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ORIGINAL ARTICLE

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Comparison of soil particle density determined by a gas pycnometer using helium, nitrogen, and air

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Abstract

Soil particle density (ρ_s) is often assumed as 2.65 g cm^{-3} (density of quartz). The objectives of this study were to compare the use of different gases for determining ρ_s in a gas pycnometer and relate measured ρ_s to soil particle size distributions. The ρ_s of 36 natural soil samples representing 12 USDA textural classes, fine glass beads, crushed granite rock, kaolinite, and bentonite were measured by a commercial gas pycnometer using He, N_2, and dry air. The ρ_s of 30 of the soil samples, glass beads, and crushed rock were also determined with a water pycnometer. The ρ_s of 36 soil samples determined by He and 30 samples determined by water had narrow ranges with averages of 2.65 and 2.59 g cm^{-3}, respectively. The ρ_s determined by air and N_2 had much wider ranges with averages of 2.93 and 2.97 g cm^{-3}, respectively. There was a near 1:1 relationship between ρ_s of all samples determined by air and N_2 with a highly significant ($p < .001$) correlation coefficient ($r = .99$). The average ratio of ρ_s determined by He and water was 1.03, but the correlation coefficient for their relationship was only .416. Although the relationship between ρ_s determined by He and either air or N_2 was relatively strong ($r < .61$), the regression coefficient was <.17. There was a strong relationship between soil clay content and ρ_s determined by N_2 or air but a weaker, yet statistically significant ($p < .05$) relationship when using He.

1 | INTRODUCTION

Particle density, ρ_s, refers to the skeletal density (Nguyen et al., 2019) of the solid phase of a material composed of particles, such as soil, potting material, seed, and cement. Particle density is an important inherent (also referred to as static, Hillel, 1998) soil property, and its value is used for determination of other soil properties such as specific heat capacity (Kluitenberg, 2002), particle size distribution (Gee & Or, 2002), and total porosity (Flint & Flint, 2002b). The most common methods for measuring ρ_s are liquid displacement and gas displacement techniques (ASTM, 2020a, 2020b; Flint & Flint, 2002a).

In addition to being labor intensive and time consuming, the liquid displacement technique (hereafter referred to as water pycnometer method) suffers from a number of disadvantages (e.g., relatively small sample that is discarded after analysis, buoyancy of some particles, difficulty of degassing to fill all the pore spaces). In general, water is used for determining ρ_s of soil, but other liquids (e.g., kerosene) may be used for materials that react with water (e.g., cementitious materials) (Ball et al., 2000; Helsel et al., 2016). The gas pycnometer method is an old procedure for determining skeletal volume of a wide range of organic and inorganic materials (as examples see Torstensson & Erikson [1937] and Washburn & Bunting [1922]). The procedure can use relatively large ground or intact samples (e.g., 100 cm^3 bulk volume), is relatively simple, and is nondestructive (i.e., the sample can be reused for other analysis), but it requires a gas pycnometer, which can be relatively expensive.

Despite wide variations in particle size distribution as well as the mineral composition of the inorganic fraction of soil (Table 1), soil ρ_s is routinely assumed to be 2.65 g cm^{-3} (density of quartz) in lieu of an actual determination (Flint & Flint, 2002b; Ghanbarian et al., 2021; Hillel, 1998; Kluitenberg, 2002).

The nature of soil mineralogy is complex (Churchman & Velde, 2019; Schulze, 2002) and the amount of different minerals in soil is often expressed qualitatively (for examples see Bielders et al. [1990] and Joosse & McBride [2003]). Although we expect ρ_s to be dependent on soil mineralogy, to our knowledge, only Ruehlmann and Körschens (2020) presented an empirical equation relating ρ_s determined by water pycnometer to the soil mineral composition. Joosse and McBride (2003) assessed mechanical compression of a number of soils with different mineralogy but only discussed their relationship qualitatively. Our assessment of ρ_s values determined by water pycnometer and their associated minerals determined for 21 of their samples did not show any meaningful relationship. A number of studies have related soil particle size distribution, which is routinely determined, to different soil properties, including ρ_s (Ball et al., 2000; Ghanbarian et al., 2021; McBride et al., 2011, 2012; Resurreccion et al., 2011; Ruehlmann, 2020). Even Ross (1978) and Thomas et al. (2000) related the shrink–swell potential of their soil samples graphically to their clay content.

Due to lower density of organic matter (OM) as compared to the inorganic fraction of soil, similar to bulk density (ρ_b), ρ_s is directly related to the soil OM content (Bielders et al., 1990; Blanco-Canqui et al., 2006; Ruehlmann, 2020; Rühlmann et al., 2006; Schjønning et al., 2017). Qin et al. (2022) compared 11 pedotransfer functions (PTFs) for estimating ρ_s of soil samples collected from the surface (0-to-10-cm depth) of 175 runoff plots with low OM in a subtropical region of China. Their assessments showed the relationship between ρ_s and clay content by these PTFs is not well established. In their own regression analysis using 175 different soil samples, they showed a statistically significant ($r^2 = .26$) inverse relationship between ρ_s and clay content. Schjønning et al. (2017) showed a significant ($r^2 = .77$, $p < .0001$) direct relationship between ρ_s and clay content for 47 Danish soil samples with <0.01 kg kg^{-1} OM, while Ball et al. (2000) reported a nonsignificant relationship for soil samples from 155 sites in the United Kingdom. Using data from Joosse and McBride (2003), McBride et al. (2012) reported a significant ($p < .05$) direct relationship between ρ_s (determined by water pycnometer) with clay content and an equally significant inverse relationship with sand + silt content. McBride et al. (2011), on the other hand, showed an inverse relationship between ρ_s with clay and a direct relationship with sand + silt content ($r^2 = .018$) for soil samples from 282 horizons of 91 soil profiles. [It should be noted that the two equations relating ρ_s with clay and sand + silt contents by each of McBride et al. (2011, 2012) and Schjønning et al. (2017) are the same because the amount of clay = 100 − (sand + silt content).]

