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Eva Schreck, Roseline Bonnard, Christophe Laplanche, Thibaut Leveque, Yann Foucault, et al.. DECA: A new model for assessing the foliar uptake of atmospheric lead by vegetation, using *Lactuca sativa* as an example. *Journal of Environmental Management*, 2012, vol. 112, pp. 233-239. 10.1016/j.jenvman.2012.07.006 . hal-00780249

**HAL Id: hal-00780249**

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Submitted on 23 Jan 2013

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**To link to this article:** DOI:10.1016/j.jenvman.2012.07.006  
URL: <http://dx.doi.org/10.1016/j.jenvman.2012.07.006>

**To cite this version:** Schreck, Eva and Bonnard, Roseline and Laplanche, Christophe and Leveque, Thibaut and Foucault, Yann and Dumat, Camille  
*DECA: A new model for assessing the foliar uptake of atmospheric lead by vegetation, using *Lactuca sativa* as an example.* (2012) Journal of Environmental Management, vol. 112 . pp. 233-239. ISSN 0301-4797

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# DECA: A new model for assessing the foliar uptake of atmospheric lead by vegetation, using *Lactuca sativa* as an example

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## A B S T R A C T

In the context of peri-urban atmospheric pollution by industrial lead recycling emissions, metal can transfer to plant shoots. Home gardeners consuming their produce can therefore be exposed to metal pollution.

The Human Health Risk Assessment Protocol (HHRAP) model from the United States Environmental Protection Agency (US EPA) classically used in risk assessment provides foliar metal uptake predictions for large farms but is not adapted to cultures in kitchen gardens. Thus, this study developed a new model, entitled "DECA", which includes individually measured parameters and the washing of vegetables before human consumption.

Results given by DECA and HHRAP models were compared with experimental measurements of lettuce. The data calculated by the DECA model were highly correlated with the measured values; the HHRAP model overestimates foliar lead uptake. Moreover, strong influences of factor of washing and time-dependent variations of loss coefficient were highlighted. Finally, the DECA model provided important risk assessment data regarding consumption of vegetables from kitchen gardens.

### Keywords:

Lead  
Foliar uptake  
Modelling  
Atmospheric particulate matter  
Lettuce  
Health risk assessment

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## 1. Introduction

Nowadays, metal recycling and production processes release a large proportion of fine and ultra-fine metallic particulate matter (PM) into the atmosphere due to the use of thinner and more effective filters (Zhang et al., 2005). As PM reactivity (in terms of bioavailability, ecotoxicity and toxicity) is very high compared to coarse emissions (Ruby et al., 1996), there are environmental (Uzu et al., 2010; Schreck et al., 2011) and sanitary (Uzu et al., 2011a, 2011b) concerns over this phenomenon. In 2007, 4800 and 108 tonnes of lead were released into the atmosphere in Europe and France, respectively (CITEPA, 2011), mainly as PM emitted by acid battery recycling and lead production (Batonneau et al., 2004; Ettler et al., 2005; Uzu et al., 2010).

According to European authorities (US EPA, 2005), lead is a Substance of Very High Concern (SVHC), and it is strictly

controlled by the European REACH law. Therefore, human exposure scenarios need to be determined for various contexts. However, according to Uzu et al. (2010), foliar lead uptake due to PM depositions can strongly increase metal concentrations in plants, especially when kitchen gardens (Vadrot, 2009; Clark et al., 2008) or farms are near recycling factories. In such cases, the risk for human and animal health regarding the ingestion of polluted plants should be considered (Alexander et al., 2006; Polichetti et al., 2009; Perrone et al., 2010). But, only a few studies in the published literature focused on the risk in kitchen gardens (Bappet, 2011) or performed experimental biotests near sources of atmospheric contamination. Using global set parameters (interception fraction, yield, and plant surface loss coefficient), the Human Health Risk Assessment Protocol (HHRAP) model from the US EPA (2005) is currently used to predict plant metal concentrations for extensive field crops exposed to diffuse atmosphere pollution. However, the HHRAP model's parameters are not adapted to the heterogeneity of kitchen gardens. Actually, kitchen gardens often comprise small surface areas with different vegetables cultivated for personal consumption (Aligon, 2010).

Within this global, scientific context, the main objective of the present work was to develop a new adaptive model for predicting

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foliar lead uptake in kitchen gardens and thus, its contribution in human health risk due to the ingestion of polluted vegetables. A field study was therefore performed under high atmospheric exposure conditions, that is, in a smelter courtyard where fallouts are highly concentrated in lead. *Lactuca sativa* L. (Asteraceae), considered the main leafy vegetable cultivated in kitchen gardens (Křístková et al., 2008) was chosen for our model and foliar pollutant uptake was studied and modelled during several weeks.

