



Regional pH Change in Groundwater Between Field and Laboratory Analyses, Temperature, Groundwater Silicon, Agricultural Soil pH and Soil-Type Distribution in Finland



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Received:  December 02, 2018; Published:  December 20, 2018

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Abstract

Objective: Silicates are a part of carbonate-silicate cycle, but the role of silicon (Si) in pH regulation of groundwater and agricultural soil (soil) is not as well clarified. Groundwater (gw) pH is different in immediate analysis on the field (pH.gw.field) to the laboratory survey (pH.gw.lab). The purpose of this manuscript is to describe regional associations between temperature (Temp), Si.gw, pH.soil, pH.gw's and their difference (Δ .pH.gw), as well as proportion of organic (Prp.org) and coarse mineral soil-types sine silt (Prp.coms) and suggest explanations.

Materials and Methods: Regional values of pH's, soil-type distribution, Si.gw and Temperature are from old sources. Regional values for Uusimaa and Varsinais-Suomi are formed of their Rural Center (RC) parts as earlier presented. Statistical analyses are from continental Finland. In graphHics whole Finland is represented,

Results: Mean Δ .pH.gw was 0.31 (+/- 0.21) (Table 1) Only in one region of 19 (Ostrobothnia) pH.gw.field value was higher to its pH.gw.lab value. pH's of Ostrobothnia are associated with special local factors. Correlations of pH.gw.field/ pH.gw.lab with Si.gw were +0.64**/-0.11 and oppositely with Δ .pH.gw (-0.56*/+0.63**) and soil pH values. (Combined regression by) [Temp; Δ .pH.gw] explained pH.soil variation 79.4 % ($r = 0.89$, $p < 0.001$),with coefficient directions (+/+). [Prp.coms;Prp.org] explained trend-like Δ .pH.gw, coefficient directions were (+/-).

Conclusion: Regional Δ .pH.gw was associated inversely with Si.gw. Combined Temp and Δ .pH.gw explained ca 80 % of agricultural soil pH variation. Δ .pH.gw can be associated with silicate carbonate interactions. (CO_2 sequestrating by silicates - weathering - can be seen as a pH stabilizing process, which could be supported by silicate liming agents and fertilizers, e.g. industrial slags and stone meals)

Keywords: pH; Groundwater; Agriculture; Silicon; Temperature; GeographY; Soil Type

Abbreviations: C: Carbon; Continental Finland: Finland Without Åland; Correlation: Pearson Correlation; GW: Ground Water; H: Hydrogen; O: Oxygen; Prp.org: Proportion of Organic Soiltypes; Prp.coms: Proportion of Coarse Mineral Soiltypes Sine Silt; pH.gw.field: pH of the Fresh Groundwater, pH.gw.lab: pH Studied in Laboratory. Δ .pH.gw = pH.gw.lab minus pH.gw.field; RC: Rural Center (earlier Agricultural Advisory Center); Si: Silicon; Silanol - Si-O-H-group; Temp: Temperature

Introduction

Silicates are known as a part of carbonate-silicate cycle [1], but the role of silicon (Si) in pH regulation of groundwater and agricultural soil (soil) is not as well clarified. Stability in inter-regional relative pH values has suggested on the possible role of silicon (Si) in pH regulation [2]. Soil pH has been written to associate non-significantly positively with Si.gw in continental Finland [3], but pH.soil was highest in Åland, where Si.gw

was low [4]. In combined regression by [Temp; pH.soil] pH coefficient got negative value for Si.gw [5]. Åland has been excluded from this survey because the availability of Si seems not to be associated with Si.gw [4,6]. Groundwater pH is different in immediate analysis on the field (pH.gw.field) to the laboratory survey (pH.gw.lab). The purpose of this assessment is to describe this difference (Δ .pH.gw) and to propose explanations.

Materials and Methods

Groundwater parameters (concerning springs and dugwells) are from Groundwater database © Geological Survey of Finland 2017 [7]. pH values and soil-type proportions from cultivated fields separately from 19 Rural Centers (RC, earlier Agricultural Advisory Centers), concerning period 1986-90 are provided by Eurofins Viljavuuspalvelu Oy [8]. Number of soil samples was 552,788. The boundaries, names and numbers of RCs and Regions

deviate slightly from each other [9]. Average annual temperatures of RCs from 1981-2010 are visually approximated by combining map of Finnish Meteorological Institute [10] and map of RC's [11]. Regional values for "Varsinais-Suomi" we got by combining RC values of "(03). Varsinais-Suomen" and "(4b). FinskaHushållnings" and for "Uusimaa" by combining RC values of "(01).Uudenmaan" and "(02).NylandsSvenska" as in [4]. After this RC values were given for respective Regions. Numerical data are in Table 1.

