Ecotoxicology and Environmental Safety 148 (2018) 114–124

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Toxic inorganic pollutants in foods from agricultural producing areas of Southern Italy: Level and risk assessment

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ARTICLE INFO

Keywords:
Heavy metals
Food safety
Pollution
Toxicity
Human health
Contamination

ABSTRACT

This study focused on the inorganic environmental contaminants in specific food products which form part of the food chain of the population residing in the area of Southern Italy (Gela) where there is a high mortality rate linked to tumor diseases and congenital malformations. Determination of toxic metals was performed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The toxicological data for every toxic element has been applied to evaluate the risk for the consumer by calculating the amount of potentially toxic element that would ingest an average of 60 kg weight individual adult. The analysis of the investigated samples shows a high level of metal contamination which can be linked both to the polluted water and air. The obtained results give us an idea about the agricultural products contamination and possible exposure of local people through the food chain.

1. Introduction

Sicily is an Italian island known worldwide for its natural features such as landscapes, seabed, archaeological parks, gastronomy and local products such as Nubia garlic, Interdonato lemon, cherry tomato, artichokes, seafood rich, red tuna, pistachio and, in particular, extra virgin olive oil and wine (Albergamo et al., 2017; Salvo et al., 2017; Corsaro et al., 2016; Gentile et al., 2016; Maisano et al., 2016; Saija et al., 2016; Salvo et al., 2016a; Salvo et al., 2016b; Salvo et al., 2016c; Vadalà et al., 2016; Mallamace et al., 2014; Salvo et al., 2014; La Torre et al., 2010). Despite all these features its territory was offended, disfigured, devastated and poisoned by entrepreneurs and/or industrialists who have rooted their "business" in this region since the post-war. The city of Gela is an ancient colony of Magna Greece in Southern Sicily that stands in front of a vast alluvial plain in the south of Sicily, in the Province of Caltanissetta. Due to its location, overlooking the Gulf of Gela and the Channel of Sicily, it is characterized by a thriving agricultural activities related to horticulture field and greenhouse, specializing mainly the artichoke and tomato production (Riggi and Avola, 2008).

The specificity of this area is given by the coexistence of agriculture with one of the largest European petrochemical complexes which, with a total area of 500 ha, consisted mainly of refineries and petrochemical plants for the production of gasoline, diesel, LPG and pet-coke.

Industrial activities, the many landfills and pollution product from 1960 to the present, generated serious environmental damage and health-related. In the petrochemical pole and surrounding areas, soil and aquifers are seriously contaminated by arsenic, mercury, nickel, lead, cadmium, chromium, antimony, vanadium, hydrocarbons, benzene, toluene and other toxic and carcinogenic organic compounds. Therefore, in 1990 the area of Gela municipality and two neighboring municipalities, Niscemi and Butera, were included among areas at high risk of environmental crisis and, in 1998 an extensive area of Gela municipality was declared a Site of National Interest (SNI) for soil remediation (D.M.A, 2007; Comba et al., 2007; IR, 2001, 1998).

According to field investigation, the main sources of soil and groundwater pollution can be traced in the petrochemical activities with spill fumes, oil drilling rigs, industrial landfills, agricultural practices and atmospheric pollution from vehicle traffic (Manno et al., 2005; Bosco et al., 2005).

The whole Petrochemical zone stretches along the coast and has about 97 different issue points that discharge into the atmosphere organic substances and heavy metals such as lead (Pb), copper (Cu), vanadium (V), nickel (Ni) and chromium (Cr). The Gela refinery is fed by a thermal power plant burning different fuels including petroleum coke, a waste substance of the cracking process that is highly polluting and contains sulfur and high concentrations of iron, vanadium, nickel, arsenic and lead (Bosco et al., 2005; Pinelli, 2003).

Among the Petrochemical zone and the greenhouses, which have a

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http://dx.doi.org/10.1016/j.ecoenv.2017.10.015
Received 16 May 2017; Received in revised form 3 October 2017; Accepted 5 October 2017

minimum distance of about 600 m, it is located the largest industrial waste landfill, containing natural radioactive materials, the *phosphogypsum*, a mineral residue derived from the fertilizers production (Trotti and Dalzocchio, 2001; Paridaens, 2001).

For several years, due to its location, the high industrialized area of Gela focused the attention of researchers towards the potential effects of pollutants of industrial origin on the population's health. In this contest, the contamination of food products is regarded as extremely serious (Musmeci et al., 2009; D.M.A, 2007; Bianchi et al., 2006).

The Gela food production is chiefly characterized by an intensive system that is divided into two main types: cultivation in greenhouses (located along the coast) and open field crops (localized in the plain). The cultivation in greenhouses, covers an area of 1.108,33 ha located along almost the entire coastal territory, and is totally destined to the production of tomato (*Lycopersicum esculentum*), which represents the most profitable cultivation. Arable crops in open field stretch over 1.803,51 ha towards the hinterland on a flood zone of which 1.352,63 ha are mainly dedicated to the artichoke (*Cynara scolimus*) cultivation (Istat, 2012).

The water used for irrigation comes from an important underground water surface, and with the flow direction from the north to the sea, crosses the alluvial and sandy subsoil of the Gela plain. The aquifer, surfacing in some places, has enabled the creation of wells that provide the necessary water supply for agricultural crops; however, several investigations have found severe contamination of these waters for the widespread presence of man-made pollutants such as surfactants, arsenic, nitrites, phosphates, hydrocarbons and heavy metals including mercury (Musmeci et al., 2009).

Numerous searches, which classified the Plain of Gela as high risk area of environmental crisis, make it clear a lack of data on chemical contamination of local products such as vegetable. The present work focused on the simultaneous determination of some metals (Hg, As, Cr, Ni, Cu, V, Cd and Pb) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in tomatoes and artichokes from the Plain of Gela and asses the consumer exposure to these contaminants by dietary vegetable consumption.

2. Materials and methods

2.1. Study area

The Plain of Gela is located in the south of Sicily, overlooking the Gulf of Gela and is bathed in the south by the Channel of Sicily. It is the second plain of Sicily and one of the largest in southern Italy; it was formed by the accumulation of alluvial deposits of Gela, Dirillo, Salso rivers and their tributaries (Fig. 1). The area of Gela that is included in the list of national interest reclamation (IR, 1998) covers a flat area of around 671 km^2.

Geologically it is mainly made up of sandy soils (high permeability) and clay (medium and low permeability). The clay minerals are generally made up of hydrated aluminum silicates and contain large amounts of sodium, potassium, magnesium, calcium and iron. They have the ability to bind cations such as Ca^{+2}, Mg^{+2}, K^{+}, Na^{+} and NH_4^{+} preventing their solubilization in water and at the same time making them available as nutrients (Manno, 2006). On the whole, the study area is entirely covered by sedimentary rocks (limestones, clay, marly clay, and white or yellow quaternary biocalcarenites). In the eastern sector are limestone and gypsum outcroppings belonging to the typical “Serie Gessoso-Solfifera” formation of Miocene age (Bosco et al., 2005).

Based on the characteristics of the soils the Plain of Gela can be divided into three classes of attenuation capabilities (available water capacity): high - medium - low. The "high" class corresponds to a low percolation of water and therefore a high protective capacity of the soil-climate system in respect of water-soluble pollutants. The entire coastal strip, characterized by sandy soil, has low soil attenuation capacity; just in this band insists the industrial sites and greenhouses systems. Instead, the plain area, characterized by clayey and sandy soils, has alternating areas of medium and high attenuation of soils. Predominantly, in this area insist agricultural activities in open field and greenhouses.