## 2. Materials and methods

### 2.1. Experimental set-up

A secondary lead-recycling plant, STCM (Chemical Metal Treatment Company), was chosen as the experimental area for studying and modelling the foliar uptake of industrial atmospheric fallout. This area, considered as a place of high level lead exposure, was chosen in order to ensure that lead concentrations were above detection limits so as to accurately assess maximum human contamination risks. The factory is located in the urban area of Toulouse, south-western France (43°38'12" N, 01°25'34" E), and emits 328 kg of total suspended particles each year, according to French authorities. Laser granulometric analyses using a Malvern Mastersizer S had previously shown that PM emissions mainly contain fine particles (91% are less than 10 µm). Their total elemental contents were determined by ICP-OES IRIS Intrepid II XXDL after heat digestion. Lead was the main metal found in the factory emissions (33.4%), and the other metal contents were Cd, Sb, As, Cu, and Zn at 2.7, 1.8, 0.09, 0.09, and 0.7%, respectively (Uzu et al., 2011a). Industrial atmospheric fallouts in the smelter courtyard were measured using plastic Owen gauges that enable wet and dry atmospheric depositions to be recorded (Taylor and Witherspoon, 1972).

Two gauges were left exposed throughout the entire experimental period, while two others were changed each week in order to determine the metal contents in atmospheric deposits. The lead concentrations in the gauges were determined according to NF EN 14902 (2005). Climate variations – precipitation (mm), temperature (°C), and hours of sunshine – were recorded daily by a meteorological station in order to establish a possible link between these parameters and the metal deposits recorded by the gauges.

Lettuces (*L. sativa*), which are popular vegetables in kitchen gardens, were chosen for foliar exposure experiments due to their high foliar surfaces and their short life-cycles. This vegetable has been widely used in plant biotests in soil (Waisberg et al., 2004; Alexander et al., 2006) and as an indicator of air quality (Uzu et al., 2010) for several years. Moreover, in terms of health risks after ingestion, lettuce is used almost exclusively as a fresh vegetable in salads, but some forms are also cooked (Lebeda et al., 2007).

Lettuces were first grown for 15 days in a greenhouse in pots containing 4 kg of uncontaminated soil. Then, the experimental pots were transferred to the smelter courtyard under atmospheric fallout for one month. The controls were cultivated under an unpolluted atmosphere (checked by Owen gauge deposition values throughout the duration of the experiment). A geotextile membrane was placed on the soil to protect it from atmospheric fallout (Uzu et al., 2010) as the foliar transfer study is aimed in our experimentation.

### 2.2. Experimental sizing

The number of plant replicates used for determining lead concentrations and model efficiency was chosen in order to produce a set of experimental data sufficiently large to cover all the variability in the exposure conditions but also able to fit within the restricted experimental set-up in the factory courtyard.

As reported by Bartlett et al. (2001) and Ghestem (2009), the minimum number of replicates required for a study can be calculated by the following formula:

$$N_{\text{replicates}} = \left[ S^2 \times Z^2(\alpha) \right] / i^2$$

where:

$N_{\text{replicates}}$ : number of replicates

$S^2$ : sample variance

$Z(\alpha)$ : reduced deviation ( $\alpha = 0.05$ ), student's  $t$ -test: 1.96

$i$ : desired precision. A precision of 10% of the mean is considered as very satisfactory from a statistical point of view.

This calculation was performed on 30 different values measured during different periods of the year with different climatic conditions. This set of 30 data followed a normal distribution as suggested by the Kolmogorov–Smirnov test ( $p = 0.136$ ) and showed that at least five replicates are sufficient to fulfil the scientific objectives of the present work. Then, in all 65 lettuces were placed in the smelter courtyard and eight plants were harvested each week for lead concentration measurements and modelling.

