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ELEMENTAL PROFILING OF GREEK HONEYS USING MP-AES AND ICP-MS TECHNIQUES

MARIA-ANTHI PRIAKOU

CHEMIST

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Elemental profiling of Greek honeys using MP-AES and ICP-MS techniques

MARIA-ANTHI PRIAKOU

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SUPERVISING PROFESSOR:

Marilena Dasenaki, Assistant Professor NKUA

THREE-MEMBER EXAMINATION COMMITTEE:

Charalampos Proestos, Associate Professor, NKUA

Vasilis Valdramidis, Associate Professor, NKUA

Marilena Dasenaki, Assistant Professor, NKUA

ΠΕΡΙΛΗΨΗ

Το μέλι είναι το γλυκό συστατικό, που παράγεται από τις μέλισσες *Apis mellifera*, είτε από το νέκταρ των φυτών είτε από τις εκκρίσεις των φυτών ή των εντόμων, που σε αυτή την περίπτωση ονομάζεται μελίτωμα. Πειράματα έχουν δείξει ότι η ποικιλία και η γεωγραφική προέλευση κάθε μελιού επηρεάζει το μεταλλικό του περιεχόμενο.

Αυτή η μελέτη εστιάζει στην ποιοτική και ποσοτική ανάλυση μελιών από 23 διαφορετικές ποικιλίες και από 31 διαφορετικές μίξεις ποικιλιών. Τα δείγματα που αναλύθηκαν ήταν δείγματα μελιών, τα οποία είχαν συλλεχθεί κατά τις περιόδους συγκομιδής 2019 και 2021. Μεταξύ αυτών, τελικά 13 ποικιλίες χρησιμοποιήθηκαν για την εξαγωγή αποτελεσμάτων (κουμαριά, καστανιά, βαμβάκι, έλατο, άνθεων, ερείκι, χαρουπιά, βελανιδιά, πορτοκάλι, πεύκο, φασκόμηλο, θυμάρι, βανίλια), χρησιμοποιώντας ως παράμετρο την ύπαρξη στατιστικά επαρκούς αριθμού δειγμάτων (≥3). Για το σκοπό αυτό, δύο ενόργανες τεχνικές πραγματοποιήθηκαν. Η Φασματομετρία Ατομικής Εκπομπής Πλάσματος Μικροκυμάτων (MP-AES) πραγματοποιήθηκε για την ανίχνευση και τη μέτρηση των συγκεντρώσεων των μακροστοιχείων (Ca, Na, Mg, K), ενώ η Επαγωγικά Συζευγμένη Φασματομετρία Μάζας Πλάσματος (ICP-MS) για την ανάλυση των μικροστοιχείων (Fe, Cu, Mn, Zn) και των σπάνιων γαιών (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U). Συγκρίνοντας τις δύο τεχνικές, και οι δύο παρείχαν τα αναμενόμενα από τη σχετική βιβλιογραφία αποτελέσματα, ωστόσο η ICP-MS εμφάνισε μεγαλύτερη στοιχειακή ευαισθησία (ng/kg) και μικρότερο χρόνο ανάλυσης. Πιο συγκεκριμένα, η MP-AES και η ICP-MS ανίχνευσαν όλους τους σημαντικούς μεταλλικούς βιοδείκτες του μελιού και έδωσαν αναλυτικά δεδομένα σχετικά με τις συγκεντρώσεις τους στα δείγματα. Ακόμη, Ανάλυση των Κύριων Συστατικών (PCA) πραγματοποιήθηκε, για να παρατηρηθούν ομοιότητες και διαφορές μεταξύ των ποικιλιών μελιού, σύμφωνα με το μεταλλικό τους στοιχειακό περιεχόμενο. Με ένα μοντέλο 3 συστατικών, εξηγήθηκε το 92.05% των δεδομένων. Η PC_1 έδειξε ότι υπάρχει αισθητή διαφορά μεταξύ μελιού και μελιτώματος, καθώς το πρώτο υπερέχει σε μακροστοιχεία, ενώ το δεύτερο σε μικροστοιχεία. Τέλος, οι ανιχνεύσιμες σπάνιες γαίες εμφανίστηκαν στα δείγματα σε συγκεντρώσεις της τάξης ng/kg, ενώ κάποιες από αυτές ήταν εντελώς απούσες σε όλες τις ποικιλίες.

ΘΕΜΑΤΙΚΗ ΠΕΡΙΟΧΗ: Χημεία Τροφίμων, Μέλι, Μέταλλα

ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ: μέλι, μελίτωμα, στοιχεία, μακρο, μικρο, σπάνιες γαίες, MP-AES, ICP-MS, PCA

ABSTRACT

Honey is the sweet component, produced by *Apis mellifera* bees, either from the nectar of the plants or from secretions of the plants or excretions of plant-sucking insects, called honeydew. Through the ages of food analysis, experiments have shown that the variety and the geographical origin of each honey affect the mineral content.

This study focuses on the qualitative and quantitative analysis of honeys of 23 different varieties and 31 different blends of varieties. The samples analyzed were honey samples, collected during the harvesting periods of 2019 and 2021. Among those, 13 were finally were used to draw conclusions (arbutus, chestnut, cotton, fir, flowers, heather, carob, oak, orange, pine, sage, thyme, vanilla), using as a parameter the existence of a statistically important number of samples (≥3). For this purpose, two techniques were held. Microwave Plasma Atomic Emission Spectrometry (MP-AES) was carried out to detect and measure the concentrations of macroelements (Ca, Na, Mg, K), whereas Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to analyze micronutrients (Fe, Cu, Mn, Zn) and rare elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U). Comparing the two techniques, both provided the results expected by the relevant literature, nevertheless ICP-MS appeared to have higher substantial sensitivity (ng/kg) and shorter analysis time. More specifically, MP-AES and ICP-MS detected all the important metallic biomarkers of honey and gave detailed data concerning their concentration in the samples. Then, Principal Components Analysis (PCA) was held, to observe differences and similarities between honey varieties according to the elemental profile. With a 3-components model, it was possible to explain 92.05% of data variability. PC_1 showed that there is a distinct difference between honeydew and honey, as the first excels at macroelements, whereas the second at micronutrients. Finally, the detected rare elements appeared in the samples in concentrations of ng/kg, when some of them were totally absent in all measured samples.

SUBJECT AREA: Food Chemistry, Honey, Metals

KEYWORDS: honey, honeydew, elements, macro, micro, rare elements, MP-AES, ICP-MS, PCA

Through all the years of my academic career, all my projects will always be dedicated to my beloved grandparents from Nestani, Arcadia, Anthi and Panagiotis, for being the sweetest and strongest role models for me…

Σε όλη τη διάρκεια των ακαδημαϊκών μου σπουδών, όλες μου οι εργασίες θα είναι αφιερωμένες στους αγαπημένους μου παππούδες από τη Νεστάνη Αρκαδίας, Ανθή και Παναγιώτη, γιατί έχουν υπάρξει τα πιο γλυκά και ισχυρά πρότυπα για εμένα…

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CONTENTS

INDEX OF GRAPHS

INDEX OF FIGURES

INDEX OF TABLES

PREFACE

This master was carried out as a substantial part of the Postgraduate Program «Food Chemistry» of the Department of Chemistry at the National and Kapodistrian University of Athens, directed by M. Charalampos Proestos, during the academic year 2021-2022 The experiments were performed at the Laboratory of Food Chemistry of the Department of Chemistry at the National and Kapodistrian University of Athens and at the Laboratory of Analytical Chemistry of the same institution.

The purpose of the study was to track and quantify metals (macroelements, microelements and rare elements) in different varieties of honeys of Greek origin, using two cutting-edge analytical techniques (MP-AES and ICP-MS), as well as chemometric tools (PCA), in order to identify the way that variety and geographical origin affect the elemental profile of the product.

Chapter 1 Honey

1.1 Brief history

The production and consumption of honey have their roots in very ancient times of Earth's history. It is not easy to have exact data of its existence on the planet, nevertheless it is for sure known to be the first food additive to be used as a sweetener by humankind.

1.1.1 The sacred bee of Egyptians

There are various reports concerning the first use of honey in the world. The oldest written and published review testifying the use and consumption of honey by *homo sapiens* dates back to 5500 B.C, and more specifically to Egyptians.[3]

In the civilization of Egypt, honeybees were strongly attached to loyalty and respect to the King and to Gods. As a matter of fact, numerous hieroglyphs for honey and for beekeeping were massively used, proving the spiritual effect this animal and its by-product had on the society and religion of this nation. They valued it so much, they would fill up ceramic vases and place them in the Pharaoh's tombs for the afterlife. When Tutankhamun's tomb was discovered, researchers found perfectly preserved crystallized honey of over 3500 years old.[1]

Figure 1. Hieroglyphs of bees in Ancient Egypt

Beekeeping, hives' formation, and honey's production are procedures that have been practiced by all classes of the Egyptian society, indicating the big scale of production that was achieved. Egyptian hives were made using pipes of clay or mud from the Nile, in a way that they could be moved along the river. As a result, the bees had the chance to collect the nectar from all different kinds of flowers, depending on the season and the weather conditions.[1]

The uses of this product by the Egyptians were not limited on food additive. More specifically, the people of ancient Egypt could also use honey for its medical properties, for example to treat wounds, as currency for their trade, as duty towards their conquerors, even as dowry at marriage contracts. Long story short, there had been found such a legal document which stated «I take thee to wife... and promise to deliver to thee yearly twelve jars of honey».[1]

1.1.2 Symbolisms of honey in the Greek mythology

The symbolisms linked with honey at Ancient Greece are also numerous, and most of them are highly related to the Olympus Gods.

According to mythology, Zeus, the King of the Gods, was hidden by his mother into a cave on Mount Dicte, to protect him by the fury of his father, God Kronos. There, sacred bees were said to have populated the place, taking care of the infant and feeding him, until he could grow old and strong, defeat his father, and take his place at the throne of Olympus. As an acknowledgement, Zeus gave to the bees their bright gold color, alongside with ability to resist cold and winds. Therefore, one of Zeus's denominations is Melissaios (by the word «melissa» [μέλισσα] meaning bee in the Greek language).[2]

In the Greek mythology, honey was also referred to as «The birds of the Muses», as the Muses were known for spreading eloquence to the mortals, by sending bees to pour honey to their lips when they were born. The Greek poet Hesiod wrote of them «whomsoever they honored and looked upon at his birth, on his tongue they shed a honeyed dew and from his lips would drop gentle words and he would speak counsel unerringly».[2]

Figure 2. The Greek Muses

1.1.3 The Romans

Romans worshiped raw honey that much, that they even had a special Goddess for bees and honeys, named Mellona. There were popular sayings supporting that, if a swarm of bees entered the temple of the Goddess, it could mean a threat to the empire, due to the monarchical organization of the bees.[1]

As the Romans quickly understood that honeybees were not a harm to the plants, they learned how to build hidden hives, protected by nature, and produce their own honey. At the same time, they imported big amounts of honey from all over the world. The biggest importer for the Romans was Malta or Melitē [>Μελίτη in Greek), which means sweet honey.[1]

As well as Egyptians, Romans took advantage of honey for many different uses. Cooking, cosmetics, food preservation and medicine were the most important and usual of them.

Ancient Romans were great producers of grain and olive oil, alongside with honey. Quite characteristically, Emperor Ottaviano Augusto, to people who asked him what his longevity secret was, always answered «Honey inside and oil outside».[1]

1.2 Honey: Definition

As defined by Codex Alimentarius (2001), honey is an aqueous solution of a natural, sweet, and viscous substance, made by the bee species *Apis mellifera*. The sugars that are predominant in honey are the simple sugars glucose, fructose, maltose, and sucrose, and they occupy 70% of the total substance. Water is its solvent, whereas other chemical ingredients appear in honey, in lower concentrations, such as proteins, organic acids, amino acids, vitamins, flavonoids and acetylcholine (Wang, Li, 2011). The percentages of those ingredients differ depending on the botanical and geographical origin of the honey, whereas based on the same parameters, each honey contains a different mixture of carbohydrates, proteins, amino acids, minerals, enzymes, aromatic oils, pollen and wax, among others, which are added by bees or due to handling and honey maturation (Belitz et al., 2009, Franchini et al., 2008, Franchini et al., 2011, Lachman et al., 2007).

1.3 Types of honey

The main basis of categorizing honeys in different varieties is the source from which the nectar is extracted. As a result, the first level of honey types classifies it into two groups; **blossom honeys**, when the nectar derives from plants, and **honeydews,** when it is the extractions of living plants or plant-sucking insects.[4]

Moving on, there exists a second level of categorization of honeys, depending on the various types of plants from which the nectar was collected by *Apis mellifera*. Here lie the most numerous categories, each one with its personal taste, flavor, and color. As it is referred, today approximately 300 different varieties of honeys have been recognized, analyzed, and used commercially (Samarghandian et al., 2017).

1.3.1 Pine honey

Honeydew that derives from the extractions of *Marchalina hellenica* insect, which is said to be a pine parasite.

This honey contains high concentrations of ash, high pH and conductivity, and low reducing sugars, such as galactose, glucose, fructose, ribose, xylose, and glyceraldehyde (<52.9%). As a result of pine's honey low concentration in glucose, it crystallizes very slowly, as it can stay fluid for over than one year and a half.

As for the nutritional value of this variety, rare elements are said to be abundant in it, making it a very nutritious choice for honey consumers.[7]

1.3.2 Fir honey

Another honeydew variety, composed by three subcategories of fir honeys:

- *Abies cephalonica*, mostly found on the mountainous regions of Greece,
- *Abies alba* or *Albies pectinata*, which grows all around Europe, up to the Caucasus,
- *Abies hybrida* or *Abies borisii,* which is the product of the mixture of *A. cephalonica* and *A. alba*.[9]

Many insects parasite the three species of trees mentioned above, to produce fir honey from the plants' excretions. Nevertheless, *Physokermes hemicryphus* appears to be the insect that mostly produces fir honey in the highest concentrations annually, as it parasites on *A. cephalonica* and *A. alba*.

Fir honey has its exclusive and highly characteristic appearance and flavor, that differ depending on the geographical origin. Thanks to the low percentage of glucose it contains, it rarely crystallizes, which makes it very competitive in the market.

As for the variety's physicochemical characteristics, it contains low moisture, which could make the honey sensitive to granulation but virtually safe from unwanted fermentation (Thrasivoulou, Manikis, 1995), if it was not for its low percentage in glucose. On the contrary, its pH value is higher than in all other varieties and, as a result, it is said to be the variety that decays at the slowest rate. Finally, reducing sugars appear in low amounts in fir honeys.[9]

1.3.3 Chestnut honey

Chestnut honey can either be a blossom variety, deriving from the excretions of the plant *Castanea sativa*, or a honeydew produced by the aphid *Myzocallis castanicola*.[7]

As far as the physicochemical characteristics are concerned, the values of ash, pH, reducing sugars and conductivity are much like those of a honeydew honey. To be more specific, chestnut honeys have high pH, conductivity, ash, and high concentrations of enzymes, as well.

The variety's flavor and color differ as far as honeydew and blossom honey are concerned. When it comes to chestnut honeydew, it can be dark brown or even black, whereas blossom chestnut honey has a lighter brown color. In both cases, chestnut honey is strongly aromatic, with very intense and kind of bitter flavor.[7]

According to the last report of the European Union, chestnut honey is a blossom honey with honeydew's characteristics.

1.3.4 Thyme honey

Thyme honey is one of the most famous blossom honeys in Greece, with a very high quality thanks to its magnificent flavor. As a variety, it is highly characterized by a burning sensation during consumption, caused by the high concentrations of fructose. Simultaneously, the enzymes diastase and proline are abundant in thyme honey.

As far as the physicochemical properties are concerned, thyme's humidity, ash and pH are the expected concerning honeys, whereas fructose's and glucose's sum sometimes exceed 60%. When it comes to metal concentration, thyme honeys appear to be most abundant in Ca. At the same time, most thyme honeys appear to be medium in color intensity, with floral notes and sweet and salty taste. Nevertheless, there are not much research carried out on the specific variety.[8]

1.3.5 Heather honey

Another variety of blossom honey, that is highly consumed in all beekeeping countries. Especially in Greece, there are four different types of heather honey, depending on the plant from which the nectar is collected by the bee, and all those are examined separately, as they have unique properties. (Thrasivoulou et al., 2002)

- Heather honey by *Erica verticillata.* Honey with high nutritional value. One of its most characteristic properties is that it contains high amounts of water, in comparison with other varieties, sometimes exceeding the limits that national legislation has set. Nevertheless, this is expected and now attributed as a peculiarity of the variety, thus it can still be on the market. Its color is red, it contains high amounts of glucose, which give it a specific sweet taste, but it makes it vulnerable to granulation (1-3 months) and inappropriate for honey mixtures.
- Heather honey by *Erica arborea*. Its color is brighter than the above's, but this one too contains high concentrations of glucose. Of course, it has its proper flavor and taste.
- Heather honey by *Arbutus unedo*. Type of the specific variety that is not used for consumption, but for maintenance and growing of the hive. This heather honey is very stimulant for the hive but highly bitter for people, and therefore its commercial value is low.
- Heather honey by *Rhododendron.* There are more than 400 types of this tree all over the world. The honey that is produced by its nectar can be toxic if consumed before its maturation, as it contains the substance called andromedotoxin, whose formal name is Grayanotaxane-3,5,6,10,14,16-hexol 14-acetate. This toxine is harmful both for people and bees, but it vanishes the time that the honey matures, and then it becomes suitable for corrosion. According to international literature, the cases of poisoning are so rare, that it can probably be linked more to allergic reactions (Olszowy, 1977, Krochmal, 1994).

1.3.6 Orange honey

As all citrus honeys, orange honey is very aromatic, with a light color and a fresh and fruity scent. However, one of its most important drawbacks is its weak resistance to granulation. It originates from Spain and Mexico, yet it is currently cultivated and produced in many countries worldwide.

The chemical composition of this variety follows the standards. Firstly, fructose and glucose reach the percentage of 70%, with fructose exceeding a bit glucose. As far as enzymes are concerned, orange honey is not very abundant, especially in diastase and invertase. Finally, and as for metals, most citrus varieties abound in Ca and can be extremely low in micronutrients, such as Fe, Cu and Mn.[7]

1.3.7 Sage honey

Variety of blossom honey deriving from the nectar of the plant *Salvia officinalis*, commonly known as sage. Although the plant species originates from the Mediterranean region, it is nowadays spread worldwide. On the other hand, the honey that comes from sage was primarily produced in California, United States.

As far as the organoleptic properties are concerned, sage honey's color is bright yellow, whereas its taste is mild. What makes sage honey highly competitive at the market is its capability to resist granulation, thanks to its concentration in simple sugars. Because of that, sage honey can be used to produce honey blends.[10]

1.3.8 Flower honey

It refers to the family of honeys deriving from different flower sources. Those can be either monofloral or hetero/multifloral. Depending on the flower, its color can vary from very light to very dark tones, usually referred to as extra light amber, as well as its flavor, which can be very rich.

As far as the physicochemical properties are concerned, moisture and HMF levels are found to be under the limit that the Codex Alimentarius gives as appropriate, with HMF exceeding the percentage of other varieties, such as pine or acacia. On the contrary, moisture in multifloral honeys appear to be the lowest compared to all other varieties. (Can et al., 2015)

Finally, flower honey usually has high amounts of Cu and other micro-nutrients, which elevates its nutritional value.

1.3.9 Oak honey

Blossom honey, produced by the nectar of the oak tree of the genus *Quercus*.

As far as the organoleptic properties are concerned, oak honey is dark colored. As a result, it contains high percentages of pollen, pigment, phenolic compounds, minerals and Maillard reactions' products, making it simultaneously very nutritional and antioxidant.[7]

1.3.10 Cotton honey

Cotton is a soft fiber, that mostly consists of cellulose. Apart from all its other applications, cotton can be a source for honey production.

This variety in general has no distinct characteristics. Nevertheless, to name a few of its observed properties, cotton honey appears to have very high moisture content, but an average pH value, compared to the rest of the varieties. On the contrary, ash's percentage is notably low.[10]

1.4 Physicochemical and organoleptic characteristics of honey

One of the most important factors as far as overall properties and quality assessment of honey are concerned, is the level of its most fundamental physicochemical characteristics, as well as the parameters that consist the organoleptic profile of the product; aroma, flavor and color. (Baloš et al., 2018).

1.4.1 pH

The pH value of a honey sample is highly connected to the danger of microbiological contamination, and it depends on the percentage of free acids in the sample. The main acid in honey is gluconic acid, in equilibrium with its lactones and esters, as well as phosphates and chlorides. There are also formic, tartaric, maleic, citric, succinic, butyric, lactic, and oxalic acids as well as various aromatic acids (Azonwade et al., 2018). European and international legislation already exist to determine the limits that need to be followed as far as the relevant concentrations are concerned. More specifically, the EU Directive 110/2001 defines that the free acidity of honey must not exceed the value of 50 milli-equivalents/kg. As a result, honeys that accord with the Directive range in pH value between 3.5 and 5.5, whereas honeydew honeys are expected to show higher values than blossom honeys.

1.4.2 Water content

Water activity in honeys is a fundamental parameter for its quality and, consequently, its commercial dynamics, nevertheless it can be affected by various factors, such as soil and climatic conditions, floral origin, intensity of nectar flux, season of harvesting, manipulation by beekeepers and storage conditions. In general, water content varies significantly, depending on the different zones producing honey and on the seasons of harvesting and production. As an overall rule, moisture percentage in honey must not exceed 20%, as then the product becomes vulnerable to crystallization.

