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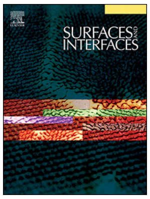

Assessment of spring waters from Lourdes (France) by contact angle method

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ABSTRACT

The geochemical investigations on karst spring waters in the area of Lourdes showed differences between the waters for numerous components, including main solutes and trace elements. In this study, a multidisciplinary approach was proposed, based on the surface free energy of solids and the surface tension of liquids using the contact angle method, by raising the hypothesis that different spring waters diverge in surface tension characteristics, which allow to discriminate waters origin in a natural system. Surface energy characteristics of seven spring waters from Batsurguère Valley were investigated here using the contact angle measured over time and the tangent method in relation to the variations of the droplet volume. Wettability of various test solids was analyzed using static and kinetic contact angle methods which led to the individuation of the spring waters on the base of the different adhesion processes occurring at the interface between water and solid, particularly on the silica glass solid. The analyses demonstrated that the surface tensiometry technique can discriminate one of such spring waters (i.e. the Massabielle spring) from other studied spring waters, regardless of their natural hydrological conditions. Contact angle hysteresis in kinetic modality, based on several repeated and extemporary set of experiment determinations, suggested a link between the water chemistry and the wettability over time of the test solids, confirming that chemical composition has an influence on the surface tension of spring waters. This investigation demonstrates that the surface tensiometry approach may represent a useful tool for monitoring quality of natural waters.

1. Introduction

The surface tension of liquids and the surface free energy of solid substrates are intended as the visible effects of the forces acting inside the studied matrices. Both these parameters are commonly investigated in many research fields in relation to the fast characterization of systems by the surface tensiometry techniques. These are the parameters that can be obtained by the mathematical conversion of the contact angles measured at the interface between a liquid and a solid on which the liquid drop is deposited. The static contact angle measurement is widely applied to determine the influence of physico-chemical factors on the surface free energy of solids [1,2] and surface tension of liquids [3]. In particular, static contact angle analyses are employed for assessing water quality [4] and evaluating the effect of electrolytes on the water surface tension [5]. The evaluation of surface tension by pendant drop, capillary buoyant bubble profile, maximum bubble pressure, Wilhelmy plate, capillary tube system and ring methods are commonly used for measuring the properties of aqueous solutions and biosurfactants, highlighting the effects of water treatment on the water surface tension and the influence of pollution on water quality [6–11]. Based on these researches, from 1990s the surface tensiometry has started to be applied in the aqueous geochemistry field using the static contact angle methods. One of the first surface free energy investigations using contact angle method in the field of water–mineral interactions was made by van Oss and co-workers [12,13] calculating the surface free energy, dispersion component, and acid/base components of the polar component of clay minerals.

More recently, surface tensiometry was applied to the study of peloids (mineral or organic muds and clays used therapeutically as part of balneotherapy) and thermal waters, by applying the Owens and Wendt mathematical model for the determination of surface free energy, dispersion component, and polar component in connection with the peloid

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maturation process [14]. In particular, surface tensiometry demonstrated to be useful for devising a personalized mudtherapy protocol based on the effect of the mud pack treatment on the skin hydration [15]. These first investigations were meant to develop new methods for assessing the biological maturation process and the quality of peloids and thermal waters used for therapeutic and recreational purposes. The peloids for therapeutic uses are made of mineral and/or organic components (e.g. clays, muds, tuffs, peats), usually thermal water and biologic component whose growth depends from the quality of water [16]. The surface tensiometry demonstrated that the wettability of peloids used for thermal treatments depends mainly from the quality of the water in which they have matured [17]. In these studies, the perfluoropolyether Fomblin HC/25® perfluoropolyether (PFPE) was employed for the first time for the evaluation of the maturation process based on the static contact angles measured at the interface between mud and the droplet of PFPE deposited on its surface [16,17]. The PFPE can monitor the overall effects of biological maturation process of peloids depending from the chemical composition of water and from the biological species which develop in it [18]. More recently [19] a new approach was developed to determine the surface energy of natural and artificial liquids by static contact angle method employing PFPE as a liquid film. These studies demonstrated that surface tensiometry could represent a new way to investigate the surface tension and surface free energy of natural materials in form of both liquid and solid with particular applications in natural sciences, like in the field of aqueous geochemistry.

Moving from these premises, the authors undertook a multidisciplinary research on selected karst spring waters in the area of Lourdes (Hautes-Pyrénées Department, France) to test the suitability of including surface tensiometry for studying and monitoring of natural water quality. The chemical researches on spring waters in the area of Lourdes are very sparse and fragmentary. The chemical analytical approach is only limited to assess the composition of Massabielle (MS) spring water (as raw water from the MS spring and after disinfection from public water taps) in terms of sanitary monitoring carried out by the local health agency (Agence Régionale de Santé). The first broad view study on selected karst spring waters of the Lourdes area was carried out in 2015 [20] involving also investigation on the surface properties of the water. The geochemical investigations demonstrated the geologically conditioned differences between studied waters in terms of numerous components, both main solutes and trace elements [20]. The studied springs discharge groundwater from the karst carbonate aquifer system of the Batsurguère Valley, located SW of Lourdes, which is superficially discharged by two episodic streams, L'Arboucau and Lanusse (Fig. 1). From a geological point of view, the study area is located in the North Pyrenean Zone [21]. The area of the Batsurguère Valley is composed mainly of Cretaceous limestones, marls and flysch rocks, which underlain by Jurassic limestones and dolomites. The Cretaceous and Jurassic rocks of the Batsurguère Valley form a synclinal structure whose central part is covered by morenic glacial deposits [22]. The main goal of this research was to analyze the waters from the studied area, by raising the hypothesis that the different spring waters have also different surface tension properties which can serve as indicators to discriminate waters in a natural system. To test this hypothesis, the wettability of some solids having different polar properties (further named test solids) was analyzed using waters from the studied area. The wettability tests were performed by contact angle method in static mode as well as over time using, for the first time, new different test solids involving excipients commonly used for the production of cosmetics and pharmaceutical formulations. From a surface tensiometry viewpoint, this work aims to apply the contact angle tangent method (T-1) over time, introducing the term of kinetic contact angle (KCA) measurement, in order to harmonize the concept of dynamic contact angle with the kinetic wettability (KW) of a solid substrate. The application of KCA was meant to improve the sensitivity of the surface tensiometry analysis for the characterization of spring waters. In this study, we evaluated the sensitivity of the contact angle measurements of different spring waters from the studied area.