### 2.3. Measuring the Pb concentration in plants

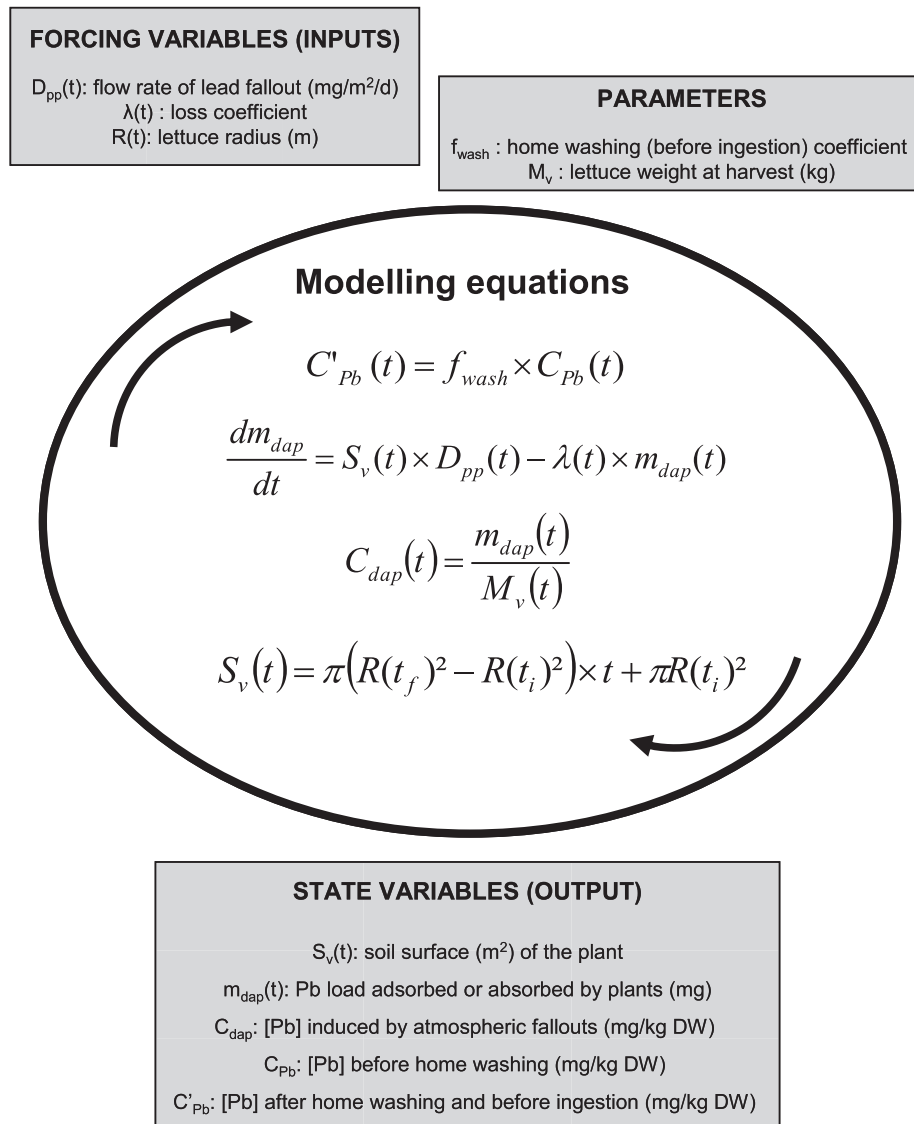
Fresh plant biomass was measured and, in order to assess sanitary risks in the case of vegetable consumption, the lettuces were washed and dried as they would be in a typical home situation. The particle desorption procedure consisted of global washing of the lettuces, first in running tap water for 30 s and then in two baths of deionized water for 1 min (Uzu et al., 2010). Lettuce dried biomasses were measured after 48 h at 50 °C, and lead concentrations were finally measured by ICP-OES (IRIS Intrepid II XXDL) after acid mineralization according to the method of Uzu et al. (2010). The accuracy of the acid digestion and the analytical procedures was checked using reference materials: Virginia tobacco leaves, CTA-VTL-2, ICHTJ and TM-26.3 certified reference material from the National Water Research Institute, Canada. The concentrations found in plant leaves were within 97–101% of the certified values. The efficiency of the desorption procedure was checked by measuring lead concentrations in washed and unwashed lettuce leaves by ICP-OES after acid mineralization. Washing causes the loss of approximately one third of the metals adsorbed onto a leaf surface. Then, a factor of washing was used in the DECA model (see model description, Section 2.4.2.1) to be closer to reality.

### 2.4. Modelling of lead uptake by lettuce shoots

#### 2.4.1. HHRAP model description and limits

The Human Health Risk Assessment Protocol (HHRAP) model, developed by the US EPA (2005), is widely used for foliar interception modelling. This model is based on global equations modelling the transfer of atmospheric pollutants based on their physical and chemical properties (Bonnard, 2005) and analytical calculations. In this study, the ratio “interception fraction/production yield” of the model was expressed as “lettuce surface/lettuce weight”. Then, calculations were done with the use of the mean deposition during the exposure period of each lettuce. Point estimations were performed (non-probabilistic approach). The surface loss coefficient was fixed at 18 per year (default value in HHRAP model).