The study area is subjected to serious contamination risk, due to the high permeability of the soil which happens to be medium - high in the Plain of Gela (loamy and clayey soils) and tends to increase as you reach the sandy soils of the coastal strip (high permeability

In order to assess, in outline, the area affected by the fallout of industrial emissions and choose the sampling areas for artichokes and tomatoes, data on the winds direction during 1971–2000 were considered. These climatic informations point out that the area to which blow most of the winds is located in the north - east of the Plain of Gela, between Gela and Niscemi towns, in which they insist most of artichoke crops. During the day the situation is variable: in the late afternoon and evening hours there is the prevalence of winds to the East and North-East area (Fig. 1) in which insist the greenhouses plants; at night there is a reversal of breezes and winds, generally, begin to blow from South -East (or South-West in the presence of *sirocco*), so that the city and the area to the west remain downwind from the petrochemical zone (Manno et al., 2005).

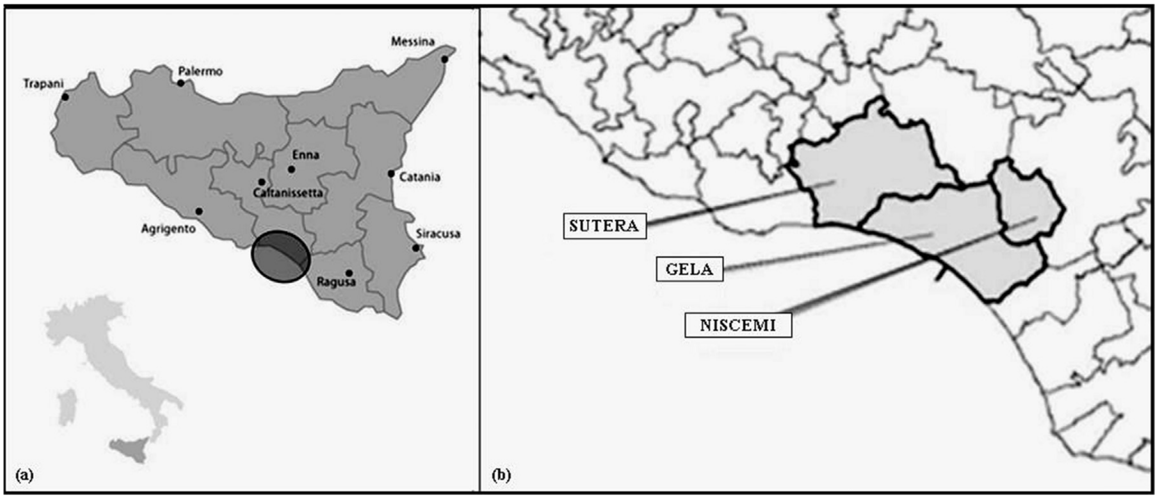

Fig. 1. Location of **(a)** Gela area in Sicily (Italy) and **(b)** study area of Gela and municipalities of the high environmental risk area.

2.2. Sampling

Sampling of food products was carried out between February and March 2015. They were collected 13 samples of artichokes from different functional areas of the Plain of Gela (S1). Each sample of the weight of about 2 kg consists of multiple samples (weight between 160 and 190 g) taken in the same area. The comparison was performed on three samples (ART control) picked up by the city of Riesi, near the highway SS 626, in North-West position and over 20 km from petrochemical zone. This sample was from the eastern study sector, belonging to the typical “Serie Gessoso-Solfifera”, and not being exposed to dust fallout from industry site and to irrigation with contaminated water, was used as reference sample.

With respect to tomatoes, they were taken 13 samples of the variety "Cherry" grown in greenhouses (S2) and irrigated with rainwater and aquifer contaminated with heavy metals and organic compounds (Musmeci et al., 2009). Each sample of about 1 kg, is made from more bunches taken at several points within the same greenhouse. These were compared with three samples (TOM control) taken in an area not contaminated by industrial installations (Province of Caltanissetta) and with organic certification. Also this case, the geochemistry of the soil at the reference point was “Serie Gessoso-Solfifera” and, although not exactly the same as the tomato cultivation sites, however it could be considered representative of the investigated area and suitable for the comparison.

The sampling procedures for the two types of products were carried out following the protocol provided by the Regulation (EC) No 333/07 (EC, 2007). Each sampling was georeferenced and reported in cartography.

Regarding the water sampling, six aquifer samples (W1-W6) were taken in September 2015 directly from wells located along the coast and mainly exploited for irrigation of greenhouse crops (tomatoes); in March 2016 were taken further 3 samples: of which two from wells 7 and 8 that draw water from the underground-aquifer and the other one from a catchment of rain water mixed with aquifer (sample W9) (S3).

The sample W8 was used for irrigation of the artichokes. All samples were placed inside 1liter polyethylene bottles, previously washed with distilled water and then with the same water sample. At the sampling time, they were carried out measurements related to pH, conductivity and temperature. Subsequently, all samples were filtered (0.45 µm filter) to eliminate the presence of vegetable and organic material, acidified with HNO_3 (2 mL/100 mL of sample) and stored at 4 °C, until analysis.

In order to assess the soil contamination, they were taken N° 34 surface samples of the so-called "top soil", randomly distributed over the entire Plain of Gela. Each sample was appropriately geo-referenced according the Geographic Information System (GIS) (S4). The soil samples were taken using a sampler for soil auger with stainless steel manual (carrot length 15 cm, diameter 3 cm). The sampling was carried out both in sandy and clay soil, at a depth of 0–15 cm. Each sample (weight 3 kg) consists of a set of five samples randomly sampled within an area of 10 m^2. Each sample was manually cleaned of any plant residues, homogenized and stored in a plastic bag for food until analysis. The analyses of soil samples were conducted both on the fine particle size (< 2 mm) and on the skeleton (> 2 mm), previously separated by sieving. The samples were stored at − 4 °C until analysis.

2.3. Reagents and standards

Nitric acid at 65%, hydrogen peroxide at 30% and ultrapure water for the ICP analysis were supplied by J.T. Backer (Backer Mallinckrodt, Milan, Italy). Stock standard solutions (1000 mg L^{-1} in 5% nitric acid) of each element studied, at the highest level of purity available, were purchased from Merck (Darmstadt, Germany) except for Hg and Cd that were purchased from Baker (Phillipsburg, USA). Ultra-pure water with resistivity of l0 MΩ cm^{-1} was obtained from a Milli-Q water purification system Thermo Scientific Barnstead Smart2Pure 12 (Milan, Italy). To tune the instrument a tuning standard solution containing ^{7}Li, ^{59}Co, ^{80}Y and ^{205}Tl (each 10 µg L^{-1} in 2% HNO_3 + 0.5% HCl) was obtained from Agilent (Santa Clara, CA). The gases 99.9990% argon and 99.9995% helium were supplied by Rivoira gases (Rivoira S.p.A., Milan, Italy).

2.4. Sample extraction and cleanup

2.4.1. Vegetable products

The analyses were performed on the edible part of the product (berry for tomato and choke for artichoke). Each agro-food product collected was placed in food bags, labeled, sealed and frozen until analysis.

The artichoke and tomato samples were previously and thoroughly washed externally with ultra pure water to remove any soil residues present on the surface; this in order to eliminate the contribution of external contamination and simulate the household washing. The samples were treated with liquid nitrogen (−196 °C) and subjected to cryo-grinding in order to obtain a homogeneous paste.

The extraction was carried out on an aliquot (about 0.5 g) of the homogenized sample that was submitted to a mineralization process. Mineralization was carried out by using a microwave digester (Microwave Digestion High Pressure System - Mileston Ethos LabStation). Each sample of artichoke or tomato, was weighed into a teflon vessel with the subsequent addition of 7 mL of concentrated nitric acid (HNO_3, 65%) and 1 mL of hydrogen peroxide (H_2O_2, 30%) (Bosco et al., 2005). The samples in the vessel were digested using an optimized method that consist of two steps with a constant microwave power (1000 W). Firstly the temperature was increased to 200 °C in 10 min (step 1), and then it was held for 10 min at 200 °C (step 2). The obtained residue was dissolved with ultrapure water, transferred into a volumetric flask and diluted to 25 mL. To minimize the error of the mineralization phase, for each cycle a blank sample was prepared. All the final samples were analyzed by ICP-MS.

