Atmospheric metal deposition based on moss analysis: Which classification and mapping method to choose for a relevant interpretation of actual deposition and critical loads?

Les dépôts atmosphériques de métaux basés sur les analyses de mousses : Quelle méthode de classification et de cartographie choisir pour une interprétation pertinente des dépôts et des charges critiques ?

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Abstract

France has been participating in the European program "Atmospheric heavy metal deposition in Europe based on moss analysis" since 1996 with the aim of obtaining data on metal deposition on a large scale. Five moss species were collected at a national scale within the framework of two surveys: 1996 and 2000. The complete data for France of 36 trace elements analysed during the 1996 biomonitoring campaign is presented here for the first time. For ten elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn), a comparison between France and the rest of Europe, as well as a comparison between 22 French provinces is done using box plots. This work also presents the first consideration of the potential use of "metal accumulated in moss" data for ascertaining actual metal deposition and critical load estimations in France. The methodological approach of presenting the results, classification of data ("European", "K-means" and "Mouvet" methods) and mapping (spot by spot and interpolation) are considered, showing the impact of these methods on the interpretation and representation of the data. It is shown that (1) interpolation maps associated with the "European" or the "K-means" classification method provide a good tool to visualize relative atmospheric metal deposition; (2) interpolation maps associated with the "Mouvet" classification method could provide a new method for critical loads and limits estimation, after further verification and potential modifications.

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Résumé

Depuis 1996, la France participe au programme européen « Atmospheric heavy metal deposition in Europe based on moss analysis » dont l'objectif est d'obtenir des données sur les dépôts métalliques à grande échelle. Cinq espèces de mousses ont été récoltées en France lors des deux campagnes nationales de 1996 et 2000. L'ensemble complet des données (36 éléments) de la première campagne française est présenté pour la première fois. Pour 10 de ces éléments (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn), sont comparés : les résultats français aux résultats européens et les résultats des 22 régions administratives françaises entre eux, en utilisant une représentation en boîtes à moustaches. Ce travail constitue également une première réflexion sur l'utilisation potentielle des données « métaux accumulés dans les mousses » pour une estimation exacte des dépôts métalliques et des charges critiques en France. Plusieurs aspects méthodologiques concernant la présentation des résultats, la classification des données (méthodes « européenne », « nuées dynamiques » et « Mouvet ») et la représentation cartographique (méthodes « point par point » et « interpolation ») sont considérés, soulignant l'impact de ces méthodes pour l'interprétation des résultats. Ce travail montre que : 1. les cartes d'interpolation associées à la méthode de classification « européenne » ou des « nuées dynamiques » fournissent un outil pertinent pour visualiser les dépôts relatifs de métaux ; 2. les cartes d'interpolation associées à la classification de « Mouvet » pourraient constituer, après vérification et adaptations, une nouvelle méthode d'estimation des charges et limites critiques.

Introduction

The programme "Atmospheric heavy metal deposition based on moss analysis" has been recently joined to an International Cooperative Programme on the effects of air pollutants on natural vegetation and crops (ICP-Vegetation), which is one of working groups of the Convention on Long-Range Transboundary Air Pollution from the United Nations (LRTAP, UN/ECE). The ICP-Vegetation has focused especially on air pollution problems and using clover and moss data for quantifying the risks posed by the atmospheric heavy metal deposition to vegetation. One of the projects of this present ICP aims to provide scientific information for the Aarhus Protocol (1998) designed to reduce emissions of heavy metals. For a decade, the critical load concept has been introduced in negotiations for the revision or elaboration of protocols to ensure an objective assessment for achieving maximum benefit of emission reductions at the lowest costs.

In order to derive the deposition levels at which effects of air pollutants start to occur, the **critical load concept** has been defined as *"a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge"* [1]. The critical load concept is based on the calculation of a **critical limit**, which is the maximum concentration of a pollutant supported by ecosystems. It is the concentration at which no relevant harmful effect on specific receptors (micro-organisms, plants, human beings) will occur over the long-term [2]. These harmful effects may be based on observed toxicity of soil organisms or biological processes, or on toxicity tests conducted in laboratory [3]. Based on the conclusion of the Bad Hazburg and Schwerin workshops [4, 5], ecotoxicological basis for the calculation of critical limits in soils is weak. An alternative approach was proposed using only free metal concentration (without any toxicological data) in soil solution, when such information exists. For example, the Dutch Target Value (DTV) is based on background soluble and adsorbed metal concentration in unpolluted soils and groundwaters [6]. The possible impact of a certain load of metals on ecosystems can be estimated by determining the difference between the actual deposition load and the calculated critical load. It means that the next step for critical load estimation is the measurement of **actual metal deposition** in ecosystems in order to determine whether the critical load is exceeded or not.

In France, networks of physico-chemical metal surveys have been mainly restricted to urban or industrial areas for ambient air: the lead network is at a national scale [7], and there are more localized networks for cadmium, arsenic and nickel [8, 9]. A few studies for metal deposition have also been conducted in field experimental stations. A primary study was done in an open field [10] and the EMEP network has planned to prepare one additional site in south-western France. However, these direct measurements of actual metal deposition are expensive, time consuming and require heavy equipment preventing them being done on a nationwide scale. Other approaches exist for metal deposition estimation in large area in France: (1) use of snow precipitation [11] and ice samples [12] to establish heavy metal map in the Alps; (2) use of soils and humus in Vosges [13]. However, these previous studies have been mainly restricted to local or regional areas for investigating deposition fluxes. An important problem for critical load estimation in France is the lack of actual deposition data on a national scale.

The utilisation of metal bioaccumulating plants is an indirect method for the estimation of metal deposition on a large scale. Mosses have been frequently used to measure metals in the environment for thirty years [14] and their efficiency to accumulate metals is well known [15]. In epigeic mosses the lack of a root and vascular system (as seen in vascular plants) means that much of the water and nutrient input is from dry and wet depositions. Some moss species are common and widespread. Their sampling is easier and less

expensive than using physico-chemical collecting equipment. Furthermore, the exposure period of mosses is several years, which is an important advantage for making maps of metal deposition.

A biomonitoring network for estimating background atmospheric metal fall-out at national scale has been in place in France since 1996 at more than 500 sites [16]. This French moss biomonitoring network is also a part of a larger international biomonitoring network. Studies on atmospheric metal deposition based on moss analysis were initiated in Scandinavian countries at the end of the 1960's [14], being enlarged to Northern Europe with national surveys in the 1980's, then in 1990 expanded to cover the rest of Europe (about 30 countries) with three surveys planned every five years. The European programme, originally proposed by the Nordic Council of Ministers with a view to estimating metal deposition, has since been incorporated, in 2001, into the ICP-Vegetation programme from the United Nations. A review process has begun to define how more detailed information on ecosystem risks can be provided using the moss data.

The purpose of this present work is:

- To present the complete data set of the 1996 French moss survey, including 36 analysed elements (an incomplete data set was published previously [16]); to compare the French moss data with those from Europe and to compare French data between and within the 22 French administrative provinces for the 10 common metals analysed: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn).
- To give a preliminary view on possible presentations and optimisations of these data as a base for further discussions in the context of critical loads. Especially, on how best to group these data into clusters in order to interpret the derived maps in a spatio-temporal context (European or French scale, from one survey to another).

The aim of this paper is thus to compare three classification schemes and two mapping methods. Other questions are: how could metals accumulated in mosses give information about the atmospheric deposition and fluxes of metals? How could the results of this survey based on metal analysis in mosses be useful for the calculation of critical loads values and critical load exceedance?

This paper is not a complete interpretation of the French 1996 "moss-metal survey". It must be considered as a preliminary investigation on the use of data provided by the "moss method" in the context of critical load calculation.

Materials and methods

The choice of moss species and the sampling method applied in France is largely based on Scandinavian recommendations [17] that were adapted to French ecological conditions as described below.

Recommendations before metal analysis

As numerous metal sources from air are present in many environments (urban sites, industrial and mining sites, volcanic sources...), the utmost care must be taken to avoid contaminations during the steps from field sampling to cleaning in the laboratory (sampling, transportation, sorting, cleaning and storage). Precautions to avoid contamination must be taken: plastic gloves have to be worn, smoking is prohibited, airtight storage should be chosen (to prevent contamination and lost of volatile elements like mercury and arsenic), the material should be handled in clean environments, and plastic tools should be used (previously soaked in acid solution and rinsed with de-ionised water).

Moss species

Moss species are mainly chosen based on them being terricolous, abundant and ubiquitous species that are easy to identify. The mosses collected in France during the 1996 survey are *Pleurozium schreberi* (Brid.) Mitt. (n = 112 samples), *Hylocomium splendens* (Hedw.) B.S.G (n = 52), *Hypnum cupressiforme* Hedw. (n = 200), *Scleropodium purum* (Hedw.) *Limpr.* (n = 160), and *Thuidium tamariscinum* (Hedw.) B.S.G.(n = 39), in order of their suitability.

Field sampling

Sites were chosen far from any local source of pollution, being located in non-urban areas, to estimate the background pollution as well as the possible long-range transport of air pollution. A regular network covering the whole of France (512 sites within the 22 administrative provinces) was used with an average sampling density of almost one moss sample per 1 000 km^2 [16, 18]. The moss network has also included some of the forest sites from the French permanent plot network for the Monitoring of Forest Ecosystem (RENECOFOR) managed by the French National Forest Office (ONF).

Sampling was done preferentially in dry conditions. Samples were mainly taken from forest clearings, situated at least 3 m away from trees, so they were not directly exposed to throughfall. Composite samples were made from one sampling point consisting of 5 to 10 subsamples collected within an area of about 50 × 50 m.

Sample preparation and analysis

The cleaning, sorting and dehydration (at 40 °C) of mosses were carried out following the Scandinavian guidelines [17, 19] and are detailed in previous publications [16, 20].

Analysis of 36 elements for the 1996 moss survey were performed at the Pierre Süe Laboratory (CEA-CNRS, Saclay) using two multi-element methods:

INAA (Instrumental Neutron Activation Analysis) for 32 elements, and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for 4 elements (Cd, Cu, Ni, Pb). These methods were agreed upon by an analytical comparison study carried out by the participating countries [21]. The analytical details have been described in earlier papers [22-24]. Results are expressed in µg of metal per g of moss (dry weight at 40 °C).

Description of methods for classification

The classification is a way to group similar data into a number of clusters with each cluster containing the lowest number of samples possible to facilitate the interpretation of the data. Different algorithms of classification can be used according to the different hypothesis of the work.

