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Eliane El Hayek, Antoine Samrani, Bruno Lartiges, Veronique Kazpard, Mathieu Benoit, et al.. Air pollution biomonitoring using successive cladodes of *Opuntia ficus-indica*: A lead isotopic study. Environmental Science and Pollution Research, 2015. hal-02182871

HAL Id: hal-02182871

<https://hal.science/hal-02182871>

Submitted on 13 Jul 2019

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Air pollution biomonitoring using successive cladodes of *Opuntia ficus-indica* : A lead isotopic study

El Hayek Eliane^{a,b*}; El Samrani Antoine^b; Lartiges Bruno^a; Kazpard Veronique^b, Benoit Mathieu^a, Munoz Marguerite^b

^a University of Toulouse (Paul Sabatier), Laboratoire Géosciences Environnement Toulouse (UMR CNRS-UPS 5563 IRD 234), 14 Av. Edouard Belin, 31400 Toulouse, France.

^b Lebanese University, Plateforme de Recherche et d'Analyses en Sciences de l'Environnement, Ecole Doctorale des Sciences et Technologies, Hadath, Lebanon.

***Corresponding author:** El Hayek Eliane (elianehayek@hotmail.fr)

Abstract

Opuntia ficus-indica (*Ofi*) is a long-domesticated cactus that is widespread throughout arid and semiarid regions of the world. *Ofi* is grown for both its fruits and edible cladodes, which are flattened photosynthetic stems. Young cladodes develop from mother cladodes, thus forming series of cladodes of different ages. Therefore, successive cladodes may hold some potential for biomonitoring over several years the local atmospheric pollution. In this study, cladodes, roots, dust deposited onto the cladodes, and soil samples, were collected in the vicinity of three heavily polluted sites, *i.e.* Selaata fertilizer industry (Lebanon), the roadside of a highway near Saida (Lebanon), and the tailings of an abandoned lead-zinc mine (Jebel Ressay in Tunisia). The lead content was analyzed by Atomic Absorption Spectroscopy and ICP-MS, Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) was used to characterize the cladode surfaces and the nature of dust deposit, and the lead isotopes were analyzed to identify the origin of Pb. The results show that (i) *Ofi* readily bioaccumulates Pb, (ii) the lead isotopic composition of cladodes evidences a foliar pathway of lead into *Ofi* and identifies the relative contributions of local Pb sources, (iii) the evolution of air quality is effectively recorded with successive cladodes, which makes *Ofi* a promising biomonitor to be used in environmental and health studies.

Keywords: *Opuntia ficus-indica*, atmospheric deposit, lead isotopes, SEM-EDX, biomonitoring.

1. Introduction

Personal exposure to airborne contaminant particles has long been known to promote illnesses such as lung cancer, and respiratory and cardiovascular diseases (Hoek et al., 2002; Peters and Arden Pope, 2002; USEPA, 1996). To identify and monitor the sources of aerosol pollutant emission is therefore essential in most environmental and health studies (Goix et al., 2011). Biomonitoring methods using species such as lichens, mosses, tree barks and leaves, have been increasingly applied since the 1970s (Catinon et al., 2009; De Bruin and Hackeniz, 1986; Goodman and Roberts, 1971; Szczepaniak and Biziuk, 2003; Tomašević et al., 2013). Indeed, such bioaccumulators offer cost-effective alternatives to traditional air-pollution stationary measuring systems by enabling a time-averaged recording of surrounding atmospheric particles (Orecchio and Amorello, 2010; Wolterbeek and Verburg, 2002; Wolterbeek, 2002). The spatial resolution of such survey can even be improved by transplanting the biomonitoring species from pristine areas to polluted regions (Bari et al., 2001; Carreras et al., 1998). Nevertheless, such lichen transplants sometimes require long-exposure durations (over one year) to yield appropriate atmospheric records (Ayrault et al., 2007). Moreover, the "memory length" of lichens has been shown to depend on many factors such as meteorological conditions, seasonal growth and thallus type and age (Conti et al., 2004; Godinho et al., 2009).

Until now higher plants have generally been considered less interesting for environmental control studies because of their relatively low spatial distribution (Loppi et al., 1998). In this study, we assess the potential of *Opuntia ficus-indica* (*Ofi*) as a biomonitor of atmospheric pollution. *Ofi* is one of the most popular species of the cactaceae family, is largely distributed in semi-arid habitats over the world (Ghaffari et al., 2013; Nobel, 2002), and could remedy to the lack of air quality biomonitors in arid and semi-arid regions. Indeed, *Ofi* is formed of flattened photosynthetic stems called cladodes, each new cladode developing from an older cladode (Nobel, 2002). The cladode surface possesses a surface roughness that expresses in terms of areole (where trichomes and glochids develop), large stomata, and cuticular wax (Booke, 1980; Nobel, 2002), that may favor the retention of airborne contaminant particles (Schreck et al., 2012; Uzu et al., 2010).