2.4.2. Soil samples

The soil samples were initially homogenized and cleaned from plant residues. The obtained sample was dried in an oven (120 °C) and sieved separating the fraction with fine particle size (< 2 mm) from the skeleton (> 2 mm). From each fraction size about 0.5 g of sample were taken and subjected to mineralization after addition of 3 mL of HNO_3 65% and 9 mL of HCl 37%. The mineralization was carried out in two steps with a constant microwave power (1000 W). Firstly temperature was increased to 200 °C in 10 min (step1), and then it was held to 200 °C for 10 min (step 2). The obtained residue was first filtered and then transferred into flask and brought to volume (25 mL) with ultrapure water. Subsequently, elemental analysis was carried out by ICP-MS.

2.4.3. Water samples

Even the water samples have been subjected to mineralization procedure by a microwave digester, in order to eliminate the organic components. About 0.5 mL of water sample were taken with a pipette and weighed inside a teflon vessel; subsequently, they were added with 7 mL of concentrated nitric acid (HNO_3, 65%) and 1 mL of hydrogen peroxide (H_2O_2, 30%) (Jie et al., 2004). Also in this case the mineralization was carried out in two steps with a constant microwave power (1000 W). Firstly temperature was increased to 200 °C in 10 min (step1), and then it was held to 200 °C for 10 min (step 2). To minimize the error, for each analytical cycle it was prepared a blank sample containing the same reagents. The obtained residue was transferred into a volumetric flask and brought to volume (25 mL) with ultrapure water. After reconstruction the solution was analyzed by ICP-MS.

2.5. *ICP-MS analysis*

The determinations of Ni, Cd, Pb, Hg, As, V, Cu and Pb in digested samples were carried out by 7500CX Agilent ICP-MS spectrometer (ICP-MS Agilent octapolo 7500 - Santa Clara, CA, USA) with a reaction/collision cell Octopolo Reaction System (ORS), and equipped with an automatic sample ASX 500. The system was pressurized with Helium to remove the interference due to the plasma and to the matrix. The analyses were performed either in gas mode that no gas.

The sample was introduced with a flow of 1 mL min^{-1} and for each element three replicas have been set. Before each analysis, the instrument carried out a wash program with diluted nitric acid (4% HNO_3).

In all the samples Hg was analyzed separately, after adding 100 µL of HCl 4% to favor the chlorides formation, while the washing cycle was performed with a hydrochloric acid solution (HCl, 2%).

The operating conditions used for instrumental analysis by ICP-MS were the following: RF power, 1.550 W; sample depth, 9 mm; spray chamber temperature, 2 °C; plasma gas flow rate, 15 L min^{-1}; auxiliary gas flow rate, 0. 9 L min^{-1}; carrier gas flow rate, 1.1 L min^{-1}; sample introduction flow rate, 1 mL min^{-1}; vacuum, $< 1.5 \times 10^{-7}$ Pa; interface pressure; 5.3×10^{-2} Pa. These parameters were optimized using a solution containing nuclides ^{7}Li, ^{59}Co, ^{80}Y and ^{205}Tl (10 µg L^{-1}), whose masses are distributed all over the interval of interest.

For each element are shown (S5) the quantified isotope, the analysis mode (with or without collision/reaction cell), the internal standard, the integration time for point and for mass used. For each mass they were considered three points and each acquisition was repeated three times. The selected isotopes, listed in S5, were chosen for each element on the basis of the relative isotopic abundance, so as to optimize the sensitivity, and the absence of important isobaric interferences or interference induced by the matrix, when possible. contain the isotope ratios of the elements and provide measurements to the additional values of *m/z* to estimate and allow the subtraction of polyatomic interference.

The calibration was performed with a multi-standard solution of Cr, V, Cu, Cd, Pb, Ni, As obtained by mixing standard solutions of each individual element and diluting with nitric acid (HNO_3, 2%). Six standard mixtures of all the elements, at different concentrations ranging from 5 to 2000 mg L^{-1} for each element, were prepared by adding the appropriate amount of the element standard solution in 10 mL volumetric flasks and bringing to volume with HNO_3 2%.

The mercury calibration was performed using five-point calibration graph obtained with 10, 50, 100, 500 and 1000 mg mL^{-1} standards. These standard mixtures were used for the construction of the calibration graphs, using the linear regression of the least squares method.

To ensure the proper digestion each sample was added with 1 mL of Re internal standard at 0.8 mg L^{-1}. A solution of Sc, Rh and Bi (1 mg L^{-1}) was prepared and used as internal standard to correct any instrumental drifts and matrix effects.

3. Results and discussion

3.1. *Method validation*

In the present study, in accordance with the Regulation (EC, 2007) and international guidelines (EURACHEM guide, 2012; EUROPEAN PHARMACOPOEIA, 2015), the used analytical process was validate considering the limit of detection and quantification, the linear range, accuracy, precision and short- and long-term repeatability. The analytical characteristics of the method are presented in S7.

The evaluation of the linearity was based on injection of the standard solutions. Each solution was injected six times and the linear coefficients for all the elements were higher than 0.99993 in each concentration range ($R^2 > 0.99993$).

The limits of detection (LODs) and of quantification (LOQs) were calculated according to IUPAC guidelines (McNaught and Wilkinson, 1997). The LODs and the LOQs were experimentally calculate as 3.3 σ/S and 10 σ/S, respectively, where σ is the residual standard deviation and S is the slope of the regression curve. LOD values ranged from 0.0004 to 0.006 µg L^{-1}, while LOQ values ranged from 0.001 to 0.02 µg L^{-1}.

The accuracy for the agricultural products was evaluated by means of a recovery study on the certified standard matrices GBW07604, provided by NRCCRN and certificate for As 0.37 mg kg^{-1}, Cd 0.32 mg kg^{-1}, Cr 0.55 mg kg^{-1}, Cu 9.3 mg kg^{-1}, Pb 1.5 mg kg^{-1}, Ni 1.9 mg kg^{-1}, V 0.64 mg kg^{-1}, Hg 0.03 mg kg^{-1}.

The certified matrix used for the soils was SOIL, GBW07402 provided by NRCCRN certificate for As 13.7 mg kg^{-1}, Cd 0.071 mg kg^{-1}, Cr 47 mg kg^{-1}, Cu 16.3 mg kg^{-1}, Pb 20 mg kg^{-1}, Ni 19.4 mg kg^{-1}, V 62 mg kg^{-1}, Hg 15 ng g^{-1}.

The obtained results, reported in S8, show that the recovery on the certified matrix GBW07604 varies from 86% to 97% with RDS values always lower than 5.88%. For the matrix GBW07402 the recovery varies from 87% to 112% with RDS values always lower than 5.62%.

In order to assess the precision of the method, the restricted repeatability and the intermediate repeatability were determined. The first was estimated on the relative standard deviations (RSD%) of the measurements obtained by analyzing the same certified matrices 10 times in the same analytical run. The same certified matrices were analyzed 20 times over a period of twenty successive days to determine the intermediate repeatability (RDS%). The precision, whose results are reported in S8, was excellent in the same analytical run (RDS% between 2.8 and 3.9 for vegetables and between 2.3 and 3.8 for soil) and good for long-time analysis (RDS% between 2.6 and 10.2 for vegetables and between 3.0 and 9.5 for soil).

