Heavy metals in edible specimens around Tagarades landfill after a big fire.

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ABSTRACT: The aim of this study was to provide information on the levels of heavy metals (lead and cadmium) in edible specimens around the Tagarades landfill after a big fire.A total of 49 fruit, vegetable and milk samples were collected, according to the Directive 2001/22/EC. The sampling areas were: < 2.5, 2.5, 3, 4, 5, 6, 7, 8, 9 and 10 km around landfill, as well as, 35-40 km away which served as a blank area that was not affected by the landfill. Care was taken to get samples of the same varieties from different selected sites. The samples were wet digested using concentrated nitric and perchloric acid. Cadmium was analyzed using a Flame Atomic Spectrometer and lead an Atomic Absorption Spectrophotometry with graphite furnace atomization. Our results indicate that there was no apparent effect from the landfill fire on lead and cadmium levels found in the tested food samples. These specimens were safe for consumption according to the Draft Commission Regulation on Setting Maximum Limits for Certain Contaminants in Foodstuffs.

Key Words: Heavy metals, Landfill, Atomic absorption analysis.

INTRODUCTION

Environmental pollution from heavy metals has been established as an ubiquitous problem throughout the world, due to the negative effects of heavy metal toxicity on human health and the growing concerns by the general public[1-3]. Toxic metals, such as lead, mercury, cadmium, arsenic etc. enter the human body by different routes and in different chemical forms.

It has been proven that there is an interrelationship between the contents of trace elements in soil, water, plants and air[1]. Soils can be contaminated by heavy metals as a result of industrial activities e.g. mining, vehicle emission, landfilling of waste etc.

Landfill design and location is such as to minimize impacts to the environment and ensure minimum contamination of the surrounding area from the waste degradation[4]. In many cases, liners are installed to prevent the migration of leachate to the surrounding environment. Municipal solid waste (MSW) landfill leachate contains a number of aquatic pollutants; a specific MSW stream often referred to as household hazardous waste, can be considered as a contributor of a large proportion of these pollutants. Great emphasis is given in assessing the environmental consequences of leachate release from a generic MSW landfill, since heavy metals and organic pollutants were found to migrate into the zones beneath a model landfill site over a 20,000-year period[5].

Landfill fires can be extremely hazardous for the environment since they lead to contamination of soil, water and air by toxic pollutants. Although landfill fires are common in Northern European countries, their effects have gone largely ignored by the scientific community. Despite the ease with which landfill fires can occur, the consequences for the environment and human health have yet to be investigated extensively and thus still remain poorly understood[10].

The present study provides data about the effect of Tagarades landfill fire on foodstuffs contamination by lead and cadmium. Such data can be helpful in making risk assessment and risk management information comprehensible to community groups, local elected

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officials, environmentalists etc. in order to assure food safety.

Determining traces of heavy metal ions in environmental samples and/or foods is restricted by two main factors: their very low concentration -which may be lower than the detection limit of many analytical techniques including atomic absorption spectrometry- and the interfering effects of the matrix[6].

Monitoring the distribution of heavy metals in soil, plants and food of animal origin, facilitates the estimation of the extent of foodstuffs contamination. The European Commission has proposed a Regulation which sets maximum limits for lead and cadmium in certain foodstuffs[7]. These maximum allowable limits result from newly found data in recent literature (epidemiological data etc.).

The aim of the present study was to determine the lead and cadmium levels in fruits, vegetables and milk samples taken at different sites around the Tagarades landfill two months after the big fire in July of 2006 and estimate the consequences the fire had on the levels of lead and cadmium in these food samples.

SAMPLING

Forty nine (49) food samples of fruits, vegetables and milk were collected during September of 2006, about two months after the fire (17-28 July 2006). Sampling was done according to the Directive 2001/22/EC.

The sampling areas were: less than 2.5, 2.5, 3, 4, 5, 6, 7, 8, 9 and 10 km around the landfill and about 35-40 km away, which was the blank area. For the analysis only the edible portions were included, whereas any bruised or rotten parts were removed. Care was taken to get samples of the same varieties from the selected areas, to the extent that it was possible, while samples from greenhouse cultivation were excluded. Vegetables and fruits samples were collected from different parts of the plantation, the size of about one half of an acre, were placed in appropriate bags and were air-dried. All samples were transported to the laboratory as soon as it was made possible.

SAMPLE PREPARATION

Five g of fruit/vegetable sample was mixed with equal volumes (total 15 ml) of concentrated nitric and perchloric acid into a beaker and kept overnight. Careful digestion of the sample took place on a hot plate. The digestion lasted as long as it was necessary in order to get a clear solution of approximately 2 ml volume, followed by cooling and addition of 2% v/v nitric acid solution, to a final volume of 10 ml.

30 g of milk were treated with the method mentioned above using 10 ml of concentrated nitric acid and 10 ml of concentrated perchloric acid for liquid digestion.