Core Ideas

- Average particle density of soils belonging to 12 textural classes determined by helium was 2.65 g cm^{-3}.
- Average particle density measured by air and nitrogen were 2.93 and 2.97 g cm^{-3}, respectively.
- Helium, nitrogen, or air can be used to measure particle density of coarse-textured soils.
- Only helium should be used to measure particle density of medium- and fine-textured soils.

Bielders et al. (1990) determined ρ_s of 38 samples collected from 14 different soils by a gas pycnometer using He and air, and reported that using air led to overestimation of the actual ρ_s (assumed to be the one determined using He). Overall, they attributed the high ρ_s determined using air to adsorption of water vapor and perhaps adsorption of N_2 and O_2 on the surfaces of soil particles. Emmett et al. (1938) reported the N_2 adsorption of air- and oven-dried samples of two soils and their respective colloidal particles (<0.3 µm). Using an apparatus similar to a gas pycnometer, Makower et al. (1938) measured the amount of N_2, O_2, and carbon dioxide (CO_2) adsorption of four soils, their respective colloidal (<0.3 µm) particles, and four clay minerals at 0 °C. Runkles (1956) also measured the volume of O_2 and He needed to fill up the pore spaces of air- and oven-dried samples for one sand, four soils with different clay content, vermiculite, and one of the above soils that contained 54% clay at different water contents. Nakayama (1958) measured the amount of each of He, O_2, and CO_2 gases that was required to fill up the volume of pore spaces of samples (i.e., volume of the sample container − volume of the solid particles) of 11 different soil materials and four clay minerals. Tuul and Innes (1962) determined the volume of air needed to measure ρ_s of a large number of oxides (e.g., SiO_2, Al_2O_3). In these studies, it was assumed that He does not adsorb by any of the soils or various oxides. Further, the difference between the volume of each gas and He required to fill up the open spaces in the sample was taken as the amount of that gas that was adsorbed on the materials under any of the experimental conditions.

The gas pycnometer method requires specialized equipment that can be obtained commercially or be constructed in house (for examples see Geddis [1994], Silva & Dharmasena [2017], Tamari [2004]). For soil, research-grade compressed He is recommended (ASTM, 2020b; Flint & Flint, 2002a). Other gases, such as purified air or N_2, can also be used, but it is purported that He does not adsorb on soil particles and more closely obeys the ideal gas law compared with other gases (Flint & Flint, 2002a). It should be mentioned that the manufacturers and distributors of commercial gas pycnometers have recommended using compressed air (UGT), research-grade He and N_2 (Micromeritics; Quantochrome Instruments), and He and (air) vacuum (InstruQuest) in their devices. In a recent study, ten Damme et al. (2021) used atmospheric air to measure particle density of their soil samples, and Park et al. (2022) showed similar results for particle density of several cementitious materials determined by vacuum and He. Because air is mainly composed of N_2 and O_2, and can be supplied using a compressor, the potential use of air in a gas pycnometer for determining soil ρ_s could help simplify the requirements of the procedure. Therefore, the use of gases other than He in gas pycnometers for determining soil particle density needs to be investigated.

Based on the available information, we hypothesize that N_2 and air may be suitable for use in a gas pycnometer for determining soil ρ_s. We undertook this study with the objectives of comparing the use of different gases in a gas pycnometer for determining soil ρ_s, and to relate soil ρ_s to soil particle size distribution. Specifically, we aimed to compare the particle densities of a number of soil samples belonging to the 12 USDA textural classes determined by a commercial gas pycnometer using compressed He, N_2, and (dry) air, and by the water pycnometer method as a reference for common comparison.

2 | MATERIALS AND METHODS

2.1 | Soil samples

Thirty-three soil samples collected from different horizons and locations in the Coastal Plain, Piedmont, and Mountain regions of North Carolina for another research study (Floro et al., 2015) and extension training (Dr. David Lindbo, formerly with North Carolina State University [NCSU]) were used. Three different silt soil samples were also obtained (Dr. Steve Monteith, National Lab, Natural Resources Conservation Service [NRCS], USDA, Lincoln, NE). In addition to the 36 natural soil materials, fine glass beads, crushed granite rock (<1 mm in diameter), and pure kaolinite and bentonite were used in the study. The natural soil samples were provided without identifications for their respective horizon, classification, or mineralogy. Their organic carbon content was <1% (by mass) for 32 samples and between 1 and 4.5% for four samples. All soil samples were air-dried, crushed by hand using a plastic roller, and passed through a 2-mm sieve. Except for the three silt samples that were analyzed by NRCS, the natural soil samples were analyzed for particle size distribution by the hydrometer method (Gee & Or, 2002). The natural soil samples representing the 12 USDA textural classes were divided into three groups; fine, medium, and coarse (Plaster, 1997) as presented in Figure 1.

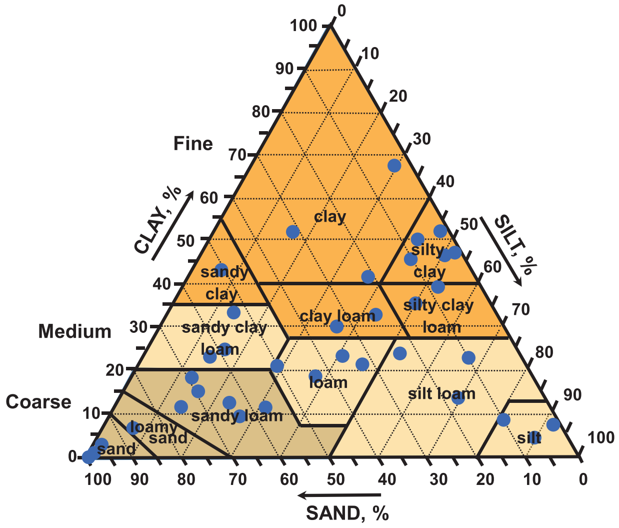

FIGURE 1 Distribution of the soil samples representing the 12 USDA textural classes placed into fine, medium, and coarse groups as suggested by Plaster (1997)