However, in realistic cases, the Pb concentrations in lettuce shoots mainly depend on atmospheric fallout and climate processes such as rainfall and wind that can remove pollutants



**Fig. 1.** Overall picture of DECA model construction. Equations, parameters and variables involved in its functioning.

from shoot surfaces and plant biomass (Rodrigo et al., 1999; Staelens et al., 2008), which are not constant parameters. The deterministic HHRAP model using mean global parameters is not really adapted to such cases. Nevertheless, it was run in our study to predict the foliar lead uptake of lettuces and as a comparison for the development of the new DECA model.

#### 2.4.2. Specific model: DECA

**2.4.2.1. DECA model description.** A specific model capable of dealing with biotests was developed and named as the DECA (Dynamic Estimation of Contaminant concentration using Attenuation factors) model. Like the HHRAP model, this model takes into account the different sources of lead in plant tissues. However, it is based on the measurement of several individual parameters: lettuce weight, soil surface occupied by each lettuce, atmospheric fallout, and loss factor (via wind and rainfall) in relation to time. Moreover, it considers the loss of pollutants due to the washing process carried out by consumers. The DECA model was developed to deal with the variability (temporal and inter-individual) in input parameters and to be more suitable for the home gardens scenario with small surfaces exposed to atmospheric pollution. Contrary to

the HHRAP model, the ratio “vegetable surface/vegetable weight” at harvest was used in the new developed DECA model, instead of the ratio “interception factor/production yield” defined for large field crops.

**2.4.2.2. Model equations and input parameters involved in foliar uptake of PM.** The total Pb concentration in lettuce shoots ( $C_{Pb}$ , mg/kg DW) was calculated according to Equation (1), as the result of foliar metal absorption induced by atmospheric fallout ( $C_{dap}$ : Pb concentration induced by atmospheric fallout, mg/kg DW) and metal soil–root transfer ( $C_{rp}$ : Pb concentration induced by root transfer, mg/kg DW):

$$C_{Pb}(t) = C_{rp}(t) + C_{dap}(t) \quad (1)$$

The objective of the DECA model was to determine the foliar uptake contribution to plant contamination near lead-recycling factories or other sources of high atmospheric contamination. Actually, working on Pb isotopic signature (<sup>206</sup>Pb/<sup>207</sup>Pb ratios), Hu et al. (2011) showed that the airborne Pb can contribute to about 75% of the metal concentrations into plant leaves, suggesting that

foliar interception is the most important source for the Pb accumulation in vegetable edible parts. Moreover, in our experiment, the lead concentration in the soil was checked regularly during the experiment and considered as very low (initial quantity of metals in soil =  $25.5 \pm 1.6$  mg/kg of dry weight) and constant, due to the use of a protective geotextile membrane placed on the soil's surface to avoid all atmosphere–soil transfer. Then, for the above reasons, in this experiment, the soil–plant transfer was neglected with respect to the air–plant transfer ( $C_{rp}(t) = 0$ ), to better focus on the contribution of the atmospheric pollution to plant contamination.

Fig. 1 provides an overall picture of the model and highlights inputs, outputs, and model parameters.

Metal load ( $m_{dap}$  expressed in mg) was provided by the ordinary differential equation:

$$\frac{dm_{dap}}{dt} = S_v(t) \times D_{pp}(t) - \lambda(t) \times m_{dap}(t) \quad (2)$$

Where  $S_v(t)$  is the soil surface ( $m^2$ ) of the plant,  $D_{pp}(t)$  is the flow rate of lead fallout ( $mg/m^2/d$ ), and  $\lambda(t)$  (per d) is loss rate due to rainfall and wind. Equation (2) was integrated as follows:

$$m_{dap}(t) = m_{dap}(t - \Delta t) \times e^{-\lambda(t) \times \Delta t} + \frac{D_{pp}(t) \times S_v(t)}{\lambda(t)} \times (1 - e^{-\lambda(t) \times \Delta t}) \quad (3)$$

Pb concentration in lettuce shoots was  $C_{dap}(t) = m_{dap}(t)/M_v(t)$  where  $M_v(t)$  is the plant dry weight at time  $t$ .

