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Bachelor's Thesis

Mg-rich carbonate minerals of the Upper Neogene Kozani Basin and their use as soil amendments

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Μαγνησιούχα ανθρακικά ορυκτά του Ανώτερου Νεογενούς της Λεκάνης της Κοζάνης και η χρήση τους ως εδαφοβελτιωτικά

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Prologue

The present thesis "Mg-rich carbonate minerals of Kozani basin and their use as soil amendments" was articulated at the Department of Geology and Geoenvironment of the School of Science of the National and Kapodistrian University of Athens.

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Table of contents

Abstract	6
1. Introduction	9
1.1. Soil amendments/conditioners and fertilizers	9
1.1.1. Organic-Inorganic soil amendments and fertilizers	9
1.1.2. The use of carbonate minerals as inorganic soil amendr	ments-conditioners
regarding agricultural purposes	9
1.1.3. Participation of minerals to the experiment; creating a s	soil amendment with
slow Mg release	10
1.1.3.1. Dolomite	11
1.1.3.2. Calcite	12
1.1.3.3. Aragonite	12
1.1.3.4. Magnesite	13
1.1.3.5. Hydromagnesite	13
1.1.3.6. Huntite	14
1.1.3.7. Brucite	14
1.2. Geology of sampling area; Kozani Basin	15
1.2.1 Fieldwork and sampling sites	17
2. Materials and Methods	20
2.1. Materials	20
2.2. Preparation of the samples; drying and crushing	21
2.3. XRD: X-ray diffraction analysis	22
2.4. SEM – Scanning Electron Microscope	25
2.5. Pelletizing	28
3. The Experiment	30
3.1. Pellet samples to soil ratio	31
3.2. Preparation for Mg measurement with flame AAS	32
3.3. Mg measurements with flame AAS	33

3.5. pH measurements344. Results – Discussion365. Conclusions45Acknowledgements47Bibliography48	3.4.	HACH Ca measurements	34
4. Results – Discussion365. Conclusions45Acknowledgements47Bibliography48	3.5.	pH measurements	34
5. Conclusions45Acknowledgements47Bibliography48	4.	Results – Discussion	36
Acknowledgements47Bibliography48	5.	Conclusions	45
Bibliography 48	Ack	nowledgements	47
	Bibl	iography	48

Abstract

The current thesis negotiates the potentiality of some mixtures of pulverized Mg-rich carbonates (magnesite, dolomite, hydromagnesite, huntite), Mg-hydroxides (brucite) and some Ca-rich carbonates (aragonite and calcite) of natural occurrence to be used as soil amendments that provide Mg²⁺ to the environment with slow release, and secondarily Ca²⁺ (huntite, hydromagnesite) as well as elevation of its' pH. Most of the Mg-rich raw materials used for the experiment were selected from the field, which was located at Kozani Basin in Western Macedonia (Fig. 1 and 3), and some of them were commercial products and processing waste that were delivered for the experiment from the companies producing them. The materials were then divided into six (6) main samples and recognition of the mineral phases and their participation in the samples was made with X-ray diffraction analysis and SEM (Scanning Electron Microscope) spectroscopy. The environment of the conducted experiment was composed of loam soil (USDA soil classification triangle) or sandy mud (Folk soil classification triangle, 1954) of 5.5 pH and bottled mineral water. To conduct the experiment the raw materials were pulverized and then shaped into pellets so that they could be mixed with the soil in specific ratios. The experiment went on by adding a precise amount of bottled mineral water to the solid mixture, leaving the arrangement as it was for specific periods of time and eventually collecting the same amount of water from each sample for each period. By measuring the Mg²⁺ concentration in each solution with FAAS (Flame Atomic Absorption Spectroscopy), the calculation of the amount of Mg (mg) that was released from each pelletized sample in relation with time was possible. The concentration of Ca^{2+} in each solution was also measured with the volumetric measurement method, and the amount of Ca (mg) released from each pelletized sample versus time was calculated as well. The experiment revealed that there was no salt accumulation in the soil, and that samples which were huntite/hydromagnesite-rich, were the ones to release the highest amounts of Mg²⁺ and Ca^{2+} in total. In particular, the quarry's processing waste that were delivered, revealed excellent results and the industrial potential for soil amending uses, for acid soil remediation.

Keywords:

Magnesium carbonates • Huntite • Hydromagnesite • Soil amendments • Kozani Basin • Rate of ion release • Soil remediation

Περίληψη

Η παρούσα εργασία διαπραγματεύεται την πιθανότητα χρήσης ορισμένων πουδροποιημένων ανθρακικών και υδροζυλικών ορυκτών με μορφή σφαιροποιημένης πούδρας (μαγνησίτης, δολομίτης, υδρομαγνησίτης, χουντίτης και βρουσίτης αντιστοίχως) του μαγνησίου (Mg) ως εδαφοβελτιωτικά τα οποία θα προσφέρουν ιόντα μαγνησίου Mg^{2+} στο περιβάλλον μέσω αργής απελευθέρωσης, και δευτερευόντως ιόντα ασβεστίου Ca²⁺, καθώς και θα συνεισφέρουν στην αύξηση του pH του. Το περιβάλλον του πειράματος απαρτιζόταν από όξινο χώμα με 5.5 pH (50% άμμος, 25% ιλύς, 20% άργιλος και 5% οργανική ύλη) και από εμφιαλωμένο νερό του εμπορίου. Το μεγαλύτερο μέρος των μαγνησιούχων πρώτων υλών που συμμετείχαν στο πείραμα συλλέχθηκε από την ύπαιθρο, και συγκεκριμένα από την ευρύτερη περιοχή της λεκάνης της Κοζάνης στη Δυτική Μακεδονία (Fig. 1 και 3), ενώ ορισμένα υλικά ήταν εμπορικά προϊόντα τα οποία συμμετείχαν στο πείραμα έπειτα παράδοσής τους από τις εταιρίες παραγωγής τους. Η ορυκτολογική αναγνώριση των υλικών διεξήγθη με την αναλυτική μέθοδο της περιθλασιμετρίας ακτινών-X (XRD) και με χρήση μικροσκοπίου ηλεκτρονιακής σάρωσης και φασματοσκοπίας (SEM και EDS). Για την εκπόνηση του πειράματος τα υλικά κονιοποιήθηκαν έως ότου η κοκκομετρία τους να αποκτούσε μέγεθος ≤ 20 μm, και έπειτα χωρίστηκαν σε έξη (6) δείγματα τα οποία διαμορφώθηκαν σε σφαιρίδια διαμέτρου 3-6mm (pellets) και αναμείχθηκαν με το χώμα σε συγκεκριμένες αναλογίες. Το πείραμα συνεχίστηκε με την προσθήκη συγκεκριμένου όγκου εμφιαλωμένου νερού (σε θερμοκρασίες 25 έως 28°C) σε κάθε στερεό μείγμα γώματος με το εκάστοτε δείγμα. Το νερό θα παρέμενε με τα μείγματα για ορισμένα γρονικά διαστήματα, και έπειτα το πέρας αυτών, θα συλλεγόταν η ίδια ποσότητα νερού (πυκνού διαλύματος) από κάθε μείγμα την ίδια χρονική στιγμή. Μετρώντας τη συγκέντρωση των ιόντων του μαγνησίου Mg²⁺, σε κάθε διάλυμα που συλλέχθηκε, με την μέθοδο της φασματοσκοπίας ατομικής απορρόφησης (AAS), ήταν δυνατός ο υπολογισμός της ποσότητας του μαγνησίου Mg (mg) που απελευθερώθηκε από κάθε δείγμα σε σχέση με το χρόνο. Μετρήθηκε επίσης και η συγκέντρωση των ιόντων του ασβεστίου Ca²⁺ στα πυκνά διαλύματα με την ογκομετρική μέθοδο (τιτλοδότηση) και έτσι υπολογίστηκε και η ποσότητα του ασβεστίου Ca (mg) που απελευθερώθηκε από τα δείγματα σε σχέση με τον χρόνο. Μέσω του πειράματος, έγινε αντιληπτό ότι δεν υπήρξε καθίζηση αλάτων στο χώμα και ότι τα δείγματα τα οποία ήταν πλούσια σε χουντίτη – υδρομαγνησίτη ήταν αυτά που παρουσίασαν τις υψηλότερες τιμές απελευθέρωσης Mg^{2+} και Ca^{2+} . Ιδιαίτερα, τα