MATERIALS AND METHODS

Standards solutions of lead and cadmium were provided by Merck (Darmstadt, Germany). All chemicals used were of analytical grade. Analysis for cadmium was carried out using a flame atomic adsorption spectrometer (Varian, SpectrAA 300) and for lead an Atomic Absorption Spectrophotometer (Perkin Elmer, 460) with a High Graphite Atomizer system HGA - 2100.

VALIDATION OF THE ANALYTICAL METHOD

The instruments were calibrated using Pb, and Cd standards. Reagents blank determinations were used to correct the instrument readings. Blank biological specimens of fruits, vegetables and milk were processed according to the previously described procedure and analyzed as mentioned above. The analyzed biological specimens, with no detectable concentrations of Pb and Cd, were homogenized and spiked with various amounts of lead and cadmium standard solutions, and a recovery study was carried out. The recoveries of the spiked biological specimens were between 105% and 120%. The relative standard deviations were lower than 10%. The limits of detection (LOD) were 0.02 mg/kg for cadmium and 0.002 mg/kg for lead.

RESULTS AND DISCUSSION

The maximum allowable levels for Pb are: 0.02 mg/kg in cow milk, 0.1 mg/kg in vegetables, 0.3 mg/kg in foliar vegetables and 0.1 mg/kg in fruits[7]. For Cd the upper limits are: 0.05 mg/kg in vegetables and fruits and 0.2 mg/kg in folia vegetables. There are no specific guidelines or statutory limits for Cd in cow milk.

The results of lead and cadmium determination in fruits, vegetables and milk samples from various areas around the Tagarades landfill are listed in tables 1-4.

Table 1. Lead and cadmium levels in tested samples at a distance less than 2.5 km, 2.5 and 3 km away from landfill.

Edible Specimens	Sampling Points (km away from landfill)	Cd (mg/kg wet weight)	Pb (mg/kg wet weight)
Grapes	< 2.5	<LOD	<LOD
Olives	< 2.5	< LOD	0.006
Olives	< 2.5	< LOD	< LOD
Cow milk	< 2.5	< LOD	0.002
Goat milk	< 2.5	< LOD	0.02
Goat milk	< 2.5	< LOD	0.004
Cow milk	2.5	< LOD	< LOD
Goat milk	2.5	< LOD	0.014
Goat milk	3	< LOD	0.015
Goat milk	3	< LOD	0.015
Grapes	3	< LOD	< LOD

As shown, no trace of Cd was detected in all of the sampling points. Pb was detected in an olive sample, a cow milk sample and in all goat milk samples. Lead concentrations ranged from 0.002 mg/kg in the cow milk sample to 0.02 mg/kg in a goat milk sample. All concentrations found were below the maximum allowable limit (0.02 mg/kg). Only in one goat milk sample, lead concentration was found equal to the upper allowable limit.

Table 2. Lead and cadmium levels in tested samples at a distance of 4 km to 7 km from landfill.

Edible Specimens	Sampling Points (km-around landfill)	Cd (mg/kg wet weight)	Pb (mg/kg wet weight)
Olives	4	0.03	<LOD
Grapes	4	< LOD	< LOD
Olives	5	0.02	< LOD
Sheep's milk	5	< LOD	0.002
Goat milk	5	< LOD	< LOD
Goat milk	6	< LOD	< LOD
Apple	6	< LOD	< LOD
Watermelon	6	< LOD	< LOD
Grapes	7	< LOD	0.02
Melon	7	< LOD	0.05
Grapes	7	< LOD	0.02

Cd was found in two olive samples with 0.02 and 0.03 mg/kg Cd concentration values which are below the upper accepted limits in the selected area. Lead was not detected in olives, goat milk, apples and water melons, but was found in grapes, melon and sheep's milk. The determined lead concentrations were also below the maximum allowable limits.

Table 3. Lead and cadmium levels in tested samples at a distance of 7-9 km from Tagarades.

Edible Specimens	Sampling Points (km-around landfill)	Cd (mg/ kg wet weight)	Pb (mg/ kg wet weight)
Zucchini	7	< LOD	< LOD
Grapes	8	< LOD	< LOD
Lettuce	8	< LOD	0.05
Onion	8	< LOD	< LOD
Grapes	8	< LOD	< LOD
Pomegranate	8	< LOD	< LOD
Olives	8	0.04	< LOD
Tomato	8	< LOD	< LOD
Pepper	8	< LOD	< LOD
Aubergine (Eggplant)	8	0.02	< LOD
Melon	9	< LOD	0.09
Corn	9	< LOD	0.05
Aubergine (Eggplant)	9	0.02	< LOD
Pepper	9	< LOD	< LOD

Table 3 indicates that Cd was found in an olive sample and two aubergine samples and Pb in a melon, lettuce and corn samples. All these values were again below the allowable upper limits for both metals.

