquad (3)$$

Therefore, the velocity statistical distribution is uniform up to v_M.

However, in a certain measurement time interval ΔT, only the particles within a distance from the laser excitation volume *L* = v ΔT will be counted. Therefore, the distribution of the number of counted particles over the time period T will be:

$$N(\mathrm{v})d\mathrm{v} \;=\; \frac{\pi n R^2}{\mathrm{v}_M}\,\mathrm{v}\Delta\mathrm{T}d\mathrm{v} \tag{4}$$

The relation between the particle speed *v* and the transit time *t* across the illuminated path of length *x* (fluorescence pulse duration) is:



$$\mathrm{v} = \frac{x}{t} \quad \Rightarrow \quad |d\mathrm{v}| = \frac{x}{t^2}|dt|$$

Therefore, Eq. 4 gives the pulse duration distribution:

$$N(t)dt \;=\; \frac{\pi n R^2}{\mathrm{v}_M}\,\frac{x}{t}\,\Delta\mathrm{T}\,\frac{x}{t^2}\,dt \;=\; \frac{\pi n R^2}{\mathrm{v}_M}\,\Delta\mathrm{T}\,\frac{x^2}{t^3}\,dt \;=\; K\,\frac{\Delta\mathrm{T}}{t^3}\,dt \tag{5}$$

Up to $t_{min} = \frac{x}{\mathrm{v}_M} = \frac{57\times10^{-6}}{0.177} = 322\ \mu\mathrm{s}$ according to a laminar flow at 10 mL/h

This model does not have free parameters and gives a reasonable agreement with experimental distribution, as reported in Figure S2.

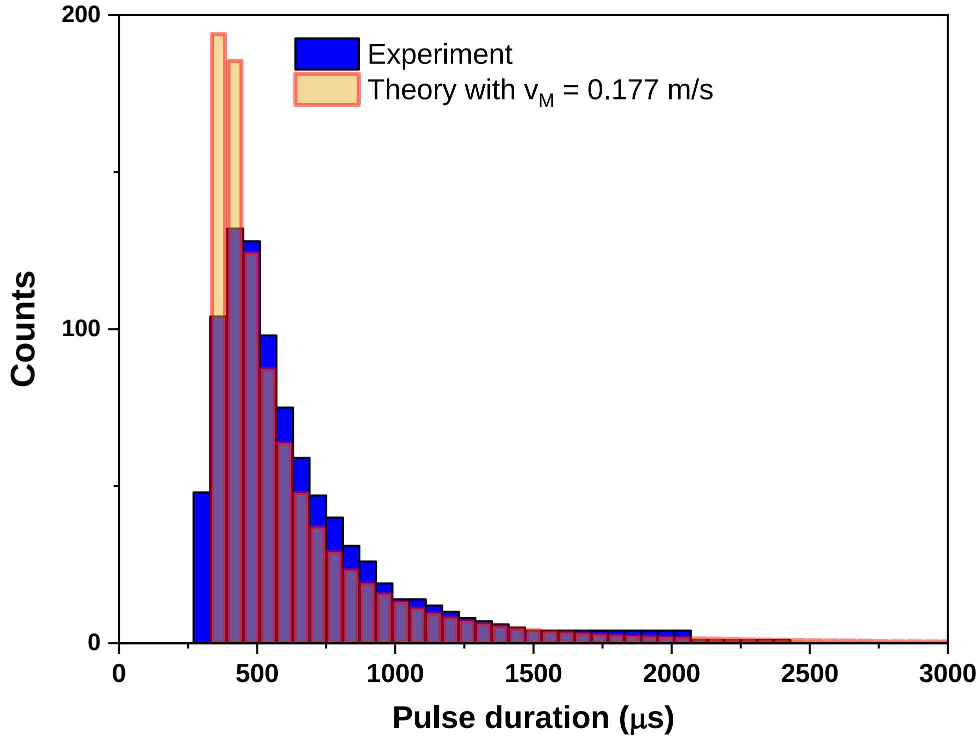


Figure S2. Experimental results for 10 μm OFPS microspheres at a flow rate of 10 mL/h. Theoretical distribution calculated according to Eq. 5 with no free parameters.