απορρίμματα κατεργασίας εμπλουτισμού του κοιτάσματος χουντίτη – υδρομαγνησίτη, έδειξαν αξιόλογα αποτελέσματα για χρήση τους ως εδαφοβελτιωτικά Mg και Ca σε όξινα εδάφη.

Λέξεις κλειδιά:

Μαγνησιούχα ανθρακικά • Χουντίτης • Υδρομαγνησίτης • Εδαφοβελτιωτικά • Λεκάνη Κοζάνης • Ρυθμός απελευθέρωσης ιόντων • Αποκατάσταση εδαφών

1. Introduction

1.1. Soil amendments/conditioners and fertilizers

A soil amendment is a substance or compound that is mixed with the soil in specific ratios of amendment to soil. It is used to regulate pH, water drainage/retention, concentration of elements in the soil that are nutritious for plant cultivations; cation exchange capacity (CEC) of the soil. Soil amendments-conditioners and fertilizers are added to soil to help with plant health and plant growth (Davis and Whiting et al., 2015).

1.1.1. Organic-Inorganic soil amendments and fertilizers

Organic soil amendments are composed by an organism that either was or is alive and/or part of it (plantae, animalia, microorganisms). Inorganic soil amendments are minerals such as vermiculite, perlite, zeolite, limestone, ash, sulfur, oxides and inorganic chemical compounds; liquid fertilizers (Davis and Whiting, 2013).

1.1.2. The use of carbonate minerals as inorganic soil amendments-conditioners regarding agricultural purposes

Table 1: The variety of the carbonate, hydroxyl and oxide Mg/Ca rich minerals that are currently used as soil amendments, and/or fertilizers, in the Greek agricultural industry

Rock/Mineral	Chemical Formula
Dolostone/Dolomite	CaMg(CO ₃) ₂
Limestone/Calcite	CaCO ₃
Caustic calcined magnesia (natural magnesite MgCO ₃ proccessing)	MgO
Brucite	Mg(OH) ₂

Most of the *carbonate mineral soil amendments*, are added to the soil as aggregates with their *granule size* varying from *powder* (<0.002mm) to *sand* (0.075-4.75mm), which are later mixed with the soil. Some of the well-known companies that trade the industrial minerals of Table 1, are mentioned below:

• "Grecian Magnesite S.A." trades caustic calcined magnesia (MgO) that has been produced by natural magnesite deposits, as a soil amendment for slow Mg release, with grain size that varies from 1.6 to 5mm.

(http://www.grecianmagnesite.com/products/caustic-calcined-magnesia/fertilmag-85-fertilmag-80)

- "Carbocal S.A." trades soft limestone, and specifically amorphous calcium carbonate, that has been crushed to a size of powder; 0-100µm, which is then compacted into spherical pellets 2mm-6mm in diameter and apparent density 1.2gr/cm³, and then applied to the soil. The purpose of the application of this product to the soil, is to stabilize pH levels of acidic soils and to discharge Ca²⁺ ions to the environment that can be beneficial for some cultivating plant species (AGROCAL KV brochure 2018).
- "RUSSIAN CHEMICAL MINING COMPANY" trades the product "AgroMag 0-300", which is brucite (Mg(OH)₂) that has been crushed to a grain size of less than 300µm, and is then applied to the soil.

1.1.3. Participation of minerals to the experiment; creating a soil amendment with slow Mg release

The minerals that participated in the experiment to determine the rate of release of Mg from them to the environment, in soil conditions when wet, are displayed in Table 2.

Minerals	Chemical Formulas
Dolomite	CaMg(CO ₃) ₂
Calcite	CaCO ₃
Aragonite	CaCO ₃
Magnesite	MgCO ₃
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$
Huntite	$CaMg_3(CO_3)_4$
Brucite	Mg(OH) ₂

 Table 2: Minerals that participated in the experiment

The free energies of the minerals above, are shown in Table 3.

