

A review: Insecticidal potential of Zeolite (Clinoptilolite), toxicity ratings and general properties of Turkish Zeolites

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DOI: xx.xxxx/xxx.2014.xxx.xxx.xxx

Abstract

Zeolites are microporous crystalline aluminosilicates derived from the reaction of volcanic rocks, ash layers and an alkaline groundwater. Atlas of Zeolite Framework Types currently recognizes about 218 framework Zeolite structures. Since its first discovery in 1756 by Swedish mineralogist A.F. Cronstedt, over 40 natural zeolites are listed. Non-toxicity (IARC, 1997a,b) and safety for human consumption (FDA GRAS Listings, 2006) of natural zeolites accelerate recognition and expand the applications of agricultural uses. Furthermore, Codex Alimentarius Commission (1999) endorses pest control in food commodities and lists Zeolite as granted substance in organic food production and in plant protection. Public awareness and growing concern to environmental issues encourage new approaches of alternative ecofriendly methods such as inert dusts. Hence, post-harvest organic minerals application as insecticide compare to synthetic insecticides provides no chemical residue, affordability, and virtually more benefit to environment with end users. Among inert dusts used in stored-product protection, Zeolites are included the group contain natural silica similarly diatomaceous earth. Review of entomology and agricultural literatures present insecticide potential of Zeolites formulations recently studied on *Sitophilus zeamais* Motschulsk, *Rhyzopertha dominica* (F.), *Sitophilus oryzae* (L.), *Tribolium castaneum* (Herbst), *Lasioderma serricornis*(F.), *Tribolium confusum* Jacquelin du Val, *Meligethes* spp., *Aedes aegypti* (L.), *Cimex lectularius* Linnaeus progressively. Clinoptilolite under Heulandite series is natural Zeolite possess one of the most promising insecticidal potential, thermal stability, and high Si/Al proportion. Anatolia that Aegean side of Turkey ranked among world's first five major producers has been known abundance of high purity Clinoptilolite and easily accessible surface deposits. The chemical and physical properties of Turkey's Clinoptilolite reserves and insecticidal potential would be presented in this paper comparatively.

Keywords: Zeolite, Clinoptilolite, insecticide, stored-product pests, Turkish Zeolite

1. Introduction

Since its first discovery in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, the Zeolites and clay minerals have been of great interest in many scientific disciplines (Barrer, 1978). Rising public awareness to chemical residues on food commodities, developing resistance to insecticides and implementing new government regulations accentuate recent approaches of using nontoxic materials such as inert dusts in stored-product insect IPM (Integrated Pest Management) programs (Subramanyum and Roesli, 2000; Collins, 2006; Kljajic et al., 2011). Natural zeolite is an inert dust categorized with diatomaceous earth (DE) according to their natural silica content (Subramanyum and Roesli, 2000).

Zeolites form a large family of crystalline hydrated aluminosilicates of alkali or alkaline earth metals principally sodium, potassium, and calcium (Barrer, 1978, Christidis et al., 2003). Volcanic rocks and ash layers react with alkaline groundwater overtime to produce natural zeolites. They have a framework structure identified by interconnected cavities or cages,

occupied by relatively large cations and water molecules (Gottardi and Galli, 1985). Because of the ability to froth when heated about 200°C, the word zeolite was derived from the Greek words mean “boiling stones” (Breck, 1974; Polat et al., 2004). Atlas of Zeolite Framework Types recognizes about 218 framework zeolite structures including more than 50 natural zeolites approved by the Structure Commission of the International Zeolite Association (IZA) in March 2014 (Baerlocher et al., 1996; Colella, 2007). Insecticidal potential of natural zeolites depends on their physical and chemical properties and their molecular structure (amorphous-crystalline type, cage-like three dimensional frames, cations, ion exchange capacity, bulk density), SiO₂ content, size and presence of particles, porosity, pH values, sorptive capacity (dehydration-rehydration), and geographical origin (Mumpton, 1999, Subramanyum and Roesli, 2000, Kijajic et al., 2011).