Table 1: Regional temperature, groundwater (gw) pH in field and laboratory surveys, pH of agricultural soils, gw pH difference (Δ . pH.gw), Si.gw, proportion of organic and coarse mineral soil-types. (Åland excluded from calculations).

	Temp	pH.gw.field	H.gw.lab	pH.soil	Δ .pH.gw	Si.gw	Prp.org	Prp.coms
	°C	-log [H ⁺]				mEq/L	%	
Åland	5.30	6.75	7.28	6.31	0.53	0.68	68.3	4.6
Varsinais-Suomi	5.02	6.71	6.97	6.13	0.25	1.12	25.4	7.4
Uusimaa	4.97	6.49	6.85	6.01	0.37	1.12	18.9	8.2
Kanta-Häme	4.60	6.60	6.93	6.01	0.33	1.12	37.0	12.1
Kymenlaakso	4.60	6.47	6.76	5.90	0.29	1.14	40.5	11.8
Satakunta	4.50	6.42	6.81	5.92	0.39	0.98	52.3	18.7
Päijät-Häme	4.30	6.32	6.79	5.96	0.47	0.98	59.7	10.7
South Karelia	4.10	6.36	6.80	5.86	0.44	0.93	65.7	18.0
Pirkanmaa	4.10	6.25	6.60	5.94	0.35	0.93	33.4	10.9
Ostrobothnia	4.10	6.77	6.46	5.70	-0.31	1.78	67.0	17.5
Etelä-Savo	3.80	6.34	6.98	5.99	0.64	0.91	83.8	14.4
South Ostrobothnia	3.40	6.79	6.94	5.75	0.15	1.07	65.3	25.9
Central Finland	3.20	6.31	6.80	5.89	0.49	0.90	57.5	17.3
Pohjois-Savo	3.00	6.35	6.80	5.86	0.45	0.78	58.4	15.3
North Karelia	2.80	6.28	6.28	5.82	0.00	0.81	54.3	16.3
Central Ostrobothnia	2.80	6.37	6.53	5.69	0.16	0.90	66.8	30.6
North Ostrobothnia	1.80	6.47	6.83	5.69	0.36	0.85	63.3	32.9
Kainuu	1.70	6.26	6.71	5.82	0.45	0.65	66.7	25.9
Lapland	0.50	6.59	6.82	5.59	0.23	0.70	58.0	40.7
Statistical Parameters of Continental Finland (Åland Excluded)								
Mean	3.52	6.45	6.76	5.86	0.31	0.98	54.1	18.6
SD	1.24	0.17	0.18	0.14	0.21	0.25	16.7	9.2
Min	0.50	6.25	6.28	5.59	-0.31	0.65	18.9	7.4
Max	5.02	6.79	6.98	6.13	0.64	1.78	83.8	40.7

Results

In general values of pH.gw.lab (6.67 +/- 0.18), were the highest, pH.gw.field (6.45 +/- 0.17) the second highest. Values of pH.soil (5.86 +/- 0.14) were the lowest. Only in one of 19 regions pH.gw.field was higher to pH.gw.lab (in Ostrobothnia). Mean regional Δ . pH.gw was 0.31 (+/- 0.21), maximum 0.64 and minimum -0.31 (Table 1).

pH.gw.field and pH.gw.lab associated weakly positively with each other ($r = +0.29$) (Figure 1), as well as with Temp (+0.17 and +0.20, respectively) (Table 2). pH.gw.field associated significantly (+0.64) with Si.gw (Table 2) and mirror-like with pH.soil ($r = -0.12$) (Table 2) and (Figure 2). pH.gw.lab correlated weakly inversely with Si.gw ($r = -0.11$) (Table 2) and moderately positively with pH.soil. ($r = +0.41$, $p = 0.091$) (Figure 3)- oppositely to pH.gw.field (Table 2).

Table 2: Pearson correlations in inter-relations of Temp, pH.gw.field, pH.gw.lab, their difference (Δ . pH.gw), Si.gw, pH.soil. (approximates, because invisible decimals were not rounded).