The "European" classification

The "European method" has been determined at the European level and is currently used for the realisation of the European maps [19, 25]. For the determination of different classes, no statistical test was used but rather an empirical method for getting appropriate maps at the European scale. The clusters used for the 1995 European survey were elaborated from previous Nordic and European surveys [17, 19]. The data set was divided into eight concentration classes of equal intervals from the minima to maxima values for each metal. However, for Cr, Cu, Fe, Pb, Ni, V and Zn, the highest class limits have been changed (increased or reduced according to the element) since the 1985 to the 1995 European surveys. These changes were linked to a decrease of some of the highest values observed between the surveys (often in the Scandinavian countries) and to an extension of the programme to countries from Eastern Europe where higher concentrations were observed for some metals [Rühling, pers. com.].

The classification using the "K-means" algorithm

This method has not been used at present for the mapping of European data. Initially, this non-hierarchical method translates the number of components of a population to the final required number of clusters, which are generated to be as different as possible. The final required number of clusters is chosen from the points that are mutually farthest apart. Next, each component in the population is examined and is assigned to one of the clusters depending on the minimum distance. The centroid's position is recalculated every time a component is added to the cluster and this continues until all the components are grouped into the final required number of clusters.

The classification of "Mouvet"

The "Mouvet's method" is currently used in France by the French Water Agencies to determine the classes of metal concentrations measured in aquatic mosses sampled for the estimation of water metal pollution. It has been set up by Mouvet [26] and was adapted by Mersch and Claveri [27]. This metal biomonitoring survey using aquatic mosses in rivers is similar in many points to those set up for the air pollution using terrestrial mosses: both have a large number of sites located in French territory (about 400 stations), successive surveys (each year since 1992), a large set of data, and the pollutants analysed are metals. These similarities allow us to adapt this methodological approach to terrestrial mosses.

The method is based on a reference concentration which is defined by the concentration value when there is no pollution. According to Bonnefoy and Bourg [28], this concentration can be calculated when the set of data is high in a large territory, by successively eliminating the highest values until a standard deviation of 60% is reached. In this way, the distribution of values is closest to a normal distribution.

The reference concentration allows the limit of classes to be calculated and pollution load in the ecosystem to be defined. A twofold geometric progression of the limit of classes is chosen, except for the cluster 1 for which the upper limit is threefold the reference value. In this way, the five upper limits of classes are defined as follow: 3 times the reference, **unpolluted situation** (cluster 1); 6 times the reference value, **suspected pollution** (cluster 2); 12 times the reference value, **certain pollution** (cluster 3); 24 times the reference values, **important pollution** (cluster 4); exceeding 24 times the reference value, **exceptional pollution** (cluster 5).

Description of calculation of the polymetallic index

The polymetallic index is based on the addition of concentrations for every metal in each site. However, as some great differences exist between element concentrations into mosses, the data had to be standardised (subtracting the mean and dividing by the standard deviation) before adding values.

Description of methods for mapping

The spot by spot map

The spot by spot map was drawn using ArcInfo and ArcView 3.1 GIS. Each spot indicates a sampling site and represents a concentration range (class) which corresponds to the value of metal accumulated in the moss species. The different sizes and colours of spots were chosen in accordance with those used by the European programme [25]. In the case of two moss species per site, the greater symbol corresponding to the higher value was put under the lower spot so not to mask it.

The interpolation maps

For the European maps

The interpolation algorithm was Kriging with a linear drift component added. This procedure involved a transformation of the data from the irregularly spaced sampling sites to a regular grid. To switch off the interpolation when there were not enough data points, the following search criteria were used: maximum distance equal to 60 km, at least one data point in each quadrant, multiple data points in a grid cell were replaced by the average. The overlay of geographic boundaries have been done using Arc info software [Olsson, pers. com.].

For the French maps

Inverse distance weighted (IDW) interpolation determines cell values using a linearly weighted combination of a set of sample points. The weight is a function of inverse distance.

In the case of French maps, the characteristics of the interpolated surface is controlled by limiting the input points for calculating each interpolated point by a radius equal to 60 km. IDW allows control of the significance of known points upon the interpolated values, based upon their distance from the output point. The interpolation can be shifted from local to global scales by changing the power. A higher power is chosen because it results in less influence from surrounding points, i.e., nearby data will have the most influence, and the surface will have more detail (less smooth). A common value of 2 is chosen for that the relative influence of more distant points decreases.

Results and discussion

French results of the 1996 moss survey

The main results of the 1996 French moss survey are presented for the 36 elements analysed but this paper will mainly focus on the 10 metals common to all European countries: As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn. The 26 other elements are given to make the first information on them available, but they are not interpreted in detail here.

Comparison with European results

The Table 1, p. 104, presents French data (36 elements) compared with results (10 metals) from more than 20 European countries participating in the 1995 European moss survey [25]. For As, Cd, Cu, Fe, Hg, Ni and Zn, French medians are close to those calculated from the rest of Europe [20]. In France, the medians are only slightly lower for V, but slightly higher and twice as high respectively for Pb and Cr. In the case of V and Cr, the French results are underestimated and overestimated respectively, which is probably due to the analytical method used [23]. Among the 10 common metals, France presents neither the highest nor the lowest metal concentration in Europe. Although variation coefficients are relatively low for some elements (41% for Zn, 52% for Cu) indicating homogeneity of metal exposure of French sites, they are large for other elements (up to 130% for As) indicating heterogeneity between sites.

Comparison between the 22 French regions

France is divided in 22 administrative provinces (Figure 1, p. 105). Figure 2, p. 106-110, presents the 1996 French moss data set for As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn, using box plots in which each region is ranked according to an increase of its median value. Box plots allow us to describe the distribution of data within the 22 provinces of France.

For most of the metals, no important concentration variations are observed between the overall values median from the 22 regions. Furthermore, values are weakly scattered (25-75% values) over the medians for As, Cd, Cr, Fe, Pb, except for Cu, V, and Zn (Figure 2, p. 106-110). The minima from regions are comparable for each metal but differences between maxima are observed for some metals. For Cd, Cu, Pb and Zn, maxima are found in some specific provinces showing higher median values. High concentrations are observed in some areas known to be urbanized and industrialized, mainly in the Ile-de-France area (Cd, Zn), the Nord-Pas-de-Calais (Pb), the Picardie (Cu) and the Rhône-Alpes areas (Cu, Zn), and in the agricultural area of Champagne-Ardenne (Cd). Some maxima are also found irregularly scattered within provinces where the medians indicate a relatively low level for some metals, revealing hot spots of contamination (for example in Centre for Pb, Auvergne and Rhône-Alpes for Fe, Bretagne and Midi-Pyrénées for Ni).

In order to go further in the interpretation of these results detailed provinces by province, the box plot presentation can be completed by a calculation of a polymetallic index. Figure 3, p. 111, presents box plots of the "polymetallic index" (10 metals) from the 22 French provinces. This presentation of results confirms some of earlier conclusions: the Ile-de-France, Picardie, Nord-Pas-de-Calais, Languedoc-Roussillon, Champagne-Ardenne and Rhône-Alpes areas appear to be the six provinces showing the most important polymetallic concentrations within mosses, and which are certainly exposed to the highest levels of metal loads. However, the box plot does not give a spatial representation of the scattered values. Mapping of the results overcomes this problem.

Methodological approach for classification and mapping illustrated by some examples

The choice of the method of classification, as well as the definition of class limits, have great influence on interpretations of mapped results. The first step to transforming data into maps is to classify the data and group them into clusters. In order to discuss different methods of classification and mapping of data, Cd and As are chosen as examples.

Table 1.
Concentrations of metals in mosses (µg/g) from the French 1996 "moss-metal survey" (mains results from [16]) and 1995/1996 European results concerning 27 countries without France [25].
For France, all elements were analysed by the INAA method except the 4 elements with an asterisk that were analysed by ICP-MS.
Numbers in parenthesis indicate values below the detection limits. In bold, results presented in [20].

Concentration des métaux dans les mousses (µg/g) de la campagne française « Mousses-métaux » 1996 (principaux résultats tirés de [16]) et résultats européens 1995/1996 concernant 27 pays moins la France [25]. En France, tous les éléments ont été analysés par INAA sauf les 4 éléments marqués d'un astérisque qui ont été analysés par ICP-MS.
Les nombres entre parenthèses indiquent les valeurs inférieures à la limite de détection. En gras, résultats présentés dans [20].

Elements (in µg/g)		Al	**As**	Au	Ba	Br	Ca	**Cd***	Ce	Cl	Co	**Cr**	Cs
Number of samples	France	559 (1)	**559 (9)**	559 (8)	559 (11)	559 (0)	559 (0)	**558 (20)**	559 (4)	559 (0)	559 (0)	**559 (0)**	559 (29)
	Europe		**4354**					**6776**				**6868**	
Maximum	France	14100	**7.50**	0.339	153	27	22600	**1.70**	17	1610	3.6	**32.4**	18.7
	Europe		**17.60**					**8.40**				**438**	
Median	France	784	**0.30**	0.003	27	3.50	3820	**0.23**	1.3	220	0.39	**3.15**	0.21
	Europe		**0.25**					**0.26**				**1.44**	
Minimum	France	51	**0.05**	5.10^{-4}	4	0.12	280	**0.04**	0.1	56	0.06	**0.70**	0.006
	Europe		**0.001**					**0.01**				**0.04**	
Standard deviation	France	1302	**0.57**	0.024	19	2.22	2450	**0.18**	2.19	194	0.35	**3.40**	0.97
Mean	France	1150	**0.44**	0.008	31	3.91	4454	**0.28**	2.02	274	0.46	**4.02**	0.42
CV* (%)	France	113	**130**	313	62	57	55	**64**	108	71	76	**85**	231

Elements (in µg/g)		**Cu***	Eu	**Fe**	**Hg**	I	K	La	Mg	Mn	Mo	Na	**Ni***
Number of samples	France	**558 (3)**	559 (10)	**559 (1)**	**559 (293)**	558 (290)	559 (0)	559 (18)	558 (11)	559 (0)	559 (351)	558	**558 (108)**
	Europe	**6874**		**6875**	**4567**								**6829**
Maximum	France	**33.1**	0.6	**5900**	**0.32**	25	15100	37	8540	1210	5.66	1710	**20.3**
	Europe	**650**		**18600**	**1.33**								**235**
Median	France	**5.40**	0.02	**551**	**0.06**	2.3	5365	0.9	1000	231	0.52	204	**2.00**
	Europe	**5.63**		**439**	**0.06**								**1.83**
Minimum	France	**1.00**	8.10^{-4}	**163**	**0.01**	0.53	859	0.01	202	13	0.10	78	**0.07**
	Europe	**0.40**		**18.2**	**0.001**								**0.03**
Standard deviation	France	**3.17**	0.039	**639**	**0.04**	1.85	1961	3.52	528	242	0.58	202	**2.50**
Mean	France	**6.13**	0.029	**744**	**0.07**	2.71	5688	1.92	1076	291	0.67	265	**2.68**
CV* (%)	France	**52**	132	**86**	**57**	68	34	183	49	83	87	76	**93**