Natural zeolites are listed by the USA Food and Drug Administration for human consumption (FDA GRAS Listings, 2006) and considered as non-toxic by the World Health Organization International Agency for Research on Cancer (IARC, 1997). Moreover, Codex Alimentarius Commission (1999) endorses pest control in food commodities and lists Zeolite as a granted substance in Organic Food Production and Plant Protection. Recent studies on agricultural and entomology show the insecticide potential of Zeolites on *Sitophilus zeamais* Motschulsky, *Rhyzopertha dominica* (F.), *Sitophilus oryzae* (L.), *Tribolium castaneum* (Herbst), *Lasioderma serricornis* (F.), *Tribolium confusum* Jacquelin du Val, *Meligethes* spp., *Aedes aegypti* (L.), *Cimex lectularius* Linnaeus (Haryadi et al., 1994; Pezzutti et al., 1979; Mulla et al., 2004; Kijajic et al., 2008, 2009a, 2009b, 2010a, 2010b, 2011; Andric et al., 2012; Gota et al., 2012; Daniel et al., 2013).

Clinoptilolite, which was discovered in 1890 (Barrer, 1978), belongs to the HEU-type III (Heulandite) zeolite group (Boles, 1972) and has a promising insecticidal potential, thermal stability, significant macroporosity (Coruh et al., 2010) and high Si/Al proportion (Gottardi and Galli, 1985; Christidis et al., 2003; Baerlocher et al., 2007). Its crystal structure and negative charge constitute a distinct ability for ion exchange and adsorption of substances that can be used for mycotoxins adsorption and as a stabilizer of pesticides in plant protection (Barrer, 1978; Akcay, 2002; Kijajic et al., 2011). Anatolia on the Aegean side of Turkey ranked among world's top five major producers and has a known abundance of high purity Clinoptilolite and easily accessible surface deposits (Virta, 2010; USGS, 2011). The chemical and physical properties of Turkey's Clinoptilolite reserves and insecticidal potential will be presented in this paper.

2. Structure and mineral formation of zeolite

Zeolites have an infinitely extending three-dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners by sharing all of the oxygen atoms (Breck, 1974). The zeolite structures contain -Si-O-Al- linkages that comprise surface pores of uniform diameter with 2-12 Å pore sizes. A representation of a typical zeolite framework is shown in Figure 1 and SEM microimages of crystals of Clinoptilolite is given in Figure 2. The enclosed cavities contain both the metal cations and water molecules and channels of discrete sizes and shapes, depending of the chemical composition and crystal structure of the specific zeolite involved (Barrer, 1978). Zeolites have microporous structures known as “molecular sieves” named by McBain (1932) and according to IUPAC nomenclature the voids (pores) between the linked atoms (host) have a free volume larger than that of a sphere with a 0.25 nm diameter, and are arranged in an ordered manner (McCusker et al., 2001).

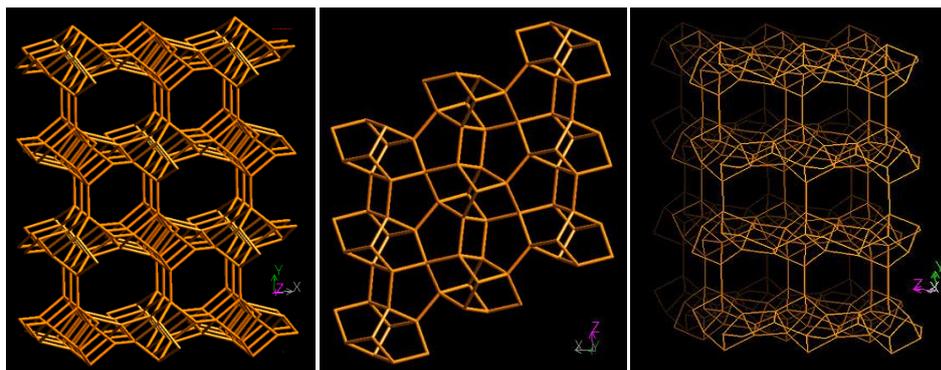


Figure 1 Diagrammatic picture of Clinoptilolite under framework type of HEU by2007 Structure Commission of the International Zeolite Association (IZA-SC).

