USE OF GYPSUM TO REDUCE EFFLUENT AND FERTILISER NUTRIENT LOSSES TO WATERWAYS

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Abstract

Agricultural systems are leaky and losses of phosphorus, nitrogen, organic matter and suspended solids can impact on water quality. While direct contamination of surface water can be prevented by avoiding livestock access and effluent discharge, it is less straightforward to prevent losses over and through soil that can eventually reach waterways. These less direct losses are affected by complex hydrological and chemical factors.

Gypsum has long been used as a soil conditioner and fertiliser but it is only recently that gypsum's potential for reducing agricultural emissions to waterways has been researched. Gypsum ($CaSO_4.2H_2O$) can improve soil aggregation through calcium induced flocculation of particles and sulfate induced leaching of excess sodium. Such effects can reduce surface runoff volume by improving water infiltration into soil. Improved stability of aggregates reduces the potential loss of soil particles to waterways both over and through soil. The calcium ions can also increase precipitation of phosphate ions either directly as calcium phosphate or indirectly by increasing availability of aluminium ions. Increased ionic strength of soil solutions due to dissolution of gypsum may also increase adsorption of phosphate ions and organic matter to soil particles. These multiple modes of action can thus partially address both hydrological and chemical factors influencing nutrient losses.

Gypsum application has been reported to at least halve phosphorus losses in some conditions but results have varied between experiments. Variability may be partly due to experimental design (insufficient time for gypsum to take effect in the soil, or high simulated rainfall conditions) but could also be related to soil type and existing exchangeable calcium level in the soil. An understanding of the causes of variability will assist in the choice of target areas for optimal economic use of gypsum to reduce phosphorus losses. Surface runoff of nitrogen, organic matter and soil particulates, as well as drainage losses of of nutrients in organic form can also be reduced with gypsum. The reduction in losses of organic forms of nutrients may be particularly important for mitigating effluent application losses. Research into the best use and conditions affecting gypsum efficacy would appear worthwhile to help reduce agricultural impacts on waterways in New Zealand.

Nutrient Loss to Waterways

Nutrients lost from agricultural systems can reduce waterway quality through eutrophication. The main nutrients involved in eutrophication are nitrogen and phosphorus and there can also be an impact from organic carbon and sediment lost from agricultural soils. Over the last 20 years in New Zealand there has been a substantial reduction in livestock access and effluent discharge into waterways. This change has significantly reduced direct contamination of waterways but nutrient losses can still occur through surface runoff and drainage losses of nutrients (see Figure 1). Drainage losses can include leaching, preferential flow (bypass flow) e.g. through cracks and the process of interflow which is flow down a slope but within the soil. These less direct losses are affected by complex hydrological and chemical factors.

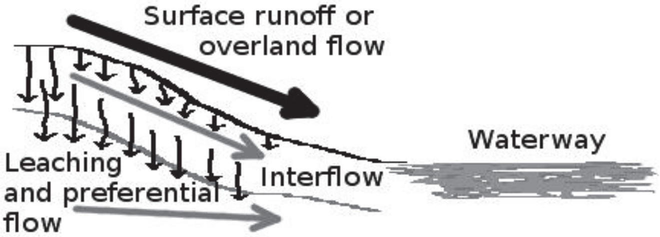

Figure 1. Nutrient loss pathways

Surface runoff losses are influenced by slope, the proportion of water that fails to infiltrate the soil, the aggregation of soil particles and the level of nutrients present in the surface including more easily lost soluble nutrients. Runoff can occur below the soil surface also and this movement through the soil matrix is termed interflow. Interflow loss of nutrients is affected by slope, any impedance to deeper drainage, the network of soil pores and the chemistry of both nutrients and the minerals or ions present that may bind them. True leaching involves drainage of water through the soil matrix and this is influenced by the amount of drainage, the network of soil pores and the again the chemistry of the nutrients and the soils ability to bind them. Preferential flow bypasses the soil matrix e.g. through cracks and can allow the loss of nutrient forms that may have limited movement through the soil matrix.

Modes of Action for Gypsum Reducing Nutrient Loss

Gypsum is calcium sulfate ($CaSO_4.2H_2O$) and provides a readily available source of calcium and sulfate ions due to its partial solubility. Gypsum has been used for decades as a soil conditioner and fertiliser (Shainberg et al., 1989) but it is in comparatively recent years that gypsum's ability to reduce nutrient losses has been researched.