Mineral	f°25°C (kJ/mol)	
Brucite	-832.3 ± 1.1	(Xiong, 2008)
Magnesite	-1026.0 ± 2.1	(Kittrick and Peryea, 1986)
Calcite	-1207.37	(Vinograd and Putnis, 2004)
Aragonite	-1207.74	(Vinograd and Putnis, 2004)
Dolomite	-2161.3	(Krupka et al., 2010; Robie and
		Hemingway, 1995)
Huntite	-4195.6 ± 6.4	(Walling et al., 1995)
Hydromagnesite	-5864.2	(Krupka et al., 2010; Robie and
		Hemingway, 1995)

Table 3: Gibbs' free energies of formation of some carbonate minerals of Table 2

Minerals which are characterized by higher free energy of formation, are more stable at standard conditions than minerals that are formed with lower free energy values. All thermodynamically metastable mineral phases can exhibit superior properties comparing to their corresponding stable phases, in industrial and laboratory scale (Sun et al., 2016). Aragonite is metastable in all geological environments (Saylor, 1928). Huntite is a metastable carbonate mineral, being a transition mineral between magnesite and dolomite (Venugopal et al., 2005), whereas hydromagnesite is a metastable phase, turning to the only Mg-carbonate thermodynamically stable phase magnesite (Moore et al., 2015; Zhang et al., 2015).

Another factor that can defy a mineral's stabillity is its' specific surface area (SSA). The smaller the mineral's crystal surfaces are, the bigger their SSA gets, and so the mineral becomes more 'reactive' to chemical treatments.

1.1.3.1. Dolomite

Dolomite has a general chemical formula; CaMg(CO₃)₂. It is an Mg/Ca anhydrous carbonate mineral. It can occur from either low metamorphic, metasomatic, diagenetic procedures, or authigenetically as a marine or lake sedimentary deposit.

Dolomite's structure is defined by the trigonal crystallization system. It has a strong dispersion and a perfect cleavage. Its' crystals can be transparent, white or yellowish-brownish (when Mg^{2+} may be replaced by Fe^{2+}). Authigenic sedimentary dolomite is usually purer than of dolomite from other occurrences.

Dolomite that is formed near the surface and/or from dense brines tends to be unstable and can recrystallize or chemically react when the conditions of its' formation change (Michael, 2005). The mineral is often described as a solid solution of CaCO₃ (calcite) and MgCO₃ (magnesite).

Dolomite can be used as a:

- filter for water purification
- Mg source for caustic calcined magnesia (MgO) and/or for pure Mg metal production, for pharmaceutical-nutritional and/or metallurgical purposes respectively
- soil amendment that can be added to acidic soils to neutralize their pH levels and to improve water drainage
- structural material

1.1.3.2. Calcite

Calcite's general chemical formula is CaCO₃ and it belongs to the carbonate mineral group. Its' crystalls abide to the trigonal crystallization system, and they present a very strong dispersion and a perfect cleavage, when well formed. Its' hardness in the Mohrs scale is 3, which means it can be scratched by a human nail, and this feature can macroscopically define the mineral from the other minerals of the carbonate group. Calcite can occur from igneous (carbonatites), metamorphic (marbles), metasomatic (hydrothermal), diagenetic (limestones), authigenic (brines) mechanisms. The biggest limestone masses are those formed by the sedimentation of fossil marine organisms (plancton, algea, shells, corals ect.), whose skeletal parts and hard inorganic parts are mostly composed of CaCO₃.

Calcite can be used as a:

- structural material: basic cement component, aggregates
- Ca source
- soil amendment for pH neutralization and Ca²⁺ ion release

1.1.3.3. Aragonite

Aragonite is one of the most common calcite polymorphs and shares the same chemical formula $CaCO_3$. Aragonite crystallizes in the orthorhombic crystallization system and it is metastable near the surface, because of low pressure values, and at temperatures higher than 300°C. In those conditions aragonite will recrystallize to calcite (Deer et al., 1992). It shows weak dispersion and an imperfect to poor

cleavage. Formation of aragonite is known to occur by metamorphism and biochemically.

Aragonite can be used as a:

- filter for removal of polutants from water
- soil amendment
- horticultural ingredient

1.1.3.4. Magnesite

Magnesite's general chemical formula is MgCO₃ and it belongs to the carbonate mineral group. This mineral crystallizes in the triagonal crystallization system. Macroscopically, it can be transparent, white, or yellowish to brownish (if other metals such as Fe or Mn have obtained Mg positions in the crystal matrix). Magnesite shows a very strong dispersion and a perfect cleavage. The mineral can occur metamorphically, hydrothermally and authigenetically; Mg precipitated from water/brine (Falk and Kelemen, 2015).

Magnesite can be used as a:

- A source for dead-burned magnesia (MgO), caustic calcined magnesia (MgO), fused magnesia and/or pure Mg metal production for the chemical industry and/or metallurgical purposes
- soil amendment that can be added to acidic soils to neutralize their pH levels and to improve water drainage
- fire retardant
- refractory material
- catalyst
- filler, because of its' whiteness

1.1.3.5. Hydromagnesite

Hydromagnesite, is a Mg-carbonate-hydrous mineral. It's general chemical formula is $Mg_5(CO_3)_4(OH)_2$ •4H₂O and it crystallizes in the monoclinic crystallization system. Hydromagnesite can have a perfect/distinct cleavage and its' crystals can be transparent or white. Occurrences of hydromagnesite are usually hydrothermal alterations of Mg-bearing rocks (such as serpentinites and dolostones/marbles), or it can occur authigenetically when precipitated from water (brines or lacustrine environments), commonly with the presence of huntite, and formations are observed near the surface (Wilson et al., 2014). Hydromagnesite's first endothermal decomposition occurs at 220-240°C, releasing its' crystal water.

Hydromagnesite can be used as a:

- Filler, because of its' whiteness and flaky nature of its' crystals
- Fire/flame retardant, because of its' endothermical decomposition
- Source for MgO and Mg

When used for industrial applications, hydromagnesite is usually mixed with huntite.

1.1.3.6. Huntite

Huntite is a Mg-Ca-carbonate-hydrous mineral and has a general chemical formula $CaMg_3(CO_3)_4$. It abides to the triagonal crystallization system and has a white color. Huntite will effervesce in cold HCl acid. It occurs from the alteration and/or weathering of Mg-bearing minerals (dolostones, ultramafic-mafic rocks etc.). A common paragenesis is huntite + hydromagnesite + dolomite + magnesite \pm calcite \pm aragonite. Huntite will decompose endothermically at 644°C.

Huntite can be used as a:

- Filler and extender because of its' whiteness and flakey mineral structure
- Fire/flame retardant, because of its' endothermic decomposition
- Source of MgO and Mg

1.1.3.7. Brucite

Brucite is a Mg-hydroxide mineral and has a general chemical formula Mg(OH)₂. It crystallizes in the triagonal crystallization system and shows a strong dispersion and a perfect cleavage. Brucite usually occurs white in colour, but it can also occur with a tint of green or a brownish colour. Brucite can macroscopically be characterised by its colour, low hardness and the ability to disolve in HCl acid. This mineral usually occurs in areas of contact metamorphism developed by granitic intrusions into dolostones (Newman and Hoffman, 1996) and of hydrothermal alteration of ultramafic rocks.