1.4.3 Electrical conductivity

This parameter has started to gain notable interest the past few years of scientific advances, because of the emerging food processing methods that have rised, such as ohmic heating and pulsed electric field. Electrical conductivity expresses how well the substance transmits electric current in its structure (Banti, 2020). It has already been applied to numerous processing methods, and as a tool to determine other physicochemical characteristics of food, such as chilling and freezing tolerance. When it comes to honey, the electrical conductivity is connected to the botanical origin, and it should not exceed the limit of 0.8 mS/cm, as it is defined by EU Directive 110/2001.

1.4.4 Ash content

Incineration is the rapid oxidation of a material, through its high temperature burning (Fathima et al., 2014). As a result, all the organic content of the waste is vanished, and the residue is called ash. Ash is indicative of the botanical origin of the honey, and it provides many quantitative and qualitative information about its mineral content. In general, the permissible range of ash in blossom honeys is 0.6% and in honeydew 1.2%.

1.4.5 Sugars

As far as total and reductive sugars are concerned, the applicable limit for blossom honeys is up to 60g/100g and for honeydew up to 45g/100g, dictated by Codex Alimentarius (2001), as well. In general, sugars are the main constituent of honeys, possessing over 50% of whole concentration in all botanical and geographical varieties. Simultaneously, sugar content is affected by moisture as research has shown that rainy seasons act as a disadvantage to the concentrations of sugars in honey.

1.4.6 Enzymes, HMF and amino acids activity

Although all three factors are relatively low in honey samples, they still play a central role in its quality.

Honey enzyme content is a parameter that is mainly affected by storage conditions. Thus, its value can be a very practical tool to evaluate freshness and adulteration of honey. Depending on the floral origin, same enzyme's activity can differ significantly from one sample to another.

The heterocyclic aldehyde 5-hydroxymethylfurfural (HMF) acts in a similar way. More specifically, HMF in honey is produced by reducing sugars, mostly hexose, when they undergo Maillard and caramelization reactions (Shapla et al., 2018). Just like conventional enzymes, like diastase and invertase, HMF's concentration is affected by storage and temperature conditions, thus it can be a bioindicator of honey's quality condition. According to Codex Alimentarius and EU Directive 110/2001, HMF's concentration must be lower than 80 mg/kg and 40 mg/kg, respectively.

As far as amino acids are concerned, proline appears to be the most abundant and critical for honey's quality. Its most important role is to indicate honey's ripeness and, sometimes, adulteration. In general, a minimum limit of 180mg proline/kg is said to be acceptable for quality honey.

1.5 Metals

1.5.1 Macroelements and microelements

The periodic table consists of 118 elements, out of which 92 are classified as metals. To define the term, metal is an element that creates positive ions, named cations, through its ability to give electrons at other elements (non-metals), forming crystalline solids that consist of ionic or heteropolar bonds. Some of the common properties that metals bear are their malleability, their ductility, their high electrical and thermal conductivity, their high reflectivity of light, their high melting points, and their density. Some of the most abundant metals to be found on Earth's surface and in its crust are Al, Fe, Ca, Na, K, and Mg. In any case, most metals occur as ores, as they highly react with other elements to create those mineral-bearing substances.[11]

The importance of metals for the evolution of mankind is very easy to understand, if someone considers that different metals were used to name different eras in ancient literature and history, such as the Iron Age, the Copper Age, and the Bronze Age. Consequently, in the modern society, metals have various applications in everyday life and can be found in many different sources. Fe in tools and vehicles, Al in kitchen equipment and windows, Zn in plastics and cosmetics, Hg in thermometers and Ti in joint replacements and tooth implants are only a few that can be cited.[11]

Apart from the applications mentioned above, metals can also be found naturally in food and beverages, or as residues, because of their presence in the environment and because of human action (farming, fishing, industrialization etc.). Among those, some are beneficial to human health and thus are intentionally added to food products, others can he harmful under certain conditions (consumer's age, amount of intake etc.), whereas some others are harmful or even toxic under all circumstances and are highly prohibited for human or animal consumption.[12]

Depending on the percentage of a mineral into the food or the beverage sample, metals are divided into two groups: macroelements or primary nutrients for those found in large supply, usually of mg/kg (Na, K, Mg, Ca, P), and microelements or rare elements, that are found in smaller percentages, usually μg/kg or ng/kg (B, Al, Cu, Fe, Mn, Zn etc.)

Regarding the six primary nutrients Na, K, Mg, Ca, and P, they possess the largest quantities compared to the rest of the elements. Those are grouped into the category of the beneficial for human health minerals, thus food market often attempts to enhance their concentrations into the food products. Nevertheless, special legislation is applied, to avoid the side effects of possible overconsumption.[13]

On the other hand, microelements can be either essential or quasi-essential for human, animals, and plants (Nieder et al., 2018). More specifically, elements such as Zn, Fe, Mn, and Cu are characterized as essential, whereas Si, Sr, and Co as quasi-essential or beneficial. Additionally, for human, Cr, I, and Se are essential. The common characteristic of the microelements is that they are found in relatively small amounts in all sources, sometimes constituting less than 0.1% of the total concentration. Just like macronutrients, microelements can turn out to be harmful or toxic, if consumed against relevant legislation. Specifically in humans, microelements play ruling nutritional roles, such as synthesis of enzymes, regulation of growth, development and functioning of the immune and the reproductive system. For those reasons, it is of high priority to control the levels of those nutrients in human body, mostly through dietary diversification and food fortification with the appropriate elements.

1.5.2 Rare earth elements

In the past few decades, the intense anthropogenic activity has led to numerous developments and discoveries in many technological and scientific sectors. As a result, apart from the macroelements and the micronutrients that were already known to mankind, nowadays there has rised a group of new elements, called rare earth elements (REE).

Rare earth elements are 17 elements, 15 of which belong to the group of lanthanides, including Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu). Two additional elements have been classified as REEs, namely Yttrium (Y) and Scandium (Sc) (Gwenzi et al., 2018). Due to their specific physical properties, they have encountered many applications in everyday life, thus they can be found as catalysts, in mobile communications, in electric cars, in fuel additives etc. When it comes to the impact of REE in human health, they displace Ca from living systems, resulting in biochemical side effects and disfunction. In all cases, there is not sufficient research concerning the actual effect of all rare elements on human's health, nor health-based guidance values. Consequently, it is of great importance to obtain adequate statistical data in various food and beverage products, to calculate their concentrations and to identify the effects they have on human's health.[16]

Chapter 2 Analytical techniques

2.1.1 Microwave plasma atomic emission spectrometry (MP-AES)

MP-AES is an analytical technique that firstly came out in the market in 2011. At that time, two other techniques, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were very popular on elemental analysis. Until the introduction of Agilent's instrument, MP-AES had not yet achieved great success. Nevertheless, after this evolution and for the last decade, the technique has established as one of the main methods for qualitative and quantitative mineral analysis of food, water, environmental and pharmaceutical samples.

The instrument's function is quite similar with the ICP's. More specifically, the MP-AES equipment consists of a standard torch, a spray chamber, and a glass concentric nebulizer. Simultaneously, a monochromator is included, usually with wavelength rage 178-780nm, as well as a solid-state charge-coupled detector (CCD) (Balaram, 2020).

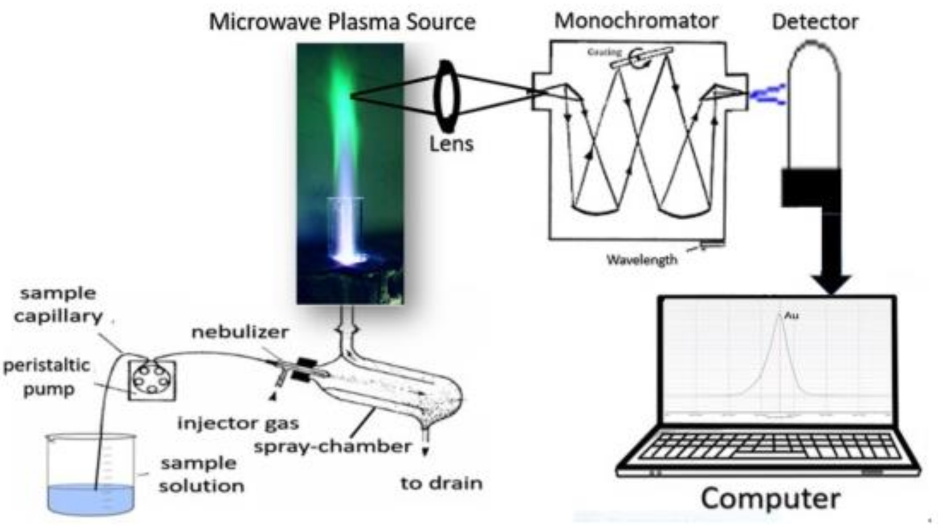


Figure 3. Schematic representation of MP-AES instrumental method

All samples must be injected into the organ in a diluted solution form. The injected portion is turned into an aerosol and headed towards the plasma chamber, where the atomization occurs. Thanks to the high temperature inside the system, various elements of the periodic table can be exited. The atoms or ions are then separated and detected by the monochromator and the detector, respectively.

One of the biggest advantages of MP-AES technique is that it provides better sensitivity compared to other similarly used techniques, such as F-AAS. In that way, extreme dilutions can often be avoided, automatically making the technique much faster and easier to run. Also, Agilent's instrument is quite simple to be used, less expensive and with a smaller footprint.

Overall, MP-AES technique has been able to dominate flame AAS technique, as well as reach almost the same productivity levels with ICP-AES technique. Nevertheless, the ICP-MS still appeared to be much more applicable and sufficient, as it provides privileges -isotope determination, linearity, speed- that no other technique can yet provide.

2.1.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS was developed during the 1980s', but it has lately started to gain scientific interest as an appropriate technique for trace element's quantification, thanks to its easy sample introduction and quick analysis. The past few years, it has evolved into a highly remarkable technique for quantitative and qualitative analysis of all kinds of multi-elemental samples, often at the part per trillion or part per quadrillion level.

As far as its structure and application is concerned, it follows the same workflow with most mineral analysis techniques. More specifically, there are four definite steps that constitute this workflow:

1. Sample introduction and aerosol generation
2. Plasma source ionization
3. Mass discrimination (m/z ratios determination for each ion and categorization)
4. Detection system

However, ICP-MS bears some distinct differences that make it more powerful. Thus, ICP-MS equipment use a high temperature plasma as source of atomization or ionization, making it capable to analyze approximately all the periodic table elements, as well as their isotopes' ratio. Additionally, noble gases such as argon are used as plasma gas. Because of the extremely high temperatures of the plasma (7000K), ICP-MS turns out to be the most suitable technique for liquid samples' analysis, as their vaporization happens more easily and more rapidly (Pröfrock et al., 2012).

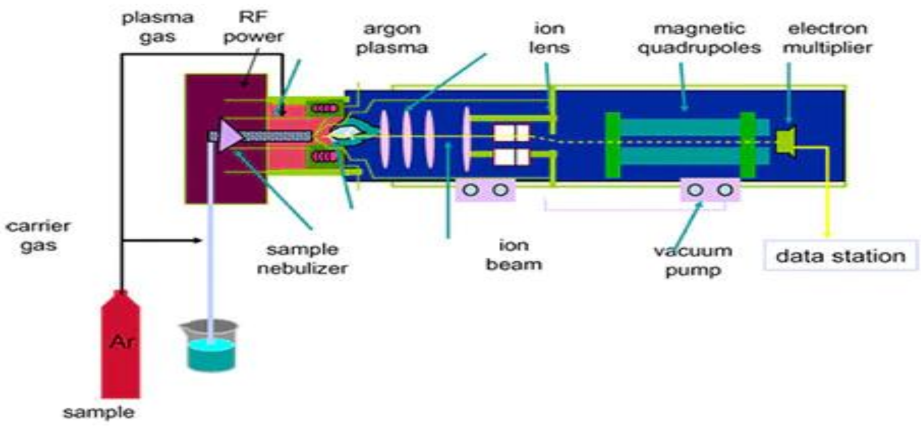


Figure 4. Scheme diagram of ICP-MS equipment

2.2 Statistical Analysis

As it occurs in all analytical methods, two are the most important stages of every experiment in natural sciences; sampling and statistical analysis.[30]

To be more specific, sampling describes the strategy followed in order to reduce a wide number of possible specimens into an easier-to-use variety of samples. In that way, the experimental path becomes easier and faster, nevertheless it bears the risk of missing out on accuracy, because of the screening.

As a means of protection by the risk mentioned above, the statistical analysis dominates in analytical methods as the second most important stage of them. More precisely, the statistical analysis consists of tests and mathematical calculations of specific values, such as the standard deviation (s), the variance (s^2), the median and the significant figures (Shiundu, 2020). The main purpose of those is the evaluation of the data given by the analysis and the extraction of conclusions as far as the accuracy and the validity of the results are concerned.[30]

Every experiment is based on an existing protocol, which always provides the analyst with theoretical values (μ) about each analyte that he is interested into. Nevertheless, experimental conditions are never the same, and as a result the final value measured (x_{mean}) by the analyst always differs from the theoretical one. The parameter that evaluates their difference is the accuracy of the method.[30]

Another crucial characteristic is the repeatability or precision of the method. The repeatability is interested only on the experimental results that are given by the same sample that is put under analysis various times, under the same environmental and experimental conditions. More precisely, it measures the numerical difference among those repetitions. Standard deviation, relative standard deviation and range are the three means of repeatability's evaluation, all mentioned above in Table 1.

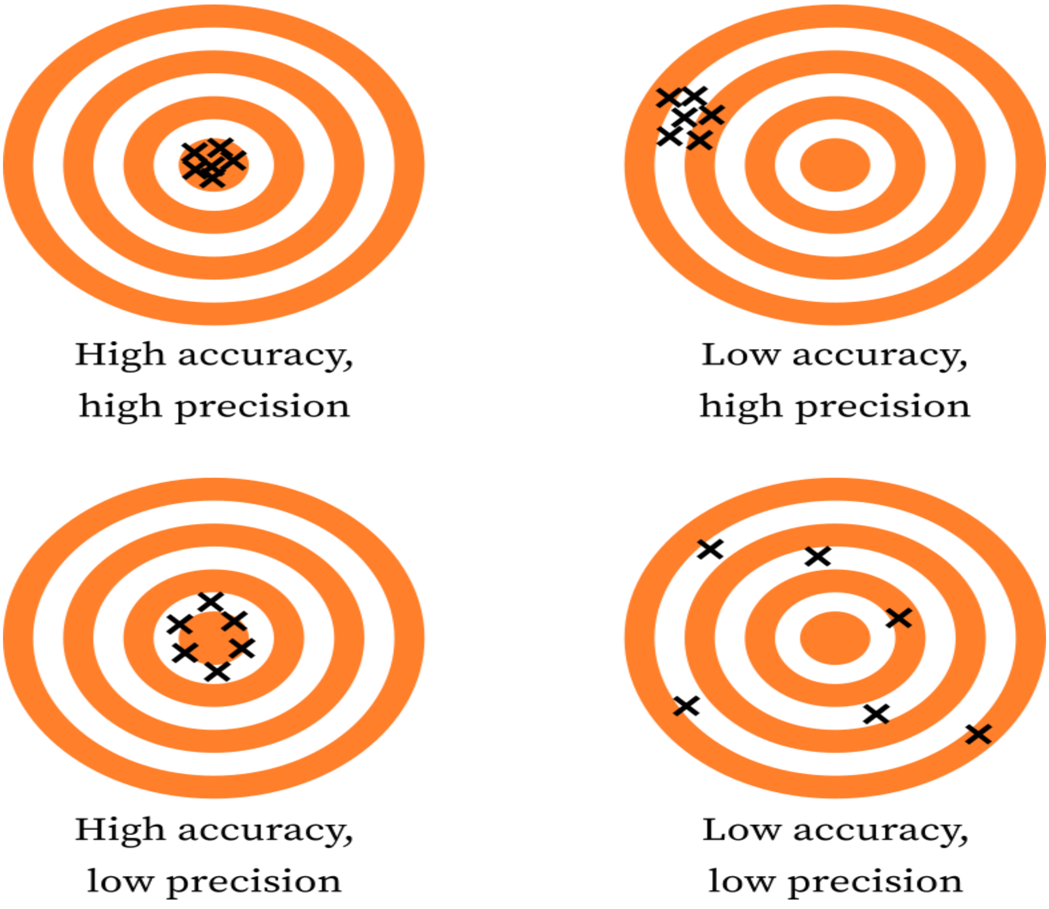


Figure 5. Different cases of statistical results

Experimental errors include two different categories. The systematic errors are those occurring in the method or the instrumental conditions, thus they are predicted by the analyst and, normally, they are included in the final calculations. On the other hand, random errors come from unexpected reasons, and their appearance and effect on the results can not be predicted.

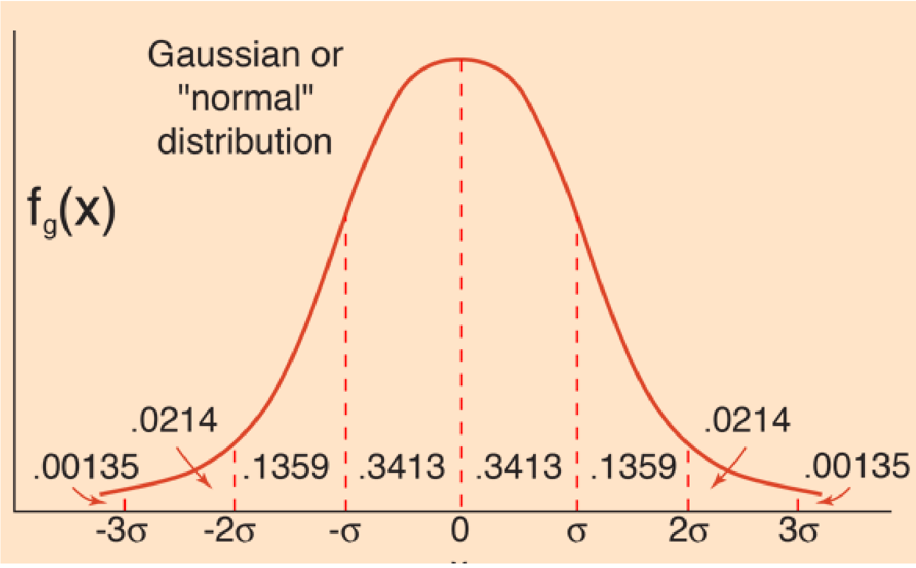


Figure 6. Gaussian distribution

Random errors appearance follows the Gaussian distribution. According to this, in every analytical method exists the theoretical value μ that is expected, and there exist also some confidence limits on the left and right of this value, inside of which any experimental result is accepted. Those confidence limits are described by the parameter t.

Furthermore, statistical analysis is divided into two categories, based on the number of the examined variables. As a matter of fact, the term variables can be split into two subcategories; the categorical variables, which have a definite number, e.g., zodiac sign or gender, and the numerical variables, that have various numbers describing them, such as height or weigh. Those categories are the univariate and the multivariate analysis which, on their behalf, involve different mathematical methods.

2.2.1 Univariate Analysis

The univariate analysis refers to the statistical methods used and practiced, to analyze one single variable qualitatively and quantitatively.[31]

The most used tools of univariate analysis are mentioned in the Table 1.

Table 1. Values of univariate analysis most measured

Statistical value	**Definition**
Average	Number taken as representative of a list of numbers, given by the sum of those numbers, divided by their amount (N)
Standard deviation	Indication of the dispersion of a list of numbers
Range	Difference between the maximum and the minimum value of a list of numbers
Median	The middle number of a list of numbers, organized by size
Box plots	Graph of statistical data, depicting the minimum, the maximum, the range, and the median of a list of numbers

2.2.2 Multivariate Analysis

On the other hand, the multivariate analysis occurs when many variables are simultaneously examined, such as spectroscopic and chromatographic data. One of the most widespread exploratory techniques is the Principal Components Analysis (PCA), which acts rather in a descriptive than in an inferential way, and aims to comprise the relevant information of the data in fewer variables.[31]

The main idea of PCA is reducing the dimensionality of a dataset, while preserving as much variability as possible (Jolliffe et al., 2016). Because of the volume of this data, it is necessary to shorten the dataset in a way, without seriously affecting the validity of the results. Thus, by combining the original variables acquired from the measurement, different variables emerge. Those new variables are called principal components (PC). In the end, what the statistician wills, is to have the minimum variables possible with the highest rate of confirmation of the results.