Particulate atmospheric deposition  $D_{pp}(t)$  was measured from the Owen gauges and was provided as an input to the model. The soil surface occupied by the plant was computed as follows, by simulating plant growth:

$$S_v(t) = \pi(R(t_f)^2 - R(t_i)^2) \times t + \pi R(t_i)^2 \quad (4)$$

where  $R(t_i)$  and  $R(t_f)$  are the lettuce radius (m) at the beginning and the end of the experiment, respectively. Loss rate  $\lambda(t)$  was estimated from a depuration experiment as detailed below.

**2.4.2.3. Loss rate and depuration experiment.** Each week ( $w = 1..4$ ), eight lettuces were collected with their pots and placed for one more week in a control zone (without atmospheric Pb fallout). After this one-week depuration period, lettuces were harvested and Pb concentrations were measured (the same way as exposed lettuces). Pollutant loss during a depuration period was modelled as an exponential decrease of the first order:

$$\frac{dm_{dep}}{dt} = -\lambda_w \times m_{dep}(t) \quad (5)$$

where  $m_{dep}(t)$  is the load of Pb in plant (mg) at time  $t$  and  $\lambda_w$  is the loss coefficient for week  $w$ . By integrating Equation (5), load is  $m_{dep}(t) = m_{dep}(t_1) \times \exp[-\lambda_w(t - t_1)]$  where  $t_1$  and  $m_{dep}(t_1)$  are the time and the load at the beginning of the depuration period, respectively. The loss coefficient for week  $w$  is therefore:

$$\lambda_w = \frac{\log \frac{m_{dep}(t_2)}{m_{dep}(t_1)}}{(t_1 - t_2)} \quad (6)$$

where  $t_2$  and  $m_{dep}(t_2)$  are the time and the load at the end of the depuration period, respectively. The loss coefficient  $\lambda(t)$  of Equation (2) is thus equal to  $\lambda_w$  for day  $t$  of week  $w$ .

**2.4.2.4. Washing factor.** Besides, the washing of lettuces before analysis can decrease the quantity of Pb adsorbed onto shoots

**Table 1**

Atmospheric parameters recorded during the exposure period. Atmospheric fallouts in Owen gauges were determined by ICP-OES. Climate variations were recorded by a meteorological station: mean temperature ( $^{\circ}C$ ), precipitations (mm) and sunshine duration (h/period).

Exposure period	Pb atmospheric fallouts ( $mg/m^2$ /period)	Rainfall (mm/period)	Mean temperature ( $^{\circ}C$ )	Period of sunshine (h/period)
Week 1	$139.1 \pm 6.3$	55.6	10.2	19.5
Week 2	$102.3 \pm 23.0$	18.2	13.0	36.7
Week 3	$214.1 \pm 9.0$	0.0	17.1	81.8
Week 4	$102.2 \pm 13.6$	9.4	19.1	52.3
Month	$456.2 \pm 67.5$	83.2	14.8	190.3

without inducing a modification in the absorbed quantity of Pb. Thus, the “washing effect” could be deduced by the application of a factor (factor of washing  $f_{wash}$ ). The application of this factor to the foliar uptake of atmospheric Pb fallout allowed to take into account the loss due to the lettuce washing performed before consumption:

$$C'_{pb}(t) = f_{wash} \times C_{pb}(t) \quad (7)$$

where  $C'_{pb}(t)$  is the total lead concentration in lettuce shoots after home washing and before ingestion. The washing factor  $f_{wash}$  was estimated using a specific experiment using lettuces exposed to atmospheric fallout at a distance of 200 and 800 m of the smelter factory. The estimation was performed by comparing lead concentration in lettuce shoots before washing ( $C_{dap}$ ) and after washing ( $C'_{pb}$ ).

All calculations were done on the ECOLEGO 5 platform (Avila et al., 2003) using the solver called Numerical Differential Formulas (NDF) as reported by Shampine and Reichelt (1997).

## 2.5. Statistical analysis

The metal concentrations in the lettuces were subjected to analysis of variance (ANOVA) with one factor using the software program Statistica, edition '98 (StatSoft Inc., Tulsa, OK, USA). Significant differences ( $p < 0.05$ ) were measured by Fisher's least significant difference (LSD) test.

## 3. Results

### 3.1. Atmospheric parameters and smelter emissions

The atmospheric parameters recorded (lead atmospheric fallout from the Owen gauges, mean temperature, precipitation, and hours of sunshine) are shown in Table 1. The levels of lead deposition shown by the Owen gauges varied strongly according to the week considered, and were approximately between 102 (for the second and the last week) and 214  $mg/m^2$  (for the third week). The meteorological parameters also varied during the exposure period. During the third week of exposure, the values showed no rainfall, a lot of sun, and high temperatures. By contrast, the first week was cold and rainy. Moreover, smelter activity was stopped during the whole of the second week of exposure for public holidays; therefore, PM was not emitted by the factory during this period. Then, all these parameters could certainly explain variations in lead deposition levels and plant foliar interception.

