Paepe

KONINKRIJK BELGIE

MINISTERIE VAN ECONOMISCHE ZAKEN
Administratie der Mijnen - Geologische dienst van België
Jennerstraat, 13 - 1040 Brussel

RECONNAISSANCE SURVEY FOR URANIUM IN THE BELGIAN PALEOZOIC

J.-M. CHARLET
L. DEJONGHE
S.-M. DE WITTE
B. DRUMEL
J. HENRY
A. HERBOSCH
J.-P. LEFIN
H. MARTIN

PROFESSIONAL PAPER 1983/1
N° 196

SERVICE GEOLOGIQUE DE BELGIQUE - PROFESSIONAL PAPER 1983/1 - N° 196

\- - - - -

RECONNAISSANCE SURVEY FOR URANIUM IN THE BELGIAN PALEOZOIC

J.-M. CHARLET

L. DEJONGHE

S.-M. DE WITTE

B. DRUMEL

J. HENRY

A. HERBOSCH

J.-P. LEFIN

H. MARTIN

ACKNOWLEDGMENTS

The Commission of the European Communities is thanked for having entrusted the Geological Survey of Belgium with the direction of this programme.

The financial contribution of the Commission is also gratefully acknowledged.

We are particularly indebted to R. AITKEN and L. BARAZZONI (EEC) who followed the progress of the work step by step.

COMPOSITION OF THE PROSPECTING TEAMS

I. GEOLOGICAL SURVEY OF BELGIUM 13 rue Jenner, B - 1040 Bruxelles.

Management	L. DEJONGHE	
Coordination	A. PREAT	(from 01.01.1979 to 30.09.1979)
	J. HENRY	(from 01.10.1979 to 31.12.1981)
Secretariat	B. PREAT	(from 01.01.1979 to 31.12.1981)
	G. BERGHMANS	(from 01.06.1981 to 31.12.1981)
Data processing	D. DERAYMAEKER	
	J. HENRY	
Traduction from french to english	D. FODE	

II. UNIVERSITE CATHOLIQUE DE LOUVAIN (Laboratory of Geochemistry)

3 Place Louis Pasteur, B - 1348 Louvain-La-Neuve.

Management	H. MARTIN	
	F. SONDAG	
Field	J.P. LEFIN	(from 01.01.1979 to 28.02.1981)
	G. DEPREZ	(from 01.07.1979 to 28.02.1981)
	H. BRUSSELMANS	(from 01.08.1979 to 31.08.1980)
	V. DUMONT	(from 01.09.1980 to 31.12.1980)
Laboratory	A. NAVARRE	
	C. ADAM	(from 01.01.1979 to 04.11.1980)
	A. ISERANTANT	(from 01.01.1980 to 28.02.1981)
	R. HUMBLET	(from 25.11.1980 to 31.01.1981)
	G. DEPREZ	
	H. BRUSSELMANS	
	V. DUMONT	

III. UNIVERSITE LIBRE DE BRUXELLES

(Laboratory of Geochemistry and Laboratory of Nuclear Geochemistry and Nuclear Geology).

50 avenue F.D. Roosevelt, B - 1050 Bruxelles.

Management	A. HERBOSCH	
	J. JEDWAB	
	E. PICCIOTTO	
Field and laboratory	S.M. DE WITTE	(from 01.12.1978 to 30.11.1981)
	J.P. MENNESSIER	(from 01.12.1978 to 30.11.1981)
	N. VALENTIN	(from 01.12.1978 to 30.11.1981)

IV. FACULTE POLYTECHNIQUE DE MONS

(Department of Mineralogy and Petrography)

9 rue de Houdain, B - 7000 Mons.

Management	J.M. CHARLET	
	C. DUPUIS	
Field	B. DRUMEL	(from 01.01.1979 to 31.03.1981)
	Y. QUINIF	(from 01.02.1979 to 30.09.1979)
	D. JANS	(from 01.10.1979) to 15.12.1980)
	J.M. DETAVERNIER	(from 15.07.1980 to 15.10.1980)
	J. FIORA	(from 15.01.1981 to 31.03.1981)
	J. BOUTE driver-technician	(from 01.04.1979 to 31.03.1981)
Processing of the recordings	D. JANS	
	J.M. DETAVERNIER	
	J. FIORA	

CONTENTS

CHAPTER I

PRELIMINARIES

I. 1. INTRODUCTION : PRESENTATION OF PROGRAMME

Interest in the radioactivity of the Belgian sub-soil is recent enough. It was in 1955, at the initiative of the Geological Survey of Belgium, that the first radiometric prospection was carried out with the aid of a portable scintillometer. It covered about 10% of the territory and enabled the detection of a certain number of anomalies.

However small and limited these indices are, they do not exclude a priori the possibility of finding concentrations of economic interest in the Paleozoic basement. Research in this field was therefore considered indispensable.

This was why, taking advantage of the possibilities of financing offered by the EEC in this field, the Geological Survey of Belgium took the initiative of organising, in 1978, a two-year reconnaissance survey over the entire Paleozoic of Belgium (± 11 000 km^2).

For a preliminary reconnaissance, with the main aim of detecting favourable zones, a radiometric prospection (airborne or carborne) would seem sufficient.

However, the following considerations led the promoters of the project to envisage a geochemical prospection as well :

a) the particular geomorphology of the Belgian Ardennes, characterized by large plateau surfaces (remains of ancient cretaceous to tertiary planations) covered with eolian deposits and solifluxion materials from the Quaternary, is not always well adapted to radiometric investigation ;

b) the hydrographic network is well developed in the entire Ardenne. This allows sampling of waters and sediments at a density that suits the needs of a preliminary prospection ;

c) the absence of a multielement geochemical inventory of the alluvia of the Paleozoic was a case in favour of action in this direction. The samples collected can be conserved and later reexploited for elements other than uranium. (✱)

(✱) A 4 year follow-up programme of analysing all the stream sediment samples for 16 elements (Pb, Zn, Ba, Ag, Sr, As, Ni, Sb, Co, Mo, Ti, Cd, Ce, La, Y, Nb, pH) has been undertaken at the laboratory of geochemistry of the University of Louvain (Prof. M. Martin). It has started in October 1981.

Thus the Belgian programme was organised from the very beginning into three more or less independent prospections :

- a radiometric prospection
- a stream sediment prospection
- a hydrogeochemical prospection.

The three prospections were allocated to specialised university laboratories, acting as sub-contractants of the Geological Survey of Belgium which took care of the direction and coordination of the project.

The Laboratory of Mineralogy of the Polytechnique Faculty of Mons (Prof. J.M. CHARLET) took charge of the radiometric section. For reasons of economy, and considering the limited potentialities of the Belgian sub-soil on the one hand, and the good coverage of motorroads with which the country is endowed on the other, a carborne prospection was chosen. A four-wheel drive vehicle, Land Cruiser TOYOTA, fitted with a crystal probe (volume : 1850 cm^3) covered and took recordings over some 11000 km of routes in less than two years.

The alluvial geochemical prospection was entrusted to the Geochemistry Laboratory of the University of Louvain (Prof. H. MARTIN), which possessed from the onset a stock of some 2100 samples. The sampling density adopted for the entire campaign was in the order of 1 sample per km^2 (10 205 samples over 11 000 km^2).

Finally, the Geochemistry Laboratory of the Free University of Brussels (Prof. A. HERBOSCH) took charge of the hydrogeochemical section. 2400 samples of stream and river waters were collected, corresponding to a density in the order of 1 sample/5 km^2.

The radiometric data and analytical results were collected by a Coordination Board installed at the Geological Survey of Belgium and then introduced into the computer of the Ministry of Economic Affairs.

A set of conversational programmes, written in APL, allowed for the direct treatment of the data from the terminal of the Geological Survey.

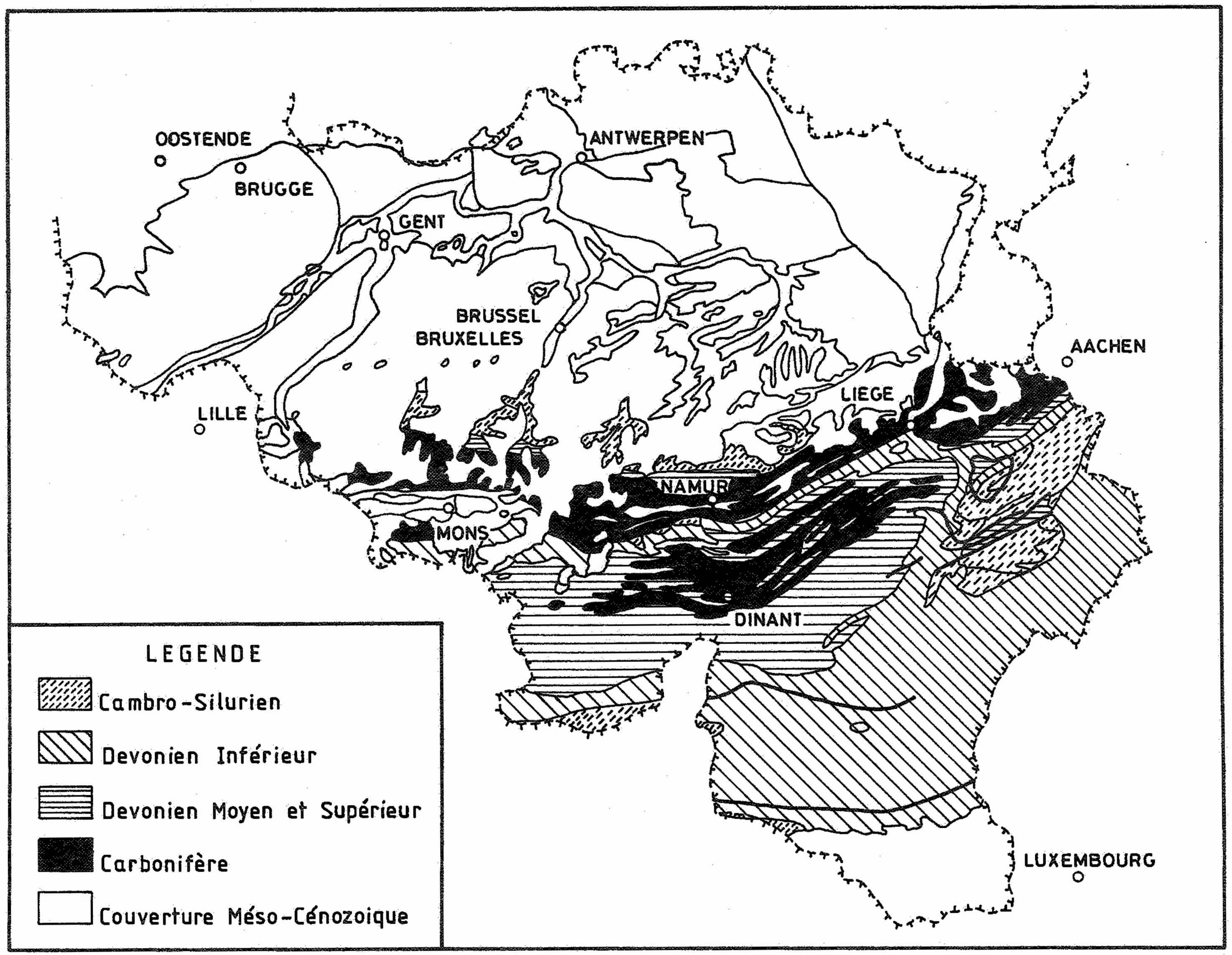


Fig. 1 Simplified geological map of Belgium.

I. 2. THE GEOLOGICAL CONTEXT

I. 2. 1. *Introduction*

From a simplified geological map of Belgium (fig. 1), two broad geological units can be distinguished, separated by a major discordance :

a) the folded Paleozoic basement, western prolongation of the schistose rhenish massive. It extends below the entire country, but only south of a line that coincides approximately with the Sambre-Meuse valley, does it outcrop in a continuous manner. The exposed part of the basement whose central zone forms a vast plateau, uplifted during the Quaternary and cut through by numerous valleys, constitutes the Geological Ardenne (which also includes the Condroz and the Entre-Sambre-et-Meuse);

b) the Meso-Cenozoic cover, sub-horizontal, covering the entire northern half of the country (Flanders, Brabant, Campine) and the extreme south of the Province of Luxemburg (Gaume). The general disposition of this cover, slightly inclined towards the north in the northern part and slightly inclined towards the south in the Belgian Lorraine, outlines a large dome whose entirely eroded apex coincides with the plateau of the Ardenne.

This disposition is the result of epeirogenic movements which affected the folded basement during the Mesozoic. The uplift of the Ardenne was particularly distinct during the Quaternary, as is shown by the ancient terraces of the Meuse, overhanging by more than 100 meters the present alluvial plain.

The existence of movements of differential subsidence since the Mesozoic is revealed, above all, by the very variable thickness of the Cretaceous from one region to another. The basin of Mons, for example, is formed within a subsident zone of the basement.

Between the two broad geological units defined above, basement on the one hand and cover on the other, there exist distinct differences in lithology and structure.

While the rocks that constitute the cover only show the effects of post-orogenic tectonics (faults, epeirogenic movements...) and are not metamorphosed, the formations of the basement have been affected to different degrees by folding and metamorphism. These transformations do not however exceed the mesozonal stage.

I. 2. 2. *The Lower Paleozoic*

Although belonging to the zone of the Variscan folds (of which it constitutes the northern front), Belgium contains a Caledonian basement geology, separated from the Variscan cover by a major discordance.

In the anticlinal zone of the Ardenne, this Caledonian appears in isolated massives surrounded by the Lower Devonian :

- massive of Givonne
- massive of Rocroi
- massive of Serpont
- massive of Stavelot.

Under the Meso-Cenozoic cover of the northern part of the country, it forms a large massive (massive of Brabant) whose formations are only exposed within the depths of certain valleys that have cut through the cover.

Finally, a narrow Caledonian band (bande condruzienne) separates the synclinorium of Namur from that of Dinant (cf. map I).

Within the Caledonian of Belgium occurs a stratigraphic series extending from the Lower Cambrian to the Upper Silurian. However, in the massives south of the Ardenne (Givonne, Rocroi, Serpont), only the Cambrian is present.

Further north in the massive of Stavelot, the Cambrian is overlain by an Ordovician formation (Salmian), whilst in the "bande condruzienne" and the massive of Brabant, the series extends to the Upper Silurian (Ludlowian).

The different formations of the Lower Paleozoic have been defined on the basis of regional lithostratigraphic criteria specific to the Ardenne. In chronological order, can be distinguished :

- a DEVILLIAN, attributed to the Lower Cambrian; quartzites and phyllites generally with clear shades of colour (green, grey, etc.);
- a REVINIAN, which corresponds to the Middle and Upper Cambrian; black rocks with a dominance of pelites;
- a SALMIAN, attributed to the Tremadocian; this stage occurs along the entire periphery of the Cambrian massive of Stavelot; black phyllites and quartz-phyllites, banks of quartzites.

In the "bande condruzienne" and the massive of Brabant, silurian formations are superposed on the Ordovician so that one talks of the Siluro-Ordovician rather than Salmian. This series goes as far as the Ludlowian.

The Siluro-Ordovician series also encloses concordant intrusions of effusive rocks of an acid nature (rhyolites, ignimbrites,...).

I. 2. 3. *The Upper Paleozoic*

After the Caledonian orogenesis, the peneplained Ardenne, bounded on the south by the Mesogea, underwent new marine transgressions. Uncomformably with the Epicaledonian surface subject to a prolonged movement of subsidence, sediments, essentially terrigenous at the beginning, then becoming progressively calcareous, accumulated in a thick series extending from the Gedinnian to the Westphalian.

The principal phase of these Variscan folds (Asturian phase) affected the entire series including the adjacent Caledonian basement and gave to the Ardenne massive its final tectonic physionomy.

The Caledonian areas previously described resurface together with the Variscan fold along whose anticlinal axes they lie.

The entire structure can be described by means of large synclinal and anticlinal tectonic units (first-order folds) whose more or less parallel disposition, or succession-type disposition, follows the general orientation of the folding which forms an arc concave towards the north.

From the south towards the north occur in succession (cf. map I) :

a) the Givonne anticline : characterised on the west by the Cambrian massive of the same name, it extends eastwards along the Lorraine basin where it comprises the Gedinnian and the Siegenian;

b) the synclinorium of Eifel (or of Neufchâteau) : comprises only the Lower Devonian, at least in Belgium. It broadens in Germany towards the Eifel due to its submergence towards the east;

c) the anticlinal zone of the Ardenne : characterised by the emergence of the Caledonian massives of Rocroi, Serpont and Stavelot, separated by the Lower Devonian formations;

d) the synclinorium of Dinant : which includes all the Middle and Upper Devonian formations, and within its central part, large series of the calcareous Dinantian. It disappears eastwards by change in axial direction along the edge of the massive of Stavelot but is replaced in the north-east by the massives of Vesdre and Herve

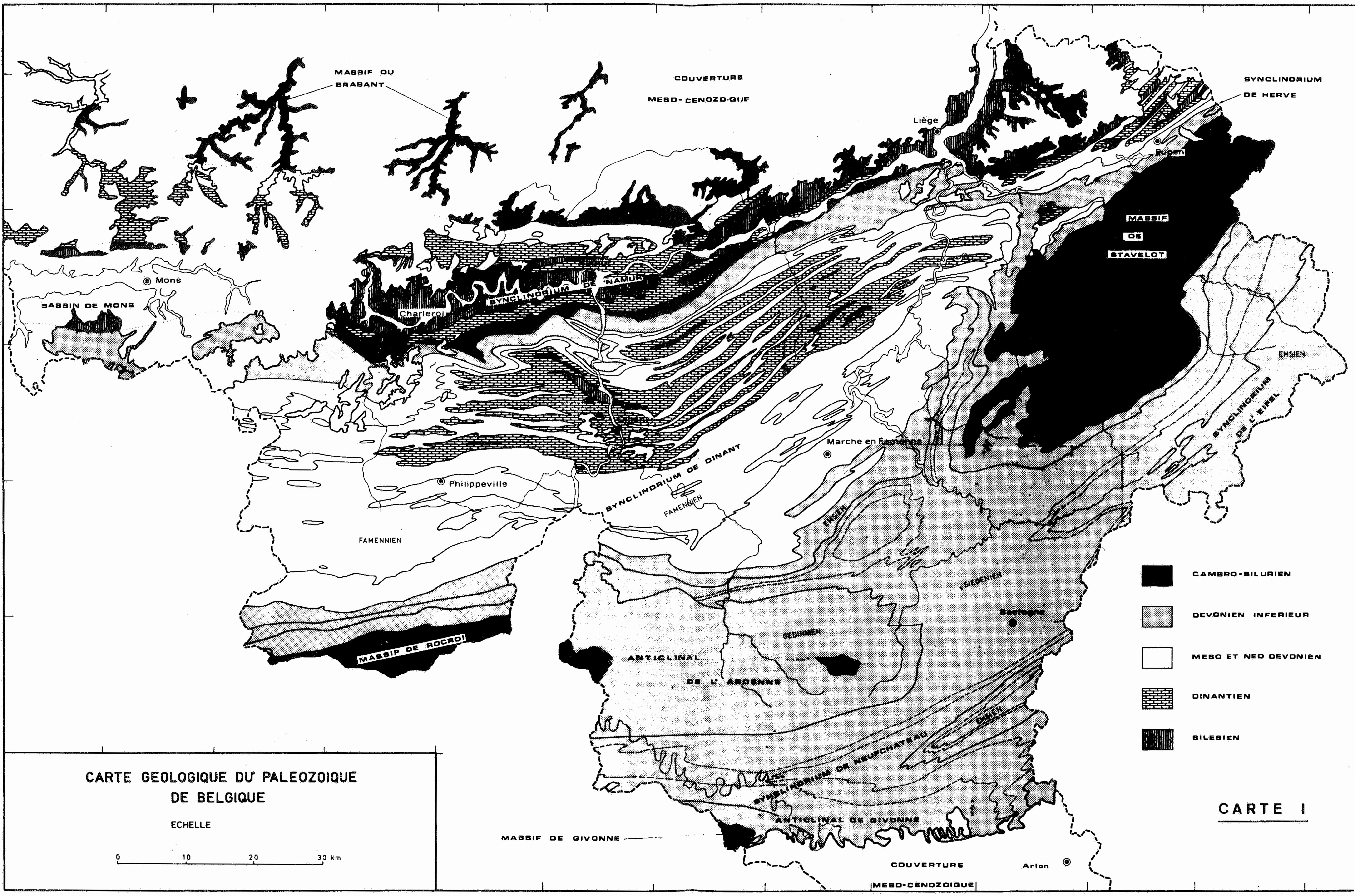
e) the faulted anticlinal zone of Condroz : this zone, which is marked by the resurfacing of a strip of silurian terrains, is the seat of a large longitudinal fault which cuts across Belgium from west to east ("Faille du Midi" to the west, "Faille Eifelienne" to the east). It is in fact a complex thrusted surface where the folded synclinorium of Dinant (allochtonous) overlaps the synclinorium of Namur (autochtonous) which is not so folded but much faulted into numerous chips;

f) the synclinorium of Namur : north of the "bande condruzienne", the sedimentary series begins with the Middle Devonian and forms a new synclinal surface in which the Silesian is dominant (coal basins of Hainaut, of the lower Sambre and of Liège).

As far as lithology is concerned, quartzo-schistose formations of the Lower Devonian cover a very large surface corresponding approximately with the first three tectonic entities previously described. They embody the Caledonian massives of Rocroi, Serpont and Stavelot, whose lithologies are about the same. The result is a relative uniformity in the geomorphology and physical features of this region which represents the essential portion of the "haute Ardenne" (plateaux spreading between 400 and 700 meters). Only in the synclinoria of Dinant, Namur and Herve-Vesdre do the calcareous formations appear and occupy large enough areas. A first strip of Meso- and Neo-Devonian calcareous rocks (Couvinian, Givetian and Frasnian) traverses the Entre-Sambre-et-Meuse and the Ardenne where it marks the transition between the "haute Ardenne" and the schistose depression of the Famenne. Further north, it is the calcareous rocks of the Dinantian alternating with the Famennian sandstones as a result of the folds, which spread largely from west to east ("Psammites du Condroz")

The Dinantian occurs again in the synclinorium of Namur and in the valleys that incise the overburden of the massive of Brabant (Senne, Dendre, Escaut). But the sandy-schistose formations of the Silesian are dominant in the synclinorium of Namur.

It must be noted that a band of the Lower Devonian outcrops again on the northern flank of the synclinorium of Dinant, just beside the Silurian band of Condroz.



CARTE GEOLOGIQUE DU PALEOZOIQUE
DE BELGIQUE

CARTE I

I. 3. URANIUM IN BELGIUM - HISTORY OF RESEARCH WORK

I. 3. 1. *The anomalies of the Paleozoic*

The first discoveries of uraniferous minerals in Ardenne go back to the last century. We shall note, for the sake of memory, the discovery of chalcolite or torbernite around Vielsalm, during an excursion organised by A. DUMONT in 1852 (1).

This mineral is mentioned in 1897 in the Memoir of G. CESARO on the phosphate, carbonate and sulphate minerals of Belgium (2).

It was not, however, until after the second world war that an interest other than mineralogic appeared in the literature in the radioactivity of the Belgian sub-soil.

In 1951, a paper by I. de MAGNEE reported original observations on the radioactivity of marine schists belonging to the Westphalian in Belgium. The author recommended the systematic "gamma probing" of cores drilled into the Silesian for study and stratigraphic correlation purposes (4).

During that same year, in a publication dealing with the future of Wallonia, A. WERY (3) put forward interesting considerations on the possibility of prospecting for radioactive substances in Belgium. According to this author, uranium must be looked for in the most ancient terrains of the Paleozoic, in association with copper. He suggested that all the indications of known copper ores be re-examined by radiometric techniques.

In 1955, the Geological Survey of Belgium organised a preliminary radiometric prospection, using a portable scintillometer. The campaign was led by R. LEGRAND between 1955 and 1962 and a density of 10 recording points per 20 km^2 was achieved. It covered about 10% of the surface area of the country, mainly in the Entre-Sambre-et-Meuse, within the centre of the Ardenne and in the eastern part of the country (fig. 2).

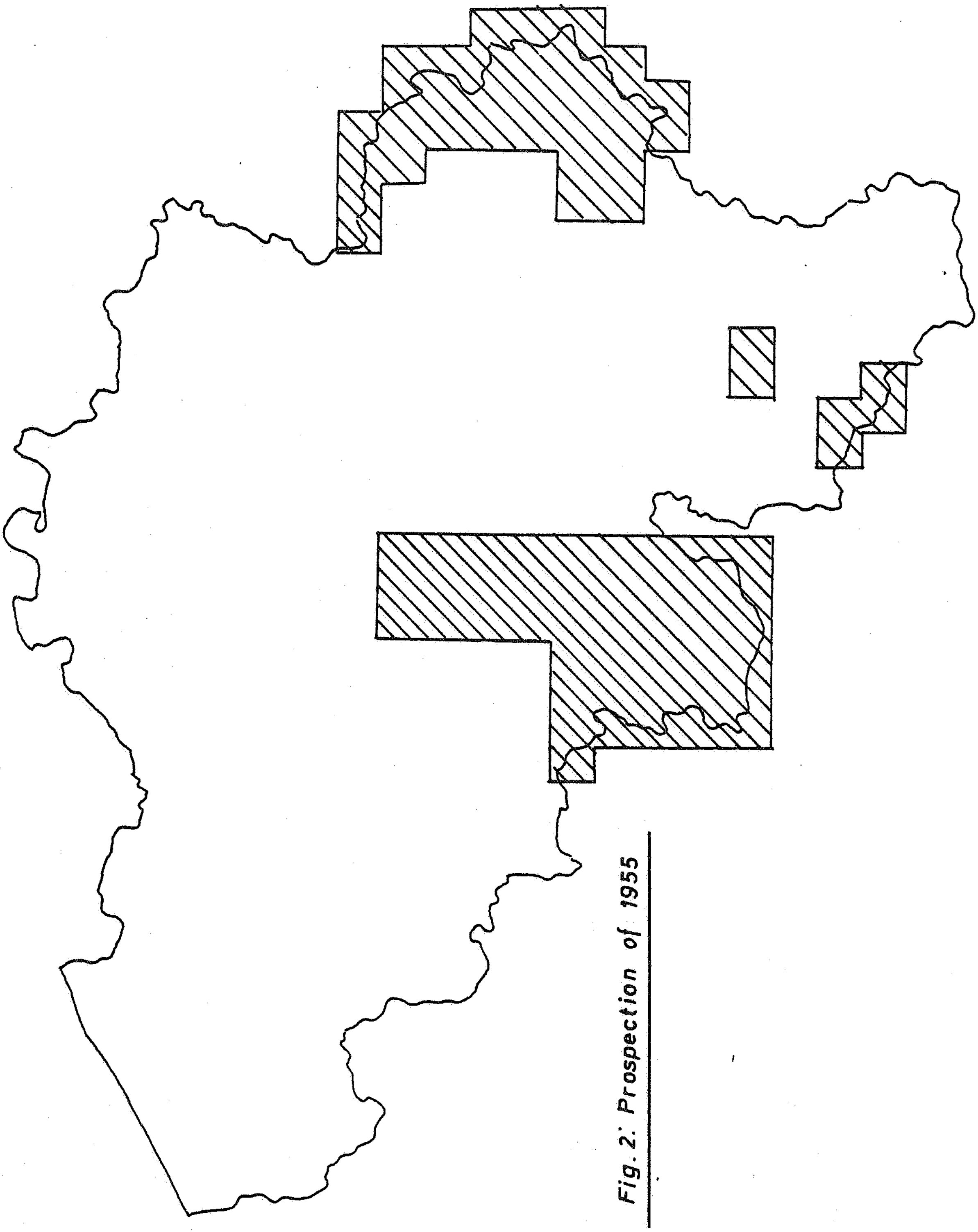


Fig. 2: Prospection of 1955

This campaign led to the detection of some anomalies :

a) in the trench of the Nimy-Blaton canal, the shales at the passage from the Visean to the Namurian show a marked radioactivity relative to the regional background (8 to 10 times the regional background);

b) in the Devono-Carboniferous massive of Visé, breccia localised within dissolution pockets of the Visean and Frasnian calcareous rocks show a high radioactivity : up to several tens of times the regional background (7, 8);

c) on the periphery of the Cambrian massive of Stavelot, the black schists ascribed to the top of the Revinian (Rv5) showed a high enough radioactivity : 4 to 5 times the regional background.

Stratigraphic studies of the trench of the Nimy-Blaton canal (called "du Mont des Groseilliers") have been carried out by many authors (11, 14). A few works on its radiometry have been carried out by the Polytechnic Faculty of Mons (17, 18). These works led to the localisation of uranium in the banks of shale formations at the passage from the Upper Visean (V3b) to the Lower Namurian. These banks, about 10 cm thick, have uranium values of 20-30 ppm, with a maximum of 80 ppm.

The gamma logging carried out for the Geological Survey of Belgium on a number of cores (Soumagne, Soiron, Wépion, Grand-Halleux, Saint-Ghislain) prove that the anomaly at Blaton is not an isolated phenomenon. In fact there is an increase in the radioactivity at the contact between the Visean and the Namurian in all places.

According to J.M. GRAULICH (12), the concentrations of uranium within the paleokarsts of the region of Visé would be due to the re-mobilization of the uranium present in the shales and cherts of the adjacent Namurian during a phase of contemporaneous emergence of the Sudetan phase of the Variscan orogeny. The paleokarsts would be of Namurian age and would correspond to the break in sedimentation in the series at the base of the Namurian as revealed by the same author.

The radioactive breccia in the regions of Visé, Richelle and Argenteau have been studied at great lengths since 1956.

In chronological order should be cited the mineralogical discoveries of J. JEDWAB (5, 6) and R. VAN TASSEL (9, 10) who identified autunite and torbernite in the dissolution pockets of the Visean at Richelle and at Argenteau. More recently, the mineralogical inventory of the known indications at Richelle has been pursued by A.M. FRANSOLET, J. JEDWAB and R. VAN TASSEL with the revelation of about thirty mineral species (15, 16).

In 1973, an anomalous radioactivity was discovered by chance in the distribution waters of the town of Visé. A systematic analysis of radon in the surrounding catchments was then carried out and the results confirmed once more the presence of uranium in the sub-soil of Visé.