Three sites, exposed to different sources of atmospheric pollution *i.e.* fertilizer industry, road traffic, and mine tailings, were selected. This study focuses on lead, a major contaminant in the environment. The origin of Pb uptake by *Ofi* was investigated from lead isotope measurements on roots and cladodes of successive generations. Lead isotopic compositions do not undergo any physical or chemical fractionation in biological or industrial processes (Ault et al., 1970), thus providing a reliable fingerprint to identify contaminant sources (Chenery et al., 2012). Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray Spectroscopy (EDX) was also used to examine the particulate contaminants deposited on cladode surfaces. To our knowledge, this is the

first study that combines isotopic analyses and microscopic observations to investigate the pathway of lead uptake in the case of a higher plant.

2. Experimental section

2.1. Study sites

Ofi exposure to atmospheric deposition was investigated in three polluted areas located around the Mediterranean coast (Fig. 1). Selaata fertilizer plant, situated in north Lebanon, emits high amounts of dust generated from the dry milling of phosphate ore (essentially fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) and the processing of treatment residues (phosphogypsum and fluorite) stored temporarily on site (Fig. 1a) (Aoun et al., 2010; Yammine et al., 2010). Such dust particles are strongly contaminated with radioactive elements and heavy metals (Al-Masri et al., 2004). The Selaata area has been the subject of numerous environmental studies to assess the pollution of local soils, sediments, seawater, and atmosphere (Abi-Ghanem et al., 2009; Aoun et al., 2010; Yammine et al., 2010). In addition to the phosphate industry pollution, the heavy truck traffic associated with the operation of the fertilizer plant has been found to be a significant source of air pollution (Yammine et al., 2010). Figure 1a shows that *Ofi* cactuses at Selaata are located 650 m northeast of the fertilizer industry. Because of dominant winds, this particular spot is frequently exposed to the dusty air generated from the fertilizer plant (Aoun et al., 2010). According to Yammine et al., (2010), a Pb level of about 17 ng/m^3 can be expected in the airborne contaminant particles.

The second study site is situated at the entrance of Saida city (Fig. 1b), 40 km south of Beirut, next to the coastal busy highway linking Beirut to Saida (150,000 vehicles/day). Saida city has recently been reported as one of the air pollution hot spots in Lebanon with a very high level of $\text{PM}_{2.5}$ (UNEP-ROWA, 2012). The road traffic, essentially motor vehicles exhausts, represents the principal source of atmospheric contamination in lead at this site. Because of local land breeze and sea breeze phenomenon, the dominant wind direction is roughly perpendicular to the cactus cladodes that in turn are approximately parallel to the highway.

The third site, Jebel Ressas, literally the lead mountain, is a Zn-Pb abandoned mine located 30 km south of Tunis (Tunisia). As illustrated in figure 1c, the cactuses grow nearby an old tailing dump subject to water and wind erosion (Ghorbel et al., 2014). According to Ghorbel et al., (2014) the lead concentration in PM_{10} aerosols reaches $5.7 \text{ } \mu\text{g/m}^3$ at that spot.

2.2. Sampling methodology

Three successive cladodes from the same stem, *i.e.* three generations of shoots, were sampled in triplicate at Selaata field site. Only one series of cladodes could be studied at Saida and Jebel Ressas. The cladodes are fixed structures, most generally oriented east-west in order to maximize light interception (Nobel, 1982). Although the angle between the cladodes surface and the prevailing wind may change, no significant difference in lead level could be detected between both sides of cladodes (Fig. S1 in Supporting Information). Obviously, within a series of cladodes, the exposure to atmospheric deposition may vary according to the position within the stem. Mature cladodes may also become less exposed with the development of younger cladodes. To reduce such sampling biases, the series of cladodes collected were selected to present what seemed equivalent exposures to atmospheric deposition (Fig. S2 in Supporting Information).

Shallow roots of *Ofi* and topsoil (15 cm depth using a stainless steel scoop) were also taken at Selaata and Saida. Dust particles deposited on cladode surfaces were collected using a soft brush. All samples were kept in sealed polyethylene bags until analysis.

2.3. Total lead analysis

The collected cactus cladodes were thoroughly rinsed with milli-Q water (18.2 M Ω) to eliminate dust residues on the surface. For plants used as biomonitors of atmospheric pollution, the washing procedure is always an issue (Calliari et al., 1995; Godinho et al., 2009). In the case of edible plants such as cladodes of *Ofi*, a thorough washing is generally applied to conform to the usual practice of food preparation (Schreck et al., 2013; Uzu et al., 2010). Nevertheless, as shown in figures S1 and S3 of supporting information, the level of lead in cladodes is here barely influenced by the washing.