The cage-like structure and pores that form around 50% of zeolites provide them with an enormous internal and external surface area for ion exchange and chemical reactions. The comparison of pore size distribution for a zeolite molecular sieve, a typical silica gel and activated carbon demonstrate the most important molecular sieve effects by the dehydrated crystalline zeolites (Breck, 1974). Since the channels and pores uniformly penetrate the entire volume of the solid, all these materials have a high internal surface area available for adsorption. The external surface of the adsorbent particles contributes only a small amount of the total available surface area (Breck, 1974). The dimensions of pore apertures are one of the important criteria to divide zeolites into following categories; small pore (pore diameters around 4 Å), medium-pore (5-6 Å), large pore (7 Å), extra-large pore (>7 Å). Additionally, shape of pores are another factor affecting their adsorbing capacity and insecticidal potential. Dimensionality of the channels (one-dimensional, two-dimensional, three-dimensional pore systems) depends on a arrangement of the mineral. Zeolites with can be classified as “high Silica” with Si/Al a.r. >10, intermediate silica (1.5< Si/Al a.r.<10), and “low silica” with Si/Al ratio ~1 (Busca, 2014).

Natural zeolites form when volcanic rocks and ash layers react with alkaline groundwater. The mineral formation of zeolite sedimentary rocks has been correlated with the chemical composition of the host rock (high or low silica), water chemistry (pH, salinity, dissolved ions) of the depositional and post-depositional environment, and the age and burial depth (Breck, 1974). The formation of natural zeolite, especially Clinoptilolite reserves, are categorized by Mumpton (1999) under six groups; mainly occurring in closed and and salty lake waters where volcanic residues react with sea water, in shores and deep sea sediments, decomposition by hydrothermal reserves, and low burial temperature before metamorphosis. High-silica and alkali-rich zeolites such as Clinoptilolite are predominantly found in high-silica rocks. The pH is related to the rate of the zeolite reaction and types of minerals that are formed. In the marine environment where the water pH is 7.5-8.1, the silicic glass is commonly preserved unaltered for millions of years. In the more basic sodium-carbonate lakes with a pH of 9.1-9.9, it seems to altered within a few tens of thousand years. The salt content of water also favors the conversion of volcanic glass to form zeolites (Breck, 1974).

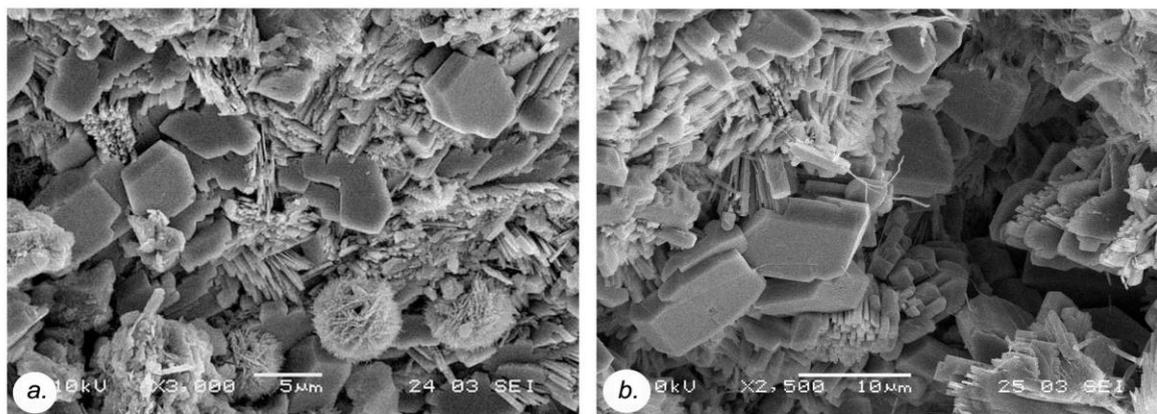


Figure 2 The shape and size of clinoptilolite crystals were elucidated using SEM imaging (Bedelean et al., 2010).