In 1977, a radiometric prospection on foot was carried out over the entire massive by a team from the ULB under the terms of a contract financed by the EEC (contract 77/02578). About twenty new radioactive anomalies were thus discovered and described successively by S.M. DE WITTE (19) in 1977, and by A. HERBOSCH, S.M. DE WITTE and A. PREAT (20) in 1979. This study established that the radioactive anomalies are systematically linked with the presence of calcium phosphates either in the karstic pockets or in the enveloping terrains (calcareous rocks, phosphorites and argilites).

The presence of uranium associated with phosphates in the calcareous rocks of the Visean gives rise to new hypotheses on the genesis of the anomalies. Without however questioning the scheme of J.M. GRAULICH on the formation of the paleokarsts themselves, A. HERBOSCH *et al.* (20) place the origin of the uranium in the phosphates dispersed within the calcareous rocks of the Visean (V3b) rather than in the argilites of the Namurian.

The radioactive anomaly discovered by R. LEGRAND in the region of Vielsalm has been studied more thoroughly during a detailed prospection in the triangle Vielsalm-Salmchâteau-Ottré, organised in collaboration with L. VAN WAMBEKE of the "Centre d'Etude Nucléaire de Mol" in 1958. These studies, which were not published, did reveal the presence of a level of black schists which were radioactive enough, at the summit of the Revinian (Rv5).

This level has also been picked up by J.M. CHARLET et al. in 1977 (18) during reconnaissance work along the route Vielsalm-Grand Halleux. Analyses effected by gamma spectrometry indicated relatively high values of uranium (20 ppm) and low Th/U ratios (~ 0.4).

I. 3. 2. *Other anomalies*

For the sake of completion, it must be added that uraniferous anomalies are known to occur in Belgium outside the Paleozoic, notably :

- a level of phosphatic concretions in the sand of Merksem, near Antwerp (13);
- the phosphatic levels of the Maestrichtian chalks in the basin of Mons (30-50 ppm uranium) (18);
- the Montian lacustrine calcareous rocks (low anomaly : ± 10 ppm uranium).

These anomalies seem to offer only a mineralogical and stratigraphical interest. Nevertheless, the possibility of finding interesting concentrations in the phosphatic chalks of the basin of Mons is not to be discarded a priori. For this reason, the present campaign was extended into this region.

I. 4. DATA PROCESSING AND CARTOGRAPHICAL DOCUMENTATION

I. 4. 1. *Maps used in the field*

For the teams in charge of the field work, the 1:25 000 topographic map of the I.G.N.(*) served as the field document for the tracing of routes and the localisation of sampling points.

This localisation is greatly facilitated by the metric scaling of the maps (LAMBERT coordinates of the European Geodesic Network of 1951). They enable the determination of the coordinates of each sample point (X = longitude; Y = latitude) in kilometers with a reading precision in the order of a meter (three decimal places).

One further advantage of these maps is that the subdivision of the field area is identical to that of the 1:40 000 geological map of Belgium.

Thus, for each topographic map, there is a corresponding sheet of the geological map covering the same surface. It is thus easy to determine the geological characteristics of any one point.

I. 4. 2. *Reference maps for the computer files*

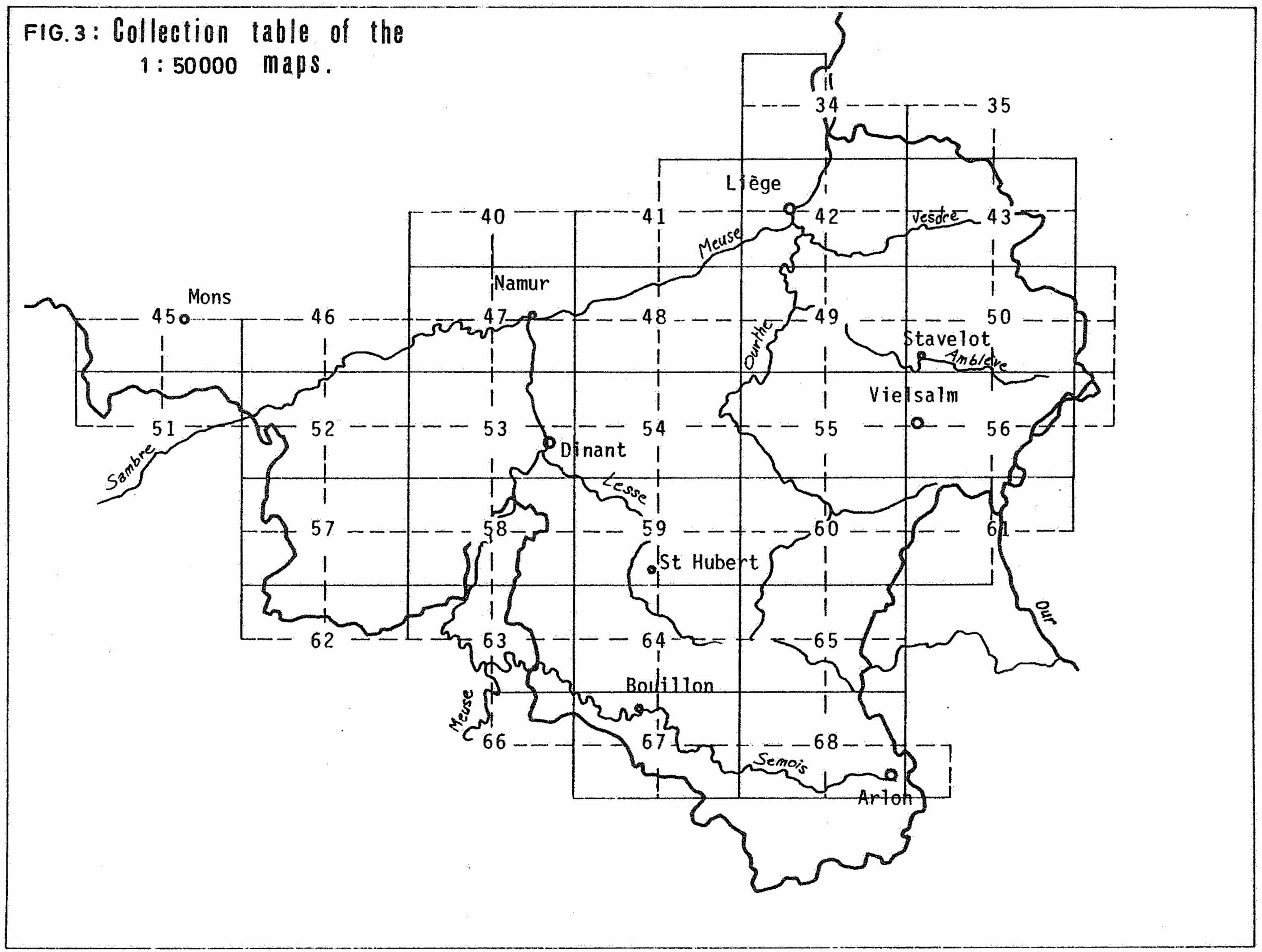
For the computer storage of the prospection data, the 1:50 000 topographic maps were used for the numbering of the points.

The collection table of 1:50 000 maps used for the entire prospected region is reproduced in fig. 3.

The numbering of points for the computer files is based on a five-number code : the first two numbers correspond to the numbers of the 1:50 000 maps (between 34 and 68) and the three others represent the numbers of the points themselves (between 1 and 999).

(*) Institut Géographique National.

FIG. 3: Collection table of the 1:50000 maps.



In general, the total number of points per map is far from the one thousand mark. However, for certain maps of the radiometric prospection, this number was exceeded so that fictitious map numbers were introduced to "take care" of the excess points. This point will be detailed in Chapter IV.

I. 4. 3. *Maps of production and geological background for interpretation purposes*

The most interesting scale for the automatic exit of the maps proved to be 1:100 000. This makes it possible to represent, in a format practical enough for the tracer, an already large surface area : 2560 km^2 in a grid of 64 cm x 40 cm.

This surface area corresponds to one unit of the 1:100 000 topographic map of the I.G.N.

We have thus adopted the cutting of the 1:100 000 map (fig. 4) for producing maps of results.

Each map, which unites four units of the 1:50 000 map, carries the name of a characteristic locality of the region represented.

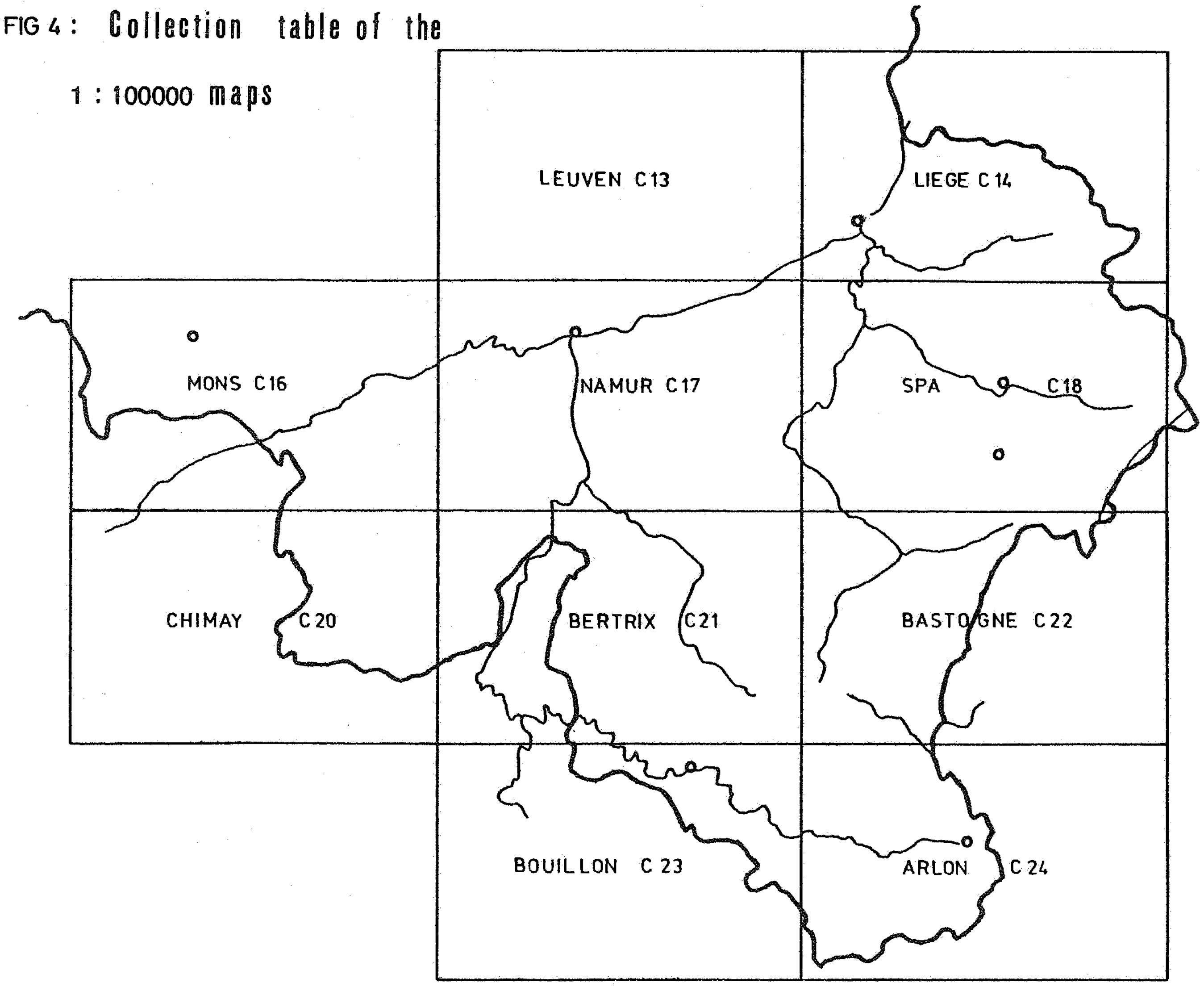
Thus the region prospected is entirely covered by the nine maps carrying the following names : MONS, NAMUR, BASTOGNE, SPA, LIEGE, CHIMAY, BERTRIX, BOUILLON, ARLON.

For each map, a background geology has been drawn on tracing paper, at the same scale to facilitate data interpretation.

I. 4. 4. *Summary maps at 1 : 300 000*

In order to grasp at a glance the situation of the anomalies in the entire region studied, a geological map of the Paleozoic at a convenient scale (neither too small for a detailed representation of the geological background, nor too large to facilitate its insertion into this report) was used. This document which has a scale of

FIG 4 : **Collection table of the 1 : 100000 maps**



1:300 000 is the result of compilation work carried out by H. NEYBERGH (Geological Survey of Belgium) from existing maps and later adjustments (notably the works of A. ASSELBERGHS on the Lower DEVONIAN).

This is the map (map I) used for the synthetic presentation of the results from the three prospections (maps II to X) ,which ,in this paper, has an approximative scale of 1:525 000 , after reduction for printing reasons.

I. 4. 5. *Computer support*

At the "Centre de Traitement de l'Information" (CTI) of the Ministry of Economic Affairs of Belgium, a data bank has been constituted for controlling the results of the prospection.

Three distinct files ("EAUX", "ALLUVIONS", "RADIO") have been created and controlled with the aid of APL conversational programs through the terminal of the Geological Survey of Belgium.

The first introduction of the data into the computer has been carried out through the specialised services of the CTI, from the index-cards used by the contracting universities for entering analytical results and measurements in standard forms.

A conversational APL program allowed any modification to the data in the created computer files.

Other programs were available, either for the selection of data complying with certain criteria, in view of their statistical treatment for example, or for the edition of maps via the plotting table of the CTI.

The points-maps and the maps of iso-value curves were calculated by a program of the Kansas Geological Survey (SURFACE II GRAPHICS SYSTEM, 1975, revised 1978, Computer Services Section, Kansas Geological Survey, Lawrence, Kansas, U.S.A.).

Detailed maps which are not joined to this publication may be consulted at the Geological Survey of Belgium and at the university laboratories involved with this survey.

BIBLIOGRAPHY OF CHAPTER I

1) A. DUMONT, 1852

Cristaux de Chalcolite trouvés près de Vielsalm.

Bull. Acad. roy. Belg., t. 19, 2e partie, pp. 343-344.

2) G. CESARO, 1898

Description des minéraux phosphatés, carbonatés et sulphatés du sol belge.

Mém. Acad. roy. Belg., Mém. cour. in 4°, t 53, n° 4, Bruxelles.

3) A. WERY, 1951

L'Avenir du Sud de la Belgique.

4) I. de MAGNEE, 1951

Observations sur la radioactivité des horizons marins du Westphalien belge.

3e Congrès de Stratigraphie et de Géologie du Carbonifère, Heerlen, 1951, pp. 429-434.

5) J. JEDWAB, 1959

Présence de torbernite à Richelle (Province de Liège).

Bull. Soc. belg. Géol. Pal. Hydrol., t 67, 1958, pp. 300-303

6) J. JEDWAB, 1959

Présence de grès uranifère à Argenteau (Province de Liège).

Bull. Soc. belg. Géol. Pal. Hydrol., t 68, 1959, pp. 319-323.

7) R. LEGRAND, 1958

Brèches radioactives aux environs de Visé.

Bull. Soc. belg. Géol. pal. Hydrol., t 66, 1957, pp. 211-217.

8) R. LEGRAND, 1959

Compte-rendu de l'excursion du 26 juin 1958 dans la région de Visé.

Bull. Soc. belg. Géol. Pal. Hydrol., t 67, 1958, pp. 290-295.

9) R. VAN TASSEL, 1959

Autunite, apatite, delvauxite, évansite et fluellite de la région de Visé.

Bull. Soc. belg. Géol. Pal. Hydrol., t 68, 1959, pp. 226-250.

10) R. VAN TASSEL, 1959

Strengite, phosphosiderite, cacoxénite et apatite fibroradiée de Richelle.

Bull. Soc. belg. Géol. Pal. Hydrol., t 68, 1959, pp. 360-370.

11) J. BOUCKAERT, A. DELMER, P. OVERLAU, 1961

Stratigraphie du Viséen moyen et supérieur et du Namurien inférieur dans la région de Basècles-Blaton (tranchée du Mont des Groseilliers).

Mém. Inst. Géol. Univ. Louvain, t 22.

12) J.M. GRAULICH, 1963

La phase sudète de l'orogenèse varisque dans le synclinorium de Namur à l'est du Samson.

Bull. Soc. belg. Géol. Pal. Hydrol., t 71, 1962, pp. 181-199.

13) R. VAN TASSEL, 1965

Concrétions tubulées du Merksémien (Pléistocène inférieur).

Bull. Soc. belg. Géol. Pal. Hydrol., t 73, 1964, pp. 469-497.

14) K. FIEGE, 1967

Tranchée du canal Nimy-Antoing au Mont des Groseilliers, Blaton. Viséen supérieur et Namurien inférieur.

Prof. Paper Serv. géol. Belg. n° 14.

15) A.M. FRANSOLET, J. JEDWAB, R. VAN TASSEL, 1974

Inventaire minéralogique de Richelle - Belgique.

Ann. Soc. géol. Belg., t 97, 1974, pp. 23-26.

16) A.M. FRANSOLET, J. JEDWAB, R. VAN TASSEL, 1974

La fluellite de Richelle, près de Visé - Belgique.

Ann. Soc. géol. Belg., t 97, 1974, pp. 27-38.

17) V. CIZA, 1976

Contribution à l'optimalisation de l'étude par spectrométrie gamma d'une anomalie radioactive.

Travail de fin d'études, Faculté Polytechnique de Mons, 1976, 58 pages.

18) J.-M. CHARLET, CH. DUPUIS, Y. QUINIF, 1977

Perspectives de la prospection de l'uranium à l'échelle nationale.

Annales des Mines de Belgique, 5e livraison, pp. 522-531.

19) S.M. DE WITTE, 1977

Contribution à l'étude de la radioactivité des roches de la région de Visé (Province de Liège).

Mém. de Licence, Université Libre de Bruxelles, 107 p.

20) A. HERBOSCH, S.M. DE WITTE, A. PREAT, 1979

Recherches sur les indices de minéralisation uranifères dans la région de Visé.

Prof. Paper Serv. géol. Belg. n° 162.

CHAPTER II

STREAM SEDIMENTS GEOCHEMISTRY

II. 1. INTRODUCTION

The objective of a preliminary prospection is the demarcation, on a regional scale, of favourable zones for eventual tactical prospection.

In stream sediment geochemistry, this objective can generally be met with sampling densities in the order of one sample per 10 to 25 km^2 (21).

For the present prospection, a high enough density was chosen, i.e. one sample per km^2, for purely methodological reasons (cf. II.2 and II.4).

The field work, for the prospection which was conducted by the Geochemistry unit of the University of Louvain, was carried out between April 1979 and October 1980. It involved a team of two men (a geologist and a field assistant) who collected a total of 8100 samples in 182 days corresponding to a mean of 44.5 samples per day.

Taking into account samples collected outside the contract period, before 1979 (± 2100 samples), the region prospected was covered at the required density (about 10200 samples over 11000 km^2).

In the laboratory, routine analyses of the following elements were effected : U, Cu, V, Fe and Mn. Moreover, for samples with uranium values greater than 2 ppm, the pH, the carbonate and organic carbon contents were determined to meet the needs of a methodological study of which the results are presented in II.4.

The laboratory thus carried out over 56100 determinations between June 1979 and February 1981, a mean of ± 56 determinations by man-day.

II. 2. FIELD TECHNIQUE

The methodological study presented in II.4 showed that in alumino-silicate as well as carbonate environments, samples can be collected within the recent alluvia along the edges of the water channels and not necessarily in the active bed.

Since this method of sampling is adopted, the samples contain a certain amount of colluvium over and above the alluvium and, considering the larger dispersion train of the alluvia, sampling density must be increased. These considerations explain the choice of a high density in the order of one sample per km^2.

It must be noted that because of its very large granulometry (pebbles), sampling of the active bed could not have been effected at a sufficient density.

The teams from the Universities of Brussels and Louvain prepared in common the sampling grids. Each 1:25 000 topographic map was divided into 1 km squares and as far as possible one sample collected within each square, taking into account the logic of the drainage basin and also the accessibility which is the dominant factor in determining the speed with which the prospection progresses.

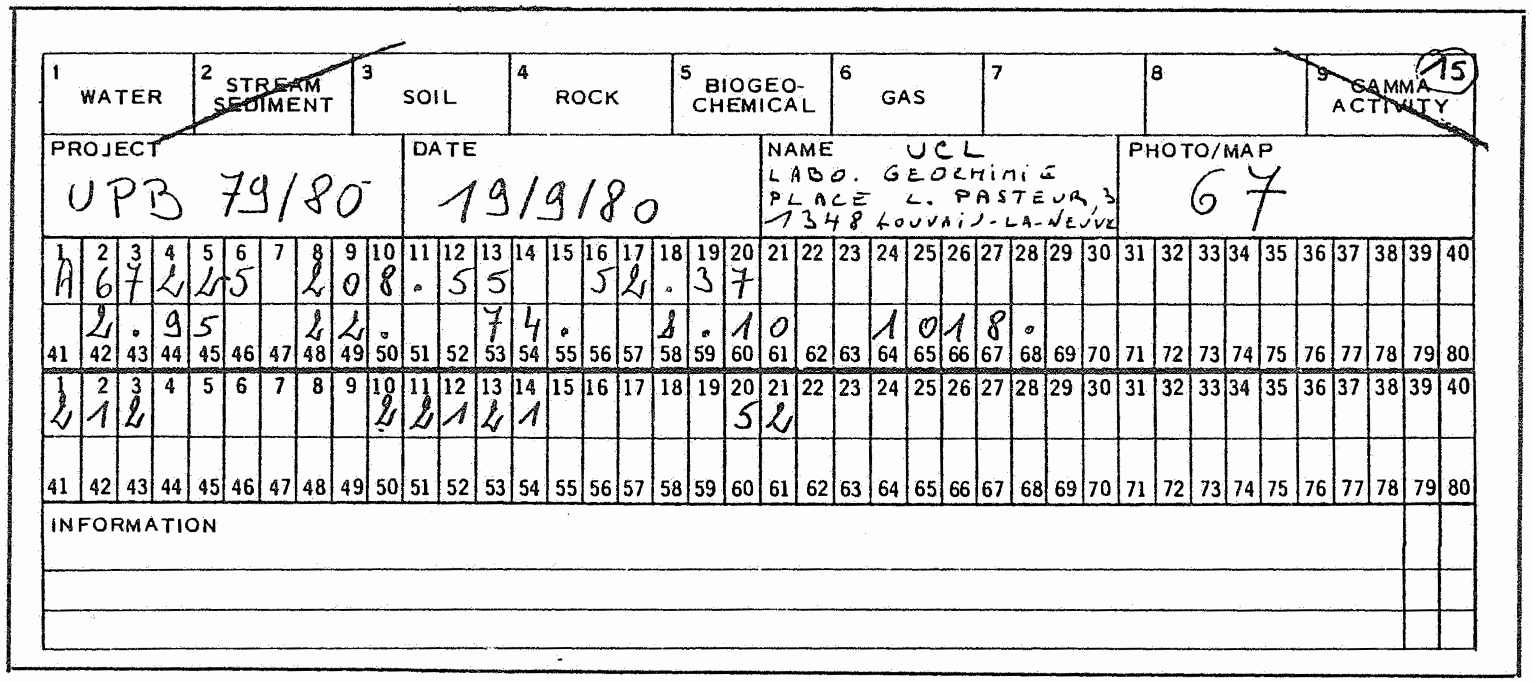
The water channels selected in this way are more often stream tributaries of low flow rate, whose alluvia could be considered as colluvia reworked by the runoff and transported over relatively small distances. Thus, the anomalies eventually encountered are no doubt never far removed from their geological source.

The samples are collected by means of a soil auger at the intersection of the lower edge of the bank and the active bed.

They are directly transferred into numbered kraft paper sacks.

On the sampling site, a series of other bits of information are noted and then codified onto a special index-card with 80 columns, a model of which is presented in figure 5 together with the code used.

On it are noted the bank from which the sample was collected, the width of the water channel, the colour of the sample, its texture, its geological environment, its organic nature, etc.



1 WATER	2 ~~STREAM SEDIMENT~~	3 SOIL	4 ROCK	5 BIOGEO-CHEMICAL	6 GAS	7	8	9 ~~GAMMA ACTIVITY~~ ⑮

PROJECT UPB 79/80

DATE 19/9/80

NAME UCL
LABO. GEOCHIMIE
PLACE L. PASTEUR, 3
1348 LOUVAIN-LA-NEUVE

PHOTO/MAP 67

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A	6	7	2	2	5		2	0	8	.	5	5			5	2	.	3	7
	2	.	9	5			2	2	.			7	4	.			8	.	1
41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
0			1	0	1	8	.												
61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
2	1	2							2	2	1	2	1						5
41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
2																			
61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

INFORMATION

Fig 5a : model of the stream sediments field record card

Ligne	Cases	Contenu
2	2	DATE de l'échantillonnage MAP n° de la carte à 1 : 50 000
3	1 - 6 8 - 14 16 - 21	n° de l'échantillon coordonnée Lambert X coordonnée Lambert Y
4	41 - 45 46 - 50 52 - 55 57 - 61 63 - 68	teneur en V (ppm) teneur en Cu (ppm) teneur en V (ppm) teneur en Fe (%) teneur en Mn (ppm)
5	1	Type de drainage : b indéterm. 1 largeur < 1 m 2 " < 2 m 3 " < 3 m 4 " > 3 m 5 suintement 6 source 7 lac 8 autre
	2	Conditions de drainage : b indéterm. 1 eau courante 2 lit sec 3 eau stagnante
	3	Prélèvement rive : 1 gauche 2 droite 3 milieu 4 partout
	4	Type d'échantillon : b indéterm. 1 alluvions 2 colluvions 3 alluvio-colluvions 4 bed-rock altéré
	10	Couleur dominante : b n'existe pas 1 brun 2 gris 3 noir 4 jaune ocre 5 rouge brique 6 gris vert-bleu 7 beige-blanc 8 rouille 9 autre
	11	Ton : 2 clair 2 moyen 3 foncé
	12	Couleur secondaire voir 10
	13	Ton : voir 11
	14	Bariolage : b n'existe pas 1 moucheté (points de rouille) 2 intime, uniforme 3 indéfini
	20	Texture : 1 argileuse 2 sableuse 3 argilo-sableuse (limon) 4 graveleuse-caillouteuse 5 mixte
	21	Roches : b pas d'affleurement 1 calcaire 2 grès-schistes 3 poudingue-conglomérat 4 indéterm.
	22	Matière organique : 1 présente 2 paratourbe b absente
	23	Odeur : b absente 1 présente
	24	Pollution : b absente 1 possible 2 autre

Fig 5b : Code for the description of a sampling point on the field card.

II. 3. LABORATORY TECHNIQUES

II. 3. 1. *Preparation of samples*

The samples brought back to the laboratory and still in their paper sacks were dried at 60°C for 48 hours, separated into two, one half being set aside for storage at the Geological Survey of Belgium to be used eventually for further programs of analyses.

The second half was disaggregated and sieved at 80 mesh (180 microns).

A dissolution is achieved by means of a hot (150°C) tri-acid attack (HF, HNO_3, HCl) on one gram of powder, and the residue is treated with diluted nitric acid (4N).

II. 3. 2. *Analysis for Uranium*

Uranium is determined after the solution from the triacid extract. Considering the large number of samples to be analysed, a rapid method for the analysis of uranium in routine was looked for. A "direct method" using the solution derived from the triacid attack was first tested. Interference studies showed that with 500 ppm of Mn in a solution equally containing 2.5 % of Fe, only about 50 % of the original uranium could be detected (fig. 6). It is worth noting that R.G. GARRETT and J.J. LYNCH (22) pointed out a lower quenching of uranium by Mn. This direct method must be done together with analyses for Mn and Fe, so that their effects on the determination of uranium can be corrected. Furthermore, application of this correction carried the risk of enhancing the imprecisions in the determination of uranium, particularly for samples rich in the interfering elements.

We adopted a method involving the extraction of uranium by methyl-iso-butyl-acetone (MIBK) in the presence of tetrapropylammonium (TPAN). In addition to being more selective, and despite the

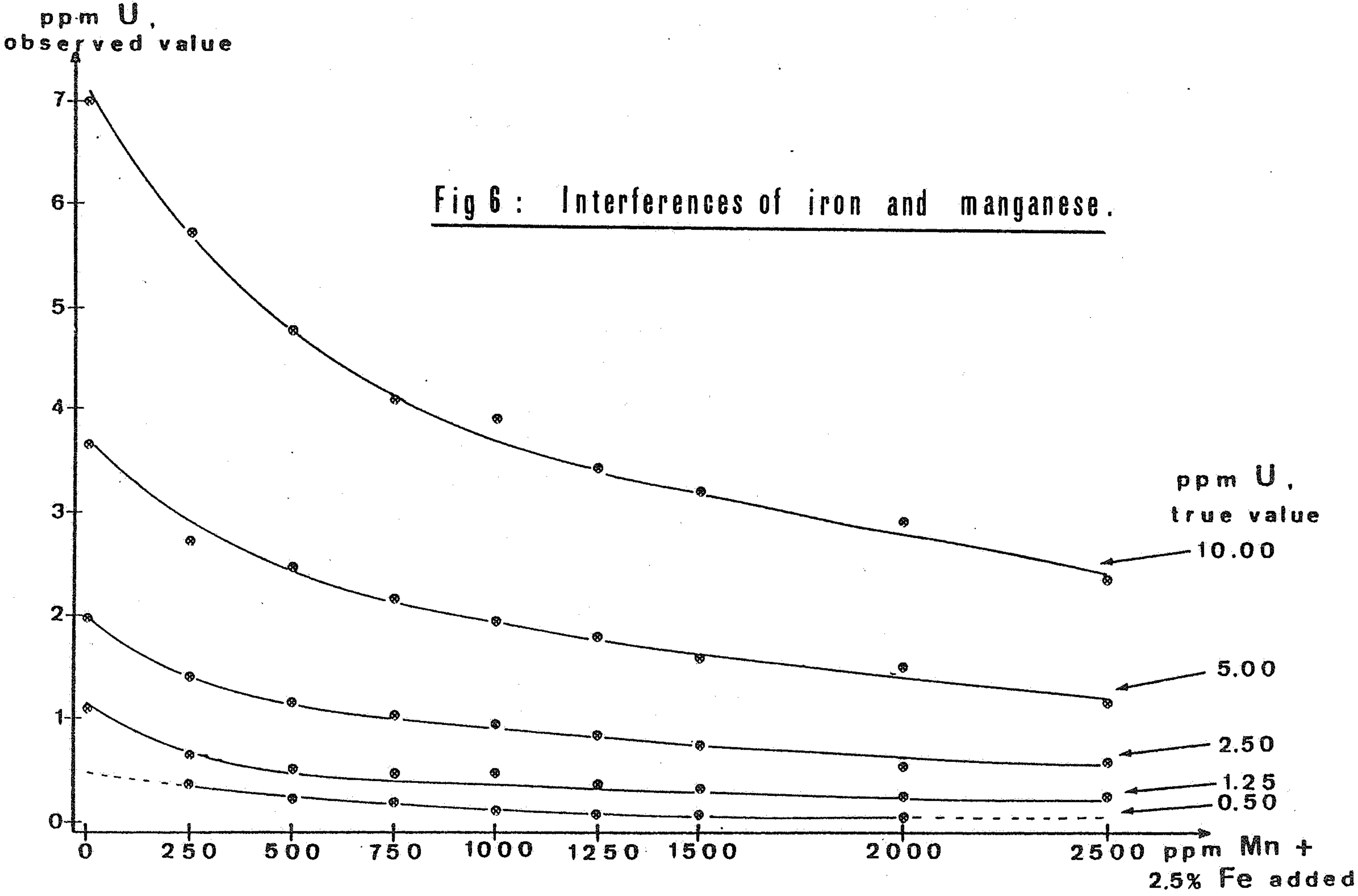


Fig 6 : Interferences of iron and manganese.

supplementary extraction stage, this method proves to be more rapid than the direct method. In fact, oven drying of the MIBK solution is much more rapid than the drying of the filtrate from the triacid attack in the direct method (23, 24).