Soil structural improvement resulting from gypsum application can include reduced surface crusting and sealing, improved water infiltration (thus reducing potential for runoff), soil aggregation, drainage and aeration with subsequent benefits for plant growth. Benefits to plant growth, including root condition, may also result from the calcium and sulphur nutrition provided by gypsum. In the case of sodium build up which can result from some effluent types (dairy factory effluent in particular), there is a clear benefit of gypsum in assisting the leaching of sodium, further benefiting soil structure particularly where there is dispersive clay present.

The mechanisms for gypsum reducing nutrient losses can be related to several mechanisms. Surface runoff losses may be reduced by improved water infiltration and aggregate stability. The release of calcium ions from gypsum may also impact on phosphate availability for environmental losses. This could be through an increased ionic strength of soil solutions causing increased mineral adsorption of phosphate and also the potential formation and precipitation of calcium phosphate minerals. These calcium interactions are discussed in detail by Uusitalo et al. (2012). These authors also discuss the work of Pavan et al. (1984) which demonstrated that gypsum calcium could release aluminium from exchangeable sites resulting in the precipitation of aluminium polymers which could contribute to phosphate retention in acid soils. Improved aggregate stability in some soils may reduce drainage losses of phosphate and other nutrients particularly losses in organic form.

Research Results for Gypsum Affecting Phosphorus Losses

Much of the research on gypsum reducing nutrient flow to the environment has been undertaken in the last decade and has focussed on mitigation of phosphorus losses. The results have varied due in part to issues in experimental design, variation in gypsum rates and differences in soil conditions. Some of the greatest reductions of phosphate losses due to gypsum have been reported in surface runoff losses where a combination of soil surface structure and soil chemistry effects can have a combined mitigation impact. Gypsum application at 5 tonne/ha equivalent reduced surface runoff of phosphorus in a Florida study by 85% and 60% for dissolved reactive phosphorus and total phosphorus respectively (Favaretto et al., 2006, in a laboratory study on Florida silt loam). The factors affecting this and other experimental results are reviewed here to help direct gypsum research in New Zealand.

Experimental Design

High rates of simulated precipitation in some gypsum studies (e.g. Favaretto et al., 2006 with 30mm/hr for 90 mins; O'Connor et al., 2005 with 71 mm/hr; Stout et al., 2000 with 50 mm/hr for 30 mins) may have resulted in low estimates of the ability for gypsum to reduce surface runoff losses of phosphorus as the physicochemical nature of the soil surface and sediment runoff would be affected according to Uusitalo et al. (2012) who conducted their trial with 5 mm/hr simulated rainfall for five hours in each of two consecutive days. For any simulated rainfall research in NZ, rainfall should be modelled on locally representative rainfall risks.

Some experiments have involved application of nutrient and gypsum just prior to simulated rainfall events. In a Texas sandy loam, McFarland et al. (2003) found that a large application of gypsum (15 tonne/ha) was not effective at reducing phosphorus runoff (though there was a small reduction in soil available P) while alum application effectively reduced phosphorus runoff. There could be several reasons for no gypsum e3ffect being evident in that experiment including the soil already having very high calcium availability and the artificial rain simulation events that were assessed for runoff phosphorus level were conducted just three and five days after gypsum and effluent application giving insufficient time for any effects on soil structure or very limited time for reaction between gypsum and effluent phosphorus. Contrasting this result, Brauer et al. (2005) also studying a Texas sandy loam (with very high available P) found that gypsum was effective at reducing dissolved reactive phosphate. Torbert et al. (2005) also found that gypsum had a significant effect on runoff of reactive phosphorus in an initial 10 minutes of runoff event but did not reduce runoff beyond that. This experiment involved application of the gypsum treatment just before applying manure and subjecting the soil to run off events which again would not have allowed time for gypsum dissolution or for effect on soil structure and water infiltration.