Elements (in µg/g)		**Pb***	Rb	Sb	Sc	Se	Sm	Th	Ti	**V**	W	**Zn**	Zr
Number of samples	France	**558 (0)**	559 (1)	559 (2)	559 (0)	559 (184)	559 (3)	529 (7)	558 (180)	**559 (1)**	554 (207)	**559 (3)**	553 (359)
	Europe	**6823**								**6595**		**6875**	
Maximum	France	**106.8**	93	1.50	2.4	2.27	1.84	2.8	1305	**17.0**	1	**120**	122
	Europe	**443**								**54.2**		**850**	
Median	France	**8.88**	13.1	0.20	0.16	0.30	0.1	0.18	83	**2.49**	0.09	**33.1**	12.8
	Europe	**7.68**								**3.14**		**37.6**	
Minimum	France	**2.50**	1.5	0.03	0.009	0.07	0.008	0.006	10	**0.60**	0.01	**6.3**	3
	Europe	**0.22**								**0.14**		**1.0**	
Standard deviation	France	**9.76**	14.8	0.20	0.23	0.28	0.19	0.29	124	**2.06**	0.12	**15**	14.5
Mean	France	**11.66**	17.8	0.26	0.22	0.35	0.16	0.26	117	**3.09**	0.12	**37**	16.7
CV* (%)	France	**84**	83	76	104	48	125	112	106	**67**	102	**41**	87

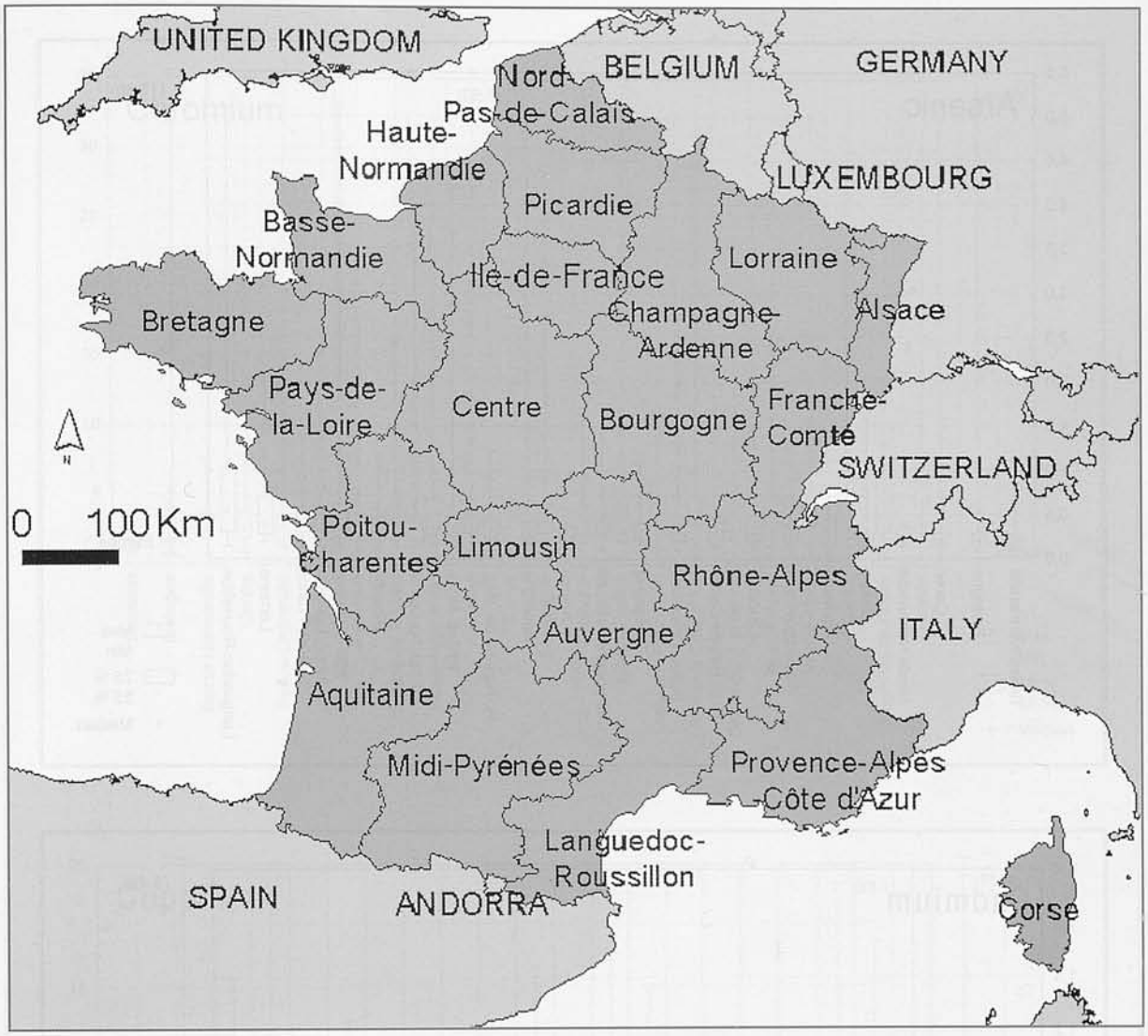


Figure 1.
Location of the 22 French administrative divisions (provinces).
Localisation des 22 régions administratives françaises.

Classification

Below, the three different ways of classification chosen for our purpose are presented.

The "European" classification

Eight concentration classes are proposed by the European programme [25] for each of 10 common metals analysed. When we apply these eight classes (ranged from the lowest to highest concentration) to the 1996 French moss data set for Cd (Table 2, p. 111) and As (Table 3, p. 112), almost two thirds of values are represented in the classes 2 and 3. These eight European classes used in the example of the French data set allow to compare French and European maps, but probably do not ensure the best presentation of the French data for mapping at the national scale. For this purpose, other methods of classification ("K-means" method and "Mouvet" method) are proposed for use and detailed below.

The "K-means" clustering

In the case of Cd and As results, five classes have been determined (Tables 2, p. 111 and 3, p. 112), where more than 90% of the values are represented in the classes 1 to 3. Using this method, the lower and upper bounds of clusters correspond to lower and upper data values of the chosen data set, and differ according to the considered area (Europe or France). Whereas this method is statistical and non subjective, the main inconvenience is that the class limits will vary according to new surveys and will have to be re-calculated each time to ensure comparisons.

For these two methods, the different classes are not associated to a quality or ecotoxicology scale i.e., the highest class which represents the highest values for metal contamination does not necessarily indicate a high level of pollution or even a polluted situation

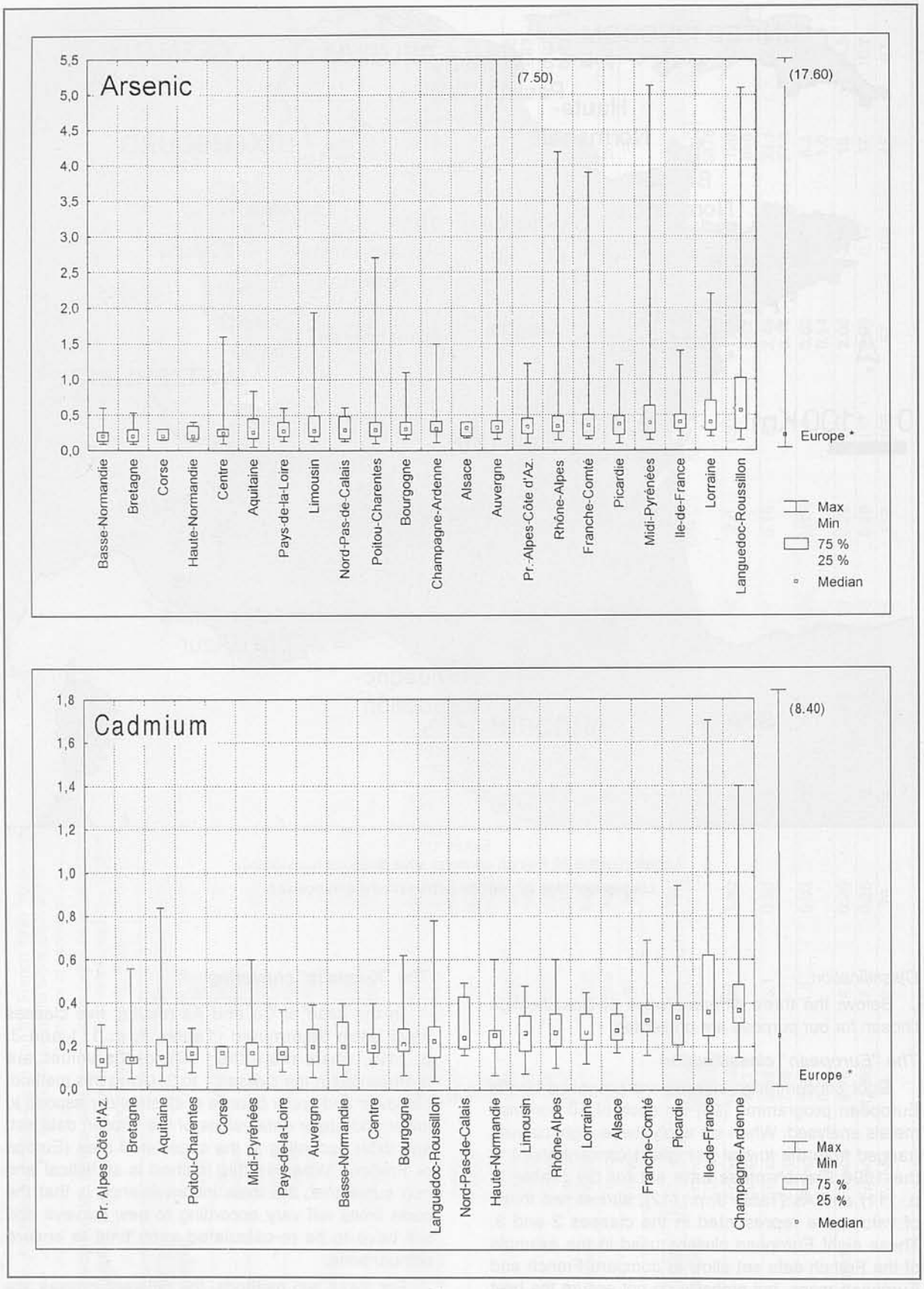


Figure 2.
Box plots of the 10 metals for the 22 French administrative divisions. Regions are ranked according to an increase of their median values. On the right of the figure, maximum, minimum and median values for Europe are indicated.

Boîte à moustaches des 10 métaux pour les 22 régions administratives françaises. Les régions sont classées par ordre croissant en fonction de leur médiane. À droite, le maximum, le minimum et la médiane sont indiqués pour l'Europe.

