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GEOCHEMISTRY OF FRESHWATER CALCAREOUS SEDIMENTS AND LONGEVITY IMPACTS OF THEIR APPLICATION TO ACIDIC SOILS OF EASTERN LITHUANIA

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Abstract. Numerous investigations on the quaternary depositions of natural calcareous sediments and their use for soil conditioning have been carried-out in the Baltic region. Locally sourced freshwater limestone were formerly introduced (1950s) for soil liming, due to the absence or limited availability of appropriate industrial materials. Nowadays, with a greater awareness and understanding of the CO_2 issues surrounding the production of industrial lime (intensively heated during manufacture), together with increasing costs of its production and transport, attention has returned to previous approaches. The main aim of this study was the identification of geological distribution peculiarities of freshwater limestone depositions, spatial and vertical geochemical variation and modelling of their previous agricultural use in acid soils regions. Geochemical composition data of local lake limestone has been lacking in Lithuania. Studies reveal that the quality parameters of sediments mostly align with the minimum for standard lime requirements (EN ISO 12945:2008), but materials are geochemically diverse even between layers of the same deposit. Tests show calcareous materials are especially rich in total manganese (3500 ppm) and slightly lower was total barium concentrations (490 ppm). Just a few mg kg^{-1} less were total concentrations of silver, boron, cobalt, chromium, copper, gallium, nickel, lead and vanadium. Former use of these sediments for liming purposes with regard to the national hygiene norm (HN 60:2004) controlled elements disclaim direct risks of soil pollution by higher heavy metals and rare elements accumulation. Previous liming studies indicate natural limes offer slow acting degradability compared to industrial products (dust limestone) and longer lasting liming effect. However, heavy metals and rare elements applied to soils are locked in topsoil (diffusion is mainly limited to depth of soil tillage). Unfortunately, cessation of liming and accelerated soil acidification promotes increased element mobility, which raises the risk of higher accumulations in crops, and their transfer to the food chain and/or their transport to groundwater.

Keywords: geochemistry, horizontal and vertical variation, soil liming; soil acidification; environmental impact assessment.

1. Introduction

Lithuania is located in the humid zone, where mean annual precipitation (748 mm) exceeds mean evapotranspiration (512 mm) (Kilkus *et al*. 2006) and soil acidification is an ongoing natural process (Bolan *et al.* 2003). In the mid-1960s, before the introduction of large-scale agricultural technologies, acid soils (pH in KCl $\leq$ 5.5) covered 41% of agricultural land, which has a national territory of 11,660 km^2. However, in some Western and Eastern Lithuanian administrative districts, where there had been limited human intervention, 70–93% of soils had a pH value of < 5 (Savickas 1973). Therefore, natural calcareous materials (lime and marl) were valued by farmers, as soil additives, for their positive effects on the chemical and biological activity of the soil and for their marked effect on soil structure (Dodgshon 1978). For instance, field experiments (since 1984) using calcareous sapropels in Eastern Lithuania demonstrate their long-term effect on luvisol pH that is evident for > 20 years (Baksiene, Janušienė 2005; Baksiene *et al.* 2006). Other experiments (since 1948) in western Lithuania show the application of calcareous tuff and travertine has a lasting effect on the neutralising of albeluvisols acidity and increasing of crop production (Ozeraitiene *et al.* 2006). Along with many neighbouring countries (e.g. Aaby 1979 (Sweden); Bartosh 1969a, 1969b; Danilans 1957 (Latvia); Mannil 1964 (Estonia); Irion, Muller 1968 (Germany)), many investigations of quaternary natural calcareous sediments have been carried-out and, once detailed descriptions and depositional maps were created (1950–1960), a geochemical basis for their use in soil conditioning (liming) was determined (Savickas 1957). Since pure calcium carbonate $CaCO_3$ rarely exists in natural calcareous deposits, for practical purposes, sediments consisting of > 85% of $CaCO_3$ are normally considered to have high-calcium content. As such, the calcareous sediments in Eastern Lithuania were intensively excavated in the 1960's (Gasiuniene, Kadunas 1997). Compared to the industrial lime dusts