To minimize any memory effects, an appropriate washing solution (HNO_3, 2%) was fluxed between an analysis and the subsequent. The memory effect can be more important in the determination of mercury; in this case it is necessary to flush for two minutes with a solution of HNO_3 2% and containing 100 ng mL^{-1} of Au (EPA, 1994).

In this study it was verified that the washing with nitric acid (HNO_3, 2%) for three minutes is adequate to cancel the mercury memory effect, for the levels at which this element was present in the analyzed samples.

3.2. *Levels of toxic inorganic elements in irrigation and aquifer waters*

The results of aquifer have been summarized in Table 1. As it is not present, until now, specific legislation on the quality of water used for crops irrigation, the obtained data were compared with the limit values set by three regulations on water quality and that encompass the same limits (LD, 2009, 2006, 2001).

The samples were divided into two groups; the first (S9) consists of aquifer samples 7, 8 and 9 taken in more inland areas and upstream from the industrial zone. These waters, used for irrigation of artichokes (sample W8) and tomatoes in the greenhouse (samples W7 and W9), have a basic pH (~ 8.09) and an high conductivity (~ 1386 µS cm^{-1}) (Table 1), but in any case below the law limits, determined by the high amounts of dissolved salts which reflect the rocks with which the aquifer meets (chalky limestone rocks). In particular, the sample W7 has the lower conductivity than those collected in the wells 8 and 9 and the highest Cu^{63} level, which probably enter through application of agricultural fertilizers. Moreover, it must be considered that rainwater, leading to soil the pollutants emitted into the atmosphere from the petrochemical complex, can move the pollutants from the source to the aquifers.

The arsenic and toxic metals content is rather similar and in any case worrying: AS^{75} (405 µg L^{-1}) presents average values 40 times higher than the legal limits, Ni^{60} (279 µg L^{-1}) exceeds by 14 times the limit, Pb^{208} (264 µg L^{-1}) and Cd^{111} (351 µg L^{-1}) beyond 26 times and 70 times the threshold values, respectively.

The W1-W6 samples, belonging to the second group (S10), are from six wells along the coast of the Gulf of Gela, in an area downstream the

Table 1
Inorganic toxic contaminants in ground and irrigation waters.

	M. U.[a]	**Aquifer W7**	**Aquifer W8**	**Aquifer W9**	**Mean**	**S.D.**[b]	**Aquifer**[b] **W1-W6**	**S.D.**	**Limit values (1)**[c]	**Limit values (2)**[d]	**Limit values (3)**[e]
Sampling		Well	Well	Water basin			Well				
Use		Irrigation	Irrigation	Irrigation			Irrigation				
Culture		Greenhouse	Artichokes	Greenhouse			Greenhouse				
pH		8.47	7.37	7.64	8.09		7.20		6.50 −9.50	–	–
Cond.	µS/cm	1014	1662	1482	1386		–		2500	–	2500
As^{75}	µg/L	404.6	405.1	405.8	405.2	0.6	168.3	29.9	10	10	10
Ni^{60}	µg/L	276.9	279.5	275.8	277.4	1.9	14.9	3.9	20	20	20
Hg^{202}	µg/L	n.d.[f]	n.d.	n.d.	n.d.	n.d.	1.0	0.8	1	1	1
V^{51}	µg/L	132.4	131.2	135.9	133.2	2.4	82.7	91.1	50	–	50
Pb^{208}	µg/L	270.0	264.1	276.0	270.0	5.6	4.2	10.0	10	10	10
Cd^{111}	µg/L	352.0	351.8	351.9	351.9	0.1	1.4	–	5	5	5
Cu^{63}	µg/L	362.1	75.0	51.0	206.5	219.9	–	–	1000	–	–
Cr^{52}	µg/L	237.0	286.6	239.6	254.4	27.9	–	–	–	–	50

[a] Measure Unit.

[b] It is the mean and the standard deviation (S.D.) of values of 6 aquifer samples collected along the coast of Gela, in November 2015.

[c] Legislative Decree 2 February 2001 n ° 31. Implementation of Directive 98/83/EC on the quality of water for human consumption. Attachment 1 Part B.

[d] Legislative Decree 152/06. Attachment 5 tab. 2.

[e] Legislative Decree 16 March 2009, n. 30. Implementation of Directive 2006/118/EC on the protection of groundwater against pollution and deterioration. Attachment 3 part A2.

[f] n.d: not detected.

industrial pole. They are used for irrigation of greenhouse crops and in Table 1 is only represented the mean value obtained from 6 samples. The results show lower values than those detected in the samples of the first group but with average values higher than the limits for arsenic (168.32 $\mu g\ L^{-1}$, with max. 734 $\mu g\ L^{-1}$ and min. 28.40 $\mu g\ L^{-1}$) and vanadium (82.67 $\mu g\ L^{-1}$, with max. 262 $\mu g\ L^{-1}$ and min. 22 $\mu g\ L^{-1}$).

The highest values of AS^{75} and V^{71} (S10c) concern the samples near the new industrial area (W4) and the greenhouses (W1). It was also detected the worrying presence of mercury equal to the average concentrations of 1 $\mu g\ L^{-1}$, but with peaks of 2.60 $\mu g\ L^{-1}$ for the sample W1. The lower concentrations in inorganic contaminants can be attributed to the variability of the water load of the aquifer that dilutes or concentrates the dissolved substances.

The analyses of irrigation waters highlighted serious pollution by toxic metals so that we can classify these aquifer samples contaminated and unfit for human consumption. Global interpretation of the groundwater samples data, according to the Italian and European Regulation, shows a chemical classification attributable to class 4 (poor) (LD, 2006, 2001).

Considering the data reported in Table 1, it is difficult, according to current knowledge, attributed to a natural origin, except in small part, the overcoming limits of the additional descriptors such as arsenic, mercury, nickel, lead, cadmium and vanadium.

These data confirm the previous studies from which it emerges that the aquifer is exposed to various sources of contamination, from point and diffuse anthropogenic origin, which infiltrate and percolate in soil until it reaches the aquifer (Gisotti and Turrio Baldassari, 2006). Therefore, the aquifer can not be considered suitable for use even in agriculture; the use of aquifer for the crops irrigation, being a source of contamination, can lead to a high risk to food safety of agricultural food products. In fact, many authors (Mohamed, 2003; Pereira et al., 2002) demonstrated the close relationship among environmental pollution of soil, of irrigation water or, in general, of the environment and the contamination of agricultural products grown in the same area. This is because the toxic metals tend to migrate from the external environment towards the plants that, depending on the species, accumulate them in a different way (Rajesh Kumar et al., 2007) and from here, penetrate into the food chain until the man (Frinkm, 1996).

3.3. Levels of toxic inorganic elements in soil

The results regarding the soil samples (Table 2) suggest that all the toxic metals show lower concentrations than the limit values established by Legislative Decree 152/06 and the Ministerial Decree 471/99 relating to contaminated soils (Abrahams, 2002; LD, 2006). These are toxic and polluting metals, clear anthropogenic, whose presence is compatible with previous environmental studies in the Gela area and the industrial activities (Manno et al., 2005; Bosco et al., 2005).

Particularly, arsenic (As^{75}) has been detected nears the petrochemical area, to the west of the Gela city. This data was obtained from sand sampled by the sea and is probably attributable to the sea water pollution. The presence of As^{75}, found in high amounts also in aquifer, could be a clear indicator of pollution coming from the petrochemical zone.

The obtained results were graphically elaborated with iso-concentration maps (Fig. 2) which show a geographic distribution of pollutants downwind, within 10–15 km, in areas close to the Petrochemical Pole, the Gela city centre and along the most trafficked roads. Fig. 2 shows that there is an increased concentration of toxic metals in the fine fraction of the soil (< 2 mm), compared to the skeleton (> 2 mm), in the areas close to the Petrochemical Pole, in Gela city center and along the most busy roads. In particular Pb^{208}, Ni^{60} and As^{75} showed a greater accumulation next to the industrial center and the main roads.