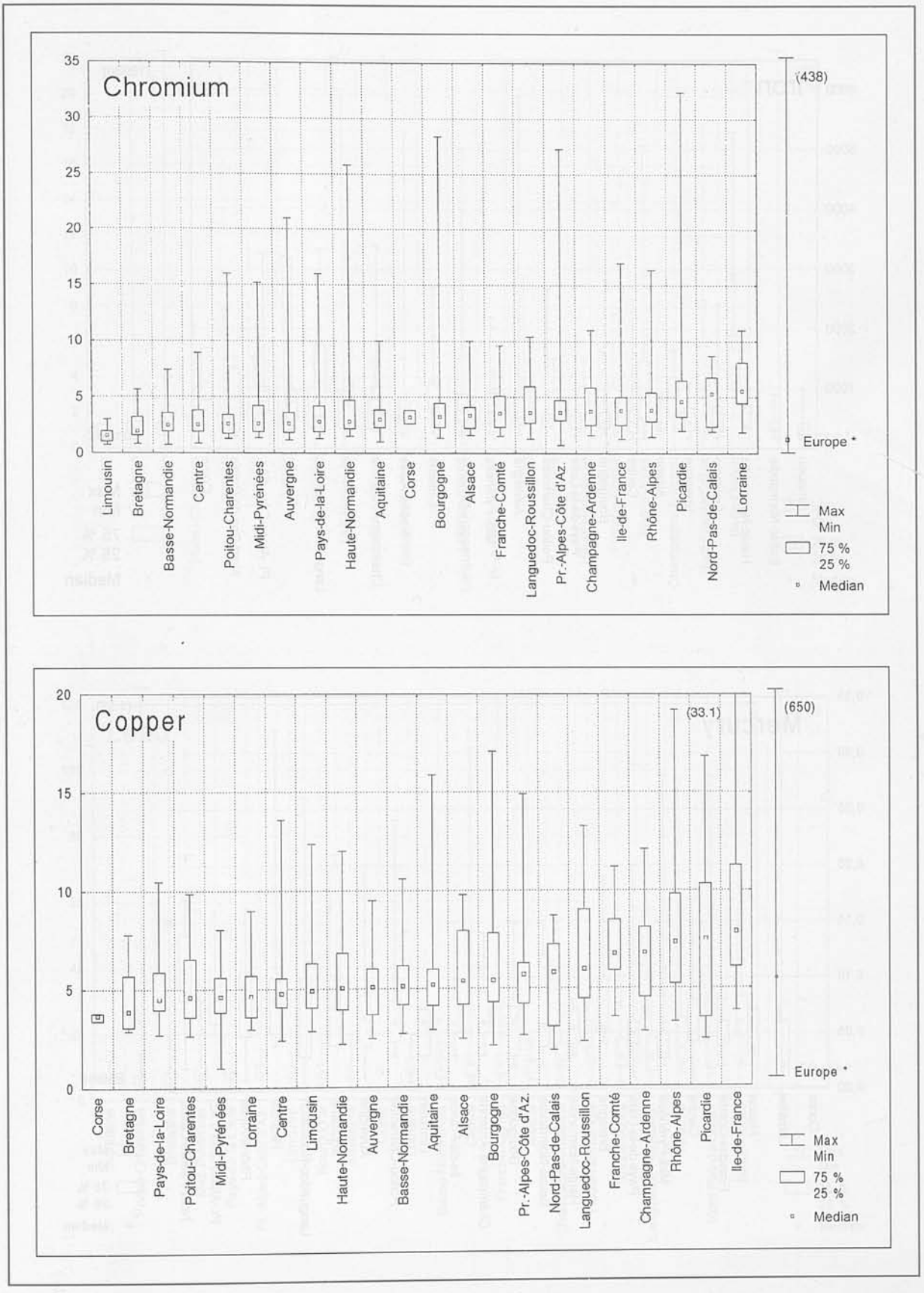


Figure 2 *(suite)*.
Box plots of the 10 metals for the 22 French administrative divisions. Regions are ranked according to an increase of their median values. On the right of the figure, maximum, minimum and median values for Europe are indicated.

Boîte à moustaches des 10 métaux pour les 22 régions administratives françaises. Les régions sont classées par ordre croissant en fonction de leur médiane. À droite, le maximum, le minimum et la médiane sont indiqués pour l'Europe.

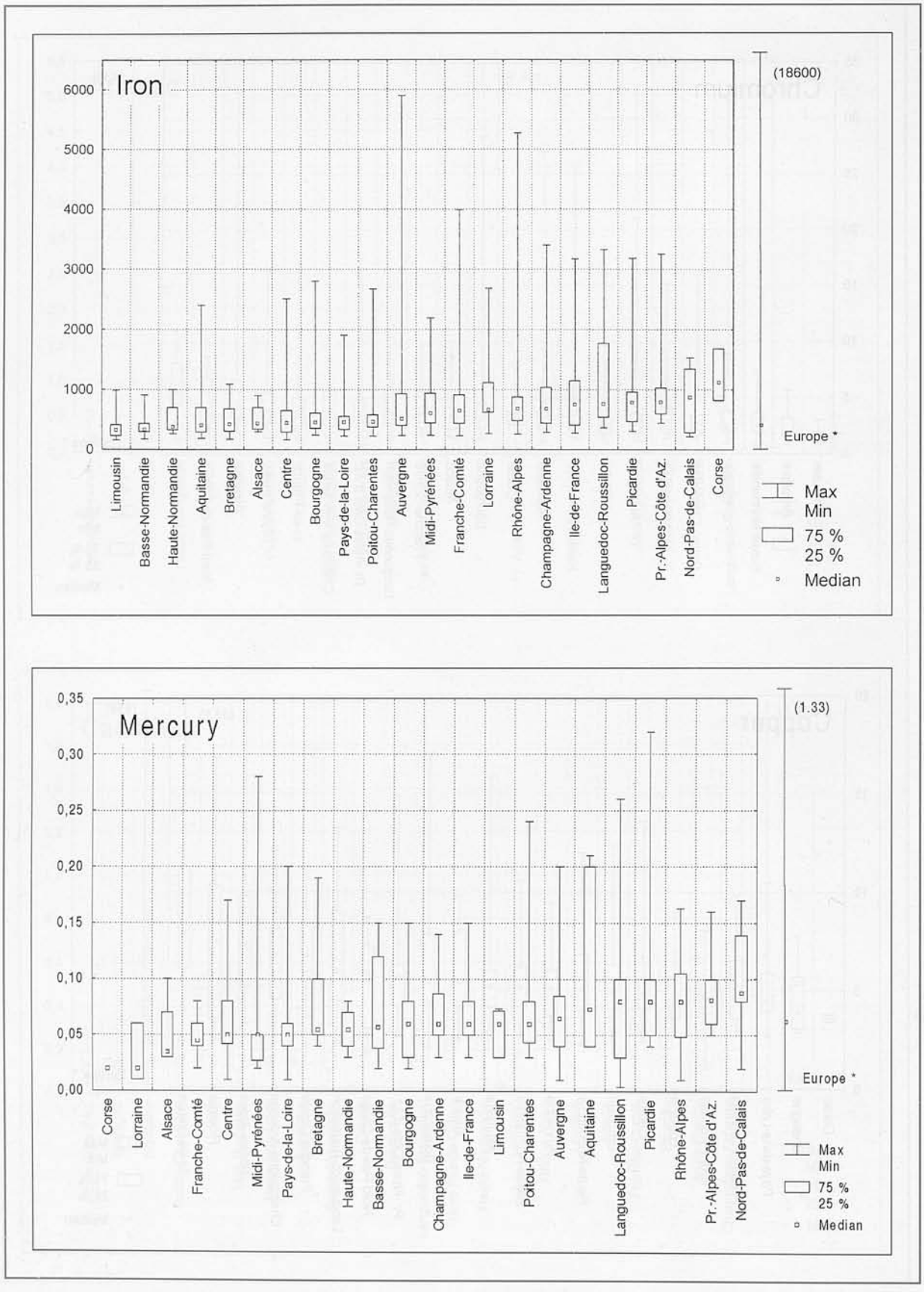


Figure 2 *(suite)*.
Box plots of the 10 metals for the 22 French administrative divisions. Regions are ranked according to an increase of their median values. On the right of the figure, maximum, minimum and median values for Europe are indicated.

Boîte à moustaches des 10 métaux pour les 22 régions administratives françaises. Les régions sont classées par ordre croissant en fonction de leur médiane. À droite, le maximum, le minimum et la médiane sont indiqués pour l'Europe.

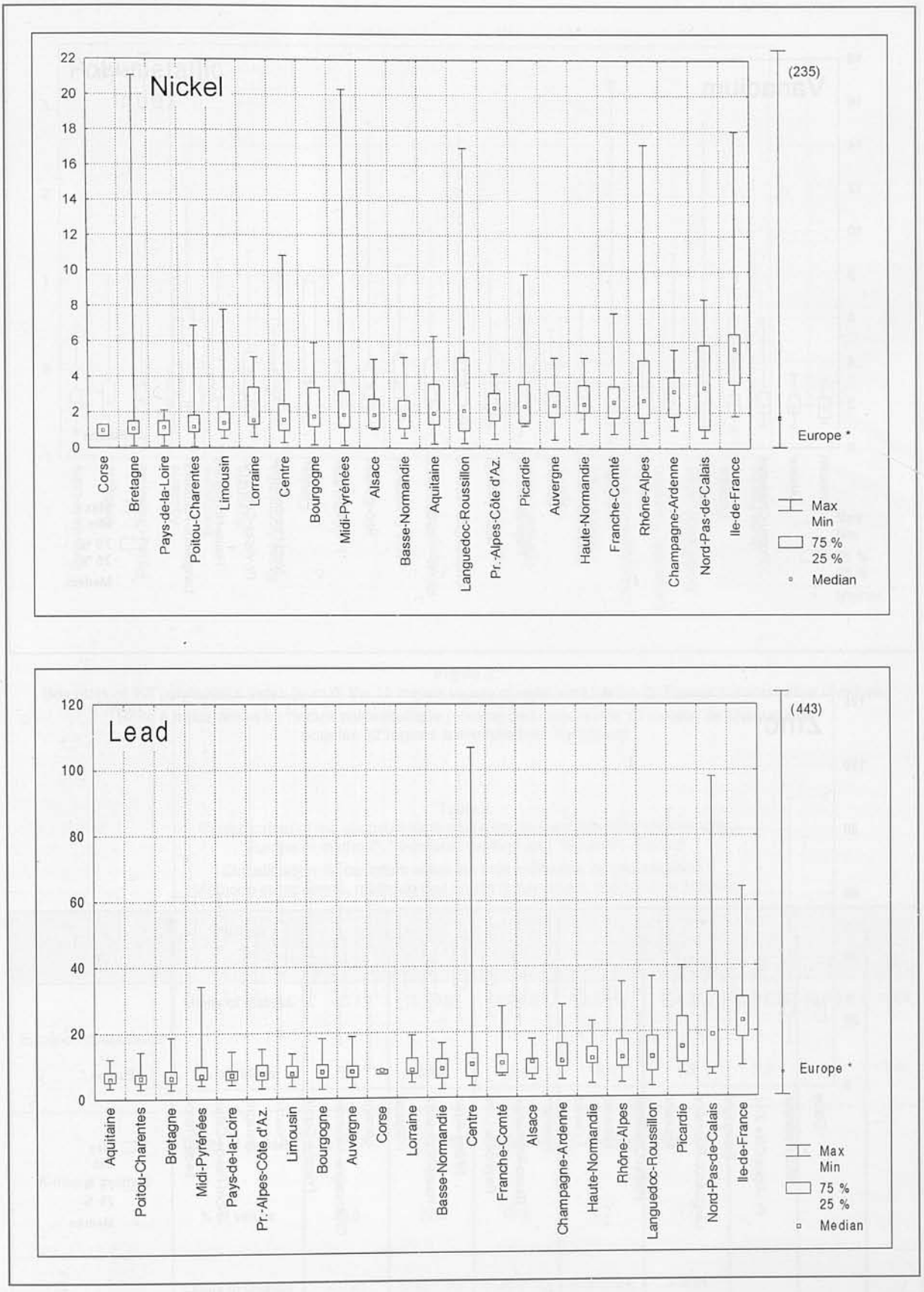


Figure 2 *(suite)*.
Box plots of the 10 metals for the 22 French administrative divisions. Regions are ranked according to an increase of their median values. On the right of the figure, maximum, minimum and median values for Europe are indicated.