Table 4. Lead and cadmium levels in tested samples at a distance 10- 35 km away from Tagarades landfill.

Edible Specimens	Sampling Points (km-around landfill)	Cd (mg/kg wet weight)	Pb (mg/kg wet weight)
Quince	10	<LOD	<LOD
Quince	10	< LOD	< LOD
Olives	10	< LOD	< LOD
Corn	10	< LOD	< LOD
Watermelon	25	< LOD	< LOD
Corn	25	< LOD	< LOD
Zucchini	25	< LOD	< LOD
Corn	25	< LOD	< LOD
Corn	25	< LOD	< LOD
Onion	30	< LOD	< LOD
Watermelon	35	< LOD	< LOD
Olives	35	< LOD	< LOD
Cow milk	35	< LOD	< LOD

At a distance of 10 to 35 km away from the Tagarades landfill no trace of lead and cadmium was found. The distance of the selected suburban sampling area from highways, industries etc. can explain these findings.

CONCLUSIONS

Forty nine food samples of fruits, vegetables and milk were analysed for detection and determination of lead and cadmium levels. The sampling sites vary in distance around the Tagarades landfill. Only 5 samples (10%) had detectable cadmium levels which were however lower than the allowed upper limits. As for the level of lead in the samples, the percentage of samples with detectable concentrations was higher (28%) and the values were also below the maximum allowed limits. Only a goat milk sample taken at a distance less than 2.5 km from the landfill had lead concentration equal to the upper limit for milk. Unfortunately there were not any reported data taken before the fire allowing for comparisons to be made. Another study was also conducted during that same period aiming at analyzing soil and vegetation samples collected 15 days after the ultimate fire extinction, from the surrounding area of the same landfill. This study also showed that there was no apparent impact from the landfill fire on the surrounding terrestrial environment and heavy metal concentrations were similar to those reported for vegetation species in other Greek locations[8]. Another investigation during an accidental fire in a landfill in Western Norway revealed that heavy metals in the leachate showed considerably increased concentrations but the determined levels (except of chromium) appeared to return to normal within one week after the fire was extinguished[9]. Finally, the results taking into account the conclusions of the two studies mentioned above[8,9] indicated that there was no apparent effect of the landfill fire on the lead and cadmium levels of the tested food samples and these specimens were safe for consumption according to the Draft Commission Regulation on Setting Maximum Limits for Certain Contaminants in Foodstuffs.

Βαρέα μέταλλα σε βρώσιμα δείγματα γύρω από τη χωματερή των Ταγαράδων έπειτα από μεγάλη πυρκαγιά.

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ΠΕΡΙΛΗΨΗ: Στόχος της έρευνας ήταν να παράσχει πληροφορίες για τα επίπεδα των βαρέων μετάλλων (μολύβδου και καδμίου) σε βρώσιμα δείγματα που είχαν συλλεχθεί από περιοχές γύρω από τη χωματερή των Ταγαράδων μετά από την εκδήλωση μεγάλης πυρκαγιάς σε αυτήν. Συνολικά 49 δείγματα από φρούτα, λαχανικά και γάλα συλλέχτηκαν σύμφωνα με την οδηγία 2001/22/EC. Οι περιοχές απ' όπου ελήφθησαν δείγματα ήταν: < 2.5, 2.5, 3, 4, 5, 6, 7, 8, 9, 10 χιλ. γύρω από τη χωματερή όπως και 35-40 χιλ. μακριά και η οποία θεωρήθηκε ως «τυφλή» περιοχή. Έγινε προσπάθεια να συλλεχθούν δείγματα από τις ίδιες ποικιλίες φρούτων και λαχανικών στις προεπιλεγμένες περιοχές δειγματοληψίας. Τα δείγματα κατεργάστηκαν με θέρμανση με μίγμα πυκνών οξέων (νιτρικό και υπερχλωρικό οξύ), ώστε να καταστραφεί η οργανική δομή τους και να καταστεί δυνατή η ανάλυση τους με φασματομετρία ατομικής απορρόφησης. Η ανάλυση του καδμίου έγινε με φασματομετρία ατομικής απορρόφησης φλόγας και του μολύβδου με φασματομετρία ατομικής απορρόφησης με φούρνο γραφίτη. Τα αποτελέσματα έδειξαν πως δεν υπήρξε εμφανής επίδραση της πυρκαγιάς στα δείγματα τροφίμων που εξετάστηκαν, όσον αφοράτα επίπεδα του μολύβδου και του καδμίου. Τα δείγματα τροφίμων ήταν ασφαλή προς κατανάλωση σύμφωνα με το Draft Commission Regulation on Setting Maximum Limits for Certain Contaminants in Foodstuffs.

Λέξεις Κλειδιά: Βαρέα μέταλλα, Χωματερή, Ατομική απορρόφηση.

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