The sodium and potassium carbonates used in the production of the pellets for uranium titration must be finely ground so as to obtain a homogeneous flux.

II. 3. 3. *Analyses for Cu, V, Fe and Mn*

The extraction solution (cf. II.3.1) is analysed directly by atomic absorption spectrophotometry (instrument VARIAN AA6).

II. 3. 4. *Measurement of pH*

The pH is measured by means of a glass electrode on 1 gram of sample suspended in 1 ml of demineralised water.

II. 3. 5. *Determination of carbonates*

Carbonates were determined gasometrically by the measurement of the volume of CO_2 freed from 1 gram of powder in contact with 10 ml of 6N HCl during 5 minutes.

II. 3. 6. *Determination of organic carbon*

Involves the oxidation of the organic carbon contained within 0.2 gram of sample by $K_2Cr_2O_7$ in excess, in the presence of concentrated sulfuric acid and titration of this excess by $FeSO_4$ in the presence of an indicator.

II. 3. 7. *Reproducibility of analyses*

Test samples were always included among each series of solutions prepared. These served the double purpose of detecting errors that might occur during the solution step on the one hand, and estimating the reproducibility of analyses over the entire contract period on the other hand. Since error is a function of concentration, eight samples were chosen on the basis of their low, mean and high contents in the elements considered. Table I shows the results of the reproducibility of the analyses.

II. 3. 8. *Analytical precision*

The method of standard additions was applied to 4 samples tested for reproducibility in order to control the error due to interferences between the different elements in the analytical solution. The method involves the addition, to four 1 gram portions of powder, of 0%, 50%, 100% and 150% of the supposed values of U, Cu, V, Fe and Mn in these samples. The results of this study are shown in Table II.

Table I : *Reproducibility of analyses over the contract period*

	U				Fe				Mn				Cu				V			
	n	$\bar{x}$	S	C	n	$\bar{x}$	S	C	n	$\bar{x}$	S	C	n	$\bar{x}$	S	C	n	$\bar{x}$	S	C
A41104	92	0.72	0.11	15.3	103	1.66	0.08	5.0	103	261	16	6.1	100	16	1	5.4	105	48	5	10.1
A50076	30	2.73	0.20	7.3	37	3.20	0.12	3.9	36	609	61	9.9	35	32	1	4.2	42	96	9	9.1
A53015	53	0.82	0.10	12.7	53	1.72	0.13	7.6	52	220	15	7.0	53	38	1	11.3	50	51	8	16.0
A53019	34	1.54	0.13	8.4	34	5.46	0.31	5.6	34	462	44	9.4	34	14	1	5.6	33	68	7	10.4
A53211	44	8.73	0.77	8.8	42	4.64	0.35	7.4	43	1301	105	8.1	43	20	1	5.6	42	63	7	11.3
A55425	38	3.45	0.19	5.5	37	3.76	0.13	3.5	38	334	18	5.4	37	23	1	3.9	37	95	9	10.0
A56177	40	1.22	0.14	11.6	51	2.61	0.10	4.0	51	924	86	9.3	51	13	1	4.7	57	66	6	9.2
A63106	78	1.53	0.18	11.8	86	3.19	0.14	4.3	86	327	25	7.8	82	24	1	3.9	89	63	8	11.9

A41104: test sample for the period 23/1/80 - 9/12/80
A50076: test sample for the period 13/2/80 - 6/8/80
A53015: test sample for the period 11/9/79 - 9/2/80
A53019: test sample for the period 11/9/79 - 13/1/80
A53211: test sample for the period 10/9/79 - 11/2/80
A55425: test sample for the period 11/8/80 - 9/12/80
A56177: test sample for the period 23/1/80 - 6/8/80
A63106: test sample for the period 14/2/80 - 9/12/80

n : number of analyses
$\bar{x}$: arithmetical mean }
S : standard deviation } are expressed in % for Fe, and in ppm for the other elements
C : variation factor expressed in %

Table II : *Test of exactitude*

	U		Fe		Mn		Cu		V	
	$\bar{x}$	x_e	$\bar{x}$	x_e	$\bar{x}$	x_e	$\bar{x}$	x_e	$\bar{x}$	x_e
A41104	0.72	0.77	1.66	1.67	261	250	16	17	48	53
A56177	1.22	1.16	2.61	2.76	924	1115	13	13	66	59
A63106	1.53	1.91	3.19	3.60	327	377	24	29	63	81
A50076	2.79	2.59	3.20	3.39	609	676	32	36	96	103

$\bar{x}$: value from measurements of precision (see Table I)

x_e: value from the method of standard additions

The values are expressed in % for Fe and in ppm for the other elements.

Even if the least satisfactory result for uranium (sample A63106) is considered, taking into account the value of the standard deviation in Table I, it can be estimated that there is a chance of only less than 5 % that x_e (1.91 ppm) does not belong to the population of $\bar{x}$ represented by the most probable value of 1.53 ppm for uranium.

II. 3. 9. *External Control*

In order to verify the reproducibility of the anomalies, an external control was effected by the Geochemistry laboratory of COGEMA (France) for uranium. The comparison between their results and those of the Geochemistry laboratory of U.C.L. is expressed as the coefficient of linear correlation (r) and by the regression line :

number of samples :	1284
coefficient of correlation :	0.9043
regression equation : Y =	0.84X + 0.82

with Y representing values from U.C.L.
and X the corresponding values from COGEMA.

The values of the slope and the intercept give an estimate of the systematic error of the analyses. For high uranium values (greater than 2 ppm), the systematic error is lower than 20%. The anomalous values can thus be considered as reproducible within the limits of analytical error. The systematic differences between the results from the two laboratories probably proceed from the different methods of analysis employed. In fact, for the sample dissolution, COGEMA employed a relatively weak attack with nitric acid while the Geochemistry laboratory of U.C.L. used the stronger hot triacid attack. Furthermore, COGEMA determines uranium by fluorimetry after a chromatographic separation. U.C.L., on the other hand, analyses for uranium by fluorimetry after extraction by MIBK in the presence of TPAN.

II. 4. METHODOLOGICAL STUDIES

II. 4. 1. *Introduction*

In 1977 and 1978, a methodological study of the geochemistry of uranium at the southern side of the Stavelot massive showed that, in the alumino-silicate environment that characterises a large portion of the Belgian Ardenne, sampling could be restricted to the recent alluvium along the edge of the water channel.

The prospection team decided to extend this same mode of sampling to the carbonate environment.

Nevertheless, it was found essential (taking advantage of this prospection campaign) to carry out a full methodological study with more emphasis on the problems encountered in carbonate environments. This approach responded to the concerns of Mr. R. AITKEN (EEC) who in a letter to the Geological Survey in July 1979, recommended "a small orientation survey with a limited number of samples to see if uranium was absorbed onto organic material in the sediment or co-precipitated with carbonate".

The following points were thus examined :

1) the validity of diverse methods of sampling
2) the influence of environmental factors (organic matter, carbonates, pH, iron, etc.) on the dispersion and fixation of uranium in stream sediments.

II. 4. 2. *Sampling*

Two zones with known uraniferous indications were chosen; one within a carbonate context (massive of Visé) and the other in an alumino-silicate environment (southern margin of the massive of Stavelot). About 150 samples were collected in each zone. At each sampling site, four different methods of sampling (p) were carried out :

- (p1) by hand in the active stream bed
- (p2) by hand from the organic rich material
- (p3) by auger, below the water level in a reduced medium
- (p4) by auger, within the break zone of the water, in an oxidised medium.

The results show that in the silicate environment (25), there is a remarkably good relationship between the stream sediment anomalies and the known uranium indications in the black schists of the Upper Revinian, irrespective of the sample type. There are significant positive correlations between the values of uranium and those of iron (r = 0.35), of copper (r = 0.67) and of vanadium (r = 0.63). On the contrary, the correlation between uranium and organic carbon is next to nothing, with a coefficient (r) equal to 0.03.

In the carbonate environment (26), only one anomaly in uranium was detected, and that in the oxidised medium (p4) of the sediments from the Berwine, at a place so-called "La Folie", in a locality close to outcropping uraniferous mineralisations. As in the case of the silicate environment, uranium shows a significant positive correlation with iron (r = 0.36), with copper (r = 0.30) and with vanadium (r = 0.40) and next to no correlation with organic carbon (r = 0.03) and carbonate (r = 0.07).

If the results of the methodological study in the carbonate environment show the same trends as those for the silicate environment, they are less conclusive considering that only one anomaly was detected in the oxidised medium (p4) related to a known uranium indication. We decided to use the same sampling method (p4) as in the silicate environment on the basis of two supplementary arguments.

Firstly, according to E.M. CAMERON *et al.* (27), the alluvium sampled from the active stream bed does not fix uranium which is largely mobilised as soluble di- or tri-carbonate ionic complexes. The theoretical foundation for this lies in thermodynamic considerations (Eh, pH, ionic activity) put forward long ago by R.M. GARRELS (28) and more recently by D. LANGMUIR (29). Also, the dominantly carbonate region which represents about one half of the surface prospected, is highly urbanised and industrialised (Liège, Verviers, Charleroi...)

and alluvium from the active stream bed is most prone to contamination. Let us cite the example of the massive of Visé which was retained as a test zone for methodological studies on sampling in carbonate environments. V. DEGROOTE (26) remarked that samples collected from the active beds of the Bolland and the Berwine were highly contaminated in carbonaceous matters, explained by the exploitation of the coal mine of Trembleur situated uphill from these two streams. Analysis of coal collected from the dumps gave a uranium value of 2 ppm. This represents the threshold value for uranium anomalies in the stream sediments (cf. II.5.2).

II. 4. 3. *Influence of organic matter, carbonates and iron on the fixation of uranium in the alluvia*

A statistical analysis of correlations was effected on a total of 844 samples. Four groups can be distinguished :

- U $>$ 2 ppm	pH $>$ 6	n = 157
- U $>$ 2 ppm	pH $\leqslant$ 6	n = 290
- U $<$ 2 ppm	pH $>$ 6	n = 188
- U $<$ 2 ppm	pH $\leqslant$ 6	n = 209

The value of 2 ppm which represents the threshold for uranium (see above) separates two populations : anomalous samples (n = 447) with respect to the total number of samples collected (n = 10205), and samples with low values, representative of the background. Samples with pH $>$ 6 occur within the dominantly carbonate zone, while these with pH $\leqslant$ 6 fall within the dominantly silicate zone. Results of the correlation analysis are shown in Table III. Since the frequency distributions of the values of the variables tend to be lognormal, the parametric correlation coefficients were calculated from the logarithmic values of the variables. Three groups of correlation coefficients concerning uranium can be distinguished :

- positive correlation with copper (r = 0.54), vanadium (r = 0.48) and iron (r = 0.47)

Table III : *Matrix of correlation coefficients*

$N = 844$

$t_{0.995} : \rho_0 = \pm 0.09$

Cu	0.54						
V	0.48	0.54					
Fe	0.47	0.48	0.65				
Mn	0.12	0.18	0.12	0.37			
C.O.	(-0.03)	(0.00)	(-0.06)	-0.22	-0.12		
CO_3^-	-0.17	(-0.04)	-0.09	(-0.02)	0.15	-0.12	
pH	-0.30	-0.13	-0.19	(-0.01)	0.40	-0.29	0.41
	U	Cu	V	Fe	Mn	C.O.	CO_3^-

C.O. : organic carbon

( ) : without signification, between -0.09 and 0.09.

- practically no correlation with organic carbon (r = - 0.03) and manganese (r = 0.12)
- negative correlation with carbonates (r = - 0.17) and pH (r = - 0.30).

These results confirm those obtained by P. CONREUR (25) in a silicate environment and by V. DEGROOTE in a carbonate environment.

Let us however emphasise the limits of the validity of correlation coefficients and their interpretation in terms of association and cause. The negative correlation between the values of uranium and those of pH and carbonate is well explained in terms of Eh and pH (28, 29). This poses the difficult problem of stream sediment prospection for uranium in oxidised and basic environments. It shows that in such media, hydrogeochemical prospection should be positive.

The absence of a significant relationship between uranium and organic carbon concentrations is a direct consequence of the method of sampling : most often from an oxidised medium. The negative correlation between iron essentially in the form of ferric oxides in the stream sediments, and organic carbon, must be noted. The highest positive correlations with coefficients r between 0.47 and 0.65 concern not only the couples uranium-iron, uranium-vanadium and uranium-copper, but also the couples iron-copper, iron-vanadium and vanadium-copper. One plausible explanation is that the amorphous iron oxides present, for example, in the acid brown soils and the stream sediments of the Ardenne have a high affinity for uranium, copper and vanadium with which they coprecipitate under the oxidising conditions. P. WARNANT *et al.* (31) bring out arguments in support of the fixation of copper by iron in acid brown soils and the stream sediments derived from them.

D. LANGMUIR (29) and A.W. ROSE (32) have shown the primordial role of iron oxides, particularly amorphous oxides in the fixation of uranium in sedimentary ores. The dispersion of uranium depends on the immobility of its tetravalent form and the high mobility of the hexavalent uranyl ion or its complexes (29). However, in oxidised media, the mobility of uranium is impeded by the fixing action of iron oxides, particularly the amorphous forms.

However, the significant positive correlation between the contents of uranium and iron could be, also explained by the mechanical dispersion of crystalline iron oxydes. Indeed, in oxidised environments, limonitic materials are often associated with the uranium mineralisation (see, for example p. 187, the case of Daverdisse).

Cartography of the alluvial anomalies (cf. II.5) shows the validity of the method of sampling employed. In fact, the uranium mineralisations in the black schists of the massive of Stavelot come out clearly as uranium anomalies in the stream sediments. The anomalies in the Gedinnian and Siegenian can be explained by a level of black schists occurrences. The group of anomalies in the Entre-Sambre-et-Meuse can be explained by uranium mineralisations similar to those that occur in the massive of Visé and which are located in the calcareous rocks of the Carboniferous.

II. 4. 4. *Conclusions*

The methodological study of the sampling carried out within the massive of Visé and along the southern margin of the massive of Stavelot has shown that given the particular characteristics (geomorphological, environmental...) the same type of sampling could be applied, from banks and in an oxidised medium, as in the case of normal metal prospection - provided a density of about one sample per km^2 is used. It is evident that in a peaty environment, such as in Scandinavia, prospection of the organic matter must be given preference.

The results of the correlation analysis on 844 samples show that organic matter does not influence the fixation of uranium in the samples collected. The same goes for carbonates which in addition show an opposition towards uranium.

On the other hand, in the absence of organic matter, iron oxides could constitute a prospection guide for uranium in the soils and stream sediments in oxidised media.

In such a case, uranium, in the uranyl form (UO_2^{+2}) would have the same destiny as metals such as zinc (Zn^{+2}) for which it has been shown (33) that the selection of iron oxides could ameliorate the prospection.

However, this association of uranium with iron oxides in the samples prospected has to be confirmed by further investigations

II. 5. PRESENTATION OF RESULTS

II. 5. 1. *Introduction*

The data for 10 205 sampling points (coordinates X, Y ; values of U, Cu, V, Fe, Mn) have been channelled to the Geological Survey of Belgium where they constitute the file "ALLUVIONS" (cf. I.4.5.)

Owing to the large number of samples, it was not possible to present in this paper detailed maps showing the sampling points together with the values of the five geochemical parameters (it would involve 50 maps at a scale of 1:100 000 ...).

In the final report submitted to the EEC, in January 1982, microfiles were attached on which the entire file "ALLUVIONS" was recorded. These microfiles are avalaible for consultation at the Geological Survey of Belgium.

In the latter report, were also enclosed 10 maps at 1:100 000 presenting the zones in which the values of uranium exceeded a threshold fixed at 1.5 ppm as well as 4 maps at 1:300 000 giving the distribution of Cu, V, Fe and Mn. All these maps may be consulted at the Geological Survey of Belgium. Reduced maps giving the anomalous areas for U, Cu, V, Fe, and Mn are shown in this publication (maps II to VI).

II. 5. 2. *Description statistics and choice of anomaly thresholds*

Figures 7 to 11 represent the histograms of frequency of the elements analysed (logarithms of the values of U, Cu, V, Fe and Mn) for the entire area prospected (10 205 samples).

The form of these diagrams illustrates once more the lognormal tendencies of the geochemical distributions. Only copper appears to show a more heterogenous distribution.

The descriptive parameters of these distributions (mean $\bar{x}_L$, standard deviation S_L) figure in the inset for each histogram.

$\bar{x}_L$ = arithmetic mean of the logarithms.

$\bar{x}_G$ = antilog $\bar{x}_L$ = geometric mean.

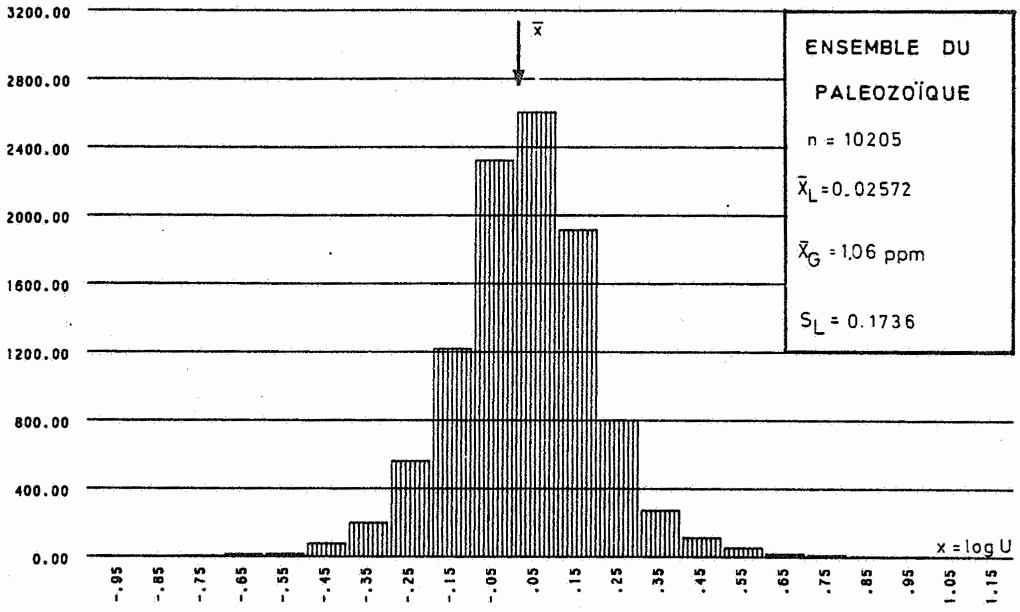


FIG 7 : LOG URANIUM (ppm)

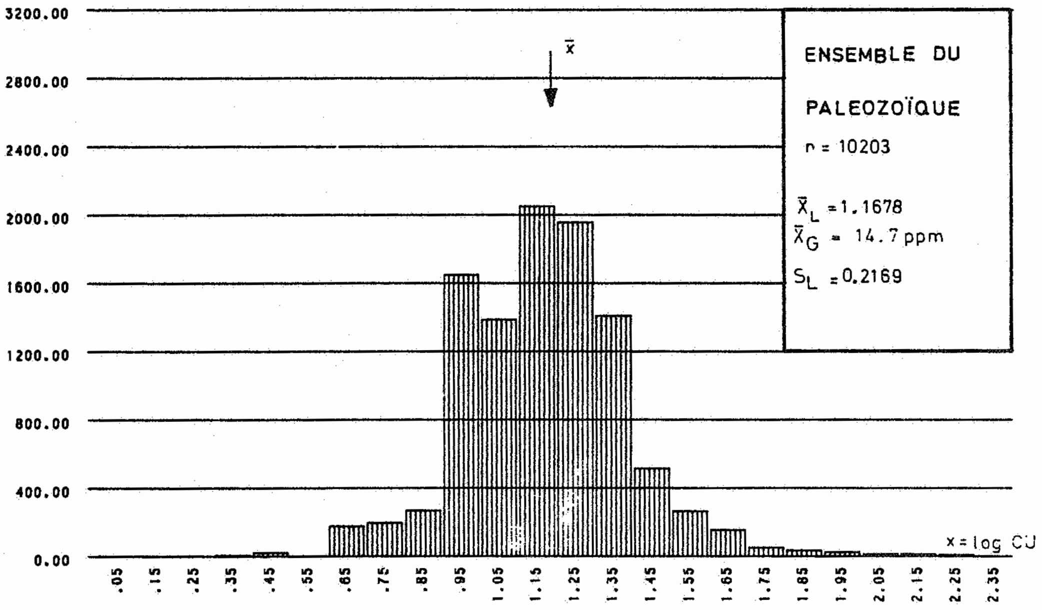


FIG 8 : LOG CUIVRE (ppm)

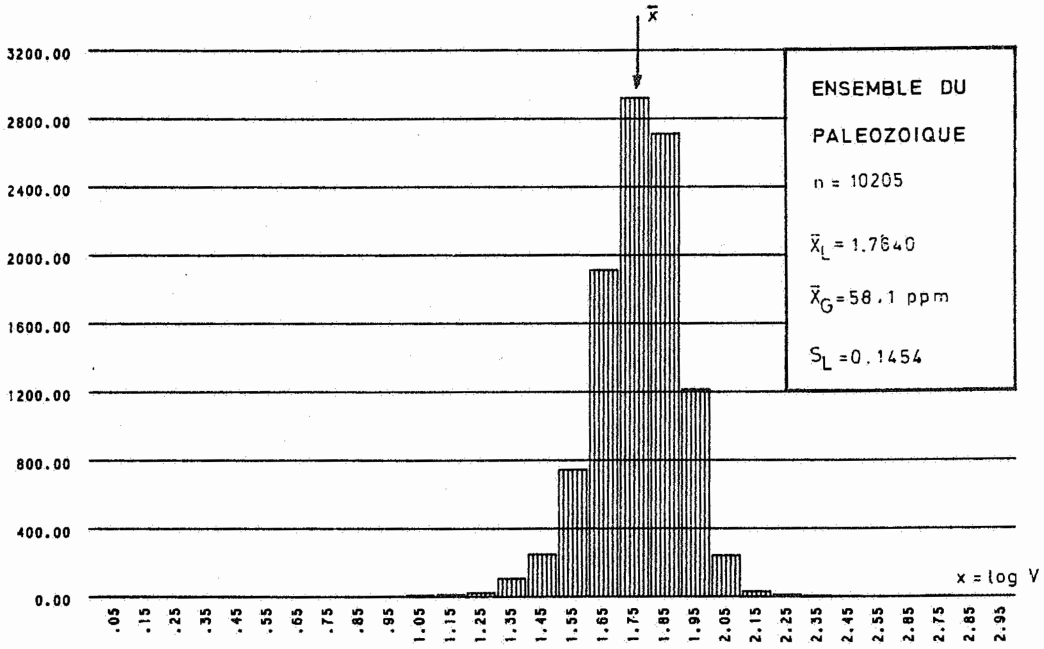


FIG 9 : LOG VANADIUM (ppm)

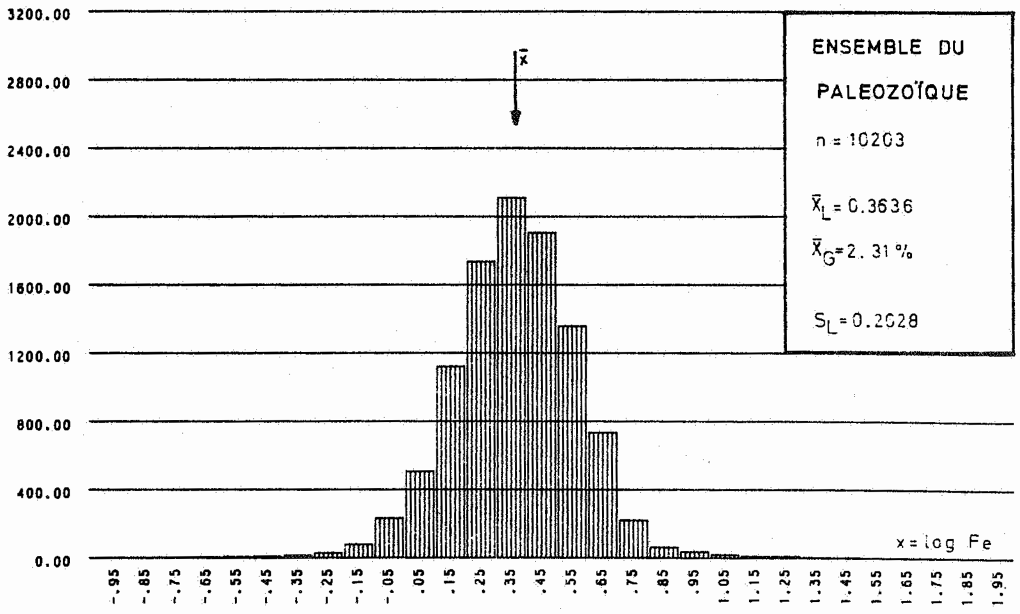


FIG 10 : LOG FER (%)

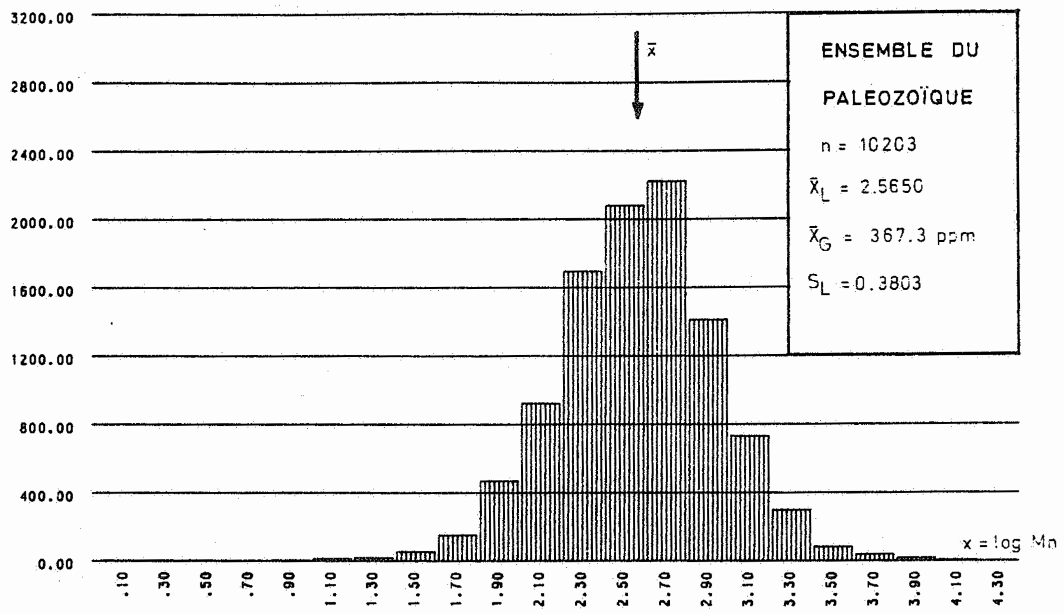


FIG 11 : LOG MANGANESE (ppm)

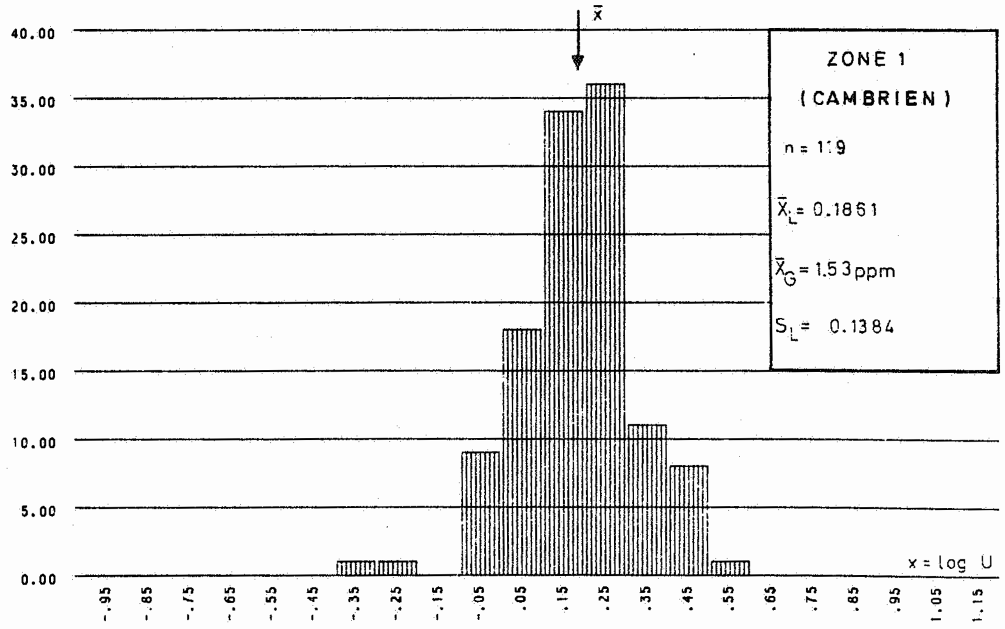


FIG 12 : LOG URANIUM (ppm)