Boîte à moustaches des 10 métaux pour les 22 régions administratives françaises. Les régions sont classées par ordre croissant en fonction de leur médiane. À droite, le maximum, le minimum et la médiane sont indiqués pour l'Europe.

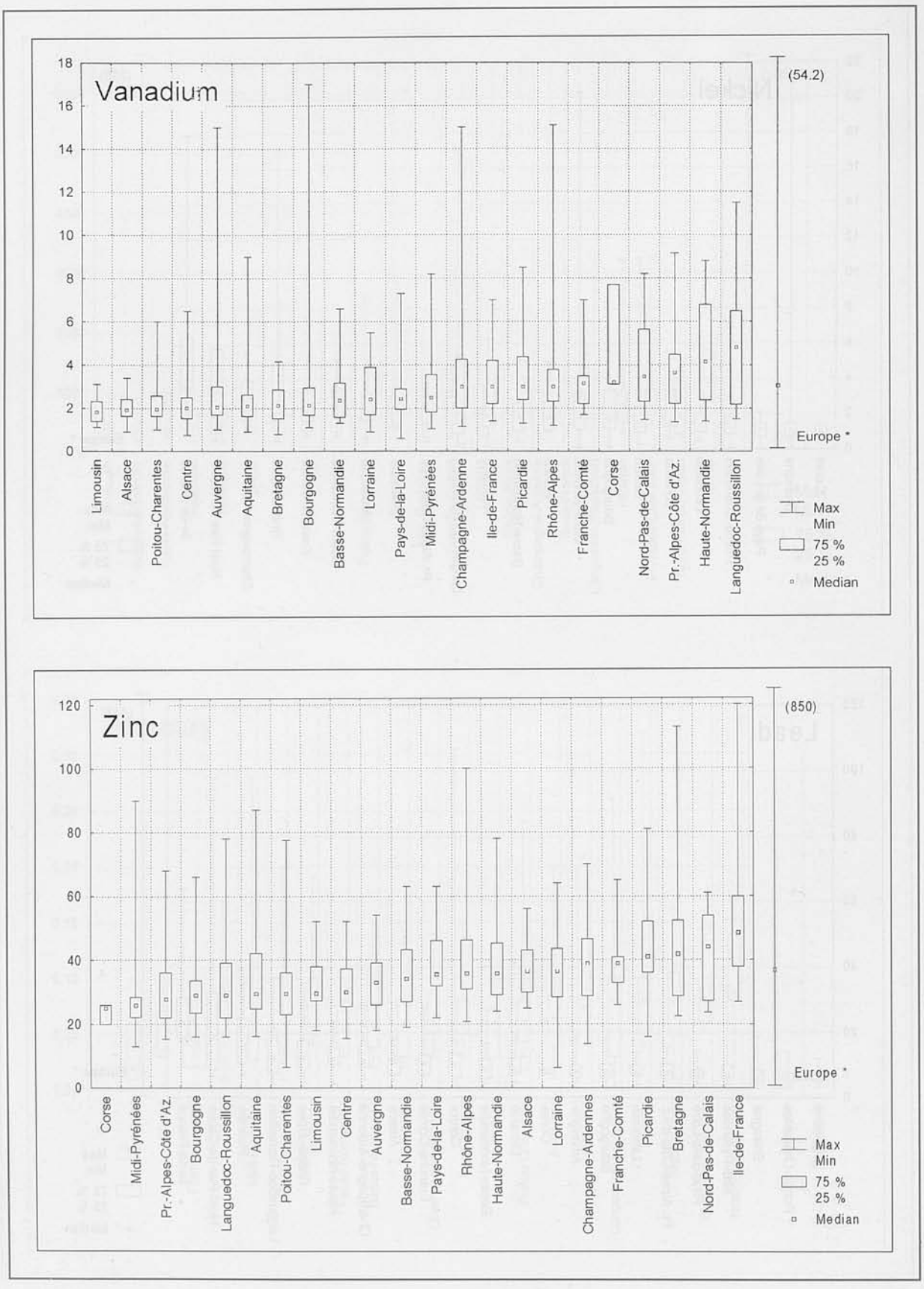


Figure 2 *(fin)*.
Box plots of the 10 metals for the 22 French administrative divisions. Regions are ranked according to an increase of their median values. On the right of the figure, maximum, minimum and median values for Europe are indicated.

Boîte à moustaches des 10 métaux pour les 22 régions administratives françaises. Les régions sont classées par ordre croissant en fonction de leur médiane. À droite, le maximum, le minimum et la médiane sont indiqués pour l'Europe.

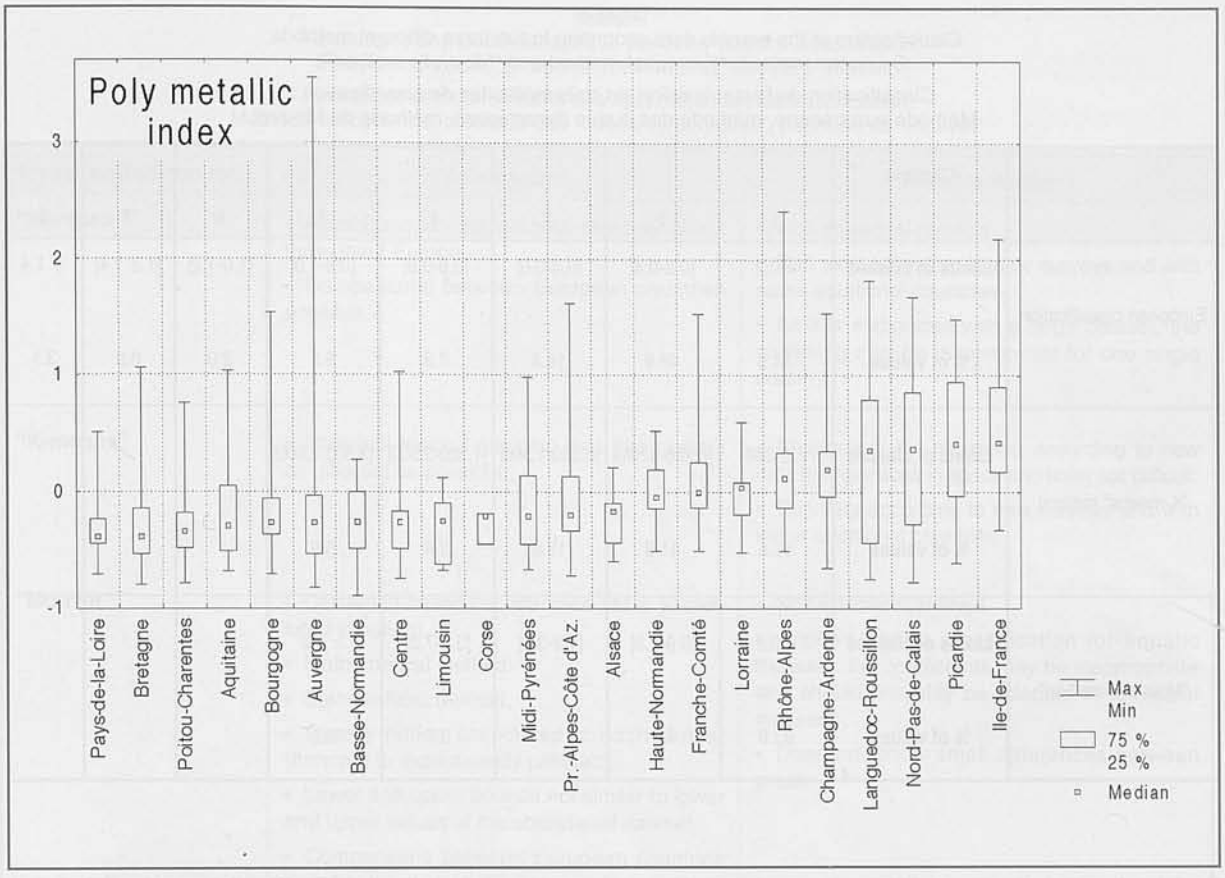


Figure 3.
Box plots of the polymetallic index (sum of the 10 metals values of each site) for the 22 French administrative divisions.
Boîte à moustaches de l'indice polymétallique (somme des valeurs des 10 métaux de chaque site) pour les 22 régions administratives françaises.

Table 2.
Classification of the cadmium data according to the three different methods: "European method", "K-means" method and "Mouvet's method".
Classification du cadmium selon les trois méthodes de classification : Méthode européenne, méthode des nuées dynamiques, méthode de Mouvet.

	Clusters	1	2	3	4	5	6	7	8
European classification	Limits of classes	< 0.1	[0.1-0.2[	[0.2-0.3[	[0.3-0.4[	[0.4-0.5[	[0.5-0.6[	[0.6-0.8[	≥ 0.8
	% of values	5.9	33.6	29.6	16.9	6.9	2.2	2.4	2.4
"K-means" method	Limits of classes	< 0.17	[0.17-0.29[	[0.29-0.46[	[0.46-0.88[	[0.88-1.7[			
	% of values	28.8	39.0	23.8	6.7	1.7			
"Mouvet's method"	Limits of classes	< 0.63	[0.63-1.26[	[1.26-2.52[	[2.52-5.04[	≥ 5.04			
	% of values	96.6	3.0	0.40	0	0			

Table 3.
Classification of the arsenic data according to the three different methods: European method, "K-means" method and "Mouvet's method".

Classification de l'arsenic selon les trois méthodes de classification : Méthode européenne, méthode des nuées dynamiques, méthode de Mouvet.