Brucite can be used as a:

- Source of MgO (dead-burned and/or caustic calcined magnesia) and Mg (s)
- Filler
- Fire/flame retardant
- Soil amendment

1.2. Geology of sampling area; Kozani Basin

The sampling area's name is Kozani Basin, which is located in Western Macedonia Greece. Geologicaly, Kozani basin is part of the southern Pliocene-Pleistocene basins of Western Macedonia-Thessaly (Metaxas et al., 2007). The basin of Kozani is arranged in a direction from NE to SW and it is a valley that is surrounded by the mountain masses of Askion ,Vourinos, Kamvounia Mts, Pieria and Vermion Mts, Northwest ,West ,South ,Southeast and Northeast of the basin respectively (Fig. 1). Kozani's basin now hosts the artificial Polifitos lake and it's water derives from Aliakmon river.



Fig. 1: Geographical location of Kozani basin. Morphological map created with GGRS87, ArcGIS 10 (Simou et al., 2013)

The geological formations that can be found in the broader Kozani area (Fig. 2) are (Stamatakis, 1994; Calvo et al, 1995):

- Inland lacustrine lake sediments of Upper Neogene age
- Alluvial and fluvial deposits of Lower Neogene age
- Flysch and limestones of Mesozoic age
- Ophiolites of Jurassic age
- Dolomites of Lower Jurassic-Triassic age
- Schists with marbles of Paleozoic age



Fig. 2: Geological map of the Kozani basin (Calvo et al., 1995). The circled red areas are the huntite-hydromagnesite deposits that were revisited on the field trip for sample collection (2018). Sampling site AGIA MARINA (N° 9) was an additional sampling area.

The rock samples that were collected from the field, belonged to the Upper Neogene lacustrine sediment formation (Stamatakis, 1995).

1.2.1 Fieldwork and sampling sites



Fig. 3: Field, sampling area (09.06.2018, GoogleEarth)



Fig. 4: "Processing Plant", Lefkara Kozanis, 07.06.2018



Fig. 5: "Lefkara", hydromagnesite-huntite quarring site, Lefkara Kozanis 07.06.2018



Fig. 6: "Neraida", hydromagnesite-huntite quarring site, Neraida Kozanis, 07.06.2018



Fig. 7: "Servia-1", Stena Portas, old quarry 07.06.2018



Fig. 8: "Servia-2".Sampling area of STP-sample.The soft matereal and the hard rock can be distinguished (both materials where collected and they represent the sample STP), 07.06.2018



Fig. 9: "Velitsinos Lakkos-Ag.Marina" old quarry 07.06.2018



Fig. 10: "Eani", Gefyra Rymniou old quarry 07.06.2018



Fig. 11: "Eani", Gefyra Rymniou 07.06.2018

2. Materials and Methods

2.1. Materials

Samples

The samples that were collected (5kg each) on the field (Fig. 3) and those that were delivered, were devided into six (6) main samples for the experiment:

- STP (Stena Portas, Fig. 8)
- BRC (Brucite, commercial product)
- GRM (Gefyra Rimniou, Fig. 10 and 11)
- PRT:BRC, in a 1:1 ration (Portafill:Brucite, "Portafill H10")
- SBW (Sibelco's Waste, Fig. 4)
- AGM (Agia Marina, Fig. 9)

Samples STP, GRM and AGM were collected from the field. Sample BRC was obtained as a commercial product and samples PRT and SBW were delivered from "SIBELCO HELLAS S.A. Mining Company".

Soil

The soil was collected from an olive tree cultivation field located in Farklada Kyparissia, in Messenia; southwest Greece. The amount of the collected soil was 10kg and it contained organic matter (decayed stems, branches, leaves and olive cores) and some rocks (0.5-2.5cm in diameter), which were removed for the experiment. Grain size analysis with laboratory sieves, revealed a composition of 50% sand, 25% silt, 20% clay^{*i*} and \approx 5% organic materials. According to the USDA soil texture classification triangle, the characterization of that soil was; *loam* soil and according to Folk's soil texture classification triangle the characterization of the soil was; *sandy mud*.

The soil was slightly acidic with a pH = 5.5. The mineral phases that participated as soil particles were; *quartz* (SiO₂), which appeared to be the *main component*, and feldspar, illite and clinochlore which appeared in minor and/or trace amounts.

After removing the macro- organic matter from the soil i.e. dead stems, leaves, 1kg of the soil was separated to implement in the experiment. The selected amount of soil was *not* crushed, dried or sterilized in any way.

^{*i*} Particle diameter; sand 0.05 to 1mm, silt 0.002 to 0.05mm, clay < 0.002mm

2.2. Preparation of the samples; drying and crushing

 Sample BRC was compiled of natural brucite and it was a commercial product obtained to participate to the experiment for the determination of the rate of release of Mg²⁺ to the water that was added to the acidic soil. BRC was dried and crushed to a grain size less than 300µm.

50gr of BRC were further crushed with an agate pestel and mortar, for 10 minutes, to achieve a grain size that is equal or less of $20\mu m$. The procedure was executed manually to avoid any crystal deformations that could occur if using a mechanical mortar (from temperature rizing due to high friction).

- Sample PRT:BRC is a 1:1 ratio mixture of the furtherly crushed brucite (BRC) and the material "Portafill H10" (PRT). PRT was selected from the processing plant of "SIBELCO HELLAS S.A.". "Portafill H10" is a mixture of naturally formed hydromagnesite and huntite, which is dried, crushed and airborn separated from the quarrying material. Its' grain size reaches a diametre of 15µm. The 1:1 ratio mixture weighted 50gr of powder in total; 25gr of each (http://coatings.sibelcotools.com/wp-content/uploads/2017/03/Portafill-H-10_TDS_01-01-2015_EN.pdf).
- Sample **SBW** (which stands for Sibelco's Mining and Processing Waste), was selected from the processing plant (Fig. 4). SBW was milled and dried, with its' grain size reaching up to 0.5mm in diametre.

50gr of SBW were air dried for a week, and were manually crushed for 20 mins with an agate pestle and mortar, to achieve a grain size of $300\mu m$ or less.

