Preliminary Checking of Some Turkish Diatomaceous Earth Similarities with Commercial Diatomaceous Earths under Scanning Electron Microscope (SEM)

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Diatoms are dead bodies of unicellular algae's and made up of fossilized diatoms in aquatic ecosystems. Diatomaceous earth (DE) is a dust varying in color depending on composition, from white-grey to yellow to red and active ingredient is amorphous silicon dioxide. DEs are commonly used for purification of water, the purification of juices, separation of various oils and chemicals and also used as an insecticide. Mode of action as insecticide which damage occurs to the insects protective wax coat on the cuticle, mostly by sorption and to a lesser degree by abrasion, or both. The result is the loss of water from the insect's body through desiccation resulting in death. The efficacy of DE against insects depends on different physical and morphological characteristics of the diatoms. In present study, image properties of 10 different Turkish DE samples under Scanning Electron Microscope (SEM) were checked and compared similarities with commercial DEs, namely Protector, SilicoSec, Insecto and Pyrisec. SEM image analysis indicated that there were variations in shape and size of dead bodies of diatoms in Turkish and commercial DEs. The shapes of dead bodies of diatoms in Turkish local DE's named as CBN and BGN were found very similar with those in commercial DE, Silicosec. Local DE coded as DC has a round shape and looks similar to commercial DE of Pyrisec while local DE coded as CAN has triangle shape and its shape was different from those of all other DE samples.

Keywords: Turkish Diatomaceous earth, SEM, Diatom, composition, insecticide

Introduction

Diatomaceous earth is the naturally occurring fossilized remains of diatoms. When diatomite is crushed into a powder, it is usually called "diatomaceous earth," or abbreviated DE (Calvert, 1930). Diatoms are single-celled aquatic algae. They belong to the class of golden brown algae known as Bacillariophyceae. Diatomite is a near pure sedimentary deposit consisting almost entirely of silica. The properties which make diatomite valuable include low density, high porosity, high surface area, abrasiveness, insulating properties, inertness, absorptive capacity, brightness, and high silica content. Diatomite has a wide variety of uses, and is a component in hundreds of products or vital to the manufacturing process of thousands more.

The most important use relative of high-quality diatomite is as a filtering media. The naturally occurring fossilized remains of diatoms have innate filtering characteristics due to their unique honeycomb structure. Their filtering qualities are used in beer and wine making, pharmaceutical manufacturing, motor oil processing, and to filter swimming pool water. For almost 100 years diatomite has been the workhorse of food and beverage processing. Almost every shelf in the grocery store contains a product which has been filtered by diatomite.

In paints, diatomite alters glass and sheen, extends primary pigments, adds bulk and strength, controls permeability and enhances coating adhesion. In plastics, diatomite serves as an antiblocking agent which helps in the separation of plastic parts in manufacturing, and in the separation of plastic bags by the consumer. Due to such characteristics as porosity and high surface area, diatomite is highly absorbent and is very useful in the clean-up of spills in the automotive, industrial, janitorial and waste remediation industries. When diatomite is incorporated into soil, it serves to reduce compaction, and increase water and air permeation. It also increases plant available water, firms soggy soils, loosens hard to work soils, provides better drainage, aids in nutrient transfer, and improves root growth. In such applications as golf courses, and other landscaped areas it helps absorb and hold water, reducing the amount of water used.

As natural insecticide when insects come in contact with diatomaceous earth, it absorbs their protective wax coating and their shells are damaged by the glassy diatoms. This combination causes them to die by dehydration. There is no survival and no built-up immunity as there is with chemical insecticides. Also, it does not break down as chemicals do.