However, experimental verifications of Poiseuille's law often give values of v_M lower than the predicted one [45], and thus this can be considered as an adjustable parameter. A better fit was found for $v_M = 0.158$ m/s which gives:

$$t_{min} = \frac{x}{v_M} = \frac{57\times10^{-6}}{0.158} = 361\ \mu s$$

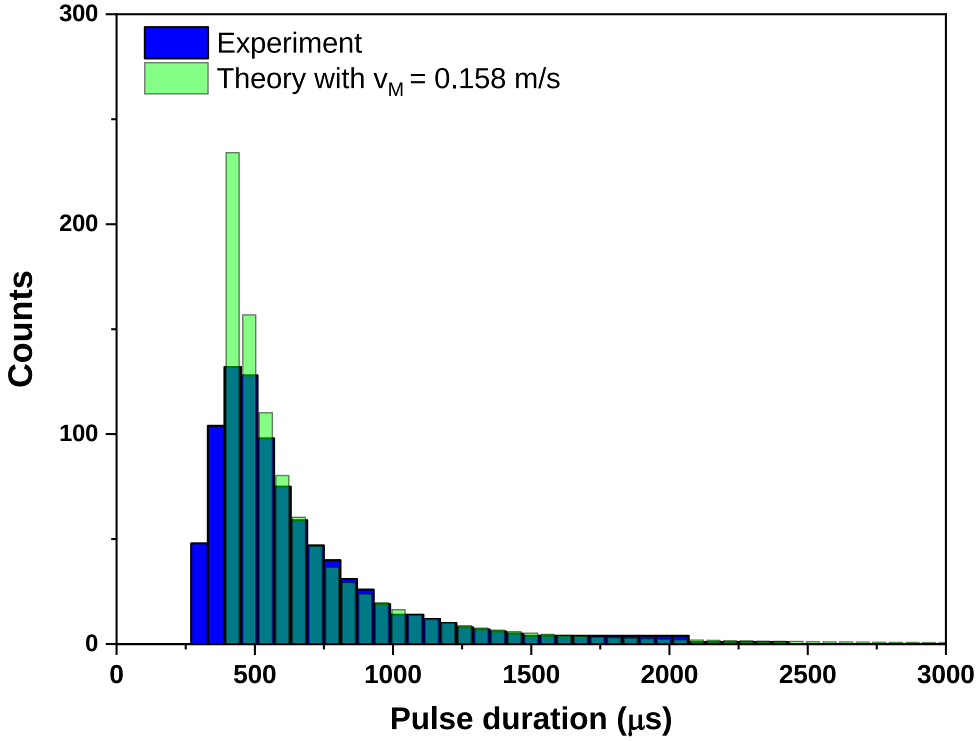


Figure S3. Experimental results for 10 μm OFPS microspheres at a flow rate of 10 mL/h. Theoretical distribution calculated according to Eq. 5 with v_M as a free adjustable parameter.