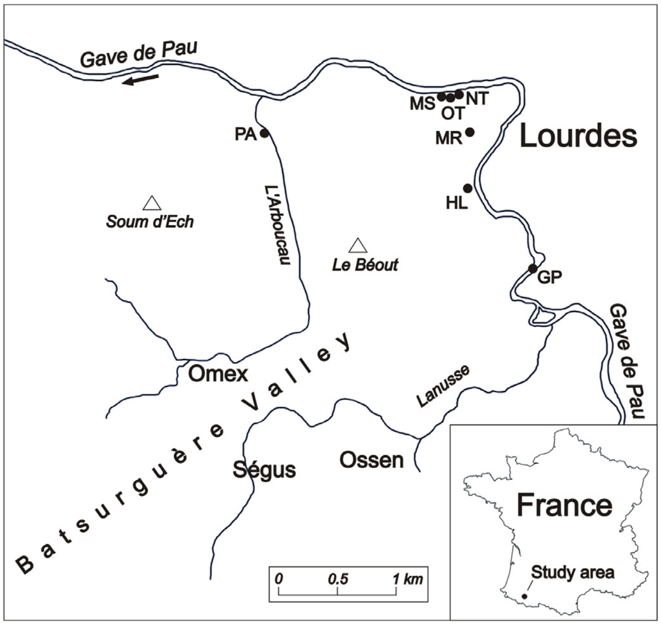

Fig. 1. Location of water sampling sites. Explanations: MS, Massabielle Spring, OT – old public taps, NT – new public taps, HL – Hount des Lavasses Spring, MR – Merlasses Spring, PA – Pont de l'Arboucau Spring, GP, Gave de Pau River. Location of public taps (OT, NT) is given approximately due to the scale of the map.

2. Materials and methods

In November 2015, groundwater was sampled in the area of Lourdes (France) from four springs: Massabielle (MS), Hount des Lavasses (HL), Merlasses (MR) and Pont de l'Arboucau (PA) (Fig. 1). Waters from both old (OT) and new (NT) public water taps in the Marian shrine, and from the Gave de Pau river (GP) upstream the town of Lourdes were investigated. The acronym OT represents the old series of taps built in the Sanctuary. The OT and NT public taps provide the disinfected (chlorinated) water from the MS spring for visitors.

The samples for wettability analysis were collected directly at the sites by filling 5 mL HDPE syringes and stored at about 4 °C. Surface tensiometry measurements of spring waters were performed by wettability analyses of different solid substrates having diverse surface free energy properties. Silica glass (SG), aluminum (AL) as foils for food packaging, plexiglass (PX), bees wax (BW) [23] lanolin alcohol (LA) [24] polyethylene glycol PEG 4000 (PG) [25] and cetostearyl alcohol (CSA) [26] were used as a test solid after the morphologic characterization of their surfaces. The morphologic analyses are important because it evaluates the smoothness of the surface. All wettability analyses of the test solids were performed at room conditions using a DSA 10 tensiometer (Krüss, Germany) with tangent (T-1) method [27]. Videos of water drop spreading were recorded by DSA 10 tensiometer and visualized using DSA 4 software (Krüss, Germany) after connecting the DSA 10 HD by a SATA device for more sensitive CA measurements over time.

The morphologic evaluation of the surfaces of inorganic and organic test solids as such were performed by a SEM apparatus (FEI instrument, Quanta 200, USA), using 400× mags performed by a secondary electron beam in low vacuum conditions (0–50 Torr) on different surface areas.

2.1. Contact angle (CA) method

The contact angle (CA) was measured at the interface between a drop of liquid and a solid surface [28]. When a droplet of a liquid is formed on a flat solid surface, the balance on the three-phase interface is expressed by the Young's equation (Eq. (1)).

$$\gamma_s = \gamma_{sl} + \gamma_l \cdot \cos\theta \tag{1}$$

where, γ_l is surface tension of liquid, θ – contact angle between the liquid-air interface and the surface, γ_{sl} is interfacial tension and γ_s is surface free energy of a solid [29]. The contact angles are expressed as ThetaL (left), ThetaR (right) and ThetaM (average). Most practical surfaces are non-ideal and the CA on such surfaces is referred as apparent contact angle θ_{ap} [30]. As a consequence, θ_{ap} falls into an interval between the advancing contact angle θ_a and the receding contact angle θ_r, whose difference is called contact angle hysteresis CAH) (Eq. (2)).

$$CAH = \Delta\theta = \theta_a - \theta_r \tag{2}$$

CAH of contact angle is due to deviations of solid and liquids surfaces from ideal conditions. Amongst the various recognized reasons accounting for the wetting hysteresis there are inhomogeneity of chemical compositions of the solid surface or solid surface roughness, local adsorption, molecular orientation, solid strain near the triple line and mass transfer due to evaporation of the liquid [31]. Surface tensiometry analyses of spring waters were performed by contact angle (CA) method in static and over time modalities forthwith after sampling. The CAs was measured twice, at both left and right contact point between water and test solids, and an average was calculated in relation to their different wettability characteristics.