Currently, the control of stored product pests in durable stored food products, such as grains and legumes, is based on the use of chemical methods such as fumigants and residual insecticides. However, the use of these substances is directly related with toxic residues on the final product, as well as serious environmental hazards. These factors, along with the consumers' demand for residue-free food and the development of resistance by several insect pests, have made essential the evaluation of alternative, low-risk and environmentally-friendly control methods. One of the most promising alternatives over the use of traditional pesticides in durable stored products is the use of diatomaceous earths (DEs). DEs are composed by the fossil skeletons of phytoplankton's, which occur in fresh and salt water since the Eocene period and produce a soft sedimentary rock, which is composed mainly by amorphous silica (SiO_2 + H_2O). The DEs currently mined vary remarkably in their insecticidal activity, depending upon species composition, geological and geographical origin as well as certain chemical characteristics, such as SiO_2 content, pH and tapped density (Korunic, 1997).

DEs act in the insects' exoskeleton (cuticle) causing rapid desiccation resulting in death through water loss. They are non-toxic to mammals (rat oral LD_{50}>5000 mg/kg of body weight), leave no toxic residues on the product and according to the US EPA they are classified in the category of GRAS (Generally Recognized As Safe) since they are used as food or feed additives (FDA, 1995). Regarding their insecticidal use, DEs can be applied with the same application technology with traditional grain protectants, which means that no specialized equipment is required (Athanassiou et al. 2005). Moreover, since they are inert (silicaceous) materials, no interaction with the environment occurs. Thus, DEs persist in the treated substrate, providing a long-term protection against pests, which is currently a 'red flag' for the use of conventional pesticides. The efficacy of DE from different sources (mines) on insects is not the same (Snetsinger, 1988; Katz, 1991; McLaughlin, 1994). DE from salt water is more common, cheaper and supposedly less efficacious as an insecticide (Snetsinger, 1988). However, efficacy of DE against insects depends on different physical and morphological characteristics of the diatoms rather than on its origin (Korunic,1998).

The mining and processing of natural diatomite is delicate and complicated. It requires large processing facilities but minimize to costs, diatomite is usually mined in open-pit, surface mines. In surface mining, a considerable thickness of earth, known as overburden, may have to be removed. Once this layer is removed and the purest of the diatomite strata is exposed, it is then cut from the bed with powerful scrapers and stockpiled. Diatomite does not need to be blasted as it is a soft, friable ore. The stockpiled material is then hauled to the processing plant for crushing, drying, milling and often calcining. Going into the crusher, the pieces may be as large as a small car, but coming out they will be the size of a pea. At this point the ore will still contain moisture. In order to dry the ore, significant amounts of heat must be applied in flash dryers. The ore is then milled gently to preserve the structure. It is critical that the ore be completely pure. A small amount of foreign matter can greatly downgrade the materials performance. These impurities are removed via a series of separators and traps. Finally, the material is classified, packaged and sent to customers. (Anonymous, 2017a). Several DEs, based on natural deposits, are now commercially available, and have proved very effective against stored grain pests (Subramanyam and Roesli, 2000, Athanassiou et al., 2011). Some of the formulation names presently available as insecticides on the market are:, Bug Resistor, Crop Guard, DE Insect Killer, Dicalite, Diacide, Diasecticide, Diatom Dust, Diatomic Earth, Dryacide, Pyrisec, Insecto and Silicosec.

Based on the first evidence and preliminary samplings, it seems that Turkey is considered to have rich natural DE deposits, and there is clear evidence for the existence of large DE deposits at some areas of Turkey (Özbey and Atamer, 1987; Mete, 1988; Sıvacı and Dere, 2006; Çetin and Taş, 2012). Diatomite reserve of Turkey is approximately 125 million tons. The largest diatomite reserve (106 million tons) known in Turkey is Hırka (Kayseri) (Çetin and Taş, 2012). However, there is no local DEs commercially available in Turkey for usagainst stored grain insects.

In this study, 10 different Turkish and 4 commercial DE samples were scanned under Scanning Electron Microscope (SEM) to examine their image properties and compare their similarities.

Materials and Methods

Local diatomaceous earth formulations: Ten local diatomaceous earth samples (coded as BCN, BGN, BHN, CAN, CBN, DC, DN, FBN, GBN, NN)collected from different locations of Turkey and four commercial DE samples (namely Protector, Pyrisec, Insecto, Silicosec) were selected for scanning electron microscopy (SEM) analysis. Local diatomaceous earth samples were mostly collected from DE reserves located at middle Anatolia of Turkey and commercial DEs were provided from agricultural market.