3. Global Zeolite occurrences and distribution

Although, there are no certainties on the total amount of zeolites in the world, all continents reported varying mineral contents and sources (Polat et al., 2001). Two hundred years after the first discovery in volcanic rocks, zeolites were rediscovered in the 1950's due to their industrial potential and reported existence on all the continents. Consequently, their commercial production accelerated in 1960's (Polat et al., 2001). The distribution of natural zeolites occurs in over 40 countries and mined in 11. The total consumption of zeolites was 3.5 million tons, of which 18% came from natural zeolites and the rest from synthetics (Polat et al., 2001). Natural zeolites are obtained by conventional open pit mining techniques. The ore is mined, crushed, dried, and milled to various particle sizes, then shipped in bags or bulk quantities. The common natural occurrence of zeolite-rich rock and sediments, and low-cost mining applications are probably the most important factor for large-scale use.

The annual world production of natural zeolite is about 3 million tones (USGS, 2011). The major producers were China (2 million tones), South Korea (210,000 t), Japan (150,000 t), Jordan (140,000 t), Turkey (100,000 t), Slovakia (85,000 t) and the United States (59,000 t) in 2010 (Virta, 2010, USGS, 2011). The countries with reserves of Zeolite principally Clinoptilolite are listed by continent by Mumpton (1985) and Colella (2007):

1. Europe: Denmark, France, Slovakia, Czech republic, England, Romania, Poland, Swiss, Russia, Bulgaria, Serbia, Slovenia, Turkey, Greece, Hungary
2. Africa: Angola, Botswana, Northern Africa, Tanzania, South Africa
3. Asia and Australia: China, Iran, Israel, Taiwan, Japan, Korea, New Zealand, Oceania, Australia
4. South America: Argentina, Chile
5. North America: USA, Canada, Cuba, Guatemala, Mexico, Panama, West Indies

4. Natural occurrence and general properties of Turkish Zeolites (Clinoptilolites)

Zeolites were first discovered in Turkey in 1971 in Golpazari-Goynuk (Akçay, 2002) and Ankara (Polat et al., 2004). Turkey has a remarkable mineral potential with an estimated total reserve of 50 billion tons representing about 7% of the world current reserves (Yorukogullari, 1997). The biggest zeolite reserves of Turkey are in the Balıkesir-Bigadic province with

estimated 500 million ton capacity (Alver et al., 2010; Ataman and Gundogdu, 1982; Gundogdu, 1982; Caliskan, 2012). According to the General Directorate of Mineral Research and Exploration of Turkey reserves of clinoptilolite in the Manisa-Gordes region only are estimated at 2 billion tones (Anonymous, 2004, Polat et al., 2004). The other mineral reserves are in Ankara (Polatli, Ayaş, Nallihan, Beypazari), Kutahya (Emet-Yukarı Yoncağaç, Saphane), Eskişehir-Kirka, Edirne-Kesan, Bursa- Mustafa Kemal Pasa, Canakkale-Gelibolu, Yalova-Karamursel, Afyon-Sandikli, Izmir-Urla, and the Cappadocia region (Tuzköy-Karain). These reserves are clinoptilolite and other types (Cetinel, 1993; Kocakusak et al., 2001; Bilgin, 2009). Turkey currently has ~345 million tons of reserves of Clinoptilolite recorded by MTA (2013).

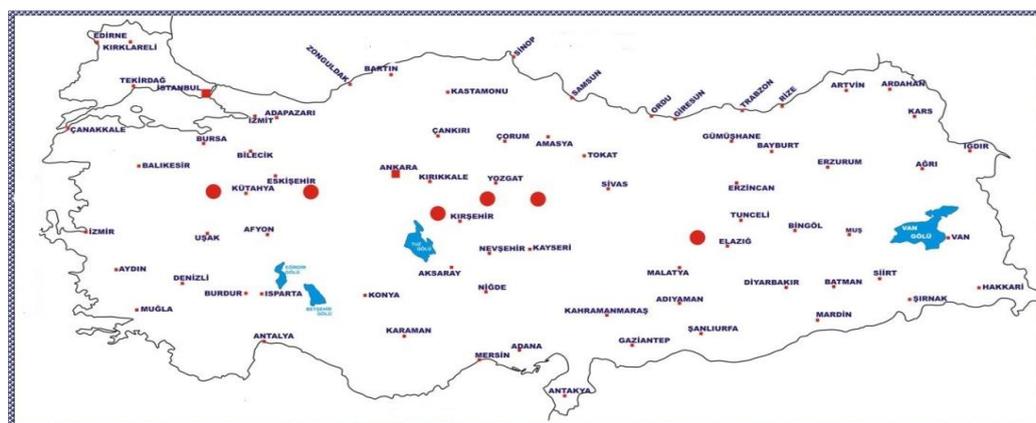


Figure 3 Zeolite Map of Turkey by General Directorate of Mineral Research and Exploration (MTA, 2012).