The cladodes were sliced with a ceramic knife into small cubes that were freeze-dried (Alpha 1-4 LD Christ), and further ground using a cooking plastic grinder (Braun) to a homogeneous fine powder sieved at 1 mm. The cladode powder was stored in sealed plastic bags. *Ofi* roots were also repeatedly washed with deionized water, before being oven dried at 60 °C for 48h. Soil samples were similarly dried before being sieved through a 50 μ m mesh nylon screen.

Cladodes and roots collected at Selaata and Saida were mineralized following the Alexander et al., (2006) digestion procedure. In brief, 1g samples were kept overnight in 70% nitric acid solution (20 mL), before being progressively heated, and finally filtered at 0.45 μ m. The Pb content was measured in triplicate for each cladode and root sample using flame atomic absorption spectrometry (Rayleigh WFX-210AA). The maximum standard deviation for each triplicate was found to be 2% unless otherwise stated (Table 1). The Pb concentration in Jebel Ressas samples, surface soil of Saida and phosphogypsum of Selaata was analyzed by ICP-MS (Agilent 7700X) at SARM-CRPG (Nancy, France).

2.4. Lead isotopic analysis

All samples for Pb isotopic analyses were prepared in a clean room. They were first dissolved by acid digestion (mixture of bi-distilled ultrapure HNO₃ and HCl acids) in a microwave digestion system (MARS 5 system CEM). Lead was then extracted from the solution by ion-exchange column (polyethylene column packed with a fine layer of purified Sr resin, the resin being first conditioned with various purified acids). The preconcentrated lead was eluted using successively HNO₃ 3 N and then 0.05 N, the pure Pb fraction being collected in 4 mL of HCl 6 N. Based on the lead concentration in each sample, a given aliquot was taken and mixed with H₃PO₄ 0.05 N before being evaporated at 120 °C. The residue was then mixed with 2 µL of silica gel and deposited on a clean rhenium filament. To ensure an effective lead ionization during analysis, an electric current was applied to the rhenium filament until the deposited solution was dried.

The Pb isotopic composition was analyzed using a Thermal Ionization Mass Spectrometer TIMS (MAT 261, Finnigan). The NBS 981 lead isotope standards were run at the beginning and between all unknown samples following a standard bracketing procedure. The standard error of measurement was below 0.2% for ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios and the normalized corrected values represented a typical uncertainty of 1% because the lead concentration in some samples was very low (Frostick et al., 2008). The total procedural blank values were less than 134 pg.

2.5. SEM-EDX examination of cladodes and atmospheric fallouts

Small pieces of freeze-dried cladodes and dust deposits were observed using a scanning electron microscope (Jeol JSM 6363LV) equipped with a Silicon Drift Detector (SDD) PGT operating at 20 kV for chemical analysis. The particles and plant fragments were placed on double sided adhesive conductive carbon tape and coated with carbon.

3. Results and discussion

3.1. Lead levels in cladodes, soils, and dust

Table 1 lists the Pb concentrations of cladodes, roots, surface soils, and dust deposited on cladodes, found at the three contaminated sites. The Pb contamination is obvious in the soil samples collected at Selaata ($54.8 \pm 20.6 \text{ mg.Kg}^{-1}$) and Saida (168.2 mg.Kg^{-1}). However, at Jebel Ressas, the lead contamination remains relatively weak compared with the local significant level (2200 mg.Kg^{-1}) (Souissi et al., 2014).

Although the lead levels measured in topsoils at Selaata and Saida are in excess of the agreed limit for unpolluted cultivated soils ($> 56 \text{ mg.Kg}^{-1}$) (Davies, 1995; Herselman et al., 2005; Jin et al., 2005), the cactuses showed no signs of adverse effects such as growth reduction or impaired photosynthesis (Nagajyoti et al., 2010). The lead concentration in *Ofi* roots remains even close to the natural range ($1.5\text{-}2.4 \text{ mg.Kg}^{-1}$) observed for plants cultivated in non-polluted areas (Kabata-Pendias, 2010). In contrast, all the cladodes collected in this study indicate a significant Pb contamination. Such contamination ranges from an average 5.59 mg.Kg^{-1} at Saida, 16.7 mg.Kg^{-1} at Selaata, to reach a Pb level high of 83.2 mg.Kg^{-1} at Jebel Ressas. Unlike Selaata and Saida sites where the lead level in the series of cladodes is almost constant (Fig. S3 in supporting information), the concentration of Pb in the cladodes increased significantly with exposure duration (*i.e.* cladode maturity) at Jebel Ressas.

The Translocation Factor (TF), defined as the ratio of metal concentration in aerial parts to that of roots (García-Salgado et al., 2011), was greater than 1 at both Selaata (TF=9.28) and Saida (TF=1.8). The process of root absorption and translocation is usually negligible in most plants cultivated on soils polluted with lead (Davies, 1995). In addition, several previous studies suggested a predominant metal uptake from foliar deposits rather than from root exposure (Dalenberg and Van Driel, 1990; Komárek et al., 2007). In our case, the cladodes are exposed to a considerable amount of Pb-enriched dust, *e.g.* the lead concentration in the atmospheric fallouts reaches 102.6 mg.Kg^{-1} in Selaata. Therefore, the atmospheric deposition of lead-bearing dust on aerial parts likely contributes to the contamination of cladodes observed at all sites.