2.2 | Application of the ideal gas law to gas pycnometer

We used the ACCUPYC II 1340 Gas Pycnometer (Micromeritics Instrument Corp.) with a 100-cm^3 sample container. This constant volume gas pycnometer is composed of two compartments, the sample chamber (inside volume with sample container = V_{sc}) and an expansion chamber (volume = V_{ec}), connected through a valve (B) as shown in Figure 2. After placing a sample with unknown volume V_s in the sample chamber, the following actions occur automatically by starting measurement. After closing valve B, compressed gas (e.g., He, N_2, or air) is applied to the sample chamber before closing valve A. The pressure in the sample chamber is measured after reaching equilibrium. After closing valve C, valve B is opened allowing the gas to move from the sample chamber into the expansion chamber. The pressure inside the sample chamber is measured again when equilibrium is reached. Using the initial and final

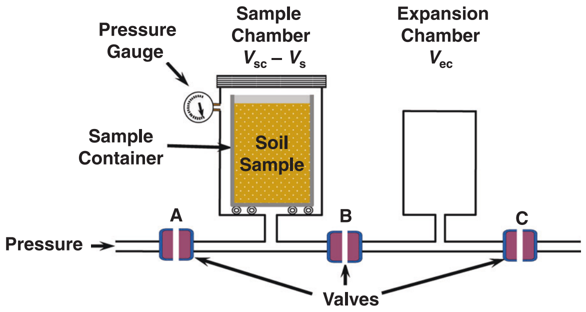

FIGURE 2 Schematic diagram showing the general components of a gas pycnometer. Drawing is not to scale. V_{sc}, sample chamber volume; V_s, soil sample volume; V_{ec}, evacuation chamber volume

pressures and the volumes of the sample and expansion chambers, the volume of the solids in the sample chamber is determined using the ideal gas law.

To measure the volume of the particles, an oven-dried sample of known mass (unknown volume V_s) is placed inside the sample chamber under atmospheric pressure (P_0). Applying the ideal gas law to the sample and expansion chambers before and after opening the valve between them we have Equations 2a, 2b, and 2c:

$$P_0 V_{ec} = n_0 RT \tag{2a}$$

$$P_1 \left(V_{sc} - V_s\right) = n_1 RT \tag{2b}$$

$$P_2 \left(V_{sc} + V_{ec} - V_s\right) = n_2 RT \tag{2c}$$

where P_1 and P_2 are the initial (sample chamber) and final (sample and expansion chamber combined) absolute pressure measured values, respectively, R is the ideal gas law constant, T is temperature (K), and n_0, n_1, and n_2 are the number of moles of gas in expansion chamber, in sample chamber before opening the valve between them, and in both chambers after opening the valve between them, respectively. Because $n_2 = n_0 + n_1$, substituting for $P_i = P_1 - P_0$ and $P_f = P_2 - P_0$ and rearranging Equation 2c we get Equations 3a and 3b:

$$\left(P_f + P_0\right)\left(V_{sc} + V_{ec} - V_s\right) = P_0 V_{ec} + \left(P_i + P_0\right)\left(V_{sc} - V_s\right) \tag{3a}$$

$$P_f \left(V_{sc} + V_{ec} - V_s\right) = P_i \left(V_{sc} - V_s\right) \tag{3b}$$

where P_i and P_f are the initial and final gauge pressures, respectively. It should be noted that Equation 3b is similar to Boyle's law. Rearranging Equation 3b, the volume of the sample can be determined by Equation 4:

$$V_s = V_{sc} - V_{ec} / \left[\left(P_i / P_f\right) - 1\right] \tag{4}$$

Instead of using Equation 4, a set of standard samples can be used to develop a calibration curve (equation) relating V_s to P_i/P_f. The gas pycnometer in this study was preloaded with a calibration equation that could be adjusted using stainless-steel standard volume samples provided with the equipment.

2.3 | Particle density measurements

Particle density of all 40 samples was measured using compressed research-grade He, research-grade N_2, and dry air. Prior to each set of measurements, a standard stainless-steel sample (known V_s) was used to check the internal standard equation of the gas pycnometer.

Prior to measuring ρ_s by each method, all air-dried samples were oven-dried at 105 ˚C for 24 h and placed in a desiccator with calcium chloride ($CaCl_2$) as desiccant. All oven-dried samples were kept in the desiccator under vacuum for at least 16 h before analysis. To measure V_s of the soil solids with each gas, the 100-cm^3 sample container was filled with an oven-dried sample. After determining the mass of the sample, it was placed in the gas pycnometer. Per the manufacturer's recommendation, the gauge pressure applied to the gas pycnometer was maintained at around 21 psi, but the internal equilibrium gauge pressure set by the equipment in the sample chamber was around 19.6 psi. The gas pycnometer was set to purge each sample with the respective gas (i.e., He, N_2, or air) 10 times followed by 10 consecutive measurements automatically. At the completion of measurements (usually between 30 and 35 min), the values of the 10 measurements of V_s, along with their average and standard deviation, were recorded. Particle density was determined by dividing the oven-dried mass of the sample by its respective average V_s.

Particle densities of 30 of the soils, glass beads, and crushed granite were also determined by the water pycnometer procedure (Flint & Flint, 2002a) using three replications. Because the samples used for measurement by the water pycnometer cannot be reused, we did not measure particle densities of three of the soil samples from North Carolina and the three silt samples provided by NRCS due to concerns about not having adequate mass of sample needed for gas pycnometry measurements. We also did not determine ρ_s of pure kaolinite and bentonite with the water pycnometer due to problems with their wetting with water.

2.4 | Relating particle density to soil texture

We related measured particle densities of the 36 natural soils determined by the three gases to their respective percentage sand, silt, and clay contents. We then inspected the correlation coefficient and the corresponding regression coefficient (i.e., the slope of the liner regression line) to assess the strength

TABLE 1 Specific gravity for selected soil and rock minerals

Crystal specific gravity (dimensionless)[a]	
Albite	2.63[b]
Allophane	2.72–2.78[c]
Anorthite	2.76[b]
Apatite	3.2[db]
Biotite	2.7–3.1[d], 3.0[b]
Calcite	2.71[b]
Chlorite	2.6–3.0[c], 3.0[b]
Feldspars	2.5–2.8[d]
Gibbsite	2.42[b]
Goethite	4.3[b]
Halloysite	2.73[c]
Hematite	5.26[b]
Illite	2.8[db]
Kaolinite	2.68[c], 2.65[db]
Magnetite	5.17[b]
Mica	2.6–3.2[d]
Montmorillonite	2.5[cdb]
Muscovite	2.83[db]
Olivine	3.81[b]
Pyrite	5.02[db]
Quartz	2.65[db]
Vermiculite	2.3[b]

[a] Specific gravity = particle density/density of water (dimensionless) (density of water = 1 g cm^{-3} at 0°C).

