PARTICULATE MATTER POLLUTION EFFECTS ON THE INORGANIC CONSTITUENTS OF FRESH AND PROCESSED TABLE OLIVES

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Abstract

Pollution from various sources such as cement kiln factories and unpaved farm roads results in particulate matter accumulation on olive leaves of trees growing in dry climates near the pollution sources. This particulate matter may affect among others the inorganic composition of the fruits including accumulation of heavy metals. We studied the effects of cement kiln dust and soil dust on fresh and processed table olive fruit inorganic element composition. Mature 'Konservolea' olive trees were dusted periodically with cement kiln dust or finely ground heavy clay soil from June to before September rains in 2009. Green olives were harvested early October, washed thoroughly with tap water, dried and stored until inorganic element analysis. Other olives were washed and processed with the Spanish method and canned in brine until analysis. Inorganic elements were expressed on edible fruit fresh weight basis. Dusts accumulated until late August due to repeated applications and lack of rain and were washed off in September (especially the soil) due to rainfall events. In raw olives, P, K, Ca, Mg, Fe, Mn, Zn, Cu and Pb content was not affected by the presence of either dust used and Ni, Co, and Cr were very low and not detected. The presence of soil dust on raw olives resulted in increased Na and Cd. The presence of cement dust on raw olives resulted in increased Na. Processed olives had significantly modified inorganic element composition besides the 1000 fold increase in Na content. Canned olives from the soil dust treatment had similar Ca, Mn, Zn, Cd, Co and Na, increased Pb and decreased P, K, Mg, Fe, Cu and Ni content compared to control olives. Canned olives from the cement dust treatment had similar Ca, Mg, Fe, Mn, Cu and Zn, increased Na, Cd, Co and Pb and decreased P, K and Ni content compared to control olives. Thus, soil or cement dust contamination during olive fruit growth does not affect the mineral composition of the fresh, but significantly affects the inorganic composition of the Spanish-style processed edible product.

Keywords: *Olea europaea*, Soil dust, Cement kiln dust, Mineral composition

Introduction

Olives are extensively cultivated around the Mediterranean basin, where summer rain events are rare. This lack of soil humidity results in widespread soil structure disintegration in very small soil particles, wherever soil is disturbed, and in almost no weed growth. This loose soil consequently can easily be transferred on plants by the wind. All other contamination sources can, in the same manner, transfer particulate matter on the soil and the growing plants, leaves and fruits and exert physical or chemical effects or both, but mainly it will act through the soil (Farmer, 1993). The toxicity of particulate contaminants on vegetation is associated with their accumulated quantity, and their acidity, metal content, surfactant properties or salinity. On the other hand, many inorganic elements found in particulate matter are plant nutrients, which can improve plant nutrition and health, if absorbed by the plants. Actually, most contaminants may enter the plant through the root system as, in the contaminated areas and with short-lived plants, the soil is the major contaminant bank supplying nutrients or toxic heavy metals. Although a number of reports have been published on forest species or short-lived crop plants, there is almost no work on fruit tree species and the related contamination of their edible parts.

The raw materials used to manufacture Portland cement consist of clinker, volcanic rock, and hydrate gypsum, which are rich in Ca, Al, Si, Fe, Mg (Taylor, 1997), but also contain Mn, Cu, Zn, Ni, Pb, Co, Cr, Cd and other trace elements. In conifer forest near cement kiln factory, cement dust caused alkalization of soil and the alkaline dust deposited on trees altered the availability of several nutrients, causing serious deviations in the mineral composition of trees (Mandre et al., 1999; Mandre, 2002). This latter alkalization is due to calcium hydroxide; which after hydration, may raise leaf surface alkalinity up to pH 12 (Grantz et al., 2003). There must be no published work of cement kiln dust contamination effects on the inorganic composition of tree fruit species and their edible parts.

Road dust may also contain significant concentrations of inorganic elements and may produce alkaline dusts (Farmer, 1993). Samples of *Citrus aurantium* fruits from trees growing in cities were analyzed for metal concentrations (Oliva and Valdés, 2003; Oliva et al., 2008). It was found that the fruits did not retain high concentrations of heavy metals, except for Ba, Cd and Zn, which were found mainly in epicarp. On the other hand, olive fruits harvested from trees next to busy paved roads and industrial areas had highly increased Pb, Cd, Fe, Cu and Zn concentrations (Sahan and Basoglu, 2009). These reports and some others on crop plants are mainly related to city road and anthropogenic pollution sources contamination. But there is almost no work on rural unpaved road dust contamination on cultivated trees.