Scanning electron microscopy (SEM): A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition (Anonymous, 2017b). Some physical properties of Turkish diatomaceous earth formulations and commercial diatomaceous earths were examined under Stereozoom electron microscope (SEM) at 5000x to 20000x magnification. Tiny DE rock samples were prepared to withstand the vacuum conditions and high energy beam of electrons, and size fits on the specimen stage. Samples were mounted rigidly to a specimen holder using a conductive adhesive. Afterwards DE samples were scanned under SEM at Namık Kemal University Central Laboratory (NABILTEM).

Results and Disscussion

Alternative methods are being emphasized to reduce the use of insecticides to reduce human exposure and to decrease the development of insecticide resistance. Diatomaceous earths (DEs) are among the most promising alternatives to chemical insecticides and fumigants, because they have low mammalian toxicity, do not break down rapidly, and do not affect grain end-use quality (Korunic et al., 1996).

Diatomaceous earth (DE) is a dust varying in color from white, grey and yellow to red. Dust is formed from fossilized diatoms, single-celled algae of various shapes and sizes which are composed almost entirely of amorphous silicon dioxide. The cell walls of diatoms are known as frustules. Diatom frustules are highly ornamented, forming an amazing range of forms. The shapes of the diatom frustule are species specific. The frustules have a broad variety of delicate, lacy, perforated shapes, including rods, disks, feathers, ladders, needles, and spheres (Raound et al.,1990; Bhishma et al.,2017). Diatoms are usually classified in to two main groups based on the symmetry of their frustules, namely, Centric Diatoms and Pennate Diatoms. Centric Diatoms are radially symmetrical, while Pennate Diatoms are elongated and generally have parallel striae (furrows or rows of holes in the silica) arranged normal to the long axis (Parkinson and Gordon,1992). Commercial DEs such as Protector and Pyrisec have radially symmetrical while Insecto and Silicosec have rod shape cell wall (Figure 1).