- Sample STP firstly contained a soft (weathered) and a hard material (Fig. 8), from which 25gr were selected from each. Both materials were air dried for a week, and the hard material was crushed with a laboratory jaw-crusher. Then, the curshed material was mixed with the weathered material, and the total of 50gr of STP were further crushed with a laboratory pulverizer, for a maximum of 10sec. Crushing with a laboratory pulverizer results in a material which has a grain size less than 20µm.
- Sample **GMR** was collected from the area of interest (Fig. 2). The rock was hard and porous, and in its' pores it contained a considerably soft and confoundedly white material (Fig. 11). 50gr of the sample where selected to air dry for a week, and the sample was firsty crushed with a laboratory jaw-crusher, and then further crushed with a laboratory pulverizer for a maximum of 10sec, to achieve a grain size of less than 20µm and to avoid any crystal deformities from excess friction.

Sample AGM was collected from the area of interest (Fig. 2). The collected material seemed soft and weathered at the site (Fig. 9). 50gr of the sample were selected to air dry for a week and were crushed with a laboratory jaw-crusher and crushed again with a laboratory pulverizer for a maximum of 10sec, to avoid crystal deformation from excessive friction. The sample obtained a grain size of less than 20µm.

2.3. XRD: X-ray diffraction analysis

The X-ray diffraction analysis of the powdered samples was conducted by X-ray diffractometer SIEMENS Model 5005. The step size was set to 0.02° and step time to 1sec. The X-ray diffractometer operated with CuK α radiation at 40kV and 40mA. The data obtained from the X-ray diffraction analysis were analyzed with EVA 10.0 software, product of DIFFRACplus. Samples STP, BRC, GRM, SBW and AGM were submitted for XRD mineral analysis (Fig. 13-16).



Fig. 12: X-ray diffraction analysis of sample STP



Fig. 13: X-ray diffraction analysis of sample BRC



Fig. 14: X-ray diffraction analysis of sample GRM



Fig. 15: X-ray diffraction analysis of sample SBW



Fig. 16: X-ray diffraction analysis of sample AGM

Samples	Brucite Hydromagnesite N		icite Hydromagnesite Magnesite Huntite Dol		Dolomite	Dolomite Calcite	
	%	%	%	%	%	%	%
STP	-	-	33.4	33.3	33.3	-	-
BRC	95	-	5	-	-	-	-
GRM	-	-	90	10	-	-	-
SBW	-	43	0.5	40	-	1.5	15
AGM	-	-	80	20	-	-	-
PRT*	-	20	-	80	-	-	-

Table 4: XRD results-Estimated mineral content (Rietveld Method)

*Sample PRT has a mineralogical analysis of 80% Huntite and 20% Hydromagnesite w/w according to the product's component specification.

2.4. SEM – Scanning Electron Microscope

All six (6) samples were characterized with a scanning electron microscope; JEOL 5600 SEM, operating at 20kV and 0.5 nA.

Sample	Au coating	C coatig	EDS analysis	Uncrushed sample
STP		Х	Х	Х
BRC	Х		Х	
GRM		Х	Х	Х
PRT	Х		Х	
SBW	Х		Х	
AGM		Х		x

Table 5: Samples for SEM imagery and EDS analysis

Samples BRC, PRT and SBW were already crushed to a grain size 300µm and less, when received. For the crystals and surfaces to be more distinguishable, those samples where sputter coated with gold (Au). There was also an EDS analysis.

The rest of the samples; STP, GRM, AGM were collected from the field, and therefore an uncrushed part of them was used for SEM imagery. STP and GRM also had an EDS analysis. Those samples were coated with graphite (C).

Sample STP when collected, had two (2) kinds of material; one soft (weathered) and one hard (rock). STP's materials where used seperately for SEM scanning and EDS analysis.



Fig. 17: STP's weathered material (soft) SEM image



Fig. 18: STP's rock material (hard) SEM image



Fig. 19: BRC SEM image



(a)

(b)

Fig. 20: GRM SEM images (a, b)



Fig. 21: PRT SEM image (c). In image (d) the platy nature of the quarry's huntite crystals is distinguishable



Fig. 22: SBW SEM images (e). In image (f) the platy nature of the quarry's hydromagnesite crystalls is distinguishable



(g)

(h)

Fig. 23: AGM SEM images (g, h)

From Fig. 21 and 22, it is distinguishable that the huntite and hydromagesite raw materials obtained from the Neraida Quarry (d and f respectively), are composed of euhedral crystals, whereas the ground products (c and e) are composed of broken crystals demonstrating size variation.

2.5. Pelletizing

After the grain size of each 50gr sample was reduced to 200µm of diametre and less, 25gr of each grounded sample where selected to be pelletized:

- STP : 25gr
- BRC : 25gr
- GRM : 25gr
- PRT:BRC(1:1): 12.5gr of PRT mixed with 12.5gr of BRC
- SBW : 25gr
- AGM : 25gr

Pelletization was conducted by adding bottled commercial water with a ratio of water:powder being 1:5. The analogy was competent enough to moisturize the more clayishly behaving minerals. Then by applying pressure with the palms of the hands, while moving them in opposing circular motions, the spheroidal shaped pellets were formed. The spheroidal shaped pellets, had a grain size that varied from 3mm to 6mm (Fig. 24).



Fig. 24: Pelletized SBW material

The purpose of pelletization of the powdered materials, was to avoid pore clogging from the powder particles as well as to avoid salt accumulation that could form a solid horizon. The pellets were also able to disolve slowy due to water flow, which eventualy would leave no solid remnants of the pellets.

3. The Experiment

The experiment's purpose, was to define whether some of the samples were able to be used as soil amendments. The definition of which, was to be determined from the calculation of *the rate of release of* Mg^{2+} *ions; the quantity of* Mg^{2+} *ions released in relation with time* from the samples to the environment, provided that Mg is consindered a nutritive element for some plantations, and an alakaline earth metal that can neutralize acidic environmental conditions.

The system of the experiment was closed. The pellets from each sample were mixed with the acidic soil (pH = 5.5) separately and with the same proportions. Then, each mixture of soil and sample was placed into a 1000ml burette (a glass cylindrical tube with a glass stopcock at the bottom), and 50ml of bottled commercial water, measured with a graduated cylinder, were added inside the burette too.

Apart from the six (6) pelletized samples, *a seventh was added that represented the reference sample; RFR*. The RFR sample was composed from soil of equal proportion as the other six samples and 50ml of the same bottled commercial water.