5. Clinoptilolite

Clinoptilolite derives from Greek and means “oblique feather stone” and is characterized by high Si/Al ratio, predominance of Na and K in exchangeable sites and thermal stability. Clinoptilolite is reported to have a classical alumina silicate cope-like structure and therefore exhibits significant macroporosity (Coruh et al., 2010). Suitability of clinoptilolite as a chemical sieve, a feed and food additive, and as a gas and odour absorber makes it one of the most useful naturally occurring zeolite types. It has remarkable properties that are useful for stored-products including a large amount of pore spaces, dehydration activity, ion exchange capacity, high resistance to extreme temperatures, high absorption level and chemically neutral basic structures (Anonymous, 2004). Furthermore, Clinoptilolite is the most abundant natural zeolite that occurs in relatively large sedimentary deposits with high purity in many parts of the world (Coruh et al., 2010). It occurs in sedimentary rocks and idiomorphic plates, with most crystals displaying characteristic monoclinic symmetry and the shape of a coffin, with chemical formulation of $\text{Na}_6(\text{AlO}_2)_6(\text{SiO}_2)_{30} \cdot 24\text{H}_2\text{O}$. Clinoptilolite is a glassy, pearl-like, transparent material with Si/Al ratio of 0.425/5.25, pH 1.5-11, roughness 3.5-4, and mass weight 2.2. It can be colourless, white, pink, yellow and reddish. Turkish Clinoptilolite demonstrates good chemical composition and has insecticidal potential.

The comparison between zeolite and DE reveals some similarities including mode of action and some differences of structure, origin and their chemical composition. Diatomaceous earth minerals originate from fossilized single-celled algae and comprised of amorphous silica occurring in lake or marine sediments, however, only freshwater-derived food grade DE is used in United States agriculture for grain storage, feed supplement, and as an insecticide. Inert dust acts as an insecticide through cuticular absorption (Subramanyam and Roesli,

2000), while the Si/Al ratio and other mineral oxides, desiccant property, and abrasive formation depend on the region of origin (Korunic, 2013). Dusts with amorphous structure are more efficient than dusts with crystal structure (zeolite) (Kljajic et al., 2010a) and though DE may be more effective than zeolite there are not enough studies to determine the efficacy of zeolites.

Table 1 The comparison of some chemical properties of Turkey and some European Zeolite reserves along with Diatomaceous earth.

	Turkey Locations				Europe Locations		Diatom. Earth
	Sivas ^a Yavu	Manisa ^b Gordes	Cankiri ^c Corum	Balikesir ^d Bigadic	Serbia ^e	Slovak Rep. ^f	Canada- DE ^g
SiO ₂	63.14	78.29	64.28	78.73	65.69	65.0-71.3	65.51
Al ₂ O ₃	10.39	12.37	12.07	12.00	14.03	11.5-13.1	13.3
CaO	11.28	1.76	2.47	3.02	3.57	2.7-5.2	1.06
Fe ₂ O ₃	4.24	1.20	0.84	1.44	2.34	0.7-1.9	4.37
MgO	0.98	0.44	2.07	0.92	1.09	0.6-1.2	1.17
K ₂ O	1.86	5.46	0.83	3.49	1.39	2.2-3.4	0.41
Na ₂ O	0.48	0.31	5.62	0.14	1.41	0.2-1.3	0.64
BaO	0.53	-	-	-	-	-	0.04
H ₂ O	7.10	-	-	-	-	-	0.6
TiO ₂	-	-	0.17	-	0.17	0.1-0.3	-
SO ₃	-	-	0.22	-	-	-	-
Others	-	-	11.43	-	-	-	-
Si/Al		5.37	3.68,	5.56		4.8-5.4	

a*(Caliskan, 2012), b*(Ozdamar, 2012), c*(Coruh et al., 2010), d* (Alver et al., 2010), e*(Kljajic et al, 2011), f*(Rehakova et al., 2004), g*(Pestell,2014)