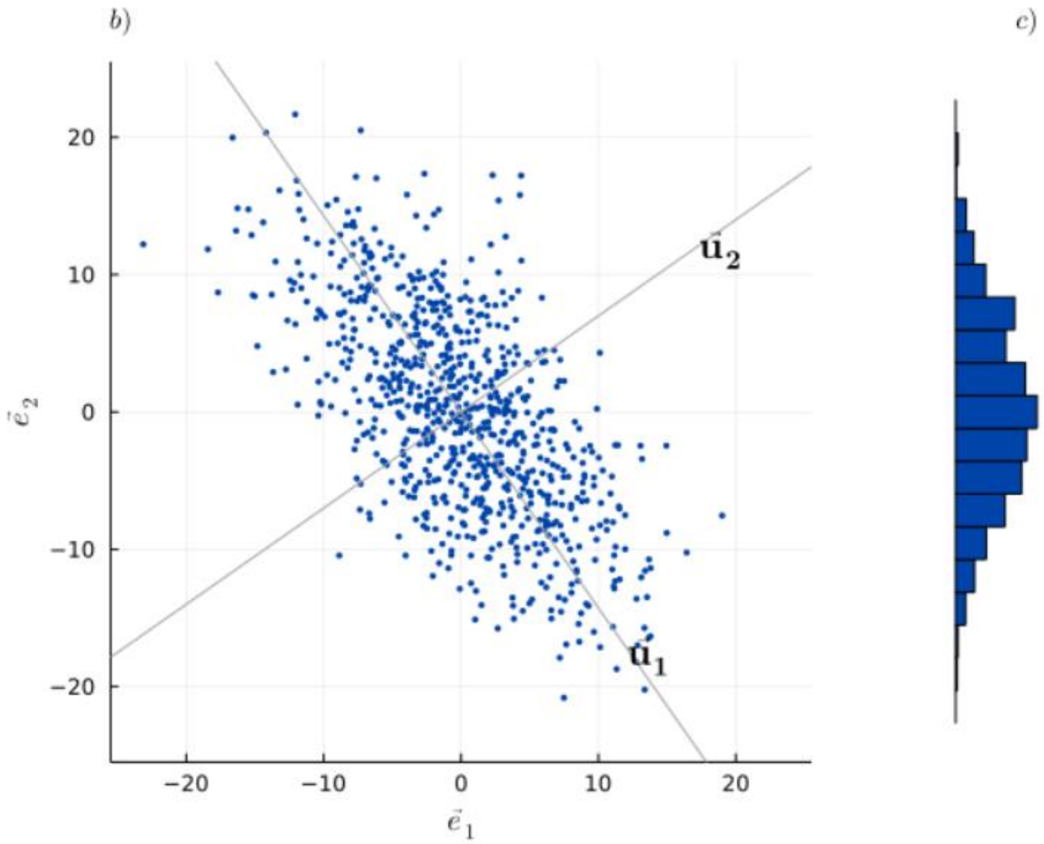


Figure 7. Distribution of values in a PCA histogram

Table 2. Literature review of research on honey types

Research	Reference	Technique	Results	Conclusions
Analysis of 187 samples of 11 different Hungarian honey varieties, for 4 macro (Na, K, Ca, Mg) and 15 micro elements (Al, Ba, Bi, B, Cd, Cr, Cu, Fe, Li, Mn Ni, Pb, Sr, Zn)	Zsofi Sajtos, Petra Herman, Sandor Harangi, Edina Baranyai, Elemental analysis of Hungarian honey samples and bee products by MP-AES method, 2020	MP-AES	-Na, Ca, Mg, K, Al, Mn, Fe, B, Ba, Bi, Cd, Co, Cr, Cu, Li, Ni, Pb, Sr, Zn concentration above limits -K the most abundant, mostly in chestnut honey (1/3 of total honey concentration in metals) -Ca, Mg, Na, B the following most abundant -Al, B, Ca similar concentration in Greek and Hungarian honey -Lower Ca concentration than in Turkish honey -Chestnut honey the most abundant in Mn concentration -Metals in honey varieties: Chestnut>Honeydew>Forest>Linden>Sunflower>Herbs>Multivarietal>Canola>Acacia>Phacelea -Honey geographical origin in most Hungarian regions, the botanical origin affects the elemental profile more than the geographical (both in Greek and Hungarian honey)	Honey has different elemental content depending on its species, age, storage conditions, and the concentrations of the components of the samples should only be compared if they are measured in dry weight.
Analysis of basic and toxic	Czipa et al., 2015	ICP-MS	-Detection of 16 elements in Hungarian honeys (Al, Ca, Cu, Fe, K, Mg, Mn, P, S, Zn, As, Cd, Cr, Mo, Pb, Se)	

elements in 34 mono- and multivariate honeys			-Significantly high concentrations of Ca in sunflower honey -Cu, Fe <LOD -K the most abundant -High amounts of Mg and Mn	
Analysis of 5 trace elements (As, Cd, Cu, Cr, Pb) in 42 honey samples	Ajtony et al., 2007	ICP-MS	-Low concentration of Cu	
Multi-element analysis (42 metals) of 57 honey samples with the aim of developing a reliable method to detect the origin of honey/Comparison with honeys from Spain, Turkey, Skopje, Saudi Arabia	B.L.Batista, L.R.S. da Silva, B.A. Rocha, J.L.Rodrigues, A.A. Berretta-Silva,T.O.Bonates, V.S.D.Gomes, R.M. Barbosa, F. Barbosa, Multi-element determination in Brazilian honey samples by inductively coupled	ICP-MS	-Higher concentrations of Ni, Mg, Al, and lower concentrations of Pb, Cd, Cu in Brazilian honeys -Concentrations in P, Zn, Mn, Fe like honeys from other countries	Concentrations of Ca, K, Mg, Li, Na, Rb are related to botanical origin, agricultural practices, and soil characteristics. Concentrations of Fe, Zn, Cu, Cr, Ni, Al, Cd, Pb are related to environmental contamination. Concentrations

	plasma mass spectrometry and estimation of geographic origin with data mining techniques, 2012			of rare earths such as La, Dy, Ce, Th, Sm, Ho, Er, are related to the use of fertilizers.
Elemental analysis of 26 acacia honeys of unknown botanical origin (collected between 1958 and 2018), together with the AMS technique to find the calendar age of the samples and test the ability of radioactive ^{14}C to date the samples	Tamas Varga, Zsofi Sajtos, Zita Gajdos, A.J. Timothy Jull, Mihaly Monlar, Edina Baranyai, Honey as an indicator of long-term environmental changes: MP-AES analysis coupled with ^{14}C-based age determination of Hungarian honey samples	MP-AES	-K the most abundant metal in acacia honey (80% of total elemental content) -Differences in the metal content of the samples were detected, depending on the year of harvest, e.g., in the macro elements K, B and in the microelements Zn, Pb. Specifically: • Higher percentages of B in the older (1959-1987) compared to the newer (1994-2018) samples → the phenomenon may be the result of changes in the physical and chemical properties of the soil, as well as anthropogenic emissions • The percentages of K did not show significant statistical differences • Zn was found to be significantly higher in old samples (highly related to anthropogenic emissions, e.g., fertilizers) • Pb was also found to be more abundant in old samples, which is an indicator of industrial activity and contamination, as well as increased traffic (hence the low Pb percentages measured in honey samples from producers living far from industrial areas) • Acacia honey has been found to be an indicator of the Anthropocene (beginning of major human impacts on the Earth's geology and ecosystems), since the sharp increase in radioactive ^{14}C in it, as well as in other foods and organisms, is evident	-The mineral content of honey in Greece, Poland, Hungary is more influenced by the botanical than by the geographical origin of the samples. -In general, apart from the botanical and geographical origin, the elemental content of

				honey can be affected by environmental factors of natural and man-made sources, climate, climatic conditions (e.g., precipitation) -Honey can act as a biomarker of natural and anthropogenic environmental effects, since environmental parameters accumulate in the samples over the years.
Identification of Greek honeys from pine, fir, chestnut, thyme, sunflower,	Thrasivoulou A., Manikis I., Tananaki Ch., Tsellios D., Karabournioti S., Dimou M.,		-The most important factors for detecting the botanical origin of honeys: •electrical conductivity • total elemental content • glucose and fructose content	-Taste and color, characteristics of the botanical origin

heather, orange and cottonwood, through the determination of its physicochemical characteristics (sugars, trace elements, minerals, enzymes, quality criteria)	The identity of Greek honey A. Physicochemical characteristics that underpin product quality, 2002		• reducing sugars • maltose • arabinose • microscopic features	
Calculation of multielement content (Al, B, Ba, Ca, Cd, Cr, Cu, K, Mg, Mn, Na, Ni, Pb, Sr, Zn) of 140 honey samples (honey, rye, rape honey) from 16 regions of Poland	Maria Chudzinska, Danuta Baralkiewicz, Application of ICP-MS for determination of 15 elements in honey with chemometric tools for the verification of authenticity, 2011	ICP-MS	-K, Mg the main constants influencing the botanical discrimination of honey samples into species (botanical authenticity indicators) (100% and 82% predictive ability, respectively) -Poor results in geographic discrimination of samples, as the effect of botanicals over geographic features was dominant -Elements that mainly determine the geographical distinction of the samples: • Mn, Ba for rye • K, Mg for rape honey • Mg, Al, Mn for honeydew	-Chemometric analysis: a useful tool for differentiating honeys, and thus establishing authenticity

Determination of 12 elements (Al, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Zn) in 30 honey samples from different regions of Poland (rape honey and honeydew)	Maria Madejczyk, Danuta Baralkiewicz, Characterization of Polish rape, and honeydew honey according to their mineral contents using ICP-MS and F-AAS/AES, 2008	ICP-MS (F-AAS/AES)	-K the most abundant element (aver. 1233 $mg \cdot kg^{-1}$)/ also high concentrations of Na, Mg, Ca) -Lower concentrations of K, Na, Mg, Mn in rape honey, but higher concentration of Ca, B, Cr - B content like Spanish honeys -Polish honey averages three times higher concentrations of K, Ca than Spanish and Italian honeys -In samples from the same area, C_{Zn} in honeydew > C_{Zn} in rape honey - Fe in the analyzed Polish samples was found as much as in acacia honey from Slovenia -Cu: dark colored honey accumulates it more -Based on the results: • Differentiation of the samples into two categories (botanical distinction): -Composed of B, Ca, Cr, Mg, Na -Composed of Al, Cr, Cu, Fe, K, Mn, Ni, Zn -Overall, the elements in which the biggest difference was found between the two species analyzed were K, Fe, Ni, Mn, Al, while the honeydew had an overall higher elemental content - Trace elements Ni, Mn, Cu, Fe, K indicators for the quality of honey	
Elemental fingerprinting of 181 honey samples from 6 regions of New	Megan N.C. Grainger, Hannah Klaus, Nyssa Hewitt,	Q-ICP-MS	-V, Hg, rare elements (La, Ce, Pr, Nd, Sm, Eu, Dy, Ho, Er, Tm, Yb, Lu,) undetectable concentrations in all samples, U >LOD only in 8 samples, so these were abandoned -Immediately more abundant elements Al, Mn, B, Rb, Fe, where (except Al,	

Zealand to detect differences due to harvesting area and use of the area around the apiaries (industrial, urban, rural)/Analysis of samples for 37 metals (macro, trace, trace, and trace lands)	Amanda D. French, Investigation of elemental content of honey from regions of North Island, New Zealand, 2021		Fe, with 92.8% and 90.1% presence, respectively) were present in all samples - The absence of Al, Fe (albeit in a small percentage) was considered strange, due to their high concentration in other samples, but also their biological importance in general - Thyme honeys from New Zealand and Spain showed a similar elemental profile for K, Ca, Fe, Zn, Mn, Rb, Cl → botanical origin affects metal content more than geographical -The remaining elements (Zn, Cu, Ba, Sr, Cs, Cr, Ni, Co, Cd, Tl, Pb) account for 0.08% or less of the total elemental content, indicators of environmental contamination -Ni levels similar for all regions of New Zealand, but always lower than the concentration of the element in honeys from other countries -New Zealand → variety of different geographical areas → distinction of honeys based on them: • More abundant macronutrients (K, Na, Ca, Mg), statistically significant quantitative differences by region (related to soil/geographic distinction)	
Quantitative and qualitative determination of Cd, Pb, Co, Cr, Cu, Zn in honey samples for the detection of	Monica Sadowska, Wojciech Hyk, Anna Ruszczynska, Aleksandra Roszak, Anna Mycka, Beata	ICP-MS	• Trace elements and rare earths -Cd was further studied, because it is linked to anthropogenic activity around the hive: present in 8.8% of the samples, its concentrations were found to be lower than those previously noted in New Zealand (but in general very large variations and dimension of scientific results and research in quotas of) -Cd, Pb present in samples that came from areas with intense agriculture	

environmental metal contamination	Krasnodebska -Ostrega, Statistical evalutation of the effect of sample preparation procedure on the results of determinations of selected elements in environmental samples. Honey bees as a case study, 2020		or traffic	
Detection of elemental deposition (Na, Mg, K, Ca, Cr, Mg, Fe, Co, Ni, Cu, Zn, As, Cd, Pb) in bees (Apis mellifera L.) (worker bees, drone bees and brood bees) and in their	Jelena Ciric, Danka Spiric, Tatjana Baltic, Ivana Brankovic Lazic, Dejana Trbovic, Nenad Parunovic, Radivoj Petronijevic, Vesna Dordevic,	ICP-MS	-Quite strong quantitative differences per sample harvest area (geographical distinction) -K the most abundant element of all in all samples -Co was not detected in any sample -Cd was detected in two samples from areas exposed to industrial contamination - Apart from those mentioned, none of the remaining 12 metals (Pb, Cd, Cu, Zn, Fe, Cr, Sr, Ba, Ca, Na, K, Mg) exceeded the predicted numbers -In Croatia, for honeys derived from the nectar of a single plant: • Citrus honey → higher in Fe, As (5.17 mg kg^{-1} and 276.1 μg kg^{-1},	

products in (Serbia, Montenegro, Croatia)	Honeybees and their products as indicators of environmental element deposition, 2019		respectively), lower in Pb (301 μg kg^{-1}) • Meadow honey →higher in Na (36.1 mg kg^{-1}), lower in Cu (4.38 mg kg^{-1}) • In general, higher aver. concentrations for Ca, Cu, Pb compared to other European countries -Concentrations of toxic metals (and in comparison with the legislation of Serbia and the European Union): • Not significant Pb difference in contaminated and uncontaminated areas, but of course higher in contaminated/similarly for Cd • As significantly higher in areas of industrial contamination	
Analysis of 36 honey samples of different botanical origin from three different regions of Tunisia, for the concentrations of 19 elements, with the aim of their botanical and geographical distinction	Giuseppa Di Bella, Angela Giorgia Potorti, Asma Beltifa, Hedi Ben Mansour, Vincenzo Nava, Vinzenzo Lo Turcom Discrimination of Tunisian honey by mineral and trace element chemometrics profiling, 2021	ICP-MS	-K the most abundant element in all samples, followed by Na, Mg, Ca, Fe and Zn -Ti, Mn, Cu, Se, Pb, Ni, Cr, V, Sb → detected as trace elements -Co, Hg in undetectable amounts in all samples -Concentration variations in Ca, Ti, Mn, Cr, V, Sb, As, Cd depending on the botanical origin of the sample: • Honey of the jujube tree higher Ca than all others • Prickly pear and thyme honey higher Tia than jujube and eucalyptus • Jujube and rosemary honey higher V than wildflower and thyme honey -Differentiation of samples into three clusters (geographic discrimination) based on qualitative and quantitative differentiation in Mn, Ca, V, Cr, Ti, Cd -Higher concentrations of Pb than the legal limit, but not to the point of making the honey dangerous and unfit for consumption	

Analysis of 16 honey and 9 pollen samples from the Mitrovica region, Kosovo, to detect contamination levels	Granit Kastrati, Musaj Pacarizi, Flamur Sopaj, Krste Tasev, Trajce Stafilov, Mihone Kerolli Mustafa, Investigation of concentration and distribution of elements in three environmental compartments in the region of Mitrovica, Kosovo: soil, honey and bee pollen, 2021	ICP-MS (ICP-AES)	-Maximum concentrations of elements (mg/kg): Cu (2.98) > Pb (2.10) > Zn (1.90) > Cr (0.84) > Ni (0.22) > As (0.12) > Cd (0.04) > Co (0.03), and median values: Cu (1.33) > Zn (0.73) > Pb (0.42) > Ni (0.13) > Cr (0.1) > As (0.04) > Cd (0.02) > Co (0.01) -Cu the most abundant (probably) toxic metal -Differentiation of the samples into 4 clusters: • 1st based on K (together with P they were found very high in quota, which is also partly linked to the use of fertilizers) • 2nd based on Ca • 3rd based on Na, Mn, Cu, Al (→ geogenic origin) • 4th based on Zn, Pb, Cr, Sr, Ni, Cd, As (→ anthropogenic origin) -Higher amounts of Cu, Zn, Pb, Cr, Ni in Mitrovica and Zvecan areas, where Pb and Zn smelters are located -Higher amounts of Al, As, Cd in samples from areas with industrial ore processing	
Establishment of elemental profile and geographic	Bibiana Silva, Luciano Valdomiro Gonzaga,	ICP-MS	-High concentration variations for rare earths in all samples (Eu > Nd > Ce > La > Sm): • Nd, Ce higher in samples from stingless bees	In general, honeydew has a higher elemental

discrimination of 23 samples of bracatinga (Mimosa scabrella Bentham) honeydew, produced in three regions of Brazil, for 39 metals	Heloisa Franca Maltez, Katia Bennett Samochvalov, Roseane Fett, Ana Carolina Oliveira Costa, Elemental profiling by ICP-MS as a tool for geographical discrimination: The case of bracatinga honeydew honey, 2021		• Nd, Eu higher in orange and sugarcane honey samples -Detection of rare earths La, Pd, Pt, Au, as well as trace elements Co, Cs, In, Te, Tl in Argentine honey samples -In honeys of the same botanical origin, the concentration of metals varies according to climate, soil vegetation and soil chemistry, which varies from region to region and from year to year -First time Rb was detected in honeydew -Large variations in the concentration of (possibly) toxic elements, such as Pb, Cd, Hg (probably due to factors such as soil, climate, organic load, pH and fertilizers) -In, U, Pr, Ho, Ir, Tm, Lu concentrations <LOD → not studied further -Rb, Co indices of geographical discrimination of honeydew samples	content than plant nectar honey (shown - due to its dark color)
Qualitative and quantitative detection of heavy metals in 100 honey samples from Egypt, assessment of their health risk	Farag Malhat, Konstantinos M. Kasiotis, Ashraf S. Hassanin, Shokr A. Shokr, An MIP-AES of heavy metals in Egyptian honey: toxicity	MP-AES	-High amounts of Cd, Cu in areas with anthropogenic activity (agricultural chemicals, mineral fertilizers, industrial and urban wastewater), however a small percentage of these comes from the earth's crust -Generally, Cu, Cd, Fe, Pb, Zn in honeys from different regions of Egypt were found in lower concentrations than recommended → honey suitable for consumption	-Zn contamination of honey: during harvesting and storage, when honey is transported in galvanized containers, as well as

	assessment and potential health hazards to consumers, 2018			proportional to the botanical origin of the honey (flowers on which bees feed)
Analysis of 11 trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in 61 honey samples of known botanical origin from Croatia	Maja Lazarus, Blanka Tariba Lovakovic, Tatjana Orct, Ankica Sekovanic, Nina Bilandzic, Maja Dokic, Bozica Solomun Kolanovic, Ivana Varenina, Andreja Juric, Marija Denzic Lugomer, Dragan Bubalo, Difference in pesticides, trace metal(loid)s and drug	ICP-MS	-The mineral content of honeys varies, depending on the botanical origin, between conventional and organic honeys -Pb in conventional chestnut honeys by 42% higher than in organic honeys, while Cr by 65% higher in organic honeys. In general, higher concentrations of metallic trace elements were measured in conventional chestnut honeys, savory and multifloral honeys, than in the corresponding organics, while the opposite was true for sage honey. -In Mn, the greatest concentration variations were measured in honeys of different botanical origin/most abundant in chestnut honey, which is the type of honey richest in pollen grains -Dark honeys were found to contain more minerals than pale ones	Metalloids in honeys can come from the environment (industry, combustion, traffic, agriculture)

	residues between certified organic and conventional honeys from Croatia, 2020			
Analysis of 93 honey samples of different botanical origin, for their content in trace elements and rare earths	Spiros A. Drivelos, Georgios P. Danezis, Michal Halagarda, Stanislaw Popek, Constantinos A. Georgiou, Geographical origin and botanical type honey authentication through elemental metabolomics via chemometrics , 2021	ICP-MS	-Content in rare earths, proportional only to the soil geology of the flowers from which the bee has collected the pollen, regardless of whether it is conventional or organic cultivation -On the contrary, strong fluctuations in the content of trace elements (as the environment is further enriched with them by human activity, e.g., fertilization, insecticides, pollution, climate change, etc.)	-So, elemental metabolomics can distinguish honeys according to their geographical and botanical origin, however it is not effective for distinguishing the type of cultivation (conventional or organic)

Evaluation of the level of 26 trace metals and more general elemental differences between honey samples from different regions of Queensland and Australia	Natasha L. Hungerford, Ujang Tinggi, Benjamin L. L. Tan, Madeleine Farrell, Mary T. Fletcher, Mineral and Trace element analysis of Australian/Queensland Apis mellifera honey, 2020	ICP-MS	- Large variations of metals from one sample to another - More abundantly (mg/kg): K(965)>Na(99.7)>Ca(85.2)>P(51.5)>Mg(28.7)>Zn(6.0) -For the trace elements, the samples were categorized as mixtures, rural, peri-urban and urban (geographical origin), and thus: -Zn, Fe, Mg higher amounts in urban honeys, compared to rural ones, as well as higher K, Na, P, Ca, B, Cu (anthropogenic activities) -Only Mn was found less in urban honeys compared to rural ones General: Urban-rural → large differences in P, B, Na, Mn, K, Cu Mixed-urban → large differences in K, Cu, P, Mn, B, Sr, Ni, Na Peri-urban → large differences in P, K, Mn Peri-urban-rural → large differences in Na	
Distinguishing honey samples based on their botanical origin through the analysis of 40 metals	Squadrone S., Brizio P. Stella C., Pederiva S., Brusa F., Mogiliotti P., Abete M.C., Trace and rare earth elements in monofloral and multifloral honeys from	ICP-MS	-Higher trace element contents were measured in chestnut honey, lower in acacia honey. Intermediate and similar contents (11-17 mg/kg) were found in linden, multifloral and rhododendron honeys. -On the contrary, the content of rare earth samples was higher in lindens, hybrids and acacias, and lower in acacias and rhododendrons. -Ag, Be, Bi, Cd, In, Ga, Sb, U, Tl <LOD in all samples -For the rest, were measured: Rb>Al>Pb>V>Sn>As (non-essential elements)/ Mn>Fe>Zn>Cu>Ni>Se>Cr>Mo>Co (essential elements) -Acacia honey was found to have the lowest concentrations of all metals, apart from Pb -On the contrary, chestnut honey has the highest concentrations of most	

	Northwestern Italy; a first attempt of characterization by a multi-elemental profile, 2020		elements -Elemental content proportional/depends on color (higher in dark honeys) -In linden honey, more As, Mn, Sn -In blends, more Cu, Fe, Mo, Ni, V, Zn -In rhododendron honey, more Cr, Se -Statistically significant differences in Al, Cu, Mn, Mo, Rb, Sn → potential interest for honey characterization based on botanical origin -The content of rare earths distinguishes single variety honeys from blends	
Qualitative and quantitative detection of 16 metals in honey samples from the Amorpha fruticosa L. tree in China	Min Zhu, Haoan Zhao, Qian Wang, Fanhua Wu, Wei Cao, A novel Chinese honey from Amorpha fruticosa L.: nutritional composition and antioxidant capacity in vitro, 2020	ICP-MS	-The main ones found were: K, Ca, Na, Mg, Zn, Fe, Cu, Ni, Cr, Co, Mo, Al, Pb, Sb, with K being the most abundant - Macronutrient content from this region → statistically lower than honeys of other botanical origin (jujube) from the same region → index of botanical origin	

Chapter 4 Scope and objective

To sum up the information that has been cited so far, honey is a natural product that is produced with the cooperation of both natural and human means. Through the ages, many civilizations have exploited this specific product for many different reasons, each one concerning a different sector of human societies', such as medicine, cosmetics, food consumption and economy, underlining its massive force. Nevertheless, as all such products, there are specific characteristics that serve its quality needs, making it even more competitive and asked by people. Those characteristics, when they refer to food products, are either physicochemical (pH, electrical conductivity, moisture etc.) or organoleptic (flavor, color, odor etc.). As it is crucial to exist a common international language to group all food products, including honey, into salutary, damaging, and toxic, there are national, European, and international legislations, that set the limits and conditions of consumption of each food, according to its contained ingredients.