3.4. Levels of toxic inorganic elements in artichoke samples

The concentations of inorganic elements in artichoke samples are summarized in Table 3 and the data are expressed in mg kg^{-1} of fresh product, as indicated in Regulation No 1881/2006 (EC, 2006).

In all samples Hg^{202} levels were below the instrumental detection limits, while the total Cr^{52} concentration (range: 0.181–0.344 mg kg^{-1}; mean: 0.270 mg kg^{-1}) was higher in the industrial than in the residenzial “unpolluted” sites (ART 8 and ART 9), albeit for this element the differences between the residenzial zone and the industrial area were no so marked. This coud be explained considering that chromium occurs naturally in the Earth's crust and its total amount can be tributable both natural and anthropogenic sources (ATSDR, 2000a).

The lead and cadmium concentrations, although sometime similar, in artchokes collected near the petrochemical complex were significantly higher than those corresponding to unpolluted area (ART 8 and ART 9). Infact, the obtained data evidenced that, for these last samples collected from non-contaminated areas, outside the spillover cone of industrial fumes, the cadmium and lead concentrations are within the legal limits. Generally, Cd^{111} and Pb^{208} average values, taking into account the standard deviation, exceed the limits set by the

Table 2
Analytical results of heavy metals in soil samples of the Plain of Gela.

ID	GIS Coordinates	Soil Fraction	Skeleton %	Umidity %	Hg mg/kg	As mg/kg	Cd mg/kg	Cr tot mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg
Limit Values Lgs D. 152/06 Att. V, Tab 1/A					***1***	***20***	***2***	***150***	***120***	***100***	***90***
1	37°03′43″N	> 2 mm	62.30%	9.70%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°18′47″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
2	37°03′41″N	> 2 mm	89.20%	3.10%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°19′04″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
3	37°03′35″N	> 2 mm	84.00%	13.70%	< 0.1	< 2	< 0.2	< 1.5	**1.8**	< 1	< 9
	14°18′47″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	**2.1**	**1.1**	< 9
4	37°06′35″N	> 2 mm	100%	14.40%	< 0.1	**3.1**	< 0.2	< 1.5	**2.8**	**1.4**	< 9
	14°04′52″E	< 2 mm			< 0.1	**3.1**	< 0.2	< 1.5	**2.8**	**1.4**	< 9
5	37°06′39″N	> 2 mm	88.20%	7.60%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°04′53″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
6	37°06′10″N	> 2 mm	71.40%	6.20%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°08′16″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
7	37°3′23."N	> 2 mm	89.80%	8.80%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°18′45"E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
8	37°6′14"N	> 2 mm	75.40%	0.90%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°21′25"E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
9	37°04′18″N	> 2 mm	86,80%	4.70%	< 0.1	< 2	< 0.2	< 1.5	**1.5**	< 1	< 9
	14°18′19″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	**1.7**	**1.1**	< 9
10	37°02′28″N	> 2 mm	91.10%	2.70%	< 0.1	**4.7**	< 0.2	< 1.5	**1.6**	**1.5**	< 9
	14°21′08″E	< 2 mm			< 0.1	**5.2**	< 0.2	< 1.5	**1.8**	**1.6**	< 9
11	37°05′49″N	> 2 mm	91.60%	5.10%	< 0.1	< 2	< 0.2	< 1.5	**1.3**	< 1	< 9
	14°20′08″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	**1.4**	< 1	< 9
12	37°06′45″N	> 2 mm	75.20%	8.00%	< 0.1	< 2	< 0.2	< 1.5	**1.7**	**1.2**	< 9
	14°18′57″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	**2.2**	**1.6**	< 9
13	37°10′07″N	> 2 mm	77.70%	3.10%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°20′18″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
14	37°07′21″N	> 2 mm	86.80%	4.20%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°23′37″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
15	37°10′19″N	> 2 mm	81.50%	4.50%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°23′05″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
16	37°00′36″N	> 2 mm	95.90%	4.30%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°22′07″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
18	37°12′03″N	> 2 mm	75.80%	13.20%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°08′14″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
19	37°10′45″N	> 2 mm	79%	4.50%	< 0.1	< 2	< 0.2	< 1.5	**1.7**	< 1	< 9
	14°16′28″E	< 2 mm			< 0.1	< 2	< 0.2	**1.6**	**2.1**	**1.1**	< 9
20	37°07′42″N	> 2 mm	76.50%	7.70%	< 0.1	< 2	< 0.2	**1.8**	**1.5**	**1**	< 9
	14°09′44″E	< 2 mm			< 0.1	< 2	< 0.2	**2.3**	**2**	**1.3**	< 9
21	37°04′38″N	> 2 mm	77.70%	6.10%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°22′25″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
22	37°08′56″N	> 2 mm	97.90%	5.70%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°26′27″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
23	37°05′33″N	> 2 mm	91.20%	3.50%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°24′56″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
24	37°02′09″N	> 2 mm	80.30%	6.90%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°25′44″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
25	37°07′52″N	> 2 mm	99.30%	1.50%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°26′03″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
26	37°01′04″N	> 2 mm	98.30%	4.30%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	**1.1**	< 9
	14°28′19″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	**1.1**	< 9
27	37°12′51″N	> 2 mm	81.80%	7.70%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°19′39″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
28	37°04′51″N	> 2 mm	84.50%	5.70%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°30′35″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
29	37°07′41″N	> 2 mm	87.60%	5.70%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°29′59″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
30	37°11′09″N	> 2 mm	89.30%	6.80%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°28′40″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
31	37°06′22″N	> 2 mm	85.00%	4.40%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°13′34″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
32	37°06′19″N	> 2 mm	72.60%	6.40%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°14′02″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
38	37°05′49″N	> 2 mm	86.70%	9.00%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°16′33″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
39	37°03′40″N	> 2 mm	85.80%	6.70%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°20′46″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
40	37°05′59″N	> 2 mm	75.60%	8.60%	< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9
	14°11′44″E	< 2 mm			< 0.1	< 2	< 0.2	< 1.5	< 1.2	< 1	< 9

Regulation (EC, 2006) in almost all samples. In fact, the average Cd^{111} levels resulted equal to 0.336 mg kg^{-1} (range: 0.038–0.506 mg kg^{-1}), that is almost 9 times higher than the legal limits. The Pb^{208} content (range: 0.075–0.415; mean: 0.284 mg kg^{-1}) was generally above the legal limit too and the mean content resulted 3 times above the limit value. Although higher than the limits, the sample ART 7 taken outside the petrochemical Pole, has a lower Cd^{111} and Pb^{208} content if compared to samples placed inside the Plain of Gela and exposed to air