3.2. Examination of cladode contaminated surface by SEM-EDX

A direct speciation of particles deposited on the cladodes was conducted using SEM-EDX in the Backscattered Electron Imaging mode to locate the particles of interest. As indicated in previous reports (Schreck et al., 2012), the washing protocol of cladodes only partially removes the particles deposited on the surface. In general, the atmospheric fallout mainly consists of soil-derived minerals, *i.e.* quartz (a), dolomite (b), iron oxyhydroxides (c), and clays (d) (Fig. S4 in supporting information). At Selaata, occurrences of fluorapatite, around 10 to 50 μm in size (Ca/P elemental ratio of 1.7) (Fig. S5), and less frequently phosphogypsum (essentially $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), were also identified, thus making obvious the presence of contaminant particles originating from the fertilizer plant on the cladode surfaces. Based on the chemical analysis of about 300 particles per cladode, it was found that the number percentage of particles emitted by the fertilizer plant remained around 8% regardless of the cladode age. The remaining 92 % correspond to soil particles. Pb could not be detected by EDX in the particles due to the relatively low detection limit of the technique ($> 1000 \text{ mg} \cdot \text{Kg}^{-1}$ for Pb).

Likewise, at Saida, the dust collected on the cladodes was mainly composed of soil particles although particles of barite, stainless steel, and zinc oxide, all consistent with a traffic-related pollution (Chow et al., 1996; El Samrani et al., 2004), were identified (Fig. S6 in Supporting Information). The sea breeze phenomenon at this site was also evidenced by the presence of numerous salt particles.

At Jebel Ressas, previous SEM examination of particles from the tailing dump located nearby the investigated cactus, revealed various lead-bearing particles such as galena (lead sulfide), cerussite (lead carbonate), anglesite (lead sulfate), and lead in iron oxyhydroxides (Ghorbel et al., 2014).

SEM also provided the opportunity to examine the main features of cladode surfaces. As illustrated in figure 2, epidermal cell walls seen through the cuticle in BEI mode, stomata which size increases from about 15 μm to 50 μm with the cladode age, and areoles, define various scales of roughness that contribute to the setting of airborne particles. The increased size of stomata and the presence of a thick rough cuticle on the surface of old cladodes, suggest that the probability of particles capture might evolve with the cladode age. The trapping of fluorapatite particles ($\sim 7 \mu\text{m}$ in size), both in the vicinity and inside a stomata, is shown in figures 2a and 2b. In addition, figure 2c also shows a calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) aggregate secreted by *Ofi* in close contact with a particle made of calcium and fluorine. Calcium oxalate crystals are very frequent in the epidermal tissue of cactaceae (Fig. 2a) (Nobel, 2002). The identification of such an association within a stomata may provide an interesting clue to the foliar pathway uptake of lead. Indeed, the extracellular calcium oxalate may react with the trapped aerosols and oxalate may sequester the released metal ions (Mazen and El Maghraby, 1998). Metal absorption through stomatal pores has been identified in several studies (Schreck et al., 2012). Sarret

et al., (1998) also reported the participation of organic acids produced by lichens in the immobilization of metals imported by atmospheric particles. Therefore, such observation is in agreement with a bioaccumulation process of trace elements driven by a foliar uptake (Vianna et al., 2011).

3.3. Isotopic identification of lead sources in *Ofi* cladodes

To substantiate the uptake pathway of lead in *Ofi*, lead isotopes ratios were measured in cladodes, roots and the soils near the cactuses investigated. Figure 3 shows the plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ for the analyzed samples, as well as the isotopic compositions of galena at Jebel Ressas (Jemmali et al., 2011) and of soil samples cored in the vicinity of the cactuses investigated at Selaata. All the Pb-isotopic compositions fall on a mixing line between lithogenic Pb and leaded-gasoline end-members. Not surprisingly, the isotopic signature of cladodes collected at Jebel Ressas is close to that of crustal sources and coincides with that of Zn-Pb minerals present at this mining site ($^{206}\text{Pb}/^{207}\text{Pb}=1.207$; Jemmali et al. 2011). At the other end of the mixing line, the Pb isotopes ratios of cladodes and root sampled at Saida are roughly distributed between the isotopic compositions of unleaded and leaded gasoline ($^{206}\text{Pb}/^{207}\text{Pb}=1.106$; Erel et al., 1997). Interestingly, the isotopic signatures of the elder cladode, of the root, and of the topsoil, lean toward the leaded gasoline end-member. In Lebanon, the use of leaded gasoline was banned in 2002 (Kaysi et al., 2000). Previous studies showed that, despite the implementation of a restrictive legislation, the level of lead exposure remains high for years because of (i) the historical accumulation of this pollutant in soils and the possible re-suspension of soil particles (Davies, 1995; Pain, 1995), and (ii) the continuous, although illegal, use of leaded gasoline. Therefore, the gradual change in Pb-isotopic composition with cladode age observed at Saida should essentially reflect the transition from a previous exposure of cactuses to leaded gasoline to the current exposure to Pb from unleaded gasoline.