The source of gypsum could also have a significant effect on results. Some international research has used phosphogypsum (a by-product of phosphate fertiliser manufacture). This may behave differently from naturally mined gypsum since there can be a significant amount of phosphorus still present in the product. The Finnish research (Ekholm et al., 2012; Uusitalo et al., 2012) utilised phosphogypsum with a phosphorus content of 1.6 g P kg^{-1} that, at the rates trialled, would have delivered between 5 and 10 kg phosphorus per hectare

(Uusitalo et al., 2012). Even so they saw significant reduction in phosphorus runoff losses. Delgado et al. (2006) applied phosphogypsum of higher phosphorus content (4 g P kg^{-1}) at higher gypsum rates (13 and 26 tonne/ha) resulting in around 56 to 112 kg phosphorus applied per hectare. Even in such a situation so they reported no significant increase in phosphorus leaching compared to control and significantly less that with manure applied at the same rate of phosphorus applied.

Another element in research design is that large catchment scale studies are often not statistically replicated and so there is some uncertainty over whether the difference between gypsum and control areas (or what proportion) was due to gypsum. This is the case in the Australian research of Cox et al. (2005). The results of field work of Ekholm et al. (2012), however, were similar to those of replicated work using rainfall simulation in the same catchment (Uusitalo et al., 2012). Uustitalo et al. (2012) reported that gypsum at 6 tonne/ha reduced dissolved reactive phosphate runoff by 50% and particulate phosphate by 70% compared to control (gypsum applied once over three years). Ekholm et al. (2012) estimated a 64% reduction in particulate phosphorus runoff and 29% reduction in dissolved reactive phosphorus runoff through the use of 4 tonne/ha gypsum (also once over three years).

Gypsum Rates

Gypsum application rates have varied between studies from 700 kg/ha to 50 tonne per hectare. Gypsum rate studies showed that around 3 to 5 tonne can be effective at reducing surface runoff and generally improving soil structure (Agassi et al., 1982) and for that reason, Favaretto et al. (2006) chose 5 tonne per hectare as a rate for their trials. Successful results for Finnish clay soils of around 4 tonne/ha every three years (Ekholm et al., 2012; and Uusitalo et al., 2012 who used 3 tonne and 6 tonne rates per hectare) indicate that such moderate rates are worthy of research focus in New Zealand. Higher rates may not be economically viable

For significant mitigation of nutrient losses it appears that gypsum needs to be applied at sufficiently high rates. The rate of gypsum used needs to cause significant structural or chemical change to the soil. In a Texan study, 5 tonne per hectare of gypsum was found to be effective at reducing dissolved reactive phosphorus levels while 1.5 tonne per hectare was ineffective (Brauer et al., 2005). These results imply that the required rates of gypsum for effective nutrient loss mitigation are well in excess of the level of gypsum applied incidentally through the use of superphosphate (which is around two thirds gypsum by weight but typically applied at 100 to 500 kg/ha).

Soil Conditions

Gypsum has been found to reduce the mobility of phosphorus in a range of soil types and conditions. Although a positive effect of gypsum on soil structure is mostly expected on dispersive clay soils or high sodium soils (Shainberg et al., 1989), significantly improved soil structure has also been reported in silt loams (with consequent reduction in runoff losses e.g. Favaretto et al., 2006; Tirado-Corbala, 2010) and sandy loams (e.g. Lehrsch et al., 1993). Gypsum applied to five widely varying Irish soils was found to reduce water extractable phosphorus by 14 to 56% and water soluble organic phosphorus by 10 to 53% (Murphy and Stevens, 2010). Even in a sandy soil, gypsum reduced phosphorus leaching by 20 to 49% from laboratory columns (Zhu and Alva, 1995).

Some of the mechanisms of phosphate loss mitigation by gypsum may vary with soil pH. Precipitation of phosphate as calcium phosphates (and consequent reduction in mobility) is more likely to occur at higher soil pH and immobilisation by aluminium (which could be an indirect effect of gypsum as described by Pavan et al., 1984) is more likely at lower soil pH. The effect of increased ionic strength of the soil solution and effects on soil structure may be less pH dependent.

Boruvka and Rechcigl (2003) found that gypsum amendment increased soil P retention several times relative to a control. These authors suggested that the retention effect may require an increase in soil pH (by liming at the same time) but this does not fit with the effects seen on a variety of soil pH levels.

