Arsenic in soil, leaves, grapes and wines

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ABSTRACT
The presence of arsenic in food and beverages creates concern because of the toxicity of this element, classified as carcinogenic in humans. The arsenic concentration in soil, vine leaves and berries (cv. Chardonnay) and white wines was studied, considering vineyards near to an old mining area (naturally rich in As), in comparison with others from uncontaminated areas in Trentino (Italy).
All analyses were performed using an inductively coupled plasma mass-spectrometer.
In soil, the *acqua regia* extracted As ranged from 3.7 to 283 mg/kg, whereas bioavailable As varied from 18 to 639 mg/kg. As in washed and acid mineralised leaves and berries was between 16.3-579 mg/kg dw and between <0.1-36.8 mg/kg dw, respectively. As content in wines was always <1.4 mg/L. Pearson's test showed significant and positive correlations between the As concentrations in soils, leaves and berries. The samples collected near the mining area showed significantly higher As concentrations.

Keywords: arsenic, plant uptake, soil, wine, human health risk.

1 INTRODUCTION

Arsenic is a widespread element and its origin could be both natural and anthropogenic [1].
The total As concentration in uncontaminated soils varies from <0.1 to 95 mg/kg with a mean <10 mg/kg whereas contaminated soils can reach up to 600 mg/kg or more [1, 2].
The biohazard of As is linked to its mobility and availability in soils mainly affected by pH, redox potential and the presence of Mn, Al and Fe oxides [2].
As is mainly accumulated in roots and old leaves and can reach up to 1500 µg/kg of dried weight (dw) in plant tissues [1]. Concentrations over 2000 µg/kg dw are considered phytotoxic [3]. In vine leaves, As ranges from 60 to 410 µg/kg dw [4]. In ripe berries, total arsenic is distributed mainly in pulp and skin; only 10% is localized in the seeds [5].
In wines As concentration varies from <0.5 to 17 µg/L [6-11]. The level on the final product can rise as a consequence of oenological treatments such as bentonites or fossil shell flours [12, 13].
The As and its compounds are classified as carcinogenic or possible carcinogenic to humans by the International agency for Research on Cancer. For this reason and because of the very few evidences regarding the As transfer through the soil-vine-wine chain, the aim of this study was to assess the possible risk of As intake related to the consumption of grapes and wines produced in vineyards located in an old mining area.

2 MATERIALS AND METHODS

28 different vineyards located in Trentino (north-eastern Italy) were studied from 2006 to 2009. 10 of these sites were close to a mining area no longer in use, where there were present deposits of arsenopirite, and other sulphide minerals containing As traces. For each vineyard, soil, leaves and berries were sampled.
The 'pseudototal' arsenic (As_T) was determined using the ISO 11466/1995 method. Bioavailable arsenic (As_B) was determined after extraction with ammonium acetate 1M pH 7 [14]. Top soil (TS, 5-30 cm) and sub-soil (SS, 30-60 cm) were studied separately.
Leaves, collected close to harvest, were washed with 0.2% citric acid, rinsed with ultrapure water, dried at 35°C and ground. The berries were picked at ripeness, washed with a 1% HNO_3, rinsed, blotted, frozen and homogenized. A comparison test between washed and unwashed berries was performed in order to quantify As deposits on the outer surface of the skin.
The As content in leaves and berries was determined after mineralization in a microwave system (max. temperature 210°C) [5].
Grapes (50 kg) coming from the mining areas were microvinified following the typical procedures for white wines using different yeast.
As was quantified using an inductively coupled plasma mass spectrometer Agilent 7500ce (Agilent Technologies, Tokyo, Japan) equipped with a collision cell (He mode) for the removal of polyatomic interferences.