The aim of the present study is to analyze different honey varieties of Greek origin. More specifically, using two techniques, MP-AES and ICP-MS, numerous honey samples had been properly processed and analyzed by the two organs, to detect and measure the concentration of most important macronutrients, micronutrients, and rare elements in those varieties. Having those data, the study managed to match each variety with specific metals' concentration and characteristics. Simultaneously, the project jumped into conclusions as far as how the botanical and geographical origin of a honey can affect its final qualitative and quantitative mineral profile, as well as its organoleptic characteristics. For all the above objectives of research, international literature had been studied profoundly.

Chapter 5 Experimental Data

5.1 Instrumentation

For the MP-AES analysis, the 4210 MP-AES Agilent Technologies instrument was used, simultaneously connected to the MP Expert computer program, to organize the analysis' data and depict the results.

Figure 8. 4200 MP-AES set-up

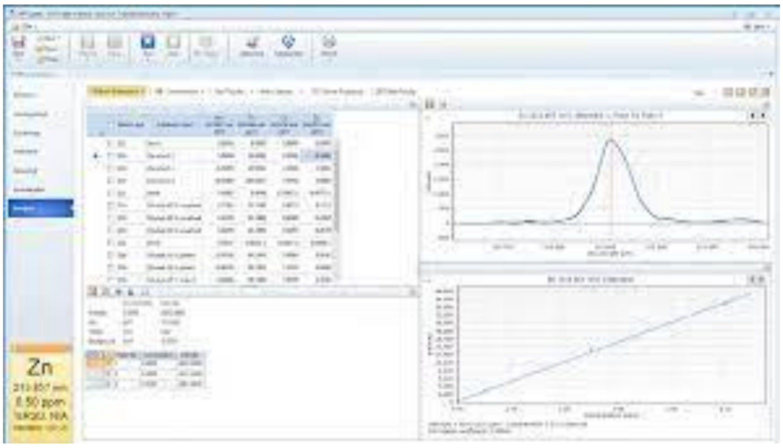


Figure 9. MP Expert application

Additionally, for the ICP-MS analysis, the instrument used was the Agilent 7900 ICP-MS, whereas the Online ICP-MS MassHunter was the relevant computer application.

Figure 10. 7900 ICP-MS instrument

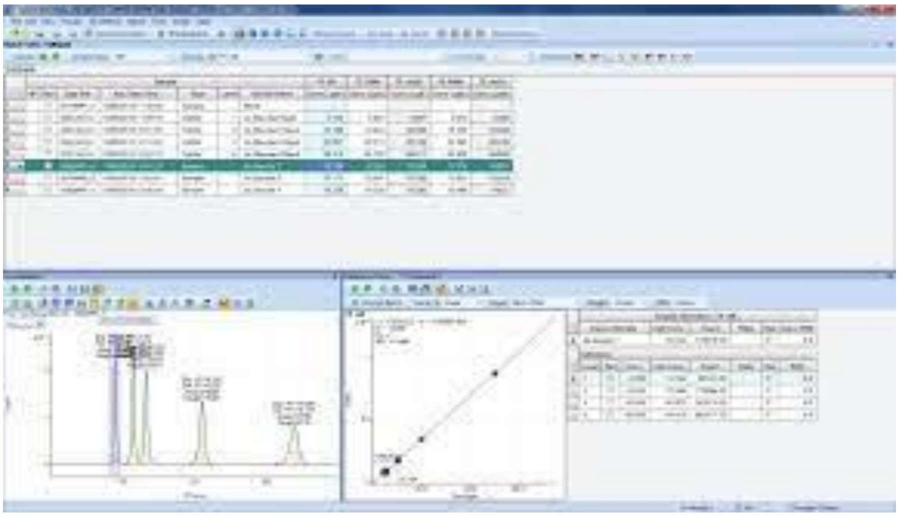


Figure 11. Online ICP-MS MassHunter computer program

5.2 Experimental Procedure

The experiment started with the collection of all samples. Each day, approximately 20 samples were processed in the lab, as a pre-step of the instrumental analysis.

First, 0.5g of honey was weighed with an analytical balance into small beakers, one separate for each sample. Those beakers would then go onto thermal plate and be heated up to 180 Celsius degrees, until total dry.

Figure 12. Moisture removal on thermal plate

Table 3. Indicative table of laboratory weighing

Sample	Before hotplate (g)	After hotplate (g)	Moisture (g)	Sample	Before hotplate (g)	After hotplate (g)	Moisture (g)
2021.82	46.7	46.6	0.1	2019.98.409	31.5	31.9	0.4
2021.108	38.3	38.2	0.1	2019.5.15	43.3	43.2	0.1
2021.90	30.4	30.3	0.1	2019.49.202	32.0	31.9	0.1
2021.130	51.3	51.2	0.1	2019.20.61	53.2	53.1	0.1
2021.98	30.9	30.8	0.1	2019.73.309	31.0	30.9	0.1

The next step was the acidic digestion. More specifically, 4mL HNO_3 65% and 1mL H_2O_2 30% were mixed with the dried samples, both used as digestion solvents that would extract the metals in the liquid phase and would stabilize the solution. This step was always held in the fume hood.

The digested mixtures were transferred into separate centrifuging tubes of 25mL volume, with the assistance of ultrapure water to limit quantity losses. Then, they were diluted up to 25mL. At last, those mixtures were filtered into additional centrifuging tubes of 15mL volume, which were the final samples to be headed for the instrumental analysis.

Finally, depending on the metals (macro metals, micronutrients, or rare metals), further dilutions were to be held before the final instrumental run.

5.3 Analytical methodologies

Once the samples pretreatment was over, they were headed towards the instrumental part of the analysis.

At first, MP-AES was run for its initial checks, e.g., N_2 levels, pressure, and nebulizer function. The approximate time for those checks was 30 minutes. During that waiting time, four calibration solutions were made, by standard solutions Ca 1000 mg/kg, Na 1000 mg/kg, Mg 10000 mg/kg and K 10000 mg/kg.

Table 4. Calibration solutions in macro analysis, MP-AES

Standard	**Concentration**
Standard 1	Ca, Mg, Na 1 mg/kg K 5 mg/kg
Standard 2	Ca, Mg, Na 5 mg/kg K 10 mg/kg
Standard 3	Ca, Mg, Na 10 mg/kg K 25 mg/kg
Standard 4	Ca, Mg, Na 25 mg/kg K 50 mg/kg

Apart from the standards of the calibration curve, two quality control solutions were run each time after the standards and between approximately 30 continuing samples. Their main analytical goal was to reassure that the instrument's results are valid.

As far as the sample list is concerned, various dilutions were examined for specimens, to find this one that would give the macroelements concentration that would adjust in the calibration limits of the curve. To be more specific, the dominants were 1mL of sample/ 5mL of ultrapure water and 1mL of sample/ 10mL of ultrapure water. Finally, the dilution that was used was 1mL of sample/ 5mL of ultrapure water.

Table 5. Dilution selection with a thyme sample

Sample	Mg (mg/kg)	Na (mg/kg)	Ca (mg/kg)	K (mg/kg)
Blank	0	0	0	0
Standard 1	0.10	0.10	--	0.50
Standard 2	0.50	0.50	0.50	1.0
Standard 3	1.0	1.0	1.0	2.5
Standard 4	2.5	2.5	2.5	5.0
Standard 5	5.0	5.0	5.0	10
Standard 6	10	10	10	20
Agilent CRM 2.5 ppm (Na, Ca, Mg)	2.39	2.43	2.52	--
Agilent CRM 2.5 ppm (K)	--	--	--	2.50
2019.55.239 dil 1:5	0.74	1.1	1.4	6.5
2019.55.239 dil 1:10	0.29	0.41	0.81	2.3

Between the two techniques, MP-AES and ICP-MS, there were no significant differences when it comes to the steps followed until the analysis started. From then on, the two instruments bared different methods and, as a result, different metals were analyzed in each one. Thus, MP-AES method calculated four macro elements, which are Na, Mg, Ca and K, in honey samples, in units mg/kg. At the same time, ICP-MS used the units μg/kg and ng/kg, given its lower detection limits, to calculate the micro elements and rare elements ^{27}Al, ^{45}Sc, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{89}Y, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{232}Th, and ^{238}U. At the end, both instruments run a separate analysis for the measurement of micro elements Zn, Cu, Mn, and Fe in the same samples. The relevant data was used to compare the two techniques, through the run of a statistical t Test.

Chapter 6 Results and Discussion

At the beginning of the research, samples from a large number of varieties were to be analyzed. The table given below contains the number of samples that were treated by each botanical origin. The quantitative results are presented in Annex I.

Table 6. Number of samples of different varieties analyzed

Variety	**Number**	**Variety**	**Number**
Acacia	1	Heather-Pine cone	1
Anise	1	Herbs-Thyme	1
Arbutus	25	Ivy	1
Chestnut	21	Lavender	1
Chestnut-Fir	1	Lemon tree	1
Cotton	5	Linden-Chestnut	3
Cotton-Clover	1	Locust tree	9
Cotton-Trefoil-Herbs	1	Oak tree	24
Eukalyptus	1	Oak tree-Flowers	2
Fennel-Anise	3	Oak tree-Flowers-Forest	1
Fir	24	Oak tree-Herbs	1
Fir-Flowers	1	Oak-Olympus Flowers	1
Fir-Vanilla	2	Orange tree	25
Flowers	12	Orange tree-Herbs	1
Flowers-Acacia	1	Oregano	3
Flowers-Arbutus	1	Pine	20
Flowers-Cotton	2	Pine-Flowers	1
Flowers-Forest	1	Pine-Ivy	1
Flowers-Locust tree	3	Pine-Thyme	3

Flowers-Oak tree	1	Sage	7
Flowers-Orange tree	1	Sage-Paliurus	1
Flowers-Pine	1	Sage-Wildflowers	3
Flowers-Thyme	1	Sunflowers-Chestnut	1
Forest	3	Thorn	1
Gum (Masticha)	1	Thyme	24
Heather	26	Thyme-Flowers	2
Heather-Pine	1	Vanilla	8

Table 7. Greek honey varieties of different geographical origin analyzed

Administrative region	**Number**
Attica	2
Central Greece	46
Central Macedonia	15
Crete	13
Eastern Macedonia and Thrace	8
Epirus	28
Ionian Islands	4
Mount Athos	5
North Aegean	3
Peloponnese	51
South Aegean	5
Thessaly	17
Western Greece	10
Western Macedonia	15

Table 8. Harvesting year of honey samples analyzed

Harvesting year	Number
2019	146
2021	143

From all the above analyzed, the final data consisted of the 13 varieties of which statistically important number of samples were present. Those varieties were arbutus, chestnut, cotton, fir, flowers, heather, locust tree, oak tree, orange tree, pine, sage, thyme, and vanilla.

As far as the geographical origin is concerned, the above varieties were sent from all parts of beekeeping and honey-producing Greece. Places from the administrative regions of Central and Western Greece, Epirus, Ionian islands, Peloponnese, Central and Western Macedonia, Thrace, Crete, Thessaly, and all parts of Aegean were represented with samples of all varieties by the harvesting periods of 2019 and 2021. Simultaneously, Mount Athos provided its own samples, as well.

6.1 Macroelements

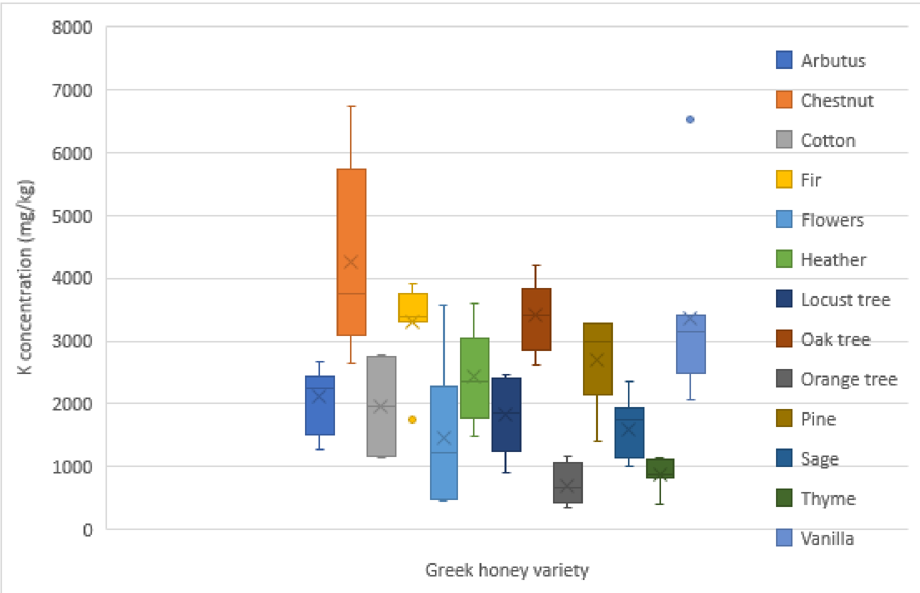
Given below are the results by the MP analysis of samples, as far as macroelements concentration is concerned, grouped by botanical origin.

Table 9. Statistical data from the analyzed Greek honey samples on macro elements

	Mg				K			
	Average	SD	Range	Median	Average	SD	Range	Median
Arbutus	33.1	17.0	10.0-69.3	29.9	2038	897	749-4052	2224
Chestnut	73.3	62.0	0-209	47.1	3421	1521	1366-6744	3267
Cotton	47.0	6.88	37.6-52.7	50.2	1864	832	1137-2771	1470
Fir	97.5	31.7	59.8-173	92.3	4088	1245	2446-7584	3663
Flowers	39.2	18.4	17.5-69.0	43.5	1210	944	348-3580	1331
Heather	54.6	33.3	10.0-136	52.73	1928	744	742-3595	1847
Locust tree	44.9	8.9	27.6-57.4	45.05	1384	698	589-2458	961
Oak tree	134	55.3	27.3-250	127	2804	980	677-4485	2907
Orange tree	21.2	11.9	2.48-45.2	17.7	625	557	49.6-2907	474
Pine	60.5	17.6	22.6-99.0	62.9	2386	744	960-3400	2472
Sage	17.5	8.45	9.84-32.6	16.1	1531	527	1004-2351	1448
Thyme	18.7	6.74	7.42-122	18.3	717	235	417-4648	717
Vanilla	79.5	20.9	52.8-103	71.7	3708	1672	2060-6532	3268
	Na				**Ca**			
	Average	SD	Range	Median	Average	SD	Range	Median
Arbutus	78.2	73.3	7.51-311	53.3	143	70.1	27.4-311	127
Chestnut	58.7	56.7	7.49-229	40.9	168	74.2	42.2-335	160
Cotton	48.5	22.1	27.6-77.8	42.0	242	42.5	195-283	259
Fir	39.7	17.9	14.9-77.0	39.8	120	73.6	39.7-286	105
Flowers	87.1	71.8	12.4-237	89.1	110	34.7	72.1-175	125
Heather	78.8	59.2	19.9-256	68.9	153	107	0-401	135
Locust tree	95.2	55.4	32.4-181	87.3	178	60.5	94.8-299	170
Oak tree	69.0	144	0-716	34.8	127	77.8	0-234	140
Orange tree	47.5	46.9	12.5-231	36.4	140	147	0-667	115
Pine	40.2	27.4	0-87.3	33.3	74.5	59.2	0-223	69.7
Sage	39.8	25.3	17.6-86.1	29.7	141	43.9	82.5-188	144
Thyme	72.2	39.6	22.4-167	59.9	105	79.4	0-259	101
Vanilla	54.3	42.0	10.1-105	41.3	100	53.3	29.8-160	61.6

As seen on the previous table, in all honey varieties K is the most abundant metal, nevertheless honeydews (fir, vanilla, oak and pine) reach highest concentrations, between 1400 and 6500 mg/kg. The only exception are some chestnut samples that, although they belong to the category of blossom honeys, in some cases presented K concentration of even 6500 mg/kg.

Apart from that, as far as other macroelements are concerned, blossom honeys like arbutus, chestnut, cotton and orange honeys have lowest concentrations of Mg and Na, sometimes not even reaching the 100 mg/kg. In most cases, Ca is the second most abundant metal in honeys, with distictive amounts in chestnut, sage and heather honeys.

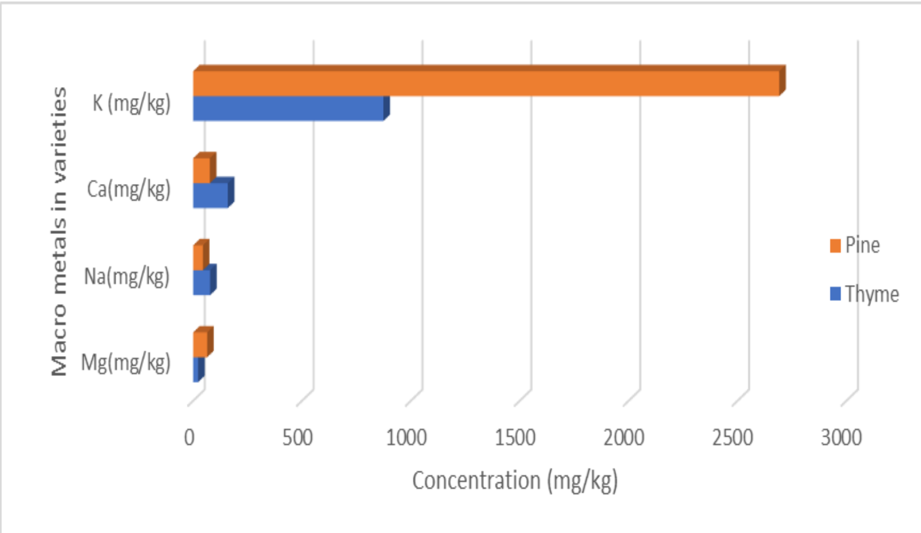


Graph 1. K concentration in Greek varieties of honey

The figure presented above depicts the range of K concentrations in various honey varieties, as well as the average amount in each variety. More specifically, the variety with the biggest range in K is chestnut, with most samples including approximately 3700 mg of macroelement per kg. On the contrary, fir, orange and thyme honeys have the smallest range of concentrations, with most samples analyzed giving a result of about 3500, 750 and 1000 mg/kg, respectively.