The seven samples were left at this order for specific periods of time. After the passage of that time, 50ml of water (concentrated solution) were gathered from each sample and at the same time. After each gathering, 50ml of the same commercial water were poured into each burette, to remain with the mixture of soil and pellets until the next gathering. In every gathering, 50ml of seven (7) concentrated solutions were obtained.

The proceedure of gathering each solution was to twist the glass stopcock at the bottom of the burette, and let the concentrated solution to be poured inside a polymer sampling bottle with a polymer funnel, on top of which filter paper was applied. The filter paper was of 391 grade, and it was applied to avoid the solution's contamination from solid materials (soil/pellet particles).

In total, fifty six (56) concentrated solutions were collected. There were eight (8) collections, and seven (7) samples;

- 1. RFR
- 2. STP
- 3. BRC
- 4. GRM
- 5. PRT:BRC (1:1)
- 6. SBW
- 7. AGM

The total time of the experiment was 101 days. On day 1 the burettes were arranged and there were no concentrated solution gatherings. The first gathering was after 30 days, during which the burette arrangements were left at that order; day 31 of the experiment. The rest of the gatherings took place at; 34, 40, 47, 54, 61, 70 and 101 day of the experiment.

It is significant to mention that prior to the first gathering of the concentrated solutions of the samples, the burettes's top openings where sealed with a commercial plastic membrane used for food packaging, and the mixtures were left in that order for a month. The membrane was applied to avoid any water evaporation due to temperatures higher than 25°C that could be reached inside the laboratory, during the month of August. The membrane was not applied in between the rest of the sample gatherings and the top of the burretes were thenceforth left open.

Another important notice, was the development of macro- and microorganisms inside the burretes, recognized by vision and odor. The cause of this development must have lied to the fact that the soil was not dried or sterilized, in order to achieve real field conditions during the experiment.

3.1. Pellet samples to soil ratio

The ratio of the mixtures placed inside the 1000ml burettes was 1:40. This ratio was calculated for the theoretical model of applying 2.5kg of soil amendment for 100kg of soil for $4m^3$ ($2m \times 2m \times 1m$) of land. The percentage was calculated to be 2.5%. For the experiment, the ideal proportion for the mixture of pellets with soil is 2.5gr

pellets to 100gr soil. For each mixture the pellet sample and the acidic soil were scaled seperately with a high precision laboratory scale (Table 5).

Sample	Pellet (gr)	Soil (gr)
RFR	-	100.12986
STP	2.557	100.0341
BRC	2.5115	100.0241
GRM	2.5208	100.0031
PRT:BRC (1:1)	2.5218	100.1471
SBW	2.4941	100.0038
AGM	2.5267	100.0479

Table 5: High precision scale measurements (gr) of each sample

3.2. Preparation for Mg measurement with flame AAS

After gathering, the 56 concentrated solutions were refiltered with a 'Munhen' 391 grade filter paper, to ensure that there were no solid particles present. The refiltered concentrated solutions were each diluted to a ratio of 1:10, and then the 1:10 diluted solutions were diluted again to a ratio of 1:10, to reach a total dilution of 1:100. This procedure took place so that the Mg^{2+} concentration in the solutions would be traceable by the AAS's detection limits (upper limit; 2.5ppm) (Table 6 and 7).

Sample	Concentrated	La ₂ O ₃ 4 %	Deionized	Total 1:10
	Solution (ml)	(ml)	H ₂ O (ml)	diluted
				solution (ml)
RFR ₃₁	1	-	9	10
(day 31)				
RFR ₃₄₋₁₀₁	1	1	8	10
STP	1	-	9	10
BRC	1	-	9	10
GRM	1	-	9	10
PRT:BRC	1	-	9	10
SBW	1	-	9	10
AGM	1	-	9	10

Table 6: Dilution 1:10

Table 7: Dilutions 1:100

Samples	1:10 diluted La ₂ O ₃ 4 %		Deionized	Total (ml)
	solutions (ml)	(ml)	H ₂ O (ml)	
RFR ₃₁	1	1	8	10
(day 31)				
STP	1	1	8	10
BRC	1	1	8	10
GRM	1	1	8	10
PRT:BRC	1	1	8	10
SBW	1	1	8	10
AGM	1	1	8	10

For the RMR sample gatherings on days 34, 40, 47, 54, 61, 70, 101 of the experiment, the diluted solutions were composed of; 1ml of concentrated solution, 1ml of La₂O₃ 4% solution and 8ml of deionized/distilled water.

The rest of the 1:10 dilutions of the sample gatherings (with the fisrt RMR gathering on day 31 of the experiment included) where composed of; 1ml concentrated solution and 9ml of deionized water.

All the diluted solutions that would be measured for their concentration in Mg^{2+} , had also a concentration of 4% La₂O₃. Lanthanum oxide (La₂O₃) is used to prevent chemical interventions during measurements of Ca, Mg, K with flame AAS.

3.3. Mg measurements with flame AAS

Measurements of the Mg^{2+} concentration (ppm) of the 1:100 diluted solutions with 4% La₂O₃ and the 1:10 diluted solutions with 4% La₂O₃, were made with Perkin Elmer 1100B flame atomic absorbtion spectroscopy (FAAS) with a graphite furnace. The detection limit was 2.5ppm.

Standard solutions were aqueous Mg²⁺ solutions with Mg concentrations of 1ppm and 2.5ppm.

Days:		31	34	40	47	54	61	70	101
Dilution	Samples				ppm				
1:10	RFR	0.45 *	1.18	1.49	1.08	1.39	0.89	1.09	0.2
1:100	STP	0.56	0.12	0.27	0.3	0.25	0.21	0.2	0.26
1:100	BRC	1.34	0.4	0.79	0.84	0.78	0.6	0.49	0.44
1:100	GRM	0.48	0.15	0.15	0.14	0.14	0.13	0.13	0.21
1:100	PRT:BRC	2	0.83	0.98	1.03	0.93	0.86	0.79	1.01
1:100	SBW	2.41	1.18	1.04	0.92	0.77	0.82	0.81	1.21
1:100	AGM	0.53	0.21	0.21	0.18	0.2	0.17	0.16	0.21

Table 8: Mg²⁺ concentration measurements in ppm (ml/lt)

*dilution was 1:100

The *bottled mineral water's concentration* was also measured to be 0.07ppm, in a 1:100 diluted solution that contained; 1ml of commercial water, 1ml of 4% La solution, 8ml of deionized water.