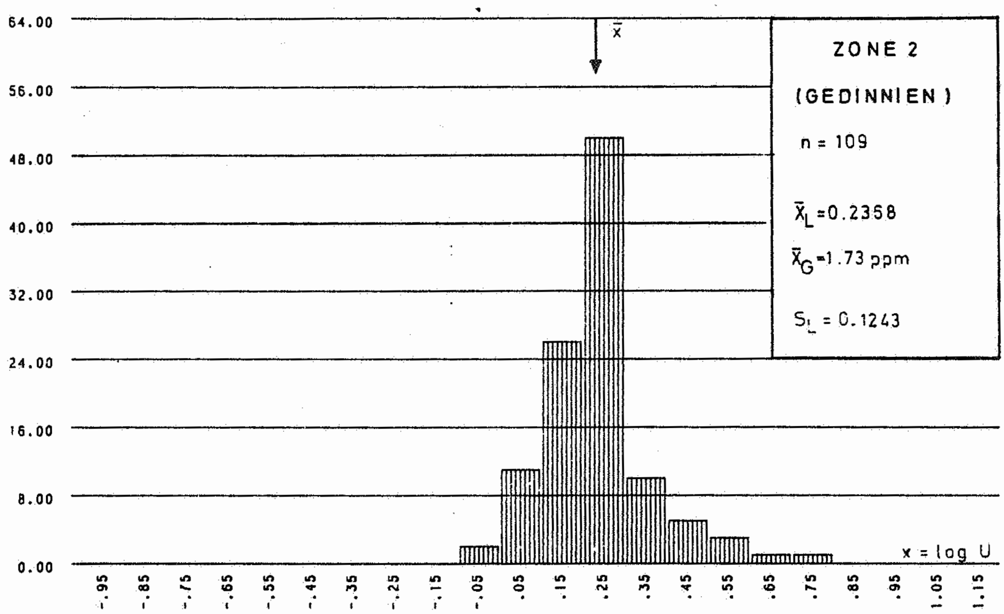


FIG 13 : LOG URANIUM (ppm)

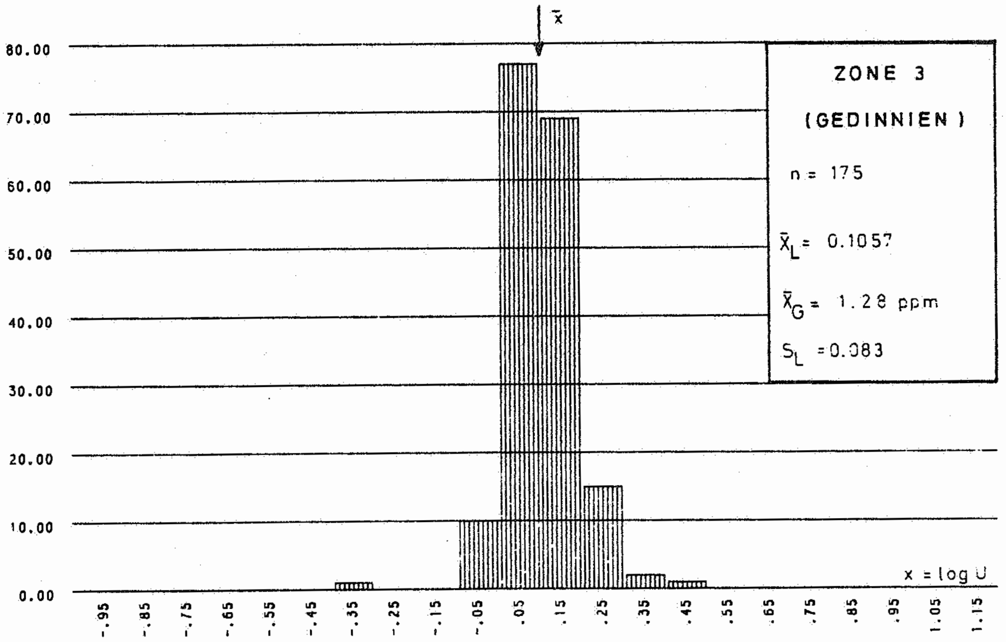


FIG 14 : LOG URANIUM (ppm)

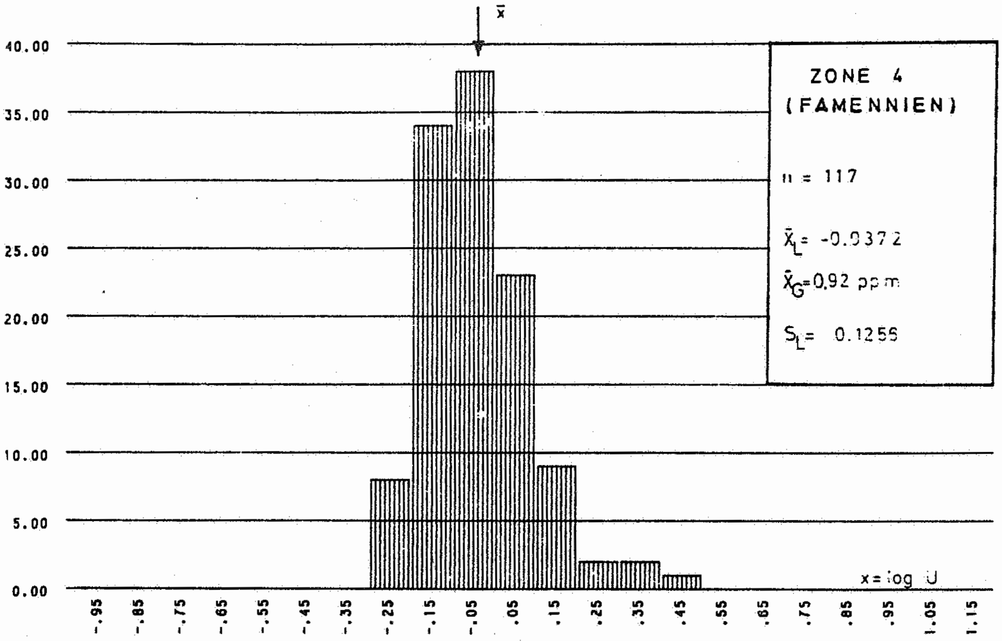


FIG 15 : LOG URANIUM (ppm)

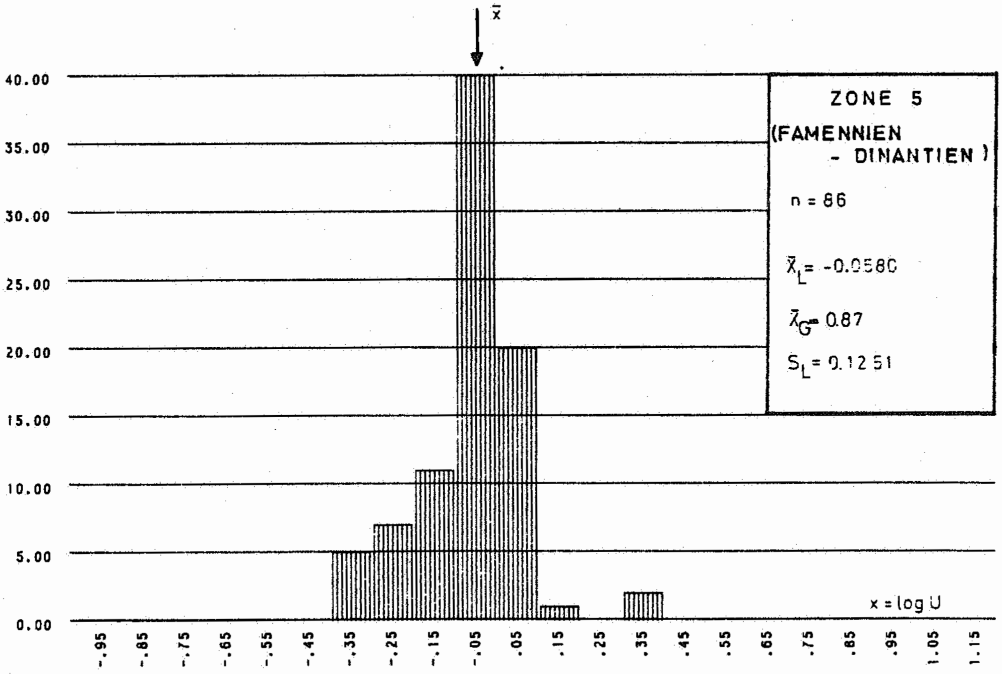


FIG 16 : LOG URANIUM (ppm)

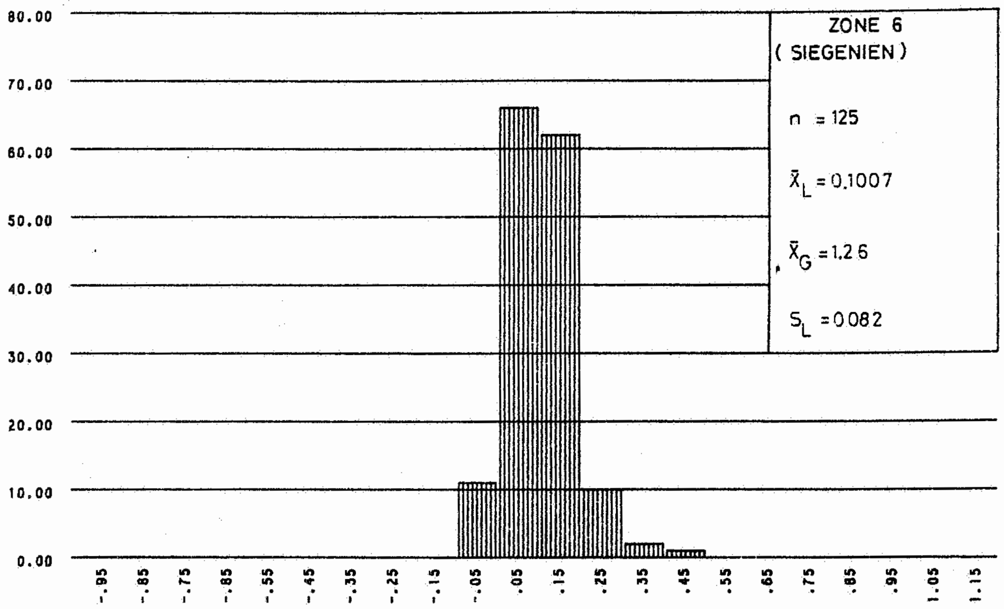


FIG 17 : LOG URANIUM (ppm)

a) Uranium

It will be noted that the mean value for the sediments is rather low : 1.06 ppm (x_G).

This value is of course obtained for the totality of the surface prospected, with all its different geological formations. The complexity of the Belgian Paleozoic makes it difficult to distinguish, in the stream sediments, sub-populations as a function of the geological substratum. Such an operation is only possible in zones of small surface areas, with a limited number of samples and thus statistically less significant.

In order to give an idea of the variability of the mean values of uranium, a small number of sub-zones with homogeneous geological substrata have been chosen and histograms of frequency calculated for the corresponding populations :

Zone 1 - Cambrian of the massive of Stavelot.

Surface area : 150 km^2
n = 119 samples

X = 255 to 265
Y = 115 to 130

Zone 2 - Gedinnian of the region of Gedinne.

Surface area : 150 km^2
n = 109 samples

X = 190 to 205
Y = 60 to 70

Zone 3 - Gedinnian of the region of Libin.

Surface area : 150 km^2
n = 175 samples

X = 205 to 220
Y = 70 to 80

Zone 4 - Famennian of the region of Beauraing.

Surface area : 140 km^2
n = 117 samples

X = 185 to 205
Y = 93 to 100

Zone 5 - Region of Ciney (Condroz).

Alternance of Famennian sandstones and Dinantian calcareous rocks.

Surface area : 150 km^2

n = 86 samples

X = 200 to 210

Y = 110 to 125

Zone 6 - Siegenian of the region of Bastogne-Houffalize.

Surface area : 200 km^2

n = 152 samples

X = 240 to 250

Y = 75 to 95

On examination of the histograms (fig. 12 to 17) and the statistical parameters, it can be seen that while remaining close to 1 ppm, the mean values of uranium ($\bar{x}_G$) vary significantly with the geological context. They occur in the range between 0.87 ppm (*zone 5*) and 1.73 ppm (*zone 2*). As a first interpretation, this variation in the mean values of uranium ($\bar{x}_G$) according to the six zones can be related to their more or less schistose character.

If the anomalous threshold (t) is defined by a formula of the type

$$t = \text{antilog } (\bar{x}_L + nS_L)$$

this value will depend as a first approximation on the variations of $\bar{x}_L$.

On fixing n = 2 in the above formula, thresholds comprised between 1.56 ppm and 3.06 ppm are obtained depending on the zone.

For the total population (10 205 samples), the application of the same formula gives a threshold value of 2.36 ppm.

The choice of a threshold of anomaly comprised between 1.5 ppm and 2 ppm thus appears to be reasonable.

In order to reduce the loss of information in areas of low geochemical background, the minimal value of 1.5 ppm was chosen to trace the curves of iso-values delimiting the anomalous zones on the detailed maps at 1:100 000 (EEC report).

For the summary map here enclosed (map II), on the other hand, a threshold of 2 ppm was adopted in order to bring out more clearly the regional distribution of the anomalies.

If the threshold is fixed at 2 ppm, the percentage of anomalous values in uranium becomes 4.4 % (475 samples of 10 205).

With the threshold at 3 ppm, this percentage falls down to 1.1 % (117 samples).

b) The other elements : Cu, V, Fe and Mn

Figures 8 to 11 give the histograms for the values of Cu, V, Fe and Mn in the entire region prospected (10 205 samples).

From the descriptive parameters of these distributions ($\bar{x}_L$ and S_L), the anomalous thresholds can be defined (table IV).

Table IV

Element	Geometric Mean ($\bar{x}_G$)	Threshold (t) n = 2	Threshold (t) n = 3
Copper	14.72 ppm	40 ppm	66 ppm
Vanadium	58.08 ppm	113 ppm	158 ppm
Iron	2.31 %	5.9 %	9.4 %
Manganese	367.00 ppm	2116 ppm	5080 ppm

These figures have been taken into account for the caracterisation of particular zones, which are the areas where the values of Cu, V, Fe or Mn exceed a threshold comprised between $\bar{x}_G$ and t (n = 2). These zones have been indicated on the maps III to VI.

The points with values greater than t (n = 2) are represented on the maps by appropriate symbols.

II. 5. 2. *Inventory of the anomalous zones*

The summary map for uranium (map II) shows the geographical repartition of the anomalous zones defined by a threshold of 2 ppm.

This document clearly brings out several large constellations of anomalous zones which obviously correspond to regional geological traits :

1°) the massive of Stavelot

2°) the anticlinal zone of the Ardennes (Paliseul-Libramont axis)

3°) the southern border of the Ardenne (Herbeumont-Habay la Neuve axis)

4°) the synclinorium of Dinant to the north of the Philippeville-Dinant axis.

To this list can be added some anomalies in the Lower Devonian south of the Entre-Sambre-et-Meuse (prolongation of the 2^{d} anomalous zone) and in the synclinorium of Herve-Vesdre.

Let us now examine the four main regions successively.

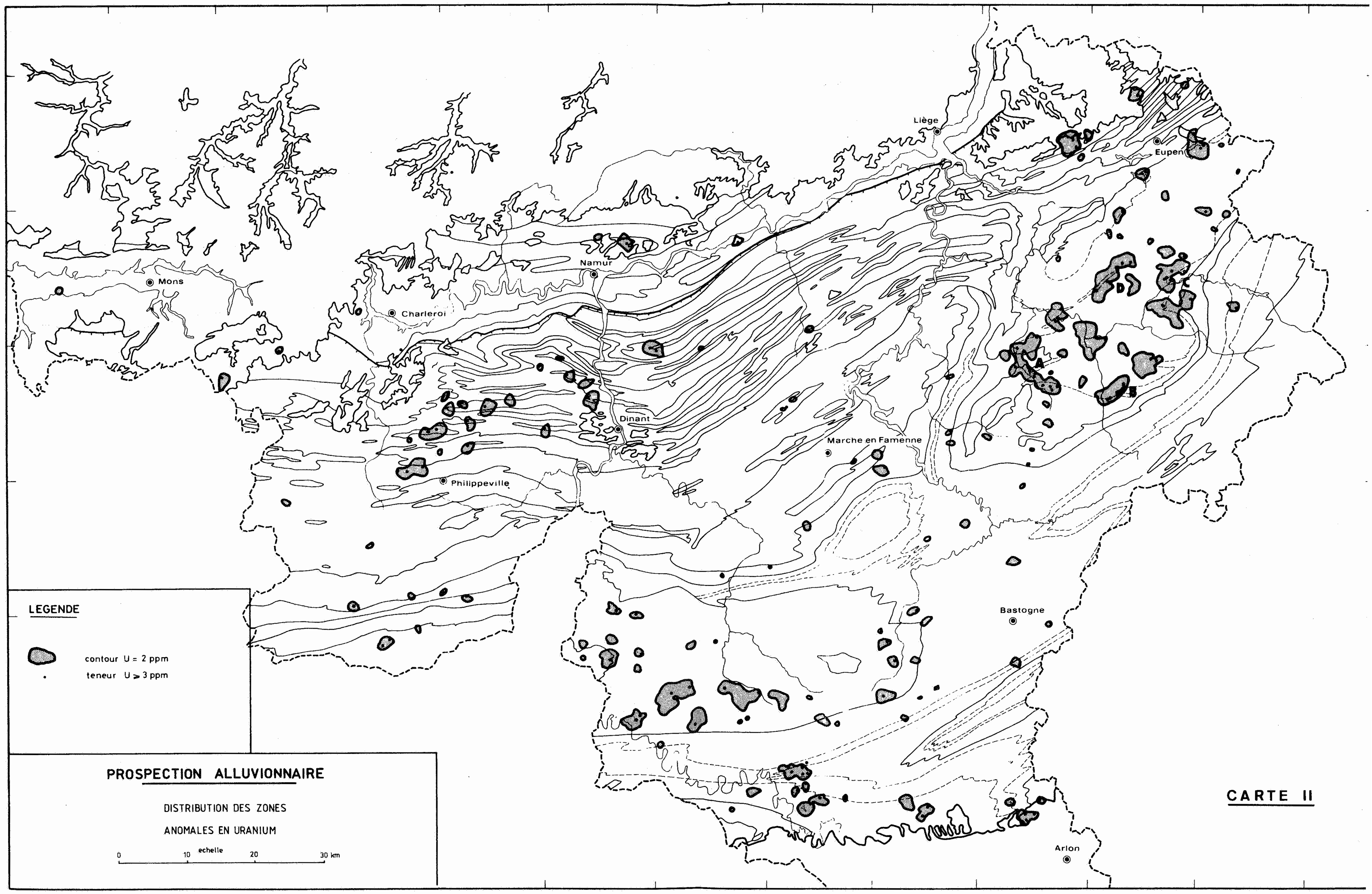
1°) The massive of Stavelot

Considering all the samples collected from the rectangle delimited by X = 242 to 274, Y = 108 to 138, which contains a large portion of the massive of Stavelot, the following statistical elements are obtained :

total number of points :	835
values greater than 2 ppm :	143
values greater than 3 ppm :	36

Thus some 17% of the samples could be considered anomalous on the terms previously defined (threshold at 2 ppm). It is evident that within a geological context characterised by a geochemical background richer in uranium, the real threshold must be higher than that

CARTE II



PROSPECTION ALLUVIONNAIRE

DISTRIBUTION DES ZONES

ANOMALES EN URANIUM

LEGENDE

▨	contour U = 2 ppm
•	teneur U ≥ 3 ppm

obtained for the total area prospected. From the histogram data for zone ŀ (Cambrian of the massive of Stavelot, fig. 12) the anomalous threshold t (n = 2) can be estimated at 2.9 ppm. For the Cambrian therefore, a threshold value in the order of 3 ppm is more acceptable than 2 ppm. The proportion of anomalous samples within the rectangle defined above would then be 4.3 % and not 17 %.

On map II, the distribution of sampling points with values greater than 3 ppm show clearly a concentration along the periphery of the massive of Stavelot. The points often seem to be situated over the Revinian-Salmian limit. A more detailed examination of these anomalies (cf. map SPA at 1:100 000 in the EEC report shows that these points gather into several constellations around the massive of Stavelot :

- *constellation A* : valley of the Lienne as far as its confluence with the Amblève.

There are 31 samples with values above 2 ppm of which 10 are greater than 3 ppm. The majority of the samples were found on the tributaries from the right bank of the Lienne. The source of the uranium can thus be attributed to the Revinian and not to the Salmian.

- *constellation B* : the Vielsalm-Recht axis east of the Salm.

The alluvia come from the Upper Revinian.

25 values greater than 2 ppm
9 values greater than 3 ppm.

This is the level referenced by R. LEGRAND within the Revinian.

- *constellation C* : around Malmedy.

A concentration of points can be observed at the south of Malmedy, and another around Mont and Xhoffrais (right bank of the Warche).

30 values greater than 2 ppm
10 values greater than 3 ppm.

The cloud of points occur right above the Revinian-Salmian limit but from the logic of drainage basins, it is probable that the origin is Revinian.

- *Constellation D* : within the Revinian, between Francorchamps and Hockai.

29 values greater than 2 ppm
5 values greater than 3 ppm.

2°) The anticlinal zone of the Ardenne

A vast, west-east aligned anomalous zone can be observed, which extends from the french border at the massive of Rocroi (which it surrounds and encloses) to the plateau of Recogne-Libramont and the upper course of the western Ourthe.

This zone contains about sixty samples with values greater than 2 ppm, of which 15 have values above 3 ppm.

From a geological point of view, the greater part of these samples come from the Gedinnian. A small contribution from the Cambrian is certain in the massive of Rocroi and probable in the massive of Serpont.

With an anomalous threshold of 2 ppm for the points, the summary map here enclosed (map II) clearly brings out two groups :

a) a main concentration of points, aligned east-west and centered around the Nafraiture-Paliseul-Recogne axis (± 40 values greater than 2 ppm);

b) a less important concentration of points in the upper basin of the western Ourthe, east of the massive of Serpont (20 samples with values greater than 2 ppm).

3°) The southern slope of the Ardenne

This does not form a continuous anomalous zone but consists of some groups of localised points of unequal sizes; they have the common characteristic of belonging to a region almost entirely occupied by stages of the Siegenian.

From west to east can be distinguished :

a) a well marked anomaly east of the Semois, near the village of Herbeumont. It contains 37 points with values above 2 ppm, of which 11 are above 3 ppm. These points are all situated in a forest zone of less than 100 km^2 (forest of Herbeumont and woods of Poursumont).

The source of this anomaly is to be sought in the Siegenian. It must be noted that the concentration in the woods of Poursumont is localised, according to the map of Asselberghs, on the western termination of the slaty phyllites of Neufchâteau.

b) a concentration of nine values over 2 ppm appears in the same region on the other side of the Semois (forests of Muno and Bouillon). In this sector, the geological substratum is formed by the Cambrian and the Gedinnian (eastern extremity of the massive of Givonne).

This anomalous zone is clearly less intense than the previous one.

c) an anomaly of nine points with values greater than 2 ppm is situated in the forest of Rulles, to the south of the village of Mellier. The geological substratum is of the Lower Siegenian ("Quartzphyllites of Anlier").

d) near the village of Nobressart, at the limit of the Ardenne and of Gaume, a group of eight points of which three have values above 3 ppm, is worthy of notice. However, since some of these points were sampled in the valley of the Attert (Triassic) the Devonian origin is not certain.

4°) The anomalies of the synclinorium of Dinant

A certain number of anomalies occur in the Entre-Sambre-et-Meuse, within the western prolongation of the Dinantian calcareous rocks of Condroz.

These concentrations systematically occur either in the proximity of a synclinal core of the Namurian enclosed within Visean calcareous rocks, or straight above an area occupied by the Dinantian calcareous rocks alone.

Although these anomalies seem to have generally limited extensions, together, they constitute an anomalous zone comparable in importance (considering the number of points) to that of the region of Gedinne-Paliseul. In fact, within the rectangle delimited by X = 154 to 198, Y = 98 to 120, there are 44 values greater than 2 ppm, 22 of which are above 3 ppm.

From a geological point of view, without ignoring, a priori, a contribution from the Famennian sandstones to some of the anomalies, it is likely that they can be attributed to phenomena comparable to those observed in the massive of Visé : paleokarsts, concentration of phosphatic debris within calcareous rocks, and eventually, uraniferous schists at the base of the Namurian.

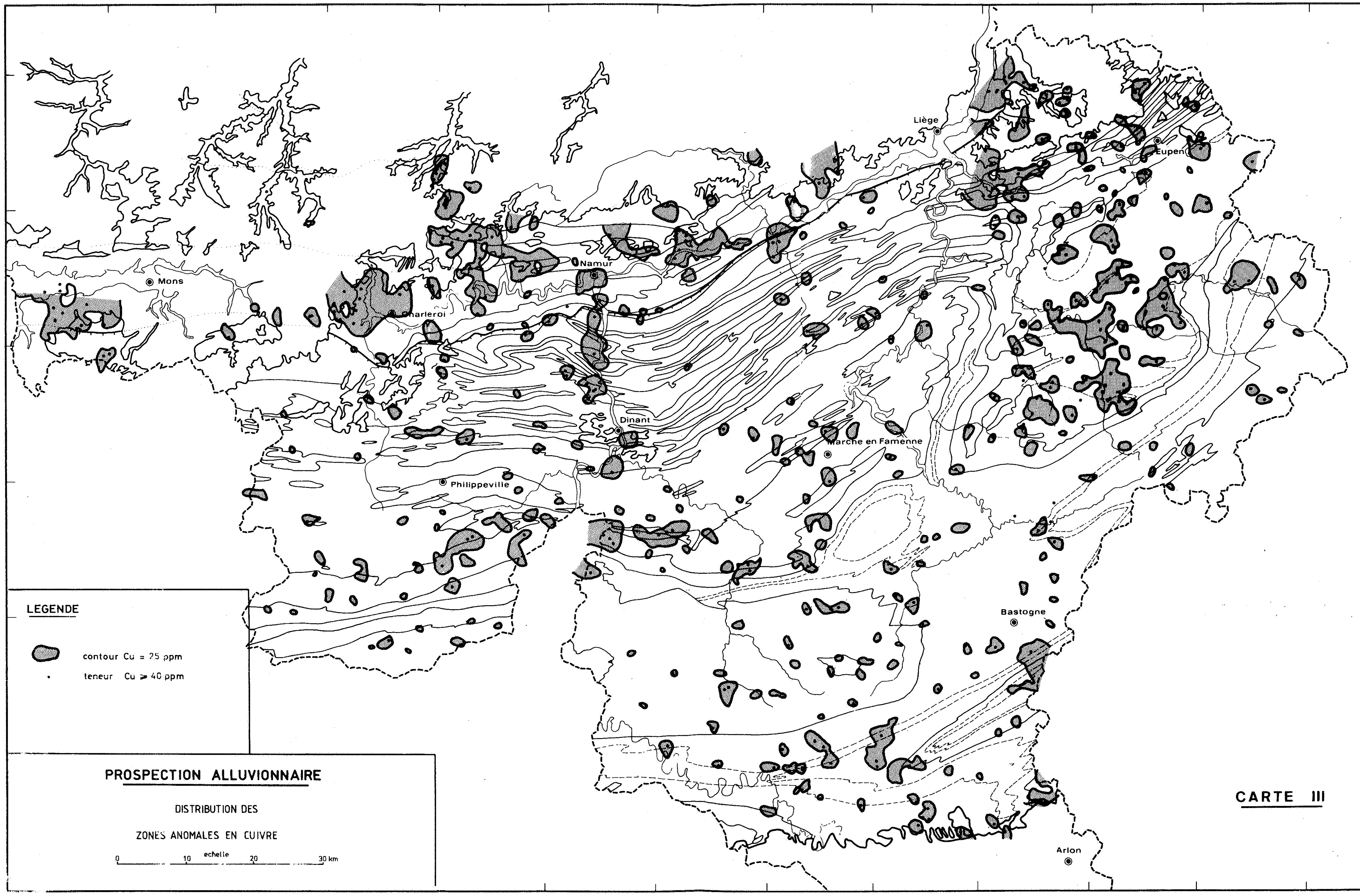
Without going into a detailed description of each anomaly, we shall at this stage merely enumerate the localities close to which they were observed :

- Walcourt
- Fraire
- Morialme
- Florennes
- Oret
- Bioul
- Warnant (Haut-le-Wastia)
- Courrière.

II. 5. 3. *The distributions of Cu, V, Fe and Mn and their eventual correspondence with the anomalies in uranium*

In § II.4, the existence of positive correlations between uranium and the three elements Cu, V and Fe was clearly demonstrated. On the contrary, the correlation between uranium and manganese seemed to be negligible.

These trends can be confirmed by comparison of the maps showing the distribution of the anomalous zones for the different elements.



CARTE III

PROSPECTION ALLUVIONNAIRE

DISTRIBUTION DES

ZONES ANOMALES EN CUIVRE

When superposing the summary maps at 1:300 000 for Cu, V, Fe and Mn on that of uranium, the following observations can be made :

1°) Uranium-copper relationship

The anomalies of copper often coincide with those of uranium in the massive of Stavelot and the synclinorium of Herve-Vesdre. A similar trend, although less marked, can be observed in the Siegenian at the southern border of the Ardenne. Within the Gedinnian of the anticlinal zone of the Ardenne, on the contrary, the geochemical background for copper is very low and nothing appears on the map.

There are some coincident points in the synclinorium of Dinant although no general trend is apparent.

Elsewhere, the distribution of copper anomalies has no apparent relationship with the uranium anomalies.

2°) Vanadium-uranium relationship

The tendency for the superposition of uranium and vanadium anomalies is general in the massive of Stavelot, the synclinorium of Herve-Vesdre and the synclinorium of Dinant. It is partial along the southern border of the Ardenne and inexistant in the anticlinal zone of Paliseul where the geochemical background of vanadium is low. On the contrary, the Meso- and Neo-Devonian terrains at the southern edge of the synclinorium of Dinant show a marked enrichment in vanadium. There are no uranium anomalies in this zone.