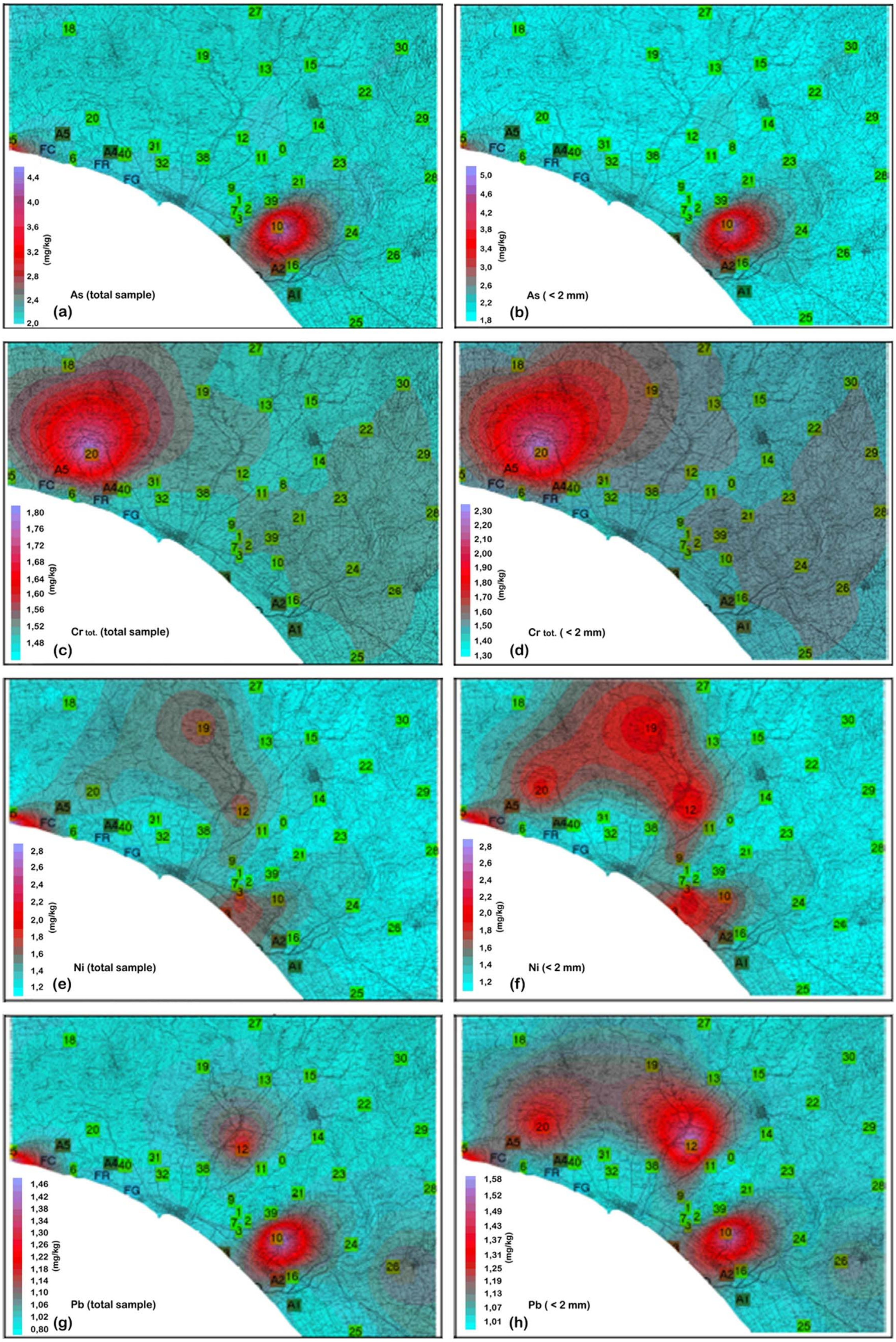

Fig. 2. Iso-concentration map of (**a**) As in total samples, (**b**) As in the fine fraction (< 2 mm), (**c**) Cr in total samples, (**d**) Cr in the fine fraction (< 2 mm), (**e**) Ni in total samples, (**f**) Ni in the fine fraction (< 2 mm), (**g**) Pb in total samples, (**h**) Pb in the fine fraction (< 2 mm) obtained from soil samples collected in the Plain of Gela and districts.

Table 3
Level (mg kg^{-1}) of inorganic contaminants in artichokes. Each analytical data is the result of the average of three samples.

Element	ART 1	ART 2	ART 3	ART 4	ART 5	ART 6	ART 7	ART 8	ART 9	ART 10	ART 11	ART 12	ART 13	ART control	Limit value[a]
Cr^{52}	0.222 ± 0.008	0.312 ± 0.009	0.344 ± 0.018	0.284 ± 0.007	0.285 ± 0.023	0.204 ± 0.012	0.214 ± 0.010	0.181 ± 0.018	0.188 ± 0.023	0.315 ± 0.006	0.322 ± 0.008	0.339 ± 0.020	0.304 ± 0.012	0.110 ± 0.007	–
Ni^{60}	0.453 ± 0.018	0.535 ± 0.014	0.624 ± 0.017	0.537 ± 0.006	0.575 ± 0.005	0.312 ± 0.032	0.205 ± 0.012	0.206 ± 0.004	0.200 ± 0.005	0.505 ± 0.013	0.450 ± 0.016	0.638 ± 0.010	0.512 ± 0.022	0.101 ± 0.006	–
Cu^{63}	2.137 ± 0.057	3.154 ± 0.055	2.489 ± 0.033	2.285 ± 0.026	2.251 ± 0.087	2.085 ± 0.072	2.047 ± 0.072	2.244 ± 0.047	2.231 ± 0.047	3.106 ± 0.042	2.128 ± 0.067	2.498 ± 0.052	2.258 ± 0.061	2.10 ± 0.025	–
As^{75}	0.567 ± 0.009	0.500 ± 0.012	0.365 ± 0.009	0.459 ± 0.006	0.432 ± 0.011	0.389 ± 0.007	0.259 ± 0.010	0.205 ± 0.015	0.232 ± 0.010	0.505 ± 0.014	0.369 ± 0.011	0.577 ± 0.019	0.399 ± 0.015	0.059 ± 0.006	–
Cd^{111}	0.324 ± 0.016	0.313 ± 0.010	0.501 ± 0.021	0.407 ± 0.006	0.437 ± 0.014	0.447 ± 0.009	0.148 ± 0.009	0.041 ± 0.010	0.038 ± 0.009	0.476 ± 0.010	0.324 ± 0.016	0.506 ± 0.024	0.411 ± 0.008	0.032 ± 0.005	0.050
Pb^{208}	0.259 ± 0.007	0.371 ± 0.013	0.404 ± 0.009	0.329 ± 0.006	0.339 ± 0.018	0.224 ± 0.005	0.189 ± 0.005	0.081 ± 0.018	0.075 ± 0.018	0.379 ± 0.012	0.258 ± 0.009	0.415 ± 0.007	0.374 ± 0.005	0.028 ± 0.006	0.100
V^{51}	0.120 ± 0.014	0.157 ± 0.009	0.183 ± 0.011	0.149 ± 0.010	0.140 ± 0.013	0.152 ± 0.031	0.098 ± 0.031	0.073 ± 0.013	0.088 ± 0.013	0.177 ± 0.011	0.148 ± 0.015	0.188 ± 0.011	0.156 ± 0.025	0.049 ± 0.010	–
Hg^{202}	n.d.[b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–

[a] The limit value of Cd and Pb are according the Regulation (EC) No 1881/2006.

[b] n.d.: not detected.

pollutants. The high Cd^{111} levels, also in samples taken otside the industrial area, could be due to the application of fertilizers in agricultural soils, waste incineration, combustion of several materials (Nadal et al., 2004; ATSDR, 1999) and irrigation with polluted water. In relation to high Pb^{208} levels, we can suppose that, although in recent years with the ban on the use of leaded gasoline, the environmental Pb^{208} levels decreased considerably, the current Pb^{208} levels in this area remain significantly high.

For other toxic elements does not exist a law fixing the safety limits, antil now. With regard to As^{75}, the analysis showed high concentrations of this element (range: 0.205–0.577 mg kg^{-1}; mean: 0.404 mg kg^{-1}). The As^{75} levels in artchokes from industrial area were higher than those corresponding to residenzial zone; however, the current As^{75} levels in samples taken otside the industrial area, suggest that pesticide applications, waste inceneration and coal combustion influence As^{75} concentrations (ATSDR, 2000b).