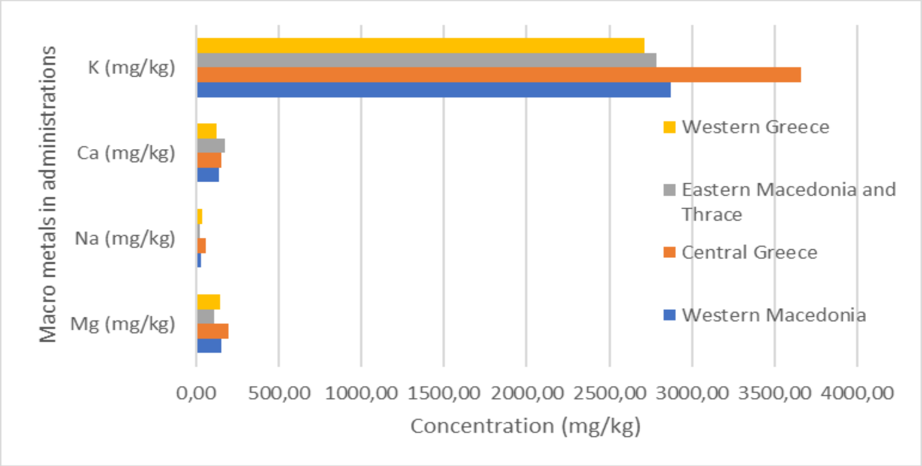
It is worth mentioning that blossom honeys, except orange and thyme, usually have a wide range of concentrations in K, whereas honeydew samples bring up more close percentages.

Furthermore, two different honey varieties have been compared, concerning their content in K, Ca, Na, and Mg. As seen below, pine has a noticeably higher amount in K than thyme, with its average concentration being almost the triple of the blossom variety. Nevertheless, when it comes to the rest of the macroelements, a roughly observable difference exists in Mg concentrations, with pine still exceeding for a little bit, but in Ca and Na thyme takes the lead. More precisely, Ca in thyme exceeds for 82.8 mg/kg (159.5 mg/kg average in thyme and 76.7 mg/kg in pine), whereas Na has a differentiation of 33.4 mg/kg, as the average in thyme honeys is 78.1 mg/kg and in pine 44.7 mg/kg, averagely.



Graph 2. Macro elements deviation in thyme (blossom) and pine (honeydew) samples

The data above appear to be in great accordance with studied literature. According to Puścion et al., 2020, honeydew honeys are expected to have the highest presence of minerals, and macro elements specifically, than blossom honeys. Namely, honeydew honeys are reported to maintain a concentration of 0.9g of minerals per 100g of honeys, whereas blossom honeys 0.2g per 100g.



Graph 3. Geographical origin effect on macro elements profile in oak honey

Aside from the botanical origin, another factor that may affect the mineral content of honeys is the geographical origin. In this thesis, samples from all the administrative regions of Greece were analyzed, giving quite different results from time to time.

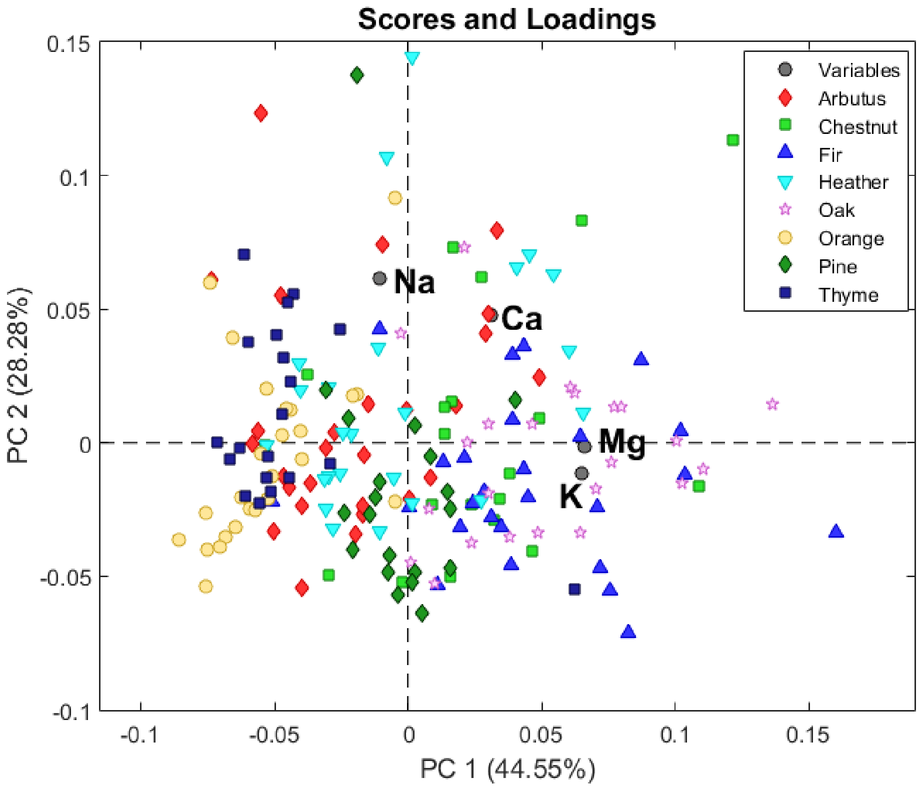
Thus, Figure 12 includes the data possessed by the MP analysis of oak samples from four different geographical regions of Greece, which are Western Greece, Eastern Macedonia and Thrace, Central Greece, and Western Macedonia. Once again, K appeared to be the most abundant metal, but with more intense percentages in the samples of Central Greece, exceeding the rest areas for at least 950.74 mg/kg. The difference in the specific metal in the other three regions was not statistically significant.

Carrying on Ca, Mg and Na, all administrative regions depicted very similar results. Ca appeared in all regions in approximately 125.23 to 173.12 mg/kg, Mg in 109.47 to 193.27 mg/kg, whereas Na came in last with concentrations that varied between 21.64 to 57.24 mg/kg.

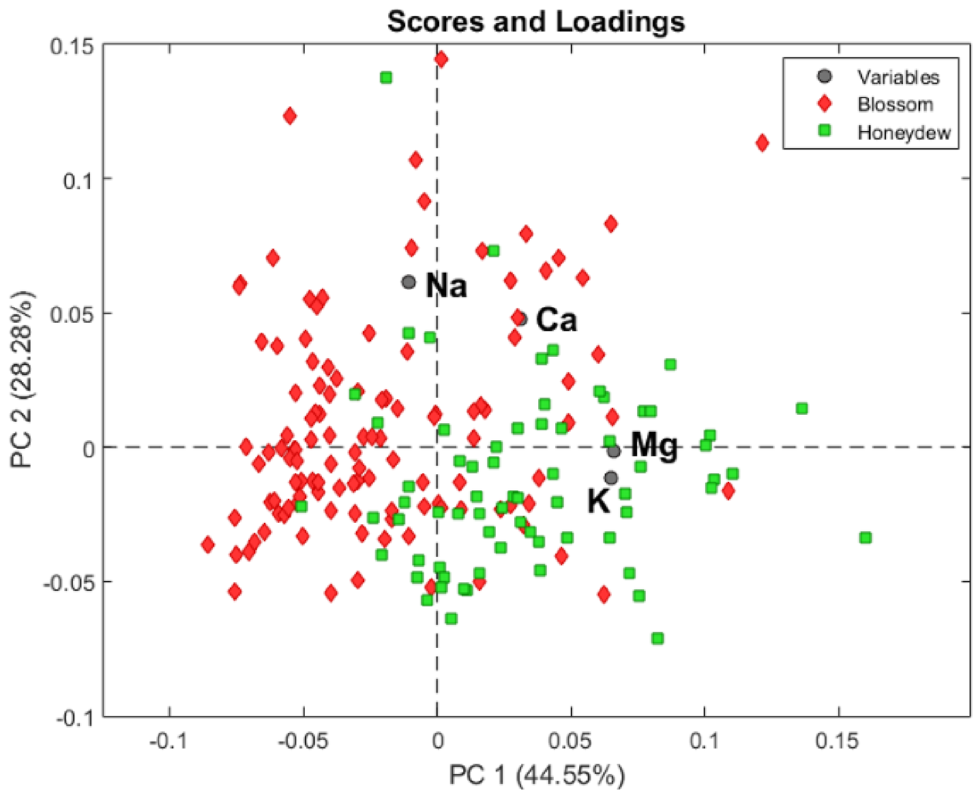
6.1.1 Principal Components Analysis

The data extracted for the macroelements was also analyzed by PCA, using the concentrations of the Greek honey samples in the four principal macroelements. The Principal Components model was performed for exploratory purposes in the autoscaled data. This preprocessing was performed to give all the variables analyzed the same importance. The model was built using the PLS_Toolbox v8.6 in Matlab environment.

Graphs 4 and 5 show the results extracted by the MP-AES instrument, which can be observed in 2 principal components. The first 2 PCs explain 72.83% of data variability and the bi-plots (scores plus loadings) can be seeing in the following graphs, color-coded in a different way to highlight different aspects of the samples analyzed. Graph 4 shoes the samples colored by the botanical varieties, while Graph 5 shoes the honeydew vs honey blossom. It is possible to observe a dispersion of samples without identifying clear clusters among them. However, subtle trends in the data can be useful for further differentiation.



Graph 4. PCA graph according to botanical origin of samples



Graph 5. PCA graph comparing honeydew and blossom samples

The varieties that appeared to be more abundant in Ca, K and Mg were oak and fir, whereas at the same time, thyme and orange contained higher amount of Na. Arbutus samples were intensely low in Mg and K, comparing to the rest, and chestnut and pine samples' concentration in Na were low, as well. Graph 5 confirms the results of Graph 4, as honeydew varieties (e.g., oak, fir) are high in Ca, K and Mg. On the contrary, blossom honeys, like arbutus, are more abundant in Na.

6.2 Microelements

Honey samples' content in microelements was analyzed as well, using both MP and ICP techniques, on some occasions. To be more specific, the table below includes the data received by the MP-AES Agilent instrument, for diverse varieties of honey.

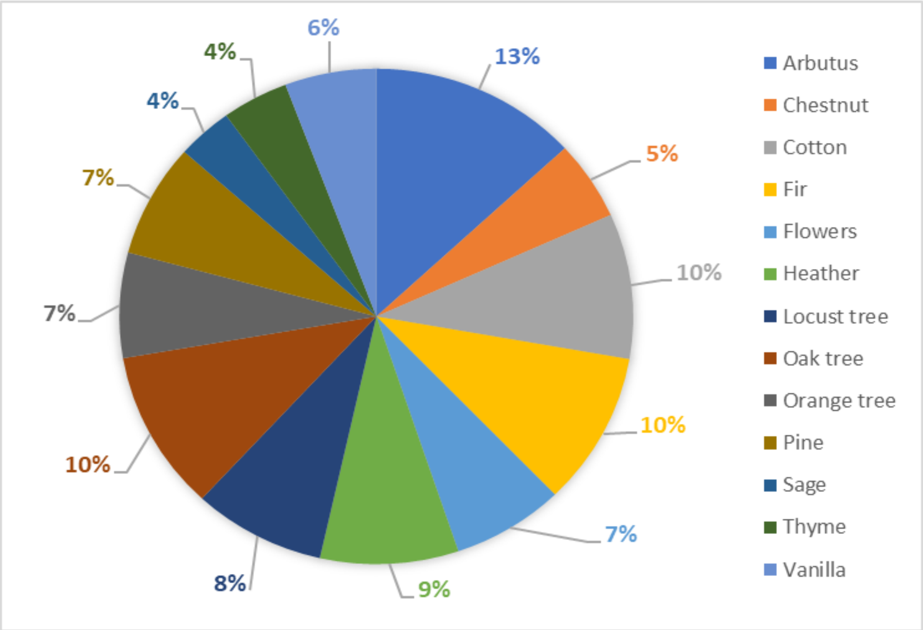
Table 10. Statistical data from the analyzed Greek honey samples on micro elements

	Zn				**Fe**				**Cu**			
	Average	SD	Range	Median	Average	SD	Range	Median	Average	SD	Range	Median
Arbutus	4.05	1.81	0.987-8.36	3.50	8.03	7.11	0-18.9	8.24	0.346	0.246	0-0.929	0.409
Chestnut	6.54	12.0	1.44-46.3	2.56	7.51	5.14	0-17.5	7.11	0.508	0.363	0-1.09	0.500
Cotton	3.67	2.40	1.52-7.64	2.88	10.8	8.65	2.01-24.5	8.12	0.230	0.134	0-0.336	0.287
Fir	4.13	2.35	1.60-9.85	3.81	11.8	6.70	1.85-24.6	11.3	0.984	0.313	0.502-1.54	0.940
Flowers	3.18	1.45	1.50-5.70	2.79	8.99	7.66	0-19.0	8.98	0.215	0.926	0-0.988	0.478
Heather	4.95	2.28	0.504-10.2	4.93	8.94	5.75	0-22.7	8.86	0.742	0.488	0-1.97	0.530
Locust tree	4.98	5.74	0.502-19.4	3.48	8.36	9.52	0-26.4	6.86	0.214	0.674	0-0.728	0.420
Oak tree	4.02	2.14	1.80-9.55	3.52	10.3	13.9	0-65.5	8.15	0.810	1.26	0-4.78	0.962
Orange tree	6.52	7.69	1.21-37.6	4.09	7.65	7.83	0-23.0	5.81	1.27	0.917	0-17.8	0.260
Pine	4.10	2.07	0.143-8.36	4.02	9.33	10.2	0.0782-45.1	6.04	0.959	0.369	0-1.43	1.01
Sage	2.86	1.40	1.67-5.57	2.52	19.1	16.7	6.53-46.4	10.8	0.325	0.195	0.152-0.677	0.280
Thyme	3.60	2.21	1.30-7.82	2.98	7.68	4.53	0.990-15.2	6.41	0.278	0.296	0-1.36	0.205
Vanilla	2.51	0.861	1.42-4.64	2.66	14.4	9.56	0.541-27.0	8.60	0.732	0.199	0.548-1.01	0.744
	Al				**Mn**				**V**			
	Average	SD	Range	Median	Average	SD	Range	Median	Average	SD	Range	Median
Arbutus	3.53	3.14	0.77-10.7	2.94	1.61	1.73	0-6.63	1.09	<LOD	<LOD	<LOD	<LOD
Chestnut	2.64	1.17	0.945-4.06	2.43	11.3	7.48	0.828-23.7	9.15	<LOD	<LOD	<LOD	<LOD
Cotton	4.27	4.83	1.66-11.5	1.95	1.10	0.656	0.332-1.87	1.00	<LOD	<LOD	<LOD	<LOD
Fir	27.5	13.4	12.6-57.4	23.9	5.67	2.16	3.24-12.1	5.46	<LOD	<LOD	<LOD	<LOD
Flowers	5.07	3.98	1.51-9.71	2.79	1.61	1.62	0-4.55	1.25	<LOD	<LOD	<LOD	<LOD
Heather	5.20	4.73	0.845-21.3	3.80	2.81	1.79	0.808-6.77	2.39	<LOD	<LOD	<LOD	<LOD
Locust tree	5.57	7.05	1.95-21.4	3.16	1.41	1.57	0-5.02	0.938	<LOD	<LOD	<LOD	<LOD
Oak tree	5.50	3.95	1.15-14.9	4.16	21.5	9.66	5.94-41.8	20.2	<LOD	<LOD	<LOD	<LOD
Orange tree	2.24	1.32	0.536-4.14	2.19	0.265	0.608	0-1.37	0.320	<LOD	<LOD	<LOD	<LOD

Pine	4.37	2.08	1.82-9.11	4.04	2.50	2.25	0.245-9.05	2.01	<LOD	<LOD	<LOD	<LOD
Sage	1.68	2.08	0-5.55	1.00	0.365	0.335	0.0511-0.993	0.330	<LOD	<LOD	<LOD	<LOD
Thyme	2.05	1.34	0.650-6.90	1.90	0.318	0.592	0-6.15	0.230	<LOD	<LOD	<LOD	<LOD
Vanilla	16.7	2.47	13.9-18.4	17.8	5.42	2.59	1.03-9.05	4.13	<LOD	<LOD	<LOD	<LOD

Co				**Cr**			
Average	SD	Range	Median	Average	SD	Range	Median
0.00288	0.00111	0.00196-0.00476	0.00219	1.02	0.710	0.270-2.21	0.700
0.00350	0.00197	0.00119-0.00598	0.00310	1.33	0.642	0.479-2.14	1.20
0.00292	0.00317	0157-0.00639	0.00222	1.17	0.849	0.198-1.92	1.29
0.0211	0.0164	0.00876-0.0523	0.0160	0.633	2.50	0-2.03	1.23
0.00432	0.00537	0197-0.0133	0.00180	1.40	0.540	0.785-1.96	1.48
<LOD	<LOD	<LOD	<LOD	0.895	0.538	0.184-1.82	0.883
0.00363	0.00199	0666-0.00489	0.00447	1.11	0.934	0.0539-2.23	0.741
0.0130	0.0189	0.0136-0.0712	0.00525	3.46	4.84	0.0919-17.6	1.60
<LOD	<LOD	<LOD	<LOD	1.14	0.585	0-2.04	0.887
0.00960	0.00786	0-0.0218	0.00545	0.915	0.552	0-1.90	0.876
<LOD	<LOD	<LOD	<LOD	1.16	0.509	0.615-1.68	1.21
<LOD	<LOD	<LOD	<LOD	0.932	0.752	0.0132-2.23	0.553

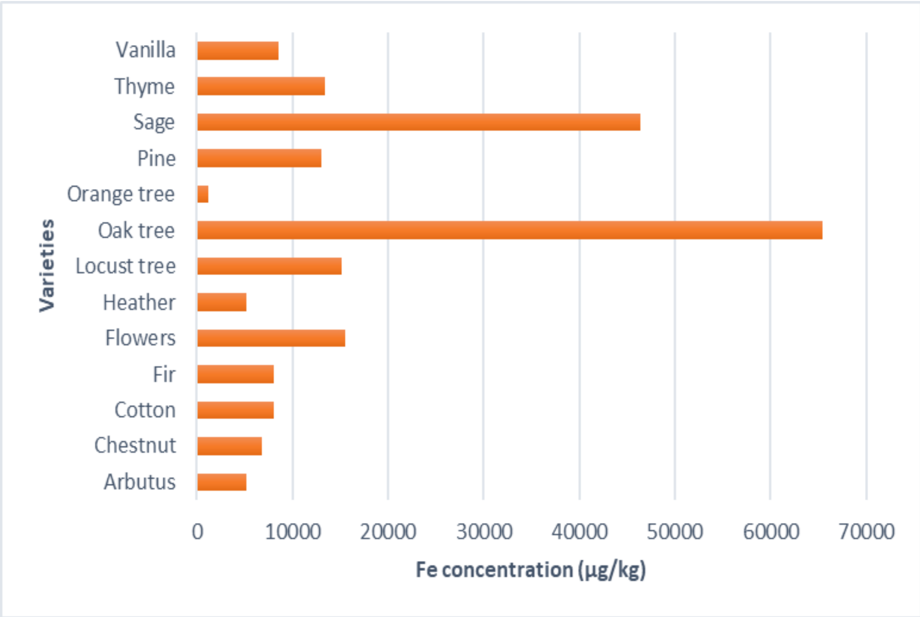
As seen, micronutrients exist in honeys in quite lowest concentrations, thus the measurement units have changed to μg/kg (ppb), which could be a problem for the MP-AES instrument's sensitivity, when it comes to the elements with the smallest content.

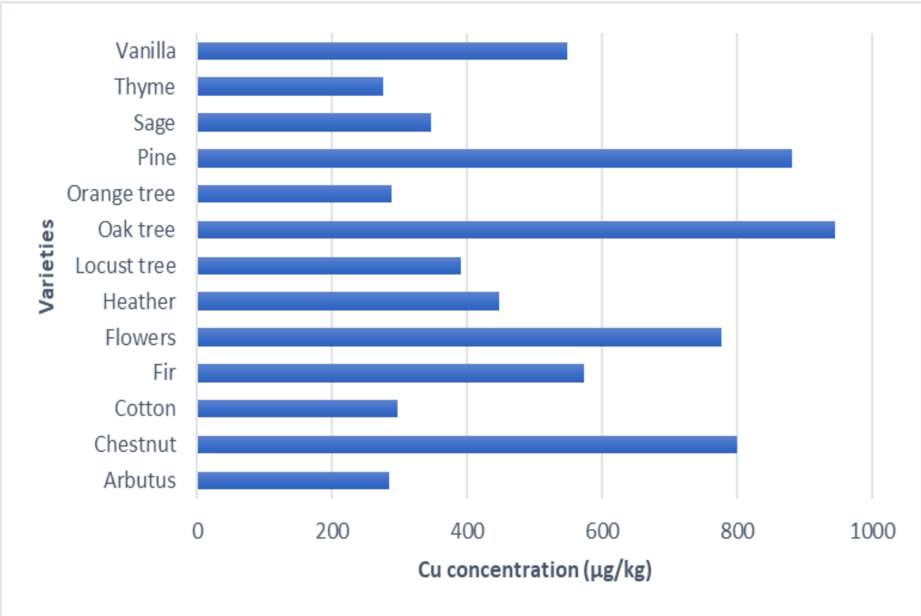


Graph 6. Zn content in honey varieties

The graph given previously refers to Zn content in all honey varieties analyzed in this thesis. As observed above, honeydew and blossom varieties don't have a distinct differentiation as far as Zn concentration is concerned. Arbutus appears to have the highest concentration, with an average of 10.6 mg/kg, making it a very nutritional choice. On the contrary, sage, thyme and chestnut are the varieties that offered the lowest percentages of Zn by the MP analysis.