### 3.2. Lead concentrations in the lettuce shoots

Table 2 shows the Pb concentrations weekly measured in the lettuce shoots after washing (for the plants exposed to atmospheric fallouts and the controls). A significant accumulation of lead was



**Table 2**

Lead concentrations (in mg/kg of dry weight DW) in lettuces according to the time of exposure under atmospheric fallouts (by comparison with controls) and impact of depuration process. Results are expressed as the mean of eight plants for each time of exposure ( $\pm$ standard deviation SD).

Weeks of exposure	Control plants	Lead concentrations in lettuce shoots $\pm$ SD (mg/kg DW)	
		Exposed plants (after harvest)	Exposed plants (after one week of depuration process)
0	0.7 $\pm$ 0.1		
1	0.8 $\pm$ 0.1	108.2 $\pm$ 7.8 <sup>a</sup>	58.1 $\pm$ 5.5
2	0.9 $\pm$ 0.1	107.4 $\pm$ 8.6 <sup>a</sup>	74.7 $\pm$ 4.0
3	1.6 $\pm$ 0.1	99.0 $\pm$ 15.6 <sup>a</sup>	93.2 $\pm$ 6.0
4	1.8 $\pm$ 0.1	122.0 $\pm$ 5.5 <sup>a</sup>	97.1 $\pm$ 1.8
6	2.1 $\pm$ 0.2	171.5 $\pm$ 6.9 <sup>a</sup>	

<sup>a</sup> Significant differences compared with controls.

recorded in the exposed shoots (ANOVA,  $p < 0.05$ ). After four and six weeks of exposure, the Pb concentrations in the lettuce shoots reached 122  $\pm$  5.5 and 171.5  $\pm$  6.9 mg/kg dry weight, respectively.

Table 2 shows that, after one week under an uncontaminated atmosphere, the lead concentrations in the lettuce shoots dramatically decreased.

### 3.3. Modelling results

The factor of washing was calculated and then seven values between 0.65 and 0.77 were obtained for  $f_{wash}$ . A uniform distribution was applied to the  $f_{wash}$  parameter, and thus, concentrations were calculated with Equation(7).

Table 3 shows the loss coefficient values determined, revealing a large variability of this parameter. Table 4 shows an overall picture of the modelling results by providing a comparison between the measured and predicted values of lead concentrations in the lettuce shoots. The specifically developed DECA model appeared to be more successful than the HHRAP model in predicting atmospheric fallout interception and lead accumulation in the lettuce shoots: the HHRAP model values were consistently higher than the measured data. The predicted values obtained by the HHRAP model were more scattered, with a “predicted value/measured value” ratio of between 1 and 4.8, whereas the ratio “predicted median/measured value” was between 0.6 and 2.7 in the DECA specific model (Table 4). Moreover, the geometric mean was equal to 1.0 in our developed model instead of 1.6 in the HHRAP model.

## 4. Discussion

### 4.1. Lead concentrations in the lettuce shoots

A significant accumulation of lead was observed in the lettuce shoots under atmospheric smelter fallout throughout the experiment. Uzu et al. (2010) showed a linear increase in lead concentrations in plant leaves, rising to 335  $\pm$  50 mg/kg dry weight after 43 days of exposure. In contrast, our study showed a rapid increase in the lead contents of lettuce shoots within the first week, followed by a plateau for the next three weeks, and then a new, significant accumulation (Table 2). This plateau can certainly be

**Table 3**

Values of the measured loss coefficient (per year).

Exposure	Loss coefficient (per year)
Week 2	24.7
Week 3	37.2
Week 4	11.3
Week 6	36.6

**Table 4**

Comparison of the efficiency of the two models (DECA and HHRAP) in lead concentration prediction. Modelled values were compared to the measured one for each time of exposure by the determination of the ratio (modelled [Pb] in shoots/measured [Pb] in shoots).