One consideration is that soils can have a large degree of microvariation in pH (see Bishop and Quin, 2013) and this may explain effective reduction in water soluble phosphate levels in a wide pH range of gypsum treated soils. In a study of three acid soils and one neutral soil, Callahan et al. (2002) reported a consistent reduction in water soluble phosphorus in all soils. In a further study of three acid soils, Stout et al. (2003) reported a 38 to 57% reduction in water soluble phosphorus due to gypsum application. Gypsum amendment reduced soluble phosphorus levels by 40 to 63% over a wide range of soil pH, manure loadings and redox conditions (anaerobic/aerobic) in a Florida study by Anderson et al. (1995).

In a soil with strong texture contrast, Cox et al. (2005) found that gypsum reduced surface runoff volume and its phosphorus concentration (by 35%), but found an increase in interflow volume. The interflow phosphorus concentration tended to be lower (by 11%) with gypsum treatment but given the larger volume, the authors described the overall reduction in phosphorus loss as “not marked”. Since the overall surface and interflow runoff was greater in the gypsum area, it remains possible though that there was a difference in incident water in the unreplicated study of one treated and one untreated catchment. The authors reported significant improvement in soil structure related to gypsum application and suggested that increased porosity may be responsible for the relatively small effect of gypsum on interflow runoff of phosphorus. In many soil types, the reduction of overflow is of greater significance than the potential for interflow through soil. The effect of any increased water infiltration on soils that have significant interflow losses (e.g. with strong contrast between textures in the soil profile) should be assessed before targeting such areas with gypsum application.

Mitigation of Drainage Losses of Phosphorus with Gypsum

Loss of phosphate into waterways is often most significant through surface runoff but it is well established that there can also be significant losses of phosphate through interflow, preferential flow and leaching in a variety of soil types. Webb et al. (2010) discuss how the traditional (pre 1980’s) concept that phosphorus is not lost through drainage has been proven incorrect. This is partly through some soils being prone to phosphate leaching e.g. porous well drained soils, particularly with low P retention status (Carrick et al., 2013; Webb et al., 2010). Drainage losses of phosphorus have been shown to be a particular concern for effluent treated soils (Nash and Murdoch, 1997; Hanly, 2012).

Loss can also be through preferential flow in which ionic P and organic P can be lost through the macropores without going through the matrix of micropores. Soils often described as poorly drained (in terms of matrix flow) can often have more significant preferential flow losses of phosphorus due to soil macropores, worm channels and soil cracks (McLeod et al., 1998). Preferential flow can be particularly significant in the presence of field drains (Monaghan and Smith, 2004; Powlson 1998). Even in the absence of drains, preferential flow can result rapid and deep loss of phosphate (Webb et al., 2010). Research has identified that

that a range of soil types are prone to significant P loss through preferential flow (McLeod et al., 1998; Thomas *et al*., 1997; McDowell *et al*. 2008; Webb et al. 2010).

Favaretto (2002) found that gypsum amendment reduced the leaching of all forms of phosphorus. Zhu and Alva (1994) reported 35 and 54% reduction in phosphate leaching in a sandy soil column leaching experiment with the addition of 4.5 and 9 tonne/ha respectively of gypsum. O'Connor et al. (2005) reported an apparent 33% reduction in phosphorus leaching in a packed column of sandy soil. They considered that aluminium and iron sludge (from water treatment processes) on the other hand, just had localised effects where they were mixed with the soil whereas gypsum was able to dissolve and move through the column.

Nitrogen

Gypsum has been found to reduce the level of surface runoff of total nitrogen (59% reduction in laboratory studies by Favaretto et al., 2006). This is likely related to effects on soil surface structure, water infiltration and generally reduced surface runoff volumes.

The main mechanism for nitrogen losses from many agricultural systems is nitrate leaching. It seems unlikely that soil structural and chemical effects of gypsum application would reduce nitrate leaching directly. There is, however, some evidence of gypsum application reducing the level of organic forms of nitrogen being leached. Organic nitrogen leaching was significantly reduced (almost halved) over a 31 month period after gypsum application (6 tonne/ha) on Finnish clay soil but no significant effect on mineral nitrogen leaching was seen (Uusitalo et al., 2012). Organic nitrogen was a major component of total N leached in that study. The leaching of organic nitrogen has also been identified as a concern in a range of New Zealand soils including some that are not so prone to nitrate leaching (Webb et al., 2010).

