Use of commercial sphagnum to estimate the geographic impact of a battery of recycling plant

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Résumé

Une technique de biosurveillance (moss-bag) est utilisée pour évaluer les retombées de métaux lourds (plomb, cadmium, arsenic, baryum et antimoine) autour d'une source industrielle. Les résultats sont comparés à ceux obtenus par l'utilisation de jauges de sédimentation et par modélisation des rejets canalisés. Ces essais sont réalisés en parallèle autour d'un même site de seconde fusion du plomb.

Les moss-bag se révèlent être d'aussi bons outils qualitatifs que les jauges de sédimentation. Il apparaît également que les moss-bag ont une plus grande efficacité à capter les retombées atmosphériques que les jauges de sédimentation et cela, malgré une surface d'exposition plus faible. Une durée de quinze jours est suffisante pour recueillir des niveaux quantifiables de plomb, de cadmium, d'antimoine et de baryum, dans les moss-bag placés au voisinage du site étudié. De plus, la hiérarchisation des points de retombées obtenue est équivalente voire plus fine (plus de niveaux différenciés) que celle déterminée au moyen de jauges au bout de trente jours.

Cependant, la vitesse d'accumulation des métaux lourds dans les moss-bag ne semble pas être constante dans le temps. Ceci rend donc délicate la comparaison de résultats de campagnes réalisées sur des durées différentes et peut-être même des périodes différentes. La coupure granulométrique et la sélectivité des moss-bag restent également mal connues.

Cette étude permet également de valider l'utilisation de sphaignes de culture pour concevoir les moss-bag, palliant ainsi la difficulté d'approvisionnement liée à l'utilisation de sphaignes «naturelles ».

L'utilisation de cette technique de cette technique a permis d'évaluer rapidement la contribution du site aux teneurs de plomb, cadmium, arsenic et antimoine, mesurées à son voisinage. En comparaison, la modélisation des rejets canalisés du site a fourni une information qualitative incomplète du fait de la présence de sources diffuses.

Cet outil de sondage qualitatif performant (intervalle de confiance réduit, coût de mise en œuvre faible, simplicité d'utilisation, technique discrète, légère) peut apporter une information essentielle là où d'autres approches sont plus fragiles (modélisation en situation dégradée) ou nécessitent d'être optimisées (méthodes quantitatives normalisées).

Cependant, une campagne de mesure utilisant une méthode de biosurveillance active, doit intégrer, dès sa conception, un minimum de points de contrôle (blanc de site, témoin, détermination de l'intervalle de confiance).

Abstract

A technique of biosurveillance (moss-bags) is used to evaluate the heavy metal depositions (lead, cadmium, arsenic, barium and antimony) around an industrial source. The results are compared with those obtained by the use of gauges of sedimentation and by modelling of the emissions from stacks. The moss-bags prove to be as good qualitative tools as the gauges of sedimentation. It also appears that the moss-bags have a greater effectiveness to collect the

atmospheric depositions than the gauges of sedimentation and that, in spite of a smaller surface of exposure. Fifteen days duration is sufficient to collect quantifiable levels of lead, cadmium, antimony and barium, in the moss-bags placed in the vicinity of the studied site. However, the speed of accumulation of heavy metals in the moss-bag does not seem to be constant in time. This makes delicate the comparison of results of campaigns carried out over different durations and perhaps periods. This study validates the use of sphagnum mosses of culture to make some moss-bag, thus mitigating the difficulty of provisioning related to the use of "natural" sphagnum mosses. The use of this technique, that requires a minimum number of measuring points, made possible a quick evaluation of the site's contribution in lead, cadmium, arsenic and antimony, deposition measured in its vicinity. In comparison, the modelling of exhaust gases and particulates of the site provided incomplete qualitative information because of the presence of diffuse sources. This tool of powerful qualitative survey (confidence interval reduced, cost effective, ease of use, discrete, light technique) can bring essential information where other approaches are more uncertain (modelling in degraded situation) or require to be optimised (standardized quantitative methods).