Time of exposure	Mean ratio (SAG value/measured value)	Mean ratio (HHRAP value/measured value)
1 week	1.1 $\pm$ 0.2	1.6 $\pm$ 0.3
2 weeks	1.1 $\pm$ 0.2	1.7 $\pm$ 0.3
3 weeks	1.0 $\pm$ 0.4	1.7 $\pm$ 0.5
4 weeks	1.1 $\pm$ 0.1	1.8 $\pm$ 0.2

explained by the activities of the smelter, where the smelter was stopped for the second week of exposure (public holiday), suggesting that stopping the source of pollution considerably reduced the level of contamination in the lettuces. This period of smelter inactivity showed that diffuse pollution due to lead processing activities was effectively responsible for the high level of lead contamination in the lettuces.

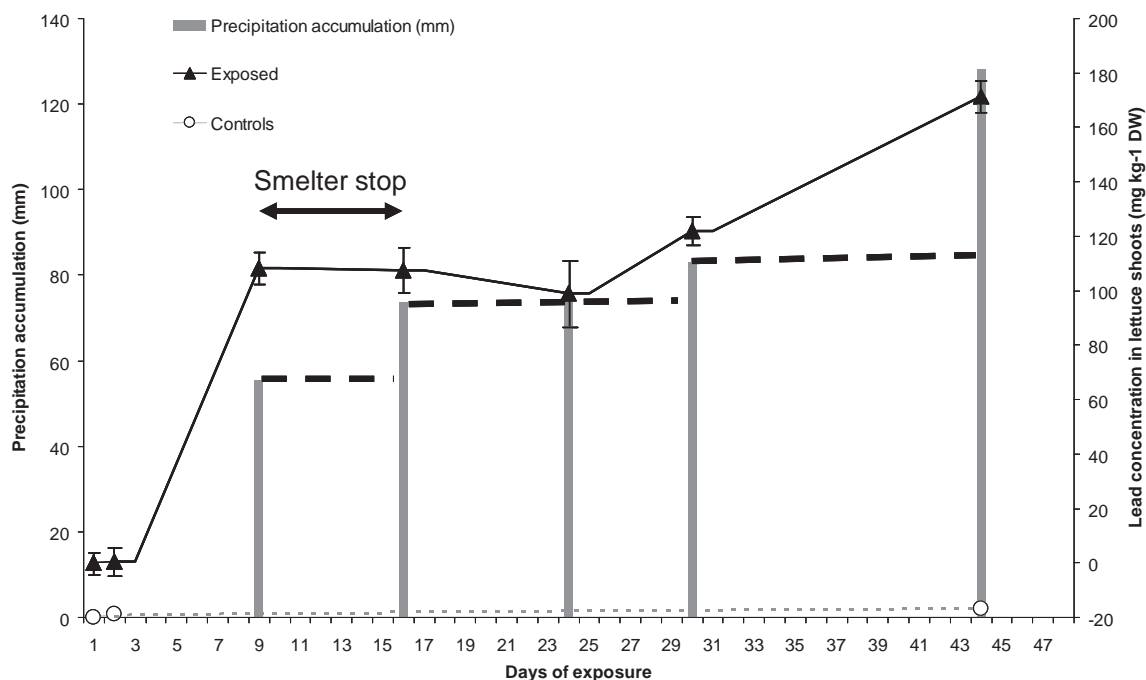
Moreover, according to the literature, meteorological changes (temperature, humidity) can have an impact on metal deposition on soils and/or plants and on their foliar uptake of metals. Lawson and Mason (2001) showed that Pb concentrations in throughfall were equivalent to or higher than dried deposition concentrations, suggesting an increase in lead deposition during rainy periods. Moreover, according to Arvik and Zimdahl (1974), the level of leaf penetration of metals from atmospheric fallout increases during rainy periods due to enlargement of cuticle, pore, and stomata openings. Prasad and Hagemeyer (1999) confirmed this hypothesis by showing that relatively low humidity and high temperature levels induced the contraction of plant cuticles and the closure of stomata, preventing metal penetration into leaves.

In the present study, Fig. 2 and Table 2 show that lead accumulation in the lettuce shoots was strictly linked to the rainfall measurements (correlation coefficient: 0.83), with a high lead accumulation during the first and last weeks due to the higher level of rainfall and a correspondingly weak correlation with deposition levels (correlation coefficient: 0.28). According to our results, no rainfall (and high temperatures) could imply high levels of lead fallout (according to the Owen gauge measurements per week, Table 1) but a low accumulation in plant shoots (Table 2 and Fig. 2). In contrast, high humidity was found to enhance foliar metal uptake by favouring penetration pathways in plants exposed to atmospheric pollution (Arvik and Zimdahl, 1974; Prasad and Hagemeyer, 1999).

