Mercury intrusion porosimetry and centrifuge methods for extended-range retention curves of soil and porous rock samples

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Abstract

The water retention function is essential for modeling flow and transport in porous media. Its experimental determination is still challenging because each of the standard methods is limited to partial moisture ranges. The pore-size distribution (PSD) obtained by the mercury intrusion porosimetry (MIP) may be used as a unifying property that spans across the individual ranges of retention properties obtained with standard methods. This study compares the MIP and quasi-steady centrifuge (QSC) methods with standard ones (suction table, evaporation, and dewpoint potentiometer) to determine the retention curves of subsoil clods and calcareous rocks over most of the moisture range. The selected soils, having a relatively rigid structure compared with other soils, are more similar to the rocks even if there is a non-negligible difference in terms of mechanical strength. The QSC, developed for rock samples, was tested for soil to see if the method is also applicable for mechanically less stable media. The porosity characteristics of soil and rock samples showed bi- and trimodal PSDs. The single MIP test allowed describing the mercury retention curve (MRC) for most of the volumetric mercury content range. The MRCs could be used to fill the gaps in the retention curves that occur with the standard retention procedure when switching from one measurement range to the other. The MIP and QSC methods proved to be relatively fast and reliable for measuring a wider range of the retention curve. However, the application of QSC method to soil samples is limited by effects of compaction due to centrifugal force.

1 INTRODUCTION

The unsaturated zone controls water movement from the land surface to the groundwater. An understanding of unsaturated-zone flow processes is, therefore, crucial in determining the amount and quality of groundwater. Unsaturated hydraulic properties represented by water retention, $h(\theta)$, and hydraulic conductivity, $K(\theta)$, functions are essential in the modeling of water movement in the vadose zone (Šimůnek et al., 2016), where $\theta$ [L$^3$ L$^{-3}$] is the volumetric water content, $K$ [L T$^{-1}$] is the hydraulic conductivity, and $h$ [L] is the matric potential expressed as pressure head.

The water retention curve (WRC), which this study is focusing on, is usually constructed from a combination of $h$ and $\theta$ datasets obtained merging standard methods that operate only in specific and limited $\theta$ ranges (Kirste et al., 2019; Kirste and Gerke, 2021).
Schelle et al., 2013). For instance, the suction table (Romano et al., 2002; Stakman et al., 1969), the hanging-water column (Dane & Hopmans, 2002), and the evaporation (Schindler et al., 2010; Wind, 1968) methods work for wet to moderate moisture ranges. The pressure plates (Gardner, 1956) and the dewpoint potentiometer (Campbell et al., 2007) work in low saturation conditions. Furthermore, some of these standard methods are time consuming. There are no studies dealing with the measurement of the retention curve over wider moisture ranges by using a single and fast method.

For the determination of the WRCs over a wider moisture range, two relatively exotic methods may be used: (a) mercury intrusion porosimetry (MIP) (Abell et al., 1999; Sun & Cui, 2020), which gives mercury retention curves (MRCs) based on volumetric mercury contents, \( \theta_{\text{Hg}} \), measured at specific values of \( h \), in addition to most precise micropore-size distributions; and (b) the quasi-steady centrifuge (QSC) (Caputo & Nimmo, 2005) method, which allows the hydraulic characterization of porous media in a wide \( \theta \) range. It is known that the porosity characteristics, which may be studied by MIP, X-ray computed tomography (Sander et al., 2008), image analysis, and epifluorescence microscopy (Bouabid et al., 1992) techniques, represent, in terms of size, structure, and connectivity of pores, an alternative indirect method to derive the retention curve. Many authors have dealt with the relationships between porosity characteristics and the hydraulic functions, and several unimodal and multimodal hydraulic functions have been proposed to characterize soil structural features (Durner, 1992; Peters et al., 2015). Othmer et al. (1991) determined the WRCs for bimodal soils.

However, only a few authors have considered the PSD obtained by MIP to derive the retention curve. Leech et al. (2006) combined the Barrett, Joyner and Halenda (BJH) method (Barrett et al., 1951) with MIP to estimate the PSD used to predict the WRC. Centrifugation techniques, however, are proposed for their capability to rapidly measure the hydraulic properties in unsaturated steady-state (Nimmo et al., 1987, 2002), quasi-steady-state (Caputo & Nimmo, 2005), and transient-state flow conditions (Alemi et al., 1976; Nimmo, 1990).