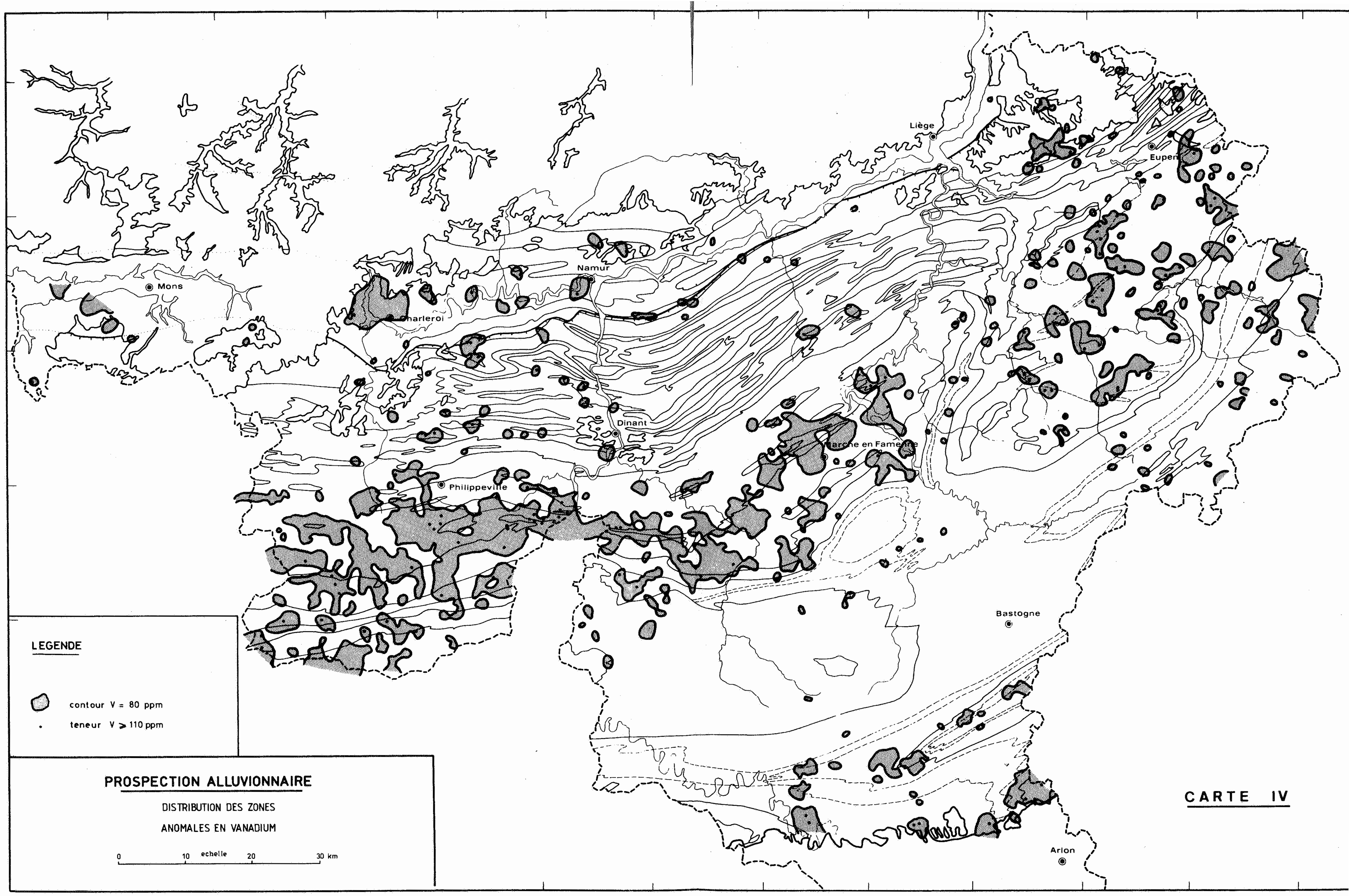
3°) Iron-uranium relationship

There are numerous anomaly superpositions in the massive of Stavelot, the synclinorium of Herve-Vesdre, the synclinorium of Dinant and the meridional border of the Ardenne.

In the synclinorium of Dinant, west of the Meuse, the form of the anomalies of iron perfectly fits the contours of the uraniferous zones.

Once more, the axial zone of the Ardenne is an exception : the uranium anomalies do not coincide with high values of iron.

On the whole, it must be noted that the general distribution of iron is different from that of uranium. For example, the Meso-



CARTE IV

PROSPECTION ALLUVIONNAIRE

DISTRIBUTION DES ZONES
ANOMALES EN VANADIUM

and Neo-Devonian band at the southern border of the synclinorium of Dinant contains a large number of zones anomalous in iron, but completely devoid of uranium anomalies.

4°) Uranium-manganese relationship

In most of the regions, there is no tendency for the superposition of manganese and uranium anomalies.

However, some coincident zones can be observed in the synclinorium of Dinant and along the meridional edge of the Ardenne (forest of Herbeumont).

Conclusions

The precedent observations appear to confirm the conclusions derived from the methodological studies. There is some degree of association of uranium with Cu, V and Fe but not with Mn. The role of iron in the fixation of U, Cu and V is very probable although it is true that this role is only evident in zones where these elements occur in sufficient amounts. It follows, therefore, that the anomalies of iron do not necessarily correspond with those of uranium.

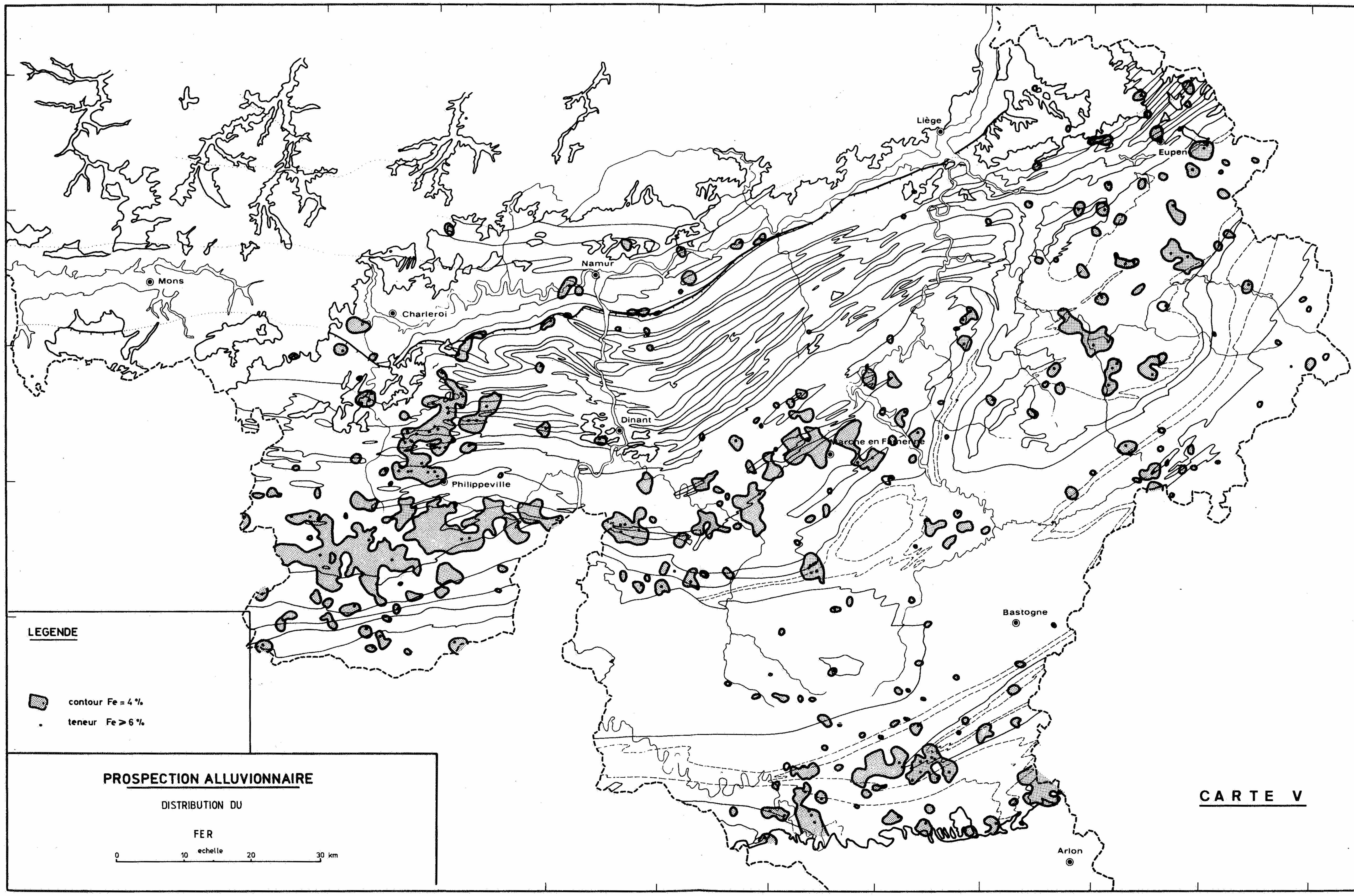
II. 5. 3. *Provisional evaluation*

From a methodological point of view, it seems that the results obtained confirm the validity of the method of sampling adopted (cf. II.4.3) and the analytical procedure designed by the Geochemistry laboratory of U.C.L. It will be noted, in particular, that even in a carbonate environment, anomalies come out clearly.

The mean values of uranium are low (± 1 ppm) and most of the samples considered to be anomalous contain values between 2 and 5 ppm.

The anomalies separate into three main groups characterised by specific geological contexts.

The first two groups (massive of Stavelot, synclinorium of Dinant) correspond likely to anomalies recognised in the past but whose extensions had not been determined.



CARTE V

LEGENDE

▨ contour Fe = 4 %

. teneur Fe > 6 %

PROSPECTION ALLUVIONNAIRE

DISTRIBUTION DU

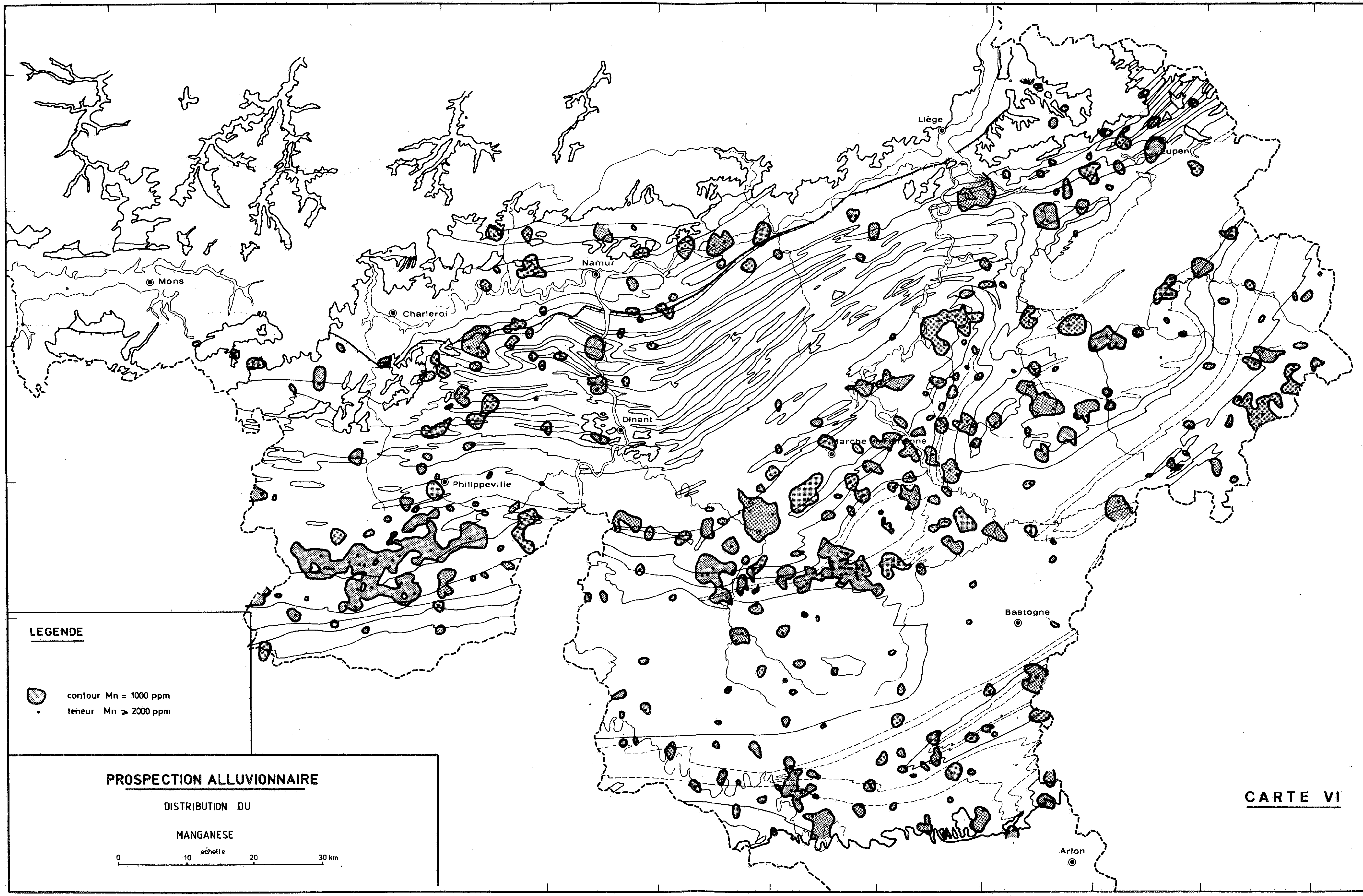
FER

A new feature that appears in this prospection is the existence of large anomalous zones within the Lower Devonian of the southern Ardenne.

The most interesting of these zones would be that of the region of Paliseul. Owing to its west-east alignment, it does not appear to be linked to any particular stratigraphic level, although it is rather confined within the Gedinnian.

Of all the anomalies encoutered, it is the only one which, at first sight, shows a small degree of association with the other elements determined including iron.

At this stage, it will equally be noted, without attempting to draw any conclusions of a genetical nature, that it coincides fairly well with the zone of mesozonal metamorphism of the anticlinal axis of the Ardenne.



LEGENDE

▨ contour Mn = 1000 ppm
• teneur Mn ≥ 2000 ppm

PROSPECTION ALLUVIONNAIRE

DISTRIBUTION DU

MANGANESE

CARTE VI

BIBLIOGRAPHY OF CHAPTER II

21) V. PRINCE and R.B. FERGUSON, 1980

Stream sediment geochemical surveys for uranium.

In R.H. Carpentier(Editor), Geochemical Exploration for Uranium.

Journ. Geochem. Explor., 13, 285-304.

22) R.G. GARRETT and J.J. LYNCH, 1976

A comparison of neutron versus fluorimetric analysis in large scale geochemical exploration for uranium.

Proc. Symp. IEAE, Vienne, pp. 321-334.

23) ASTM Method, D2707-70T

Microquantities of uranium in water by fluorimetry. Method B - Extraction Method.

Annual Book of ASTM Standards, 1973, pp. 633-636.

24) W.J. MAECK, J.L. BOOMAN, M.C. ELLIOT and J.E. REIN, 1958

Separation of uranium from diverse ions.

Analytical Chemistry, 30, pp. 1902-1907.

25) P. CONREUR, 1980

Géochimie de surface de l'uranium au bord sud du massif de Stavelot.

Mém. Licence, inédit, Faculté des Sciences, U.C.L., 66 p.

26) V. DEGROOTE, 1980

Géochimie d'alluvions appliquée à la prospection de l'uranium (massif de Visé).

Mém. Licence, inédit, Faculté des Sciences, U.C.L., 43 p.

27) E.M. CAMERON and E.H.W. HORNBROOCK, 1976

Current approaches to geochemical reconnaissance for uranium ore deposits.

In : Exploration for uranium ore deposits, IAEA, Vienne, pp. 241-266.

28) P.B. HOSTETLER and R.M. GARRELS, 1962

Transportation and precipitation of uranium and vanadium at low temperatures, with special references to sandstone-type uranium deposits.

Econ. Geol., 57, pp. 137-167.

29) D. LANGMUIR, 1978

Uranium solution mineral equilibria at low temperatures with applications to sedimentary ore deposits.

Geochem. et Cosmochem. Acta, 42, pp. 547-570.

30) B. CHAPMAN, 1976

Limitation of correlation and regression analysis in geochemical exploration.

Inst. Min. Metall. Trans. (London), sect. B, 85, pp. 279-282.

31) P. WARNANT, H. MARTIN and A.J. HERBILLON, 1980

Kinetics of the selective extraction of iron oxides in geochemical samples. Association between Fe and Cu in acid brownsoils.

8th Int. Geochem. Explor. Symp., Hannover, April 1980,
Journ. of Geochem. Exploration (in press).

32) A.W. ROSE and R.J. WRIGHT, 1980

Geochemical exploration models for uranium deposits. In R.H. Carpentier (Editor), Geochemical Exploration for Uranium.

Journ. of Geochem. Explor., 13, pp. 153-179.

33) BRGM : E. WILHELM and L. LAVILLE

U.C.L. : H. MARTIN, P. LECOMTE, F. SONDAG and P. WARNANT, 1981

Improvement of geochemical techniques by means of phase selection.

R&D Programme on Primary Raw Materials Contact Group, Geochemical Methods in Mineral Prospecting, Utrecht, April 1981.

CHAPTER III

HYDROGEOCHEMISTRY

III. 1. INTRODUCTION - GEOCHEMICAL LOGIC

The geochemical behaviour of uranium in a supergene environment (38, 44), in practical terms of hydrogeochemical prospection, is shown by its high mobility in solution as well as by a high contrast relative to the normal background (close to 1 ppb) in the event of a mineralisation.

When in solution in the river waters, uranium forms a stable and persistent dispersion halo over several kilometers, thus justifying a low sampling density. A sampling density of one sample per 5 to 50 km^2 is recommended by M. DALL'AGLIO (38) for a prospection on a regional scale; this same order of density is used in the NURE program (36, 46); finally, a density of one sample per 10-20 km^2 is recommended by L.V. BENSON and D.L. LEACH (34). The French Atomic Energy Commission (41) use, for strategic prospection, a higher density, in the order of one sample per 2 to 3 km^2.

Considering the complexity of the Belgian Paleozoic, and the necessary link with the stream sediment prospection, a fairly high sampling density was chosen :

1 sample per 5 to 10 km^2

This sampling includes, in addition to river waters, a certain number of springs with a density 3 to 4 times lower.

Thus, about 2300 water samples have been collected and analysed during the two years of this campaign (between the 1.12.78 and the 30.11.80), for which one bachelor's graduate in geology and two technicians were employed full time.

The sampling areas were first selected from 1:25 000 oro-hydrographic maps, taking into account the geology and the accessibility. The points thus chosen were then transferred to 1:25 000 topographic maps which were used for field locations. The choice of the sample points was in each case carefully studied and guided by several imperatives which are schematised in figure 18, consisting in

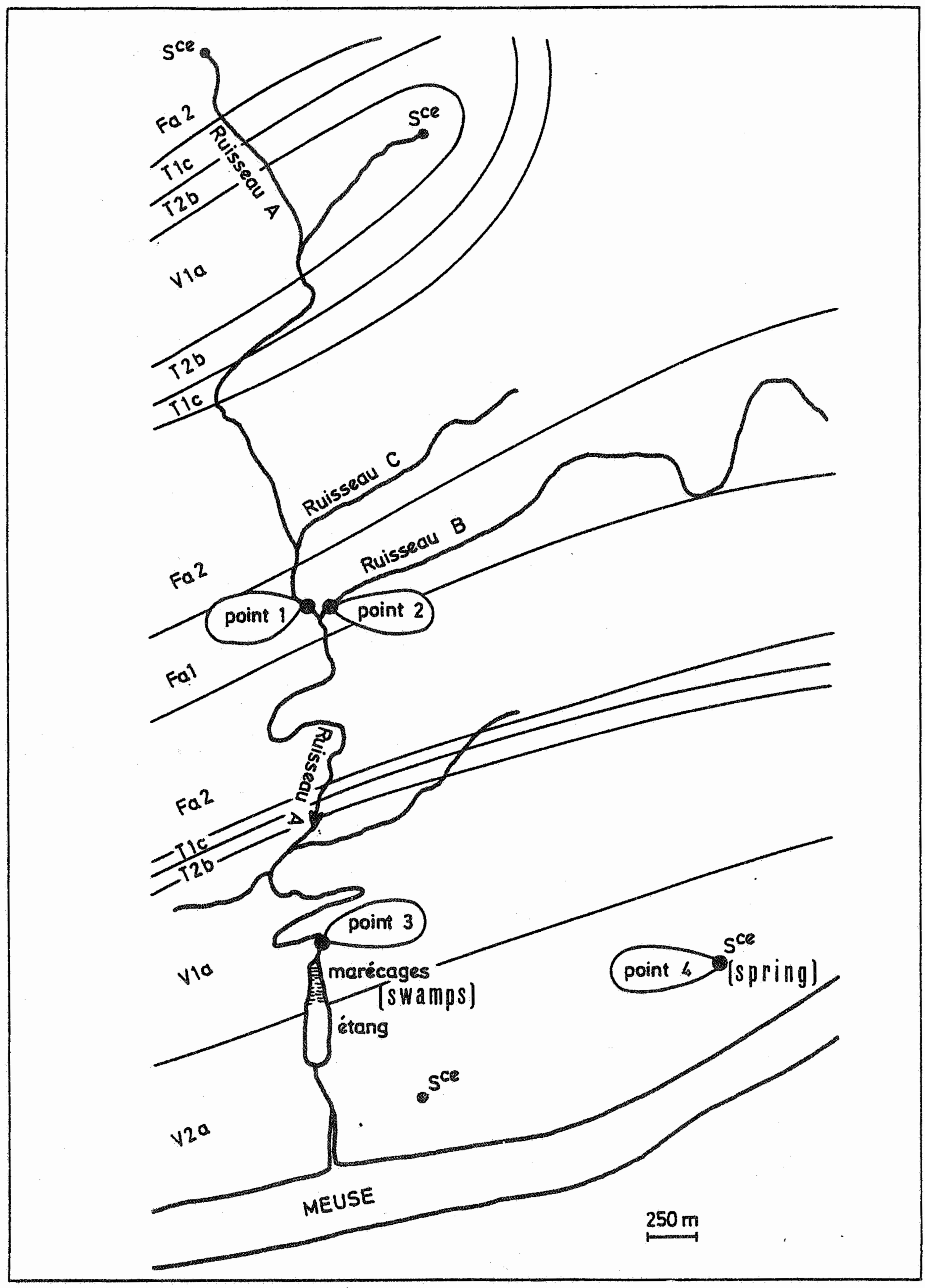


Figure 18: Choice of the sampling sites.

order of their importance of the following :

1. The geochemical logic

- swamps and zones of settling (lakes and pools) are carefully avoided, sampling being made just upstream;
- rivers prone to pollution (industries, towns) are generally eliminated or sampled upstream from the source of pollution;
- large rivers with widths exceeding about 10 meters (Lesse, Ourthe, etc...) are eliminated in favour of their tributaries.

2. The sampling density

This density was originally fixed at one sample per 5 to 10 km^2 as a function of that of the hydrographic network and of the complexity of the geology. Geologically complex regions such as those from maps 55, 56, 65 (valleys of the Ourthe, Amblève, Our and their tributaries) require a greater number of samples while regions situated to the south of Belgium, characterised by the importance of the lower Devonian, require less.

3. The geology

The choice of tributaries often depends on the geological nature of the grounds which they drain.

4. Efficacity

The selection of double sampling points (confluence-tributary), more rarely triple points, and points easily accessible by car, greatly increase the output.

III. 2. FIELD OPERATIONS

III. 2. 1. *Summary of the sequence of operations*

The sequence of operations effected during each sampling is succinctly described as follows :

1°) sampling in the river, stream or spring of about ten litres of water by means of a plastic pail;

2°) from the pail, taking away of two samples, the first destined for the analysis of uranium and the second constituting a reference sample and being used for analyses of major ions and fluorine;

3°) measurement of physico-chemical parameters : alkalinity, electrical conductivity, pH, temperature;

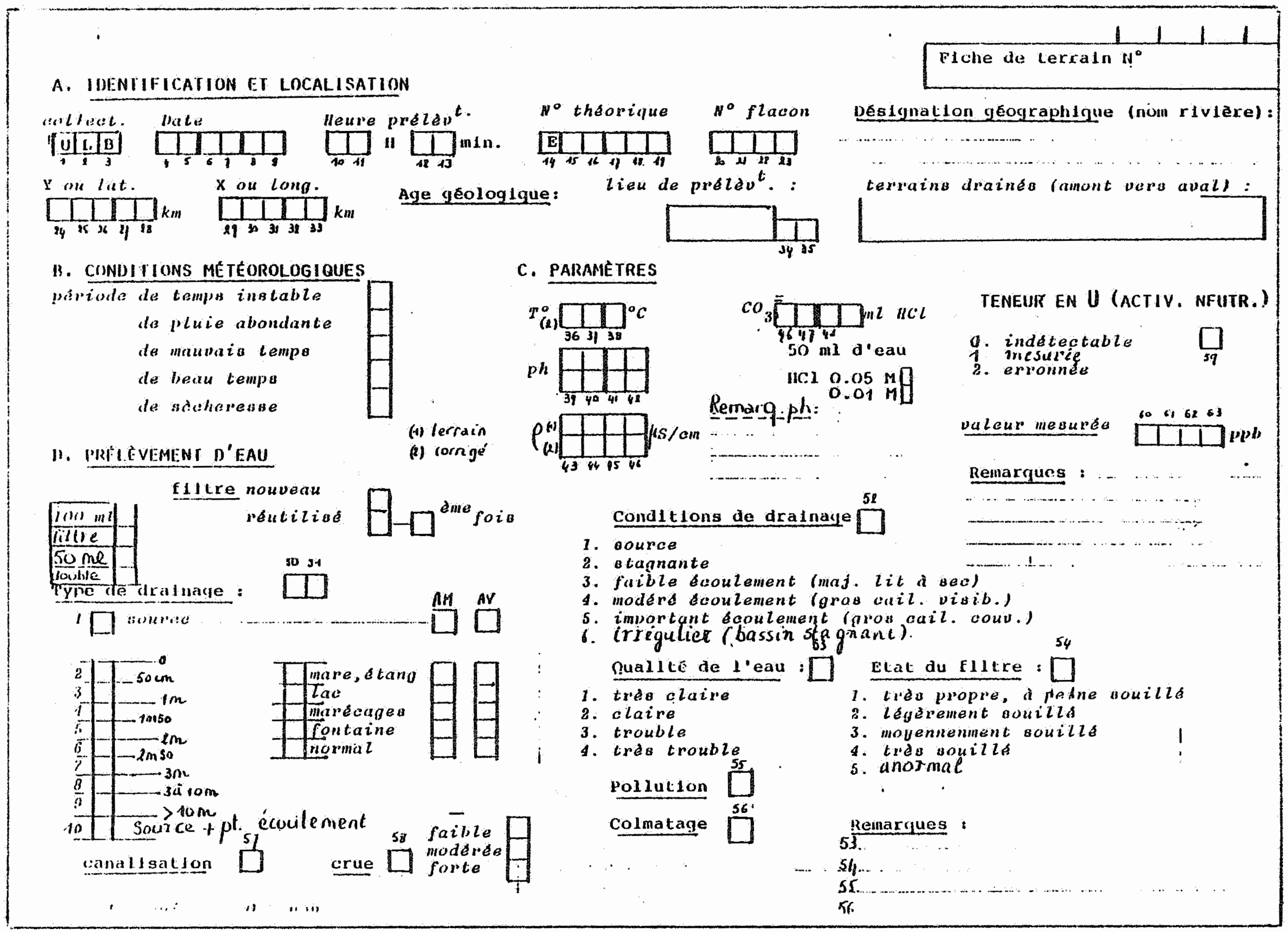
4°) description on a "field record card" of all the characteristics and measurements relating to the sampling point together with particular comments if need be.

Operations 2°, 3° and 4° are generally carried out by two persons and together take less than ten minutes.

With the sequence of operations known, a detailed description of each individual step will now be given in chronological order, with reference to the "field record card" (fig. 19). It is a very important document which constitutes the record file for each sample; these cards are numbered in the chronological order of the sampling in the field (n° 1 to 2415).

III. 2. 2. *Water sampling*

Water sampling is a delicate operation which must be given the greatest care. It influences the analytical results and the eventual interpretation which will be derived from them. On the whole, a sample must be homogeneous, representative and free from contamination. In the present case, and considering the very low concentrations



Fiche de terrain N° ☐☐☐☐

A. IDENTIFICATION ET LOCALISATION

collect. [U][L][B] 1 2 3

Date ☐☐☐☐☐☐ 4 5 6 7 8 9

Heure prélèv^t. ☐☐ H ☐☐ min. 10 11 12 13

N° théorique [E]☐☐☐☐☐ 14 15 16 17 18 19

N° flacon ☐☐☐☐ 20 21 22 23

Désignation géographique (nom rivière):

Y ou lat. ☐☐☐☐☐ km 24 25 26 27 28

X ou long. ☐☐☐☐☐ km 29 30 31 32 33

Age géologique:

lieu de prélèv^t. : ☐ ☐☐ 34 35

terrains drainés (amont vers aval) : ☐

B. CONDITIONS MÉTÉOROLOGIQUES

période de temps instable ☐

de pluie abondante ☐

de mauvais temps ☐

de beau temps ☐

de sécheresse ☐

C. PARAMÈTRES

$T^o_{(1)}$ ☐☐☐ °C 36 37 38

ph ☐☐☐☐ 39 40 41 42

$\rho^{(1)}_{(2)}$ ☐☐☐☐ µS/cm 43 44 45 46

(1) terrain
(2) corrigé

$CO_3^{=}$ ☐☐☐ ml HCl 46 47 48
50 ml d'eau
HCl 0.05 M ☐
0.01 M ☐

Remarq. ph:

TENEUR EN U (ACTIV. NEUTR.)