Introduction

We used an active bioaccumulation method known as moss-bag. This technique rests on the exposure of small nylon nets filled with bryophytes for one given period. The bryophyte depends primarily on the atmosphere for their nutrition. They absorb there the traces elements (deposit dry and wet) they need but also other elements nonessential with their survival of which heavy metals. The bryophyte, having a strong capacity of cations exchange, they will act like metals hyper-accumulators and their complexes. These compounds will be fixed at the cellular walls of which numbers components have negatively charged groupings.

Contrary to the traditional techniques of assessment of pollution, the bryophyte are living organisms, and their capacities of accumulation are thus prone to variations of a biological nature in relation to their environment. Consequently, the exploitation without precaution of the results obtained by the biosurveillance is unsure. There are several sources of variability of the retention capacity of the elements in the bryophyte [1] :

- The species: These variations, related to the difference of morphology and growth are at the origin of the difficulties of interpretation at the time of the comparison of the results for the in situ studies. At small scale, it is relatively easy to find a species present on all the selected sampling points. But on greater scales, it is often necessary to take other species when the species of reference are missing. The interpretation of the results is then more critical. In this case, comparisons inter species are to be realised. Those are difficult to carry out since variability inter species must be quantified in relation to the regional variations [2]. This variability source makes also critical the comparison of studies "transplants" realized with various species.
- The element: the rates of retention also differ according to the element considered [3, 4].
- The environmental conditions: sources and mechanisms, others than air pollution, can influence the metal contents of the bryophyte [5]:
  1. The marine factor: exchange cations on the surface of the bryophyte with sea salt ions;
  2. The ground factor: mineral particles coming from the local ground and transported by the wind;
  3. Effects related to the acid rains (exchanges of ions) and the transport of the soluble compounds at the time of the long periods of contact water/soil/bryophytes (snow melt);
  4. The climatic conditions play an important part in the absorption of the elements, the intensity of precipitations, the wind speed [7] is one of the principal parameters which modified the process of absorption [6].

Contrary to certain studies [8], we did not seek to maintain the bryophyte under optimum conditions for life. This approach can seem contradictory with the use of living organisms, and we could almost speak about "necro-sensor". We made this choice in order to use a biologically inert material, to free itself from any interference of the metabolism of the bryophyte with the collection of metals (elimination, defense...). Indeed, an alive bryophyte used in the technique of the transplants is under permanent stress. This has consequences on its capacity of accumulation then involving differences in response from an intake point to another.

The principal operational difficulty when one works with this type of material is the provisioning. Sphagnum mosses, because of particular ecosystem that they shelter, are often protected species. We thus tested the possibility of using of Sphagnum mosses of culture used in the horticulture in substitution of the natural sphagnum mosses.

The aim of this study was also to show the benefits of this kind of technique to evaluate the geographic impact of diffuse emission. We worked on the contribution to lead, cadmium, arsenic, barium and antimony deposition coming from a battery recycling plant. For comparison, we also used gauges to measure the deposition with a conventional methodology.

1. Materials and methods

Moss-bag origin

The moss used is of Sphagnum mosses type. They came from Chile where they were dried then cut into pieces of 15cm after harvesting. They were then, conditioned and dispatched all over the world. They are identified "Chile" in this study. The results obtained with this material have been compared with those obtained with Sphagnum mosses collected alive in its natural environment (Sphagnum papillosum). in Forest of Coye (close to Chantilly) far from any polluting anthropic activity. They are identified "Coye" in the remainder of the study.