3 RESULTS

The median As_T value was 11.4 mg/kg (min-max: 3.7-283 mg/kg, Fig. 1). The plots near the mining areas presented a median value significantly higher than the other plots studied (26.4 *vs* 10.5 mg/kg respectively; Mann-Whitney U test; $p<0.05$, $n = 56$). Seven vineyards showed As_T concentrations above 20 mg/kg, the maximum level indicated by Italian law for agricultural soil. and three out of seven had levels >50 mg/kg. All were sited near the mining area, one excluded. The average ratio between As_T in the TS and SS was 1.1 suggesting a natural geological origin of As.
The As_B median content was 108.0 µg/kg (18.0-639 µg/kg). The mining areas showed As_B levels higher

than other plots (median 169 µg/kg *vs* 76.7 µg/kg respectively, p<0.001). Acid or subacid soils presented higher content on As_T than subalcaline soils (Mann-Whitney U Test, p<0.001), probably due to the greater values of Fe, Mn and Al-oxides (data not shown) which can adsorb As [1, 15]. Five out of nine acid soils were close to the mining area. The remaining four acids soils showed anyway As_T content higher than 10 mg/kg with the only exception of one sample.

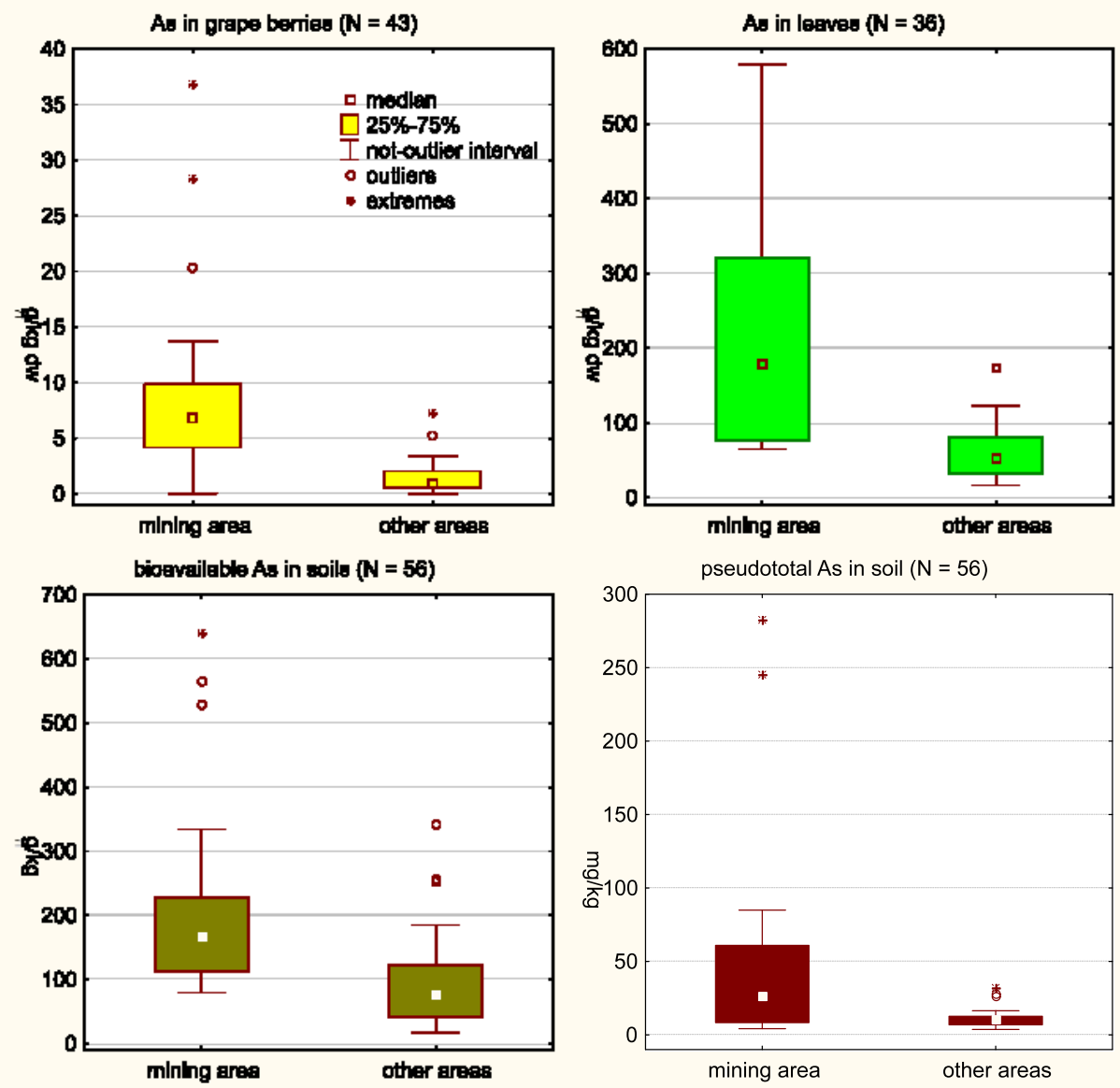

Figure 1. Distribution of the As content in soils, leaves and berries between mining areas and the areas of the sites studied.

The As_B/As_T ratio was lower than 5%, according to literature [16, 17], even though there been reported ratios ranging from 5 to 10% in Croatian vineyards soils [18]. Subalcaline soils had As_B/As_T ratios significantly higher than subacid soils (Mann-Whitney U Test, p<0.001) because of the mobility of As, that increases with higher pH, and the Ca-arsenate dissolution.

Leaves (N=36) presented a median value of 70.5 µg/kg dw (16.3-579 µg/kg dw) confirming the values reported by Ko et al. [4]. The mining areas showed significantly greater levels compared with the remaining sites (median values: 179.0 µg/kg *vs* 52.6 µg/kg respectively, p<0.001).

The bioconcentration factor (BF, defined as the ratio between As in leaves and As_T in soils) has been calculated considering the average value for each vineyard. These values ranged between 0.002 and 0.017 with a median value of 0.007, and are distinctive for mineral elements hardly taken up by plants [19, 20]. The Mann-Whitney U Test did not highlighted differences between the two areas studied.