(95–98% $CaCO_3$) (used in Lithuania since 1976), natural calcareous deposits have greater compositional variability and are often enriched with organic matter (OM). Therefore, the physicochemical characteristics of calcareous sediments may influence soil toxicity – one such characteristic is sediment OM content (Lacey *et al*. 1999). Transport of trace metals from the soil to a plant involves chemical, physical and biological processes (such as diffusion, adsorption, absorption, plant growth, transpiration rate, amongst others) in the soil, the soil rhizosphere and in the plant itself (Baltrėnaitė, Butkus 2007). To date, there are no known national Lithuanian archives that record the analytical purity and geochemical composition of freshwater calcareous sediments and no documented studies into the limitations and impacts of their use. Therefore, this work aims to: (i) assess the characterisation and distribution of freshwater limestone deposits; and (ii) evaluate the impact of their previous agricultural use in the acidic soil regions of Eastern Lithuania.

2. Materials and methods

2.1. Desktop study

Existing documentation on freshwater calcareous deposits, their excavation and applications in Lithuania are limited. Available information from the national geological survey, accessible land use archives and noted recommendations of soil studies have been combined with regional soil acidity maps to identify those sites used in this study (Vilnius, Molėtai and Trakai district municipalities (Fig.1)). Soil acidity is sizeably pronounced in these locations and represents more than half of the total agricultural soils in the districts (Table 1).

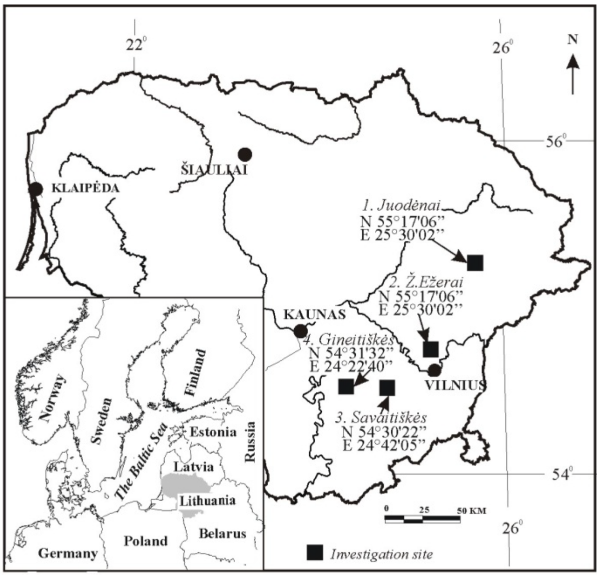

Fig. 1. Location map showing the inter-site sampling scheme

Table 1. Distribution of acid and exposed to acidification soils (pH in KCl ≤ 5.5) in East Lithuania (Mažvila *et al.* 1998)

Distribution of acid and exposed to acidification soils	Administrative districts			
	Vilnius	Trakai	Molėtai	Total
	% of acid soils from total agriculture area			
Currently acid soils	35.9	33.8	25.8	26.6
Soils exposed to acidification	32.0	21.6	25.1	25.3
Total	67.9	55.4	50.9	51.9

2.2. Fieldwork

A soil auger was used to define the depositional extent of the calcareous deposits at each site (mainly grasslands) and to interrogate their vertical structure. Selected individual profiles were then excavated, their morphology described and sediment samples collected for laboratory analyses (Fig. 2). To quantify the vertical variability of deposit geochemical composition more detailed sampling was done at the site Balsys (Ž. Ežerai) (each 10–15 cm in relation to changes in profile morphology, from depth of 25 to 270 cm).

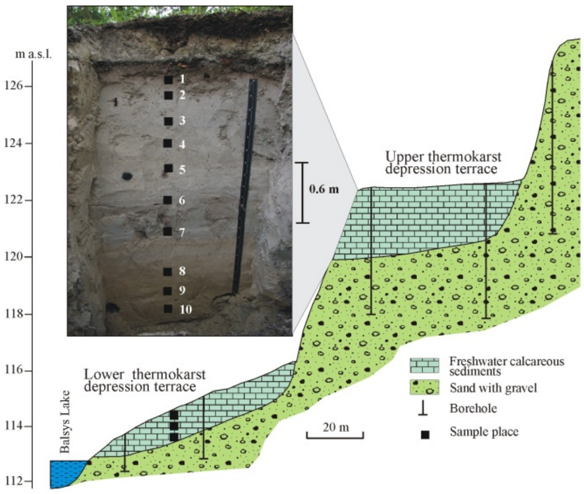

Fig. 2. Scheme and profile of Balsys lake freshwater limestone deposition

2.3. Laboratory analysis

Using the same approach as the geochemical survey of Lithuania (Kadunas *et al.* 1999), atomic emission spectrography (AES), calibrated to international standards with low background limits, was used to measure 13 elements of < 1 mm size fraction of each sample and the spectrum lines were deciphered by microdensitometer DM-100.