Preparation

All the containers, utensils were rinsed with diluted nitric acid (1%), then with deionised water. During all the operations (harvest, treatment, exposure...) the sphagnum mosses and the moss-bag were handled using plastic gloves without talc. The collected sphagnum mosses (Coye) were placed in a hermetic plastic bag, then stored at around 4°C. The Sphagnum mosses Chile were directly taken in the conditioning of the supplier. The sphagnum mosses were cleaned (elimination of the old sphagnum mosses, other plants, insects...) then cut into pieces of 5-6 cm. The pieces were washed with the water de-ionised and then with the diluted acid (HNO3 with 1%). After a last rinsing with deionised water, the Sphagnum mosses were dried with air (clean room) until complete dehydration. Approximately 0,4 g (dry weight) of mosses were laid out in a nylon net (meshs of 2 mm X 2 mm) so as to form a sphere of a diameter ranging between 2,5 and 3 cm. The moss-bags were then placed in hermetic plastic bags in order to avoid any possible contamination before exposure. The moss-bags were then set up approximately at 1,70 m above the ground level.

Post-exposure treatment

The moss-bags were collected in clean plastic bottles. The samples were dehydrated in a drying oven. The whole of the sample is analysed, which makes it possible to avoid problems of distribution of the analyte in the sample. The whole of the moss-bag is poured in matras then mineral-bearing with the furnace microwaves in a nitric acid solution to 65% (Suprapur).

Sampling strategy

The location of the sampling points around the site was selected according to the modelling of stack emissions (figure 1-left side).

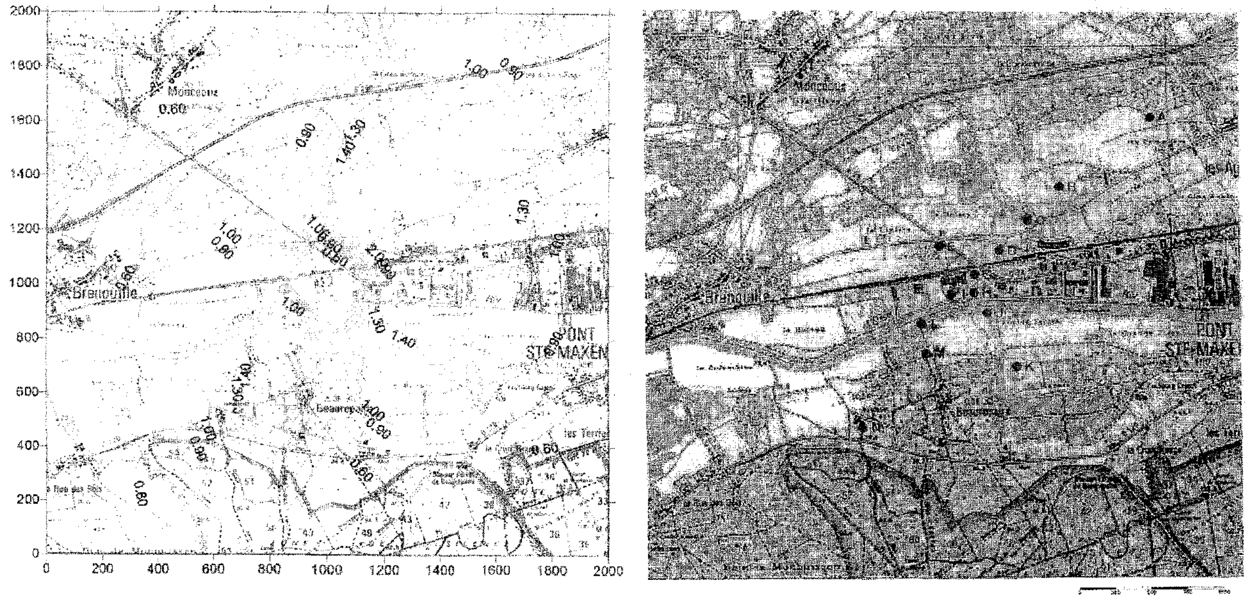

Figure 1 : <u>Left side :</u> Lead concentrations calculated by modelling of the lead emissions from stack (10^{-2} µg/m^3) – Plant position : 1000 ;1000. <u>Right side :</u> *Position of the 14 sampling points around the plant (blue circle)*

Fourteen sampling points equipped with sensors of the moss-bag type and gauges were set up in a perimeter of 2 km around the site (figure 1-right side).