Most inorganic plant constituents are useful nutrients to humans and are positively related to human health. But the consumption of food products containing high amounts of heavy metals, including the toxic As, Cd, Pb and Hg, is known to negatively affect human health. The above inorganic elements can be present in food naturally, but mainly as a result of human activities (e.g., agricultural practices, industrial emissions, car exhausts), from contamination during processing and storage, or by direct addition.

Table olives are products with significant nutritional value and are important components of the Mediterranean diet. Their world consumption is increasing due to their benefits to human health (Peres et al., 2011). Processing of olives almost always involves the addition of sea salt among others to remove bitterness and preserve the processed fruit. This process may produce some changes in the mineral composition of the processed fruits (López et al., 2008). The consumption of particulate matter polluted olives could threaten human health, published information is lacking and, thus, it needs to be investigated.

We studied the effects of cement kiln dust or soil dust foliar contamination during fruit growth on the inorganic elements composition of fresh green table olives and Spanish-style processed olives as it relates to human health.

Materials and Methods

The experiment was carried out in a drip irrigated grove with mature olive trees (*Olea europaea* L. cv. Konservolea). Olive trees were selected for uniformity and age and dusted periodically with cement kiln dust (CE), or with finely ground (particle size <500 μm) heavy clay soil dust (S), while others remained uncontaminated (control, C). The duration of the experiment was from June to before September rains in 2009. To quantify particulate matter contamination, olive leaves were periodically sampled and the dust was carefully removed and weighed. The leaf surface was measured using a scanner and the dust was expressed as g per m^2 of leaf surface.

Fresh green olives were harvested from all sides of canopy early October. The fruit were initially washed thoroughly with tap water. After washing, the pit was removed and the edible part of the fruit was dried in a force-air drying chamber at 70 ^oC until constant weight. For the inorganic element analysis we used ten fruit per replication and three replications per treatment. Other olives were washed with tap water and processed with the Spanish style method. For each treatment we prepared two glass jars with metal lid and 30 fruit per jar (no corrosion on the lid was obvious at the end of the storage period before analysis). For processed fruit analysis, the brine was removed and the edible part of the processed olives was dried as described above. Two replications per jar were analyzed. Fruit water content in fresh and processed olives was determined by the difference in weight of the fresh and dried samples.

The dried samples were finely ground and 2 g were placed in crucible porcelain and were ashed in a Carbolite muffle furnace at 480 ^oC for 4 h. For the determination of the inorganic elements concentrations, the ashed samples were digested with concentrated HNO_3 (Papafilippaki and Stavroulakis, 2009). The concentrations of Mg, Mn, Fe, Cu, Zn, Ni, Pb, Cd, Cr, Co were measured using an Atomic Absorption Spectrometer with flame atomization (Analyst 700, Perkin Elmer). The concentrations of mineral elements K, Na and Ca were determined by flame photometer (Model 410, Sherwood). The concentration of P was determined spectrophotometrically with the ammonium vanadate-ammonium molybdate method. Inorganic elements were expressed on fruit fresh weight (edible part) basis.

Results and Discussion

Dust concentration on leaves

Dusts accumulated from the first application in June until late August due to repeated applications and lack of rain. The soil dust (S) was almost completely washed off in September due to rainfall events, while almost half of cement kiln dust (CE) remained (Fig. 1). Cement kiln dust formed a hard crystalline crust on the leaf surface, which was difficult to be removed with rainfall.

Inorganic elements concentrations in fresh green table olives

In raw olives, K concentration was the highest, followed by Ca, P, Mg and Na in all treatments (Table 1). From the minor elements, Fe concentration was highest, followed by Zn, Pb, Cu, Mn and Cd in all treatments (Table 1). Results are similar with those reported by Nergiz and Engez (2000) except of Pb and Cd.