Moreover, the stabilization (or decrease) in lead concentrations in the lettuce shoots during these periods (Table 2 and Fig. 2) could be due to the increase in biomass under high levels of sunshine, which is responsible for a dilution effect of lead concentrations in the shoots. In fact, this dilution effect was confirmed by our depuration experiment. After one week in the control zone (with respect to atmospheric pollution), the total lead concentrations in the lettuce shoots significantly decreased, which was certainly due to the dilution effect: the plants still grew, increasing their biomass, but no further lead was accumulated in their leaves.

### 4.2. Model predictions and risk assessment

Focussing on the modelling of levels of foliar lead uptake by lettuce, compared to the global field HHRAP, the new DECA model showed a better correlation with the experimental data due to weekly measures of individual parameters: lettuce diameter, biomass, factor of washing, and loss coefficient  $\lambda$ .



**Fig. 2.** Relation between lead concentration in lettuces (in mg/kg of dry weight) and precipitation accumulation (mm) since the beginning of the experiment according to the time of exposure under atmospheric fallouts. Lead concentrations are expressed as the mean of eight plants for each time of exposure ( $\pm$ SD). "Smelter stop" corresponds to a period during which smelter activity was stopped for public holidays; therefore, PM was not emitted by the factory during this period (whole of the second week of exposure).

The HHRAP model significantly overestimated the lead uptake concentrations, as suggested by the ratios greater than 1.6 in Table 4. This overestimation of lead concentrations in leaves to be consumed could have consequences in terms of sanitary risk assessment (due to the overestimation of lead exposure) and risk management (due to overestimation of this pathway and the possible implementation of inappropriate management measures). The DECA model is thus able to take into account the variability in parameters and gives more precise results without bias.

In most models (US DOE, 2004), a default value equal to 18 per year (mid-point of the range reported by Miller and Hoffman, 1983) is assigned to the loss coefficient ( $\lambda$ ). By contrast, in our new specific DECA model, losses by run-off and plant growth were evaluated. Using the same value of 18 per year for the loss coefficient ( $\lambda$ ) and a value equal to 1 for the factor of washing ( $f_{\text{wash}}$ ) in the DECA model would give the same type of results as HHRAP with a global ratio of "predicted median/measured values" equal to 1.6. Actually, using the factor of washing ( $f_{\text{wash}}$ ) reduces the overestimation error and using specific values for the loss coefficient  $\lambda$  (depending on each exposure period instead of a constant value) allows a reduction of the bias as well as improvement of the precision of the estimates. These two parameters appear quite influential for modelling foliar lead contamination of edible plants in the context of PM fallout. Thus, with the parameters included, the DECA model allowed a better adaptation to the biotest conditions in the smelter courtyard.

Finally, DECA has more requirements but gives more realistic results than classical models and could provide important data for risk assessment enterprises, especially regarding to foliar metal uptake by consumed vegetables from kitchen gardens. Nevertheless, to be even more relevant, the DECA model could be improved by taking into account the two ways of contamination of the vegetable leaves: atmosphere–shoot transfer and soil–root transfer, even if this second way of contamination could be neglected in the case of high atmospheric contaminations, as reported by Hu et al. (2011). Then, a very complete model could be developed to

become a large indicator of health risk assessment after edible parts ingestion by humans. Further studies are in progress.

#### 4.3. Conclusions

This article focused on the development of a new prediction model for foliar metal uptake. This new DECA model is well adapted to the studies of lead interception by vegetables from kitchen gardens or from experimental biotests located near sources of atmospheric metal-enriched PM. This model has shown the influence of variations in the loss coefficient due to environmental parameters, PM quantity and the impact of the factor of washing for modelling lead foliar concentration in leafy vegetables.

Furthermore, this study should be of interest for consumer risk assessments in the case of plant ingestion. Even if the exposure should be considered maximal in this experiment, applications would be brought out from this study in view of being more precise in health recommendations.

Nevertheless, plant morphological characteristics (such as specific surface, roughness, number of trichomes, density and locality of stomata) could certainly influence foliar lead interception and internalization from atmospheric fallouts near factory emissions (Rao and Dubey, 1992) with pollutant bioavailability consequences (Schreck et al., 2012). Thus, further studies should be conducted on various inorganic pollutants and on garden plants at different distances from the smelter in order to improve subsequent foliar uptake and risk assessment models with applications for both stable and radioactive metallic pollutants carried by atmosphere particles.

#### Acknowledgements

We gratefully acknowledge ADEME, the French Agency of Environment and Energy, for founding the DIMENSION project, as well as STCM, the Chemical Metal Treatment Company, for its technical help in the experimental set-up and for financial support.



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