A reference sensor of each system of measurement was also located at approximately 4 km in the south-west of the site, far from any source of heavy metal emission. In order to evaluate the level of background contamination.

The measurement network was focused on a perimeter of 500 m around the site in order to evaluate the possible impact of the diffuse emissions. In order to calculate the repeatability of each system of measurement, 6 moss-bags and 6 gauges were simultaneously exposed on zones expected to collect strong (point C) and weak deposition (point K) (figure 1-right side).

The sensors were exposed during one month (from 03/06/03 to the 04/07/03). During this period, some of the moss-bags were exposed over a fifteen days shorter duration (from the 03/06/03 to the 19/06/03) in order to evaluate the duration of minimal integration necessary to get a good quality of the results. The formalism J+15 and J+30 will distinguish the two exposure times in the remainder of the document.

The parameters of atmospheric dispersion (force and direction of the wind to 10 meters height, pluviometry and temperature on the ground), were obtained thanks to the establishment of a measuring site on the factory site.

On each sampling point, three moss-bags from each origin (Coye and Chile) and of both duration (J+15 and J+30) were exposed in order to give a good estimate of the average metals concentration.

For each system of measurement, blank samples were also carried out (samples that underwent all handling without never being exposed). This makes possible to evaluate the initial contaminations but also those likely to occur at each stage of the protocol: taking away, pre-exposure treatment, transport, handling, post-exposure treatment, analyses.

On the whole 204 moss-bag and 25 gauges were exposed during the campaign.

Analyses
According to the concentrations expected in the various samples, two analytical techniques were used: ICP-AES (atomic emission spectrophotometer of coupled to an induced plasma) for the hight concentrations and ICP-MS (mass spectrometer coupled to an induced plasma) for the low concentrations. A semi-quantitative analysis in ICP-AES was carried out on some samples in order to choose the analytical technique.

2. Results and discussion

Repeatability
The 6 moss-bag and 6 gauges exposed in parallel on the points C and K made it possible to calculate a confidence interval (IC) to 95% for two levels of concentrations (weak and strong). This IC correspond to the interval including/understanding with a probability of 95% the true value of the average (μ).

$$IC = t_{1-\alpha/2,\gamma} \times \frac{s}{\sqrt{n}}$$

$$\bar{x} - IC \leq \mu \leq \bar{x} + IC$$

with ,

n : *sample number (n=6)*

$t_{1-\alpha/2,\gamma}$: *Student coefficient, for which γ is the degree of freedom ($\gamma = n-1$), and the probability 1-α/2.*

$\bar{x}$: *averaged concentrations measured in C or K*

μ : *the true value of the averaged concentration measured in C or K*

s : standard deviation *calculated at points C or K*

The relative confidence interval, $\left(\frac{IC}{\bar{x}} \times 100\right)$ was calculated of each point C and K for each metal, each type of support and each exposure time. The repeatability of the technique of the moss-bag is of 15-20%, therefore comparable with that of the technique of the gauges. For lead and cadmium the repeatability is constant in the range of studied concentrations. We will apply this assumption to the whole of metals for this study.

Accumulation rate
The accumulation rate of the moss-bag varies with the exposure time. This variation is more important than the variation of repeatability, but it is equivalent at the same moment on the whole of the points (placed in a comparable climatic environment). This intrinsic property of the moss-bag thus makes critical the comparison of the results of campaigns carried out over different durations and perhaps even from different periods. A series of fifteen days measurement is sufficient to evaluate the barium and antimony, and lead levels accumulated in the moss-bags. For weak cadmium background noises, a 30 days exposure is preferable.