As median concentration in washed grape berries (n=43) was 2.06 µg/kg dw (<0.10 to 36.8 µg/kg dw). Only one site showed values over 24.2 µg/kg, the average concentration for European vegetables according to Al Rmalli et al. [21]. These values were consistent to those found in Chinese raisins [22] and Chardonnay grapes [5], but much lower than those reported by Ko et al. [4]. The mining areas showed an As content in berries significantly higher than the other sites (median value: 6.81 µg/kg dw *vs.* 1.04 µg/kg dw

respectively, p<0.001). All grapes with As levels <DL were collected from alkaline soils, nevertheless some grapes grown on acid soils had also lower As concentration.

Washed berries showed a reduction of As_T ranged from 13 to 33% as compared to unwashed berries in accordance to literature [23].

Arsenic median concentration in white wine (n=70) was 0.60 µg/L (0.09-1.39 µg/L). These results are in accordance to recent literature that reports As content in wines ranging from <0.5 to 17 µg/L [6-11] but far below from those reported in the past [24] or from the limit suggested by the International Organization of Vine and Wine.

There is a highly significant and positive correlation (Pearson test, p<0.001) between berries and leaves content (n=36, r=0.789), and between berries content and As_T and AS_B (n=43; r=0.684 and r=0.559 respectively) suggesting a passive uptake of As by plants [1]. A positive trend between the As content in unwashed berries and wines could be highlighted, but it is not statistically significant, probably due to the similar amounts of As content in the wines produced.

4 CONCLUSIONS

Near mining areas the As_T, As_B, leaves and berries As content of the samples collected was significantly higher. However this content in berries and wines is very low and does not represent a risk for human health according to the tolerable weekly intake (PTWI, 15 µg/kg of body weight) for As set by FAO/WHO and the limit (200 µg/L) suggested by OIV for wines.

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