	Temp	pH.gw.field	pH.gw.lab	pH.soil.tot	Δ . pH.gw	Si.gw
Temp	1.00	0.17	0.20	0.78***	0.03	0.60**
pH.gw.field	0.17	1.00	0.29	-0.12	-0.56*	0.64**
pH.gw.lab	0.20	0.29	1.00	0.41	0.63**	-0.11
pH.soil.tot	0.78***	-0.12	0.41	1.00	0.45	0.12
Δ . pH.gw	0.03	-0.56*	0.63**	0.45	1.00	-0.62**
Si.gw	0.60**	0.64**	-0.11	0.12	-0.62**	1.00

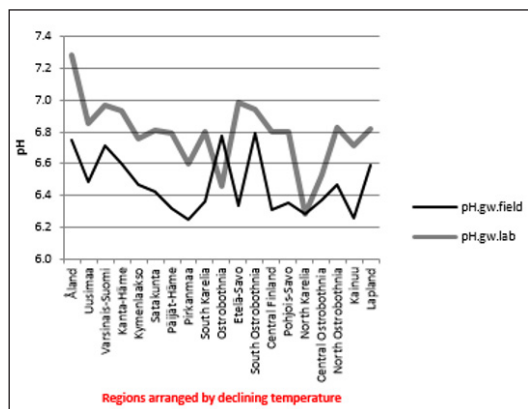


Figure 1: pH.gw.field and pH. gw.lab.

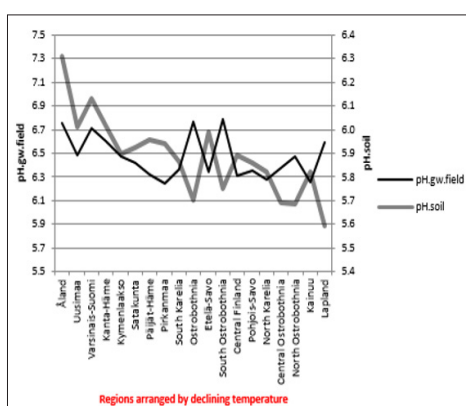


Figure 2: pH.gw.field pH.soil.

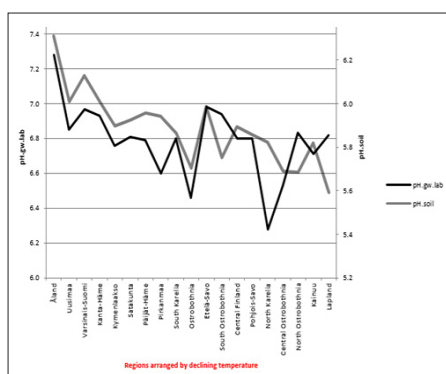


Figure 3: pH.gw.lab. pH.soil.

Δ . pH.gw correlated (Table 3) as pH.gw.lab, but stronger – inversely – with Si.gw (-0.62**) (Figure 4) and positively with pH.soil (+0.45) (Figure 5) Si.gw correlated weakly (+0.11, ns), but interestingly with pH.soil (Figure 6).(Regression by) [Temp; Δ . pH.gw] explained variation of pH.soil 79.4 % ($r = 0.89$, $p < 0.001$), coefficient (direction)s (+/+) (Figure 7) and by [Temp; Si.gw] 80.6 % ($r = 0.90$, $p < 0.001$) coefficients (+/-) (Figure 8).[Prp.org;Prp. coms] explained trend-like Δ . pH.gw. Visual association is clear, although association is non-significant, coefficients (-/+) (Figure 9).

Table 3: Significances of correlations.

N=	18	
abs(R) >	0.47	:P<0.05*
abs(R) >	0.58	:P<0.01**
abs(R) >	0.69	:P<0.001***

Note: Symbols *, ** or *** are signs of significance level.

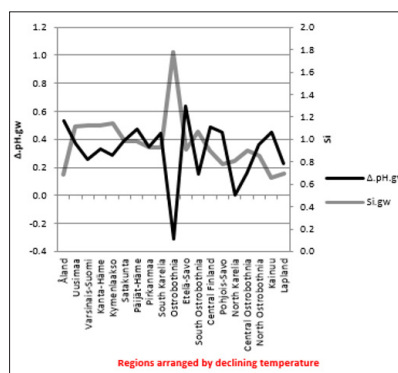


Figure 4: Δ . pH.gw and Si.gw.