Comparison Coye/Chile

The correlation between this two types of material is very good (figure 2). The Coye moss-bags are slightly more sensible than the moss-bags of the Chile type but the sphagnum mosses cultivated remains a good alternative to the "natural" sphagnum mosses for the design of moss-bag.

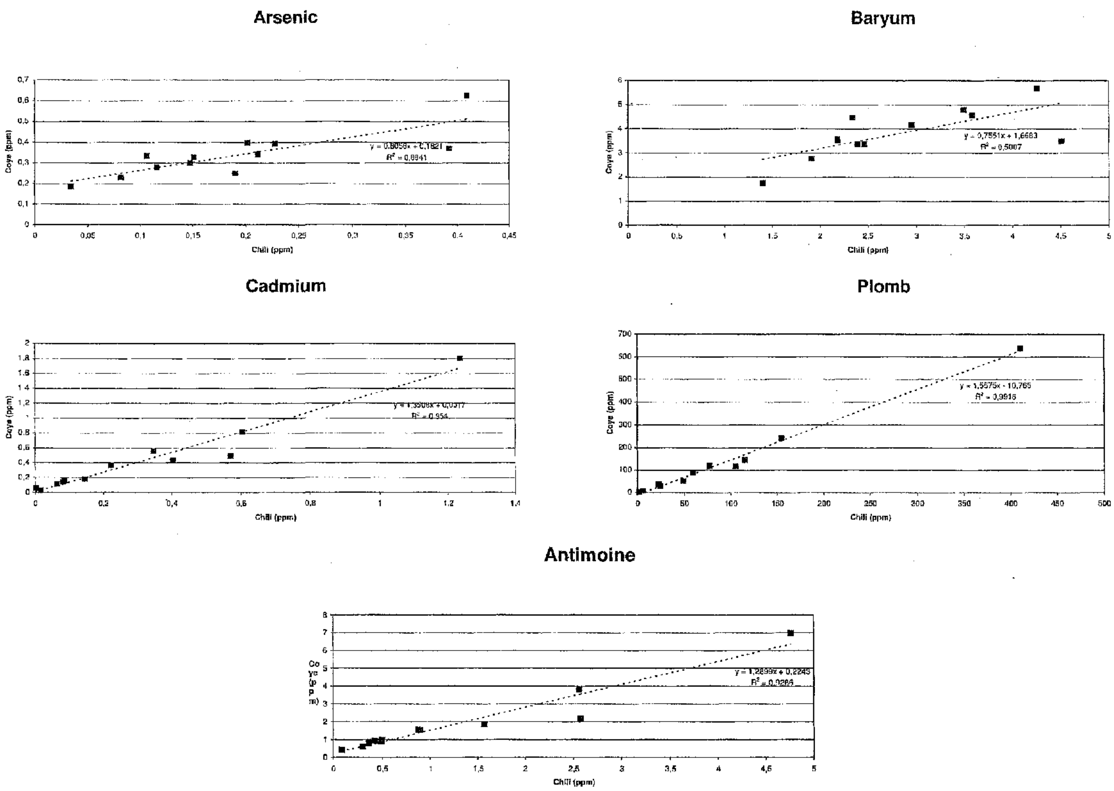

Figure 2 : Correlations between Chile and Coye moss-bags (exposed during 30 days)

Comparaison Moss-bag / Gauges

The correlation between the measurements carried out with the gauges and the moss-bags Chile is less good than that between different type of moss-bags (figure 3).