Furthermore, there is still a gap between the two geo-scientific disciplines, the soil physics and the geohydraulic-related rock physics, regarding the determination of unsaturated hydraulic properties. Although Bockgård and Niemi (2004) studied the interface between a soil layer and underlying fractured bedrock, there are few studies (Conca & Wright, 1992; Olofsson, 1994) that compare hydraulic properties of rocks and soils obtained with the different methods.

The main goal of this work is to find a single and fast method to measure the retention curve over most of the moisture range by comparing the relatively exotic methods, MIP and QSC, with the standard ones (suction table, evaporation, and dewpoint potentiometer). Soils and rocks with characteristic pore structures and hydraulic properties are tested to extend the final consideration to a wider range of materials. Moreover, these two kinds of media are studied to compare their porosity characteristics and to identify the differences in modality of the PSDs. Specifically, the subsoil samples selected for this work are similar to the chosen soft sedimentary rocks having a relatively rigid structure with smaller pedological features. Differences in pore-size distribution (PSD) and hydraulic characteristics between soils and rocks allowed us to evaluate the applicability of a single full-range retention method for different porous materials.

2 | MATERIALS AND METHODS

The tested samples were selected from different sites (Figure 1), and tests were carried out in both laboratories in Müncheberg and Bari according to the available equipment. Some of the data were taken from previous studies (Fér & Kodešová, 2012; Rieckh et al., 2012). A total number of eight soil clod samples (subsoil horizons including soil parent material) and 36 rock samples were investigated (Tables 1 and 2). The soils are Haplic Luvisols and Haplic Regosols (FAO, 2006) developed from glacial till, collected in northeastern Germany (Holzendorf; 53°22′45″ N, 13°47′11″ E), hereafter named Till 1, Till 2, Till 3, Till 4, and Till 5 (Figure 1); and Haplic Luvisols developed from Loess, collected in the northeastern Czech Republic (Hněvěvěvně; 50°18′47″ N, 15°43′03″ E) (Figure 1) named Loess 1, Loess 2 and Loess 3. Haplic Luvisols were investigated because they are well structured and have cracks, fissures, and earthworm burrows, which define preferential pathways with different flow velocities. Haplic Regosols were chosen because they are calcareous, which makes them comparable with calcareous porous rocks.

The tested rocks belong to lithotypes C and M of the Calcarenite di Gravina Formation and come from two quarry districts known as “Le Tufarelle” located in Canosa di Puglia.
FIGURE 1 Map of the areas where the tested samples were collected: (a) samples of Haplic Luvisols (haLV) developed from Loess (Hněvčes, Czech Republic) and from glacial till (Holzendorf, Germany), used for the dewpoint potentiometer test; (b) sample of Haplic Regosols (haRG) developed from till, used for the quasi-steady centrifuge (QSC) test; (c) samples of calcareous porous rocks, Rock 1 from Canosa di Puglia, and Rock 2 from Massafra (Italy), used for the QSC test

| Rock parent   | Soil type | Sample | $\rho_b$ | $\rho_p$ | Depth | $\Phi$ | Clay | Silt | Sand |
|---------------|-----------|--------|----------|----------|-------|--------|------|------|------|
| Glacial till  | haLV      | Till 4 | 1.95     | 2.61     | 40–60 | 0.25   | 16.5 | 35   | 48.5 |
|               |           | Till 5 | 1.95     | 2.61     | 40–60 | 0.25   | 16.5 | 35   | 48.5 |
|               | haRG      | Till 2 | 1.76     | 2.64     | 30    | 0.33   | 11.8 | 26.7 | 61.4 |
|               |           | Till 3 | 1.76     | 2.64     | 30    | 0.33   | 11.8 | 26.7 | 61.4 |
| Loess         | haLV      | Loess 2| 1.74     | 2.60     | 60–80 | 0.33   | 34.6 | 56.2 | 9.2  |
|               |           | Loess 3| 1.74     | 2.62     | 60–80 | 0.34   | 34.6 | 56.2 | 9.2  |
| Porous rock   | –         | Rock 1 | 1.50     | 2.65     | 30–80 | 0.43   | n.a. | n.a. | n.a. |
|               | –         | Rock 2 | 1.56     | 2.65     | 30–80 | 0.41   | n.a. | n.a. | n.a. |