The isotopic signatures measured in cladodes and soil samples of the fertilizer plant site in Selaata also show a significant spread along the mixing line, knowing that the distribution of individual corrected isotope delta values presented a relative deviation that exceeded the 0.01 percent relative uncertainty. The younger cladodes indicate an increased exposure to anthropogenic activities, whereas the Pb-isotope composition of soil samples is shifted towards more radiogenic values with depth. Actually, the nature of anthropogenic activities at Selaata covers not only the release of apatite and phosphogypsum particles generated during the processing of phosphate ore and phosphogypsum waste, but also the heavy truck traffic associated with the operation of the fertilizer plant (Yammine et al., 2010). The strong contribution of lead from gasoline emissions to the isotope ratios measured in cladodes can be evidenced by including the lead isotopic signature of phosphogypsum in the $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ plot (inset

of Fig. 3), that is commonly used to discriminate between point sources (Graney and Landis, 2013). In that plot, a strong correlation ($R^2 = 0.98$) is observed between the lead isotope ratios of cladodes, roots, soils, and gasoline, whereas radiogenic phosphogypsum remains an outlier. Therefore, gasoline emissions and more exactly unleaded gasoline, represents the main lead atmospheric local pollution in the Selaata area. Such influence of leaded petrol had already been evidenced in the nearby industrial area of Chekka which showed lead isotopic signatures attributed to French and German alkyl producers (Bollhofer and Rosman, 2001).

To estimate the relative contributions of soil particles and unleaded gasoline emissions end-members to the lead pollution of cactus cladodes and roots, a simple binary model was applied (Hu et al., 2011). Lead from gasoline represented an input of about 56.4%, 62.6%, 77.2% and 72.7% for the root, the oldest cladode, the middle cladode, and the youngest cladode, respectively. Not knowing the operating history of the fertilizer plant (e.g. delivery of the phosphate ore by boat or by truck), the increased exposure of younger cladodes to the gasoline emissions cannot be reliably explained. As older cladodes are characterized by larger stomata and a rougher surface, a size-sorting phenomenon of airborne particles similar to that evidenced by (Cloquet et al., 2009) could also be invoked. Nevertheless, as both topsoils, roots, and younger cladodes, possess Pb-isotopic signatures significantly different from each other at both Saida and Selaata, and keeping in mind that the lead isotopic compositions should not undergo any fractionation during biological or industrial processes (Ault et al., 1970), it is clear that the foliar uptake pathway of lead is predominant for *Ofi* in presence of atmospheric fallouts.

4. Concluding remarks

Our study reveals that cladodes of *Opuntia ficus-indica* readily capture airborne particles, thus recording the local atmospheric pollution. The stupendous capacity of *Ofi* to conserve its ancient aerial reproductive system provides the opportunity to identify previous source emissions of heavy metals over several years. Thus, at both fertilizer plant and road traffic sites, the change in isotopic signature in the series of cladodes clearly indicates an evolution of local air quality with time. As a cosmopolitan plant often planted in the vicinity of human dwellings, *Ofi* appears to be a promising biomonitor to be used in environmental and health studies. Several key-points have yet to be clarified such as determining the precise age of any cladode, identifying the mechanisms of foliar uptake of heavy metals (Pb and others than Pb) and their possible translocation in the plant or developing daughter cladodes. Such issues will be addressed in a follow-up paper.

Acknowledgments: E.E.H. and B.L. would like to thank the University of Toulouse (Paul Sabatier) for funding a thesis joint-supervision grant. E.E.H. and A.E.S. are also grateful to the Lebanese University and the AUF agency in Lebanon (Agence Universitaire de la Francophonie) for providing a significant part of the thesis grant.