3.4. HACH Ca measurements

Volumetric measurements of Ca^{2+} concentration were conducted with HACH COMPANY LOVELAND's Hardness (Calcium) Reagent Set (100-4000mg/lt). The *ratio of concentrated solution to deionized water was 1:4; 20ml of each concentrated solution were diluted into 80ml of deionized water*, to gain a solution of 100ml in total from each sample and every gathering (56 in total). The bottled mineral water's Ca^{2+} concentration was also measured with that method (Table 9).

 Table 9: HACH's volumetric Ca²⁺ concentration measurements in ppm (for a 100ml solution)

Days:	31	34	40	47	54	61	70	101
Samples				ppm				
RFR	17.6	18	20.8	24.4	25.6	25.6	25.4	24
STP	44.8	22.4	28.4	25.6	26.1	26.8	32	49.6
BRC	17.6	18.3	22.8	24.9	26.1	24.9	26.7	27.2
GRM	24	24.4	25.6	26	28.9	28.8	36	42.4
PRT:BRC	21.2	25	22.4	25.6	26.9	26.2	25.7	25.3
SBW	34.8	35.2	28.8	32	36	37.9	38.4	50.6
AGM	18.2	24	22.4	19.2	22.4	24	24	54.4

The *commercial water*'s sample gave a Ca^{2+} concentration of 51.2ppm.

3.5. pH measurements

Measurements of pH were conducted with Consort C561 Electrodes and JENWAY 3040 Ion Analyser. Calibration was executed with standard solutions of 7 pH and 9 pH.

The pH level of the concentrated solutions of the seven (7) samples were measured for day 31 and 70. The pH of sample SBW's collection on day 54 of the experiment was also measured.

Days:	31	54	70
Samples		pН	
RFR	8.679		8.681
STP	7.57		8.469
BRC	8.403		7.916
GRM	8.46		8.593
PRT:BRC	8.734		8.035
SBW	9.3	8.954	8.417
AGM	8.729		8.298

Table 10: pH measurements of some gatherings of the samples (mainly on gatherings upon days 31 and 70 - on the first and prior to last gathering)

To measure the soil's pH, 50ml of deionized water were poured inside a separate burrete with a 100gr of soil, and the arrangement was left for ten (10) days. After the passage of that time, the water was collected and filtered. The pH measurement was conducted with Consort C561 Electrodes and JENWAY 3040 Ion Analyser, and calibration was executed with standard solutions of 5 pH and 7 pH. The measurement was $pH_{soil} = 5.5$.

4. Results – Discussion

From the Mg^{2+} measurements with the flame atomic absorption spectroscopy method (FAAS), and from the XRD mineral analysis, the quantity of Mg (mg) that was released from the original 2.5gr of pellets, for each sample was calculated. The following diagrams were formed with "Microsoft Excel" software (Fig. 25 and 26).



Fig. 25: Mg content in mg inside the concentrated solutions (50ml) against time in days

On Fig. 25 it is shown that samples STP, GRM and AGM show very low Mg release in comparison with samples BRC, PRT:BRC and SBW. Sample BRC's Mg release seems to decrease with time in oppossition with samples PRT:BRC and SBW which tend to increase their Mg release on days 71 and 101. Sample SBW shows the highest Mg release on the fisrt three (3) and on the last two (2) gatherings, even though sample PRT:BRC showed higher Mg release on the days 47, 54 and 61 (with a small difference). The SBW's major mineral components; aragonite, huntite, hydromagnesite are metastable carbonates (Table 3). It is proposed that the nature of those three minerals is responsible for their higher release of Mg in comparison to dolomite, magnesite and brucite.

It seems that Mg concentration (mg) is the highest upon the first gathering (31 days) because the mixtures were left for a month with 50 ml of bottled mineral water to homogenize, and that consequently was enough time for the alkaline materials to react with the sightly acidic soil and the release of their Mg^{2+} ions.



STP BRC GRM PRT:BRC SBW AGM

Fig. 26: Mg concentrations of every sample in every gathering (gr/50ml)

Pie charts that demonstrate the percentage of Mg that was released in total in 101 days of the experiment, from the original 2.5gr pellets were created with "Microsoft Excel" software for each sample (Fig. 27).



Fig. 27: Percentages of the Mg (gr) that was released from the original 2.5gr pellets

From the Ca^{2+} volumetric measurement, the quantity of Ca inside every concentrated solution was calculated for each sample. Diagrams that demonstrate the Ca²⁺ concentration (mg/50ml) in the concentrated solutions (vertical axis) versus time in days (horizontal axis) for each sample were formed with "Microsoft Excel" software (Fig. 28 and 29).



Fig. 28: Ca content in mg inside the concentrated solutions (50ml) against time

Regarding the diagram of Fig. 28, samples RFR, PRT:BRC and BRC present a similar and a relatively low Ca concentration in comparison with samples AGM, STP, GRM and SBW, which demonstrate a significant increase of Ca (mg/50ml) release with time, especially in between the 71st and 101st day of gathering of the concentrated solutions. The highest Ca concentrations were shown on the 101st day of gathering, for samples AGM, STP and SBW.

Although sample PRT:BRC contains 40% huntite and 2.5% of other Ca-Mg carbonate minerals w/w, on Fig. 28 it is shown that there is insignificant to none Ca^{2+} ion release from this sample. In opposition with the diagram of Mg release on Fig. 26 where sample PRT:BRC demonstrates the second highest Mg²⁺ ion release, in comparison with the rest of the samples. It seems that the present of aragonite is crucial to the higher Ca release (observed from sample SBW, in comparison with huntite, dolomite and calcite.



Fig. 29: Ca concetrations of every sample in every gathering (gr/50ml)

RFR STP BRC GRM PRT:BRC SBW AGM

From the XRD mineral analysis, a deduction was made that the samples containing Ca-bearing minerals were four (4) in total; STP, GRM, SBW and AGM. Pie charts that demonstrate the percentage of Ca that was released in total from the four (4) pelletized samples were created with "Microsoft Excel" software (Fig. 30).



Fig. 30: Percentages of the Ca (gr) that was released from the original 2.5gr pellets

The materials that were used in the experiment for determination of the release of Mg and/or Ca for 101 days were all carbonate minerals of natural occurrence and their processing included air drying for a week (7 days), crushing and pelletizing. Table 11. demonstrates the percentages w/w of the minerals present in the samples, and the quantities of Mg and Ca (gr) that would had been released per ton, for 101 days of the experiment (approximately; 3 months).