6. Insecticidal potential, mode of action and use as pesticides

The efficacy of zeolites and other inert dusts is substantially affected by three major aspects, environmental conditions, species of insects, and structure of the dust. Environmental conditions are temperature, humidity of air and substrate, exposition time, retention of dust on kernels, grain temperature and moisture, condition of stored-product (cracked grain, flour, whole grain) and method of treatment (Fields and Korunic, 2000; Subramanyum and Roesli, 2000; Arthur, 2001; Fields et al., 2003; Athanassiou et al., 2005; Kljajic et al., 2010a). Furthermore, the developmental stage of the insects, size (greater surface area to volume ratio), softness of wax layers, hairyness, susceptibility and physical mobility are also factors which influence the use of inert dusts in stored-products (Korunic, 1998; Subramanyum and Roesli, 2000; Field and Korunic, 2000; Arthur 2001; Fields et al., 2003; Athanassiou et al., 2005; Athanassiou et al, 2007; Kljajic et al., 2010a,b). The dust properties molecular structure, content of silicium dioxide, shape and size of particles, Al/Si ratios, sorption ability and geographical original also affect the insecticidal potential (Korunic, 1992, 1998, Kljajic et al., 2009b, Subramanyum and Roesli, 2000, Vayias et al., 2009).

The action of inert dust is through five pathways; spiracle blocking and asphyxiation, abrasion of cuticle and water loss, binding of water from the cuticle, ingestion of the dust particles, absorption of epicuticular lipids, and desiccation (Subramanyam and Roesli, 2000, Kljajic et al., 2011). Several researchers showed weight loss of insects exposed to inert dusts (Subramanyam and Roesli, 2000).

Physical control methods of beetles infesting stored cereals was studied in Milan, Italy (Pezzutti et al., 1979). Experiments of *R. dominica* (F.) on wheat, *S. oryzae* (L.) on maize and *O. surinamensis* (L.) on rice were carried out in normal and dry conditions. Atmospheric drying with silica gel caused death of all stages of the three species in 70, 128 and 139 days, respectively. The adults of *R. dominica* and *O. surinamensis* showed more tolerance than the immature stages, and the adults of *S. oryzae* were less tolerant. The experiments with other adsorbents including zeolite were conducted against *O. surinamensis* only and killed all stages within 98 days. Germinating ability of the grains and quality of flours was improved as well (Pezzutti et al., 1979). Natural zeolite applications were also effective on maize weevil *Sitophilus zeamais* (Haryadi et al., 1994).

Natural zeolite formulations originating from Serbia (Minazel Plus and Minazel) and the DE formulation (Protect-ItTM) were applied to wheat at selected rates under laboratory conditions for efficacy against *Sitophilus oryzae*, *Rhyzopertha dominica* and *Tribolium castaneum* (Kljajic 2010b). The highest adult mortality was observed after the longest exposure period of 21 days. Mortality of *S. Oryzae* was 97-100% and mortality of *T. Castaneum* was 94-100% for all zeolite dosages (0.25, 0.50, 0.75 g/kg). Progeny reduction of >90% was achieved after 21 days of contact for all test insects for DE applications and the highest rate of zeolite products for *S. oryzae* and *T. castaneum*. Therefore, these zeolite formulations were of comparable efficiency to DE formulations (Kljajic et al., 2010b).

Bentonite (Bosnia and Herzegovina), natural zeolite (Serbia), and DE (Belgrade, Serbia) formulations were investigated under laboratory conditions to test the insecticidal potential against *S. oryzae* and *T. castaneum* adults (Kljajic et al., 2011). Total mortality of *S. oryzae* was 100% for DE S-1 and DE S-2 dusts, while *T. castaneum* mortality was 94% and 91%, respectively. Total mortality of the natural zeolite Minazel in treated wheat was 86-89%, and Minazel Plus 53%. None of the bentonite treatments exceeded 15% efficacy rates (Kljajic et al., 2011). Insecticidal potential of natural zeolites (NZ natural zeolite, NZM natural zeolite modified) originating from Serbia were evaluated for progeny reduction (Andric, 2012). Progeny production with DE was at least 90%. While equivalent progeny reduction of natural zeolite formulation was achieved only for *T. castaneum* after highest rate.