Note. $\rho_b$, bulk density; $\rho_p$, particle density; $\Phi$, total porosity; clay (<0.002 mm), silt (0.063–0.002 mm), and sand (2–0.063 mm) (Rieckh et al., 2012); haLV, Haplic Luvisols; haRG, Haplic Regosols; na, not applicable.
Table 2: Characterization of the representative rock and soil profiles (Kodešová et al., 2011; Rieckh et al., 2012)

| Rock and soil profiles | Elevation | Slope angle | Aspect | Depth |
|------------------------|-----------|-------------|--------|-------|
| Rock 1                 | 70 m      | 0–30°       | NE     | <0.0  |
| Rock 2                 | 60 m      | 0–30°       | NE     | <0.0  |
| Loess 1, 2, 3          | 275 m     | 0           | n.a.   | 0.5   |
| Till 4, 3              | 50 m      | 0           | n.a.   | 0.5   |
| Till 2, 3              | 54 m      | 13          | NE     | 0.26  |

Note. NE, northeast; n.a., not applicable.

(41°09′4.85″ N, 15°59′24.92″ E), and “Caprocetta” located in Massafrà (40°33′29.25″ N, 17°08′32.83″ E), both in the Apulia region, southern Italy. The lithotypes C and M are hereinafter named Rock 1 and Rock 2, respectively (Figure 1).

The soil clods and porous rocks were chosen for this study because they are similar in terms of pore structure. Both have a relatively rigid structure: the soils because of drying by capillary forces, and the rocks because they consist of clasts bound to each other by the carbonate cement.

The testing program involved the MIP test to determine the porosity characteristics and, successively, standard methods (suction table, evaporation, and dewpoint potentiometer) and exotic ones (MIP and QSC) to measure retention curves according to the scheme in Table 3.

2.1 Suction table

Rock 1 and Rock 2 were tested using core samples 3.6 cm in diameter and 5 cm in height that were obtained by disc-cutting the cores previously drilled from the blocks collected in the quarry.

The suction table method (Stakman et al., 1969) was used to assess the drying $h(\theta)$ curve in the low-suction range. A sandbox (Eijkelkamp Agrisearch Equipment Model 08.01) was used to determine $h$ between 0 and −100 cm. A series of static equilibria between the water inside the samples and a free water body contained in a suction control system at known $h$ were established. The magnitudes of pressure steps were 0, −2.5, −5, −10, −14.4, −20.4, −25.6, −30.8, −36.2, −40.6, −45.5, −51, −56, −61, −66, −72, −81, −91, −97, −100 cm. The measurements referred to half of the sample height. Equilibrium was achieved when the sample mass, checked every day, became steady. The time required to reach the equilibrium ranged from 3 d for $h > −20$ cm to 10 d for $h = −100$ cm. The value of $\theta$ was gravimetrically determined for each known $h$ value. Each data point of the WRC identifies the pair of values, $h$ and $\theta$, obtained as an arithmetic average computed on five replicates for each type of rock. The suction table method was not applied for the selected soil samples because it was already carried out on the same soils in Fér and Kodešová (2012) and Rieckh et al. (2012).

2.2 Evaporation

Rock 1 and Rock 2 were tested by using samples, 7.8 cm in diameter and 12 cm in height, obtained by disc-cutting the cores previously drilled from the blocks collected in the quarry (see above). The samples were laterally sealed by epoxy resin and saturated under vacuum. Three holes, 2.45 cm in length and 1.22 cm in diameter, were drilled at a constant distance along the core sample height. The evaporation method (Wind, 1968) was used to measure the drying $h(\theta)$ functions for $h$ values ranging between 0 and −800 cm. Values of $h$ were measured with needle-tensiometers (SDEC France; Young & Sisson, 2002), the ceramic cups of which were inserted into the samples holes. During the test, the sample weights changed due to evaporation and the water content decreased. This method was not applied to the soil samples in the present study because we assumed that the suction table data were complementary in this pressure head range (Fér & Kodešová, 2012; Rieckh et al., 2012).