Considering the analyses of the distension ratio of waters drops in the time, CAH was calculated by the T-1 contact angles method after each frame [27]. The differences ($\Delta\theta$) between contact angles measured at the first frame (t_0) and that calculated at the end (t_{final}) of the distension process of water drops were calculated.

2.1.1. Dynamic contact angle method

In general, the term dynamic contact angle measurements indicates a technique that measure the contact angle during movement of a drop [32]. The dynamic contact angle measurement is usually performed by adding or removing liquid to a static droplet on a surface [32]. The contact angle measured during droplet expansion is indicated as advancing contact angle (θ_a), while the contact angle measured after removing liquid from a droplet is indicated with the term receding contact angle (θ_r) [32]. The difference between the advancing and receding contact angle is referred to contact angle hysteresis (CAH) [32]. Taking in account the concept of dynamic contact angle, the movement of a drop of water leaved on the surface of solid substrate was here investigated using the contact angle method over time.

2.1.2. Kinetic contact angle method

Another possibility to determine the contact angle of a drop of liquid during the movement is to measure its changes over time. However, the concept of dynamic contact angle does not fully express the contact angles measurement performed over time. In the context of our work, the term kinetic contact angle (KCA) here purposed express the need to distinguish the movement of a drop deposited on a solid surface over time from the movement of a droplet of the same liquid measured using the dynamic contact angle, a term widely used and defined in lecterature. The kinetic contact angle (KCA) take in account that the measurement of the spreading of a drop of a liquid on a solid substrate can define its kinetics of wetting (KW) [33]. as well as the dynamic contact angle method (Fig. 2). Fig. 2 put in evidence the distinction between the movement of a droplet of liquid in terms of advancing and receding CA (dynamic contact angle measurement) and its spreading over time (kinetic contact angle measurement). It is important to underline that the equilibrium of contact angle depends on the solid – liquid interactions at the interface, and decreases with increasing interaction with the substrate during the KCA analyses [34]. The trend line of CAs measured over time using KCA were performed by applying the power equation of correlation in order to describe mathematically the spreading of spring waters droplets on the surface of solids test and the variation of droplets volume during the analysis of CAs in time, whose variation can influence the measurement of CAs.

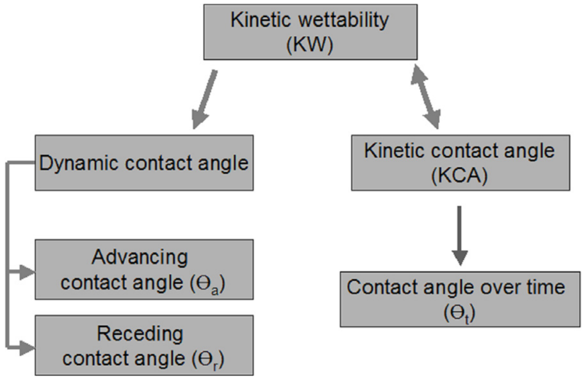

Fig. 2. Link between kinetic wettability (KW) and kinetic contact angle measurement (KCA) (double arrow) and connection between kinetic wettability (KW) and dynamic contact angle measurement expressed as advancing/receding contact angle measurements (single arrow).

2.1.3. Tangent method

In general, the wetting analysis is an useful tool able to enhance wettability and adhesion properties in many field of applications; it has been demonstrated that the contact angle is independent of the contact angle measuring method [35]. On the basis of this experimental evidence, the contact angle tangent method (T-1) was considered here because of the possibility of determining the contact angle hysteresis (CAH) using static contact angle and KCA measurements.

In the tangent (T-1) method, a horizontal baseline is drawn that passes through the triple point on the side of the droplet where the liquid, solid, and surrounding gas meet each other assuming an elliptical droplet shape. The tangent method fits a general conic section equation to the droplet shape. The angle between the baseline and tangent line defines the intrinsic contact angle (θ0) formed on a flat horizontal surface [36]. Although widely applicable, this method increases the uncertainty of CA depending on the wettability of the substrate [37]. In particular, the uncertainty in CA measured by the tangent method appears to be quite small over most of the wettability range, but it increases asymptotically near 90° The surface tensiometry characteristics of studied waters were investigated in order to calculate the contact angle hysteresis (CAH) variations for each plot.

2.1.4. Droplet volume assessment

It has been demonstrated that the contact angle depends strongly on the droplet volume and structured/pore-consisting surfaces [35]. For this reason, the droplet volume is a surface tensiometry parameter to be considered in relation to the kind of application. In particular, the ideal volume of a droplet depends from CA, being 5–10 μL for $\theta < 40°$, 20–50 μL for $40° < \theta < 90°$ and 50–100 μL for $\theta > 90°$ [38].

Changes of droplet volume in the time during CA measurements might occur due to the evaporation rate [39]. Assuming a spherical shape of the droplet at the beginning of the evaporation process, behavior of CA in the time can be described with the rate of volume change and average CA (Eq. (4)).

$$V = \frac{v_i - v_{i-1}}{\Delta t} \tag{4}$$

where v_i is volume at the time i.

Normally, the droplet volume changes (θ) are calculated between consecutive measurements and the change of CA in the same time interval (Eq. (5)).

$$\theta = \frac{\theta_j - \theta_{j-1}}{\Delta t} \tag{5}$$

where θj is the contact angle at the time j.

It is clear that the lower the influence of the evaporation on θ, and the lower the rate of droplet volume (V) change in time. All these parameters were measured during surface tensiometry analyses.

