

What Is the Impact of Leaky Sewers on Groundwater Contamination in Urban Semi-confined Aquifers? A Test Study Related to Fecal Matter and Personal Care Products (PCPs)

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Supplementary material 1: Standard operating procedure for grain size analysis

Small portions of granular materials (0.15 to 0.32 g) were collected from the middle section of the 6 core plugs using a precision chisel. Subsequently, the sample amounts were dried in an oven at the controlled temperature of 35 °C to remove most of the water content. Such low temperature is suitable for sample drying without affecting the mineralogical composition. Dehydration is needed also to ease the disaggregation of clayish and silty material. Prior to the analysis, all samples were disaggregated in a becher filled with distilled water applying a soft mechanical stirring for two minutes. Then, disaggregated materials were left to rest for at least 30 minutes before the analysis. Grain size analyses were performed with a Mastersizer 3000 (Malvern Panalytical®) optical laser granulometer. The instrument calculates the particle size according to their volume gained with optical light scattering diffraction. The granulometer applies the Mie light diffraction theory, which requires to provide the refractive and absorption indexes of analyzed materials as input parameters [1]. To analyze our samples, we inserted the optical parameters of crystalline silica (quartz), having refractive index of 1.54 and absorption index of 0.01. We assumed quartz as the dominant mineral composing our samples. The incident light used to produce diffraction of dispersed particles is provided by two different sources, one red and the other blue. The red laser light with a wavelength of 632.8 nm is generated by a He-Ne source excited with 4 mW electrical power. The blue light with a wavelength of 470 nm is provided by a LED source with a maximum power of 10 W. The adoption of two laser sources allows to analyze particles with equivalent diameter spanning from 10 nm to 3500 µm. We used the laser granulometer coupled with a liquid dispersion unit (Hydro EV), which is specifically designed to analyze low cohesion granular materials, if they can be fully disaggregated. To facilitate disaggregation before the analysis, pre-disaggregated samples were inserted into a becher filled with still water and ultrasonication to 2% of maximum intensity, together with 1500 rpm stirring speed were applied. The ultrasonication phase lasted for 200 s, while for successive 200 s samples underwent stirring at 1500 rpm without any further ultrasonication. The dispersion of granular samples in tap water may produce a strong alteration of the original particle size distribution, thus providing unreliable data. To minimize sample alteration and to grant the best statistical reproducibility we performed several test in compliance with previous studies [2], to set a specific standard operating procedure. We tested each instrumental parameter playing a role in determining the final grain size distribution and a summary of the tests conducted is reported below:

1. The sample amount is a critical parameter to be set because it determines the reliability of the light diffraction. Too low as well as too high sample quantity may lead to incorrect determination of particle equivalent diameter. To avoid this issue, we carefully weighted sample mass to decrease the power of incident laser in a range comprised between 80 and 90% of the initial power. In this range, the Mie laser diffraction theory can be applied without errors. Sample mass used during tests and final analyses falls between 0.15 and 0.32 g.

2. The Hydro EV liquid-dispersion modulus is equipped with a stirrer allowing the mechanical dispersion of granular media. Low stirrer speed allows to analyze only the finer fraction of the grain size distribution, with coarse particles remaining on the bottom of the analysis becher. Conversely, high stirrer speed is more suitable for mobilizing coarser particles, even if mechanical fragmentation may occur especially on pre-damaged or micro-fractured grains. The correct stirrer speed was selected after the completion of a dedicated test during which the stirrer speed was raised from 500 rpm (the lowest speed) up to 3500 rpm (highest speed), with progressive incremental steps of 100 rpm. For each incremental steps, we performed 10 successive measurements having a duration of 5 s. Inserting the data in a plot with stirrer speed on the X axis and equivalent mean diameter on the Y axis helps to evaluate the stirrer speed which allows to analyze samples without compromising the original grain size distribution. In our sample, we selected a stirrer speed of 1500 rpm.
3. The measurement time indicates the time of activation of the laser source related to each analysis. Brief activation times are more effective to analyze well sorted samples, with narrow grain size distribution curves. Conversely, long measurement times are suitable in the case of poorly sorted samples with extremely wide curves. We performed three separate tests to check the proper measurement time with 5, 10 and 20 s laser activation. Tests were compared checking the configuration granting the least variation of equivalent diameter values during the analysis. In our samples, due to the moderate to high width of the grain size distribution curves, a laser activation time of 20 s was chosen.
4. The total number of measurements composing the analysis can be a critical parameter to be set because it defines the residence time of the sample inside the distilled water. Analysis with high number of measurements may partially compromise the goodness of the results because of the mechanical stress imparted during stirring. This is particularly true in the case of fine-grained materials. Three tests were performed coupling the total number of measurements with the laser activation time. We halved the number of measurements and doubled the laser activation time, to maintain the same sample residence time inside distilled water. Following this, tests were run with 100, 50 and 25 measurements on the same sample. In our samples, the best reproducibility is provided by 25 measurements each with 20 s of laser activation time.
5. Ultrasonication consists in the emission of sonic waves inside the stirring dispersed material. The usage is particularly useful in fine grained materials to avoid flocculation of clayish material and to disaggregate particles. However, if ultrasonication is used incorrectly it may lead to severe damaging of particles compromising and underestimating the original grain size distribution. Three tests were conducted applying an ultrasonication intensity of 2, 5 and 10%. Tests were run at relatively low ultrasonication intensity to avoid mechanical stress which typically occurs above the 10% intensity threshold. For our samples, we decided to do not use ultrasonication during the analysis because of the severe micro-fragmentation occurring in the coarser fraction. However, during the disaggregation phase prior to the analysis we deployed ultrasonication at 2% for 200 s to ease disaggregation of coarse-grained particles without causing mechanical damage.
6. The final test is aimed to check the statistical reproducibility of the analysis and was conducted performing 5 successive tests on different sample aliquots, keeping the same instrumental parameters. The reproducibility is evaluated by comparing the five average grain size distributions. In the case

of overlapping or similar average curves the standard operating procedure is assumed to be suitable. In our sample, the 5 curves matched, and we approved the procedure.