[b] Rumble (2020).

[c] Bielders et al. (1990).

[d] Flint and Flint (2002a).

of the relationships between ρ_s and percentage sand, silt, and clay of the samples. In this analysis, we did not use the fine glass beads and crushed rock, which are not soil, as well as pure bentonite and kaolinite (100% clay-sized) to avoid biasing our analysis.

2.5 | Potential adsorption of gases on soil particles

To explore the possible reasons for any difference in the ρ_s determined by the gas pycnometer using He and N_2 (and air by extension), the number of moles of He and N_2 involved in determining the ρ_s of a 100-g sample of each of the 36 natural soil materials, ground rock, fine glass beads, kaolinite, and bentonite was determined. For this, the volumes of the expansion and sample chambers, the initial equilibrium pressure in the sample chamber (Table 2), and the volume for each sample were used in the gas law presented by Equation 3b to determine the respective P_f. Then, we used Equations 2a, 2b, and 2c with $T = 293$ K (20 °C room temperature) to determine the number of moles of each gas in the sample chamber. (Note: The number of moles of the two gases in the expansion chamber at atmospheric pressure and a given temperature is constant.) Using the conversion factor of 22.41 L $mole^{-1}$, we converted the numbers of moles of N_2 and He to their respective volume at standard temperature (0 °C) and pressure (1 atm) (STP), and the difference was taken as the amount of N_2 adsorption.

TABLE 2 Values of the fixed parameters related to the gas pycnometer

Parameter	Value
Sample chamber volume, V_{sc}	111.40 cm^3 (0.1114 L)
Expansion chamber volume, V_{ec}	74.31 cm^3 (0.07431 L)
Initial gauge pressure, P_i	1.3337 atm (19.6 psi)
Ideal gas law constant, R	0.0821 L-atm/mole-K
Room temperature, T	20 °C
Measurement temperature, K	293 K

2.6 | Statistical analysis

The R software (R Core Team, 2021) was used to perform statistical analysis. Because we used homogenized ground samples, only one sample of each soil was used for each measurement by the gas pycnometer. The normality of distributions of all ρ_s measured by three gases were determined by the Kolmogorov–Smirnov test. As stated before, the soil samples were assigned to three groups: fine, medium, and coarse (see Figure 1) as suggested by Plaster (1997). Analysis of variance (ANOVA) with Tukey's HSD test were performed comparing the ρ_s determined by the three gases within each soil textural group and the three soil textural groups analyzed by each gas. In addition, we used linear regression analysis to compare particle densities of the soils determined by water and different gases as well as relationships between particle densities and soil particle size distribution.

3 | RESULTS AND DISCUSSION

Particle size distribution, textural class, and ρ_s of the samples determined by He, N_2, air, and water for three soil textural groups are presented in Table 3. As indicated earlier, except for water pycnometer measurements (three replications), each ρ_s value is the average of 10 consecutive measurements by the gas pycnometer. The CV for 10 consecutive measurements by the gas pycnometer for all 40 samples ranged between 0.03 and 0.69% for He, 0.01 and 0.24% for N_2, and 0.04 and 0.36% for air. The very low CV values for all three gases show the precision of the

TABLE 3 Particle densities of samples determined by He, N_2, air, and water with their respective particle size distribution, and textural class

	Particle density determined by				Distribution of			
Sample no.	**He**	**Air**	**N_2**	**Water**	**Sand**	**Silt**	**Clay**	**Textural class**
	$g\ cm^{-3}$				%			
Fine								
1	2.65	3.23	3.33	2.62	20.9	37.4	41.7	Clay
2	2.67	2.99	3.02	2.50	31.3	17.3	51.4	Clay
3	2.74	3.29	3.44	2.68	1.0	46.0	53.0	Clay
4	2.69	3.22	3.30	2.54	3.2	29.9	66.9	Clay
5	2.72	3.24	3.40	2.58	0.6	53.3	46.0	Silty clay
6	2.75	3.42	3.54	2.56	10.1	43.8	46.2	Silty clay
7	2.74	3.49	3.57	2.66	2.1	50.0	47.9	Silty clay
8	2.71	3.35	3.44	2.49	8.2	41.9	50.0	Silty clay
9	2.64	2.93	3.01	nd	14.0	50.0	36.0	silty clay loam
10	2.68	3.00	3.12	2.65	8.7	51.8	39.5	silty clay loam
11	2.66	2.88	2.89	2.56	34.4	36.0	29.6	Clay loam
12	2.55	2.88	2.91	2.47	25.2	42.4	32.3	Clay loam
13	2.66	3.00	3.05	2.60	52.0	5.7	42.2	Sandy clay
Medium								
14	2.66	2.85	2.87	2.65	62.6	14.7	22.8	Sandy clay loam
15	2.67	2.93	2.99	2.62	58.8	16.1	25.1	Sandy clay loam
16	2.64	2.92	2.97	2.61	53.4	13.8	32.8	Sandy clay loam
17	2.59	2.76	2.77	2.46	43.5	37.8	18.8	Loam
18	2.65	2.89	2.90	2.55	50.8	28.9	20.3	Loam
19	2.58	2.74	2.74	2.50	32.8	46.5	20.7	Loam
20	2.61	3.11	3.16	2.61	36.8	40.4	22.8	Loam
21	2.69	3.09	3.26	2.50	17.8	69.2	13.0	Silty loam
22	2.69	3.01	3.11	nd	10.0	67.0	23.0	Silty loam
23	2.65	2.79	2.82	nd	24.0	52.0	24.0	Silty loam
24	2.40	2.53	2.52	nd	6.2	89.9	3.9	Silt
25	2.67	2.97	2.67	nd	1.4	91.3	7.3	Silt
26	2.61	2.67	2.65	nd	10.4	81.9	7.7	Silt
Coarse								
27	2.74	2.86	2.89	2.57	64.5	26.2	9.3	Sandy loam
28	2.62	2.69	2.67	2.59	57.9	30.7	11.4	Sandy loam
29	2.65	2.69	2.68	2.65	76.4	12.2	11.4	Sandy loam
30	2.66	2.75	2.78	2.68	64.0	23.4	12.5	Sandy loam
31	2.63	2.82	2.80	2.60	69.6	15.3	15.2	Sandy loam
32	2.67	2.82	2.81	2.61	69.3	12.4	18.3	Sandy loam
33	2.65	2.67	2.67	2.68	86.4	7.3	6.3	Loamy fine sand
34	2.65	2.66	2.67	2.66	98.8	1.2	0.0	Fine sand
35	2.61	2.62	2.62	2.56	96.5	0.7	2.8	Fine sand
36	2.65	2.65	2.65	2.65	100.0	0.0	0.0	Sand
Kaol	2.57	2.70	2.69	nd				
Bent	2.62	3.47	3.34	nd				
GR	2.71	2.71	2.71	2.71				
GB	2.48	2.48	2.48	2.48				