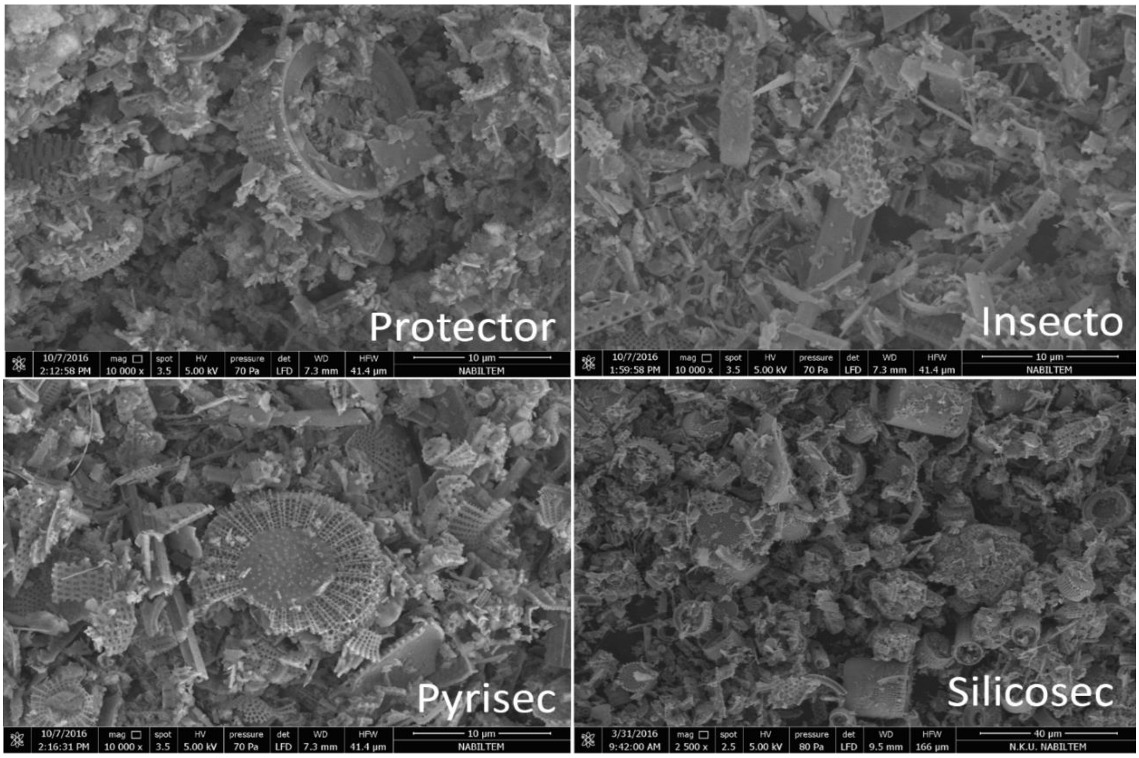

Figure 1. Scanning electron microscope images of fossilized bodies of different shapes of commercial diatomaceous earths.

The dust base of DEs is made of the dead bodies of diatoms in various shapes and size (Korunic,1998) SEM image analysis indicated that there were variations in shape and size of dead bodies of diatoms in Turkish DEs.The shapes of Turkish local DEs coded as CBN and BGN, collected from Middle Anatolia were found very similar to that of commercial DE of Silicosec. Local DE coded as DC has a round shape and looks similar to commercial DE of Pyrisec. Local De coded as CAN has triangle shape and its shape was tottaly different from those of all other DE samples (Figure 2).