Moving on, Graph 7 refers to the two most abundant micronutrients in honey samples, Fe, and Cu. More particularly, Fe possessed the highest amounts in all varieties, nevertheless its excellence in oak honeys (honeydew) was the most notable (65.4 mg/kg in Fe, in contrast with 0.9 mg/kg in Cu in the same variety). Sage was the second variety with a similar deviation between the two microelements (46.6 mg/kg in Fe, 0.3 mg/kg in Cu). Apart from those two, all other varieties were accordingly most abundant in Fe, nonetheless the range was not that wide.





Graph 7. Fe and Cu in different varieties of honey samples

6.2.1 Micronutrients analysis with both MP-AES and ICP-MS techniques

Among all microelements found in honeys in μg per kg percentages, Fe, Cu, Mn, and Zn are the most abundant, as well as those with the highest nutritional effect on the product. For that reason, in scientific literature, they are found with the term micronutrients.

In the present thesis, honey samples of various botanical and geographical origin were analyzed using both MP-AES and ICP-MS technique, to detect differences between the sensitivity, the accuracy, and the detection limit of the two instruments. For the comparison of the relevant data, a t Test was run. The results are presented in the Table below.

Table 11. T-test run, between different Greek honey varieties

N/N	MP-AES				ICP-MS			
	Zn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
1	4.46	0.00	0.99	<LOD	4.99	0.225	4.74	0.358
2	4.20	<LOD	<LOD	9.96	4.27	0.729	12.9	13.4
3	4.30	0.50	3.02	41.83	4.01	1.10	3.35	38.1
4	4.96	0.50	5.46	6.94	5.07	0.503	4.79	2.98
5	5.24	0.00	<LOD	0.51	5.58	1.29	5.64	0.784
6	3.51	0.00	<LOD	0.50	4.64	0.189	1.04	0.374
7	3.03	<LOD	<LOD	<LOD	3.53	0.123	4.80	0.123
8	3.00	<LOD	<LOD	10.00	4.16	0.110	27.3	0.351
9	4.52	1.01	5.53	9.05	4.69	0.644	<LOD	3.92
10	6.00	0.50	4.46	1.98	6.02	0.317	6.69	<LOD
11	4.47	<LOD	0.00	31.31	4.13	25.3	2.42	37.8
12	4.99	0.00	1.47	12.75	5.17	1.16	9.09	16.2
13	2.99	<LOD	<LOD	2.50	4.77	0.401	36.3	5.98

14	2.49	0.50	4.48	1.49	3.51	0.267	2.03	<LOD
15	1.99	<LOD	<LOD	0.50	2.04	0.190	5.98	0.514
16	1.97	0.49	2.96	0.49	1.70	0.335	8.91	<LOD
17	5.48	0.50	<LOD	3.99	5.46	0.930	7.26	7.73
18	4.02	1.01	6.04	9.05	3.92	1.12	2.81	4.28
19	2.50	0.50	<LOD	14.47	3.35	1.34	4.80	22.8
20	2.58	0.49	<LOD	<LOD	3.02	0.0704	6.60	<LOD
21	1.93	<LOD	<LOD	5.02	2.77	0.437	4.61	7.90
22	1.49	<LOD	<LOD	0.00	2.26	0.428	7.37	1.79
23	1.24	1.51	5.54	1.51	1.81	0.941	4.35	1.78
24	3.49	0.00	<LOD	0.00	3.50	0.312	2.87	1.24
25	4.45	0.49	1.48	2.96	3.74	1.02	16.5	2.94
26	3.99	<LOD	<LOD	0.00	3.96	0.158	5.94	0.143
27	4.01	1.50	3.51	0.00	5.00	0.118	3.58	0.214
28	3.94	0.99	5.92	2.47	4.32	1.13	<LOD	<LOD
29	3.47	0.50	4.46	0.99	4.09	0.205	5.04	0.465
30	4.52	0.50	4.02	1.00	4.67	0.142	1.71	<LOD
31	3.46	0.99	4.94	1.98	4.60	0.722	4.89	1.16
32	1.65	0.50	5.45	0.50	2.26	0.036	2.88	<LOD
33	4.11	0.50	4.00	0.00	4.43	0.164	12.8	<LOD
34	1.98	<LOD	2.48	6.45	4.12	0.376	4.88	8.95
35	2.01	<LOD	<LOD	0.01	3.54	0.407	4.72	1.21
36	1.98	<LOD	<LOD	<LOD	2.00	0.232	4.77	0.330
37	4.03	0.50	4.03	0.50	4.95	0.130	6.60	0.236
38	1.50	0.00	<LOD	0.00	1.90	0.291	4.58	1.10

39	3.02	<LOD	<LOD	0.50	3.94	0.274	5.20	1.70
40	3.92	0.49	1.47	0.98	4.02	0.723	7.39	0.781
41	3.94	0.49	0.00	20.71	4.05	0.985	48.8	18.9
42	3.44	0.00	<LOD	1.48	5.73	0.356	4.97	3.23
43	2.51	0.00	1.51	12.05	2.48	1.07	3.22	14.1
44	4.50	0.50	34.00	0.50	4.65	0.198	<LOD	<LOD
45	4.46	0.00	0.99	0.99	4.11	0.438	16.3	1.66
46	3.01	1.00	4.52	2.01	3.00	0.856	15.0	1.45
47	5.76	0.50	4.50	15.50	5.86	0.619	1.61	8.39
48	2.50	0.00	4.49	0.50	3.84	1.31	6.17	1.24
49	4.95	0.00	2.01	1.00	5.04	0.366	4.89	1.54
50	5.22	0.49	4.94	18.77	5.41	0.597	20.6	13.0
Aver.	2.69	<LOD	<LOD	3.88	2.23	<LOD	3.39	6.85
SD	0.95	0.49	3.65	9.62	1.03	1.09	8.12	11.9

S1-2$_{Zn}$	**S1-2$_{Cu}$**	**S1-2$_{Fe}$**	**S1-2$_{Mn}$**
1.180014	2.512999	7.573538	8.966050499
t_{exp}	**t_{exp}**	**t_{exp}**	**t_{exp}**
1.941131	1.108092	2.521947	0.314003737

The main goal of a t Test is to compare two relevant data, to evaluate the precision of the technique followed. To achieve that, a t value is found in literature, whereas the confidence limit of the method is set. The Figure below includes the different values of t parameter, according to various confidence limit and degrees of freedom (v=N-1, N: number of samples).

v=N-1	Στάθμη εμπιστοσύνης, %				
	50	90	95	99	99,9
1	1,000	6,314	12,706	63,657	636,619
2	0,816	2,920	4,303	9,925	31,598
3	0,765	2,353	3,182	5,841	12,941
4	0,741	2,132	2,776	4,604	8,610
5	0,727	2,015	2,571	4,032	6,859
6	0,718	1,943	2,447	3,707	5,959
7	0,711	1,895	2,365	3,500	5,405
8	0,706	1,860	2,306	3,355	5,041
9	0,703	1,833	2,262	3,250	4,781
10	0,700	1,812	2,228	3,169	4,587
11	0,697	1,796	2,201	3,106	4,437
12	0,695	1,782	2,179	3,055	4,318
13	0,694	1,771	2,160	3,012	4,221
14	0,692	1,761	2,145	2,977	4,140
15	0,691	1,752	2,131	2,947	4,073
20	0,687	1,725	2,086	2,845	3,850
25	0,684	1,708	2,060	2,787	3,725
30	0,683	1,697	2,042	2,750	3,646
∞^{a}	**0,674**	**1,645**	**1,960**	**2,576**	**3,291**

Figure 13. t value number according to confidence limit and number of measurements

With the above information, the theoretical and the experimental values are compared. When the experimental value is higher, then it has occurred a systematic error and the method has failed. On the contrary, when the experimental value is lower, this difference is the outcome of a random error, and the results are valid.

Thus, according to data of Table 11, MP-AES and ICP-MS in most cases give almost identical results (Karlsson et al., 2015), with ICP-MS providing a lowest detection limit, reaching even ppt concentrations (ng per kg).

Given the above, the data of the Table 11 depicts the results of the statistic t Test, that was run, with 50 samples of different varieties of Greek honey been pretreated and analyzed with both Agilent instruments. With a confidence limit up to 95% and a theoretical t-value equal to 1.960, the final experimental t parameters of Zn, Cu and Mn were found to be higher than the theoretical one, depicting the equivalence of the two techniques for the measurement of the specific metals. On the contrary, the experimental t value for Fe was found higher than the theoretical, which appeared to be making sense, since on the total 50 samples that were run for the t Test, at 19 of them the MP-AES failed to provide concentrations, as the percentage of Fe in the samples was below the limit of detection of the technique.

Despite the above, in various cases, MP-AES and ICP-MS bared notable differences. More specifically, the MP technique could not detect the concentration of micronutrients in samples, giving result below the level of detection (LOD) of the technique and the instrument. Nevertheless, continuing, when the same sample was analyzed using the ICP-MS instrument, a numerical result was received. Representative examples are the samples 5, 13, and 36, were the concentrations of Cu, Fe, and Mn were intensely low for the MP to detect, but not for the ICP.

Another observation that rises from the study of the data of Table 3 is that, in no sample was Zn low enough to become non detectable by MP instrument. That leads us to the conclusion that Zn is, in the plurality of cases, the most abundant micronutrient, being present in concentrations over the LOD of both MP and ICP instruments.

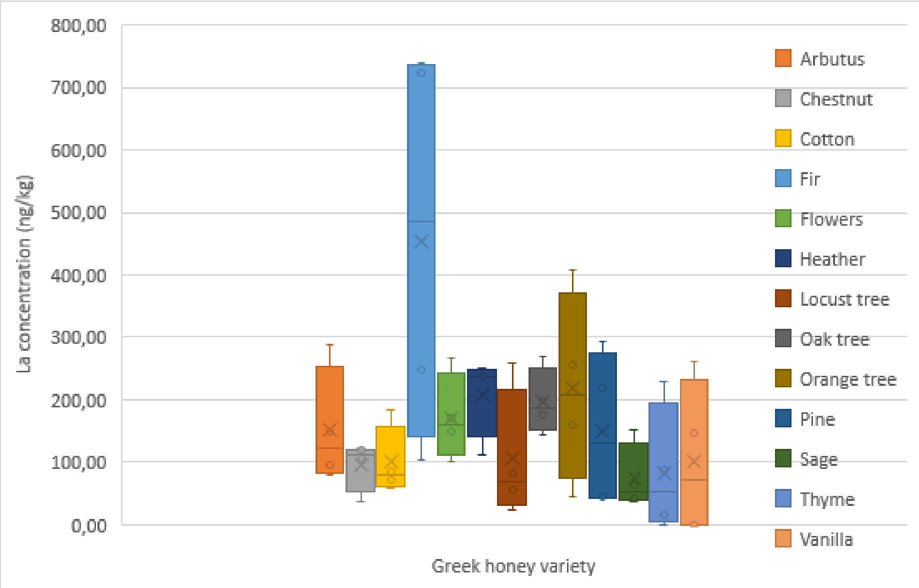
Finally, cases like samples 9, 40, 47, and 50 concerning the Zn concentration prove that, when a micronutrient exists in a sample in a noticeable amount, the result that the two instruments provide are quite similar, having a statistically non important difference between them. Thus, the motivation for moving on from the MP-AES technique to the ICP-MS is the need to detect and quantify minerals of low content in honey samples, which are mostly the nutrients Cu, Mn, and Zn and, of course, the rare elements.

6.2.2 Rare elements

Rare elements group consists of microelements that are included in food in very low concentration of ng per kg (ppt). As a result, the samples of the specific thesis were analyzed for rare elements using only the ICP technique, whose LOD was appropriate for the detected proportions.

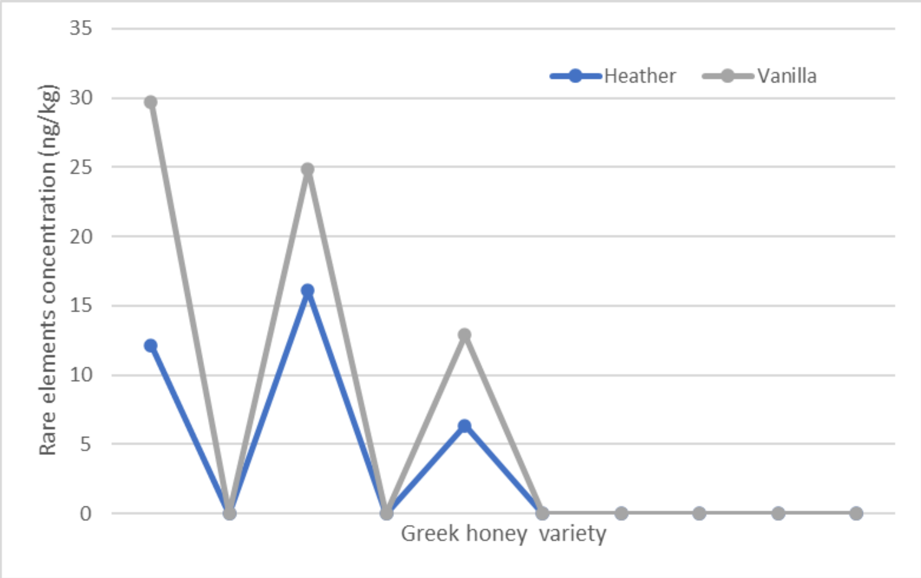
By the data received and presented in the Annex, rises the conclusion that the content of honey varieties in rare elements is so low in most cases, that not even ICP-MS can detect. The rare elements with the most intense presence in honeys are La and Nd, with Y, Ce, and Pd coming next. In continuance, some rare elements like Sm, Gd, and Dy are mostly absent, with a few cases of a few nanograms in some samples. Finally, Sc, U, Th, and Tm are rare elements that were absent in all the analyzed specimens. For that reason, they are not included in the relevant Table in Annex III.

The graph included below depicts the variation of La in all honey samples.

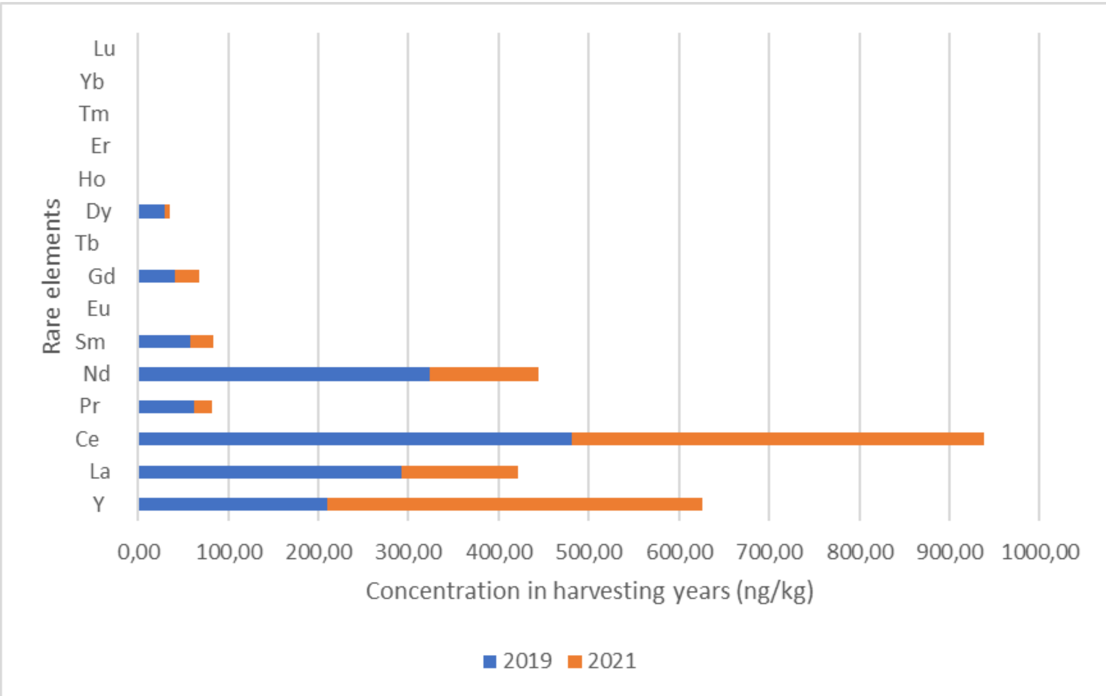


Graph 8. La presence in various honey samples

The most remarkable notice by the graph above is the very wide range of La concentrations in oak honeys, as it spreads between 79.1 ng/kg and 208.5 ng/kg. Additionally, the variety with the second narrowest range of concentrations is orange, leading to the conclusion that there is no significant differentiation between blossom and honeydew samples referring to rare elements, or even if there is, it can’t be detected given the LOD of the existing techniques.



Graph 9. Rare elements' comparing in a blossom and a honeydew sample



Graph 10. Effect of harvesting year on rare elements' concentration in fir sample

Graph 10 is dealing with the effect that the harvesting year had on the final mineral content of a sample of fir honey. In the specific research, the samples possessed were grouped into two harvesting periods; 2019 and 2021.

According to the graph above, the rare elements with the highest concentrations in 2019 (Ce, Y, and La) maintained their excellence in 2021. Nevertheless, there was not a proportional effect observed, as Ce gave almost the same percentage in 2021 as in 2019, Y showed augmentation compared to 2019, and La presented a significant decrease almost in half.

Given the data of the rest rare elements, the plurality of them depicted a degradation of rare elements in honeys the harvesting period of 2021, probably testifying environmental and climatical changes that could have such consequences, like the severe fire incidents in Greece on summer 2021.

Lastly, rare elements with highly low concentrations, such as Lu, Yb, Tm, and Er, gave no conclusions, as their amounts were too low to be depicted and interpreted.

ABBREVIATIONS

MP-AES	Microwave Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
Q-ICP-MS	Quadrupole Inductively Coupled Plasma Mass Spectrometry
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
F-AAS	Flame Atomic Absorption Spectroscopy
PCA	Principal Component Analysis
PC	Principal Components
HMF	Hydroxymethylfurfural
REE	Rare Earth Elements
CCD	Charge-Coupled Detector
SD	Standard Deviation
RSD	Relative Standard Deviation
AMS	Accelerator Mass Spectrometry
CRM	Certified Reference Material

ANNEX I

Table 12. Overall data of macro elements concentration in Greek honey varieties

Variety	Mg (mg/kg)	Na (mg/kg)	Ca (mg/kg)	K (mg/kg)
Acacia	22.6	178	402	685
Anise	12.5	20.0	80.0	270
Arbutus	25.2	65.4	239	734
Arbutus	10.0	7.5	40.0	2.15
Arbutus	14.8	207	59.2	749
Arbutus	32.5	55.0	133	2.25
Arbutus	24.9	49.8	27.4	1.39
Arbutus	60.6	24.2	133	2.22
Arbutus	22.4	37.3	87.0	1.51
Arbutus	62.1	27.3	159	2.43
Arbutus	69.3	126	312	2.79
Arbutus	32.1	106	111	2.71
Arbutus	30.0	54.9	200	2.67
Arbutus	27.4	27.4	107	2.44
Arbutus	20.0	22.5	128	2.48
Arbutus	17.2	78.8	98.5	815
Arbutus	34.9	312	94.8	1.35
Arbutus	44.4	74.0	182	3.50
Arbutus	37.7	136.	259	1.78
Arbutus	24.7	24.7	86.5	2.53
Arbutus	58.1	53.3	269	4.05
Arbutus	55.1	80.2	288	3.02

Arbutus	22.4	999	84.7	1.54
Arbutus	124.00	117	181	1.91
Arbutus	17.3	39.6	104	1.29
Arbutus	19.9	47.2	102	1.12
Arbutus	36.9	41.8	172	1.11
Chestnut	22.5	140	167	858
Chestnut	20.0	12.5	62.4	5.47
Chestnut	89.9	37.5	99.9	2.13
Chestnut	99.8	12.5	165	2.66
Chestnut	37.7	65.3	161	3.60
Chestnut	39.5	49.4	240	6.74
Chestnut	210	229	266	4.34
Chestnut	27.5	17.5	117	5.38
Chestnut	40.0	17.5	160	3.89
Chestnut	75.3	17.6	136	3.51
Chestnut	42.5	17.5	208	4.25
Chestnut	35.1	426	168	5.73
Chestnut	34.8	54.7	221	3.31
Chestnut	108	125	336	3.23
Chestnut	9.9	91.8	64.5	1.53
Chestnut	54.9	25.0	20.0	1.59
Chestnut	150	7.49	99.8	2.35
Chestnut	49.6	71.9	179	3.11
Chestnut	180	44.4	150	1.37
Chestnut	0	84.0	178	177
Chestnut-Fir	84.3	12.4	42.2	2.04

Cotton	60.4	20.1	108	4.83
Cotton	42.0	42.0	198	1.18
Cotton	52.7	27.6	259	2.77
Cotton	50.2	30.1	196	2.76
Cotton	37.6	65.1	276	1.47
Cotton-Clover	52.7	77.8	284	1.14
Cotton-Trefoil-Herbs	32.2	24.8	104	861
Eukalyptus	34.9	44.9	195	1.32
Fennel-Anise	20.0	90.2	235	1.11
Fennel-Anise	27.9	43.1	68.5	1.64
Fennel-Anise	38.0	76.1	226	2.63
Fir	37.5	75.0	100	1.70
Fir	96.7	14.9	39.7	2.45
Fir	148	9.84	22.1	5.05
Fir	117	40.0	210	3.58
Fir	82.1	47.3	87.1	3.76
Fir	99.9	35.0	92.4	3.34
Fir	78.7	18.5	<LOD	3.14
Fir	106	148	128	3.82
Fir	72.7	72.7	113	3.39
Fir	90.3	20.8	74.1	3.92
Fir	102	32.4	72.2	5.52
Fir	167	52.3	154	4.80
Fir	174	24.8	166	7.58
Fir	95.8	22.7	65.5	5.93