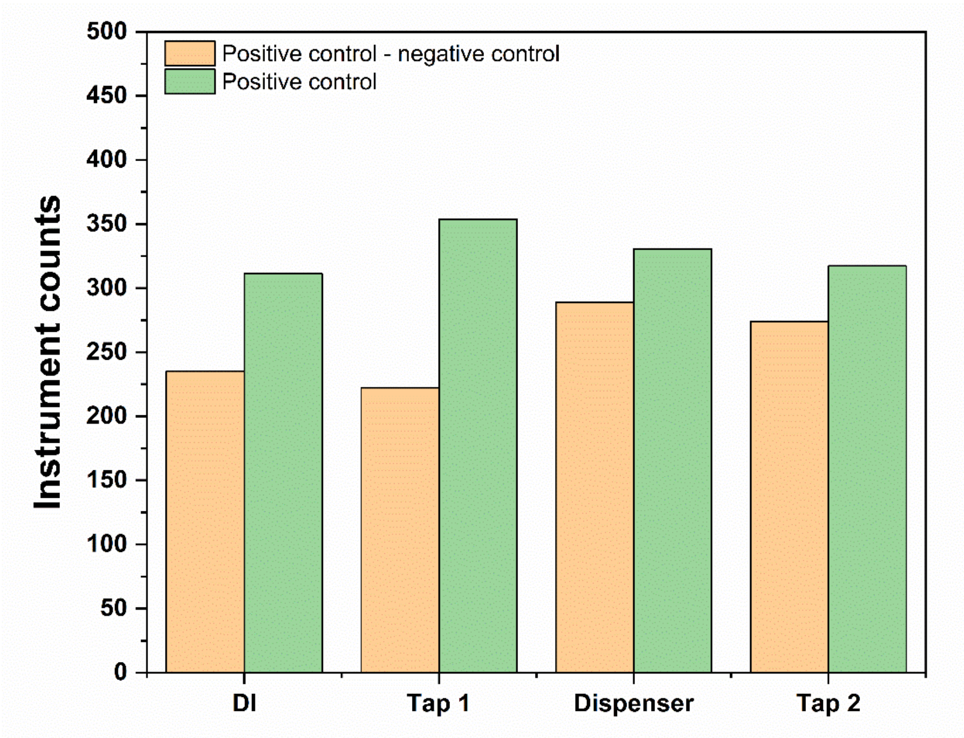


Figure S4. Observed counts in spiking experiment of stained PS MPs in different types of real water and in DI water. Water was filtered through a 0.7 μm filter and NR concentration was 0.1 mg/L.

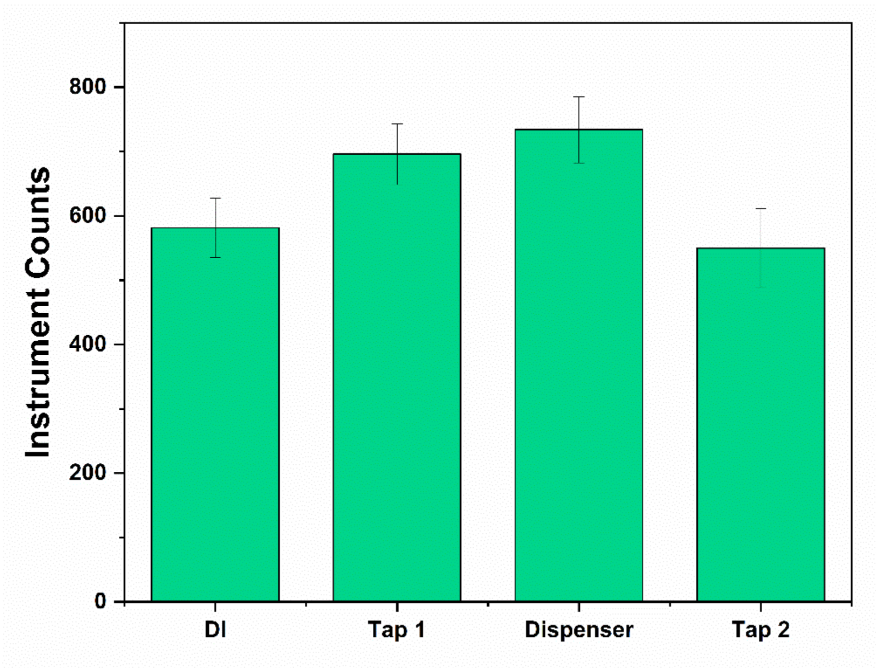


Figure S5. Observed counts in spiking experiment of stained PS MPs in different types of real water and in DI water. Water was filtered through a 40 μm filter and NR concentration was 5 mg/L.