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Figures and captions:

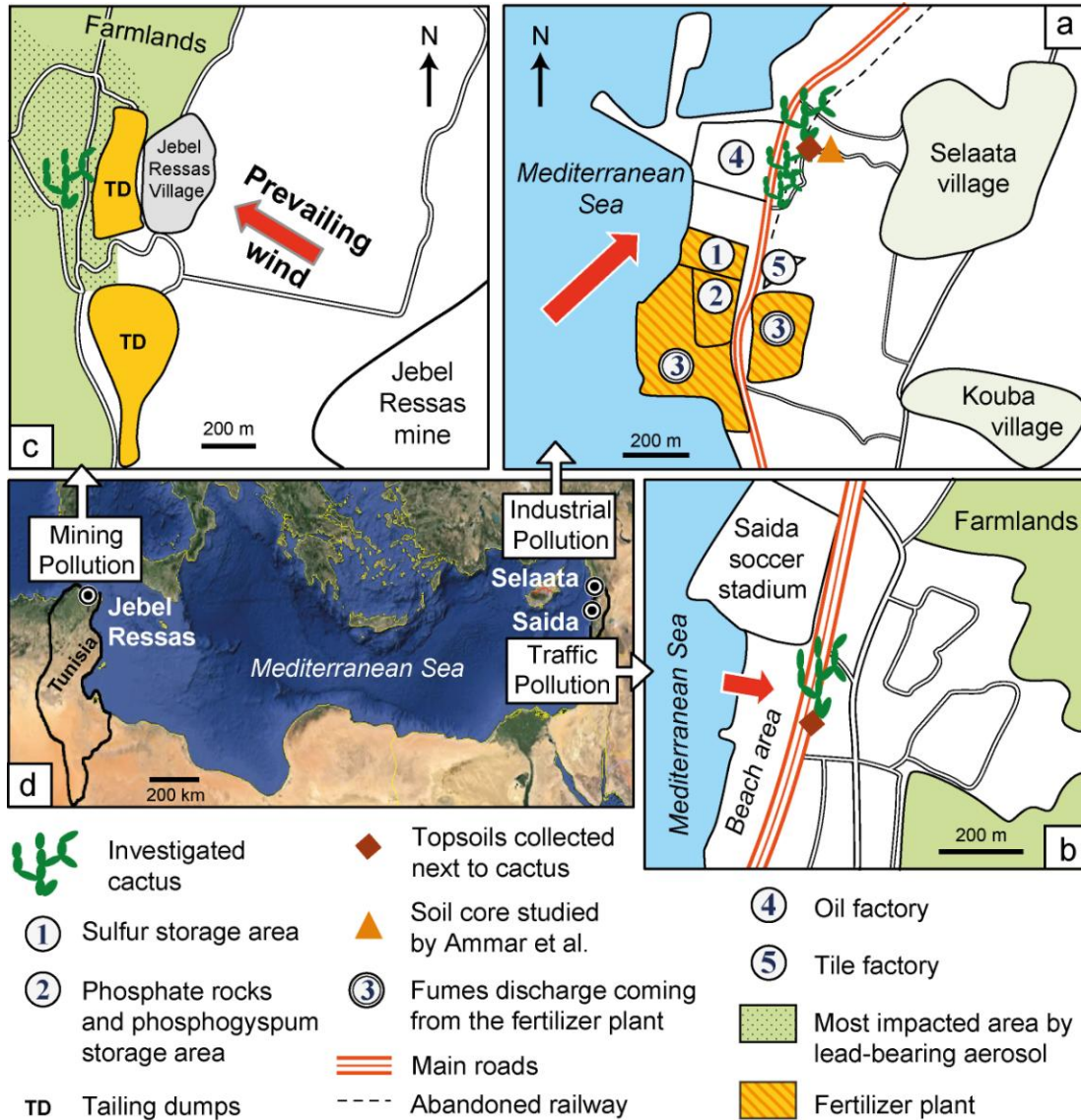


Figure 1: Location of sampling sites. Samples in Lebanon were collected a) at the industrial complex of Selaata (34°16'49.07"N, 35°39'31.9"E) and b) next to the highway linking Beirut to Saida (33°34'58.36"N, 35°23'8.09"E). Samples in Tunisia c) were collected at Jebel Ressas next to mine tailings (36°36'35.30"N, 10°18'59.78"E). The red arrow indicates the direction of the prevailing wind at each site. The brown color at Jebel Ressas delimited the area contaminated by atmospheric pollution.