All the tests reported above were performed on (S10 3-4 m) sample, which was considered representative of the entire sample set.

Summarizing the analytical parameters that were employed, we sampled 0.15 to 0.32 g of granular materials that were manually disaggregated for 2 minutes and were kept resting for 30 minutes. Pre-disaggregated samples were inserted in analysis becher filled with distilled water and stirred at 1500 rpm with 2% ultrasonication form 200 s. Afterwards, we stopped ultrasonication and stirring was continued for other 200 s to allow the disaggregation of coarse-grained particles. The final analysis consisted of 25 measurements, each with 20 s duration without ultrasonication. The average grain size distribution curves are calculated from the 25 measurements. Results of the grain size analyses referred to each sample are reported in Figure S1.

We hereafter describe the formulas used in the main text of the article to calculate the equivalent diameter and the span of the granulometric curves.

The generic formula employed to calculate the equivalent diameter via laser diffraction is:

$$D[m, n] = \left(\frac{\sum_{i=0}^t V_i * d_i^{m-3}}{\sum_{i=0}^t V_i * d_i^{n-3}} \right)^{\frac{1}{m-n}} \quad (1)$$

where V_i stands for volume density of particles in the size class d_i and t is the total number of size classes composing the grain size distribution. By substituting the indexes m and n with exponents (4, 3) the De Broucker mean diameter, or equivalent diameter, is obtained.

Span is related to the sorting of grain size distribution curves and can be assumed as an estimate of the width of the curves. It is calculated as follows:

$$Span = \frac{d(x, 0.9) - d(x, 0.1)}{d(x, 0.5)} \quad (2)$$

where d is the equivalent diameter threshold and x can be substituted according to the type of distribution (unimodal, polymodal, left or right skewed). High values of span are related to low sorting degree (large granulometric curves), while low span values indicate well-sorted samples (narrow grain size distributions).

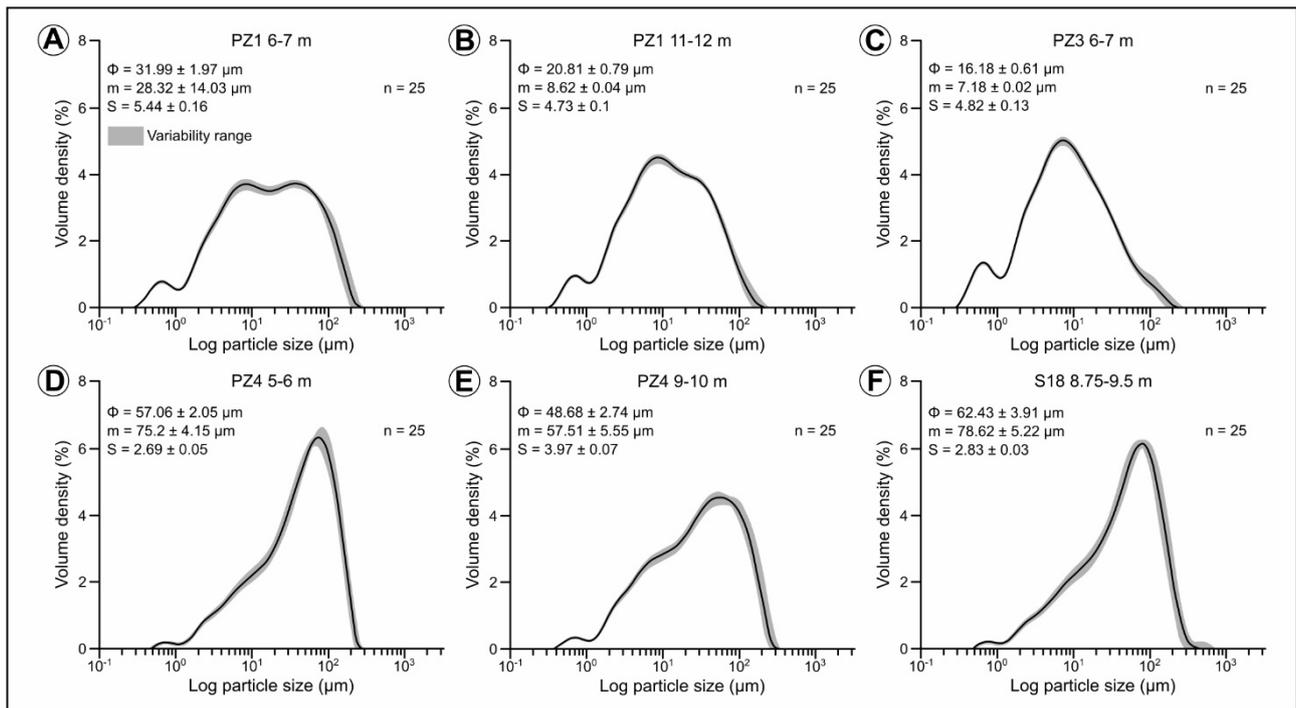


Figure S1. Grain size distributions with average curve in black and variability range in light gray. Grain size distribution curves for PZ1 6-7 m (A), PZ1 11-12 m (B), PZ3 6-7 m (C), PZ 5-6 m (D), PZ4 9-10 m (E) and S18 8.75-9.5 m (F). Φ , equivalent mean diameter; m, modal value of the grain size distribution; S, span (sorting) of grain size distribution; n, number of measurements.

References

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