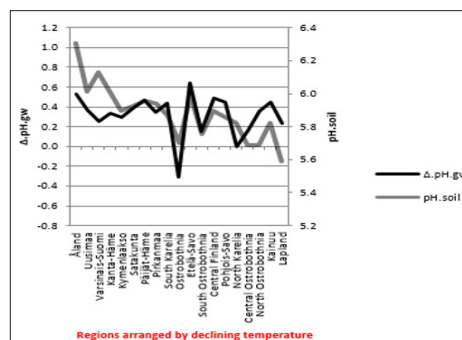


Figure 5: Δ . pH.gw and pH.soil.

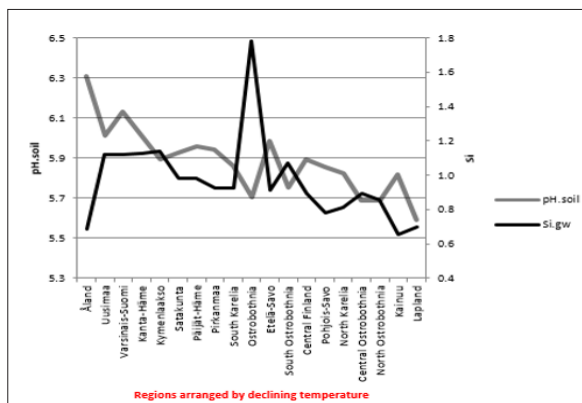


Figure 6: pH.soil and Si.gw.

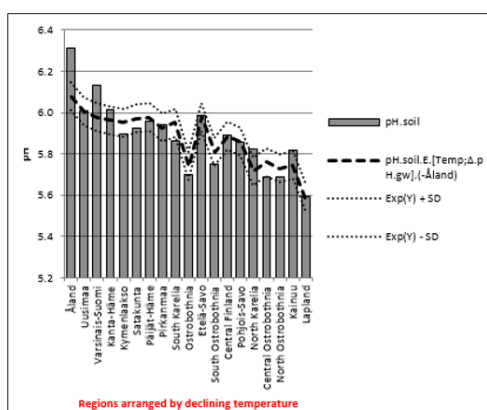


Figure 7: Combined regression of P^H .soil by Temp and Δ .pH.gw in continental Finland.

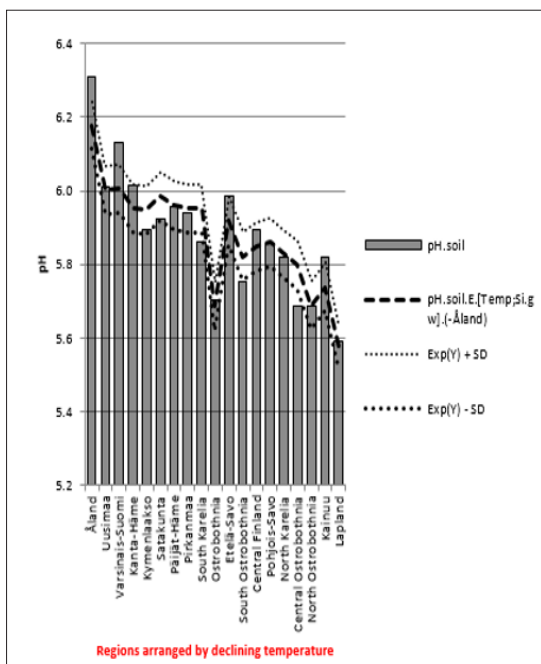


Figure 8: Combined regression of pH.soil by Temp and Si.gw in continental Finland.

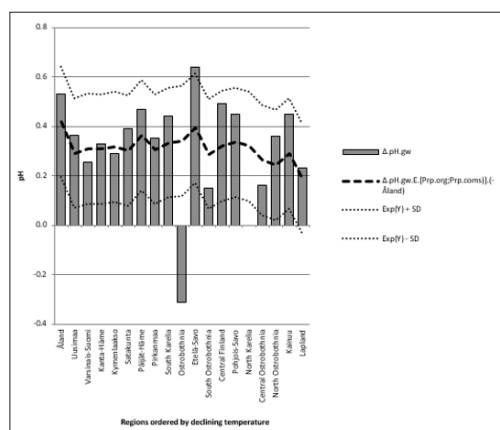


Figure 9: Combined regression of Δ .pH.gw by Organic and coarse mineral soil type proportion in continental Finland.