Total soluble alkalinity titrimetric method for the determination of the basicity of soluted material was applied. The principle of the procedure consists in solution of a test portion in water, filtration of the solution and titration with a standard volumetric solution of hydrochloric acid in presence of methyl orange as indicator (ISO 740:1976). ISO 10694:1995 method (determination of organic and total carbon after dry combustion) for the determination of the amount of organic matter (OM) was applied.

2.4. Data analysis

All data was analysed using Minitab-15 software (Guide to Minitab, 2007), to reveal the basic statistics and to determine non-parametric Kruskal-Wallis tests for inter-site variations and Mann-Whitney test for intra-site variations.

3. Results

3.1. Availability of freshwater calcareous sediments

Summarising geological surveys, profiles of their lithological composition and aerial photography sets, it was determined that quaternary depositions of freshwater calcareous sediments are common in SE Lithuania and are represented by two major types, all containing minimal, if any, magnesium. These beds dominantly are comprised of calcareous tufa and lake limestone. The Geological survey of Lithuania (in 2001) reported 235 freshwater limestone deposits (90 of calcareous tufa and 145 of lake limestone) in Alytus, Vilnius and Utena provinces. The revision showed the major part of these deposits having minimal resources and only small thickness of the useful bed (Geological survey of Lithuania, Annual report, 2001) and unfortunately many have been previously excavated but without records available. For application of these materials, physical properties are very important because it is noticeable that in organic matter rich deposits, natural humidity of materials varies in higher range and can reach up to 75% (organic rich calcareous tuff) (Kacas *et al*. 1955). Excavation of soft and 'more pure' lake limestone has been prioritized compared to other freshwater limestone. A scheme of the vertical structure of deposits demonstrates favourable conditions of deposit excavation after removal of peat layer (Fig. 2).

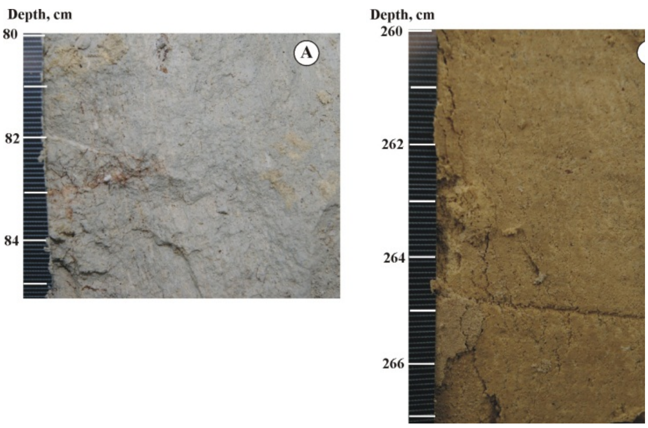

Fig. 3. Morphologically different profiles of freshwater limestones

3.2. Variability of freshwater calcareous sediments

In Lithuania the thickness of limestone depositions is relatively thin, with deposit mean values at 0.5–1.0 m. Thickness of investigated depositions varied from 0.3 to 2.7 m. Vertical sectional view of selected lake limestone deposits was found often morphologically uneven, with easily noticeable variation in colour, texture or both (Fig. 2–3). Such lamination is demonstrating cyclic sedimentation of carbonates, for which morphologic variation is found closely related to chemical and agronomical parameters of materials. Visible morphological variation chemically can be related to % of organic matter, concentration of Fe and neutralising values. Inter-site variations were calculated for each parameter and Kuskal-Wallis test (Table 2) demonstrated significant differences between all sites for neutralising value.