	Clusters	1	2	3	4	5	6	7	8
European classification	Limits of classes	< 0.2	[0.2-0.4[	[0.4-0.6[	[0.6-0.8[	[0.8-1.0[	[1.0-1.2[	[1.2-1.4[	≥ 1.4
	% of values	14.5	48.9	19.8	7.3	3.5	2.0	0.9	3.1
"K-means" method	Limits of classes	< 0.286	[0.286-0.580[	[0.580-1.300[	[1.300-3.500[	[3.500-7.500[			
	% of values	41.6	41.3	13.8	2.4	0.9			
"Mouvet's method"	Limits of classes	< 0.9	[0.9-1.8[	[1.8-3.6[	[3.6-7.2[	≥ 7.2			
	% of values	93.9	4.1	1.1	0.7	0.2			

that is damaging ecosystems. In contrast, the "Mouvet's classification" permits the assessment of a pollution load in an ecosystem.

The classification of Mouvet

Five classes have been determined for Cd and As and their limits are shown respectively in Table 2, p. 111 and Table 3. For Cd, the 5 highest values have been eliminated to reach a standard deviation of 57.6% (lower than 60%) and the reference value obtained is 0.21 µg/g. Standard deviation of the whole data set is 64% (Table 1, p. 104). For As, the 22 highest values have been eliminated to obtain a standard deviation of 59.7% and the reference value is 0.30 µg/g. Standard deviation of the whole data set is 130% (Table 1, p. 104).

Table 2, p. 111, shows that 96.6% of Cd concentration values is distributed in cluster 1 (unpolluted situation) and no values are included in clusters 4 and 5 (important or exceptional pollution). Table 3 shows that 93.9% of As concentration values is distributed in cluster 1, and 0.2% of the values (i.e., one value) is located in cluster 5 (exceptional pollution). According to this classification method, Cd concentration distribution shows no important nor exceptional pollution, and most of the values are considered as reflecting a background level. The As distribution shows a few exceptional and important pollution levels (clusters 4 and 5). The example of Cd points out a problem. The Cd reference value is calculated on the hypothesis of an homogeneous set of data (showing a standard deviation close to 60%) reflecting an unpolluted situation. For Cd, the standard deviation is 64% (Table 1, p. 104). In the case of a diffuse and homogeneous level of pollution, the reference value would be overestimated, and the calculation of classes would be biased. The consequence would be to mask important or exceptional pollution levels. To solve this problem, it is necessary to calculate the reference value with a higher data set at a European or international level, including remote regions far from polluted areas. Another problem is that the class limits calculation (using a twofold geometric progression) should perhaps be adapted to terrestrial mosses after analysing the data set of whole metals, and after considering the variation of distribution of values using different geometric progressions.

In conclusion, for each of the three methods of classification, a majority of data is located in the lower classes (low metal concentrations) whereas only a few data in the upper ones (high metal concentrations). Table 4 presents the advantages and disadvantages of these methods. The choice of the method depends on the objectives: (1) to compare the French data to the European ones, the "European classification" will be chosen; (2) to present the French data in the best way in space and time, the "K-means" method will be preferred; (3) the "Mouvet's method", which parameters might be adapted to terrestrial mosses will not be appropriated to show the fine French spatial differences between areas. The general idea of the "Mouvet's classification" is to transform quantitative data of concentrations in mosses to qualitative data associated to a level of

Table 4.
Advantages and disadvantages of the three ways of classification.
European method, "K-means" method and "Mouvet's" method.

Avantages et inconvénients des trois méthodes de classification.
Méthode européenne, méthode des "nuées dynamiques", méthode de "Mouvet".

Classification methods	Advantages	Disadvantages
"European"	• Homogenous cartographic representation throughout Europe. • Comparisons between European countries possible.	• Non statistical method. • Can vary according to new surveys and with some additional countries. • As it is elaborated with a large dataset, the clustering may be inappropriate for one single country.
"K-means"	• Statistical method grouping data into clusters as different as possible.	• Changes of the clustering according to new data (comparisons in space and time) are difficult. • Can vary according to new surveys and with some additional countries.
"Mouvet"	• Clustering based on reference value (unpolluted situation). • Mathematical method. • Standardized method. • Quality notion associated to each cluster (from not to exceptionally polluted). • Lower and upper bounds not similar to lower and upper values of the considered dataset. • Comparisons between European countries possible.	• Non statistical method. • Applied from a classification for aquatic mosses : the coefficients may be inappropriate and should probably be adapted to terrestrial mosses. • Does not show small differences between areas.

contamination. This method of classification will thus be favoured to give a qualitative contamination notion to the sites and to point out important or exceptional pollution.

Mapping

The second step to present data after the clustering is the mapping of the different classes. The aim is to visualize the distribution of data within a large area, making possible comparisons in space and time. The choice of number of clusters mapped, colours, symbols or interpolation algorithms used can provide such different maps which can lead to strongly different interpretations of results.

Two Cd maps using different methods (spot by spot, interpolation) are presented and discussed below. Then, the three classification methods described above are compared using the interpolation map for Cd and As.

Spot by spot map

The French spot by spot map for Cd that is realised with the "European classification", is presented in Figure 4, p. 114. In the provinces where density of sites is not too high, like in the Rhône-Alpes and the Midi-Pyrénées provinces, several "hot spots" are clearly visualized. Indeed, some sites present a high local concentration in mosses whereas the next closest sites to these indicate much lower metal levels. It is not the case in provinces where a higher density of sites (example of the Ile-de-France province) may mask information at a national scale. So, the main disadvantage of this method is that results are considered as scattered points, where an information may be masked in the case of high density of sites or, at the opposite, where the general information cannot be seen obviously in the case of a low density of sites (with an higher visual impact of hot spots than other sites). However, the great advantage of this presentation is that it gives complete informations (site location, moss species) and contributes to precise interpretation.

Interpolation maps

The Cd interpolated European map realised with the "European classification" (Figure 5, p. 115) allows to see a general tendency throughout Europe. We can see for example, higher levels in Eastern Europe (Romania, Ukraine, Slovakia, and Poland), and also in other countries (Portugal and The Netherlands), lower levels in Northern Europe, or some large areas showing intermediary levels of Cd in mosses (throughout south-western Germany, Luxembourg, Belgium and north-eastern France). So, this kind of presentation allows a global interpretation of the distribution of data with large scale variations in the

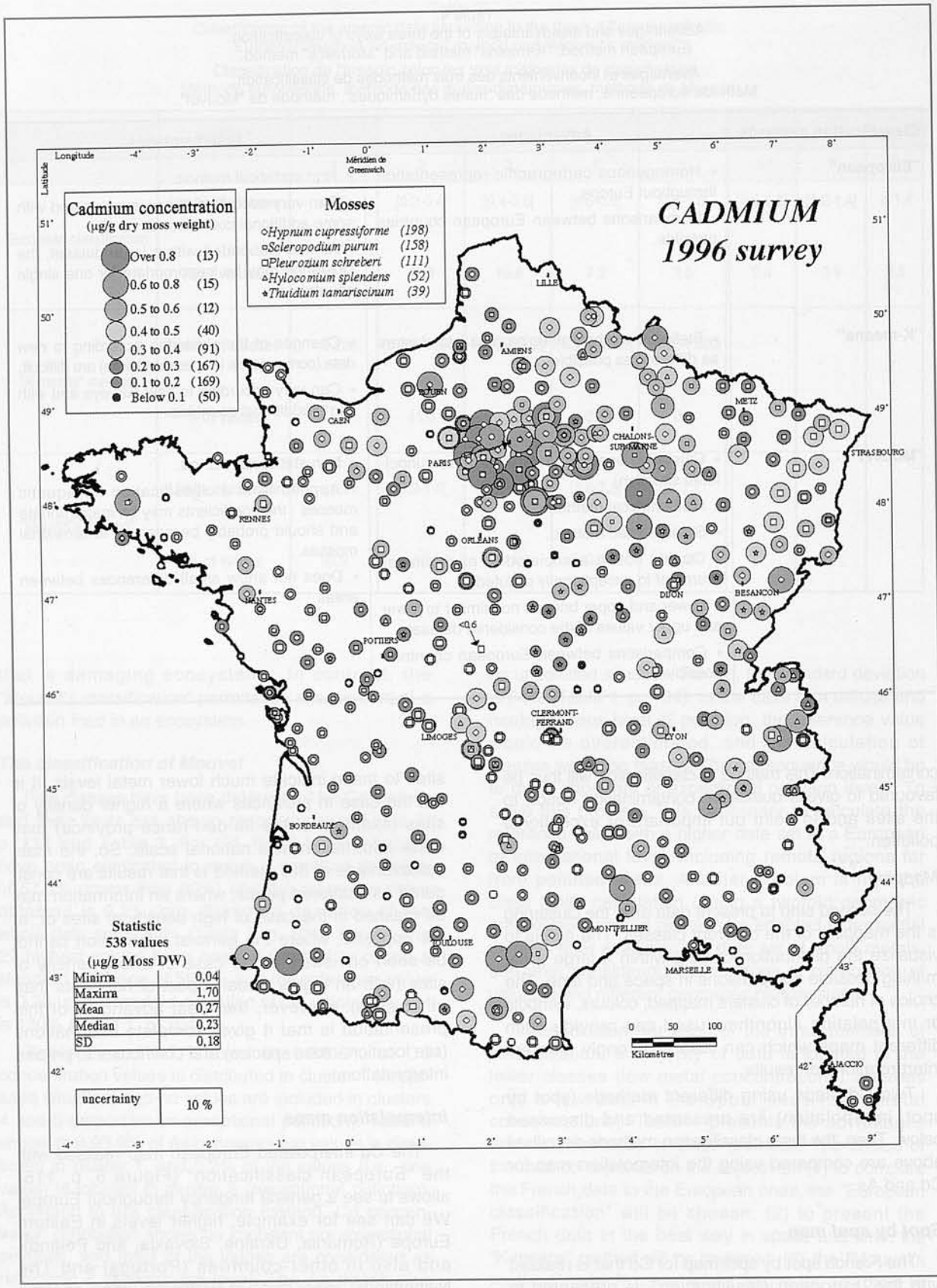


Figure 4.
French spot map of the cadmium concentrations into mosses according to the clustering of the "European" method. Map realised by the ADEME (B. Charré, 2000) from the 1996 French data survey [16].

Carte française de la distribution des concentrations en cadmium dans les mousses représentée point par point en fonction des classes établies d'après la méthode "européenne". Carte réalisée par l'ADEME (B. Charré, 2000) d'après les données de la campagne française 1996 [16].