Note. Bent, bentonite; GB, glass beads; GR, ground rock; Kaol, kaolinite; nd, no data.

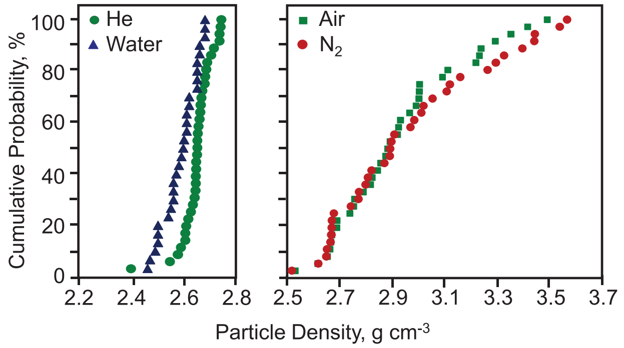

FIGURE 3 Cumulative distributions of particle density of 36 soil samples determined by He, air, and N_2 in a gas pycnometer, and 30 soil samples determined by water pycnometer

measurements by the gas pycnometer. The ranges of mean and standard deviation of the tree replications for ρ_s determined by water pycnometry were 2.46–2.68 and 0.015–0.098 g cm^{-3}, respectively.

3.1 | Distribution of particle density values

The cumulative distributions of ρ_s of 36 soil samples (not including crushed rock, glass beads, and pure clays) representing the 12 textural classes determined using He, air, and N_2, and 30 samples determined by water are presented in Figure 3. According to the Kolmogorov–Smirnov tests, all distributions presented in Figure 3 are normal. The mean ρ_s of the 36 natural soil samples determined by He is 2.65 g cm^{-3} with a CV of 2.35% and a range of 2.39–2.75 g cm^{-3}. The cumulative distribution for the ρ_s of 30 soil samples determined by water pycnometer also indicates a narrow range with a mean of 2.59 g cm^{-3} and a CV of 2.49%. The cumulative distributions of ρ_s determined by the gas pycnometer using air and N_2 gases (Figure 3) are substantially different than the distribution obtained using He. The ρ_s of the 36 soil samples range between 2.53 and 3.49 g cm^{-3} with a mean of 2.93 g cm^{-3} and CV of 8.10% for air and between 2.52 and 3.57 g cm^{-3} with a mean of 2.97 g cm^{-3} and a CV of 9.44% for N_2.

In the study by Keller and Håkansson (2010), the range of ρ_s determined by water pycnometer for 40 samples with <3% OM was 2.42–2.69 with a mean of 2.63 g cm^{-3} and CV of 1.57%. Ball et al. (2000) reported ρ_s range between 2.36 and 2.87 g cm^{-3} with a mean of 2.64 g cm^{-3} and CV of 2.3% for hydrogen peroxide-treated soil samples from 155 sites determined using kerosene instead of water. The range of ρ_s values determined by a gas pycnometer using He in Bielders et al. (1990) study was 2.38–2.72 g cm^{-3} with a mean of 2.58 g cm^{-3} and a CV of 3.8%. Ghanbarian et al. (2021) reported the particle density of 21 soil samples from Arizona determined by water pycnometer. Excluding one sample with a ρ_s of 3.08 g cm^{-3}, their mean and CV of the samples belonging to nine textural classes are 2.59 g cm^{-3} and 3.16%, respectively. Overall, our results obtained using water or He agree with the above studies that show a narrow range with very low variability for ρ_s measured by different methods.

3.2 | Relationships between particle densities determined by different methods

The relationships between ρ_s of all the samples determined by He and air (Figure 4a), and He and N_2 (Figure 4b) are strong with correlation coefficient (r) values of .613, and .623 (p < .01), respectively. However, the regression coefficient relating ρ_s determined by He to the corresponding values determined by air and N_2 are only .164 and .145, respectively. In contrast, as shown in Figure 4c, the relationships between ρ_s determined by air and N_2 is very strong with a highly significant (p < .001) r value of .99. The range of $\rho_{s\text{-N2}}/\rho_{s\text{-Air}}$ ratios for all 40 samples is 0.98–1.05 with a mean and CV of 1.01 and 1.7%, respectively. These results should be expected because atmospheric air is mainly composed of approximately 78% N_2 and 21% O_2. Although the ratio of ρ_s determined by He and water ranged between 0.99 and 1.09 with an average of 1.03, the correlation coefficient for the relationship between the ρ_s determined by the two methods was only .416 (Figure 4d). The lower ρ_s determined by water pycnometry, mainly for fine- and medium-textured soils (see Table 3), is likely due to air entrapment between soil particles (degassing) in a water pycnometer.