In raw olives, P, K, Ca, Mg, Fe, Mn, Zn, Cu and Pb content was not affected by the presence of either dust used and Ni, Co and Cr were very low and not detected. The presence of soil dust on raw olives resulted in increased Na by 84% and Cd by 10%. The presence of cement dust on raw olives resulted in increased Na by 97% and did not affect Cd content (Table 1). Thus, it seems that the presence of any dust on fruit surface of fresh olives during the summer period did not result in the accumulation of the inorganic elements of the pollutants in the fruit except Na and kept them in safe for human health levels (López-López et al., 2008). Only Cd concentration was slightly above the permitted safe limits (López-López et al., 2008) in all treatments and especially in dusted fresh olives. The increased Na concentration in fresh olives compared to control olives is probably related to cement or soil dust composition, but could also be due to the saline water irrigation.

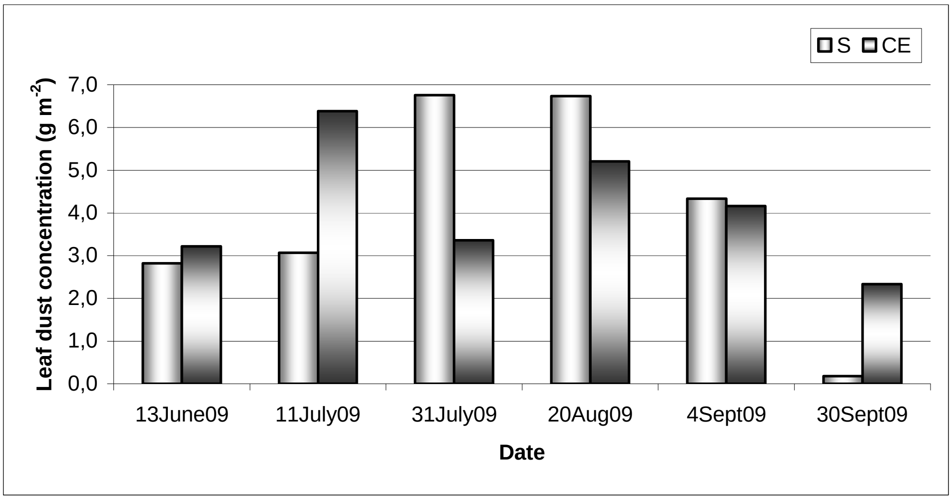

Fig. 1. Leaf dust concentration from June to September 2009 on 'Konservolea' olive leaves expressed as g of dust per m^2 of leaf surface.

Table 1. Mean values (±standard deviation) of inorganic elements in the pericarp (flesh and skin) of fresh green table olives, expressed as mg kg^{-1} f.w., harvested from control (uncontaminated, C) or dusted with soil (S) or cement kiln dust (CE) 'Konservolea' olive trees.

	C (mg kg^{-1} f.w.)	S (mg kg^{-1} f.w.)	CE (mg kg^{-1} f.w.)
P	102.3 ± 15.0	95.7 ± 7.0	94.0 ± 6.6
K	2590 ± 244	2556 ± 290	2363 ± 287
Ca	250 ± 84	190 ± 65	230 ± 80
Mg	38.7 ± 5.00	44.2 ± 11. 6	38.4 ± 6.0
Fe	1.65 ± 0.53	1.38 ± 0.10	1.26 ± 0.23
Na	15.4 ± 6.1	28.3 ± 6.2	30.5 ± 5.0
Mn	0.13 ± 0.03	0.09 ± 0.03	0.10 ± 0.04
Zn	0.35 ± 0.17	0.29 ± 0.05	0.33 ± 0.07
Cu	0.14 ± 0.06	0.21 ± 0.06	0.11 ± 0.06
Pb	0.29 ± 0.08	0.34 ± 0.07	0.38 ± 0.06
Cd	0.067 ± 0.002	0.074 ± 0.003	0.071 ± 0.005
Ni	ND[a]	ND	ND
Co	ND	ND	ND
Cr	ND	ND	ND

[a] ND: Not Detected

<u>Inorganic elements concentrations in Spanish-style processed green table olives</u>

Processed olives had significantly modified inorganic element composition besides the 1000 fold increase in Na content compared to the fresh olives in all treatments (Table 2). This Na content increase is due to significant amounts of sea salt added during olive processing

K and P concentration decreased in processed olives compared to fresh fruit in all treatments. K is present mainly as ion in the cellular vacuoles and was progressively lost in brine during processing as it was substituted from Na. In addition, successive immersions in water partially remove K from olives (López et al., 2008). The P content in green fresh and brined olives is related to the completion of lactic acid fermentation (López et al., 2008), but its loss is difficult to explain as most P is present intercellularly as organic molecules.