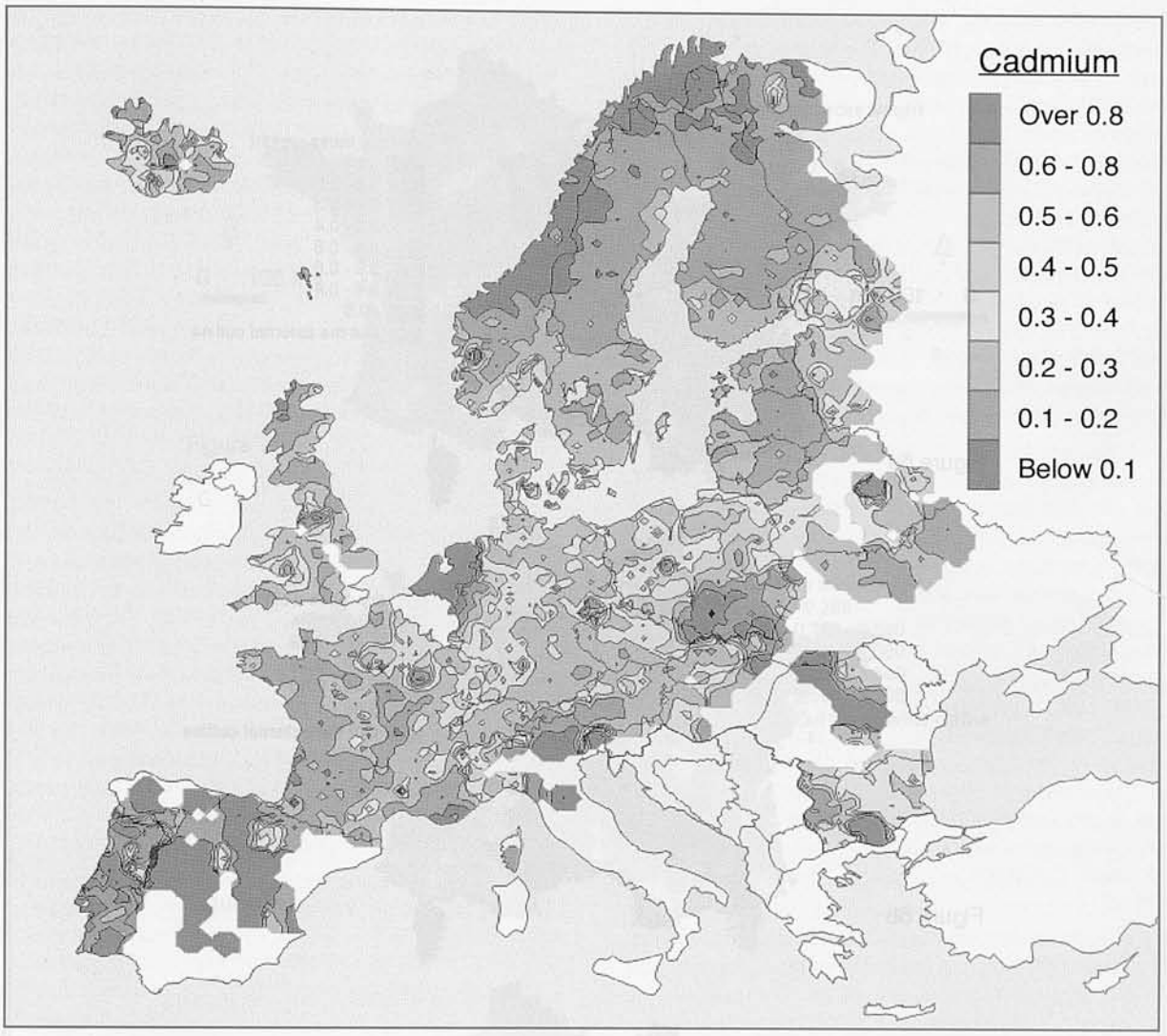


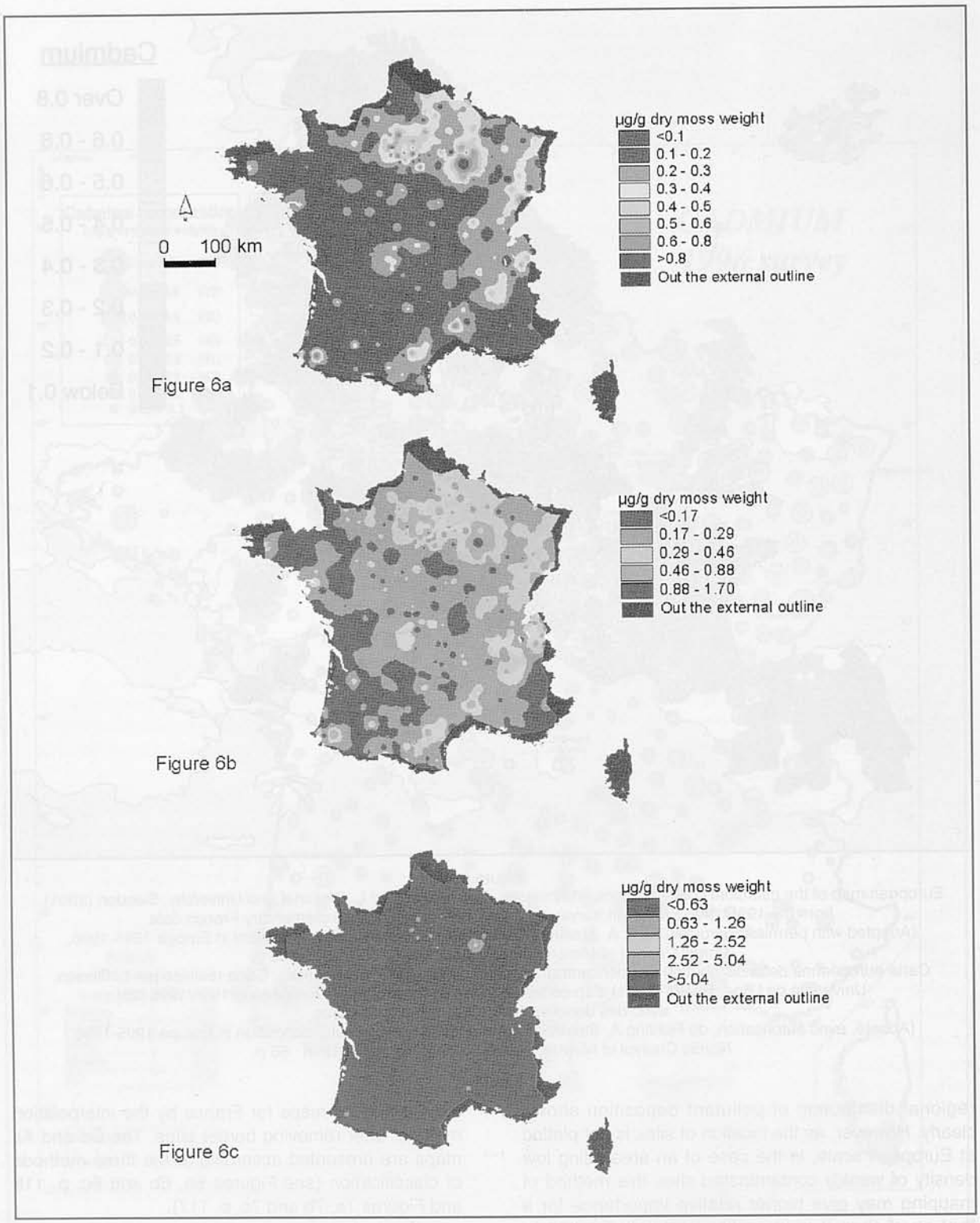
Figure 5.
European map of the cadmium concentrations into mosses. Map realized by L. Olsson, Lund University, Sweden (2001), from the 1995/1996 European survey data [25], with additional complementary French data
(Adapted with permission from Rühling A, Steinnes E. Atmospheric heavy metal deposition in Europe 1995-1996. Nordic Council of Ministers (ed) vol 15, Nord, 1998, 1998 : 66 p.
Carte européenne de la distribution des concentrations en cadmium dans les mousses. Carte réalisée par L. Olsson, Université de Lund, Suède (2001) d'après les données de la campagne européenne 1995/1996 [25] avec des données françaises complémentaires
(Adapté, avec autorisation, de Rühling A, Steinnes E. Atmospheric heavy metal deposition in Europe 1995-1996. Nordic Council of Ministers (ed) vol 15, Nord, 1998, 1998 : 66 p.

regional distribution of pollutant deposition shown clearly. However, as the location of sites is not plotted at European scale, in the case of an area using low density of weakly contaminated sites this method of mapping may give higher relative importance for a "hot spot" than it is in reality, certainly leading to misinterpretations. This is the main disadvantage of this method.

Comparison of the three maps for cadmium and arsenic according to the three classification methods (European, "K-means" and Mouvet methods)

Considering the advantages and disadvantages of each mapping method, we have chosen to show the Cd and As maps for France by the interpolation method, after removing border sites. The Cd and As maps are presented according to the three methods of classification (*see* Figures 6a, 6b and 6c, p. 116 and Figures 7a, 7b and 7c, p. 117).

For Cd and As, maps of the "European classification" and of the "K-means" methods (Figures 6a and 6b, p. 116 for Cd and Figures 7a and 7b, p. 117 for As) show the same general tendency throughout France even if the calculation of classes is different. The first maps presents 8 classes (Figures 6a and 7a) whereas the second maps 5 classes (Figures 6b and 7b) for each of the two metals. For Cd, the Ile-de-France and Champagne-Ardenne provinces show the highest levels of metal



Figures 6.
Interpolation maps of the cadmium concentrations into mosses according to the three methods of classification: "European classification", "K-means" method and "Mouvet's method". Map realised by J. Signoret (EBSE).
6a: Map realised according to the clustering of the "European" method.
6b: Map realised according to the clustering of the "K-means" method.
6c: Map realised according to the clustering of the "Mouvet method".

Cartes d'interpolation de la distribution des concentrations en cadmium dans les mousses en fonction des classes établies d'après les trois méthodes de classification : méthode "européenne", "méthode des nuées dynamiques" et "méthode de Mouvet". Données de la campagne française 1996. Carte réalisée par J. Signoret (EBSE).
6a : Carte établie d'après la classification « européenne ».
6b : Carte établie d'après la classification « nuées dynamiques ».
6c : Carte établie d'après la « classification de Mouvet ».