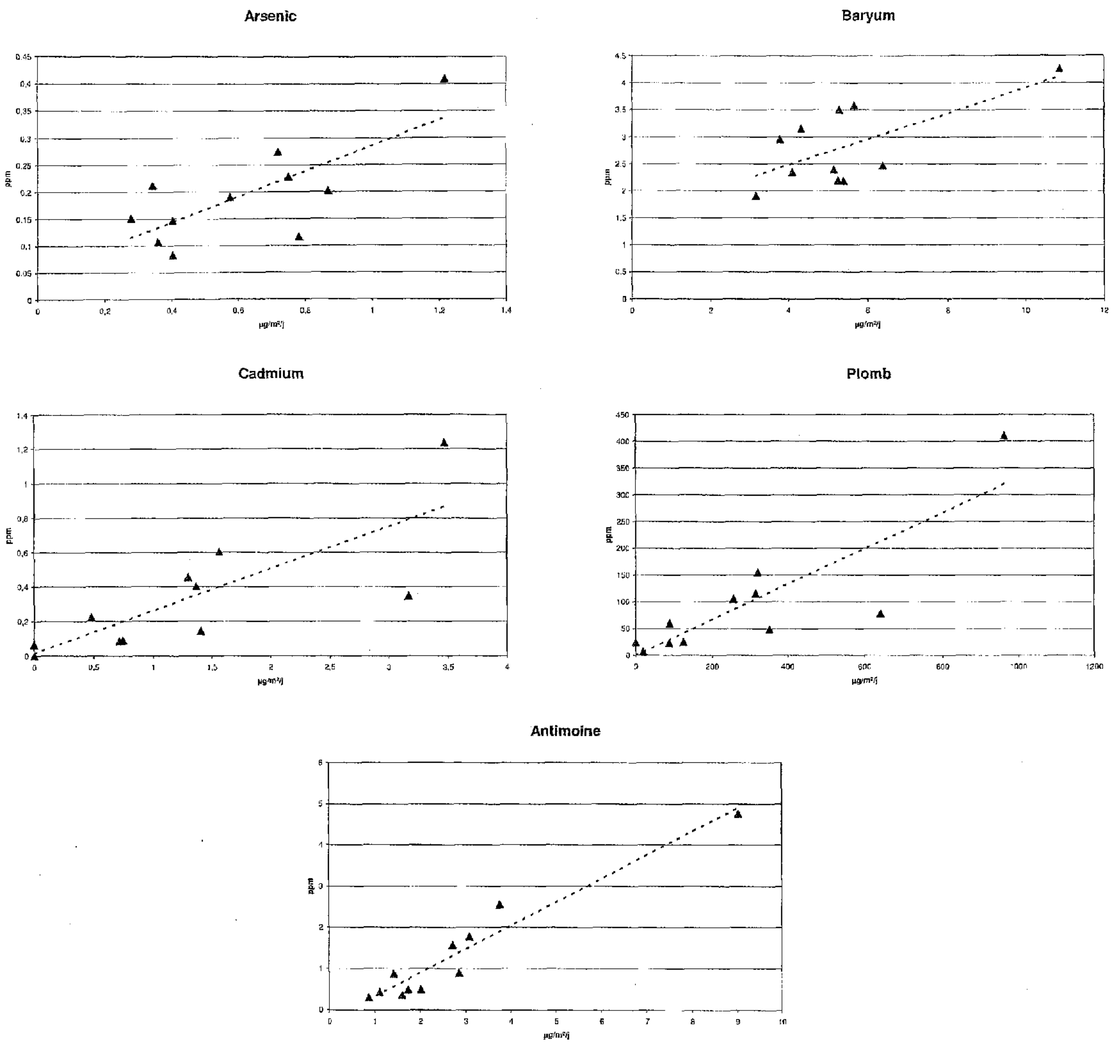

Figure 3 : Correlations between Chile moss-bag and gauge (exposed 30 days)

The moss-bag and the gauges are subjected to the same particulate metal concentrations in the ambient air. In order to compare the quantities measured with these two systems of measurement, the metal concentrations measured in the moss-bags (µg/g of ms) were converted into µg/m^2.day to be in a comparable unit with the measurements carried out with the gauges. The ratio of these quantities is higher than one (from 1.4 to 3.9) for all the elements (figure 4).