In static conditions, the CAs of water onto solid test surfaces were fitted with a linear function $y = ax + b$ in order to quantify the surface tensiometry compatibility between the MS water and other investigated waters tested expressed through the correlation coefficient (R^2). This value takes into account the surface tensions of diverse waters. In order to compare the different spring waters using KCA, the CAs of waters measured over time onto solid tests surfaces and droplet volume values were mathematically fitted with a power function $y = a \cdot x^n$ to determine the entity of the variations of their parameters through by analyzing the correlation coefficient (R^2). The power function's parameters were calculated from three series of contact angles measurements performed over time at the water-test solid interface.

2.2. Statistics

Comparisons among the CA of the different solids tests were performed by Analysis of Variance (ANOVA) and Least Significant Difference (LSD) tests [40]. For each water, mean CA was calculated of the solid tests AL, BW, LA, PX and SG, and the results were used as quantitative variables in a cluster analysis for agglomerative hierarchical clustering of the waters. Clustering was applied using complete linkage, where the distance between two clusters was the maximum distance between observations [41, 42]. The results of the ANOVA test did not consider the OT water because only one static CA measurement was available for this water.

Solids tests with different polar properties can evaluate the polar gradient of studied waters based on the interfacial interactions with the solids test used. Following this principle, our surface tensiometry's investigations focused on the study of the interface phenomena occurring between test solids and waters having unknown polar gradient. The MS water was considered as a “reference” sample because, compared to the other spring waters, it contains higher concentrations of a number of elements such as Li, Na, Cs, Ba, REE (rare earth elements), Th, Zr, Cr, Mn, Cd, B, Sb, Bi, F and Br [20]. In this study, the CA was considered as the only reference parameter for the analyses of the properties of waters in terms of wettability gradient.

3. Results and discussion

3.1. Morphological analyses of test solids

The comparative analyses of the morphology of the test solids surfaces proved to be fundamental in order to select the most appropriate solid substrates in relation to the effect of their structured/pore-consisting surfaces in the CA measurements [35]. The PG, LA and BW solids showed satisfactory smooth surfaces, close to the morphology of AL and SG (Fig. 3). The cetostearyl alcohol (CSA), instead, presented a rougher surface compared with others excipients. For this reason, it was substituted with plexiglass (PX), because of the high sensitivity of the CA analysis using KCA by T-1 method.

3.2. Static contact angle

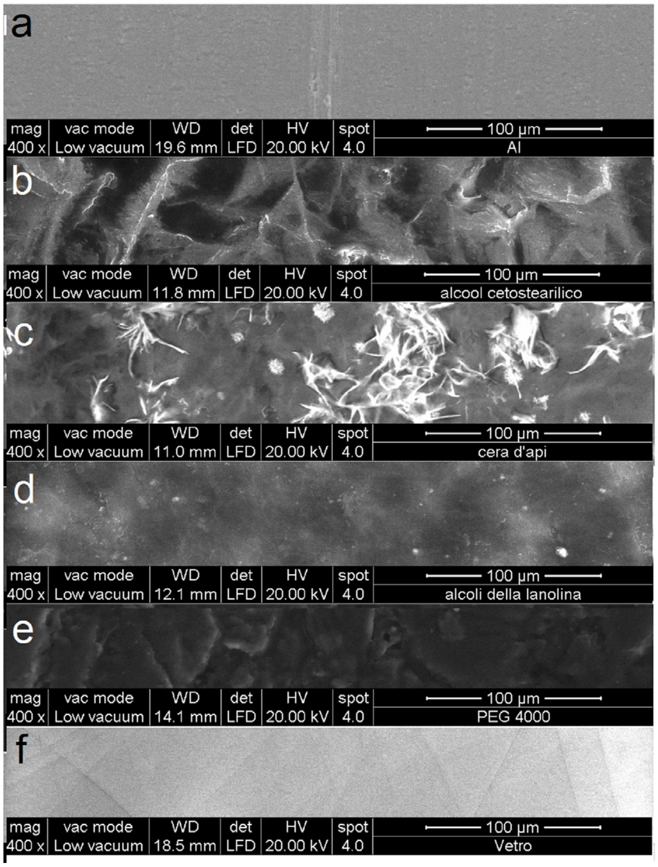

Fig. 3. Morphologic data of “organic test solids surfaces by SEM analyses where (a) is aluminium (AL), (b) is cetostearyl alcohol (CSA), (c) is bees wax (with artifacts) (BW), (d) is lanolin alcohol (LA), (e) is polyethylene glycol PEG4000 (PG), and (f) is silica glass (SG) .

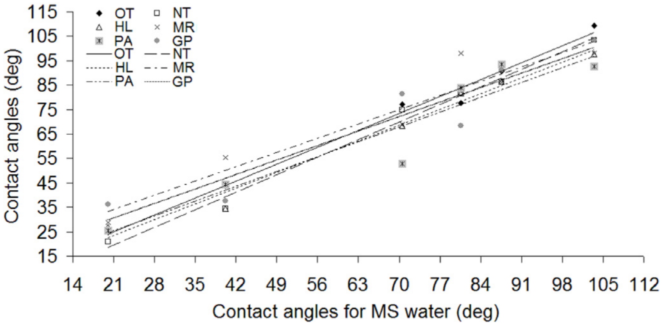

Fig. 4. Linear correlation between the MS water and other waters in function of the solids used. Coefficients of determination given in Table 1.

The analysis of the correlations between static CAs of the MS water measured on the surface of test solids and the CAs of other spring waters, demonstrated the particular surface tensiometry characteristics of the MS water. The decrease of the affinities of wettability between the MS water and other studied waters (Fig. 4) is indicated by the decrease in the R^2 values that can be divided in two groups. The first group ($R^2 > 0.98$) involves MS, OT, NT and HL waters; the second group ($0.90 < R^2 < 0.91$) includes MR, GP and PA waters (Table 1). This demonstrates the differences between waters from the static contact angle measurement viewpoint and that the roughness grade of the surface of LA (Fig. 3) does not influence significantly the wettability values of the test solids used. The study of the wettability gradient [43] of the test solids confirmed that NT and OT waters originate directly from the MS water, and also suggested close affinity between the HL and MS waters. The MS and the HL springs are hydraulically connected

Table 1
Mean and standard deviation of contact angles (CA) measured at the interface between studied waters and solid substrate by the static CA method using for linear fitting. The CA values in deg.