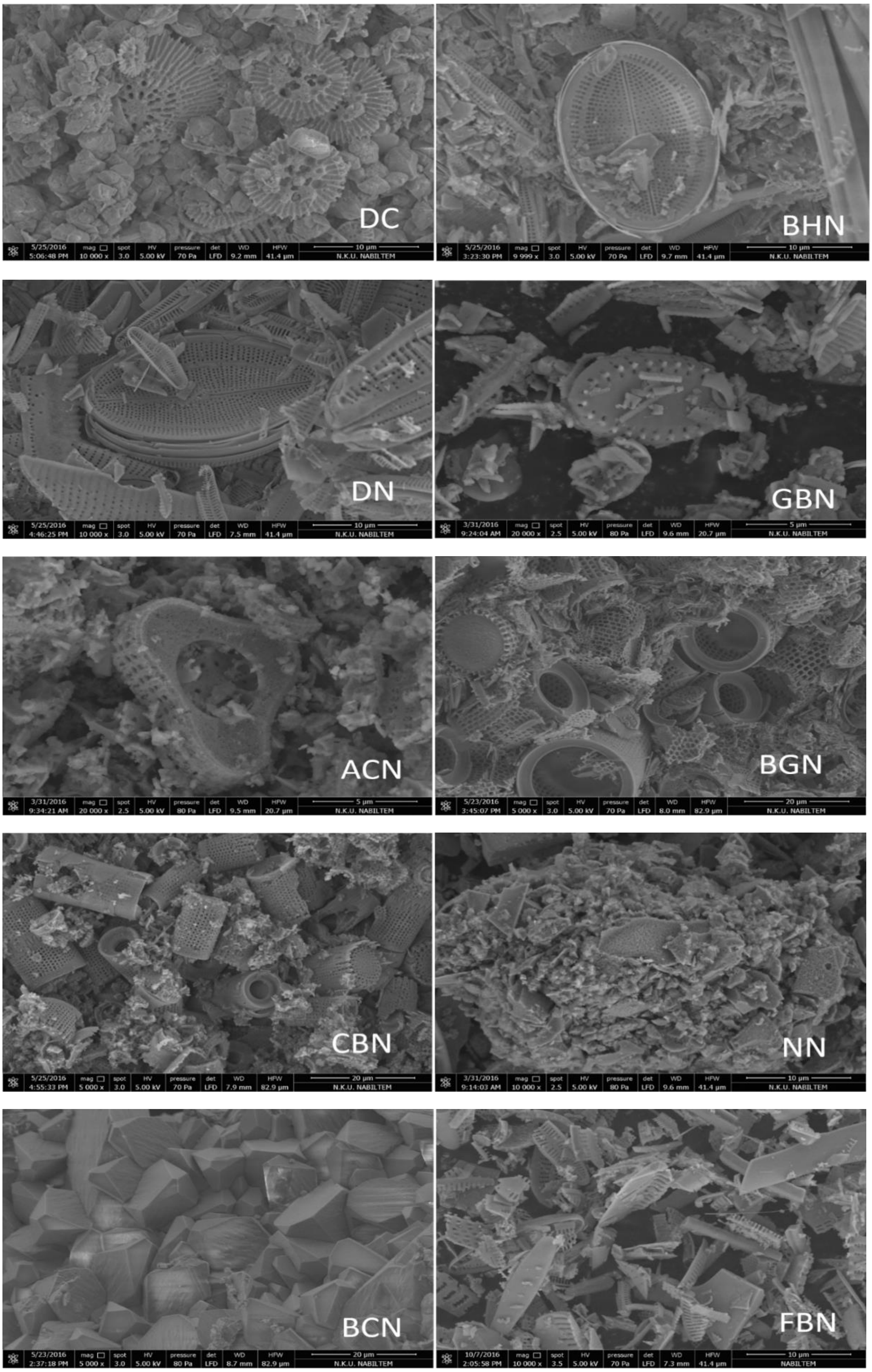

Figure 2. Scanning electron microscope images of fossilized bodies of different shapes of Turkish diatomaceous earths.

In conclusion, this preliminary SEM study indicated there were variations in shape and size of dead bodies of diatoms in Turkish and commercial DEs. While some Turkish DEs had similar shape with commercial DEs, some of them had different shape with commercial ones. Although a few studies have been published (Doğanay et al,2014; Işıkber et al. 2015; 2016; Ertürk, 2014), there is a limited data on efficacy of Turkish diatomaceous earths deposit against stored product pests in the literature. These similarities and differences between Turkish and commercial DEs can provide information on efficacy of Turkish diatomaceous earths deposit against stored product pests. Therefore, further studies are required to clarify interaction or relationship between their shape and size and biological efficacy of DEs against stored product insect pests.

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References

Anonymous, 2017a. Diatomite Mining and Processing,http://diatomite.org/Diatomite-Mining-and-Processing.IDPA, International diatomite producers association. (Accessed date: 05.05.2017).

Anonymous, 2017b. Scanning Electron Microscopy (SEM). https://en.wikipedia.org/wiki/Scanningelectronmicroscope (Accessed date: 05.05.2017).

Athanassiou, C.G., B.J. Vayias, C.B. Dimizas, N.G. Kavallieratos, A.S. Papagregoriou and C.Th. Buchelos, 2005. Insecticidal efficacy of diatomaceous earth against *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae) and *Tribolium confusum* du Val (Coleoptera: Tenebrionidae) on stored wheat: influence of dose rate, temperature and exposure interval. Journal of Stored Products Research, : 41- 47.

Athanassiou, C.G., N.G. Kavallieratos, B.J. Vayias, Z. TomanoviC, A. Petrovic, V. Rozman, C. Adler, Z. Korunic and D. Milovanovic, 2011. Laboratory evaluation of diatomaceous earth deposits mined from several locations in central and southeastern Europe as potential protectants against coleopteran grain pests. Crop protection 30: 329-339.

Bhishma, R.S., S.H. Alavi, S.P. Harimkar, M. McCollum, J.F. Donoghue and F.D. Blum, 2017. Particle morphology dependent superhydrophobicity in treated diatomaceous earth/ polystyrene coatings, Applied Surface Science 416:947–956.

Calvert, R. 1930. Diatomaceous earth Journal of Chemical Education, 7: 28-29.