Sample	Minerals %	Mg release gr/ton	Ca release gr/ton
	w/w	for 101 days	for 101 days
	43% hydromagnesite		
SBW	40% huntite	79,652.2	80,584.51
	17% other Mg and Ca		
	anhydrous carbonates		
	47.5% brucite		-
PRT:BRC	40% huntite	45,682	
	10% hydromagnesite		
	2.5% other Mg and		
	Ca carbonates		
BRC	95% brucite	21,046.5	-
	5% magnesite		
	33.3% huntite		
STP	33.4% magnesite	7,733.71	53,947.05
	33.3% dolomite		
AGM	80% magnesite	3,736.21	95,829.13
	20% huntite		
GRM	90% magnesite	1,217.3	192,751.2
	10% huntite		

Table 11: Mg and Ca release in gr/ton from the raw materials for 101 days (approximately; 3 months)

According to Table 11, sample **SBW** (XRD mineral analysis; Table 4) would release 79.6kg of pure Mg and 80kg of pure Ca from 1ton of the original material, when mixed with acidic soil in a ratio of 1:40, for 101 days.

It can be assumed, that one of the reasons which controls the high release rate of Mg and Ca of the mining/processing waste (SBW) is the interaction and synergistic behavior between the various metastable carbonate phases that are present (Table 4).

Another factor to SBW's behavior, could be its' grain size ($\approx 300 \mu m$) which provides a porosity that enables enough water flow through the pellets that can release relatively high amounts of Mg and Ca ions into the environment (=water + soil). Given the facts that:

- 1. SBW's material is considered quarry waste from industrial material excavations, which after its' accumulation in piles, is transferred again by trucks to be used as an aggregate restoration material.
- 2. The material's requirements of processing methods prior use are simple.
- 3. According to the USGS Mineral Commodity Summaries 2019, magnesium compounds were on high demand the past two years (2017 and 2018) due to worldwide market changes, which resulted into an increase in prices of all grades of magnesia. Mine production for the years 2017 and 2018 are given by USGS, as well as reserves demonstrated in Table 12. Only countries neighboring Greece were depicted in Table 12.

Country	Mine	Production	Reserves
			(kton)
	2017	2018	
	(kton)	(kton)	
Greece	400	400	280,000
Austria	600	600	50,000
Russia	1,500	1,500	2,300,000
Slovakia	450	470	120,000
Spain	300	330	35,000
Turkey	3,300	3,400	230,000
(World total	29,100	29,000	8,500,000)

Table 12. Magnesite Mine Production and Reserves, USGS 2019

4. According to the Greek legislation of the terms and policies on soil amendment trafficking of Paragraph b), Article 2, N°217217/16.01.2004(Official Government Gazette of Hellenic Republic), decision of the Minister of Agriculture; 'materials that have been classified as soil amendments can be sold on the market for agricultural purposes if the products are characterized, signalized and mention the identity of the product as follows; species, composition, origin of raw materials, proper use per soil species and plant species, dosage'.

Dolomite, which is used as soil amendment that provides Mg²⁺ and pH elevation, in the Greek agricultural market, is sold at a price of 350€/ton for a granule size of 0.2-0.5mm and 320€ for a granule size of 0.5-1.7mm (personal communication). According to Table 11., if dolomite was used solely, it would give 2575gr/ton in 101 days when mixed with acidic soil in a ratio of 1:40. This means that dolomite provides 299% less Mg than sample SBW.

It is suggested that the material represented by sample SBW, should be conducted to further experiments, with purpose the determination of its' potentiality to be used as a soil amendment that could provide Mg^{2+} with slow release and to contribute in pH elevation of the soil's environment.

5. Conclusions

From the results (Fig. 25 and 26) it was noticeable that sample **SBW** *released the highest amount of Mg (mg) in comparison with the rest of the samples*, except from the gatherings on days 47, 54, 61, on which sample PRT:BRC showed slightly higher Mg concentrations (Fig.25). In Fig. 31, the amounts of the Mg (mg) that were released in total from each sample are visible.



Fig. 31. Total Mg release (mg/400ml) from each sample in 101 days

As shown in Fig. 31 sample SBW released 80% more Mg (mg) than sample BRC and 10% more Mg (mg) than sample PRT:BRC, which was the second sample to present an increase in Mg (mg) release with time. Sample SBW was delivered from "SIBELCO HELLAS S.A." 's processing plant, and it was considered as waste from the huntite-hydromagnesite enrichment process. Its' mineral composition was diagnosed to be the material that was firstly mined from an inland lacustrine sedimentary Mg hydrous carbonate (mainly huntite and hydromagnesite) occurrence in Lefkara, Kozani, Central-Northern Greece, and then taken to the processing plant where it was crushed, and airborne separated during the enrichment prosses.

Another important notice was that the 1.25gr of sample PRT, which stands for the commercial product "Portafill H10" (used as filler, whitener, extender and a rheology modifier), released 24.545mg of Mg in 101 days. If this material was to be used solitarily, then it is estimated that 2.5gr would release 49.1mg of Mg, which means that sample PRT would had had 25% higher total Mg release than sample SBW.

Regarding the *Ca release* (mg) that was observed (Fig. 28 and 29), samples STP, GRM, SBW and AGM showed an increase in Ca concentration (gr/50ml) with time (Fig. 27), with sample SBW demonstrating the highest Ca release (mg/400ml) amongst them (Fig. 31). Sample SBW released 51% more Ca (gr) than STP, 105% more Ca (gr) than GRM and 313% more Ca (gr) than sample AGM, despite that SBW released only 8% of its' total Ca content (Fig. 32).



Fig. 32: The total amounts of Ca (mg/400ml) that were released from each sample in 101 days

Overall the experiment unveiled no salt accumulation throughout time as it was shown from the measurements which demonstrate similar and/or increasing Mg (mg) and Ca (mg) concentrations throughout time (Fig. 25 and 28 respectively). In case of salt accumulation in the soil, the concentrations of Mg and/or Ca should have decreased with time due to salt crystallization from the water (concentrated solutions). Another notice was that although the alkalinity was quite high for some samples (Table 10.) macro- and micro- organisms were able to form.

Due to SBW's industrial potential, further research accompanied by a technoeconomical assessment would be an ideal way for its' introduction to the domestic and international market as a soil amendment.

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