0. indétectable ☐ 59
1 mesurée
2. erronnée

valeur mesurée ☐☐☐☐ ppb 60 61 62 63

Remarques :

D. PRÉLÈVEMENT D'EAU

100 ml ☐
filtre ☐
50 ml ☐
double ☐

filtre nouveau ☐
réutilisé ☐ — ☐ ème fois

Type de drainage : ☐☐ 50 51

AM AV

1 ☐ source ☐ ☐

2 — 50 cm
3 — 1m
4 — 1m50
5 — 2m
6 — 2m50
7 — 3m
8 — 3 à 10m
9 — > 10m
10 — Source + pt. écoulement

mare, étang ☐ ☐
lac ☐ ☐
marécages ☐ ☐
fontaine ☐ ☐
normal ☐ ☐

canalisation ☐ 57

crue ☐ 58 faible ☐ modérée ☐ forte ☐

Conditions de drainage ☐ 52

1. source
2. stagnante
3. faible écoulement (maj. lit à sec)
4. modéré écoulement (gros cail. visib.)
5. important écoulement (gros cail. couv.)
6. irrégulier (bassin stagnant).

Qualité de l'eau : ☐ 53

1. très claire
2. claire
3. trouble
4. très trouble

Etat du filtre : ☐ 54

1. très propre, à peine souillé
2. légèrement souillé
3. moyennenment souillé
4. très souillé
5. anormal

Pollution ☐ 55

Colmatage ☐ 56

Remarques :
53.
54.
55.
56.

Fig. 19 : The field recording card for waters.

of uranium in waters (ppb levels), the following precautions were taken in order to avoid all contamination :

- use of inert plastic materials as containers;
- careful washing of material in the field (wrapping in film paper or in sealed plastic sacks);
- use of very pure acid for the acidification.

If opinion on the utility of filtration of water samples is still divided, recent work by K.J. WENRICH-VERBEEK (47) has shown it to be desirable and the Savannah River Laboratory always apply it as part of the NURE program (46). It was also decided to use membrane filtration on all of the samples.

On the field record cards, information relative to the sampling is entered in D ("WATER SAMPLING"), as well as in 54 ("STATE OF FILTER") and 56 ("CLOGGING").

a. <u>Sampling destined for analysis of uranium by neutron activation</u>

1. Sampling from the river of about ten litres of water by means of a plastic pail. The pail is first rinsed with the river water and the sampling carried out in such a way that it is representative of the flow and is not contaminated by the mud. This volume of water was considered sufficient not to influence the measurements and further samplings to which it will be subject in the minutes that follow.

2. Sampling and filtration of 30 mls of water through a 0.45 micron membrane of cellulose acetate (Sartorius SM 113) by means of a graduated syringe and a 47 mm Swinnex filter carrier.

3. The filtrate is directly poured into a special plastic flask (supplied by Harwell) fitted with a cork and a screw top.

4. The cork which covers the flasks is sealed by means of a blowlamp in the laboratory.

5. Conservation in the laboratory at normal temperatures and expedition in batches of 200 samples for analysis.

b. Sampling destined for analysis of uranium by fluorimetry

1. Removal of 50 ml of water from the pail and filtration under the same conditions as for neutron activation.
2. Direct transfer into plastic flasks, previously rinsed twice with the same water that had been removed and filtered.
3. Conservation in the laboratory, away from light, and expedition in batches of 200 for analysis. The time lapse between sampling and analysis varies between 10 and 40 days, except for the first batch (No. 1254 to 1454) where the lapse was about 3 months (due to a change in the method of analysis).

c. Sampling destined for complementary analyses

1. Removal of 150 ml of water from the pail and filtration under the same conditions as previously described.
2. Direct transfer into a plastic flask.
3. Acidification with 0.5 ml ultra pure 2N HNO_3. This acidification ensures a pH between 2 and 3 and serves the purpose of minimising the effects of adsorption on the walls of the flask and of precipitation, etc...
4. Conservation in the cold (25°C below zero) in the laboratory.

III. 2. 3. *Measurement of physico-chemical parameters*

The physico-chemical parameters measured are the temperature, the conductivity, the pH and the alkalinity. They are entered onto the field record cards in C ("PARAMETERS"), boxes 36 to 48.

a. Temperature

The instrument used is a digital thermometer, WALLAC DTM-10 fitted with a universal lead allowing a reading of 1/10th of a degree Celsius. Calibration occurs by means of a code supplied by the manufacturer.

b. Electrical conductivity

The instrument used is a portable conductimeter P.T.I-7, trademark ACTIVION, fitted with a glass lead and platinum electrodes. Six measuring scales allow the measurement of conductivities from 1 to 10 000 $\mu S.cm^{-1}$.

Calibration was effected by means of dilute KCl solutions (3.10^{-2} N and 10^{-3} N) and by comparison with a very precise, non-portable conductimeter. Calibration in the field was made with a 10^{-2} N KCl solution, whose temperature was measured at the moment of use.

So as to allow comparison, all conductivity measurements are brought to 20°C.

c. pH

The instrument used is a digital pH-meter, trademark ORION, model 201, fitted with a combined electrode. The instrument comprises a temperature calibration and can be read to ± 0.05 pH units. Calibration is made by means of commercial buffer solutions.

d. Alkalinity

Measurement consists in a classical acidimetric analysis, carried out directly in the field. The pH of the equivalent point depends on the species to be titrated $(HCO_3)^-$ and on its concentration.

- Reagents:

0.05 N HCl. In some cases of low pH (< 5) and very low conductivities (< 100), a 0.01 N solution of HCl was used.

Indicator : 0.02 g of methyl red + 0.1 g of bromocresol green in 100 ml of 95% ethyl alcohol.

- Procedure:

1. Transfer 50 ml of water sample in a beaker.
2. Add some drops of the indicator.
3. Titrate with 0.05 N HCl until the green colour turns pink.

- Calculation of the HCO_3^- concentration :

  The results are expressed in mg $HCO_3^-/1$, without notable errors in all cases.

III. 2. 4. *Other information noted on the field record cards*

The field record card is the document that carries all the information that could be relevant to the data interpretation, i.e. information concerning the sample location in a general sense, operations carried out in the field as well as part of the analytical measurements.

a. Identification and localisation

In order to avoid all possibility of errors, each sample is identified by

- the date and time of its collection (boxes 4 to 13);
- its theoretical number consisting of the letter E (or by the number 2 for the computer) followed by five numbers;
- the flask number which is a chronological numbering for internal use (expedition, storage, artificial standards etc...);
- its geographical coordinates (boxes 24 to 33) in Lambert coordinates :

  X corresponding to the longitude expressed in kilometers and Y corresponding to the latitude expressed in kilometers.

  Moreover, local geographical details such as the names of rivers and springs, place names, special topographic details etc... are noted under the heading "geographical designation";
- its geological age (boxes 34, 35) : geological age of the terranes at the sampling point. This information was not used. Instead, the geological age of the grounds drained, considered to be of greater importance, was preferred.

b. Endogenic factors

This point concerns factors particular to the river such as its width, its depth, its flow, the nature of its substratum, the turbidity, the conditions and type of drainage, the physico-chemical parameters, etc... Most of these characteristics do not need further comments, thus only a brief description will be given.

- type of drainage (boxes 50, 51) : this heading indicates whether it is a spring (01), a flow close to a spring (10) or a river, in which case its mean width (02 to 09) is mentioned. The presence of settling zones uphill (AM) or downhill (AV) from the sampling site is also noted.
- conditions of drainage (box 52) : observations which take into account the depth and the flow within the sampling zone.
- quality of the water (box 53), pollution (box 55) : the turbidity of the water (optical cloudiness) could be of a natural (suspensions) or an artificial (pollution) origin. In the latter case, the waters are often coloured : the white and opalescent waters from the Prumerbach at Saint-Vith (dairy farms), the red frothy and opaque waters of La Bel (slaughter houses), brown and orange waters (metallurgy), etc... It will also be noted that there is some natural coloration of waters due to the presence of vegetable matter (green waters) or to the draining of peats (brown waters). Despite its coloration, the water is not turbid; it is the case of most of the rivers that drain the West-hertogenwald (the Helle for example).
- floods (box 58) : in general, sampling was interrupted in the case of high spates.
- canalisation (box 57) : canalised spring or river.
- substratum : the geological nature of the river beds was noted under the heading "Remarks" only in cases where rocks outcropped.

c. Exogenic factors

These are factors not directly linked with the river but which influence its dynamics and its composition such as : the geography, geology and meteorological factors.

- meteorological conditions : parameters characterising the weather during the entire day of sampling;
- geological and geographical factors : already envisaged in the preceding paragraph, these factors are easily established from maps (cf. Chapter I).

III. 3. ANALYSIS FOR URANIUM

III. 3. 1. *Choice of analytical method*

In the framework of a hydrogeochemical prospection for uranium, three methods are generally used :

1° delayed neutron activation with counting of delayed neutrons ;

2° fluorimetry ;

3° fluorometry.

Each of these methods requires investments out of proportion with the small number of samples to be analysed (about 3000). It was therefore not possible to carry out the analyses for uranium in our laboratories. Since no institution in Belgium possessed the needed equipment or was able to receive us, it was indispensable that the analyses of our samples be carried out in a foreign laboratory.

After a bibliographical study of the advantages and disadvantages of the three methods, delayed neutron activation with counting of delayed neutrons was chosen. The main advantage of this method lies in the absence of all risk of loss or of contamination, the activation taking place directly on the sample in its collecting flask.

The analyses were carried out at the NUTMAQ MINING INSTRUMENTATION in Great Britain (Building 7, AERE Harwell, Oxfordshire, England - Mr. M. ASTON).

Unfortunately, following an exchange of letters with Mr. Aston during the month of December 1979, it became clear that this laboratory could no longer accept samples from our 1980 prospection : an increase in demands for analyses prevented them from delivering results within acceptable time limits. It therefore became essential, in spite of all the inconveniences involved (change in analytical method while the prospection was in progress, in the type of sampling flasks, in the volume of water sampled, etc...) to seek another laboratory for analyses.

After a detailed study of other possibilities for the analysis of uranium by the most modern methods in our laboratories as well as in those of neighbouring countries (Great Britain, France, Germany, Denmark), the fluorimetric method, used in routine since 1968 by the Geochemistry Laboratory of COGEMA, France (Division de la Crouzille - 87640 Razes - France - Mr. R. LORIOD) was chosen.

III. 3. 2. *Analysis by activation and counting of delayed neutrons*

A total of 1203 samples were analysed in 1979, and for comparison 207 samples in 1980.

a. Description of the method, reliability

All theoretical and practical details of the method used at Harwell are described in the article by Hostle, Coleman and Ball (1972).

Briefly, the sequence of operations is as follows :

- introduction of a plastic flask containing 30 cc of the water sample into the reactor by means of a pneumatic system;
- irradiation during 60 seconds by a flux of 5.10^{12} neutrons $sec^{-1} cm^{-2}$. This provokes fission of the nuclei of U^{235} atoms. Some of the products of this fission emit neutrons after some tens of seconds, from which the appellation "delayed neutrons";
- the sample is removed from the reactor and its activity measured during 60 seconds in a neutron counter. The time lapse between the end of irradiation and the beginning of counting is 25 seconds;
- the activity of the sample is compared to that of uranium standards treated in the same manner, thus allowing the calculation of concentrations as per the following formula :

$$\text{value of uranium } (\mu g/l) = \frac{C_e - \bar{C}_b}{\bar{C}_{st}} \text{ . U content of standard}$$

where C_e = activity of the sample (counts)

$\bar{C}_b$ = mean activity of a blank (counts)

C_{st} = mean activity of a standard (counts).

The reliability of the method in the analysis of waters appears excellent, based on trials carried out by the same authors :

- interferences : very feeble for the Th, without incidence considering the very low solubility in this element.
- accuracy : linked with the preparation of uranium standards, which can be carried out with an error clearly below the 1% level.
- precision : linked with statistical errors in neutron counting : it is excellent for high values but diminishes rapidly for values lower than 10 ppb.
- detection limit : approximately 1 ppb.

b. Controls, problem of representativity at low values

1°. Accuracy

Blanks and standards prepared with uranium of known isotopic composition were sent together with the series of normal samples. Table V reveals the very good accuracy of the individual values which almost always fall within the confidence interval of the mean values for the standards, at a 95% confidence interval.

Table V - *Tests of accuracy*

Sample	H_2O dist.	H_2O tridist.	standard 1.1 ppb	standard 11 ppb	standard 110 ppb
Values ppb	1.08				
	0.00	0.00			
	0.86	0.43			
	2.60	0.00	3.03	14.11	110.29
	0.00	0.00	0.00	9.11	108.99
	0.00	0.86	0.86	11.28	110.29
$\bar{x}$	0.76	0.26	1.30	11.50	109.86
$2\sigma^*$	1.23		1.41	2.5	7.07
Confidence interval *	below detection limit			8.5-13.5	103-117

* calculated from the activities in counts corresponding to the values of the standards (cf. 3° below).

2°. Precision

Two samples, one from a spring and another from a river, were collected each in 10 separate lots, on the same day, and then sent together for analysis. Unfortunately, the samples (*) show values which fall below or close to the detection limit, thus making any discussion impossible.

(*) Samples previously collected from these two points contained values of several tens of ppb; this was why they were chosen for the reproducibility trials.

Table VI : *Trials of reproducibility*

Sample 53140	Sample 53113	
1.30	0.64	Results in ppb (x)
0.86	1.08	
0.00	2.17	
2.38	2.82	
0.64	0.21	
0.00	1.73	
0.00	0.00	
0.00	1.30	
1.08	1.95	
0.00	2.82	
0.63	1.47	$\bar{x}$
0.80	1.00	s_x
-	0.7	theoretical σ

3°. Detection limit, representativity at low values

Tables V and VI clearly show that for values of a few ppb, the precision is entirely controlled by the statistical error on the counting. At this stage, two questions arise :

- for which limit is a value obtained by a single counting considered to be statistically null, i.e. what is the detection threshold ?
- what is the confidence interval on a single measurement, particularly for values close to the detection limit ?

In order to have a good grasp at these fundamental questions with respect to the interpretation of the prospection data, it is indispensable to know the relationship between the values (ppb) and the activities (counts), knowing that only the error on the count is calculable (normal distribution). The regression was carried out on analyses provided by Harwell :

Value of U (ppb) = 0.11022 activity (counts) - 3.4517

For a blank, the mean activity is 31-32 counts with a standard deviation of 7 counts, hence the detection limit is :

1.23 ppb at a level of confidence of 95.5 % (2σ)

1.85 ppb at a level of confidence of 99.7 % (3σ)

Figure 20 shows the confidence intervals of the mean values between 0 and 10 ppb, calculated with a degree of confidence of 95.5 %. This enables a visualisation of the range of values within which the mean of a single measurement can be situated. Let us consider the example of an analysis giving 4 ppb : there are 95.5 chances out of 100 that its mean value occurs between 2.6 and 5.8 ppb (in broken lines on figure 20, next page).

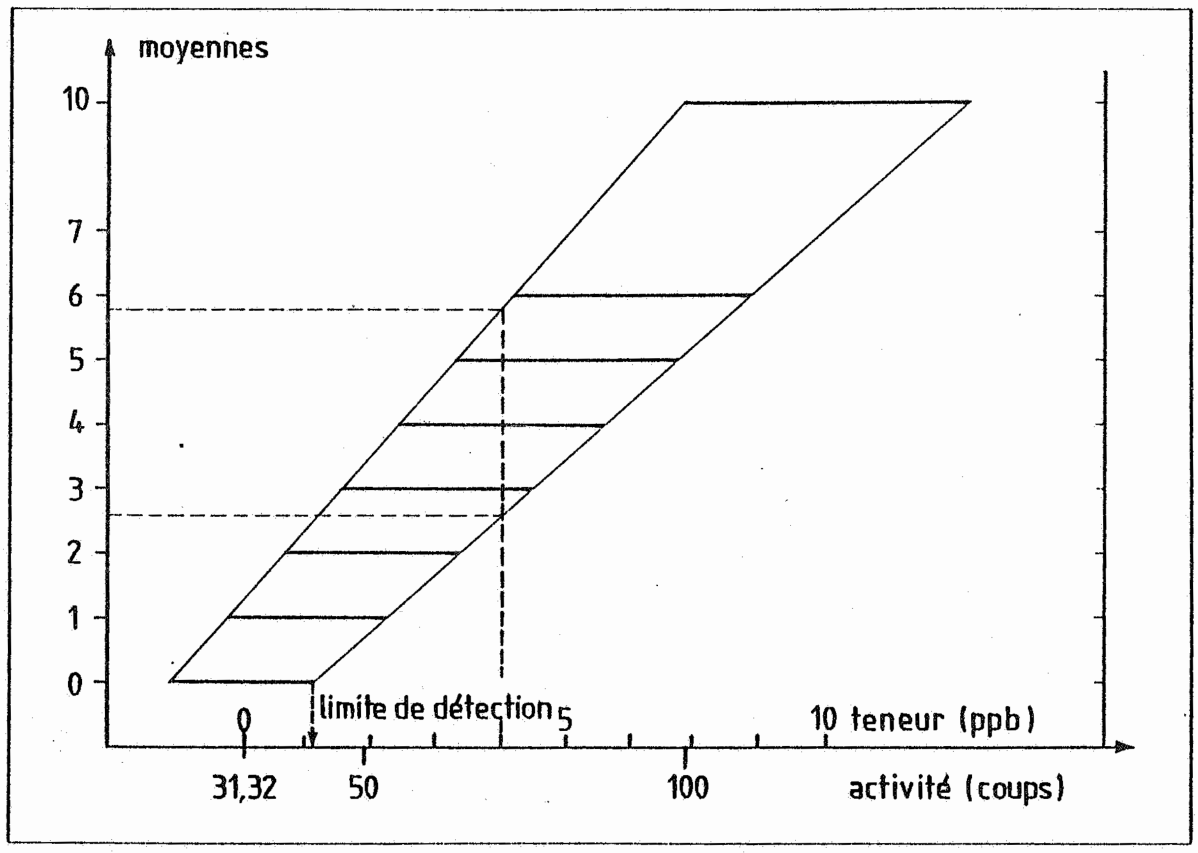


Figure 20 : Confidence intervals of the mean values between 0 and 10 ppb at a confidence level of 95.5 %

Considering that it is impossible to maintain the flux of a reactor absolutely constant, the real detection limit can be taken as 2 ppb.

4°. Conclusions

The activation analysis as carried out on the samples in this prospection is characterised by :

- an excellent accuracy
- a precision at a 95.7 % confidence level of :

  ± 38 % for 5 ppb

  ± 24 % for 10 ppb

  ± 4 % for 100 ppb
- a detection limit in the order of 2 ppb;
- no risk of loss or of contamination in the period between sampling and analysis.

III. 3. 3. *Analysis by fluorimetry*

A total of 1128 samples were analysed in 1980.

a. Description of method, reliability

All details of the method used in the laboratories of COGEMA are described in the publication by P. Bertholtet (35). Briefly, the sequence of operations is as follows :

- concentration by evaporation of a 10 cc portion on chromatographic paper;
- separation of the uranium by ascending chromatography on paper;
- calcination of the band of paper containing uranium, fusion with the flux in platinum cupels, and measurement of the fluorescence by a fluorimeter.

This technique, whose application is delicate, shows a good reliability :

- interferences : none, since uranium has been separated.
- accuracy : excellent, linked with the preparation of the standards.
- precision : average, since it is linked with the control of the fusion temperature : ± 10 %.
- detection limit : very low : 0.05 ppb (0.1 after P. Berthollet; 35).

b. Controls, problems of ageing

1°. Accuracy

Blank solutions, standards prepared with triple distilled water and doped water samples were sent for analysis in batches. The time lapse for analyses (time between preparation of standards and analysis) was 5 days for the doped samples and 10 days for the standards. It can be seen from table VII that the accuracy is good, although the values tend to be underestimated by about 10 % (the relative deviation is always negative).

This underestimation can however be attributed to a loss in uranium, due to the time lapse between sampling and analysis (cf. discussion below - 3°).

2°. Precision

Although the number of samples analysed is too small to allow a good estimation of the reproducibility, the results in table VII can be used to estimate it at 10-15 % at a 95.7 % level of confidence.

3°. Detection limit

The absence of a significant difference (table VII) between the analytical results for the distilled and triple distilled water (distillation over quartz in an ultra-clean laboratory), together with the abnormally high U content of the triple distilled

Table VII : *Tests of accuracy (ppb)*

Sample (*)	H_2O dist.	H_2O tripl. dist.	Standard 1.26	Standard 15.8	Standard 149	Doped 105	Doped 10.5	Doped 1.05	Doped 10	Doped 1
Value in ppb	0.18	0.15	0.94	14.0	130	88	8.3	0.82	7.4	0.80
	0.19	0.18	0.95	12.0	120	105	9.8	0.71	8.2	0.76
	0.23	0.13	0.93	13.0	150	95	10.5	1.14	11.5	1.14
		0.30	1.10	15.0	150					
		0.19								
$\bar{x}$	0.20	0.19	0.98	13.5	137.5	96	9.5	0.89	0.0	0.90
Δ %	-	-	- 22	- 14.5	- 7.7	- 8.6	- 9.6	- 15.2	- 10	- 10

Δ % : relative deviation between the mean value and the standard value

* : time lapse for analyses : 5 days for the doped samples, 10 days for the standards.

water (*) show that the limit of detection would be in the order of 0.2 ppb.

4°. Problem of loss by ageing

Since the fluorimetric analysis is carried out on an aliquot part of the sample collected, the possibility of loss of U by adsorption along the walls of the recipient or on suspended particles, by co-precipitation etc... cannot be excluded a priori. This question is even more important considering that there is necessarily a variable time lapse between sampling and analysis. In the present case, there was an average lapse of 25 days between extremes of 10 to 40 days.

In order to test the effect of this, three series of samples (corresponding to three sampling points) were immediately doped in the field. One series was analysed after 5 days (minimum possible lapse) and another after storage for 60 days in the dark (as for the prospection samples). The results presented in table VIII and in figure 21 show :

- no significant loss for the samples doped with uranyl acetate;
- a loss inversely proportional to the initial value for samples coped with uranyl nitrate. It is likely a constant loss of the order of 0.2 ppb, , which would clearly explain the shape of figure 21.

(*) The Pb contents of this triple distilled water are below 0.01 ppb (determined by isotopic dilution).

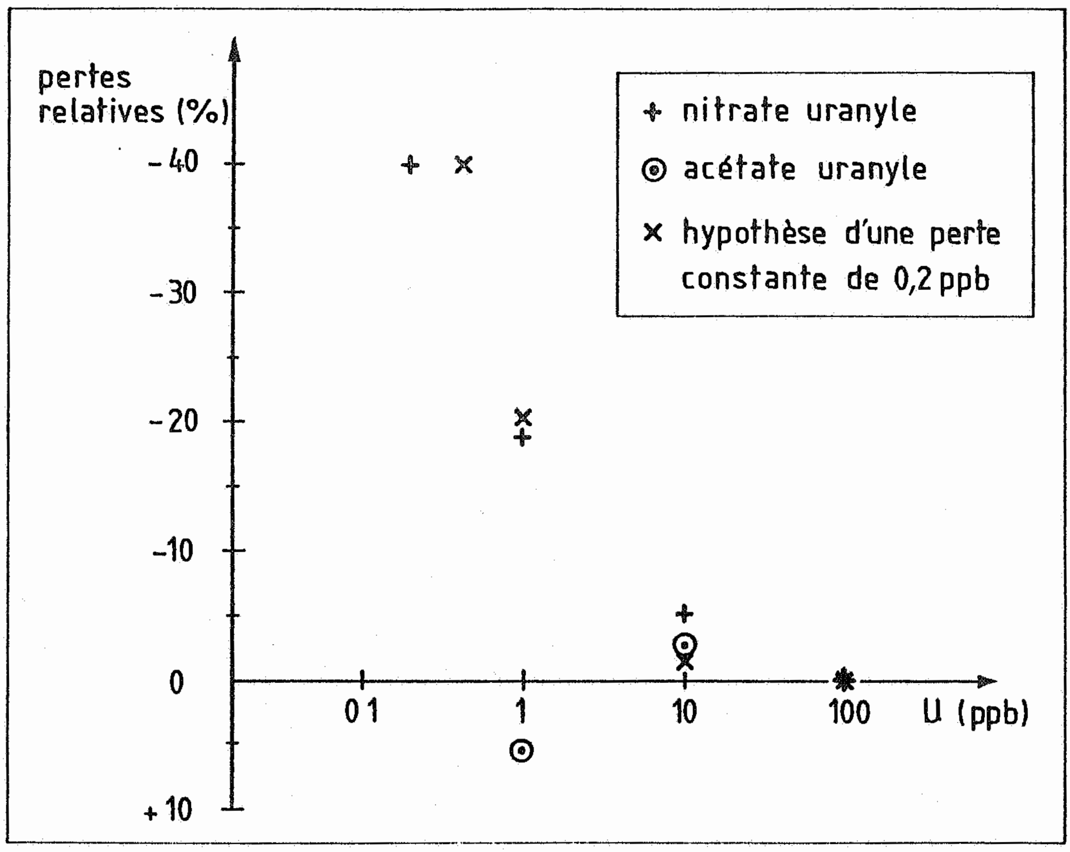


FIG. 21 : Uranium losses.

Table VIII : *Tests of ageing*

No. sample	Plain water			Doped 105 ppb*			Doped 10.5 ppb*		
	5 days	60 days	Δ %	5 days	60 days	Δ %	5 days	60 days	Δ %
2339	< 0.2	< 0.2	-	88	84	- 4	8.3	8.5	+ 4
2337	0.24	< 0.2	-	105	90	- 14	9.8	7.0	- 27
2341	0.46	0.28	- 39	95	113	+ 18	10.5	11.7	+ 11
Mean	0.29	0.17	- 39	96	96	0	9.5	9.1	- 5

	Doped 1.05 ppb*			Doped 10 ppb°			Doped 1 ppb°		
	5 days	60 days	Δ %	5 days	60 days	Δ %	5 days	60 days	Δ %
2339	0.80	0.55	- 31	7.4	8.0	+ 9	0.80	1.00	+ 25
2337	0.71	0.58	- 18	8.2	7.5	- 7	0.76	0.73	- 4
2341	1.14	1.02	- 10	11.5	10.7	- 7	1.14	1.12	- 2
Mean	0.89	0.7	- 19	9.0	8.7	- 3	0.90	0.95	+ 6

* doped with uranyl nitrate

° doped with uranyl acetate

Note : the values for the doped samples have been corrected in each case for the initial value.

Other trials were carried out at the laboratory of COGEMA by Mr. LORIOD : non-filtered plain water samples, doped with uranyl nitrate, were conserved in our flasks and analysed over a period of three months.

Table IX : *Tests of ageing carried out at COGEMA*

Dates of measurements	Conduc. m/S	U ppb	U in dry Res.ppm	Conduc. m/S	U ppb	U in dry Res.ppm	Conduc. m/S	U ppb	U in dry Res.ppm
20 March 80	20	0.5	3.5	22	6.5	40	54	10.0	26
4 April 80		0.6			5.0			8.8	
8 May 80		0.6			6.0			7.5	
18 June 80	22	0.6	3.8	22	4.0	26	30	6.5	30

The results (table IX) show :

- no significant losses at low values
- losses of about 10% per month of conservation for values in the order of 10 ppb.

The results of these ageing tests are contradictory and are an indication of the problems inherent to the conservation of the water samples on the one hand, and the difficulty of conceiving tests appropriate to such low values on the other hand.

All these tests lead to the conclusion however, that with the short conservation time (10-60 days) involved, eventual losses are relatively negligible for values greater than a few ppb's.

Consequently, these losses :

- carry no risk of masking the presence of any eventual anomalies (seen the generally high contrast);
- do not seem to allow the comparison of results obtained by fluorimetry with those obtained by activation for values lower than about 5 ppb.

III. 3. 4. *Comparison between analyses by activation and by fluorimetry*

In consequence of the above conclusions, and in order to help in the interpretation of the results of the entire prospection, we found it necessary to compare the two analytical techniques from both the theoretical and the practical points of view.

a. Comparison of their practical features

The possibilities and intrinsic characteristics of the two methods described in the last two paragraphs are summarised in Table X.

It can be seen from this table that for values over 5 ppb, results of the two methods are equivalent, with nevertheless a better precision and accuracy for the neutron activation analysis.

On the other hand, comparison of results supplied by the two methods is no longer possible for values below 5 ppb : fluorimetry, which is more sensitive and more accurate, seems to be affected by losses during storage (small in absolute values but significant in relative values). However, as we shall see later, the uranium contents of the waters from the Belgian Paleozoic are very low (below the ppb level, cf. III.7.1) and make impossible any comparison of the results obtained by the two methods.

Table X : *Comparison between activation and fluorimetry*

Characteristics	Neutron activation	Fluorimetry
Precision	influenced by statistical error on counting	fusion temperature of pellets
at 100 ppb	± 7 % (2σ)	± 15 %
at 10 ppb	± 24 % (2σ)	± 15 %
at 5 ppb	± 38 % (2σ)	± 15 %
at 1 ppb		± 15 %
Accuracy	excellent, influenced at low values by statistical error on counting	very good
Real detection limit	2 ppb	0.2 ppb
Loss in uranium	impossible	possible during time lapse between sampling and analysis. Negligible for values over about 5 ppb

b. Comparison in the field

A series of 83 samples were collected in duplicate when the change in the analytical method for uranium was being made (beginning of March 1980). Unfortunately, only 7 of these samples (table XI) contained values greater than the detection limit of the neutron activation analysis (2 ppb), thus excluding any form of arithmetical comparison. The very low values obtained by fluorimetry can however be emphasized : 34 samples contain values below the detection limit (0.20 ppb), with only one value exceeding 1 ppb. This seems to confirm the existence of losses by adsorption during storage (samples of the first batch, delayed for about two months before analysis).

Following this inconclusive comparison, one of the rare zones with values greater than the detection limit (2 ppb), observed during the first prospection campaign, was again sampled in triplicate in the month of August 1980. The 23 samples were analysed by neutron activation, by fluorimetry and by fluorometry*.

Contrarily to those collected in September 1979, the samples collected in August 1980 showed extremely low values, almost always below the detection limit, irrespective of the method of analysis used. Such low values make even more difficult any attempt at comparing the two sets of results.

The large difference in the values of the two sets of samples can be explained by the greater drought of September 1979.

Owing to the lack of time, and above all the absence of zones highly anomalous in uranium, these investigations were not carried further.

---

* Fluorometer Scintrex UA-3, analyses carried out by HUNTING TECHNICAL SERVICES LIMITED.