Dissolved Organic Carbon

The impact of agricultural land use on eutrophication of waterways is not restricted to phosphorus and nitrogen additions since dissolved organic carbon (DOC) can also contribute. Gypsum application was found to reduced runoff of DOC from Finnish clay soils by 35% compared to control and lime treated soils (Ustitalo et al., 2012). The researchers considered reasons for this could include an increase in the ionic strength of soil solution in turn increasing adsorption of organic matter to soil mineral components and due to the divalent calcium ions providing structural support for larger aggregates (flocculation). Muneer and Oades (1989) also found that gypsum addition generally improved soil aggregate stability and reduced the loss of organic matter.

Sodium

Gypsum is a common recommendation internationally to address the sodium build up and improving soil structure of dispersive clay soils in the face of high sodium levels (Shainberg et al., 1989).

High sodium irrigation water, applied in naturally dry conditions and long term application of some effluents can lead to a build-up of sodium levels in the soil to the detriment of soil structure. The mechanisms of this are well understood (Tillman and Surapaneni, 2002). High sodium levels, particularly in soils with dispersive clay, can lead to issues in soil-water and soil-air relations such as poor drainage, clay pan layers, restricted root growth and restricted plant yields.

Gypsum application can assist in leaching excess sodium from affected soils. The amount of gypsum required to address high sodium effluent effects may be larger than typical agricultural applications (Bond 1998) depending on the Sodium Adsorption Ratio (SAR) of the effluent (calculated using the equation below).

$$\text{SAR} = \text{Na}^{+} / \sqrt{((\text{Ca}^{2+} + \text{Mg}^{2+}) / 2)} \text{ [all cation amounts in cmol}^{+}\text{/100g]}$$

There is not much published information on the level of sodium in New Zealand dairy farm effluent. The sodium level can be influenced by the sodicity of the water used in washing down, sodium level in the feed and dairy hygiene products containing sodium. Longhurst et al. (2000) reported NZ dairy farm effluent nutrient levels but data on sodium levels was restricted to three samples ranging from 25 to 80-mg/L. At these levels, a sodium issue would not be expected. It may be, however, that some effluent levels will be higher than this. In Australia there is more evidence of high sodium issues in some dairy farm effluent samples with SAR values ranging from around 1 to around 9 (DPI, 2012). Even at relatively low SAR values, there can be an impact on soil structure for soils with relatively low electrical conductivity (ANZECC & ARMCANZ, 2000).

Soils receiving dairy effluent may build up sodium over time. There is a special case of farms receiving effluent from dairy factory processing (NZIC, 2002). These effluents can be very high in sodium levels leading to a rise in soil sodium levels over time.

Bond (1998) suggested that the effect of gypsum increasing sodium leaching from the topsoil meant that the potential for increased sodium levels in the subsoil should be assessed. Research since that time has generally established that subsoil drainage can tend to be increased by gypsum application though in high pH conditions there may be a risk of calcium carbonate precipitation causing reduced subsoil drainage, as reported for one soil studied by Tirado-Corbala (2010). The readily leached sulphate and calcium from gypsum means that subsoil sodium levels can also be reduced and subsoil flocculation and structure improved. Jenkins and Jenkins (2013) reported gypsum effects of increased subsoil sulphate levels and reduced penetrometer readings (indicating reduced soil compaction) within 6 months of application of gypsum to a range of New Zealand soil types.

Mount and Schuppan (1978) reported that gypsum application on to a heavy clay sodic soil being treated with sodic effluent resulted in significant yield gains in some years relative to control. This may be related to improved soil structure and the yield increase could assist with nutrient removal in crop harvest.

Hulugalle et al. (2006) found that 2.5 tonne/ha of gypsum improved subsoil drainage in an Austraian vertisol (soil containing expansive clay that can form cracks when dry) receiving effluent and with high sodium levels. They found, however, that the gypsum application did not reduce soil sodium levels and they even noted lower exchangeable calcium and more clay dispersion than in untreated soil. The authors considered that the gypsum application rate was suboptimum and cautioned that such sub-optimum applications in a highly sodic soil may be ineffective.

Potassium

Dairy farm effluent in New Zealand is variable but typically high in potassium (see Longhurst et al., 2000). This means that effluent paddocks will often tend to accumulate potassium resulting in high herbage levels of potassium (Salazaar et al., 2010). High herbage potassium levels in effluent paddocks can result in metabolic issues for livestock (hypocalcaemia and hypomagnesaemia) particularly at the key times of calving and early lactation.