Discussion

Because generally only pH.gw.lab values are published [7] and I have not find discussions on differences between Finnish pH.gw.lab and pH.gw.field, this assessment can be justified. The primary aim was to describe the pHEnomenon by (Figures 1-8) and secondarily to propose some explanations. CO₂ values, which were measured only on the field, were not available for this survey. HCO₃⁻ values, which were measured in the laboratory, were available, but they seem not to be informative without CO₂. Regional Temp (average mean annual temperature) was significantly ($p < 0.01$) associated with Si.gw and pH.soil, weakly with pH.gw's and infinitesimal with Δ .pH.gw (Table 2). Temperature was strongly associated with Finnish geography and soil-type variation [3,4,5]. Here Temp association with Prp.org was -0.88, with Prp.coms -0.51 and with proportion of fine mineral soils (Prp.fims) +0.72. calculated from (Table 2). (Prp.coms +Prp.org + Prp.fims = 100). Interesting was the low association of Temp with pH.gw parameters; especially Δ .pH.gw seems to be "thermo-resistant".

pH.gw.field associated significantly positively with Si.gw (+0.64**) and negatively with Δ .pH.gw (Figure 2). pH.gw.lab associated about oppositely: significantly positively with Δ .pH.gw (+0.63**) (Figure 3) and weakly negatively with Si.gw. pH.gw.field curve forms like a mirror image with pH.soil (Figure 2), similarly as Si.gw with Δ .pH.gw (Figure 4). Interesting was that pH values of different soil-types (org, sands, mould, moraines and silt) gave highly similar curves as pH.soil [8]. pH.soil associated about similarly with pH.gw.lab and Δ .pH.gw (Figures 3&5). It is interesting, because proportion of agricultural soils of total land is different in different parts of Finland. This suggests that gw could be mainly of intra-regional origin. Regression of Δ .pH.gw by [Prp.coms;Prp.org] (Figure 9) showed trend-like positive association with coms and negative associations with org. Soil-type distribution (Figure 9) did not explain Ostrobothnia nor North Karelia values (Figure 9).

Combined regression by [Temp; Δ .pH.gw] explained pH. soil 79.4 % ($r = 0.89, p < 0.001$), both parameters were positive (Figure

7). [Temp;Si.gw] explained it slightly stronger 80.6 % ($r = 0.90$, $p < 0.001$), coefficients (+/-) (Figure 8). The negative association of Si.gw with pH. soil in this combination can be understood by Figure 6 (similar trends with Temp, but Si.gw fluctuations/deviations were like mirror-image to pH.soil). Δ . pH.gw could be associated with carbonic acid (H_2CO_3): Its pK_{a1} is 6.3 [12], which is near the means of pH.gw.field (6.45) and pH.gw.lab (6.76). This pK_{a1} includes reactions $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ [13]. Most of CO_2 is dissolved in water and about ca 0.2 % of CO_2 is in the form of H_2CO_3 [13,14]. In the absence of a catalyst, the balance in reactions $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$ is reached quite slowly [13]. Slow evaporation of CO_2 after pH.gw.field analysis could reduce H_2CO_3 and raise pH.gw. The effect of temperature as such on pH.gw (on the field 7.2 +/- 3 °C) [7] can obviously be excluded, because even pH.gw.field was measured at 25°C as pH.gw.lab [7].

Explanations via silicon: Silicate weathering can proceed via the chemical reaction as: $\text{CaSiO}_3 + 2\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}_2^{+} + 2\text{HCO}_3^- + \text{SiO}_2$ (dissolved silica) [1]. So silicates can sequester CO_2 from air, soil and subsoils and work as antacids, before coming to groundwater. Possibly in gw this reaction could work slowly backwards [1] and produce again water-soluble CO_2 , which could evaporate as CO_2 in the temperature (25°C), which is higher to the fresh gw and so raise pH. Inside every region Δ . pH.gw of different samples could be different with different explanations (i.e. different buffer systems). Low pH.gw in North Karelia as in Ostrobothnia (with acid sulphate soils [15]) could be a part of explanation. Regional Δ . pH.gw medians got no negative values, but zero in Ostrobothnia. Product of soluble SiO_2 , orthosilicic acid $\text{Si}(\text{OH})_4$ or H_4SiO_4 is a weak acid ($\text{pK}_{s1} = 9.51$ and $\text{pK}_{s2} = 11.74$) [16,17]. $\text{Si}(\text{OH})_4$ can condense and form dimers and oligomers [18]. The pK of silanol (Si-O-H) [19] groups on the outside of oligomers 1nm in diameter is 6.8 [18], which is close to the mean pH.gw's, which could make buffering possible. Because pK_{a2} (7.20) of phosphoric acid is moderately near mean P^h.gw's, it could have some effects, too [20].