Waters	SG[a]	AL[b]	PX[c]	BW[d]	PG[e]	LA[f]	R^2[g]
MS	40.2 ± 0.72[h]	80.6 ± 1.30	87.6 ± 0.17	103.5 ± 1.00	20.0 ± 1.24	70.5 ± 2.75	1
OT	43.7 ± 0.5	77.8 ± 6.17	90.8 ± 1.36	109.3 ± 3.76	24.8 ± 0.00	77.1 ± 2.76	0.99
NT	34.4 ± 0.00	81.6 ± 6.65	86.4 ± 0.20	103.3 ± 1.96	20.8 ± 0.00	75.0 ± 1.27	0.99
HL	45.2 ± 3.16	92.1 ± 1.96	93.6 ± 3.04	97.7 ± 1.66	26.8 ± 6.36	68.5 ± 0.70	0.98
MR	55.4 ± 1.45	98.0 ± 4.11	86.3 ± 4.38	98.1 ± 6.50	28.9 ± 0.00	68.9 ± 0.66	0.91
GP	37.7 ± 4.66	68.4 ± 3.48	91.4 ± 2.78	103.5 ± 10.44	36.3 ± 0.00	81.4 ± 4.33	0.90
PA	44.5 ± 3.06	83.9 ± 13.36	93.6 ± 5.09	92.7 ± 5.07	25.3 ± 2.15	52.9 ± 9.54	0.90

[a] Silica Glass.
[b] Aluminium.
[c] Plexiglas.
[d] Bees wax.
[e] Polyethylene Glycol.
[f] Lanolin Alcohol.
[g] Coefficient of determination for regression models between CA values for the MS water and other waters studied.
[h] Mean and standard deviation ($N = 3$).

to the same karst hydrogeological system of the Batsurguère Valley. Field tracer tests [44] showed that these two springs were the main discharge sites of tracer-carrying groundwater from the mentioned above aquifer system.

Besides to excluding the GP river water, which is a surface water unlike others that are groundwater resource-related, ANOVA analysis (Table 2) showed that the tests with AL, PG and SG test solids can discriminate investigated waters better than other solids (BW, LA, PX) in comparison to the reference MS water.

In turn, the cluster analysis [42] clearly evidenced that HL, MR and PA spring waters are different with respect to the MS-related waters (i.e. MS, NT and OT), showing that the MS is significantly different from other waters from the wettability viewpoint (Fig. 5). The cluster analysis confirmed the suitability and the discriminating ability of surface tensiometry for the non-invasive characterization of the origin and relations of waters tested (that is, without destroying the sample matrix as for example during chemical analyses).

Considering GP river water in the ANOVA analysis of wettability data, the clustering demonstrated a possible relation between GP and MS-and-NT waters. However, at the current stage of research, there are not enough data to explain this unexpected feature.

The wettability investigation of waters by static CA method [45] led to the clear distinction between waters linked to the MS site (i.e. MS, OT and NT) and waters from MR and PA springs. Considering CA static measurements it can also be concluded that the HL spring water reveals dual features. The HL water shows, hydrogeologically conditioned, closeness to the MS water. On the other hand (clustering analysis), the HL reveals affinity to MR and PA spring waters. Based on geochemical studies [20] the feature connecting HL, MR and PA waters is the lower concentration of numerous (mainly trace) elements (Li, Na, Cs, Ba, REE, Th, Zr, Cr, Mn, Cd, B, Sb, Bi, F and Br) compared with the MS water. However, it could be not associated with surface tensiometry features, but with bedrock geochemistry in alimentation zones of particular springs.

Table 2
ANOVA results for static CAs measured at water-solid interface, excluding GP river water.

	Solid test					
	AL	BW	LA	PG	PX	SG
MS vs. HL	4.67*	1.66	0.33	4.28	8.35*	4.99
MS vs. MR	10.58**	1.4	0.28	4.68	0.02	47.34***
MS vs. NT	0.04	0	2.02	0.02	0.01	3.49
MS vs. PA	0.38	5.72*	25.27***	3.21	6.55*	3.67

One, two and three asterisks correspond to $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