Differences were also found for Ni^{60} and V^{51} between industrial and residenzial area. These elements showed the highest levels in the samples collected near the petrolchemical zone. In particular, V^{51}, Ni^{60} and As^{75} are toxic anthropogenic metals, the sources of which may be attributable to activities related to petroleum processing and combustion of fuel oils that come to crops through the smoke relapse process. A study (Bosco et al., 2005) conducted through biomonitoring on the Pinus halepensis leaves confirmed for the presence of heavy metals from industrial emissions into the atmosphere. Specifically, this study found that heavy metals and non-metals such as V^{51}, Ni^{60} and As^{75} abound in the industrial area of Gela. Moreover, the main source of atmospheric vanadium (about 2/3 of the total) is attributable to the combustion of residual fuels and coats, substances that according to their biological origins frequently contain these metals (ATSDR, 1992).

A separate evaluation must be made for copper since for this element the European Community law does not set a safe limit. The concentrations of this element were high in all the analyzed samples and the test does not show a significant difference between the Cu^{63} levels (range: 2.047–3.154 mg kg^{-1}; mean: 2.378 mg kg^{-1}) in the samples from the two geographical areas (contaminated and non-contaminated). However, its presence in substantial quantities, even in the control samples (2.085 mg kg^{-1}), may be indicative of use of this component in the agricultural practices (Manno et al., 2005).

3.5. Levels of inorganic elements in tomato samples

Table 4 shows the metal and non-metal concentrations in tomato samples collected in greenhouses located to the east, about 600 m from the petrochemical complex, and then downwind. The investigations conducted on tomatoes showed that Hg^{202} levels were under the detection limits, while Cd^{111} concentations (range: 0.022–0.042 mg kg^{-1}; mean: 0.030 mg kg^{-1}) were always below the limits established by Regulation (EC, 2006). As for artichokes, with the exception of a single sample (TOM 13: 0.074 mg kg^{-1}), also for tomatoes the Pb^{208} concentations were above the law limits (range: 0.074–0.263 mg kg^{-1}; mean: 0.190 mg kg^{-1}) and similar or lower than those reported for other tomato samples from different urban sites (Demirbaş, 2010; Mohamed, 2003).

Among the other micro-constiuents, for which do not exist specific law limits, the higher concentrations were observed for Cu^{63} (range: 1.454–2.428 mg kg^{-1}; mean: 1.934 mg kg^{-1}), followed by As^{75} (range: 0.379–0.486 mg kg^{-1}; mean: 0.441 mg kg^{-1}), Ni^{60} (range: 0.284–0.437 mg kg^{-1}; mean: 0.334 mg kg^{-1}) and Cr^{52} (range: 0.241–0.347 mg kg^{-1}; mean: 0.289 mg kg^{-1}). Vanadium showed the lowest residual values (range: 0.124–0.157 mg kg^{-1}; mean: 0.141 mg kg^{-1}). The levels of these elements did not show significant differences among the samples from the different collection zone. Particularly, also the control sample showed high Cu^{63}, Ni^{60}, As^{75} and V^{51} contents; Cu^{63} only were below the mean value and as expected Cd^{111} and Pb^{208} levels were significantly lower.

Table 4
Level (mg kg^{-1}) of inorganic contaminants in tomatoes. Each analytical data is the result of the average of three samples.

Element	TOM 1	TOM 2	TOM 3	TOM 4	TOM 5	TOM 6	TOM 7	TOM 8	TOM 9	TOM 10	TOM 11	TOM 12	TOM 13	TOM control	Limit value[a]
Cr^{52}	0.347 ± 0.018	0.285 ± 0.011	0.275 ± 0.035	0.241 ± 0.016	0.275 ± 0.024	0.268 ± 0.013	0.298 ± 0.011	0.281 ± 0.015	0.292 ± 0.020	0.308 ± 0.011	0.314 ± 0.010	0.259 ± 0.020	0.316 ± 0.014	0.288 ± 0.012	–
Ni^{60}	0.437 ± 0.017	0.330 ± 0.015	0.284 ± 0.011	0.326 ± 0.018	0.307 ± 0.005	0.310 ± 0.021	0.295 ± 0.015	0.306 ± 0.008	0.287 ± 0.006	0.405 ± 0.011	0.382 ± 0.012	0.348 ± 0.012	0.324 ± 0.018	0.337 ± 0.009	–
Cu^{63}	2.250 ± 0.023	2.025 ± 0.012	1.779 ± 0.013	1.933 ± 0.018	1.454 ± 0.009	2.023 ± 0.017	2.428 ± 0.051	1.663 ± 0.024	2.042 ± 0.020	1.732 ± 0.023	2.076 ± 0.010	1.912 ± 0.011	1.826 ± 0.010	1.145 ± 0.010	–
As^{75}	0.486 ± 0.020	0.393 ± 0.012	0.433 ± 0.006	0.379 ± 0.008	0.433 ± 0.020	0.420 ± 0.005	0.473 ± 0.019	0.435 ± 0.018	0.481 ± 0.011	0.433 ± 0.017	0.459 ± 0.012	0.475 ± 0.018	0.439 ± 0.016	0.359 ± 0.008	–
Cd^{111}	0.024 ± 0.006	0.022 ± 0.005	0.040 ± 0.007	0.039 ± 0.006	0.042 ± 0.004	0.023 ± 0.009	0.030 ± 0.008	0.041 ± 0.010	0.025 ± 0.009	0.038 ± 0.010	0.022 ± 0.011	0.023 ± 0.007	0.024 ± 0.008	0.012 ± 0.001	0.050
Pb^{208}	0.203 ± 0.007	0.180 ± 0.013	0.167 ± 0.009	0.234 ± 0.006	0.263 ± 0.018	0.166 ± 0.005	0.259 ± 0.005	0.187 ± 0.018	0.178 ± 0.013	0.180 ± 0.015	0.205 ± 0.009	0.168 ± 0.007	0.074 ± 0.005	0.048 ± 0.006	0.100
V ^{51}	0.157 ± 0.005	0.143 ± 0.015	0.139 ± 0.003	0.124 ± 0.004	0.140 ± 0.008	0.136 ± 0.006	0.152 ± 0.012	0.139 ± 0.010	0.153 ± 0.012	0.147 ± 0.010	0.145 ± 0.014	0.128 ± 0.008	0.134 ± 0.012	0.143 ± 0.011	–
Hg^{202}	n.d.[b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	–

[a] The limit value of Cd and Pb are according the Regulation (EC) No 1881/2006.

[b] n.d.: not detected.

To the best of our knowledge, few data ar reported in literature on mineral contents of “cherry” tomato. Generally, it is stressed that the heavy metals content in tomatoes depends on growth conditions (Rossi et al., 2008). Some data, regarding the mineral composition of different tomato varieties, highlight that Ni^{60} levels found in this study were lower than those previously found in Arab tomatoes (Mohamed, 2003). Relating to Cu^{63} levels, comparing the results of this study with data published by Mohamed (2003) and Demirbaş (2010) for different variety, it emerges that the Arab and Turkish samples had the highest Cu^{63} concentrations (4.47 and 18.7 mg kg^{-1}, respectively); however, our concentrations were similar or higher than the levels determined by Peredens et al. (2008) and Bakkali et al. (2009) for Spanish tomatoes (1.39 and 0.08 mg kg^{-1}, respectively).

In spite of this, troubling is the average content of As^{75}, Ni^{60} and V^{51} in the tomato samples from Gela. As already previously said, these are elements of clear anthropogenic sources, that might reflect the content of such components in groundwater and aquifer. In fact, the greenhouse cultivation of tomatoes that develops to the east, about 600 m from the petrochemical area, is subject primarily to two man-made sources of contamination: the irrigation with contaminated groundwater and farming practices (use of pesticides, fertilizers, etc.). In this case, the metals increase due to relapse fumes may not be predominant since the greenhouse environment might protect the cultures from air pollution. Therefore, the high levels of inorganic elements might mainly be attributed to agricultural practices, and especially the use of groundwater irrigation that appear to be seriously contaminated.