2.3 Dewpoint potentiometer

The tested samples were Till 1, Loess 1, Rock 1 and Rock 2. For each type of the rock 10 samples were considered while only one till and one loess sample could be measured. All samples were undisturbed with intact pore structure and were 3.6 cm in diameter and 0.6 cm in height. Specifically, the soil samples were cut out manually from larger clods using steel rings, while the rock ones were obtained by cutting from the core samples previously drilled from block collected in the quarry. The used dewpoint potentiometer (Campbell et al., 2007) is a temperature-controlled model WP4-T (DECAGON Devices) that allows to determine wetting $h(\theta)$ curves in the high-suction range with $−3 \times 10^6 \leq h \leq −10^3$ cm. This method is based on the chilled-mirror dewpoint technique and allows measurements of $h$ at the equilibrium between the liquid-state water in the sample and gas-state water in a chamber surrounding the sample. This is achieved by using the Kelvin equation:

$$ h = \left( \frac{RT}{V_w} \right) \ln \left( \frac{p}{p_0} \right) $$

where $R$ is the universal gas constant ($8.314 \times 10^{-6}$ MJ mol$^{-1}$ K$^{-1}$), $T$ is the temperature (°K), $V_w$ is the molar volume of water (m$^3$ mol$^{-1}$), $p/p_0$ is the relative humidity as a fraction where $p$ (MPa) is the actual vapor pressure of air, in equilibrium with the liquid phase, and $p_0$ (MPa) is the
satisfaction vapor pressure at $T$. Starting from the initially dry sample, 0.05 g of water was added several times, so the $h$ value increased. The equilibrium for each water increment was reached after 24 h, and the measurement of the corresponding $h$ value was performed by inserting the sample in the WP4-T device. Volumetric water content, corresponding to each $h$ value, was measured by dividing the volume of water in the sample by the total sample volume, which was computed by multiplying the base surface by the height of the sample. Each pair of values, $h$ and $\theta$, identifies a data point of the WRC. For each type of rock, the pairs were obtained as an average computed on the 10 tested rock samples.

### 2.4 | QSC

Till 2 and Till 3 core samples, collected in the field with a cylindrical steel sampler, and Rock 1 and Rock 2, extracted from the blocks, all 7.8 cm in diameter and 6 cm in height, were tested with QSC method. The test was carried out by using centrifugal accelerations between 230 and 2,000 revolutions per minute (rpm), which allowed measurement of $h(\theta)$ function, with $h$ ranging from 0 to $-500$ cm. The QSC method used an experimental apparatus that fits into a swinging centrifuge bucket. The upper part of the apparatus rested on the sample, consisted of a reservoir that controlled the water flow by means of a layer of specific granular material, whose conductance determined the flow rate. The granular materials used for testing the rocks were kaolinite, silica flour, and silica sand, whereas kaolinite, silica flour, and clay were used for testing the soils. The lower part of the apparatus, located below the sample, included a ceramic plate placed on the outflow dish, which rested on the bottom of the centrifuge bucket. Details on the method and on the experimental apparatus can be found in Caputo and Nimmo (2005). The QSC method needed a tensiometer, external to the centrifuge, for measuring $h$ value of the sample once it reached the $\theta$ steadiness.

### 2.5 | MIP

The soil clod samples tested, with an approximate volume of 2 cm$^3$, were irregularly shaped specimens, Till 4, Till 5, Loess 2, and Loess 3, manually prepared using a knife and a scalpel. Rock 1 and Rock 2 specimens, instead, were hand-cut to form a parallelepiped with 1-cm$^2$ base and 2-cm height. A Micromeritics Autopore IV 9500 porosimeter was used to measure the PSD with a stem-volume 1.836 penetrometer. The sample dimension to be used for the MIP test is related to the volume of the penetrometer. Specifically, the sample pore volume, which is the sample volume multiplied by the porosity, $\Phi$, must be between 25 and 90% of the penetrometer volume. The pore fraction detected by MIP is calculated as a ratio of pore volume (ml ml$^{-1}$) to $\Phi$ that is computed by subtracting from 1 the ratio of bulk density, $\rho_b$, to particle density, $\rho_p$. The maximum value of the pore fraction detected by MIP represents 100% of $\Phi$ that is expected to be lower than $\Phi$ because the MIP method detects interconnected pores within a specific range of pore diameter ($0.003 \leq d \leq 420$ μm).