3.3. Kinetic contact angle (KCA)

The comparative analyses of KCA measurements of spring waters were performed in order to determine the resolution capability of T-1 method in relation to the solid – liquid interactions occurring at solid/liquid interface [35]. Data of plots I and II from NT–SG and plot I from GP–SG tests (Table 3) cannot be evaluated, because of instrumental errors during the CA measurements. The contact angles measurements performed at MS–SG interface demonstrated a good reproducibility; their values are similar for all three series considered (CA ranges 38.5–40.5°) (Fig. 6). The CA stability over the time in plot II (series II) ($R^2 = 0.24$) appears to be higher than those found in plot I ($R^2 = 0.55$) and plot III ($R^2 = 0.53$) (Fig. 5A). However, the droplet volume showed in Fig. 5B is similar between the three plots (range about 13.5–14.2 µL), they undergo at variations over the time in the three measurements series (plot I: $R^2 = 0.83$, plot II: $R^2 = 0.77$, plot III: $R^2 = 0.84$). The results demonstrated that it is possible to evaluate the variations of the wettability parameters on the basis of R^2 and select the series plots on the basis of the minor changes of droplet volume over time. This possibility takes in account the physico-chemical interactions at the interface between MS water and SG occurred in time [46]. and the evaporation of the water droplet, due to the environmental conditions in which the CA measurements were performed. The same test was performed on others waters (Table 3) as NT (Plot III: $R^2 = 0.84$), OT (Plot III: 0.73), HL (Plot II: 0.92), MR (Plot II: 0.81), GP (Plot II: 0.72), and PA (Plot I: 0.70). In Fig. 6 are reported the trend lines of the selected plots chosen on the base of their lowest correlation degree (R^2). Low values of R^2 indicate more constant droplet volumes in time, also witnessed by the low fitting performance of the power function applied at the CAs distribution. However, the surface roughness of SG test solid should be taken also in account. Trend line (Fig. 7) marks the behavior in the time of CA measured at the interface between MS water and SG solid whose correlation degree appears to be the lowest ($R^2 = 0.24$) with respect to others waters (OT: $R^2 = 0.93$, NT: $R^2 = 0.84$, HL: $R^2 = 0.92$, MR: $R^2 = 0.87$, GP: $R^2 = 0.88$, PA: $R^2 = 0.70$). The CAs plots chosen correspond to minor volume variations over the time (MS: $R^2 = 0.77$, OT: $R^2 = 0.25$, NT: $R^2 = 0.86$, HL: $R^2 = 0.43$, MR: $R^2 = 0.39$, GP: $R^2 = 0.24$, PA: $R^2 = 0.10$), that identifies them as suitable for CAs analyses according to [30]. The great difference between R^2 values for MS water ($0 < R^2 < 0.70$) and other waters ($0.70 < R^2 < 0.93$) likely resulted from the adhesion forces generated at the interface between MS water and SG solid. This could explain the greater stability of the contact angles measured over the time by which the power function cannot interpolate well the CA values, thus determining lower

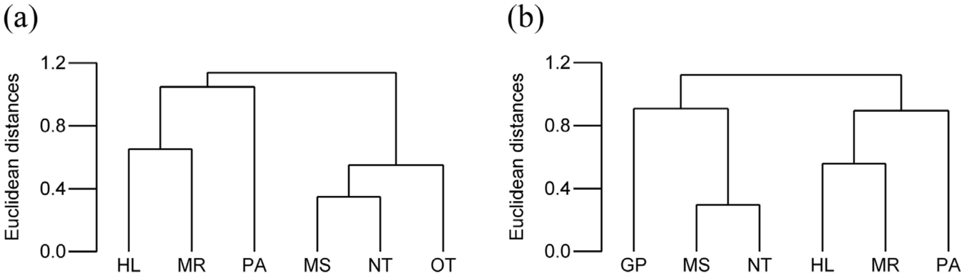

Fig. 5. Clustering dendrogram of studied waters (excluding GP river water) (A) and with GP river water (B) based on static contact angle measurements onto silica glass (SG) solid.

correlation degrees between them and the time.

3.4. Contact angle differences (Δθ)

The calculation of the differences between the CAs of spring waters measured in static modality and that performed at the end of KCA analyses (Δθ) led to estimate the increase of the interfacial interactions between them and each test solid~~s~~ [35].

The waters are ordered according to Δθ values obtained with static CA method [24] (Fig. 8). The NT and OT provide water from MS spring after disinfection (chlorination), whereas the MS presents raw water sampled directly at the outflow site in the cave. The Δθ indicates the common origin of NT and OT waters in agreement with the results of static contact angle measurements (Fig. 5a and b). The possibility to non-invasively detect the spring waters origin assumes importance in order to determine the real characteristics that link raw and treated waters in relation to the entity of the influence of chlorination in the physico-chemical profiles of waters. The analyses of Δθ clearly highlight that the CA average of MS, OT and NT (average 1.43°) is largely lower than other waters (average 7.13°). This result confirms the greater affinity existing between NT and OT with MS than with HL, MR, GP and PA in terms of wettability properties accordingly with ANOVA and cluster analyses [42]. This also suggests that the chlorination of NT and OT waters does not substantially influence the wettability properties of these waters, evidencing their origin from MS that demonstrate to be less influenced by physico-chemical factors occurred at solid–liquid (s–l) interface united at the environmental conditions at solid–vapor (s–v) interface. On the base of these results, it might be hypothesized that high Δθ values means high influence of the natural physico-chemical factors on HL, MR, GP and PA waters and consequently on the wettability of SG solid.

3.5. Analysis of contact angle hysteresis (CAH)

The analysis of the contact angle hysteresis (CAH) afforded the evaluation of the compatibility of a test solid for surface tensiometry investigations and the analyses of the link between chemical and physical properties of a liquid. In particular, the CAH allows to evaluate the variations of receding (θ_r) and advancing (θ_a) contact angle values in the time during the distension of water droplets onto glass solid surface, representing the difference between ThetaL (left) and ThetaR (right). The CAH values look highly reproducible for all ThetaL (left) and ThetaR (right) CA measurements, demonstrating that all measurements were performed on a highly horizontal surface (Table 4).

The wettability data obtained suggest that the presence of an higher content of trace elements in the MS water, with respect to other spring waters [20] likely influence the wettability of the solids test used according to their physico-chemical features. In this context, it is important to take in account the water solubility of organic test solids as LA (water-insoluble; $4.12{\cdot}10^{-4}$ mg/L) [24] used as Water in Oil (W/O) emulsifier agent, PG (water-soluble; 66% wt) [25] and BW (water-insoluble) [23] because their solubility influences the CA values

Table 3
Power function parameters from contact angles (CA) measured at the interface between studied waters and silica glass (SG) solid. *n* is the exponent and *a* is intersection of the Y-axis.