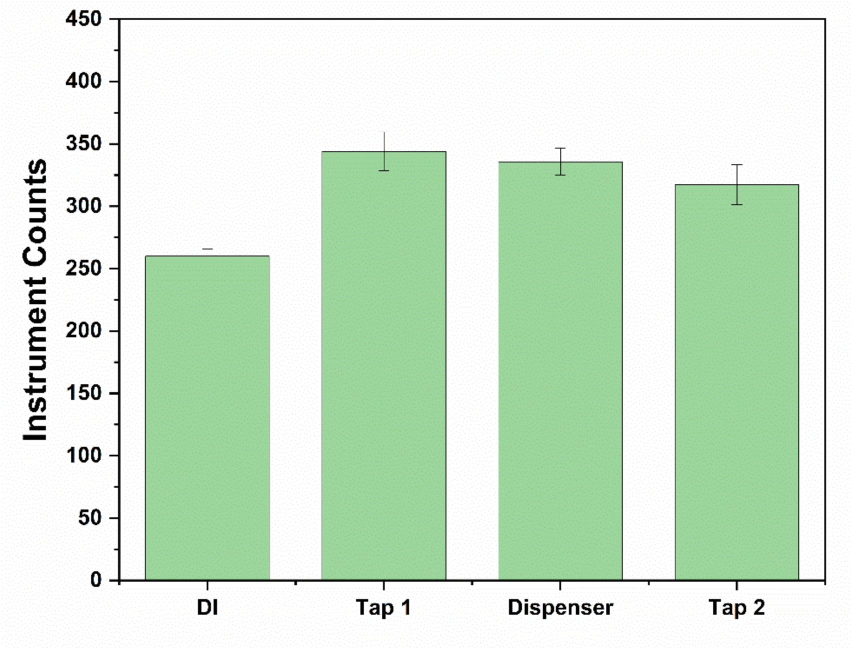


Figure S6. Observed counts in spiking experiment of stained PS MPs in different types of real water and in DI water. Water was filtered through a 40 μm filter and NR concentration was 0.1 mg/L.

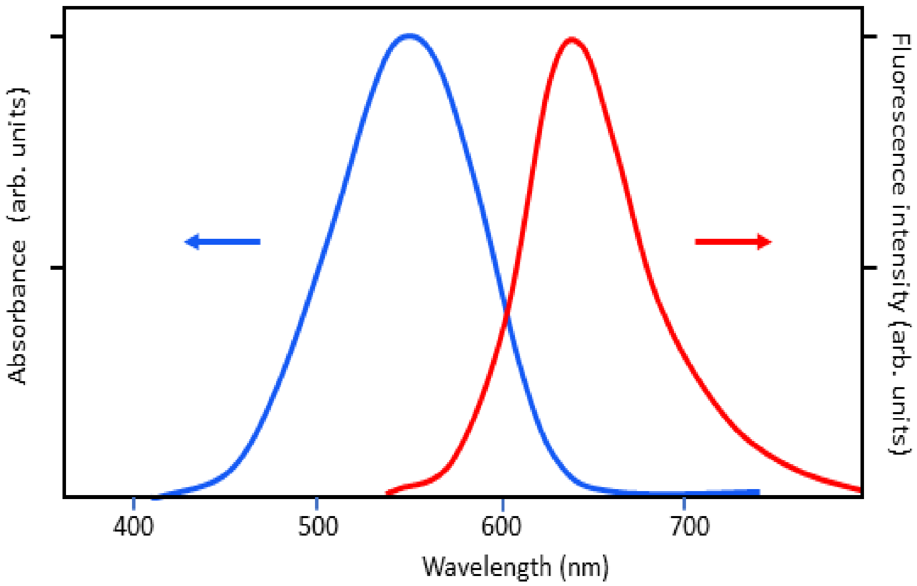


Figure S7. The absorption (blue curve) and emission spectrum (red curve) of Nile Red used in the present study.

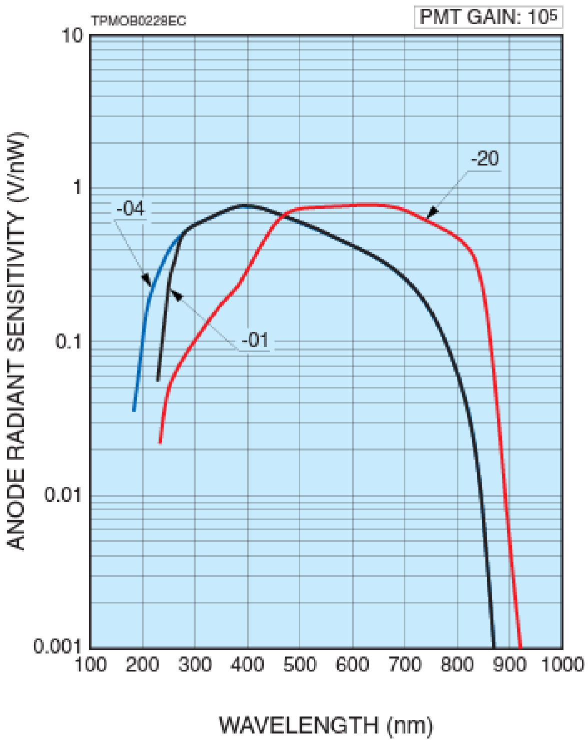


Figure S8. The spectral response (red curve) of the H10721-110 Hamamatsu photomultiplier used in the present study.
From:
https://www.hamamatsu.com/eu/en/product/optical-sensors/pmt/pmt-module/voltage-output-type/H10723-20.html