3.6. *Daily intake evaluation*

The mineral composition of artichokes and tomatoes, due to the relatively high detection, was evaluated for some intake considerations. To predict the human exposure we considered the Recommended Dietary Allowance (RDA) values for Cu^{63} and Cr^{52}, which for adult are 1 mg day^{-1} and 0.01 mg day^{-1}, respectively (EC, 2008). The Maximum Residue Limit (MRL), the Tolerable Weekly Intake (TWI) and the Provisional Tolerable Weekly Intake (PTWI) values given by Europe Food Safety Agency (EFSA, 2015, 2012a, 2012b, 2010, 2009a, 2009b) were considered for As^{75}, Cd^{111} and Pb^{208}, (Table 5a,b). CONTAM Panel has established the TWI for Cd^{111} and Hg^{202}, setting, the values at 2.5 µg kg^{-1} b.w. per week and at 4 µg kg^{-1} b.w. per week, respectively (EFSA, 2009b, 2012a). The joint FAO/WHO Expert Committee on Food Additives set the PTWI of 15 µg kg^{-1} b.w. per week for As^{75} and 25 µg kg^{-1} b.w. per week for Pb^{208} (EFSA, 2009a, 2010). The CONTAM Panel, since the PTWI is no longer appropriate and in order to make these values more health protective, identified a benchmark dose of 1% extra risk ($BMDL_{01}$). The $BMDL_{01}$ values for As^{75} and Pb^{208} are 0.3–8 µg kg^{-1} b.w. per day and 1.5 µg kg^{-1} b.w. per day, respectively (EFSA, 2009a, 2010). Moreover, in February 2015, EFSA published a scientific opinion on the risks to human health from nickel in food, particularly in vegetables, and also in drinking water. Based on current mean and high exposures, EFSA's experts concluded that current chronic dietary exposure to Ni^{60} is of concern for the general population; therefore EFSA set a safe level, known as the Tolerable Daily Intake (TDI), of 2.8 µg kg^{-1} b.w for Ni^{60} (EFSA, 2015). For Vanadium no benchmark dose was fixed.

In order to make an assessment on the results of this study, Cd^{111}, Hg^{202}, As^{75}, Ni^{60} and Pb^{208} dietary intake, for an adult (60 kg) deriving from a daily ingestion of 300 g tomatoes and artichokes, was compared with these values, the results are reported in Table 5a, b. In order not to underestimate the contamination intake, a concentration equal to LOQ (0.003 µg kg^{-1}) was assigned to all samples that showed a non-quantifiable amount of Hg^{202}. All the analyzed samples do not exceed PTWI values for Hg^{202}. Compared to the safety standards the results of the present study show that: Cu^{63} content in artichokes (71.3%) and tomatoes (58.0%) remains within the RDA margins while Cr^{52} surpasses the RDA limit both for artichokes (202.5%) and tomatoes (216.8%);

Table 5
Mean values for RDA, TWI, PTWI BMDL01 (n = 13) for **a)** artichoke and **b)** tomato samples.

	Cu	Cr	Ni	As	Cd	Pb	Hg
a)							
Mean values (mg/Kg/ww; n = 13)	2.378	0.270	0.442	0.404	0.336	0.284	0.003 × 10^{-3}
RDA (mg × day^{-1})	1	0.04					
% of RDA estimated by mean value	71.3	202.5					
MRL (mg × kg^{-1} w/w)					0.1	0.3	0.5
TWI or PTWI (mg/kg b.w./week)				0.015	0.0025	0.025	0.004
TDI (μg/kg b.w./day)			2.8				
BMDL01 (μg/kg b.w./day)				0.3–8		1.5	
% of TWI or PTWI estimated by mean value				94.27	470.40	39.76	0.00
% of TDI estimated by mean value			78.93				
% of BMDL01 estimated by mean value				25.25–673.33		94.67	
b)							
Mean values (mg/Kg/ww; n = 13)	1.934	0.289	0.334	0.441	0.030	0.190	0.003 × 10^{-3}
RDA (mg × day^{-1})	1	0.04					
% of RDA estimated by mean value	58.0	216.8					
MRL (mg × kg^{-1} w/w)					0.1	0.3	0.5
TWI or PTWI (mg/kg b.w./week)				0.015	0.0025	0.025	0.004
TDI (μg/kg b.w./day)			2.8				
BMDL01 (μg/kg b.w./day)				0.3–8		1.5	
% of TWI or PTWI estimated by mean value				102.90	42.00	26.60	0.00
% of TDI estimated by mean value			59.64				
% of BMDL$_{01}$ estimated by mean value				27.56–735.00		63.33	

Ni^{60} does not exceed the corresponding TDI limit both in artichokes (78.93%) and tomatoes (59.64%); Cd^{111} remains within safety margins of TWI only for tomatoes (42.00%) while exceeds these values in artichokes (470.20%); the extra-safety margin of BMDL$_{01}$ are within the safety limits for Pb^{208} in tomatoes (63.33%) and artichokes (94.67%) while As^{75} surpasses these values both in artichokes and tomatoes with (25.25–673.33%) and (27.56–735.00%) of BMDL$_{01}$, respectively.

4. Conclusions

This study confirm the epidemiological hypothesis that indicated in the consumption of local food products one of the most important factors of exposure to toxic elements, particularly arsenic. Agro-foodstuffs such as artichokes showed high Cd and Pb concentrations that often abundantly exceeding, in almost all the analyzed samples, the limits set by Regulation (EC, 2006). The monitoring of toxic metals in tomato samples evidenced that, while Cd levels were always below the fixed European limits, the Pb content is significantly higher than that reported by the Regulation (UE) limits for this metal.

The evaluation of dietary intake of Cd, Pb, Ni and Hg, deriving from a daily ingestion of 300 g of artichokes and tomatoes in an adult (60 kg), shows that eating artichokes exposes the Gela consumers to a worrying cadmium intake. Moreover, our data demonstrate that arsenic amount is above the respective benchmark limit, both in artichokes and tomatoes. Particularly, since the CONTAM Panel focused on more recent data showing that exposure to arsenic and inorganic arsenic compounds increases the risk of cancer (EFSA, 2009a), the high presence of arsenic in artichokes and tomatoes might determine important cancer risk for the consumers, so it would be recommended that dietary exposure to inorganic arsenic should be reduced.

The sources of pollution, responsible for the food products contamination, could be attributable mainly to the use for the irrigation of groundwater, severely contaminated by heavy metals; although, the relapse to the ground of the combustion fumes coming from the petrochemical complex can affect the metal pollution of the soil.

Our study show that there is a serious risk of toxic minerals from artichokes and tomatoes grown on the Plain of Gela; this hazard could be even more serious when you consider that to individual foods analyzed, you must add the contribution of toxic elements from the other foods that make up a diet (water, meat, dairy products, etc.). The interesting informations obtained, however suggest the need to deepen the critical scenarios that have emerged.

We believe that to reduce the health risk it is necessary and urgent to initiate the remediation of the aquifer, limit the use of local groundwater for crops irrigation, avoid implanting agricultural productions in downwind areas and/or in proximity to petroleum plants, reduce emissions of pollutants through the use of new technologies and the periodic maintenance of industrial plants. We can suggest a limited consumption of artichokes and tomatoes coming from the Plain of Gela to prevent a metal accumulation in the human body.

Acknowledgments

We especially thank our colleague and friend Maria Alfa, which has left us for another life and that began the study with Tiziano Granata.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2017.10.015.

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