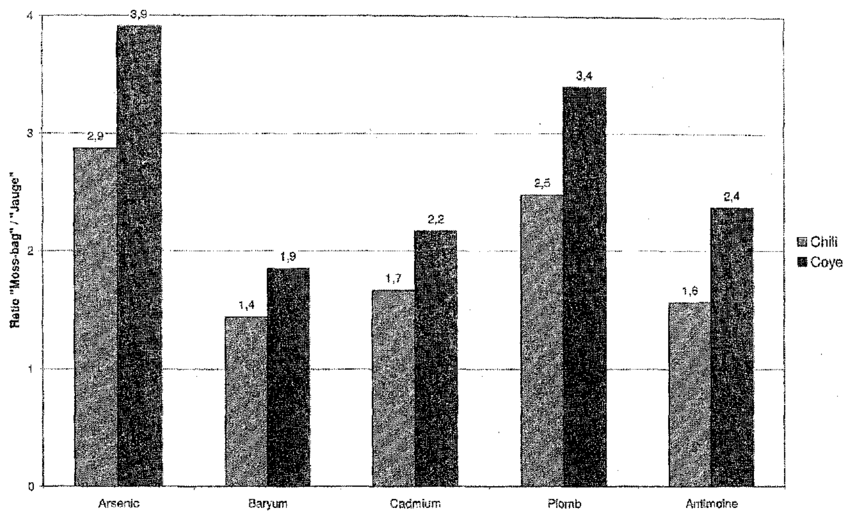

Figure 4 : Ratio of surface deposition measured by moss-bags and gauges

These results are in contradiction with the surface of exposure of the moss-bags which is theoretically smaller than the section of opening of the gauges (Surface Gauges = ~2.6 x Surface moss-bag). By making the assumption that the two systems have identical cut-off diameter, it seems that the moss-bag has a surface of exposure that would actually range between 3 and 10 times that of the gauges. The greatest effectiveness of the moss-bag is probably the result of a combination of two factors. First, the fibrous internal network of moss-bag offers an important exchange surface to the particles. In this network, the particles are better captured on the vegetal surface (adsorption and/or mechanical trapping) than on the plastic surface of the gauges (stop and go phenomenon). In addition, comparatively with the gauges, one estimates that the moss-bags collect a broader spectrum of particles [8]. Indeed, the gauges collect only the particles of size higher than 5µm of diameter [9] and the finer particles, generally forming a deposit by impaction [10], are retained better in the fibrous network of the moss-bag. These two factors compensate probably the losses of matters collected by the moss-bag (scrubbing, agitation, problem of adsorption of the metal elements traces on the nylon net not analysed...).

There is a good correlation between the moss bags and the gauges. The moss bags seem to be more sensitive than the gauges.

Contribution of the plant

For all the metals, the contents measured within the limit of property of the factory are higher than those measured outside. According to metals, the contents measured at the point G are between 7 and 6194 times those of the reference sample (table 1). For all metals, the point D corresponds to the maximum of the contents measured outside the site.

Localisation	Arsenic	Baryum	Cadmium	Plomb	Antimoine
A	1	1	23	4	1
B	2	1	77	10	3
C	4	1	159	19	6
D	4	1	430	69	16
E	2	1	140	18	5
F*	13	3	4613	424	83
G*	47	7	6194	1480	245
H*	12	3	1369	227	85
I*	10	2	1203	184	30
J	2	1	211	26	8
K	1	1	30	4	1
L	1	1	121	13	3
M	1	1	51	8	2
N	2	2	32	4	2

** Localisation dans la limite de propriété du site industriel.*

Tableau 1 : Ratio of concentration measured at different locations to the reference

Outside the limits of the site, the ratio obtained for barium drops quickly and is relatively uniform whatever the direction of sampling. For lead, cadmium, arsenic and antimony the ratios are a function of the distance that separates the sampling points and the site. The shape of the curves is similar for these four metals (figure 5).