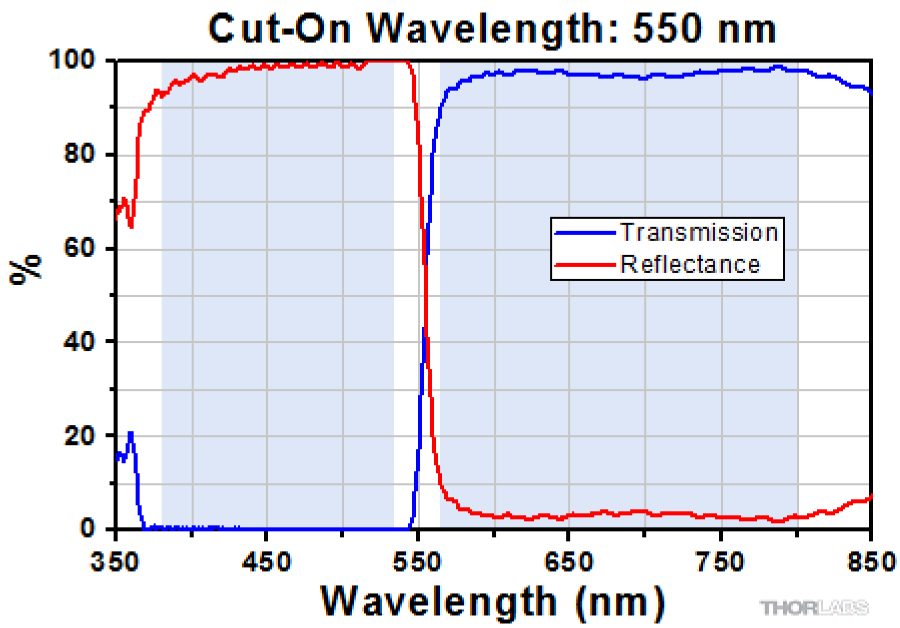


Figure S9. The transmission/reflection curves of the dichroic mirror Thorlabs DMLP550L used in the present study.
From:
https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=3313&pn=DMLP550

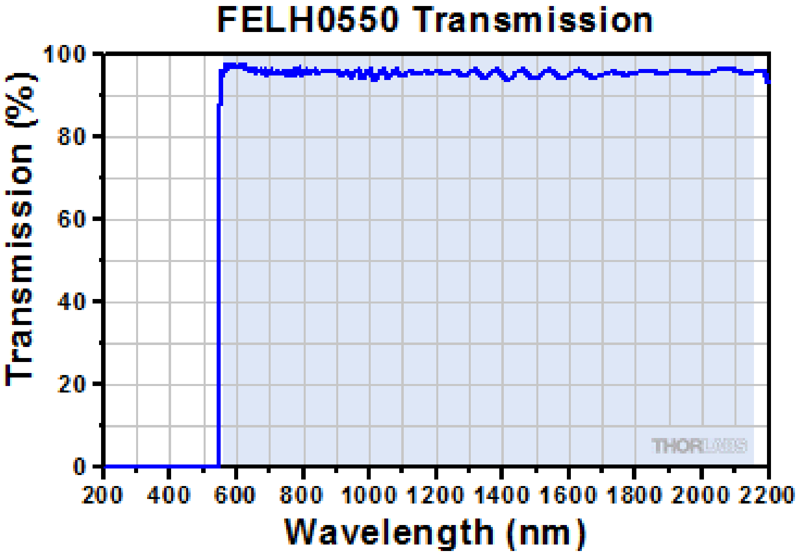


Figure S10. The transmission curve of the long-pass filter Thorlabs FEL0550 used in the present study.
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https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=6082&pn=FELH0550