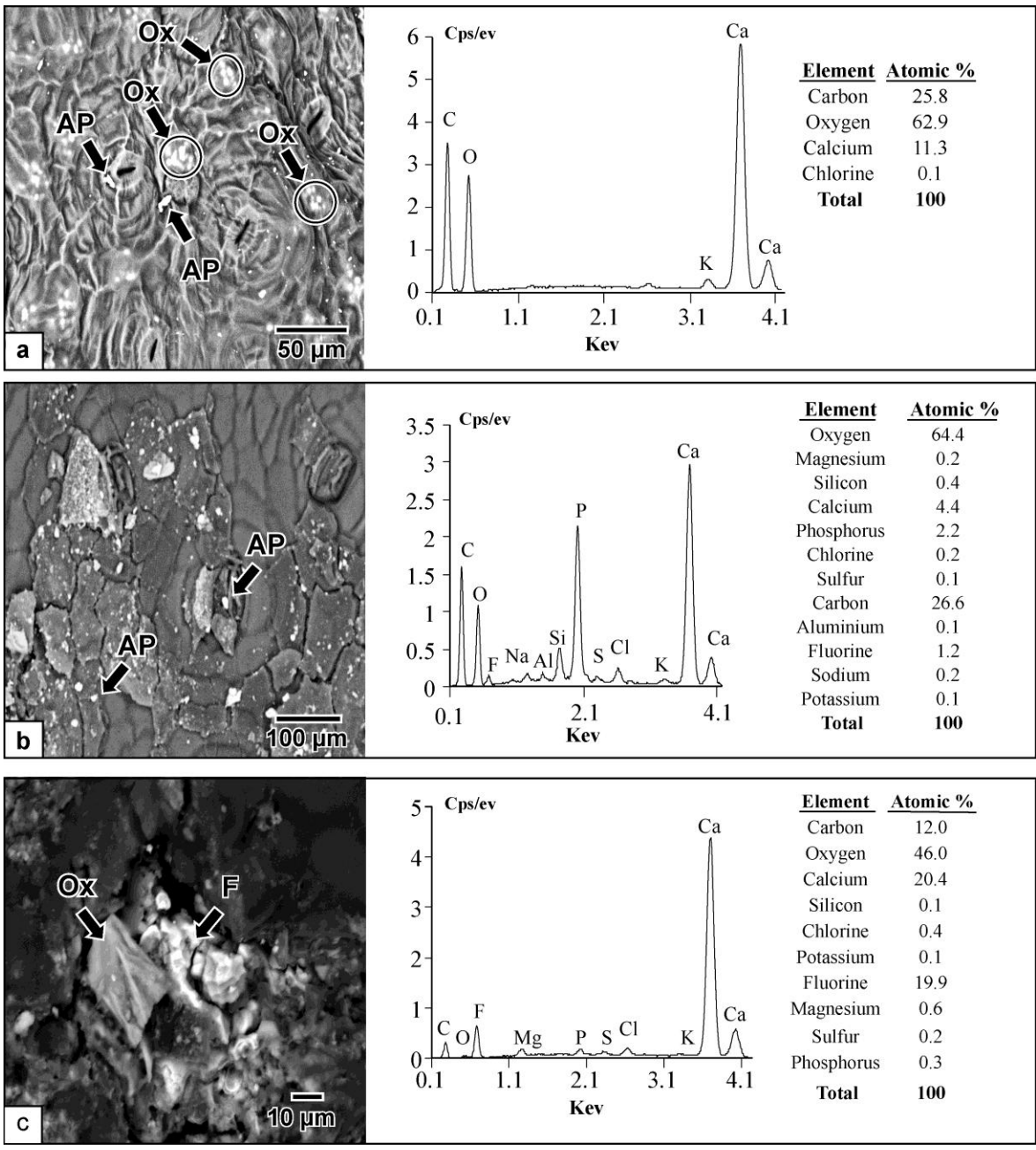


Figure 2: Backscattered electron images and corresponding EDX spectra of particles found at the surface of cladodes at Selaata. a) calcium oxalate crystals (Ox) observed through the cuticle. b) Apatite (AP) (presumably francolite) in or at the edge of a stomata. c) Aggregate of fluorite (F) and calcium oxalate inside a stomata (light elements are poorly counted in the hollow of stomata).