$y = a \cdot x^n$		CA (°)			Volume (μL)		
Water-substrate	Plots	*a*	*n*	R^2	*a*	*n*	R^2
MS-SG	I	40.506	−0.0036	0.5524	14.305	−0.0056	0.8396
	II	39.090	−0.0033	0.2427	13.879	−0.0045	0.7717
	III	40.582	−0.0032	0.5355	14.450	−0.0052	0.8416
NT-SG	I	ND	ND	ND	ND	ND	ND
	II	ND	ND	ND	ND	ND	ND
	III	34.363	−0.0038	0.8387	12.676	−0.0078	0.8638
OT-SG	I	42.667	−0.0143	0.7823	13.481	−0.0086	0.9850
	II	44.419	−0.019	0.9277	14.368	−0.0006	0.2490
	III	42.597	−0.0112	0.7315	14.091	−0.0064	0.9262
HL-SG	I	41.235	−0.0295	0.9638	14.75	−0.016	0.9754
	II	42.106	−0.0248	0.9243	16.992	−0.0058	0.4203
	III	47.372	−0.028	0.9681	15.439	−0.0042	0.9403
MR-SG	I	53.524	−0.0178	0.8654	17.138	−0.0045	0.3893
	II	52.314	−0.0154	0.8149	17.430	−0.0133	0.9471
	III	55.782	−0.0197	0.9771	18.987	−0.0082	0.9401
GP-SG	I	ND	ND	ND	ND	ND	ND
	II	34.557	−0.0155	0.7201	33.298	−0.1630	0.9844
	III	41.252	−0.0315	0.8842	23.006	−0.0103	0.2397
PA-SG	I	39.936	−0.0754	0.6983	14.415	−0.0749	0.10
	II	47.235	−0.0678	0.8675	13.582	−0.0212	0.7675
	III	43.636	−0.0726	0.8928	19.563	−0.0225	0.6745

ND – not determined.

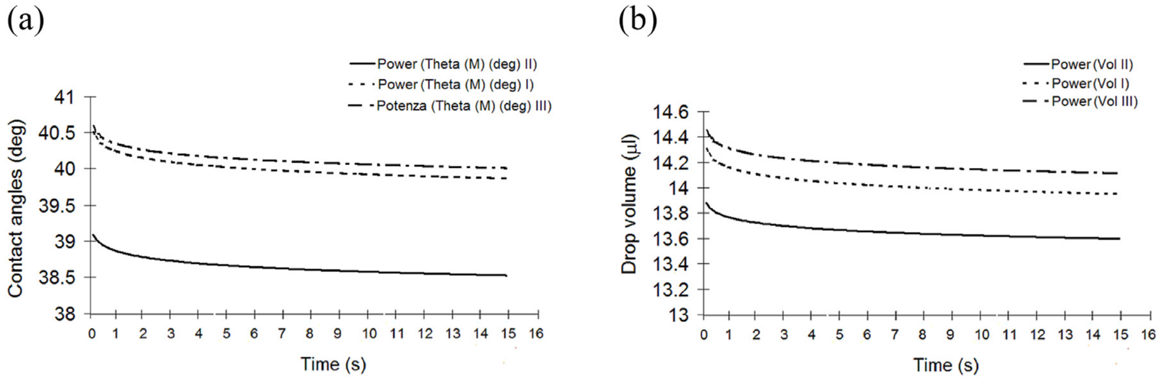

Fig. 6. Trend behaviours of three contact angle (CA) series (A) and three drop volume (Vol) series (B) at the interface between the MS water and silica glass (SG) solid and temporal changes of such parameters.

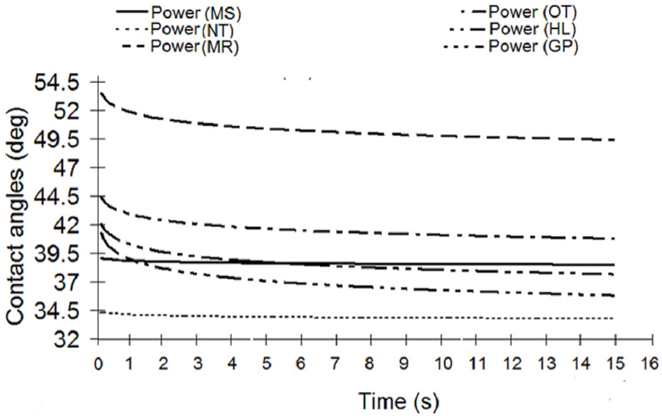

Fig. 7. Contact angles (CA) series performed over time (s) onto silica glass (SG) solid test.

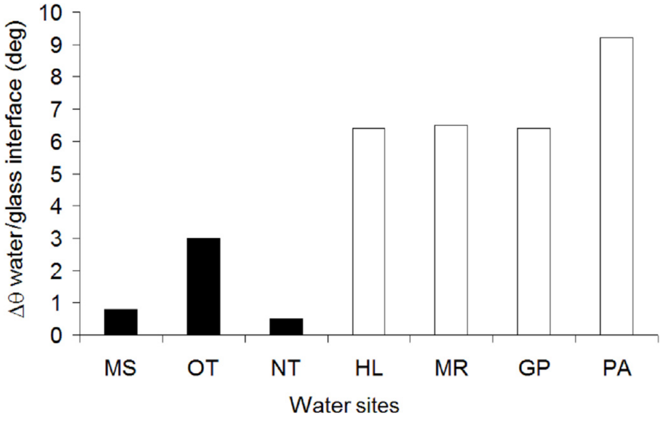

Fig. 8. Entity of the differences in CA after drop distension (Δθ) of waters.

Table 4

Contact angles hysteresis (CAH) (averages ± standard deviation) calculated at the interface between studied waters and silica glass (SG) solid substrate. ND – not determined.