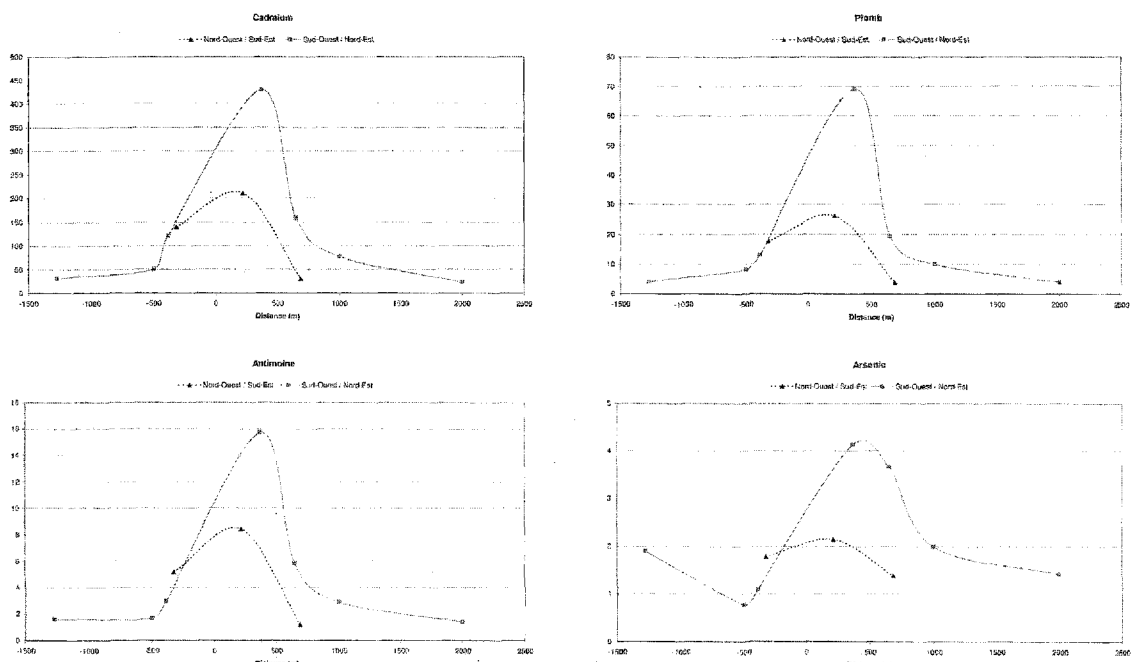

Figure 5 : $\frac{C_{Po\text{int } i}}{C_{Témoin}}$ *evolution at different sampling points in function of the distance to the site*

The concentrations measured increase through site. According to the directions of dispersion, south-west/north-east and north-west/south-east, they reach a maximum respectively at 370 and 217 m under the wind of the installation. The points located at the NorthEast of the site, reveal more important contents compared to those of the three other directions. This distribution is consistent with the wind rose and recorded precipitation direction. The plant obviously seems to be a probable source of lead, cadmium, arsenic and antimony.

Conclusions

For the levels of exposure met in this study, the sphagnum mosses of culture are a good alternative to natural moss-bags. This limits the difficulty of supplying sphagnum mosses in natural and protected area.

The technique of the moss-bags is a powerful tool of qualitative survey (implemented simple, inexpensive, allowing to carry out many intake points) which has many advantages (lower confidence interval, low cost of implementation, easy to use...).

This technique brings essential qualitative information where other approaches are less reliable: modelling in degraded situation (diffuse emission). This tool makes it possible to optimise and reduce the costs of conventional quantification campaigns by quickly determining the geographic impact of a plant.

It however does not exempt to implement a series of "traditional" measurement to complete the characterization of the impact of a site.

This study shows the importance to follow a strategy of measurement which makes it possible to have the necessary elements to the objective exploitation of the results (reference sample, blank, determination of the repeatability...)

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