Each MIP test implied two separate phases that consisted of low- and high-pressure analyses, performed within pressure ranges from 0.1 to 420 MPa, fixed for the used instrument. For this reason, the MIP constrained the measurements of pores between 0.003 and 420 μm (ASTM, 1998). In fact, the method is based on the fact that mercury, which behaves as a nonwetting liquid with most substances, does not intrude the pores of a porous medium without an applied pressure. Therefore, the pore radius, assuming cylindrical pores, was calculated by using the following Washburn (1921) equation:

$$P = -4\sigma_{Hg} \cos (\gamma_{Hg}) / d$$  \hspace{1cm} (2)$$

where $P$ (P) is the mercury pressure, $\sigma$ (M T$^{-2}$) is the mercury surface tension (0.559 N m$^{-1}$), $\gamma$ (˚) is the mercury contact angle, ranging from 133˚ to 140˚, and $d$ (L) is the pore diameter.
RESULTS AND DISCUSSION

3.1 Porosity

The MIP test results provide the reference data for the PSD of the tested samples. The maximum intruded pore volume in soil clods (Figure 2) is lower than in calcareous rocks due to the lower porosity of soils (0.25 ≤ Φ ≤ 0.34 for soil clods vs. 0.41 ≤ Φ ≤ 0.43 for rocks). The maximum intruded pore volume does not reach the value of porosity because of the limitation of the MIP method in detecting pores. In fact, the MIP is based on the principle that mercury, a nonwetting liquid with most substances, does not intrude the pores without an applied pressure (see Equation 2; Washburn, 1921). For the pressure range of the used instrument, from 0.1 to 420 MPa, the method is able to detect interconnected pores within a specific range of pore diameters between 0.003 and 420 μm (Abell et al., 1999).

The graph that shows the specific pore volume (ml g⁻¹) vs. mean pore diameter (Figure 3) highlights a gap between the two main pore size classes for both soils and rocks. The peaks on the right of the graph (Figure 3) represent the modal pore size of the structural or interpedal pores, whereas the peaks on the left indicate the modal pore size of the textural or intrapedal pores. These two classes are separated at a pore size of 15 μm that corresponds to the boundary value between textural and structural pores (Kutílek, 2004). Loess 2 and Loess 3 exhibit trimodal porosity, with three peaks at 0.005, 0.392, and 222 μm, and 0.007, 0.391, and 221 μm, respectively. Rock 1, Rock 2, Till 4, and Till 5 show bimodal PSDs, having two pore diameter peaks corresponding to 0.137 and 27.496 μm; 1.847 and 19.67 μm for rocks; and 0.008 and 177 μm and 0.008 and 232 μm for till samples, respectively. Bimodal behavior of PSD is more evident for Rock 1 than for Rock 2 because of the bioclasts in Rock 1 that contribute to the larger pores, and because of the greater proportion of intergranular cement that contributes to the smallest pores compared with Rock 2.

All of the curves in Figure 3 show a cutoff on the right side of the graph, corresponding to the maximum pore size that is detectable by MIP. This means that there could be larger pores that were undetected. Only Rock 1 exhibits a cutoff on the left side of the graph, meaning that there could be smaller pores than the smallest pore-size detectable by MIP. Even if the MIP method does not allow the investigating of pores greater than 420 μm or lower than 0.003 μm, it is still a useful tool for distinguishing different pore systems in a relatively wide range of pore sizes, as shown in the multimodal PSDs.

Results in Figure 4 clearly show that the MIP is able to investigate all pores only for Till 5 by allowing it to arrive at 100% of the pore fraction detected by MIP. Unlike other samples, Till 5 is characterized by pores, which are all included in the specific range of the pores detectable by MIP, mentioned above.

3.2 Comparison of standard methods with MIP and QSC

The WRCs determined for both soils and calcareous porous rocks (Figure 5) are in the same h range. In general, it is
difficult to measure $h$ and $\theta$ values close to saturation because the samples easily lose water under the action of gravity during the operations needed for applying the methods.