3.3 | Relationships between particle density and soil particle size distribution

The differences between ρ_s values determined by He and the corresponding ones determined by air or N_2 cannot be explained without additional information. According to the ANOVA, the ρ_s determined by all three gases are similar for coarse-textured soils, but ρ_s determined by He is significantly lower (p < .05) than N_2 and air for medium- and fine-textured soils (Figure 5a). Comparing the three textural groups for each gas, the ρ_s determined by air or N_2 is significantly higher for fine-textured soils (p < .05) than medium- and coarse-textured soils, but there is no difference between ρ_s among particle size groups for He (Figure 5b).

To further examine the results, the relationships between ρ_s values and sand, silt, and clay contents of the samples were assessed using their respective regression equations. Although the relationship between ρ_s determined by He and clay content (r = .49) was statistically significant (p < .01), there was only a slight increase in ρ_s with increasing clay content (Figure 6). The relationship between ρ_s and sand (r = −.111) or silt (data not shown), however, was not

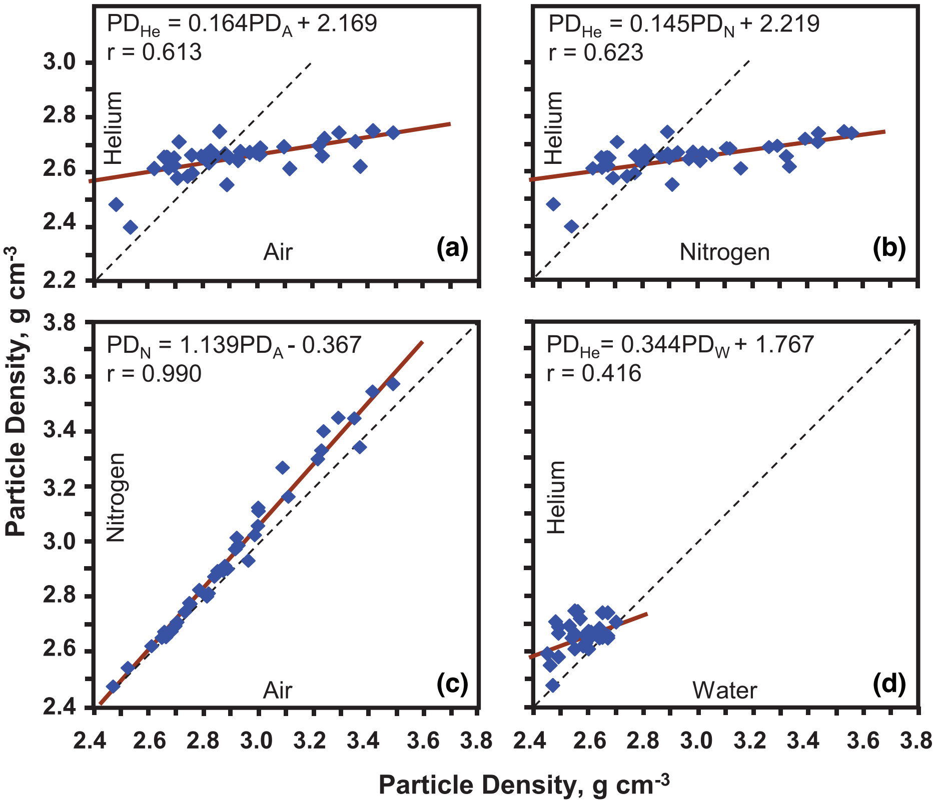

FIGURE 4 Relationships between particle densities (PDs) determined by He, N_2, and air for 36 different soil samples, fine glass beads, crushed granite rock, and pure kaolinite and bentonite. Also shown is the relationship between PDs determined by He and water for 30 soil samples, fine glass beads, and crushed granite rock. The regression equation relating the PDs determined by each pair and the associated correlation coefficient (*r*) are also presented. The dashed lines represent a 1:1 relationship. Note that the *y*-axis scales are the same for the two rows of graphs

significant. No significant relationship between ρ_s and sand, silt, or clay content was obtained when we regressed ρ_s of the 40 soil samples with <3% OM in the Keller and Håkansson (2010) study (data are not presented). As discussed earlier, Schjønning et al. (2017) showed a significant relationship between ρ_s and clay content for soil samples with <0.01 kg kg^{-1} OM. By our analysis, ρ_s determined by He in the Bielders et al. (1990) study was strongly inversely related to the sand content (*r* value of −.82) and directly related to clay content with *r* value of .81 (number of data pairs was 27 for clay content and 38 for sand content). Unlike He, our results show air and N_2 had a strong inverse relationship with sand ($r = −.638$ and −.648 for air and N_2, respectively) and a direct relationship with clay ($r = .818$ for air and .816 for N_2, both significant at $p < .01$) (Figure 6).

3.4 | Adsorption of N_2 and air on the surfaces of soil particles

As indicated earlier, in the absence of measured values, a ρ_s of 2.65 g cm^{-3} is routinely used for determining soil porosity and other soil properties. In this study, the mean ρ_s value for 36 different soil samples representing the 12 textural classes determined by He, but not by air or N_2 agrees with such a value. In addition, there was a significant dependence of ρ_s determined by N_2 and air, but not by He, with clay content. The higher ρ_s determined by the gas pycnometer using air or N_2 as compared to He is directly related to a higher volume (i.e., higher number of moles) of gas that had to be applied to the sample chamber to reach the initial pressure. Based on our analysis, the calculated extra number of moles of N_2 that resulted in a lower volume of soil particles compared with He was directly related to the clay content of the samples (Figure 7).