Fir	59.8	62.3	59.8	2.98
Fir	67.1	77.0	96.9	3.25
Fir	79.4	44.7	72.0	3.31
Fir	97.7	183	55.1	1.74
Fir	84.5	42.3	162	3.75
Fir	129	42.2	236	5.14
Fir	127	57.3	286	4.02
Fir	60.2	25.1	161	3.58
Fir	94.3	39.7	136	5.21
Fir	72.2	22.4	144	3.11
Fir-Flowers	32.2	39.7	76.9	689
Fir-Vanilla	65.1	150	125	4.84
Fir-Vanilla	68.6	44.1	221	3.53
Flowers	64.9	27.5	160	4.39
Flowers	49.4	111	123	1.55
Flowers	37.4	22.5	127	3.58
Flowers	24.9	79.5	72.1	900
Flowers	56.7	187	76.4	1.50
Flowers	397	331	620	4.03
Flowers	17.5	27.6	175	348
Flowers	20.2	237	134	1.23
Flowers	69.0	98.6	128	1.83
Flowers	39.5	12.4	81.5	1.44
Flowers	67.0	104	119	454
Flowers	47.4	77.4	162	497
Flowers-	49.1	51.6	174	3.42

Arbutus				
Flowers-Cotton	32.2	61.9	71.9	1.64
Flowers-Cotton	57.9	131	244	1.28
Flowers-Locust tree	62.1	67.1	92.0	1.93
Flowers-Locust tree	50.6	111	127	1.17
Flowers-Locust tree	53.1	152	225	1.93
Flowers-Orange tree	47.4	37.4	77.4	1.15
Flowers-Pine	39.6	91.6	141	1.96
Flowers-Thyme	62.8	12.6	15.1	3.33
Forest	34.9	59.8	105	1.69
Forest	67.5	103	27.5	3.14
Forest	120	15.0	180	3.62
Gum(Masticha)	65.1	27.6	108	3.09
Heather	79.5	34.8	164	2.93
Heather	129	101	295	1.47
Heather	39.3	39.3	128	1.49
Heather	9.9	37.2	<LOD	2.02
Heather	27.2	37.0	88.9	1.87
Heather	136	39.8	234	2.87
Heather	52.5	45.0	45.0	1.65
Heather	10.0	74.9	<LOD	938
Heather	54.5	111	166	1.82
Heather	95.1	67.6	273	3.60
Heather	104	99.0	307	2.87

Heather	22.6	37.6	<LOD	1.53
Heather	55.2	35.1	113	2.65
Heather	25.1	70.1	133	2.24
Heather	46.9	257	161	2.87
Heather	27.0	127	108	1.52
Heather	19.8	71.9	69.4	2.35
Heather	27.7	75.7	85.8	782
Heather	42.3	19.9	209	742
Heather	80.2	386	<LOD	711
Heather	54.2	76.4	153	2.37
Heather	57.6	238	318	1.75
Heather	81.9	57.0	402	2.08
Heather	29.9	22.4	152	1.30
Heather	64.9	54.9	102	2.15
Heather	52.9	40.3	60.5	2.47
Heather-Pine	54.2	91.2	138	929
Heather-Pine	34.9	99.8	120	1.12
Herbs-Thyme	59.4	56.9	96.5	4.21
Ivy	76.4	173	101	160
Lavender	45.0	37.5	105	3.80
Lemon tree	39.5	9.86	205	471
Linden-Chestnut	14.8	64.0	108	652
Linden-Chestnut	48.0	65.6	386	1.65
Linden-Chestnut	64.9	27.5	42.4	3.70

Locust tree	50.5	55.5	374	2.23
Locust tree	52.4	87.3	230	1.85
Locust tree	49.5	39.6	198	2.46
Locust tree	27.6	97.7	170	902
Locust tree	36.8	181	299	961
Locust tree	45.1	178	183	904
Locust tree	57.4	32.4	94.8	1.60
Locust tree	50.1	47.6	120	2.35
Locust tree	42.7	118	153	851
Oak tree	42.4	74.9	152	589
Oak tree	82.9	47.7	171	2.56
Oak tree	251	15.0	120	3.15
Oak tree	197	41.8	150	3.82
Oak tree	179	49.7	114	2.87
Oak tree	122	12.7	112	2.62
Oak tree	229	10.0	209	3.13
Oak tree	196	42.7	151	4.21
Oak tree	120	64.7	219	3.41
Oak tree	229	52.3	182	3.63
Oak tree	67.6	716	<LOD	1.19
Oak tree	198	5.02	233	3.39
Oak tree	172	69.7	162	4.49
Oak tree	96.7	30.6	234	2.94
Oak tree	136	98.8	163	3.44
Oak tree	76.7	12.4	69.3	2.22
Oak tree	102	24.9	22.4	2.42

Oak tree	27.3	<LOD	<LOD	677
Oak tree	120	82.2	129	2.40
Oak tree	141	35.3	186	3.67
Oak tree	133	20.0	120	3.77
Oak tree	149	7.46	124	2.28
Oak tree	88.2	34.3	100	2.11
Oak tree	121	12.4	96.5	1.97
Oak tree-Flowers	87.5	115	173	1.28
Oak tree-Flowers	92.0	199	154	2.99
Oak tree-Flowers/Forest	205	19.7	306	4.16
Oak tree-Herbs	150	57.3	214	3.35
Oak-Olympus Flowers	90.1	47.5	113	3.25
Orange tree	140	36.9	253	3.39
Orange tree	17.8	35.5	73.6	660
Orange tree	15.2	25.3	90.9	659
Orange tree	14.8	27.2	34.6	398
Orange tree	42.8	232	5.04	411
Orange tree	35.0	77.5	97.5	798
Orange tree	32.4	42.4	132	865
Orange tree	12.5	17.5	0	402
Orange tree	24.7	44.5	474	353
Orange tree	20.0	22.5	112	609
Orange tree	20.2	55.6	172	745
Orange tree	7.5	47.5	40.0	352

Orange tree	12.6	37.7	143	513
Orange tree	37.7	47.7	213	1.18
Orange tree	17.7	25.3	199	669
Orange tree	2.5	37.2	19.8	49.6
Orange tree	39.9	44.9	97.3	2.91
Orange tree	12.5	72.2	167	588
Orange tree	15.0	22.5	69.9	404
Orange tree	22.3	17.4	667	434
Orange tree	45.2	27.6	126	1.06
Orange tree	10.1	17.7	119	278
Orange tree	7.50	12.5	55.0	123
Orange tree	27.6	20.0	143	210
Orange tree	17.3	131	119	349
Oregano	17.3	54.5	176	710
Oregano	50.0	62.5	275	1.67
Oregano	34.8	59.6	67.1	586
Pine	7.4	14.9	47.0	131
Pine	61.3	19.6	<LOD	2.63
Pine	77.2	24.9	52.3	3.24
Pine	52.4	7.49	74.9	2.98
Pine	69.2	27.2	4.94	2.77
Pine	61.9	49.5	109	3.27
Pine	63.9	27.0	31.9	2.51
Pine	67.0	71.9	64.5	2.16
Pine	67.2	44.8	94.6	3.28
Pine	76.0	56.4	223	3.40

Pine	35.2	17.6	78.0	2.97
Pine	34.4	29.5	56.5	2.44
Pine	22.6	<LOD	<LOD	1.51
Pine	98.1	7.6	47.8	1.78
Pine	69.6	59.6	64.6	1.93
Pine	54.2	37.0	78.9	1.53
Pine	49.2	86.1	145	960
Pine	108	67.8	103	1.66
Pine	70.3	72.8	141	2.19
Pine	59.9	87.3	110	1.41
Pine-Ivy	55.3	25.2	103	1.79
Pine-Thyme	63.8	353	88.3	2.73
Pine-Thyme	64.1	71.5	101	2.04
Pine-Thyme	32.2	44.6	112	3.11
Sage	49.0	53.9	76.0	1.34
Sage	10.0	25.0	82.5	1.13
Sage	20.2	17.6	123	2.35
Sage	32.6	25.1	188	1.81
Sage	17.2	34.4	182	1.76
Sage	40.3	247	222	1.95
Sage	9.84	86.1	165	1.00
Sage-Paliurus	15.1	50.3	103	1.14
Sage-WildFlowers	14.9	64.6	54.7	1.58
Sage-WildFlowers	5.09	76.3	<LOD	440
Sage-	15.1	72.8	113	994

WildFlowers				
Thorn	64.7	12.5	284	3.59
Thyme	22.6	30.1	120	715
Thyme	19.8	101	183	542
Thyme	122	29.4	36.7	4.65
Thyme	12.3	29.6	44.4	518
Thyme	19.0	33.3	<LOD	461
Thyme	12.3	49.3	121	875
Thyme	24.6	83.5	157	835
Thyme	22.5	105	220	417
Thyme	22.3	37.1	79.2	703
Thyme	12.3	131	121	800
Thyme	7.40	94.0	51.9	697
Thyme	17.3	44.5	74.1	608
Thyme	15.0	35.0	125	1.16
Thyme	29.9	67.4	259	841
Thyme	22.5	118	130	1.12
Thyme	12.6	65.3	97.9	525
Thyme	17.7	45.5	83.3	1.07
Thyme	12.5	22.4	<LOD	436
Thyme	27.2	54.5	81.7	730
Thyme	32.3	89.5	104	877
Thyme	183	563	355	280
Thyme	15.0	168	165	435
Thyme	12.6	50.4	106	192
Thyme	32.5	628	160	470

Thyme-Flowers	54.8	812	<LOD	1.22
Vanilla	78.4	471	119	2.13
Vanilla	57.2	39.8	29.8	2.49
Vanilla	103	22.6	60.4	3.41
Vanilla	72.9	106	62.9	2.06
Vanilla	47.8	1.36	<LOD	1.25
Vanilla	52.8	90.5	156	3.38
Vanilla	98.1	42.8	161	6.53
Vanilla	49.6	<LOD	5.0	1.62

ANNEX II

Table 13. Overall data of microelements’ concentration in Greek honey varieties

Variety	Zn (μg/kg)	Cu (μg/kg)	Fe (μg/kg)	Mn (μg/kg)	Al (μg/kg)	V (μg/kg)	Cr (μg/kg)	Co (μg/kg)
Acacia	4546	111	13862	263	1650	<LOD	828	17.5
Arbutus	5610	188	1955	222	930	<LOD	<LOD	<LOD
Arbutus	4198	426	975	622	967	<LOD	1803	2.13
Arbutus	986	338	10564	1239	767	<LOD	1851	<LOD
Arbutus	4328	738	11628	1325	1205	<LOD	1503	148
Arbutus	4328	738	11628	1325	1205	<LOD	1503	148
Arbutus	10579	247	9137	995	2937	<LOD	786	<LOD
Arbutus	8363	370	7333	388	2795	<LOD	355	<LOD
Arbutus	7231	284	5253	671	2827	<LOD	820	1.96
Arbutus	5808	829.	11918	5522	10162	<LOD	814	2.00

Arbutus	1974	929	849	4202	3952	<LOD	2207	3.30
Arbutus	4142	479	13460	6631	1345	<LOD	270	<LOD
Arbutus	2637	392	12220	2154	10667	<LOD	700	<LOD
Arbutus	1285	180	17856	909	3939	<LOD	637	<LOD
Arbutus	1396	271	18893	1433	2826	<LOD	643	<LOD
Arbutus	4306	224	12948	1487	3454	<LOD	691	<LOD
Arbutus	1479	534	9434	4400	3461	<LOD	1884	2.25
Arbutus	4361	364	18706	1191	8508	<LOD	615	4.76
Chestnut	46297	700	17460	17060	1727	<LOD	855	<LOD
Chestnut	1446	1090	12079	23674	3919	<LOD	2019	5.98
Chestnut	2354	523	11476	2461	4060	<LOD	2138	3.47
Chestnut	1596	399	8023	11797	2372	<LOD	1668	1.19
Chestnut	6880	884	35107	12906	3489	<LOD	2063	4.42
Chestnut	2259	329	12316	828	3961	<LOD	1855	2.72

Chestnut	6146	433	7441	14439	2942	<LOD	919	<LOD
Chestnut	3699	443	13978	4870	1709	<LOD	734	<LOD
Chestnut	2628	801	6789	6495	2491	<LOD	479	5.71
Chestnut	1436	142	2828	4703	1280	<LOD	697	<LOD
Chestnut	2354	343	12458	7724	2842	<LOD	640	<LOD
Chestnut	4804	729	9135	6047	1373	<LOD	1489	1.94
Chestnut	4164	606	6047	3634	945	<LOD	531	<LOD
Chestnut-Fir	2020	975	15393	5873	29412	<LOD	636	13.70
Cotton	2299	298	8118	1659	11511	<LOD	1851	6.39
Cotton	1525	287	13282	1871	1878	<LOD	1917	0.16
Cotton	7641	231	6170	637	2027	<LOD	198	<LOD
Cotton	2881	336	24477	332	1664	<LOD	730	2.22
Cotton-Clover	6114	308	5450	460	1958	<LOD	939	<LOD
Cotton-Trefoil-Herbs	4435	344	11023	899	3233	<LOD	746	<LOD

Eukalyptus	1613	220	19992	659	3109	<LOD	645	<LOD
Fennel-Anise	4150	355	11440	1043	1988	14.0	1557	10.25
Fennel-Anise	3173	742	5969	844	2924	<LOD	404	15.29
Fir	3939	810	4327	5309	31853	1.00	<LOD	15.52
Fir	9932	1640	9920	10209	47223	<LOD	1674	40.17
Fir	2312	1519	1854	5447	49171	<LOD	1803	49.54
Fir	3930	1125	11395	6131	22897	<LOD	567	4.30
Fir	1821	1498	11234	3607	19386	<LOD	1913	17.27
Fir	5256	1143	9321	4298	20216	<LOD	890	14.35
Fir	2404	1182	23662	7100	19393	<LOD	687	15.90
Fir	1597	1539	11827	7471	54698	<LOD	2032	52.33
Fir	8070	973	8687	5622	15092	<LOD	<LOD	6.70
Fir	1666	895	13084	5490	57347	<LOD	1663	44.45
Fir	7273	1069	4694	3543	18200	<LOD	<LOD	8.76

Fir	3733	562	3581	3243	12629	<LOD	1936	10.03
Fir	5737	724	4357	6747	27589	<LOD	527	9.35
Fir	2528	824	18167	4602	31192	<LOD	650	12.92
Fir	1001	674	8557	11365	4270	<LOD	362	0.270
Fir	3735	573	8023	6986	16015	<LOD	89.0	3.85
Fir	4475	804	13849	5473	25515	<LOD	1610	26.0
Fir	2059	502	24550	3950	24861	<LOD	766	17.2
Fir	9851	1005	11940	3647	29185	<LOD	1696	48.8
Fir	3875	797	10018	8056	31061	<LOD	1574	24.3
Fir	5774	900	22156	12091	16941	<LOD	721	7.85
Fir-Flowers (white tea. oregano)	3606	1884	5764	2580	27300	<LOD	809	16.3
Fir-Vanilla	1415	414	9546	2879	19554	<LOD	1593	7.40
Fir-Vanilla	3238	537	20742	5336	27918	<LOD	678	17.5
Flowers	4734	565	8975	4554	2280	<LOD	1875	1.10

Flowers	2158	367	18966	1144	9086	<LOD	785	1.75
Flowers	2791	776	15573	1251	9711	<LOD	903	13.3
Flowers	3879	691	11588	1519	6116	<LOD	582	5.32
Flowers	3799	249	15212	2109	1506	<LOD	1956	5.23
Flowers	5699	478	12783	3008	2785	<LOD	1478	0.202
Flowers-Acacia	2576	760	12253	520	2792	<LOD	544	43.7
Flowers-Arbutus	14250	547	8150	555	1840	<LOD	<LOD	<LOD
Flowers-Locust tree	4686	425	4211	591	1299	18.2	1594	0.341
Flowers-Orange tree	3782	358	8971	1224	1734	<LOD	1489	6.26
Flowers-Pine	7646	1244	5034	3614	5223	<LOD	652	39.7
Flowers-Thyme	4082	346	7806	1458	81803	<LOD	1378	3.36
Forest	5566	726	21087	4224	21338	<LOD	757	12.2
Forest	4744	1134	13420	19821	3797	<LOD	1939	9.87
Forest	3165	874	13528	5747	6739	<LOD	616	20.9

Gum(Masticha)	4222	1050	19343	8672	2515	<LOD	833	8.52
Heather	5799	319	4212	1885	3159	<LOD	184	<LOD
Heather	6409	1970	6836	808	9323	<LOD	1717	4.05
Heather	5147	1290	4705	1711	4643	<LOD	1058	<LOD
Heather	2494	1249	10764	2487	1372	<LOD	1823	<LOD
Heather	7019	885	8447	2540	3741	<LOD	229	0.633
Heather	7484	479	4265	917	5316	<LOD	1144	<LOD
Heather	3749	903	14773	1495	1536	22.2	1538	0.261
Heather	6329	736	9279	1224	2502	<LOD	589	<LOD
Heather	6902	454	5849	6765	3801	<LOD	<LOD	<LOD
Heather	6078	447	5138	6343	4934	<LOD	202	<LOD
Heather	10149	517	7410	3938	4982	<LOD	1145	3.41
Heather	2677	638	12608	1324	4159	<LOD	546	<LOD
Heather	1728	242	14837	3358	2572	<LOD	510	<LOD

Heather	2349	798	15665	2861	3469	<LOD	214	9.84
Heather	4358	450	17181	2547	7352	<LOD	649	<LOD
Heather	7410	1535	10543	5208	2354	<LOD	1576	2.34
Heather	2564	215	11236	7489	1620	<LOD	528	0.759
Heather	6089	356	3565	2288	845	<LOD	1685	0.378
Heather	3639	550	22715	1867	11425	<LOD	707	<LOD
Heather	4718	503	10205	5661	21323	<LOD	1468	13.0
Heather-Pine	1257	685	1745	950	2492	<LOD	851	<LOD
Heather-Pine cone	980	1148	10808	1729	24890	<LOD	1762	32.8
Ivy	3860	840	3626	5254	29383	<LOD	1682	21.6
Lemon tree	5315	216	8842	285	1428	<LOD	1716	3.04
Linden-Chestnut	8502	322	10783	2867	1796	<LOD	168	<LOD
Linden-Chestnut	7445	700	8182	11062	2279	<LOD	227	21.4
Locust tree	2620	500	11804	223	4623	<LOD	2225	4.68

Locust tree	6721	337	6857	938	2339	<LOD	533	<LOD
Locust tree	5518	391	15114	2797	3163	<LOD	212	<LOD
Locust tree	3477	544	1964	1111	21415	<LOD	2117	0.672
Locust tree	19372	728	1393	1247	3291	<LOD	1877	4.269
Locust tree	1741	509	15205	630	1947	<LOD	54	4.89
Locust tree	1381	419	26373	723	2208	<LOD	741	<LOD
Oak tree	6541	849	5143	12974	2015	<LOD	92	14.0
Oak tree	9552	1741	9033	30075	4873	<LOD	708	4.67
Oak tree	3519	1295	15681	18674	2297	<LOD	680	<LOD
Oak tree	1957	1010	11868	32426	14871	<LOD	1958	9.50
Oak tree	2470	945	65446	28231	4128	<LOD	2071	4.90
Oak tree	3285	4777	12939	32564	7090	<LOD	868	4.52
Oak tree	8415	1537	5071	35165	7145	<LOD	841	12.4
Oak tree	4053	779	7540	13969	4186	<LOD	107	2.47

Oak tree	1976	1158	14401	19278	3125	<LOD	588	<LOD
Oak tree	6706	1399	8151	32342	3325	<LOD	1980	8.69
Oak tree	7209	1107	9792	20239	3285	<LOD	1561	5.25
Oak tree	4334	453	5222	13788	1523	<LOD	658	<LOD
Oak tree	4402	1232	14565	20760	6399	<LOD	1734	71.2
Oak tree	3658	962	8773	15825	12333	<LOD	1467	13.06
Oak tree	2961	1385	17642	23523	8038	<LOD	693	13.58
Oak tree	1802	1085	20207	27995	1145	<LOD	684	0.49
Oak tree-Flowers	1677	734	5804	1237	1264	<LOD	1804	3.77
Oak tree-Flowers	2792	848	11458	15661	2196	<LOD	2000	6.30
Oak tree-Flowers/Forest	4771	975	10205	12853	13226	<LOD	1633	12.96
Oak tree-Herbs	8054	1557	5184	8722	7716	<LOD	591	28.31
Oak-Olympus Flowers	2170	1101	7932	20192	1546	<LOD	2026	7.87
Orange tree	5534	110	6254	196	2194	<LOD	626	<LOD