The control of cigarette beetle, *Lasioderma serricornis* (F.) (Coleoptera: Anobiidae), in chickpea under laboratory conditions was evaluated by Perez et al. (2012). These natural treatments included one native South American flowering plant release peppery odour "Matico" which is *Piper aduncum* subsp. *ossanum* (Piperaceae) as PAO-1, PAO-2, zeolite and control in a completely randomized design with four replications (Perez et al., 2012). The highest mortality rates and reduction of adult emergence determined with PAO-2 (0.40 %) and secondly zeolite (15.97%). There were no significant differences regarding the germination of chickpea grains in any of the treatments (Perez et al., 2012).

Rock dusts treatment in organic agriculture has a long history. Clinoptilolite was investigated to control pollen beetle *Meligethes* spp. in organic and IPM oilseed rape fields in Switzerland (Daniel et al., 2013). Two or three clinoptilolite treatments reduced the number of pollen beetles by 50 to 80% in 2009 and 2010, though there was no reduction of pollen beetles under rainy weather conditions in 2008. Treated plots showed increased yield in 2010 under IPM conditions, flowering was visibly more intensive in all experimental years and control plots

had less infestation activity (Daniel et al., 2013). Clinoptilolite was evaluated for control of *T. confusum* on barley at selected rates under laboratory conditions. Physical control of bed bugs, *Cimex lectularius* Linnaeus (Hemiptera: Cimicidae) using natural zeolite was reported by Gota et al. (2012). *Aedes aegypti* is a major vector of the casual agents of dengue and dengue hemorrhagic fever, and vector control through larvicides is the main approach to disease control. New formulations of zeolite granules of temephos ZG(1%) were compared with *Bacillus thuringiensis* var. *israelensis* (5%, VectoBac tablets) and temephos sand granules SG (1%). Results showed excellent control with the Bti for 90 days and significant control of 100% for more than six months with temephos ZG and temephos SG (Mulla et al., 2004). Clinoptilolite from Georgia was evaluated to protect *Bacillus thuringiensis* from UV radiation and slowed inactivation time and increased the quality (Kvachantiradze et al., 1999).

7. Toxicity and health

Inert dusts have many advantages and disadvantages over synthetic insecticides. Their low mammalian toxicity, slow and environmental friendly action, and their affordability are considered great advantages for IPM and organic agriculture. (Kljajic et al., 2011). Codex Alimentarius Commission (1999) recommends Zeolite under "Silicates, clay, sodium silicate" to control of insect pests in food communities and lists as permitted substances for plant pest and disease control. After this classification new evaluations were conducted (Bodroza-Solarov et al., 2011). According to the FDA, GRAS Substances (SCOGS, 1979) do not pose a hazard to public. Silicon compounds under this listing consumed as direct food ingredient, food packaging, and filter aids (SCOGS, 1979). Naturally occurring zeolites occur worldwide and exposures may occur during the mining, production and use of zeolites. But, there were no human carcinogenicity effects in a study by IARC (1987, 1997ab). Clinoptilolite is a safe food additive (EFSA, 2013ab).

8. Conclusion

Zeolites are comparable in toxicity to DE and have potential for use in stored-product protection. They are non-toxic (IARC, 1997) and safe for human consumption (FDA GRAS Listings, 2006). The Codex Alimentarius Commission (1999) recommends Zeolites as permitted substances to control of plant pest and diseases in food commodities. Turkey has abundant reserves of clinoptilolite therefore future studies of the potential of clinoptilolite alone or combined with other entomopathogenic agents is strongly recommended.

Acknowledgement

I gratefully acknowledge the financial support of the Turkish Scientific and Technological Research Council (TUBITAK) Science Fellowships and Grant Programme Departments (BIDEB), and their precious critique and proofreading of Mevlut Emekci and Ahmet Guray Ferizli, Ankara University, Turkey without which the present study could have been completed.

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