The results showing lower particle density determined using He agree with the findings of Makower et al. (1938), Emmett et al. (1938), Jamison (1953), Runkles (1956) (also Runkles et al., 1958), Nakayama (1958), Tuul and Innes (1962), and Bielders et al. (1990) that used different versions of gas pycnometer to determine the volume of solids in their samples (which could be used to determine the particle density as we did in our study) using N_2, O_2, air, and He. These studies attributed the lower volume of the samples determined using N_2, O_2, and air as compared to He under different pressures as the amount of the respective gases adsorbed on the

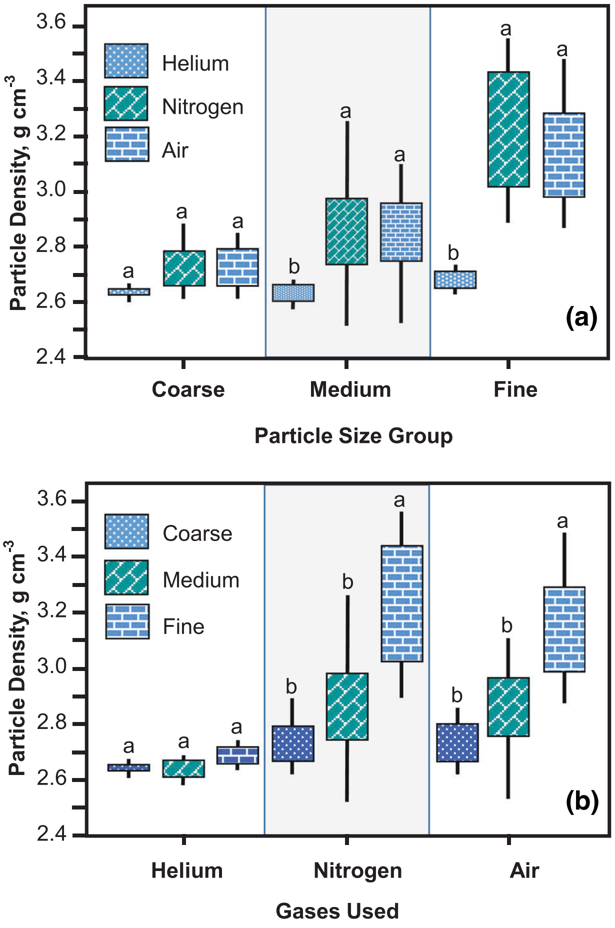

FIGURE 5 Analysis of variance (ANOVA) comparison of the particle density (ρ_s) determined by three gases for (a) the three soil textural groups and (b) within the textural groups for the three gases. For each box, the top and bottom lines are Q1 (25%) and Q3 (75%) values, respectively, and the vertical line represents the minimum–maximum of the treatment. Treatments with the same letter are statistically the same ($p < .05$) within each particle size group or with each gas

solids without providing any direct evidence of such adsorption. Here we discuss the application of the ideal gas law and the mount of N_2 adsorption by soil particles as compared to He in a gas pycnometer, but the discussion can be extended to air because air is composed mainly of N_2 and O_2.

1. For the ideal gas law to be applicable, all molecules of a gas in a given volume are in random motion, and except during their collisions with one another, no appreciable forces act on the gas molecules. Adsorption of N_2 molecules on the surfaces of soil or their colloidal particles, however, violates the ideal gas law assumptions (for ideal gas law assumptions see a physics textbook such as Resnick & Halliday [1966]). Therefore, the ideal gas law should not be applied to assess the volume of soil solids in a sample by a gas pycnometer using N_2 because nitrogen should be considered non-ideal in the soil environment.
2. In measuring the volume of solids in a gas pycnometer by He or N_2, all the pore spaces of the samples should be occupied by the respective gas after the initial purging. Assuming N_2 but not He adsorb on soil particles, the volume of pores in the bulk volume of a given sample in a gas pycnometer can be divided into a free and an adsorbed region. In the free region, all the molecules for each gas (He or N_2) move freely. According to Avogadro's law, the number of molecules of different gases occupying a given volume under the same pressure and temperature is constant (Resnick & Halliday, 1966). Therefore, an equal number of moles of He and N_2 should be present in the free region of the pores in the sample. In the adsorbed region, on the other hand, only He molecules are free to move while the adsorbed N_2 molecules are packed closely. Therefore, the number of moles of N_2 adsorbed on the soil particles (i.e., in the adsorbed region) is equal to its total number of moles applied to the gas pycnometer minus its number of moles in the free region, which is the same as the number of moles of He in the region. Based on this, the amount of N_2 adsorbed should be greater than the difference in the total amounts of N_2 and He applied to a given sample. For example, for one of our samples with 42.2% clay content, the calculated amount of N_2 for determining ρ_s of a 100-g sample was 472 µmol more than the amount of He. Therefore, considering the number of moles of He in the adsorbed region, there must be more than 472 µmol of N_2 adsorbed on (or packed closely near the surfaces of) the soil particles.
3. As mentioned earlier, the amount of time to analyze each sample by the gas pycnometer (10 purging and 10 consecutive measurements) was approximately 30–35 min. This implies that the average time for applying gas and reaching equilibrium pressure in the sample chamber (measuring P_i), waiting for the pressure to reach equilibrium after opening the valve between the two chambers (measuring P_f), and waiting for the pressure inside the two chambers to come back to atmospheric pressure was approximately 3 min or less for each measurement. Because the 10 consecutive measured values for all the samples (including the stainless-steel standards) were almost the same (as presented earlier), the adsorption of N_2 molecules on the surfaces of soil particles under pressure, their desorption during the second stage of measurement, and their final desorption at atmospheric pressure must be reversible and extremely fast (i.e., almost instantaneous). Otherwise, the amount of N_2 applied to the sample chamber would reduce and the measured volume of particles would increase during the 10 consecutive measurements.
4. The question is, considering the composition of atmospheric air, are there any N_2 and O_2 molecules adsorbed on the surface of soil particles under natural conditions (i.e., at atmospheric pressure and natural soil temperature)? If