Table XI : *Compared analysis of 83 samples collected in the region of Rochefort-Marche-Cineu*

No. sample	ppb U DNA	ppb U fluorim.	No. sample	ppb U DNA	ppb U fluorim.
1254	2.82	0.70	1296	1.08	0.10
1255	1.73	0.07	1297	0.21	0.27
1256	2.38	0.49	1298	1.95	0.55
1257	1.08	0.70	1299	0.00	0.09
1258	0.43	0.34	1300	0.00	0.25
1259	0.21	0.09	1301	0.63	0.30
1260	0.64	0.44	1302	1.08	0.22
1261	1.95	0.55	1303	0.00	0.29
1262	1.51	0.57	1304	0.86	0.35
1263	0.64	0.23	1305	1.73	0.32
1264	0.43	0.07	1306	1.08	0.33
1265	0.43	0.15	1307	0.43	0.28
1266	0.00	0.07	1308	0.43	0.05
1267	0.86	0.05	1309	0.86	0.50
1268	0.00	0.07	1310	1.30	0.12
1269	0.64	0.09	1311	0.00	0.07
1270	2.17	0.38	1312	1.51	0.40
1271	0.86	0.04	1313	1.30	0.09
1272	0.43	0.25	1314	0.00	0.32
1273	0.00	0.27	1315	0.00	0.12
1274	0.64	0.10	1316	0.64	0.07
1275	0.00	0.14	1317	0.00	0.07
1276	0.00	0.07	1318	0.00	0.09
1277	0.21	0.05	1319	0.21	0.08
1278	1.51	0.24	1320	0.21	0.53
1279	0.00	0.27	1321	0.00	0.44
1280	0.00	0.04	1322	1.08	0.42
1281	0.64	0.27	1323	0.21	0.63
1282	0.00	0.34	1324	0.21	0.40
1283	0.00	0.47	1325	0.00	0.15
1284	0.00	0.62	1326	1.08	0.54
1285	0.00	0.17	1327	0.00	0.54
1286	0.00	0.13	1328	1.73	0.50
1287	1.51	0.13	1329	3.03	0.07
1288	0.00	0.17	1330	0.00	0.57
1289	0.00	0.12	1331	1.30	1.20
1290	0.00	0.33	1332	0.21	0.27
1291	0.64	0.43	1333	0.43	0.27
1292	0.00	0.20	1334	0.64	0.54
1293	0.00	0.15	1335	0.00	0.09
1294	0.00	0.43	1336	1.08	0.34
1295	0.43	0.29	1337	1.95	0.39

Sampling : beginning of March; analysis : May 1980.

Table XII : *Compared analysis of 23 samples from the region of Spa*

Topograph. code no.	Sampling September 1979	Sampling August 1980		
	Neutr. Activ.	Neutr.Activ.	Fluorimetry*	Fluorometry
49312		0.21	0.06	< 0.05
49319	1.51	1.30	0.08	0.12
49316	2.60	0.43	0.15	0.14
49317	4.34	0.86	0.18	0.08
49315	2.82	0.00	0.23	0.18
49313	-	1.30	0.08	0.16
49321	4.99	0.21	0.05	0.21
49322	4.34	0.86	0.13	0.34
49318	-	1.08	0.06	0.12
49323	1.51	1.08	0.10	0.12
49324	2.60	1.08	0.09	0.20
49325	4.12	0.00	0.13	< 0.05
49326	5.86	1.30	0.05	< 0.05
49328	1.73	0.00	0.20	< 0.05
49329	5.42	1.30	0.16	0.18
49332	3.03	0.00	0.23	0.10
50102	3.68	0.43	0.18	0.10
50118	2.38	1.08	0.09	< 0.05
49330	-	0.00	0.13	< 0.05
49331	-	0.64	0.14	0.11
49342	-	0.00	0.08	0.14
49343	-	0.43	0.10	0.08
49327	-	0.64	0.18	0.11
Samples below detection limit	3 (2 ppb)	23 (2 ppb)	20 (0.2 ppb)	6 (0.05 ppb)

* Sampling effected on August 18, analysis on September 9.

III. 3. 5. *Conclusions*

Despite the difficulties encountered in establishing tests of comparision in the laboratory as well as in the field, it can be concluded that :

1°) analysis by delayed neutron activation followed by counting of delayed neutrons, carried out directly on water samples, is ideally suited for the strategic prospection of uranium. It will only be noted that there is a slight lack in sensitivity for prospection in sedimentary regions with very low geochemical background, which seems to be the case of the Belgian Paleozoic.

2°) analysis by fluorimetry, in spite of a better sensitivity, is subject to losses of uranium (adsorption, co-precipitation...) in the period between sampling and analysis. These losses cannot be controlled and are small in absolute value, but become relatively important below a few ppb's. Equally, they seem to be linked with the length of storage time.

3°) the losses observed in the results of the analysis by fluorimetry carry no risk of masking the presence of any eventual anomalies owing to the generally high contrast of uranium together with the low absolute values of the losses.

4°) below values of about 5 ppb, it is not possible to compare the results obtained by neutron activation to those obtained by fluorimetry.

III. 4. ANALYSIS OF MAJOR CATIONS

III. 4. 1. *Method and instrumentation*

The determination of the major cations : Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} was carried out by atomic absorption spectrophotometry in the laboratory of geomorphology at the University of Brussels. (Prof. SOUCHEZ) where the method is used in routine.

The instrument used is a double beam spectrophotometer, mark PERKIN-ELMER, Model 303.

Working conditions were as follows :

- source :	monoelement hollow cathode lamps
- burner :	type Lundegarth
- gas mixture :	air + acetylene
- Na :	line 2950 Å 8 m A
- K :	line 3830 Å 12 m A
- Mg :	line 2850 Å 10 m A
- Ca :	line 2110 Å 6 m A

All analytical details for these four elements can be found in the work of R. LORRAIN (45).

III. 4. 2. *Procedure, reliability*

1°. The sample, stored at -25°C, is brought up to room temperature by taking it out one night in advance and is then homogenised.

2°. K^{+} is determined on the sample as it is.

3°. Na^{+} is determined after dilution (11 or 21 times).

4°. The determination of Ca^{2+} and Mg^{2+} is carried out on an aliquot part of the sample that has been diluted for the Na analysis, to which is added a fix amount of a 5% solution of lanthanum nitrate in 9% HCl (4 ml sample + 0.8 ml La solution). The addition of lanthanum suppresses interferences due to Si and Al.

5°. The concentration is calculated from a calibration carried out on a range of standard solutions prepared by dilution of a Tritisol mother-solution. Each series of samples (about 50) is framed by a calibration line.

Under the conditions of storage used (freezing and acidification to pH's lower than 3), trials showed no significant losses of the cations (45).

The analytical precision under the measuring conditions in routine is about 10 %.

The values determined always exceed the detection limit.

III. 5. ANALYSIS OF FLUORINE

III. 5. 1. *Method and instrumentation*

Fluorine was determined by ionometry, using a specific electrode.

The method was established in our laboratories from documents supplied by the firm ORION and from data taken from the literature. The instrument used is a digital ionometer, Model 701-A of the firm ORION, fitted with a specific electrode for F^- ions, Model 9609 ORION (combined electrode).

III. 5. 2. *Procedure*

1°. The sample, stored at -25°C, is brought to room temperature by bringing it out one night in advance, and is then homogenised.

2°. A 30 ml portion of the sample is removed and to it, is added 3 ml of TISAB III reagent. The electrode is plunged into this solution which is continuously stirred; the reader stabilises after 2 or 3 minutes. The TISAB reagent has a buffering effect (pH 5 - 5.5) which prevents interference by hydroxyl ions and complexation of part of the F^- ions by H^+ (HF or HF_2^-). It also contains CDTA which complexes Al and Fe up to values of around 5 ppm.

3°. Calibration was carried out with a series of fluorine standards prepared by dilution of a Tritisol mother-solution. The calibration curve is linear (except at low concentrations) (fig. 22) if the measured potentials (mv) are plotted against the logarithm of the concentrations (ppb). Each series of samples falls within the calibration curve.

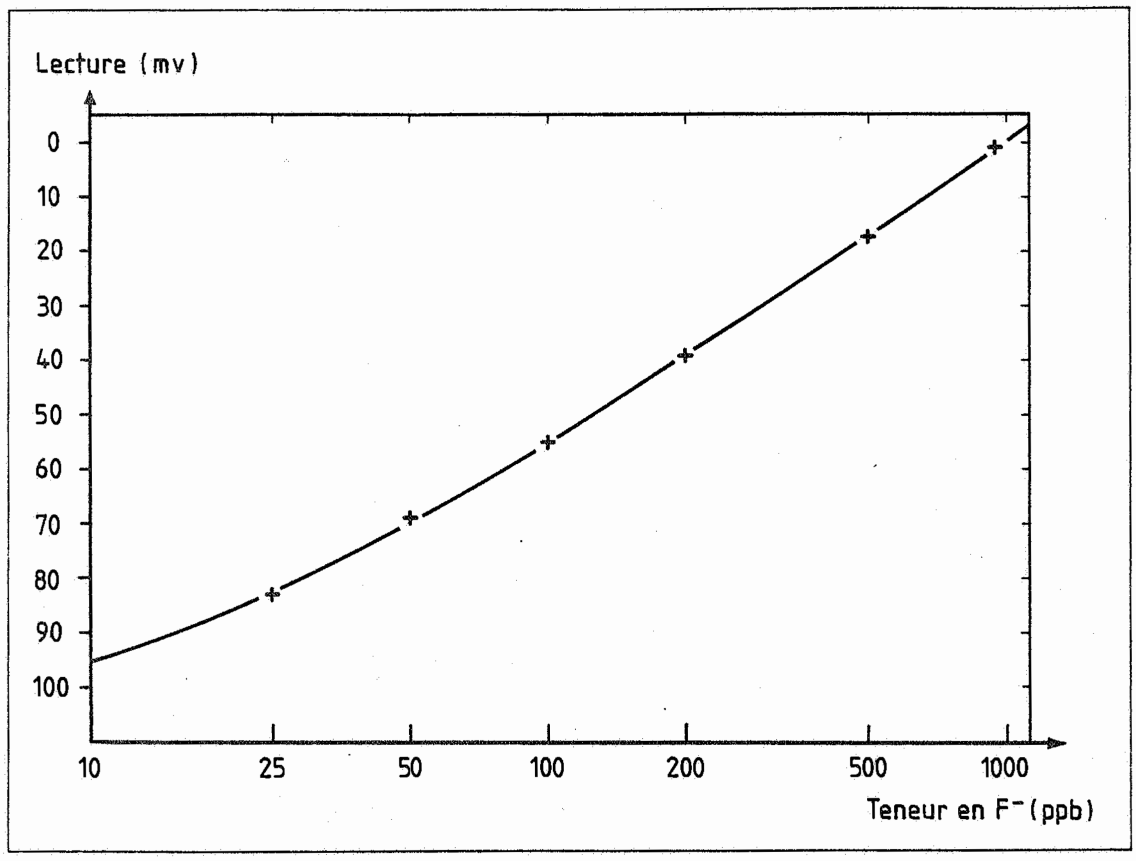


FIG. 22 : The calibration curve for fluor

III. 5. 3. *Tests of reliability*

In order to test the possible effects of the aqueous matrix, the direct calibration method was compared with the method of standard additions. The results were in good agreement within the limits of analytical errors, thus proving the absence of matrix effects. The method by direct calibration, which is more rapid and more accurate, was chosen. Considering the generally low fluorine contents of our samples, the absence of interferences due to pH, to Fe and Al, as well as contaminations by F, was verified.

Trials also showed no significant losses of fluorine during sample storage.

The analytical precision is :

- ± 2%, in the range 100 to 0.1 ppm
- ± 10%, in the range 0.1 to 0.02 ppm.

Under the best conditions, the detection limit is about 10 ppb.

III. 6. PRESENTATION OF RESULTS

III. 6. 1. *Introduction*

All the results from the hydrogeochemical prospection (9 variables for about 2500 samples) were centralised at the Geological Survey of Belgium where a system of management and computer treatment of the data was designed by a coordination team (cf. I.4.).

The results for uranium were manually transferred onto 1:100 000 orohydrographic maps as and when they arrived.

III. 6. 2. *Balance*

Of a total of 2335 sampling points :

- 1744 or 74.7 % were from rivers;
- 591 or 25.3 % were from springs.

With respect to the area prospected, the mean sampling density was :

- 1.25 samples per 10 km^2 for the rivers;
- 0.42 samples per 10 km^2 for the springs

giving a total density of about 2 samples per 10 km^2.

The map in figure 23 shows the geographical repartition of the sampling points, and table XIII gives the repartition of the samples according to the number of the 1:25 000 topographic maps, from which the homogeneity of the sampling density can be seen.

At each of the 2335 sampling sites, measurements were carried out in the field of : temperature, pH, resistivity, alcalinity, and each of the water samples was analysed for uranium.

TABLE XIII : RESULTS OF THE PROSPECTION

No. topog. map	S km2	Number of samples			Density sampl. 10 km2	URANIUM				Major cations	Fluor
		River	Spring	Totals		Activ-ation	> 2 ppb	Fluori-mètry	> 1 ppb		
34	400	28	7	35	0.87	3	1	32	18	4	0
35	50	6	1	7	1.4	7	1	0	0	7	0
38	tests	2	0	2	-	2	2	0	0	2	0
39	tests	5	0	5	-	5	1	0	0	5	0
40	320	25	1	26	0.81	26	6	0	0	26	0
41	480	38	10	48	1.00	48	30	0	0	48	0
42	640	69	29	98	1.53	20	0	85	7	98	0
43	400	75	6	81	2.02	81	11	0	0	81	0
45	300	13	3	16	0.53	16	3	0	0	16	0
46	320	24	11	35	1.10	35	11	0	0	35	0
47	640	81	19	100	1.56	100	26	0	0	100	0
48	640	80	23	103	1.61	103	20	0	0	103	0
49	640	88	43	131	2.05	13	7	122	1	58	56
50	640	94	20	114	1.78	114	48	0	0	114	114
51	150	21	2	23	1.53	23	5	0	0	23	0
52	550	92	12	104	1.89	104	8	0	0	104	0
53	640	79	27	106	1.66	106	8	0	0	106	13
54	640	92	23	115	1.80	86	0	103	0	4	3
55	640	85	41	126	1.97	0	0	126	0	0	0
56	550	101	31	132	2.06	132	26	0	0	132	132
57	520	73	15	88	1.69	88	4	0	0	88	8
58	640	73	20	93	1.45	93	12	0	0	93	72
59	640	101	25	126	1.97	0	0	126	0	39	38
60	620	84	37	121	1.89	0	0	121	0	0	0
61	80	11	7	18	2.25	18	0	0	0	18	18
62	200	25	3	28	1.40	28	0	0	0	28	0
63	450	30	9	39	0.87	39	0	0	0	18	18
64	640	73	37	110	1.72	0	0	110	0	1	0
65	510	73	54	127	2.49	0	0	127	0	0	0
66	40	4	4	8	2.00	2	0	6	0	2	0
67	440	48	35	83	1.89	0	0	83	0	0	0
68	580	51	36	87	1.50	0	0	87	3	1	0
TOTALS	14 000	1 744	591	2 335	1.67	1 292	230	1 128	29	1 354	464
% total number of samples		74.7	25.3	100	-	55.3*	10.1	48.3*	1.2	58	20

* 84 samples were taken in duplicate and analysed by the two methods.

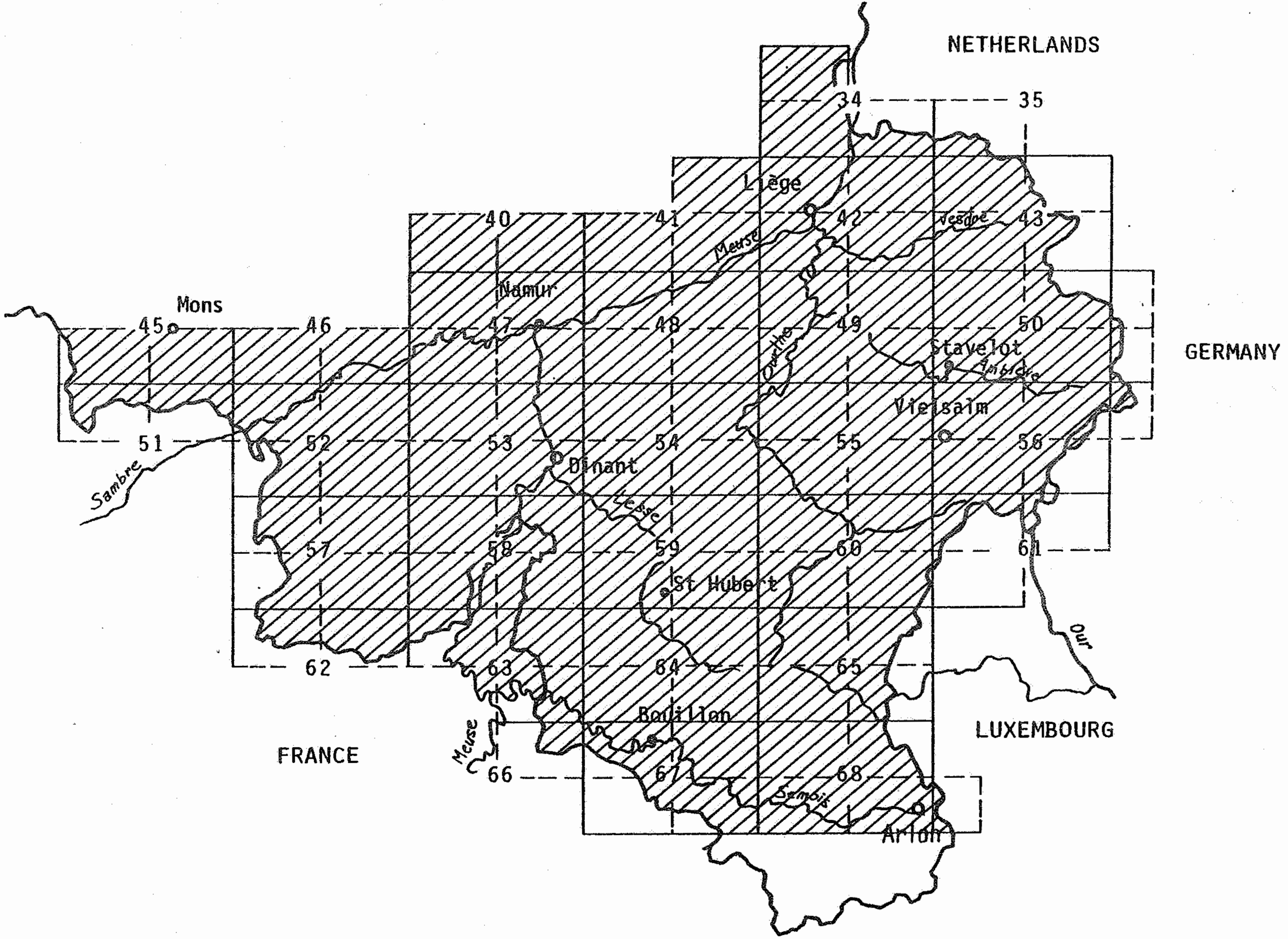


FIG. 23 : Hydrogeochemistry : the prospected area.

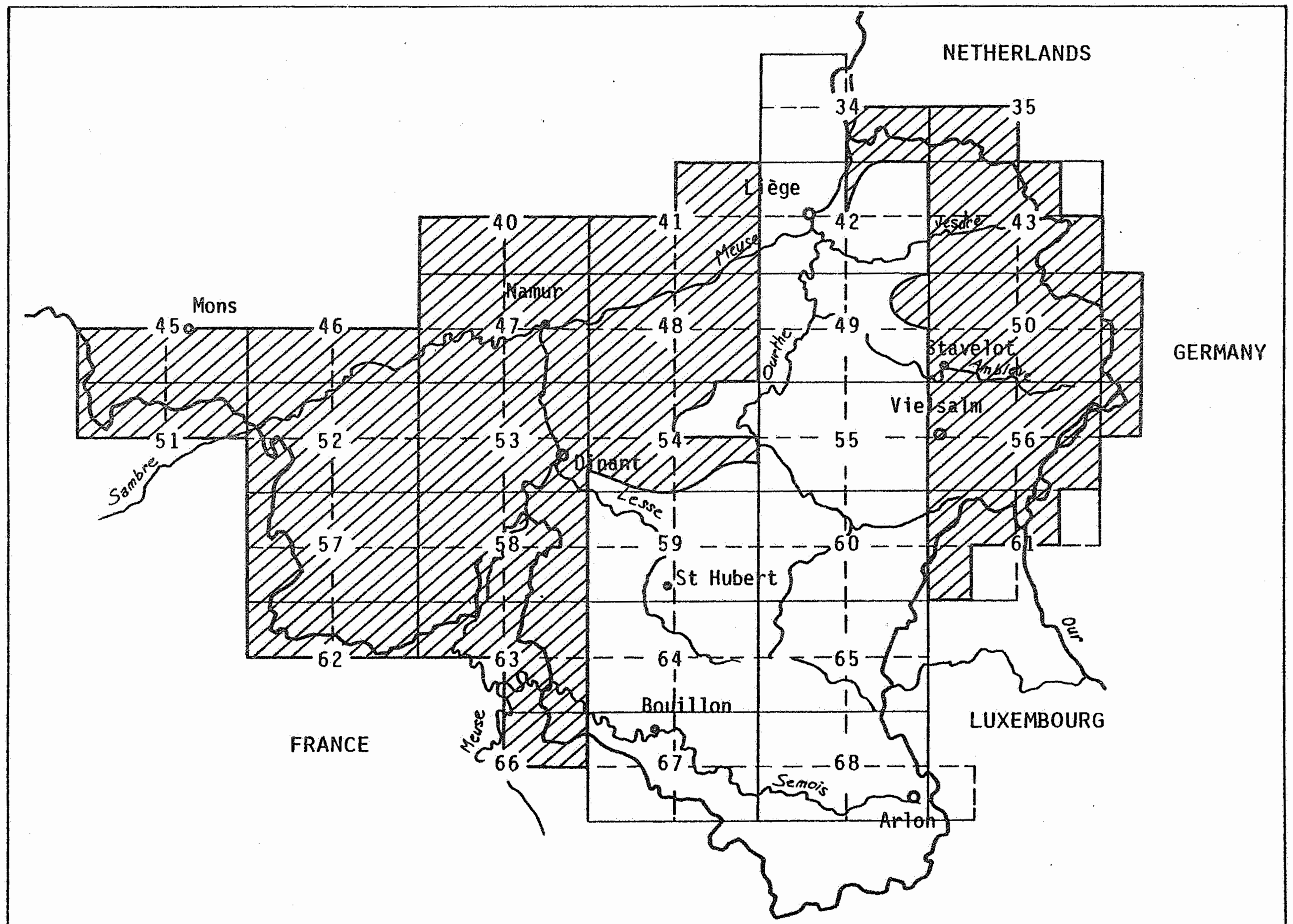


FIG 24 : Zone analysed by delayed neutron activation.

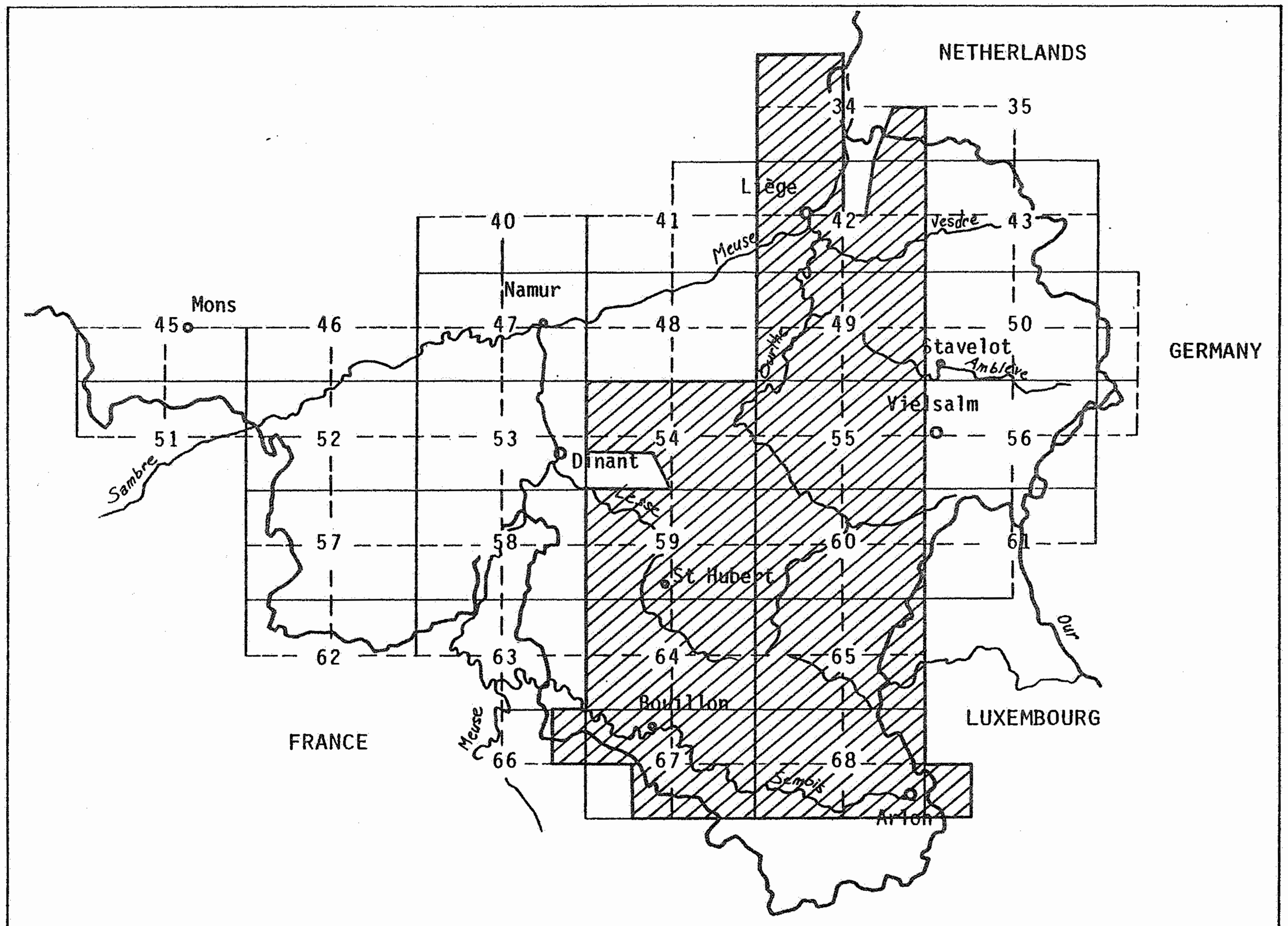


FIG 25 : Zone analysed by fluorimetry

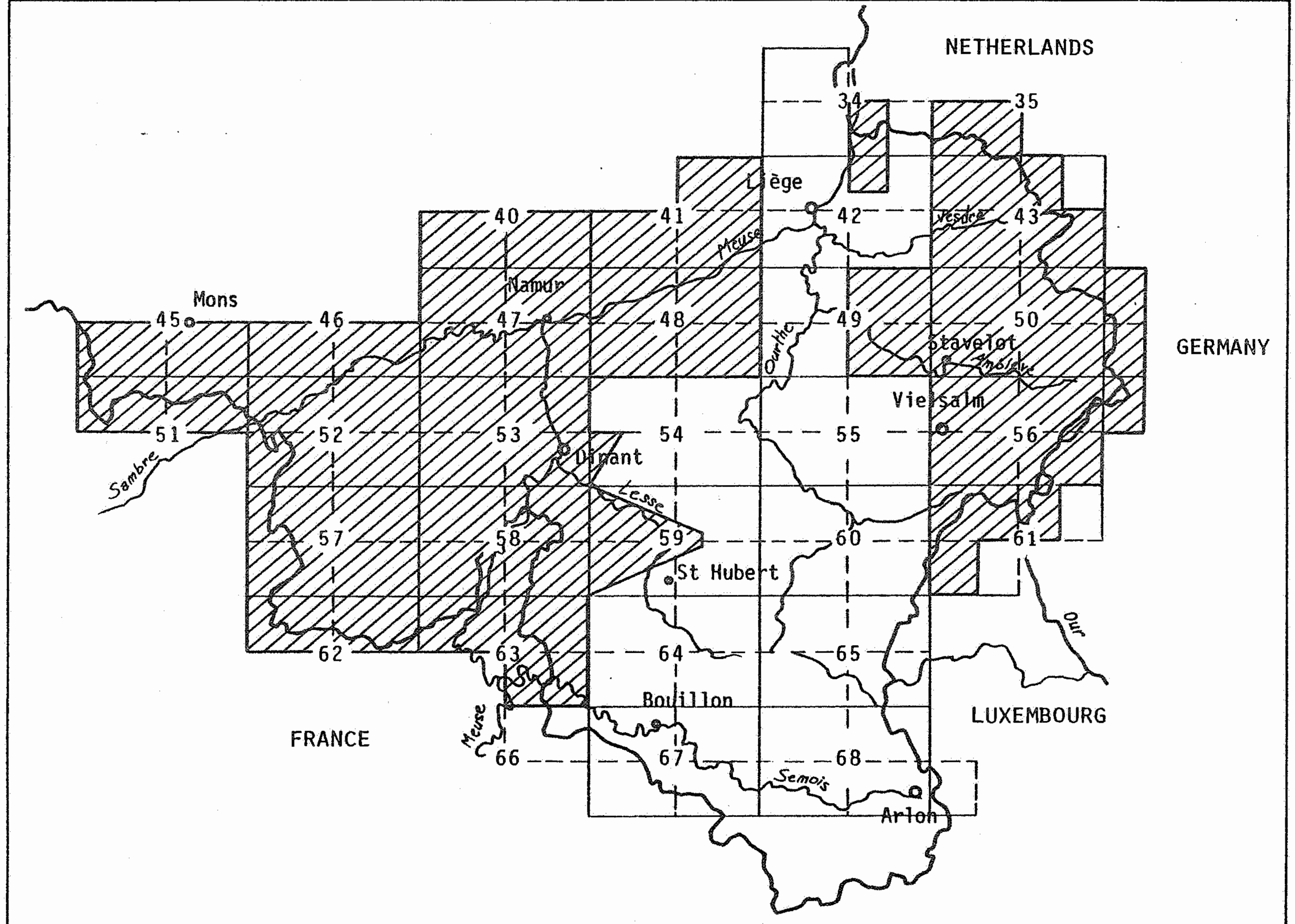


FIG. 26 : Zone analysed for major cations.