If we look at Figure 5a, some differences among the retention curves of calcareous rocks arise. The most important one is that the WRCs measured by standard methods present gaps differently than MRCs that show more continuous curves. The MIP method works well for soils and rocks and may suffice in accurately describing the complete retention curve in the wider volumetric liquid content range compared with the suction table, evaporation, dewpoint potentiometer, and QSC methods. Furthermore, mercury is a nonwetting fluid and does not interact with the solid phase of the tested medium.

The MRCs of rocks (Figure 5a) show bimodal behavior, more evident for Rock 1 than for Rock 2, due to the intergranular cement, which affects the retention curve of Rock 1. Moreover, Rock 1 has greater volumetric mercury content, $\theta_{Hg}$, than Rock 2 because there is more cement (greater bulk density, $\rho_b$), and more liquid is entrapped in the cement compared with the surrounding matrix and grains (Ravina & Magier, 1984). In addition, Rock 1 has a greater porosity than Rock 2, due to its calcareous concretions and some macro pores or cracks at the interface between the concretions and surrounding medium (Ravina & Magier, 1984). By comparing the WRCs of calcareous rocks measured by the QSC and evaporation methods in the $h$ range, which corresponds to medium-size pores (Figure 5a), it can be seen that the two curves tend to diverge for $h \leq -40$ cm and $\theta \leq 0.35$ m$^3$ m$^{-3}$, especially for Rock 2. This discrepancy is due to the difference in measuring $h$ and $\theta$ values in the mentioned methods. The evaporation method measures changing $h$ and $\theta$ values quasi-continuously, whereas the QSC method records $h$ and $\theta$ values when equilibrium is reached.

The effective volumetric liquid saturation values, $\theta_s$, obtained by all the methods except for QSC, do not correspond with the measured porosity (Figure 5a), probably because of the loss of water by gravity when handling the samples under almost saturated conditions. In fact, the curves measured by QSC achieve maximum saturation because the upper reservoir of the experimental apparatus supplies water to the sample continuously, thus keeping the $\theta$ values at relatively high levels.

Similarly, the maximum $\theta_{Hg}$ obtained by the MIP method (Figure 5a) does not correspond with the measured porosity.
because of instrument inability in measuring the larger pores at relatively low pressures for the mercury intrusion. The gap in the wet range, between the retention curves obtained by the suction table and MIP methods, is due to the rock’s macro-pores, which are out of the pore range detectable by MIP (Figure 5a). Therefore, the discrepancy between real porosity and maximum liquid content occurs for both the WRCs and MRCs.

The shapes of the MRCs (Figure 5a) differ from those of the WRCs in the range $-10^5 \leq h \leq -10^3$ cm because the MRCs represent infiltration curves while the WRCs represent drying ones in the mentioned range. Rock 1 shows visible gaps both in the WRCs obtained by the evaporation method and the dewpoint potentiometer. These gaps are connected with the more heterogeneous PSD of Rock 1 as compared with Rock 2, meaning that Rock 1 has a range of large pores that the two mentioned methods are not able to investigate. Specifically for Rock 1, the evaporation method seems to not capture the pores in the range $-10^5 \leq h \leq -10^3$ cm at all (Figure 5a). This is because, for Rock 1, the liquid flow to evaporation is changing into vapor flow due to the emptying of the larger pores thereby switching to second phase of evaporation (see Tindall & Kunkel, 1999, p. 232). In fact, the Rock 1 loses more water to gravity than to evaporation, the gravity acting more rapidly. This is different for Rock 2 because this rock type has fewer larger pores; the $\theta$ decreases mainly because of evaporation and thus points within the $-10^5 \leq h \leq -10^3$ cm range could be measured with this method, which could explain the gap in the retention data between evaporation and dewpoint methods.

Regarding the soils (Figure 5b), the WRCs measured by QSC are affected by the compaction that may occur during the centrifugation (Khanzode et al., 2002; Nimmo & Akstin, 1988; Omoregie, 1988). This effect causes a sample height decrease of about 1 cm over 6 cm, obtained by accurate measurements, by making the reservoir that rests on the sample in the centrifuge bucket unstable. Highest compaction was observed in the central part of the soil core sample because of the effect of adherence between the sample itself and the cylindrical sampler edge. Therefore, the sample height decrease leads to the loss of contact between the sample itself and filter membrane, by causing the filter membrane to break under the centrifugal force. Another aspect that affects the soil WRCs obtained by the QSC method is the observed difficulty in achieving a good contact between the ceramic plate of the tensiometer and the upper surface of the sample being distorted under the centrifugation. In contrast, the rocks are not affected by the compaction because of the rigid structure. For this reason, the WRCs obtained by the QSC method for soils have no conventional S-shape (Figure 5b). The compaction causes (a) change in the PSD by reducing the proportion of large pores (also enhanced in the WRCs) and (b) reduction in porosity from 0.33 to 0.25 after the centrifugation for both Till 2 and Till 3.