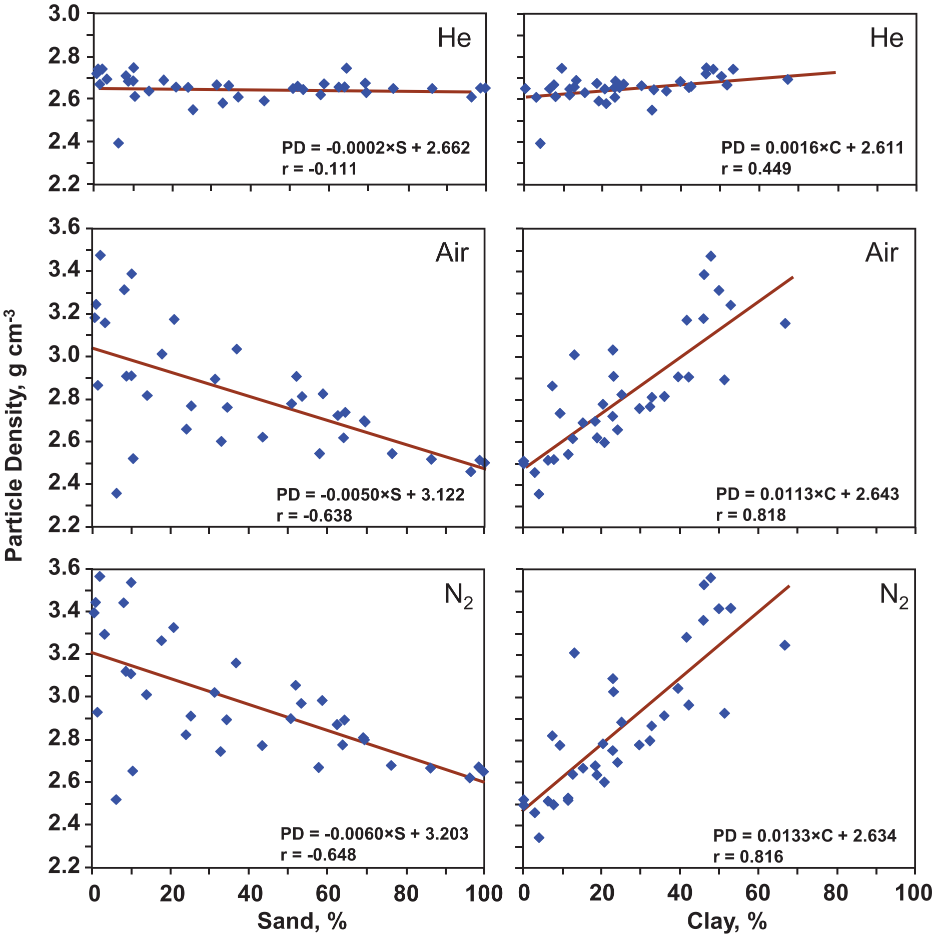

FIGURE 6 Relationships between particle densities (PDs) of 36 different soil samples determined by He, air, and N_2 with sand (S) and clay (C) contents. Note that the *y*-axis scales are the same for the three rows of graphs

He gas does not adsorb on the surfaces of clay particles, we need to consider what happens to the N_2 and O_2 molecules that may be originally adsorbed on the surfaces of particles when He is used to purge the sample followed by measurements. Can a gas molecule that does not adsorb on the surfaces of particles remove gases that are adsorbed?

4 | SUMMARY AND CONCLUSIONS

We hypothesized that, in addition to He, air and N_2 may be suitable for determining soil ρ_s by the gas pycnometry method, and wanted to explore if ρ_s is related to soil texture. The ρ_s of 36 natural soil samples representing the 12 textural classes determined by He showed a narrow range, with an average value of 2.65 g cm^{-3}, while the measured values ranged between 2.53 and 3.49 with an average of 2.93 g cm^{-3} for air, and between 2.52 and 3.57 with an average of 2.97 g cm^{-3} for N_2. The ρ_s determined by all three gases showed a statistically strong relationship with clay content and an inverse relationship with sand content:

- Considering that soils are composed of a number of minerals with different densities, and that ρ_s may be related to soil clay content (even though slightly when measured using He), assuming 2.65 g cm^{-3} for ρ_s of mineral soils (or mineral fraction of soils) in lieu of measurement may not be justified for all applications. This requires further investigation.
- In addition to He, air and N_2 can be used to measure ρ_s of coarse-textured soils by the gas pycnometry.
- We recommend He for measuring particle density of medium- and fine-textured soils by gas pycnometry. Considering the potential adsorption of N_2 (and O_2) on surfaces of soil clay particles, the use of N_2 and air for determining ρ_s of medium- and fine-textured soils should be avoided until further studies show otherwise. Also, more comprehensive studies are needed to determine the degree of N_2 and O_2 adsorption on the surfaces of soil particles under natural conditions (i.e., at ambient temperature and atmospheric pressure).
- Based on the narrow range of the ρ_s of our samples belonging to 12 textural classes determined by He, and relative

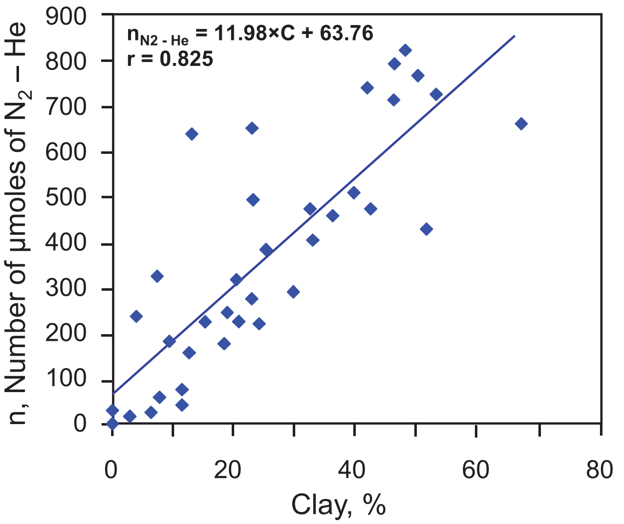

FIGURE 7 The number of additional moles, *n*, of N_2 as compared to He used for determining the particle density of 100 g of 36 soil samples by the gas pycnometer as related to their clay content

similarity of the corresponding values determined by He and water (i.e., ratios near 1), we suggest that He (or assuming 2.65 g cm^{-3} for ρ_s in the absence of a measured value) be used for determining particle density and porosity of the soil for water flow analysis and modeling.

- For particle size distribution analysis of fine-textured soils, measurement of the ρ_s of the mineral fraction of the soil by He in a gas pycnometer should be considered.

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AUTHOR CONTRIBUTIONS

Aziz Amoozegar: Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Project administration; Validation; Visualization; Writing – original draft; Writing – review & editing. Joshua L. Heitman: Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Validation; Visualization; Writing – original draft; Writing – review & editing. Christina N. Kranz: Formal analysis; Investigation; Validation; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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