While limestone from Savaitiskes contains the lowest amount of OM% and Gineitiskes contain the largest OM%, they significantly differ from the Juodenai and Balsys sites. Balsys and Savaitiskes limestone are similar in Fe concentrations, but differ significantly from Juodenai – which is richest in Fe (0.82%).

There is a growing interest in the geochemical parameters of freshwater carbonates from various environmental disciplines, with recent studies providing new insights into the behaviour of trace elements within tufa systems (Rogerson *et al*. 2008). Geochemical purity data has been unavailable in Lithuania, and data from other countries (Geochemistry of Sedimentary Carbonates 1990; Jochmann *et al*. 1997; Hood *et al*. 2004) has been used.

Our testing is exploring much wider inter-site geochemical variations compared to neutralizing values of sediments. Results indicated that the elements which contribute to concentration ranges can be divided into three groups (Table 3) – ≤ 10, 10–100, ≥ 100. Group one: manganese (Mn) and barium (Ba), group two: boron (B), nickel (Ni), copper (Cu), chromium (Cr), lead (Pb) and vanadium (V) and group three: cobalt (Co) and silver (Ag). The first group are sediments showing the presence of Ba and Mn in their highest concentrations (mean 364.4 ppm and 518.9 ppm accordingly) with maximum of 1600 ppm for Mn. Both these elements demonstrate the widest range of statistical parameter variation. B, Ni, Cu, Cr, Pb, and V varied in the range of 0.6 (V) to 50 (B) ppm, with mean values at 6.7 (V) –10.6 (B) ppm.

To illustrate intra-site vertical variation, profile data from the site of Balsys (each 10–15 cm in relation to changes in profile morphology, from depth of 25 to 250 cm) has been assessed statistically (Table 4). All tested elements presented in vertical variation of geochemical composition appear to be greater for both – high and lower concentration in presented elements. Ba (ranging between 180–410 ppm) and Mn (ranging between 20–190 ppm) demonstrate highest concentrations among other deposits.

3.3. Impacts and longevity of freshwater calcareous sediment applications to soil

In contaminated soils, the total metal content often represents a long-term, multiscore input of metal pollutant elements with complex historical background (Van Oort *et al*. 2006). The higher concentrations of

Table 2. Kuskal-Wallis test on major specific calcareous sediments properties in different sites (n = 12)

sites	Test results								
	Fe% *(H = 3.04 DF = 3 p = 0.385)			OM% *(H = 6.16 DF = 3 p = 0.104)			Neutralizing capacity % *(H = 5.44 DF = 3 p = 0.142)		
	median	rank	Z	median	rank	Z	median	rank	Z
Balsys	0.31	3.0	–1.55	2.61	3.7	–1.03	45.21	5.0	0.00
Juodenai	0.82	6.3	1.03	2.71	5.3	0.26	42.87	2.7	–1.81
Savaitiškės	0.40	4.0	–0.39	2.24	1.0	–1.55	44.71	5.0	0.00
Gineitiškės	0.72	6.5	0.88	4.86	8.5	2.05	50.30	8.5	2.05

* H – Kuskal-Wallis test statistic; DF – degree of freedom; p – significance.

Table 3. Descriptive statistics of inter-site geochemical composition variation, ppm (parts per million) (n = 12)

Elements	Basic statistics				Kruskal-Wallis test	
	Mean	Standard deviation	Minimum	Maximum	H	p
Mn	518.9	546.9	80	1600	7.2	0.07
Ba	364.4	112	230	490	7.3	0.06
B	10.6	15.5	1.8	50	4.0	0.26
Ni	9.7	10.4	2	35	5.1	0.17
Cu	7.7	8	1.7	26	2.0	0.57
Cr	7.6	10.9	1.5	35	4.9	0.18
Pb	6.9	2.8	5	13	2.8	0.43
V	6.7	11.7	0.6	37	4.1	0.25
Co	4.2	3.3	1	9	4.9	0.18
Ag	0.1	0.1	0.1	0.3	5.4	0.14

Table 4. Summary statistics of vertical intra-site geochemical composition variation, ppm (parts per million) (n = 10)