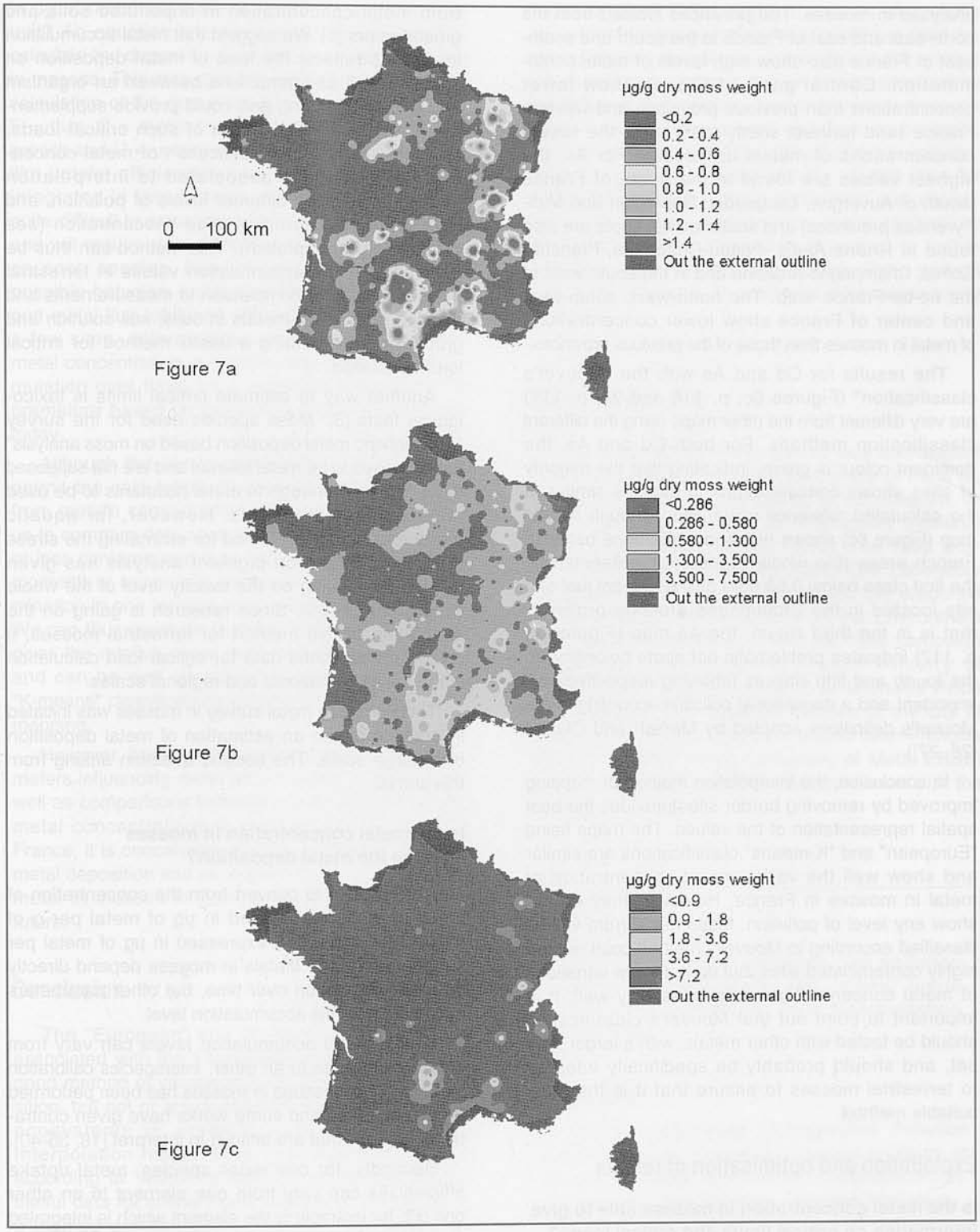


Figure 7.
Interpolation maps of the arsenic concentrations into mosses according to the three methods of classification: "European classification", "K-means" method and "Mouvet's method". Map realised by J. Signoret (EBSE).
7a: Map realised according to the clustering of the "European" method.
7b: Map realised according to the clustering of the "K-means" method.
7c: Map realised according to the clustering of the "Mouvet method".

Cartes d'interpolation de la distribution des concentrations en arsenic dans les mousses en fonction des classes établies d'après les trois méthodes de classification : méthode "européenne", "méthode des nuées dynamiques" et "méthode de Mouvet". Données de la campagne française 1996. Carte réalisée par J. Signoret (EBSE).
7a : Carte établie d'après la classification « européenne ».
7b : Carte établie d'après la classification « nuées dynamiques ».
7c : Carte établie d'après la « classification de Mouvet ».

analysed in mosses. The provinces located from the north-east and east of France to the south and south-east of France also show high levels of metal contamination. Central parts of France show lower concentrations than previous provinces and western France (and furthest south-east) show the lowest concentrations of metals in mosses. For As, the highest values are found in the south of France (south of Auvergne, Languedoc-Roussillon and Midi-Pyrénées provinces) and scattered hot spots are also found in Rhône-Alpes, Poitou-Charentes, Franche-Comté, Champagne-Ardenne and in the south-west of the Ile-de-France area. The north-west, south-west and center of France show lower concentrations of metal in mosses than those of the previous provinces.

The results for Cd and As with the "Mouvet's classification" (Figures 6c, p. 116 and 7c, p. 117) are very different from the other maps using the different classification methods. For both Cd and As, the dominant colour is green, indicating that the majority of sites shows concentrations in mosses similar to the calculated reference value. But, although the Cd map (Figure 6c) shows nearly no difference between French areas (the whole France is represented by the first class below 0.63 µg/g of DW, except just one site located in the Champagne-Ardenne province, that is in the third class), the As map (Figure 7c, p. 117) indicates problematic hot spots belonging to the fourth and fifth classes (showing respectively an important and a exceptional pollution according to the Mouvet's definitions adapted by Mersch and Claveri [26, 27]).

In conclusion, the interpolation method of mapping improved by removing border sites provides the best spatial representation of the values. The maps using "European" and "K-means" classifications are similar and show well the variations of concentration of metal in mosses in France. However, they do not show any level of pollution. Maps made from values classified according to Mouvet's method point out the highly contaminated sites, but do not show variations of metal concentrations in mosses very well. It is important to point out that Mouvet's classification should be tested with other metals, with a larger data set, and should probably be specifically adapted to terrestrial mosses to ensure that it is the most suitable method.

Exploitation and optimisation of results

Is the metal concentration in mosses able to give information on critical limits and critical loads?

The concentration of metal in mosses is an integration of metal in mosses over a period of several years. This information on the metal concentrations does not reflect only the load of metal deposition. This accumulation reflects complex interactions between mosses and their environment, including the biodisponibility of metals.

Critical limits, the maximal concentration of pollutants supported by the whole ecosystem, can be estimated from metal concentration in unpolluted soils and groundwaters [6]. We suggest that metal accumulation in mosses reflects the load of metal deposition on soils, as well as interactions between an organism and the environment, and could provide supplementary data for the estimation of such critical loads. Mouvet's method of classification of metal concentrations in mosses associated to interpolation mapping visualizes different levels of pollution, and is based on a reference value concentration (*see* Methodological approach). This method can thus be adapted to metal accumulation values in terrestrial mosses, with later comparison to measurements and addition of data for metals in soils, soil solution and groundwater, providing a useful method for critical load calculation.

Another way to estimate critical limits is toxicological tests [3]. Moss species used for the survey "Atmospheric metal deposition based on moss analysis" are supposed to be metal tolerant and are not supposed to be sensitive enough to metal pollutants to be used for toxicological studies. However, for aquatic mosses, a sensitive method for estimating the stress in mosses based on pigment analysis has given reliable information on the toxicity level of the whole ecosystem [29-35]. Since research is going on the adaptation of this method for terrestrial mosses, it could provide useful data for critical load calculation in the future on national and regional scales.

The European metal survey in mosses was initiated in order to obtain an estimation of metal deposition on a large scale. The second question arising from this aim is:

Is the metal concentration in mosses equal to the metal deposition?

Is it possible to convert from the concentration of metal in moss (expressed in µg of metal per g of moss) to a deposition expressed in µg of metal per surface area unit? Metals in mosses depend directly on metal deposition over time, but other parameters may influence this accumulation level.

Firstly, metal accumulation levels can vary from one moss species to an other. Interspecies calibration of metal concentrations in mosses has been performed for two decades and some works have given contradictory results that are difficult to interpret [18, 36-40].

Secondly, for one moss species, metal uptake efficiencies can vary from one element to an other one (Pb for example is the element which is integrated more (100%) by mosses in laboratory conditions [14]). The saturation effects for one element can also lead to changes in the accumulation of other elements.

Thirdly, environmental factors (climate, soil chemistry, leakage) have an impact on the physiology and morphology of mosses, and may induce changes in the final concentrations of metals accumulated in mosses.

Is it now conceivable to think of a conversion from a concentration of metals to a flux of metals expressed

in µg of metal per surface area unit, and per time unit? An equation has been suggested [17, 41] to calculate the deposition from the metal concentration in mosses. This calculation is based on a theoretical calculation of the deposition flux ($F = C \times G/U$, with F = flux, C = metal concentration in mosses, G = growth and U = uptake efficiency). Other parameters like uptake efficiencies and moss growth rate are integrated in this formula. These parameters are quite difficult to extrapolate from literature based data and will require more investigations at each site and on each species. Even if some correlations are possible between metal concentrations in mosses and metal flux (obtained with chemical collectors) in a few sites, determination of flux deposition from metal concentration in mosses (resulting of an accumulation over time) on a large scale seems to be premature based on the actual state of knowledge today.

Although the "moss-metal method" does not yet permit the calculation of absolute metal deposition from metal's concentration in mosses, it does allow us to compare data spatially (locations that are more or less contaminated than each other at a particular moment) or temporally (increase or decrease contamination in one location from one survey to another). We can thus conclude that the "moss-metal method" gives the relative metal deposition for a large scale, and can be well visualized by the "European" or "K-means" classifications associated with interpolation mapping.

However, because the investigations on the parameters influencing metal accumulation in mosses, as well as comparisons between actual depositions and metal concentrations in mosses, are going on in France, it is conceivable that the estimation of actual metal deposition and exceedances from accumulated metal in mosses in France will be possible in the future.

Conclusion

The "European" and "K-means" classifications associated with the interpolation mapping provide a good method of visualisation for relative metal deposition, but not of actual absolute metal deposition on ecosystems in present state of knowledge. Interpolation maps made from values classified according to "Mouvet's method" could also provide useful data for critical loads estimation. Furthermore, a method estimating the stress in moss (pigment measurements) extrapolated to give an idea of the ecosystem stress could provide additional data for critical limits calculations. Considering the unique nature and large scale of the set of data provided by the "moss-metal" method, and information given on interactions between mosses and their environment, it is thus suggested that the unit *µg of metal accumulated per g of moss* could provide reliable data for critical loads: *critical limits estimation* and visualisation of *relative atmospheric metal deposition* (exceedances estimation). This is subject to further investigations to confirm the adequacy of the method and of the inclusion of additional information using field trials.

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Keywords

Metal deposition. Mapping. Air pollution. Mosses. Critical loads and critical limits. Classification methods. Data interpretation. French data.

Mots clés

Dépôts métalliques. Cartographie. Pollution atmosphérique. Mousses. Charges critiques et seuils critiques. Méthodes de classification. Interprétation des données. Données françaises.

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