Ca concentration in brined olives slightly increased in all treatments, even though it was not intentionally incorporated in brine. Actually, the sea salt and tap water used contained significant Ca amounts, which could be absorbed by the olives during processing. In general, olive flesh can absorb Ca and retain it even with washing treatments during processing and this increased Ca content is very effective in preventing processed olive softening (López et al., 2008).

Table 2. Mean values (±standard deviation) of inorganic elements in the pericarp of processed green table olives in brine, expressed as mg kg^{-1} f.w., harvested from control (uncontaminated, C) or dusted with soil (S) or cement kiln dust (CE) 'Konservolea' olive trees.

	C (mg kg^{-1} f.w.)	S (mg kg^{-1} f.w.)	CE (mg kg^{-1} f.w.)
P	67.6 ± 4.5	49.7 ± 11.0	57.0 ± 6.9
K	165.5 ± 22.5	71.0 ± 20.5	86.9 ± 0.0
Ca	391.4 ± 104.6	280.2 ± 104.4	481.1 ± 102.3
Mg	53.49 ± 4.81	36.10 ± 10.74	59.0 ± 14.0
Fe	2.13 ± 0.29	1.62 ± 0.20	1.84 ± 0.09
Na	23363 ± 2560	26738 ± 1248	28596 ± 708
Mn	0.25 ± 0.08	0.18 ± 0.01	0.27 ± 0.01
Zn	2.09 ± 1.14	1.46 ± 0.49	1.47 ± 0.19
Cu	0.84 ± 0.18	0.47 ± 0.15	0.65 ± 0.08
Pb	0.83 ± 0.04	0.91 ± 0.03	0.97 ± 0.04
Cd	0.11 ± 0.01	0.09 ± 0.05	0.13 ± 0.00
Ni	0.36 ± 0.03	0.30 ± 0.03	0.28 ± 0.01
Co	0.20 ± 0.03	0.22 ± 0.10	0.33 ± 0.02
Cr	ND[a]	ND	ND

[a] ND: Not Detected

Mg concentration increased in processed olives compared to fresh fruit in all treatments except canned olives from the soil dust treatment which did not differ from fresh olives. Mg content in olive fruit has increased by processing (López et al., 2008).

Fe increased in olives with processing only in the case of cement dust treatment. The presence of Fe in fresh and brined olives may cause fruit browning due to the formation of complexes with the olive polyphenols (López et al., 2008); but we found low concentrations in fresh and processed olives unable to cause detectable browning.

Mn, Cu, Zn and Cd concentrations also increased in processed olives compared to the fresh ones in all or most of the treatments.

Processed olives from the soil dust treatment had similar Ca, Mn, Zn, Cd, Co and Na, increased Pb by 9.6% and decreased P, K, Mg, Fe, Cu and Ni content (by 26.5%, 57.1%, 32.5%, 23.9%, 44.0% and 16.7%, respectively) compared to control olives (Table 2). Processed olives from the cement dust treatment had similar Ca, Mg, Fe, Mn, Cu and Zn, increased Na, Cd, Co and Pb (by 22.4%, 18.2%, 65.0% and 16.9%, respectively) and decreased P, K and Ni content (by 15.7%, 47.5% and 22.2%, respectively) compared to control olives (Table 2). Cr was not detected in any treatment.

The results show that the Spanish-style processing exacerbated the differences between the particulate matter treatments and the control. In particular, the concentrations of the toxic heavy metals Pb, Cd and Co increased with processing compared to fresh olives especially in the case of cement-dusted olives as Pb, Cd and Co are constituents of the cement dust. Cd content was above the permitted limit for human consumption. It is clear that the processing with NaOH *per se* or the added salt increased the levels of these metals as it has been proposed before (López-López et al., 2008).

In conclusion, the contamination with cement or soil dusts throughout the summer did not affect fresh green olive fruit inorganic element composition. On the opposite, with processing many changes occurred in inorganic element composition due to processing itself and due to the presence of dusts in the field, resulting in a few cases in unsafe products for human health.

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