There is some thought that the potassium ions may have some similar effects as sodium ions on clay dispersion and soil structure since they are both monovalent cations (Arienzo et al., 2009; Chen et al., 1983; Rengasamy and Marchuk, 2011, Smiles and Smith, 2004) but research on this is still limited.

Gypsum can assist in the leaching of excess potassium levels (Alva and Gascho, 1991; Uustitalo et al., 2012). In the presence of excess soil potassium, the addition of calcium ions from gypsum could either reduce or balance uptake of potassium by herbage to the benefit of herbage quality and livestock metabolism.

High potassium may also have an impact on the ability of soil to retain phosphorus (Ryden and Syers, 1975). Since gypsum can assist with the leaching of excess potassium levels, the use of gypsum on high potassium soils such as those treated with high rates dairy effluent may reduce the potential for phosphorus losses (by this indirect means in addition to other mechanisms).

Plant Uptake of Nutrients

Although gypsum can reduce the availability of nitrogen and phosphorus for environmental losses, the uptake of these nutrients from the soil may actually be increased by gypsum application if plant growth or root tip formation is improved by the provision of calcium and sulphur, and the improvement of soil structure related due to the gypsum.

Favaretto (2002) did note some reduction in phosphate uptake in gypsum amended soils but the plant uptake of nitrogen and the growth of roots and shoots was not impacted negatively by gypsum application. Stout et al. (2003) found that gypsum application actually increased plant uptake of phosphorus and Bailey (1992) found that the rate of nitrate and ammonium uptake was increased by the application of gypsum.

Plant uptake of nutrients is important for agricultural productivity and also for the removal of excess plant nutrients from soil (e.g. some effluent treated soils).

Considerations for Strategic Placement of Gypsum Amendments

Gypsum is particularly effective at reducing phosphorus losses so target areas should typically be where phosphorus (rather than nitrogen) is the main limiting nutrient for eutrophication of nearby waterways. Gypsum can also be particularly effective at reducing surface runoff losses so priority target areas could be those with surface runoff risk. Placement of gypsum may specifically be most effective in wide strips around runoff prone areas or in effluent treated or pugging prone paddocks rather than over the whole farm. Targeting high risk sections of a farm would assist the economic viability of gypsum application.

Gypsum can reduce the potential for phosphorus losses over a wide range of soil conditions but it would seem less likely to make a significant difference where exchangeable calcium levels are already high. Soils with excess sodium levels on the other hand are likely priority target areas for gypsum application as long as there is drainage potential for leaching out sodium ions.

Large losses of sulfate can occur from gypsum treated soils (Ekholm et al., 2012). In many cases this would not impact significantly on eutrophication as waterways are typically nitrogen and/or phosphorus limited rather than sulfate limited. There is some evidence, however, that lakes and wetlands may have sulfate-induced eutrophication indirectly e.g. from sulfate reducing bacterial activity in sediment resulting in greater availability of phosphate (Lamers et al., 1998; Smolders et al., 2006). A cautious approach was therefore adopted in Finland (Ekholm et al., 2012) by targeting areas draining into the saline Baltic Sea. Land around lagoons (e.g. Lake Ellesmere/Waihora and Lake Waihola), rivers flowing to the sea and perhaps some lakes in geothermally active areas may also be suitable low risk sitesin New Zealand

Conclusions

Gypsum can at least partially address many of the hydrological and chemical factors that influence phosphorus and other nutrient losses from agriculture to waterways. Due to the multiple modes of action, gypsum has shown efficacy on phosphorus mitigation over a range of soil types and conditions. Variability in experimental results indicate that attention should be paid to experimental methods including 1) applying a sufficient amount of gypsum, 2) allowing sufficient time for gypsum effects to take place, 3) mimicking realistic rainfall conditions and 4) establishing sensible criteria for both soil, slope and waterway characteristics for choosing appropriate study sites. Strategic choices of target areas are important since mitigation strategies for phosphorus losses need to be economically viable (McDowell, 2008). International research has shown that under some conditions very significant mitigation of nutrient losses, in particular phosphorus, can be achieved.

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