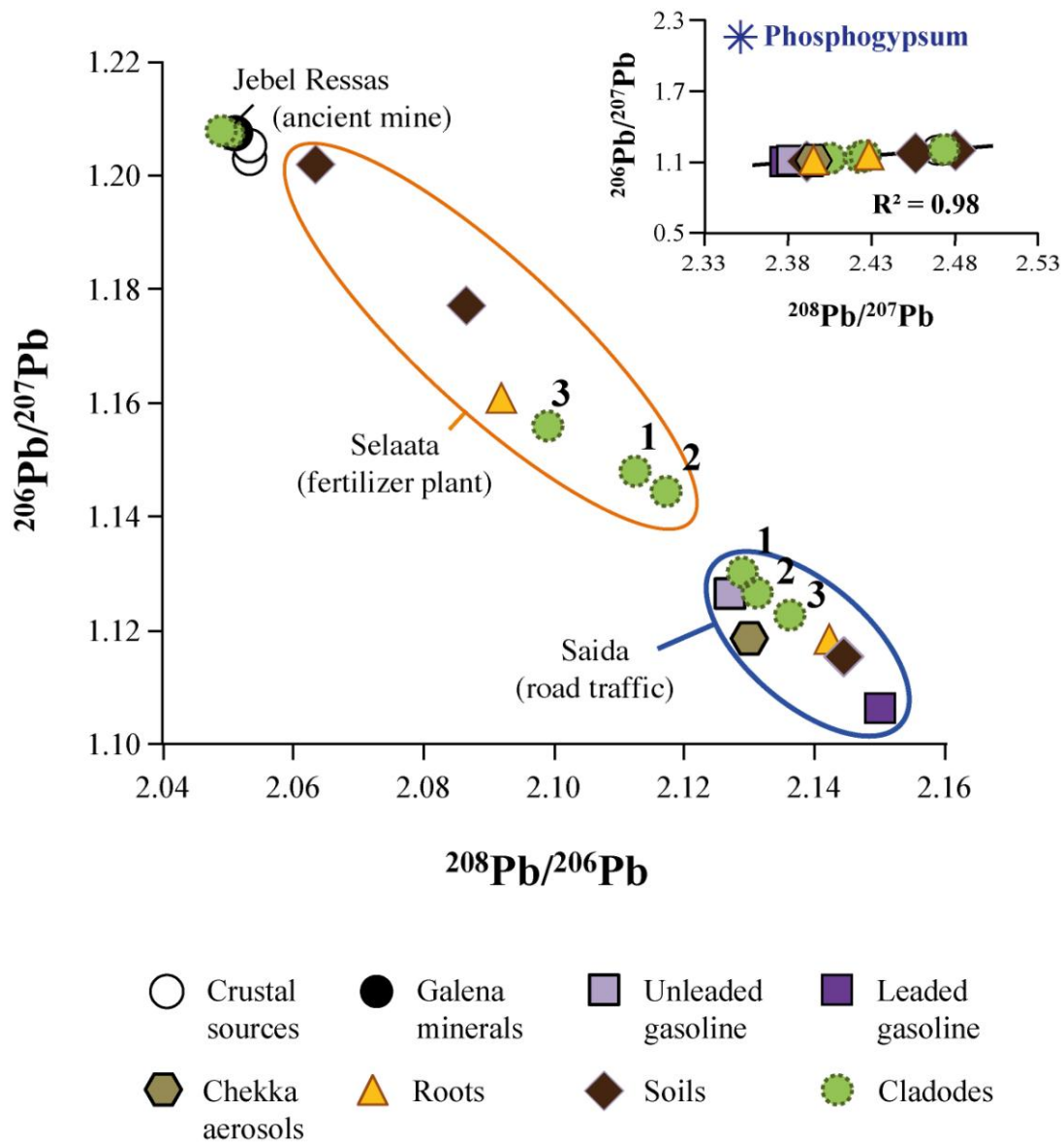


Figure 3: Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ for cladodes, roots, soils, and other relevant lead isotope values. At Selaata, soil core values correspond respectively to the deepest layer of soil (70 cm) ($^{206}\text{Pb}/^{207}\text{Pb}=1.206$) and to the soil surface ($^{206}\text{Pb}/^{207}\text{Pb}=1.177$) studied by Rawaa et al (submitted). The numbers refer to the age of the cladode in the series (3 the oldest). The inset shows the same data in the $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{207}\text{Pb}$ representation along with the Pb isotopic composition of phosphogypsum.

Table and its caption:

Location	Sample type	Pb mg.kg ⁻¹	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	References
Selaata	Cladode 1	24.7	1.148	2.113	This study
	Cladode 2	11.6	1.144	2.118	
	Cladode 3	13.7	1.156	2.099	
	Roots	1.8±0.95	1.161	2.092	
	Topsoils (n=8) ^a	54.8±20.6	-	-	
	Dust collected on cladode surface	102.6	-	-	
	Phosphogypsum	1.93	2.180	1.079	
Crustal sources	Mean soil core	-	1.189	2.076	This study
	Miocene carbonate rock	-	1.203	2.053	Luck et al. (1998)
Paleocene carbonate rock	-	1.205	2.053		
Saida	Cladode 1	5.6	1.130	2.129	This study
	Cladode 2	4.6	1.127	2.131	
	Cladode 3	6.6	1.123	2.136	
	Roots	3.1±0.53	1.118	2.142	
	Topsoil	168.2	1.115	2.144	
Lebanon	Leaded gasoline	-	1.106	2.150	Erel et al. (1997)
	Unleaded gasoline	-	1.126	2.127	
	Chekka aerosols	-	1.119	2.130	Bollhofer et al. (2001)
Jebel Ressas	Cladode 1	56.6	1.207	2.050	This study
	Cladode 2	69.1	1.207	2.049	
	Cladode 3	83.2	1.207	2.049	
	Topsoil ^b	2200	-	-	Souissi et al., (2014)
	Galena minerals	-	1.207	2.051	Jemmali et al. (2011)

Table 1: Lead concentrations and isotope ratios analyzed in samples taken from Selaata, Saida and Jebel Ressas. Cladodes 1, 2 and 3 represent the youngest, the middle and the oldest cladode, respectively. Also shown literature values of lead isotope ratios relevant for the studied areas and for phosphogypsum sample taken from the industrial site (Selaata).

^a Average of eight different samples collected under and around cactus.

^b Median concentration of soil samples collected at cactus area.