Çetin, M. and B. Taş, 2012. Biyolojik orjinli tek mineral: Diyatomit. Türk Bilim Araştırma Vakfı (TÜBAV) Bilim Dergisi, 5(2): 28-46.

Parkinson, J. and R. Gordon, 1999. Beyond micromachining: the potential of diatoms. Trends Biotechnology, 17:190–196.

Round, F., R. Crawford and D. Mann, 1990. The Diatoms: Biology and Morphology of the Genera, Cambridge University Press, UK.

Katz, H. 1991. Desiccants: dry as dust means insect's death. Pest Control Technology, 82-84.

Korunic, Z., P.G. Fields, M.I.P. Kovacs, J.S. Noll, O.M. Lukow, C.J. Demianyk and K.J. Shibley, 1996. The effect of diatomaceous earth on grain quality. Postharvest Biology and Technology, 9(3): 373-387.

Korunic, Z. 1997. Rapid assessment of the insecticidal value of diatomaceous earths without conducting bioassays. Journal of Stored Products Research, 33, 219-229.

Korunic, Z. 1998. Diatomaceous earths, a group of natural insecticides. Journal of Stored Products Research, 34: 87–97.

Doğanay, İ.Ş. , A.A. Işıkber, Ö. Sağlam and Y. Bilgili, 2014. Efficiency of some Turkish diatomaceous earth deposits against stored-grain insects, *Sitophilus granarius* (L.) and *Rhyzopertha dominica* (F.). International Conference on Biopesticide (ICOP 7), p.91.

Ertürk, S. 2014. Farklı diyatom toprağı formülasyonlarının depolanmış çeltikte zararlı böceklere etkinliği üzerinde araştırmalar. Ankara Üniversitesi, Fen bilimleri Enstitüsü, Bitki Koruma Anabilim Dalı, Doktora Tezi, s.120.

FDA (Food and Drug Administration, USA), 1995. Specifications for diatomaceous earths as a maximum 2 % animal feed additive. 21 CFR Section, 573.340.

Işıkber, A.A., Ö. Sağlam, M.K. Er and H. Tunaz, 2016. Potential of Turkish diatomaceous earth formulations as natural grain protectants for control of stored grain insects. 15th International Cereal and Bread Congress, p.42.

Işıkber, A.A., Ö. Sağlam, M.K. Er, H. Tunaz and R. Şen, 2015. Toxicity of Turkish diatomaceous earth deposits against some stored-grain insects on wheat. 10th Conference of IOBC/WPRS Working Group "Integrated Protection of Stored Products" Congress, p.29.

McLaughlin, A. 1994. Laboratory trials on desiccant dust insecticides. 6th InternationalWorking Conference on Stored-Product Protection. CAB, Wallingford, Canberra, Australia, pp. 638–645.

Mete, Z. 1998. Kütahya-Alayunt Yöresi Diyatomit Yataklarının Zenginleştirilmesi, Akdeniz Üniversitesi Isparta. Mühendislik Fakültesi Dergisi, 184-201.

Özbey, G. and N. Atamer, 1987. Kizelgur (Diatomit) hakkında bazı bilgiler. 10. Türkiye Madencilik Bilimsel Teknik Kongresi, Ankara, s.493-502.

Round, F., R. Crawford and D. Mann, 1990. The Diatoms: Biology and Morphology of the Genera, Cambridge University Press, UK.

Sıvacı, R. and Ş. Dere, 2006. Melendiz Çayı'nın (Aksaray-Ihlara) Epipelik Diyatome Florasının Mevsimsel Değişimi. C.Ü. Fen-Edebiyat Fakültesi Fen Bilimleri Dergisi, 27(1): 1-12.

Snetsinger, R. 1988. Report on Shellshock insecticide. Report of Department of Entomology, Pennsylvania State University, pp. 1–7.

Subramanyam, B. and R. Roesli, 2000. Inert dust. In Subramanyam Bh, Hagstrum, D.W. (Eds), Alternatives to Pesticides in Stored - Product IPM. Kluwer Academic Publishers, Boston, MA: p.321-379.