Orange tree	2048	157	2610	191	729	<LOD	1906	<LOD
Orange tree	4184	234	13219	671	3877	<LOD	678	<LOD
Orange tree	37585	3960	23025	386	3947	<LOD	923	0.888
Orange tree	12085	387	4515	453	3512	<LOD	<LOD	<LOD
Orange tree	16285	17844	8954	229	3857	<LOD	1917	1.89
Orange tree	7056	715	2537	343	3153	<LOD	698	<LOD
Orange tree	3226	164	10107	185	849	6.25	1302	<LOD
Orange tree	6814	142	5371	288	2255	<LOD	200	<LOD
Orange tree	9708	285	2893	732	4142	<LOD	887	<LOD
Orange tree	1211	628	15941	872	1919	<LOD	530	20.1
Orange tree	2264	842	15052	526	2640	<LOD	792	<LOD
Orange tree	3404	56	11239	141	536	<LOD	2040	0.671
Orange tree	3557	130	18562	58.2	551	<LOD	822	<LOD
Orange tree	4957	673	18501	774	1923	<LOD	1643	0.397

Orange tree	4230	288	1188	1369	775	<LOD	1824	0.424
Orange tree	4180	820	8074	408	1267	<LOD	1501	7.33
Orange tree-Herbs	2743	402	42758	288	4451	<LOD	63.0	0.564
Oregano	1618	439	36280	7016	1916	<LOD	774	20.9
Pine	6694	1427	3519	4957	3004	<LOD	<00	20.6
Pine	143	1001	6689	3002	3255	<LOD	1586	5.02
Pine	6229	1389	16218	1481	9113	<LOD	991	21.8
Pine	8362	1276	10806	4729	4673	<LOD	880	13.7
Pine	5972	882	13027	4247	4626	<LOD	186	5.45
Pine	5456	1332	13226	1173	4761	<LOD	150	3.80
Pine	4378	1170	5036	971	6501	<LOD	876	0.312
Pine	2296	1011	4147	721	3462	<LOD	1902	11.6
Pine	4784	1054	9471	738	2060	<LOD	1428	3.80
Pine	2759	772	8802	916	1824	<LOD	488	<LOD

Pine	3417	424	78	245	3082	<LOD	881	1.55
Pine	1229	1075	45106	2264	6068	<LOD	699	18.0
Pine-Ivy	8251	1257	4359	872	5754	<LOD	<LOD	<LOD
Pine-Thyme	4482	830	11906	3293	4880	<LOD	1691	8.06
Pine-Thyme	5407	675	8075	695	2826	<LOD	1616	0.554
Sage	2870	380	33384	993	5550	<LOD	615	<LOD
Sage	3924	372	19972	5920	2107	<LOD	598	<LOD
Sage	2823	677	11349	368	1536	<LOD	630	<LOD
Sage	2224	214	6684	109	467	<LOD	1551	<LOD
Sage	1673	178	10322	345	278	<LOD	1678	10.3
Sage	5567	152	6525	51	0	<LOD	1622	<LOD
Sage	2022	347	46362	321	2221	<LOD	871	<LOD
Sage-Paliurus	8219	371	5058	664	2989	<LOD	334	<LOD
Sage-WildFlowers	5384	206	1871	216	1575	<LOD	250	<LOD

Sage-WildFlowers	1855	284	7142	193	754	<LOD	1850	8.59
SunFlowers-Chestnut	2115	292	6974	2252	604	<LOD	1572	<LOD
Thyme	1301	203	8097	111	1896	<LOD	1772	2.34
Thyme	6517	1360	1090	681	3497	<LOD	13	<LOD
Thyme	1957	250	11491	242	2494	<LOD	2143	2.68
Thyme	1924	218	11741	106	650	<LOD	1548	<LOD
Thyme	1481	140	12826	132	977	<LOD	1883	<LOD
Thyme	2977	276	13356	329	1374	<LOD	2231	1.37
Thyme	7710	205	4491	311	2237	<LOD	570	<LOD
Thyme	6442	158	5370	194	2267	<LOD	361	0.582
Thyme	7817	151	5233	160	2071	<LOD	428	<LOD
Thyme	6574	879	1816	6154	30386	<LOD	<00	14.2
Thyme	1722	154	5310	189	777	<LOD	273	<LOD
Thyme	2986	225	15178	258	1286	<LOD	488	<LOD

Thyme	2750	317	12988	440	2742	<LOD	553	<LOD
Thyme	3371	190	8114	1773	766	<LOD	509	<LOD
Thyme	3761	162	7451	210	1846	<LOD	457	<LOD
Thyme	1496	225	2348	<LOD	5901	<LOD	746	<LOD
Thyme-Flowers	3551	688	14466	481	561	<LOD	481	<LOD
Vanilla	2444	744	26962	4126	18378	<LOD	868	23.8
Vanilla	2657	632	16476	3132	13855	<LOD	593	1.10
Vanilla	1425	548	8604	5358	17835	<LOD	1711	16.6
Vanilla	4639	994	541	1025	1846	<LOD	1613	13.6
Vanilla	2497	798	14257	3157	21343	<LOD	661	26.6

ANNEX III

Table 14. Overall data of rare elements concentration in Greek honey varieties

Variety	Y (ng/kg)	La (ng/kg)	Ce (ng/kg)	Pr (ng/kg)	Nd (ng/kg)	Sm (ng/kg)	Eu (ng/kg)	Gd (ng/kg)	Tb (ng/kg)	Dy (ng/kg)	Ho (ng/kg)	Er (ng/kg)	Yb (ng/kg)	Lu (ng/kg)
Acacia	<LOD	34.2	<LOD	<LOD	27.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	252	253	<LOD	77.3	<LOD	<LOD	12.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	81.3	<LOD	<LOD	31.0	<LOD	<LOD	2.84	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	16592	148	59.0	5.31	98.9	<LOD	<LOD	4.06	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	16592	148	59.0	5.31	98.9	<LOD	<LOD	4.06	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	78.8	<LOD	<LOD	26.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	331	<LOD	<LOD	46.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	289	64.8	<LOD	41.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	3258	3402	25.2	207	9.18	<LOD	34.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Arbutus	54.5	112	105	8.45	119	17.6	<LOD	17.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	1318	96.6	<LOD	<LOD	30.3	4.68	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	1318	96.6	<LOD	<LOD	30.3	4.68	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	84.1	<LOD	<LOD	78.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	38.1	<LOD	<LOD	85.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	504.22	49.2	<LOD	<LOD	52.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Arbutus	<LOD	41.5	<LOD	<LOD	45.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	<LOD	139	<LOD	0.482	127	0.483	<LOD	3.71	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	18.7	106	56.6	3.90	102	20.8	<LOD	8.54	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	9.12	77.7	46.4	0.361	57.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	<LOD	119	38.6	3.28	68.2	<LOD	<LOD	3.42	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Chestnut	441	471	1329	34.9	219	6.06	<LOD	5.03	<LOD	5.60	<LOD	<LOD	<LOD	4.14
Chestnut	568	114	14.5	<LOD	35.1	<LOD	<LOD	8.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	<LOD	<LOD	<LOD	<LOD	0.352	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	4294	36.8	<LOD	<LOD	10.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	<LOD	39.9	<LOD	<LOD	26.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	227	178	85.0	6.89	90.3	<LOD	<LOD	10.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chestnut-Fir	<LOD	583	<LOD	<LOD	114	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cotton	22.7	85.8	18.9	<LOD	66.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cotton	<LOD	72.9	<LOD	<LOD	40.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cotton	270	182.68	32.1	<LOD	73.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cotton	<LOD	58.1	<LOD	<LOD	19.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cotton-Clover	<LOD	148	5.57	<LOD	7.22	<LOD	<LOD	<LOD	81.5	<LOD	<LOD	<LOD	<LOD	46.5
Cotton-Trefoil-Herbs	381	267	<LOD	<LOD	36.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Eukalyptus	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fennel-Anise	553	290	369	30.2	24	22.0	<LOD	36.4	<LOD	14.3	<LOD	<LOD	<LOD	<LOD
Fennel-Anise	<LOD	815	1531	8.26	221	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	3174	495	187	13.0	116	17.8	<LOD	13.2	2.41	2.41	<LOD	<LOD	<LOD	<LOD
Fir	417	538	1134	116	752	82.8	<LOD	78.8	<LOD	50.8	<LOD	<LOD	<LOD	<LOD
Fir	22.3	104	87.8	9.05	113	7.17	<LOD	18.0	<LOD	6.76	<LOD	<LOD	<LOD	<LOD
Fir	231	118	<LOD	<LOD	108	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	699	723	1626	191	936	206	24.5	177	<LOD	118	3.57	45.3	24.0	<LOD
Fir	<LOD	247	156	<LOD	158	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	<LOD	200	<LOD	7.84	191	22.0	<LOD	5.97	<LOD	0.344	<LOD	<LOD	<LOD	<LOD
Fir	749	740	1625	221	966	196	34.6	193	<LOD	130	10.4	48.6	29.5	<LOD
Fir	<LOD	110	102	<LOD	146	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	67.4	171	169	15.2	153	18.6	<LOD	19.1	<LOD	7.70	<LOD	<LOD	<LOD	<LOD
Fir	353	595	1171	109	671	97.1	<LOD	63.6	<LOD	52.5	<LOD	<LOD	<LOD	<LOD

Fir	352	215	330	38.5	249	40.4	<LOD	46.7	<LOD	35.6	<LOD	<LOD	<LOD	<LOD
Fir	2769	673	148	<LOD	140	<LOD	<LOD	<LOD	515	<LOD	<LOD	<LOD	<LOD	530
Fir	<LOD	231	<LOD	9.60	211	28.0	<LOD	8.91	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	<LOD	30.8	<LOD	<LOD	57.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	<LOD	9.11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	416	303	459	43.3	238	35.7	<LOD	49.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir	<LOD	75.7	<LOD	<LOD	128	15.4	<LOD	4.54	<LOD	4.70	<LOD	<LOD	<LOD	<LOD
Fir	979	204	183	9.44	117	10.8	<LOD	5.34	<LOD	0.0301	<LOD	<LOD	<LOD	<LOD
Fir	811	291	255	23.5	209	18.8	<LOD	29.3	<LOD	6.58	<LOD	<LOD	<LOD	<LOD
Fir	<LOD	62.2	<LOD	<LOD	83.4	7.51	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fir-Flowers (white tea. oregano)	402	449	<LOD	101	594	115	4.00	83.9	<LOD	68.8	<LOD	14.0	7.75	<LOD
Fir-Vanilla	115	5639	9017	800	2186	184	<LOD	125	<LOD	24.0	<LOD	1.19	<LOD	<LOD
Fir-Vanilla	3589	246	<LOD	0.283	173	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Flowers	15.7	149	130	<LOD	54.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers	<LOD	34.5	<LOD	<LOD	64.4	2.78	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers	<LOD	266	<LOD	38.6	348	53.4	<LOD	39.9	<LOD	31.2	<LOD	<LOD	<LOD	<LOD
Flowers	<LOD	<LOD	<LOD	<LOD	4.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers	<LOD	101	<LOD	<LOD	26.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers	719	170	85.6	<LOD	83.1	<LOD	<LOD	7.34	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers-Acacia	<LOD	48.3	<LOD	<LOD	34.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers-Arbutus	<LOD	25.1	<LOD	<LOD	59.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers-Locust tree	843	256	171	5.87	90.6	2.42	<LOD	1.66	<LOD	2.61	<LOD	<LOD	<LOD	<LOD
Flowers-Orange tree	422	142	51.8	<LOD	70.6	<LOD	<LOD	1.38	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers-Pine	788	209	240	<LOD	163	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flowers-Thyme	1104	146	153	5.09	112	<LOD	<LOD	5.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Forest	1984	20.4	<LOD	<LOD	30.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Forest	5169	102	58.5	<LOD	106	1.21	<LOD	9.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Forest	<LOD	144	4929	6.31	166	1.19	<LOD	6.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Gum(Masticha)	<LOD	40.2	<LOD	<LOD	76.71	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	155	9.85	<LOD	110	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	37.4	355	421	33.6	195	0.224	<LOD	29.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	68.9	216	170	<LOD	86.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	68.9	216	170	<LOD	86.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	59.9	<LOD	<LOD	54.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	51.3	<LOD	<LOD	11.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	80.6	22.4	<LOD	46.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	9800	236	180	1.56	109	3.99	<LOD	6.35	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	53.7	<LOD	<LOD	27.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	416	22.0	<LOD	80.3	<LOD	<LOD	<LOD	134	<LOD	<LOD	<LOD	<LOD	70.3
Heather	<LOD	139	92.8	<LOD	129	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	368	122	<LOD	43.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Heather	<LOD	198	<LOD	<LOD	73.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	<LOD	<LOD	<LOD	<LOD	0.371	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	626	111	131	1.15	102	34.4	<LOD	25.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	25196	50.8	<LOD	<LOD	44.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	2049	251	306	26.2	176	6.18	<LOD	26.7	<LOD	6.35	<LOD	<LOD	<LOD	<LOD
Heatther	<LOD	<LOD	<LOD	<LOD	16.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	717	112	11.9	<LOD	33.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	<LOD	36.1	<LOD	<LOD	41.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather	2242	146	155	8.25	118	<LOD	<LOD	27.2	<LOD	3.08	<LOD	<LOD	<LOD	<LOD
Heather-Pine	<LOD	24.1	<LOD	<LOD	29.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heather-Pine cone	128	119	187	22.9	205	14.8	<LOD	40.0	<LOD	23.9	<LOD	<LOD	<LOD	<LOD
Ivy	1064	293	9737	75.5	287	56.9	<LOD	45.8	<LOD	8.44	<LOD	<LOD	<LOD	<LOD
Lemon tree	357	227	70.3	<LOD	33.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Linden-Chestnut	191	482	383	17.2	90.4	<LOD	<LOD	11.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Linden-Chestnut	<LOD	23.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	45.8
Locust tree	70.8	260	439	32.8	160	7.53	<LOD	25.8	<LOD	11.0	<LOD	<LOD	<LOD	<LOD
Locust tree	<LOD	24.2	<LOD	<LOD	50.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Locust tree	<LOD	56.4	<LOD	<LOD	25.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Locust tree	257	164	277	21.9	131	25.0	<LOD	18.1	<LOD	19.8	<LOD	8.31	7.06	<LOD
Locust tree	6.13	81.3	54.3	4.69	97.1	16.0	<LOD	6.37	<LOD	1.89	<LOD	<LOD	<LOD	<LOD
Locust tree	<LOD	<LOD	<LOD	<LOD	39.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Locust tree	<LOD	91.8	<LOD	<LOD	138	<LOD	<LOD	<LOD	<LOD	0.379	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	59.8	<LOD	<LOD	30.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	357	349	0.442	178	11.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	214	<LOD	<LOD	128	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	110	175	246	25.5	178	29.2	<LOD	32.2	<LOD	19.6	<LOD	<LOD	<LOD	<LOD
Oak tree	112	199	246	24.4	160	31.1	<LOD	29.3	<LOD	7.58	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	244	<LOD	18.6	244	73.9	<LOD	30.4	<LOD	18.1	<LOD	<LOD	<LOD	<LOD

Oak tree	<LOD	145	104	<LOD	144	0.452	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	2957	116	<LOD	<LOD	16.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	94.9	<LOD	<LOD	74.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	160	268	1879	43.4	248	16.0	<LOD	16.3	<LOD	8.10	<LOD	<LOD	<LOD	<LOD
Oak tree	86.4	118	94.9	6.35	97.0	33.7	<LOD	11.9	<LOD	4.14	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	2115	206	172	11.8	142	15.4	<LOD	5.90	<LOD	9.20	<LOD	<LOD	<LOD	<LOD
Oak tree	53	224	338	10.1	129	14.5	<LOD	12.3	<LOD	3.53	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree	<LOD	32.1	<LOD	<LOD	62.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oak tree-Flowers	197	264	234	29.7	225	31.5	<LOD	36.0	<LOD	17.0	<LOD	<LOD	<LOD	<LOD
Oak tree-Flowers	67.2	358	173	18.7	140	24.1	<LOD	17.0	<LOD	5.13	<LOD	<LOD	<LOD	<LOD
Oak tree-Flowers/Forest	757	319	347	16.8	136	17.8	<LOD	11.5	<LOD	6.89	<LOD	<LOD	<LOD	<LOD
Oak tree-Herbs	<LOD	171	129	<LOD	152	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Oak-Olympus Flowers	20.9	165	219	18.5	100	1.35	<LOD	6.53	<LOD	5.89	<LOD	<LOD	<LOD	<LOD
Orange tree	<LOD	41.2	<LOD	<LOD	9.56	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	2116	201	<LOD	<LOD	72.8	<LOD	<LOD	9.22	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	<LOD	299	1824	<LOD	121	8.84	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	6840	1295	1191	50.4	329	40.1	<LOD	11.2	<LOD	22.8	<LOD	<LOD	<LOD	<LOD
Orange tree	123	408	271	<LOD	153	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	191	929	840	150	552	56.5	<LOD	44.5	<LOD	30.9	<LOD	10.8	<LOD	<LOD
Orange tree	<LOD	159	27.1	<LOD	75.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	4142	122	86.0	<LOD	84.3	9.87	<LOD	6.23	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	<LOD	44.9	<LOD	<LOD	42.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	<LOD	257	11.1	<LOD	93.4	<LOD	<LOD	<LOD	275	<LOD	<LOD	<LOD	<LOD	189
Orange tree	<LOD	37.8	<LOD	<LOD	78.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	<LOD	88.6	<LOD	<LOD	65.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	30.6	26.9	<LOD	<LOD	18.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Orange tree	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	358	163	167	9.52	118	9.52	<LOD	15.9	<LOD	5.87	<LOD	<LOD	<LOD	<LOD
Orange tree	36.2	318	<LOD	<LOD	75.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree	328	170	106	5.95	109	16.2	<LOD	11.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Orange tree - Herbs	104	954	1394	91.8	291	4.92	<LOD	20.2	<LOD	13.1	<LOD	<LOD	<LOD	<LOD
Oregano	<LOD	126	<LOD	<LOD	132	<LOD	<LOD	7.48	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	186	81.3	<LOD	111	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	71.0	219	239	24.9	167	14.8	<LOD	22.7	<LOD	9.60	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	307	301	<LOD	205	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	169	123	<LOD	77.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	166	168	<LOD	<LOD	150	7.60	<LOD	2.33	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	100	<LOD	<LOD	113	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	315	<LOD	12.0	234	30.1	<LOD	22.3	<LOD	20.6	<LOD	<LOD	<LOD	<LOD
Pine	652	294	442	52.9	290	51.7	<LOD	62.20	<LOD	21.2	<LOD	3.43	<LOD	<LOD

Pine	322	153	146	10.6	172	29.1	<LOD	24.1	<LOD	15.7	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	43.8	<LOD	<LOD	46.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	72.1	<LOD	<LOD	71.0	2.75	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine	<LOD	41.3	<LOD	<LOD	73.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pine –Ivy	258	399	305	46.73	347	34.2	<LOD	32.1	<LOD	2.54	<LOD	<LOD	<LOD	<LOD
Pine – Thyme	1895	460	757	90.8	450	94.6	<LOD	90.5	<LOD	41.3	<LOD	13.9	1.81	<LOD
Pine – Thyme	3461	215	<LOD	8.25	193	10.0	<LOD	5.56	<LOD	10.8	<LOD	<LOD	<LOD	<LOD
Sage	<LOD	40.1	<LOD	<LOD	11.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage	<LOD	151	<LOD	<LOD	127	13.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage	<LOD	64.6	<LOD	<LOD	7.22	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage	<LOD	37.8	<LOD	<LOD	14.4	0.11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage	1775	154	30.3	<LOD	46.0	<LOD	<LOD	0.27	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage	<LOD	43.3	<LOD	<LOD	63.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Sage-Paliurus	<LOD	48.8	<LOD	<LOD	25.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage-WildFlowers	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sage-WildFlowers	17.8	120	93.4	0.83	100	<LOD	<LOD	6.88	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
<LOD	43.6	<LOD	<LOD	32.8	4.11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	96.3	3.51	<LOD	57.2	8.04	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	57.4	120	87.2	1.56	80.6	6.58	<LOD	0.59	<LOD	0.11	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	43.7	<LOD	<LOD	35.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	9.47	74.5	0.35	<LOD	97.4	1.60	<LOD	8.67	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	13.5	84.6	59.5	<LOD	110	0.40	<LOD	12.0	<LOD	1.83	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	27.4	<LOD	<LOD	38.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	229	1028	<LOD	121	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	87.1	<LOD	<LOD	29.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	57.1	298	86.1	<LOD	72.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Thyme	<LOD	69.1	<LOD	<LOD	19.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	168	<LOD	<LOD	19.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	146.8	<LOD	<LOD	98.7	19.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	53.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	56.4	<LOD	<LOD	45.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	<LOD	<LOD	<LOD	27.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme	<LOD	16.4	<LOD	<LOD	29.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Thyme-Flowers	<LOD	5.77	<LOD	<LOD	22.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Vanilla	<LOD	89.8	<LOD	<LOD	93.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Vanilla	<LOD	<LOD	<LOD	<LOD	16.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Vanilla	131	260	307	7.98	121	14.0	<LOD	5.70	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Vanilla	719	146	123	11.0	101	21.1	<LOD	11.8	<LOD	6.52	<LOD	<LOD	<LOD	<LOD
Vanilla	<LOD	<LOD	<LOD	<LOD	16.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

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FIGURES CITATION

Figure 1.

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Figure 2.

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Figure 3.

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Figure 4.

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Figure 5.

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Figure 6.

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Figure 7.

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Figure 9.

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Figure 11.

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Figure 13.

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