Studied waters	Plots	CAH (°)
MS	I	0.8247 ± 0.008*
	II	0.1597 ± 0.007
	III	0.8663 ± 0.092
NT	I	ND
	II	ND
	III	1.0122 ± 0.1607
OT	I	0.3739 ± 0.2113
	II	0.3447 ± 0.2118
	III	0.7153 ± 0.1391
HL	I	0.7967 ± 0.1806
	II	0.9978 ± 0.1561
	III	1.2260 ± 0.1568
MR	I	0.8731 ± 0.2901
	II	0.4388 ± 0.3823
	III	1.4764 ± 0.2911
GP	I	ND
	II	1.2400 ± 0.440
	III	1.3666 ± 0.3881
PA	I	1.555 ± 0.6691
	II	1.3111 ± 0.5666
	III	1.28 ± 0.6144

measured at the interface with the different spring water investigated. In the case of LA, its particular physico-chemical features influence the morphology characteristics of its surface profile, as also demonstrated by SEM imaging (Fig. 2). As for the general mechanism of glass–water interaction, from which also depend the CAs measurements, it depends on the glass structure and on phenomena such as H_3O^+ ions adsorption onto the glass surface, surface ion exchange due to electrophilic attack of H_3O^+ ions on non-bridging oxygen bonded to metal ions or nucleophilic attack of H_2O on bonded metal ions, besides to lattice ion exchange of H_3O^+ for a cation within lattice $(C + S)_i$, migration of H_3O^+ ions over the glass surface and migration of metal ion within the lattice $(C + S)_i$ [47]. In the case of food packaging, aluminum foils (water-insoluble; Al = 99%), it has to be noted that aluminum quickly develops on the surface a thin layer of aluminum oxide, further preventing a direct reaction of metal with water, while PX (poly-methylmethacrylate) has a water absorption close to zero (0.3%/24 h) and high chemical resilience [48]. According to manifold interface interactions occurring between water and solids considered, it is suggested that different interfacial phenomena observed through the use of the surface tensiometry could be directly linked to the different physico-chemical interactions occurring at the solid-water interface [46]. Accordingly, the different chemical patterns of investigated waters cause a large amount of physico-chemical interactions on solid surfaces, which are detectable in a non-invasive manner by means of CA analyses [49].

The opportunity to measure all different interfacial phenomena behaviors over the time using a single datum, led to discriminate the MS water from others, underlying that its significantly different chemical features could be intertwined with its specific surface tension properties.

Anyway, the data reported here are prompting us to pursue the investigation in the fields of groundwater geochemistry and monitoring for a large scale wettability and surface tension characterization of groundwater (e.g. spring waters) which can be performed by CA method over the time on samples as such.

The surface free energy components of the organic test solids used in this work are reported in Table 5. The surface free energy, dispersion

Table 5
Surface free energy (SFE), dispersion component (DC), and polar component (PC) of organic polar and less polar solids.

Organic test solids	SFE (mJ/m^2)	DC (mJ/m^2)	PC (mJ/m^2)
Lanolin alcohol (LA)	39.7	32.4	7.3
Bees wax (BW)	21.3	18.9	2.4
Polyethylene glycol PEG 4000 (PG)	65.9	4.0	61.9

component, and polar component of test solids are in accordance with their physico-chemical features [50]. The differences in dispersion component and polar component of test solids are linked to their different wettability with the waters studied here, because the contact angle value of a liquid depends on the surface free energy properties of the solid substrate on which is deposited. In the end, new wettability investigations by surface tensiometry have to be performed using the same kind of organic test solids, and previously characterized by the surface free energy viewpoint.

4. Conclusions and perspectives

The CA method demonstrated mainly the capability of surface tensiometry to underline the differences between the surface tension of the waters considered by wettability evaluation. This made possible a first interpretation of the different characteristics of waters according with their origin and in relation to their flow conditions in the studied area. In this context, this work validated the hypothesis that studied waters have also significantly different surface tensions characteristics. The wettability investigations of the test solids led to the first non-invasive assessment of the quality of different types of waters (groundwater from karst springs, surface water, disinfected groundwater from public taps) sampled in seven sites in the Lourdes area by the CA methods.

The T-1 tangent method applied at the contact angle analyses performed at the interface between studied waters and the solids test will consent the selection of the more appropriate substrate on the base of the absolute uncertainty of the CA measures. In particular, the static contact angle method revealed different surface tension of the MS water with respect to the other studied spring waters. ANOVA and cluster analyses demonstrated the capability of the static contact angle method to discriminate MS and public tap (NT) waters from other waters on the base of their different proveniences giving at the study high sensitivity and statistical significance.

This study introduced the kinetic contact angle (KCA) measurement term coupling the droplet spread analyses over time with T-1 method. The combined approach KCA/T-1 demonstrated its ability to evaluate the movement of a droplet of water on the surface over time because it is linked to the kinetic wettability of the substrate (KW).The KCA analysis of the wettability properties of inorganic and organic test solids by contact angles highlighted that each spring water produces different physico-chemical interactions at the interface with the solids used. The kinetic contact angle (KCA) term introduced here demonstrated to be harmonized with the concept of kinetic wettability (KW) of a solid substrate, linking the dynamic contact angle term with advancing and receding contact angle measurements only. The application of a power equation to the spreading of the contact angle in time on glass surface led to a mathematical characterization of each spring water, confirming the peculiar physico-chemical and surface energy characteristics of the MS water with respect to other waters.

The analysis of the difference between the static CA and the CA measured after the spreading of the water droplets over time (Δθ), allowed to detect the origin of waters and the influence of the chemical treatment on their physico-chemical properties.

The analysis of the static and KCA also demonstrated the possible influence of the trace elements content in water on the wettability of the solids test used. The present results hint to the possibility of calculating surface tension, its dispersion and polar components of studied spring waters using also the newly proposed Solid-Like Method [19]. In the light of the results obtained, surface tensiometry would be a rational method especially for selecting the most reliable research points in designing networks of natural water monitoring.

Authorship statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the *Surface and Interface*.

Declaration of Competing Interest

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