Conclusion

Regional Δ .pH.gw was associated inversely with Si.gw. Combined Temp and Δ . pH.gw explained ca 80 % of agricultural soil pH variation. Δ . pH.gw can be associated with silicate carbonate interactions. (CO_2 sequestering by silicates - weathering - can be seen as a pH stabilizing process, which could be supported by silicate liming agents and fertilizers, e.g. industrial slags and stone meals).

References

1. Carbonate-silicate cycle.

2. Töysä T, Hänninen O (2017) Soil pH, Ca and Mg Stability and pH Association with Temperature and Groundwater Silicon.
3. Toysa T, Hänninen O (2015) Agro-Geology and CHD in Finland. JJ Agriculture 1(2): 006.
4. Toysa T, Hänninen O (2016) Soil weathering, silicon and CHD in Finland. JJ Agriculture 2(1): 008.
5. Toysa T (2018) Regional Groundwater Hardness and Silicon, Cropland Fertility and CHD in Finland. Biomed J Sci & Tech Res 2(1): 6
6. Töysä T (2018) Rainy Days, Geographic Coordinates, Vitamin D, Silicon, Selenium and CHD in Finland in 1962-2014. Biomed J Sci & Tech Res 10(1).
7. Lahermo P, Tarvainen T, Hatakka T, Backman B, Juntunen R, et al. (2002) The film was a thousand-Suomenkaivosienfysikaalis-chemical quality in 1999. Summary: One thousand wells - the physical-chemical quality of Finnish well waters in 1999. Geological Survey of Finland, Report of Investigation 155, and Groundwater database of Geological Survey of Finland 2017.
8. (2015) The most commonly known species is the average acidity of the ja_86_90.xls 117.50 KB, (Acidity and Mineral element content per soil type in Finnish Rural Centers 1986-1990. Eurofins Viljavuuspalvelu Oy, email: viljavuuspalvelu@eurofins.fi Address: Eurofins Viljavuuspalvelu Oy PL 500 FI-50101 Mikkeli, Finland.
9. Töysä T (2018) Regional associations of CHD and musculoskeletal morbidity with environmental and geographic factors - e.g. Ca, Mg, Si, Sn. Biomed J Sci & Tech Res.
10. Temperature: Average annual temperature pp. 1981-2010.
11. (1988) Official Statistics of Finland: Farm Register. ISSN = 0784-8404. 1988. Agriculture and forestry 1990:2 Helsinki: National Board of Agriculture. Copyrights by Maanmittauslaitos (MML), p. 16.
12. White A, Handler P, Smith EL (1968) Principles of Biochemistry. Mc Graw-Hill Book Company/Kōgakusha Company, LTD. Table 5.3: pKa Values of some useful and biologically important compounds, on pp. 100.
13. (2018) Carbonic acid.
14. (2018) Housecraft and Sharpe, Inorganic Chemistry, (2nd edn), Prentice-Pearson-Hall 2005, in Carbonic acid pp. 368.
15. Hartikainen H (2005) Occurrence and chemistry of selenium in Finnish soils. 18-24. Agrifood Research Reports 69. Proceedings Twenty Years of Selenium Fertilization. Euroala M (Eds.). Helsinki, Finland, p. 18-24.
16. (2018) Orthosilicic acid.
17. (2018) Kieselsäure.
18. Belton DJ, Deschaume O, Perry CC (2012) An overview of the fundamentals of the chemistry of silica with relevance to biosilicification and technological advances. FEBS J 279(10): 1710 1720.
19. (2018) Silanol.
20. (2018) Ortophosphoric acid.

ISSN: 2574-1241

DOI: [10.26717/BJSTR.2018.12.002259](https://doi.org/10.26717/BJSTR.2018.12.002259)

Töysä T. Biomed J Sci & Tech Res



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