The compaction that causes structural deformation in the soils is responsible for the $\rho_b$ deviations from the in-situ values (Fu et al., 2011). Overall $\rho_b$ value for Till 2 and Till 3 increased from $1.76 \times 10^3$ kg m$^{-3}$ (in situ) to $1.98 \times 10^3$ kg m$^{-3}$ after a series of centrifugal runs.

Except for the soils, the data points measured by the QSC method seem to be generally consistent with the WRCs obtained by the other methods. The soil samples are affected by compaction during the centrifugation that causes structural deformation responsible for the $\rho_b$ deviations from the in-situ
values as well as for the reduction of the porosity and the proportion of larger pores. Due to the effects of the centrifugation, the soil samples, other than Till 2 and Till 3, were not tested with the QSC method.

The MRCs depicted in Figure 5b show inflection points typical for soils and exhibit bimodality for Till 4 and Till 5, and trimodality for Loess 2 and Loess 3, which is consistent with the shape of the curves (see Figure 3) as discussed above. Overall, the MRCs exhibited $\theta_{Hg}$ greater than 0 for the same $h$ with respect to the WRCs. This difference is due to the different properties of water and mercury that affect the capillary rise expressed by Jurin’s law (Jurin, 1719):

$$h_c = 2\sigma_{Hg} \cos (\gamma_{Hg})/\rho_{Hg} g r$$

(3)

where $h_c$ is the capillary pressure that equals $h$ in the MIP test, $\rho_{Hg}$ (M L$^{-3}$) is the mercury density (13,541 kg m$^{-3}$), $g$ (L T$^{-2}$) is the gravitational acceleration (9.81 m s$^{-2}$), and $r$ (L) is the effective pore radius. If the matric potential of the WRCs is recalculated, replacing the water properties by those of mercury, the recalculated retention curves are shifted upwards and tend to overlap the MRC (Figure 6). The recalculated retention curves and the MRCs do not fully correspond due to the hysteresis effect (Figure 6). In fact, the retention curves calculated by the evaporation and QSC methods are both drying curves, whereas the MRCs are wetting curves.

4 | CONCLUSIONS

This study compared MIP and QSC with standard methods for determining retention curves over most of the moisture range of soil clods and calcareous porous rocks. The study demonstrated that most of the liquid content range of the retention function was explored by a single MIP test; it covers the individual ranges investigated by each of the standard methods. The difference between the two methods, MIP and QSC, in measuring the retention curves is that MIP results were comparable for both soils and rocks and even obtained in a shorter time.

The MRCs reveal the actual pore structure of both soils and rocks and show a greater accuracy in distinguishing pore-size classes compared with WRCs. The differences in PSD and characteristics between rock and soil helped in the evaluation of the extended-range retention methods for the different porous materials.

The results confirmed that the QSC method is a relatively fast and still reliable method for measuring a wider range of the WRC. However, its application to soil samples is limited by compaction due to centrifugal forces even for the already relatively dense and rigid samples used in the present study.

Mercury retention curves could be used to fill the gaps in the retention curves that occur with the standard retention procedure when switching from one measurement range to the other. By highlighting the multimodal PSD of the tested soil and calcareous rock samples, the results clearly suggest a hierarchical structure of both porous media as reflected in the retention properties.

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AUTHOR CONTRIBUTIONS

Antonietta C. Turturro: Data curation; Formal analysis; Investigation; Software; Writing—original draft; Writing—review & editing. Maria C. Caputo: Conceptualization; Data curation; Funding acquisition; Project administration; Resources; Supervision; Validation; Visualization; Writing—original draft; Writing—review & editing. Horst H. Gerke: Conceptualization; Project administration; Resources; Supervision; Writing—review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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