Elements	Summary statistics				Mann-Whitney test	
	Mean	St. deviation	Minimum	Maximum	*W	*p-value
Ba	295	71.8	180	410	31	0.108
Mn	110.2	72.6	20	190	20	0.933
Ag	0.1	0	0.1	0.1	0	–
B	2.2	0.5	2	3.5	25	0.554
Co	1	0	1	1	0	–
Cr	2.1	1.1	1.5	4.5	26.5	0.398
Cu	5.9	3.3	2.7	12	20	0.933
Ni	5.7	2.2	3	10	11	0.108
Pb	4.5	0.7	4	6	30	0.151
V	0.6	0.2	0.5	1	34	0.035

*W- Mann-Whitney test statistic; *p-value – significance

heavy metals in Central Europe topsoil are found directly related to human activities. Cd, Cu, Hg, Pb, Zn present high correlations with agriculture (r = 0.7) and with quaternary limestone (r = 0.41) (Lado *et al.* 2008).

All too often, soil-liming benefits are emphasised without mentioning its important environmental and ecological roles. Liming can prevent the uptake of radionuclide and heavy metals by plants (Lietuvos dirvožemiai 2001). Otherwise, soils and groundwater face greater pollution risk. Moreover, acidifying reactions of solutions in the landscape entail an increased aggressiveness of chemical toxic substances, suppression of microbiological processes, disturbances of metabolism and nutrients exchange, spreading of endemic diseases and degradation of material values. Increasing the pH of a soil by adding $CaCO_3$ changes the solubility of most mineral elements substantially, the several distinct patterns observed being governed by, for example, ionic properties and charge, affinity for organic compounds, and pH-dependent formation and solubility of complexes. Inversely related to pH are soil solution concentrations of Al, B, Ba, Bi, Cs, Ce, Eu, Ga, Ge, Fe, Li, K, Rb, Na, Th and Ti (Tyler, Olsson 2001).

Our studies have revealed that quality of lake limestone deposits have been acceptable for their former agricultural use irrespective of geological genesis of deposit, geographical location, deposit thickness and vertical variability. On average, neutralizing capacity recorded at 49% demonstrates it was a favourable material for former acid soil liming applications.

According to recommended application rates and periodicity of liming we model the concentrations of elements in topsoil layer. Investigating applications of former lake limestone to soil ranging in amount equal to 5 t per ha $CaCO_3$ single application and three liming cycles within 15-years demonstrate negligible concentrations of HN controlled elements have been introduced. Their levels are as low as 0.59% of MPC if we speculate for Zn concentrations at the level of detection. Ba is the second highest modelled concentration element, demonstrating about 50% lower values at 0.29% of MPC. Mn, Ag, B, Co, Cr, Cu, Ni, Pb, V and speculated at detection limit Mo and Sn, all range below 0.12% of MPC.

4. Discussion

The low inter-site differences displayed by our data suggest geochemical variations can not be assessed with confidence. Intra-site variability could be large enough to mask inter-site variability in sediment geochemistry. Previous findings on freshwater limes applications disclaim direct risks of soil pollution (relating to hygiene norm) by higher heavy metals and rare elements accumulation in soil. However, this does not eliminate the effect on the large variety of forms of life sensitive to eco-toxic concentration for any substance. In spite of this, results do not correspond to the risk of accumulation in crops and transport to ground waters as long-term effect on soil pH exists, because it is one of the main parameters of mobility of selected elements. Whole-catchment liming experiments clearly demonstrate that liming produces a long-term effect on water quality (Traaen *et al*. 1997). Latest results of long-term field experiments on calcareous sapropels (Baksiene, Janusiene 2005; Baksiene *et al.* 2006) in Eastern Lithuania (lasting since 1984) demonstrate that their effect on luvisol pH is evident for more than 20 years. Other experiments in Western Lithuania (since 1948) show that application of calcareous tuff and travertine has, at least for 55 years, a lasting effect on neutralising of albeluvisols acidity and increasing of crop production (Ozeraitiene *et al.* 2006).

Geochemical evaluation of soils in long-term field experiments conclude statistically reliable deviations of Co, Cu and Sr total concentrations as compared to the background levels of 18 elements tested (Marcinkonis *et al.* 2005). Assessment of trace elements enrichment or depletion, using total concentrations of Al, Fe and V (control topsoil and B horizon) as reference elements show Sr accumulation, which means that Sr concentrations have profoundly changed during decades of soil fertilization and liming in Lithuanian soils (Marcinkonis 2008). Concentration of some elements in soils can be efficiently controlled by the application of phytoremediation technique. According to the mathematical modelling results of soil remediation with regard to heavy metals obtained by Jankaitė (2009), it has been shown that when soil is cleaned with grassy vegetation, copper concentrations decrease and, therefore, we can draw a conclusion that a selected mixture of grassy vegetation may be applied for the removal of heavy metals from soil.

It is surmised that lake limestone is a pure liming material, and because of its long-lasting pH regulating effect, which might have indirect influence on accumulation of HN controlled elements, when applied with mineral and organic fertilizers.

5. Conclusions

Three general conclusions can be drawn from this work:

(i) Freshwater calcareous sediments are geochemically diverse even in between layers of the same deposit, and tested calcareous materials are especially rich in total manganese (3500 ppm) and total barium (490 ppm);

(ii) Long-term and intensive use of calcareous freshwater lake limestone for soil liming appears harmless, from a direct soil pollution viewpoint; and

(iii) Former applications of freshwater calcareous sediment offer indirect influences on long-term soil pH-regulating effects.

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GEOCHEMINĖ GĖLAVANDENIŲ KALKINGŲJŲ NUOSĖDŲ SUDĖTIES VARIACIJA IR JŲ NAUDOJIMO PALIKIMAS RŪGŠTIEMS RYTŲ LIETUVOS DIRVOŽEMIAMS

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S a n t r a u k a

Baltijos jūros regione atlikta nemažai tyrimų, kurių sudėtinė dalis – kalkingųjų kvartero nuosėdų tyrimai ir jų naudojimas dirvai gerinti. Gėlavandenės klintys buvo naudojamos dirvožemiams kalkinti trūkstant pramoninių kalkinių medžiagų. Šiuo metu jomis vėl domimasi, nes jos leidžia išvengti CO_2 emisijų, susidarančių gaminant pramonines kalkines medžiagas (kaitinant klintis), jų naudojimas yra ekonomiškai patrauklus. Pagrindinis atliktų tyrimų tikslas – nustatyti geologinio paskirstymo ypatumus gėlavandenėse kalkingosiose nuosėdose, horizontalųjį bei vertikalųjį geocheminį pasiskirstymą ir ankstesnio šių medžiagų naudojimo žemės ūkio paskirties rūgščių dirvožemių regionuose išliekamąjį poveikį. Geocheminė gėlavandenių klinčių sudėtis anksčiau Lietuvoje nebuvo tirta.

Atliekant tyrimus nustatyta, kad kalkingosios nuosėdos dažniausiai atitiko minimalių standartinių kalkinių medžiagų reikalavimų kokybės rodiklius (EN ISO 12945:2008), bet geocheminė šių medžiagų sudėtis yra labai įvairi net skirtinguose to paties klodo sluoksniuose. Buvo nustatyta, kad išanalizuotose kalkingosiose nuosėdose yra ypač daug suminio Mn (3500 ppm) ir šiek tiek mažesnė Ba koncentracija (490 ppm). Tik keli mg kg^{-1} ar mažiau buvo rasta suminių Ag, B, Co, Cr, Cu, Ga, Ni, Pb ir V. Modeliuojant buvusį šių nuosėdų naudojimą kalkinimo tikslais, vertinant pagal higienos normoje (HN) kontroliuojamų elementų koncentracijas, paneigtas tiesioginis dirvožemio taršos pavojus sunkiaisiais metalais ir retaisiais elementais. Šiomis medžiagomis kalkintuose dirvožemiuose sunkiųjų metalų ir retųjų elementų atsargos yra ilgam imobilizuotos (mobilesnės iš esmės yra tik armens sluoksnyje). Tačiau dėl nutrauktų kalkinimo darbų spartėjant dirvožemio rūgštėjimui, šių elementų mobilumas didėja, taip pat padidėja grėsmė susikaupti augaluose, patekti į mitybos grandinę ir užteršti gruntinius vandenis.

Reikšminiai žodžiai: geochemija, horizontalioji ir vertikalioji variacija, dirvožemio kalkinimas, dirvožemio rūgštėjimas, higienos normos.

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