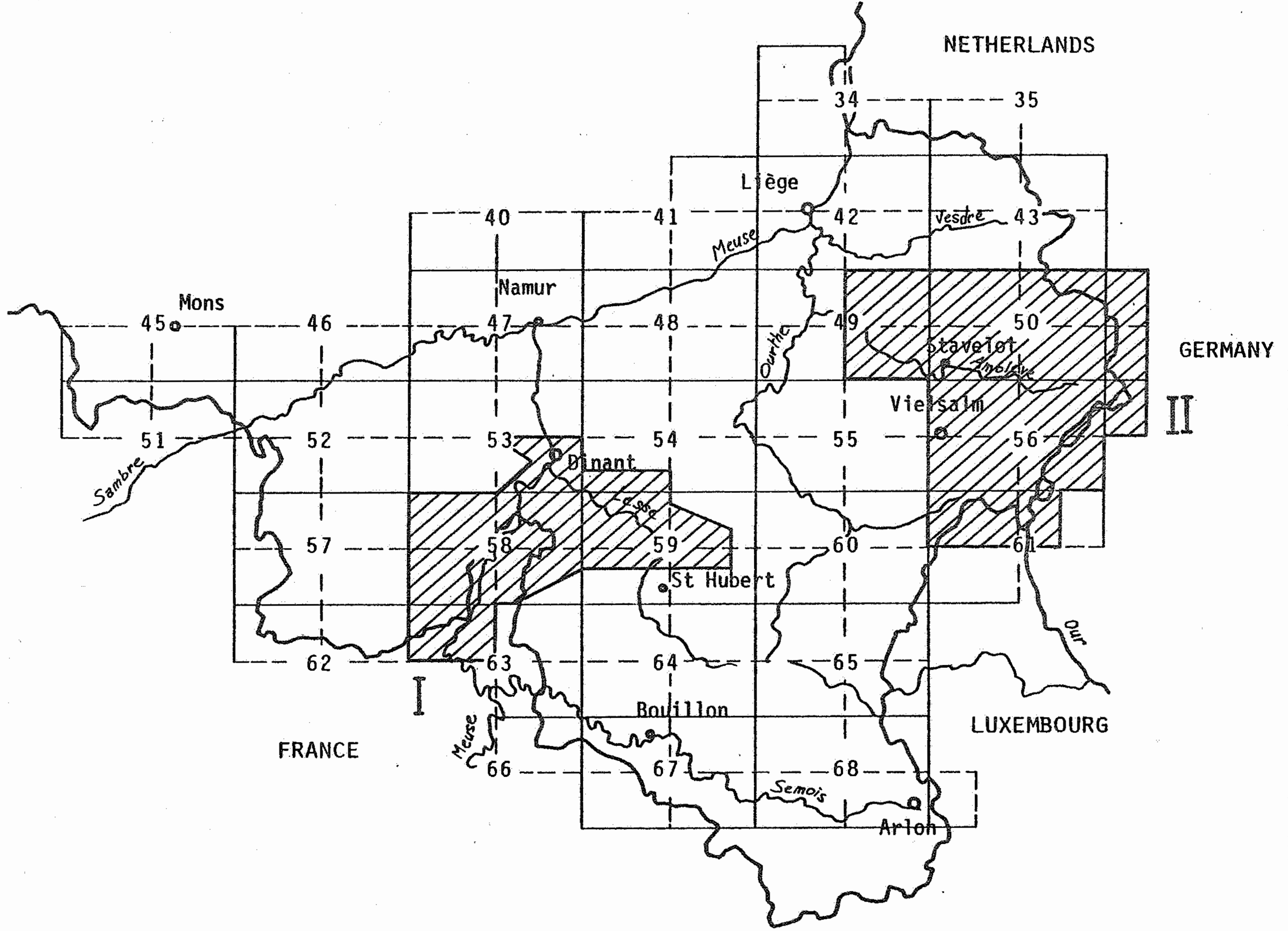


FIG. 27 : Zone analysed for fluorine.

Figures 24 and 25 give the geographical repartition of the samples analysed by neutron activation (1292 samples) and by fluorimetry (1128 samples) and table XIII, their repartition by topographic map.

Figures 26 and 27 give the geographical repartition of the samples analysed for the major cations (1354 samples) and for fluorine (464 samples). Table XIII shows their repartition by topographic map.

Number of samples collected	2335	100 %
Number of river samples	1744	74.7 %
Number of spring samples	591	25.3 %
Number of samples analysed for uranium by activation	1292	55.3 %
Number of samples analysed for uranium by fluorimetry	1128	48.3 %
Number of samples analysed for major cations	1354	58.0 %
Number of samples analysed for fluorine	464	20.0 %

III. 6. 3. *Raw data*

The complete list of the numerical data as well as their localisation were recorded on microfiles in the final report submitted to the EEC in January 1982. These microfiles are avalaible for consultation at the Geological survey of Belgium.

III. 6. 4. *Cartographical representations*

Four 1:100 000 maps showing the distribution of uranium in oro-hydrographic backgrounds are presented in plates in the EEC report

Different symbols are used to distinguish between river waters (whole symbols) and spring waters (hollow symbols).

Moreover, for greater clarity, each map shows only the results obtained by the same analytical method (thus two maps are presented for the north-east zone).

The class limits for the symbolic representation are different for the two techniques, due to their different sensitivities :

activation analysis :
- values lower than 2 ppb (detection limit)
- values between 2 and 5 ppb
- values between 5 and 10 ppb
- values greater than 10 ppb.

fluorimetric analysis :
- values lower than 0.2 ppb
- values between 0.2 and 0.5 ppb
- values between 0.5 and 1 ppb
- values greater than 1 ppb.

These maps are essential and will serve as a basis for the interpretation of the prospection results.

III. 6. 5. *Descriptive statistics*

Figures 29 to 66 show the frequency histograms as well as the descriptive parameters (mean, standard deviation) of the variables measured (U, conductivity, alkalinity, pH, Ca, Mg, K, Na, F).

The prospected zone was divided into three "homogeneous" zones (fig. 28) with regard to the sampling (period and geography) and the method of analysis of uranium :

- a west zone consisting essentially of the Entre-Sambre-et-Meuse. This zone was sampled between May and August 1979, and all the samples were analysed for uranium by activation and for the major cations (fig. 24 and 25).

  From a geological point of view, this zone is composed essentially of the devonian and carboniferous terranes belonging to the synclinorium of Dinant, and to the north and north-east, of the largest portion of the synclinorium of Namur.

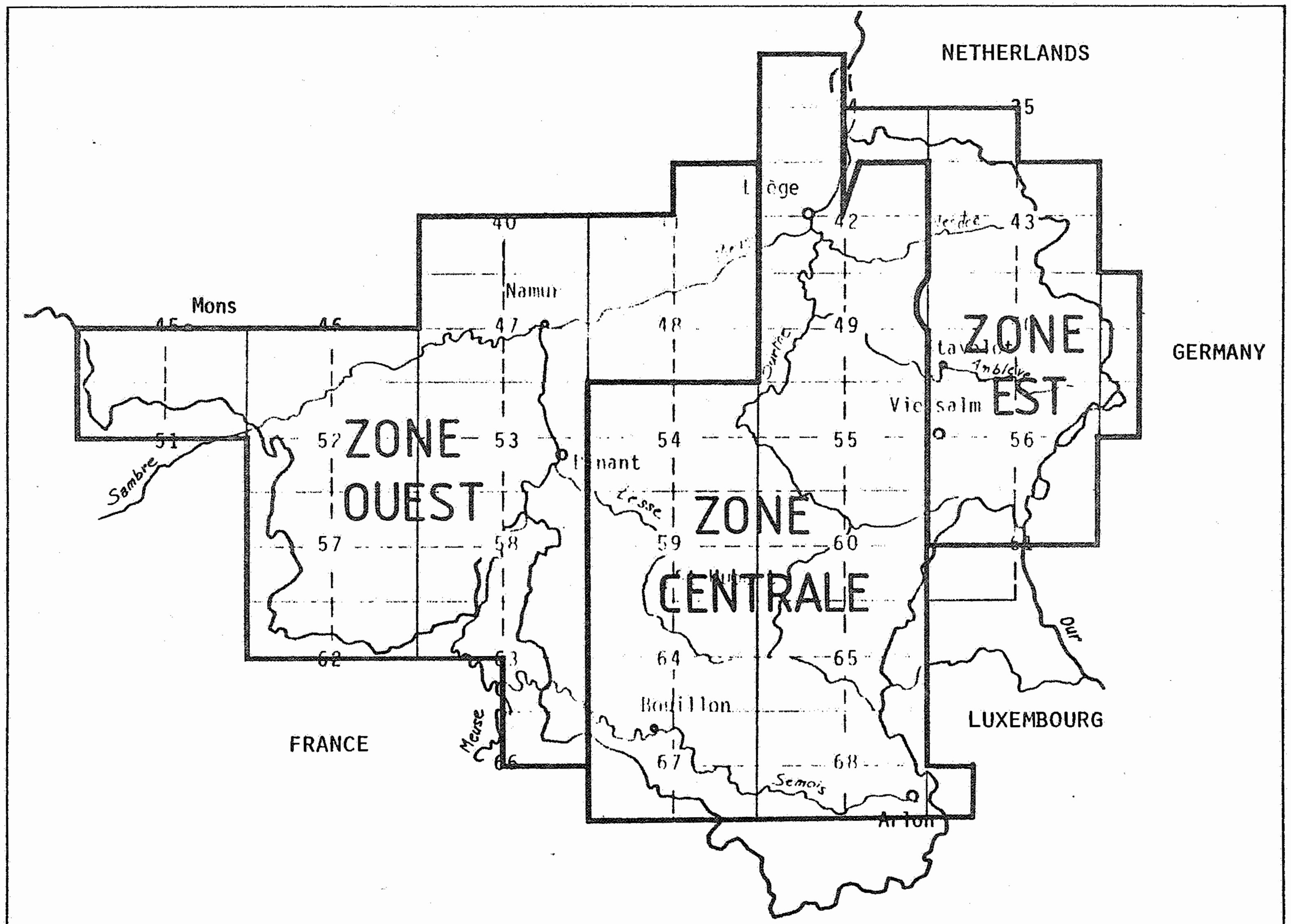

NETHERLANDS
GERMANY
LUXEMBOURG
FRANCE
ZONE OUEST
ZONE CENTRALE
ZONE EST
Mons
Namur
Liège
Dinant
Stavelot
Vielsalm
Bouillon
Arlon
Sambre
Meuse
Lesse
Ourthe
Amblève
Vesdre
Our
Semois
35
40
42
43
45
46
47
48
49
51
52
53
54
55
56
57
58
59
60
62
63
64
65
66
67
68

FIGURE 28

- an east zone consisting of the plateau of Herve and the "Hautes Fagnes". This zone was sampled in September/October 1979. All the samples were analysed for uranium by activation, for the major cations, and to a large extent for fluorine (fig. 24, 26 and 27).

  From a geological point of view, this zone consists of the Devono-Carboniferous belonging to the synclinorium of Herve in the north, of the Cambro-Ordovician belonging to the massive of Stavelot in the centre and of the Lower Devonian belonging to the synclinorium of Eifel in the south-east.

- a central zone comprising the largest portion of the Condroz, the Famenne and the Ardennes. It was sampled between April and September 1980 and all the samples were analysed for uranium by fluorimetry (fig. 25).

  Geologically, this zone consists essentially of the Eodevonian terranes belonging to the anticline of the Ardenne, the synclinorium of Neufchâteau and the anticline of Givonne.

In all cases (except for fluorine), the histograms were constructed from the logarithms of the values, with the result that the shapes of the distributions are more symmetrical (approximately or tendency towards lognormal distributions).

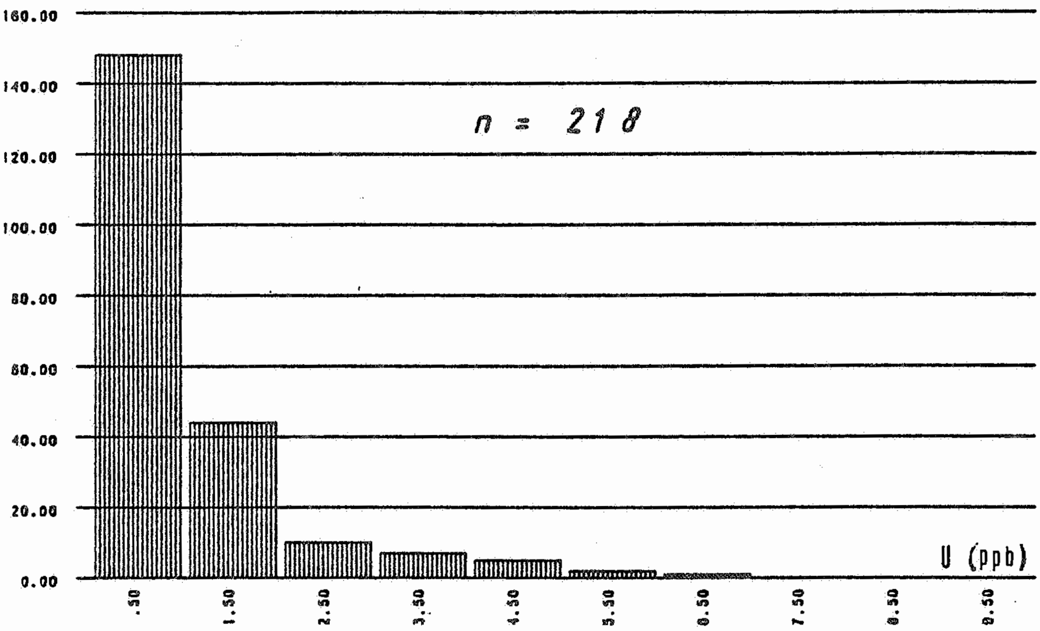


FIG 29 URANIUM

U/SOURCES

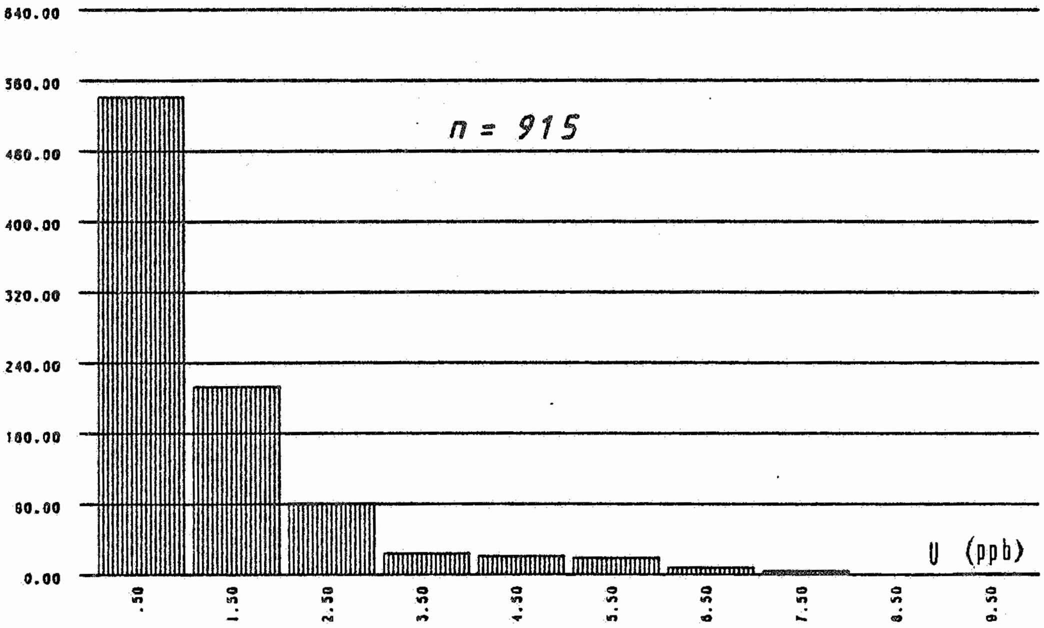


FIG. 30 URANIUM

U/RIVIERES

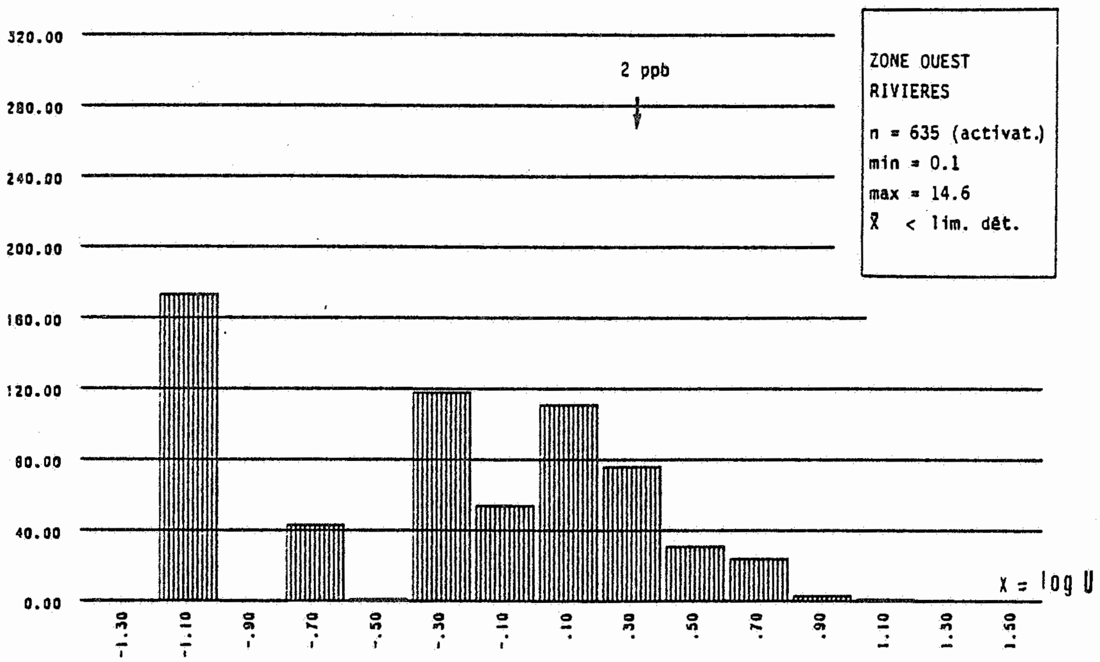


FIG. 31 LOG URANIUM (ppb)

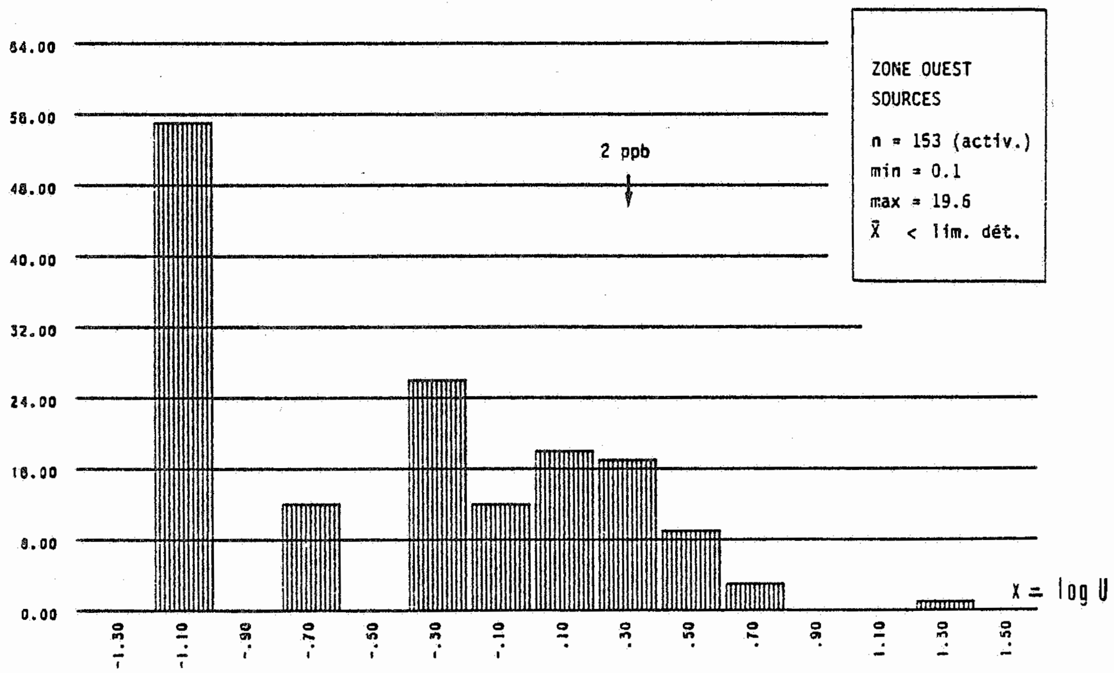


FIG. 32 LOG URANIUM (ppb)

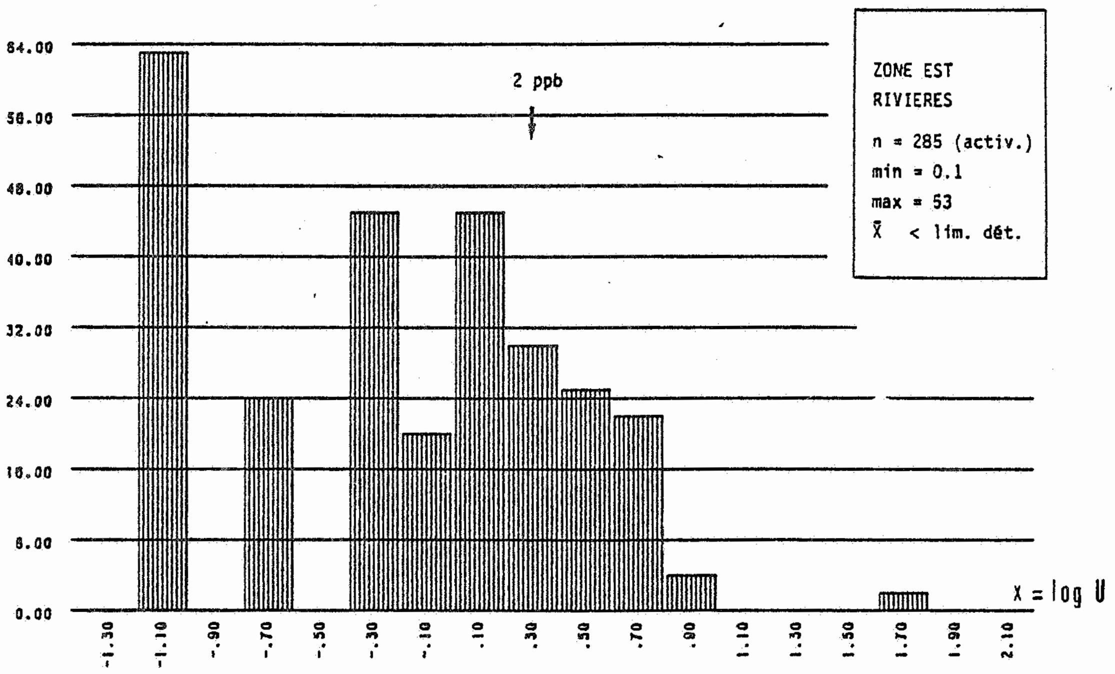


FIG. 33 LOG URANIUM (ppb)

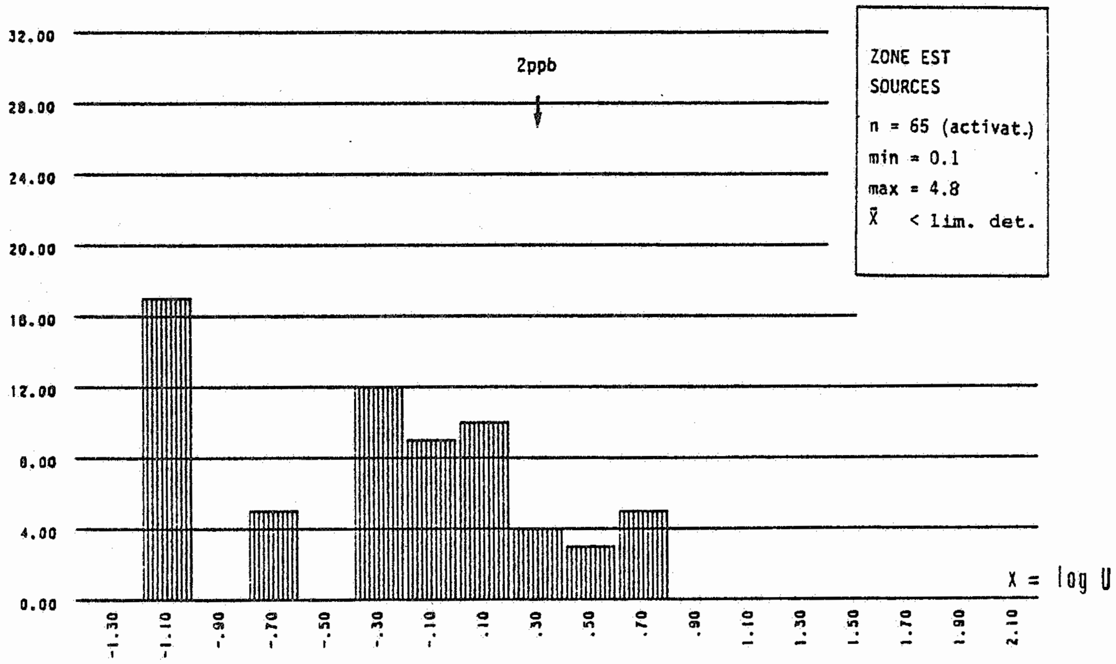


FIG. 34 LOG URANIUM (ppb)

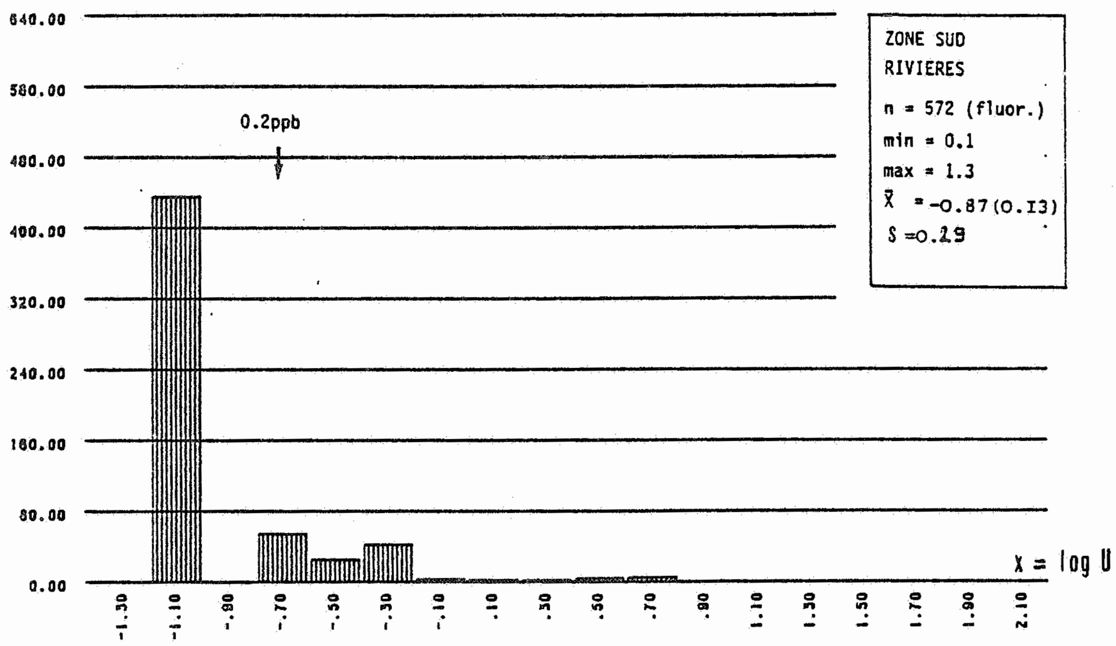


FIG. 35 LOG URANIUM (ppb)

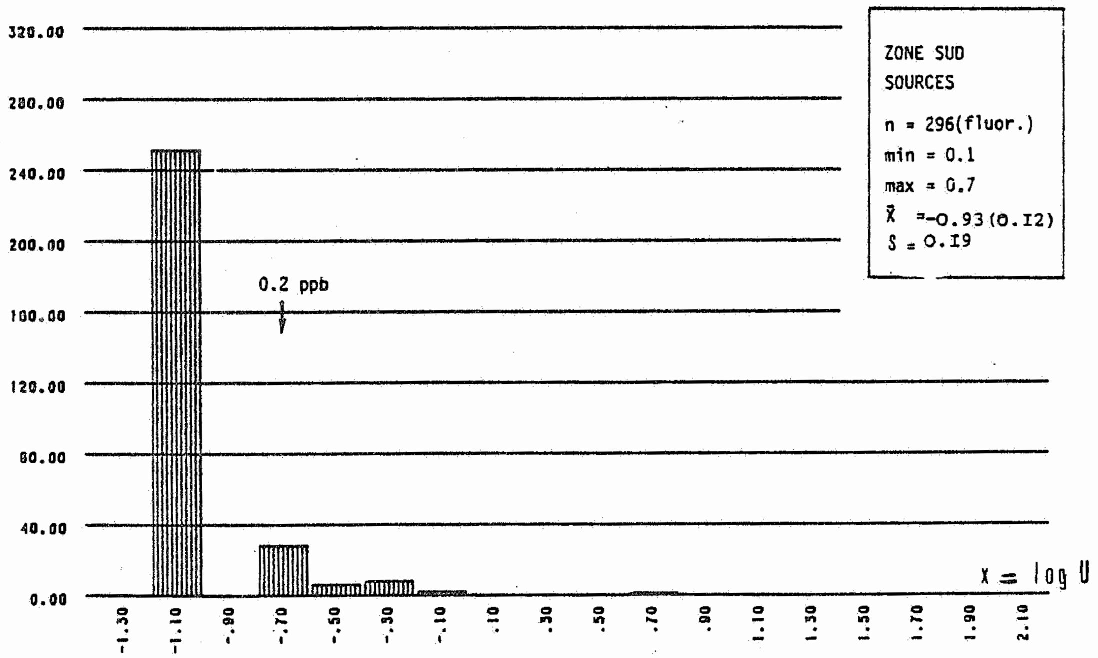


FIG. 36 LOG URANIUM (ppb)

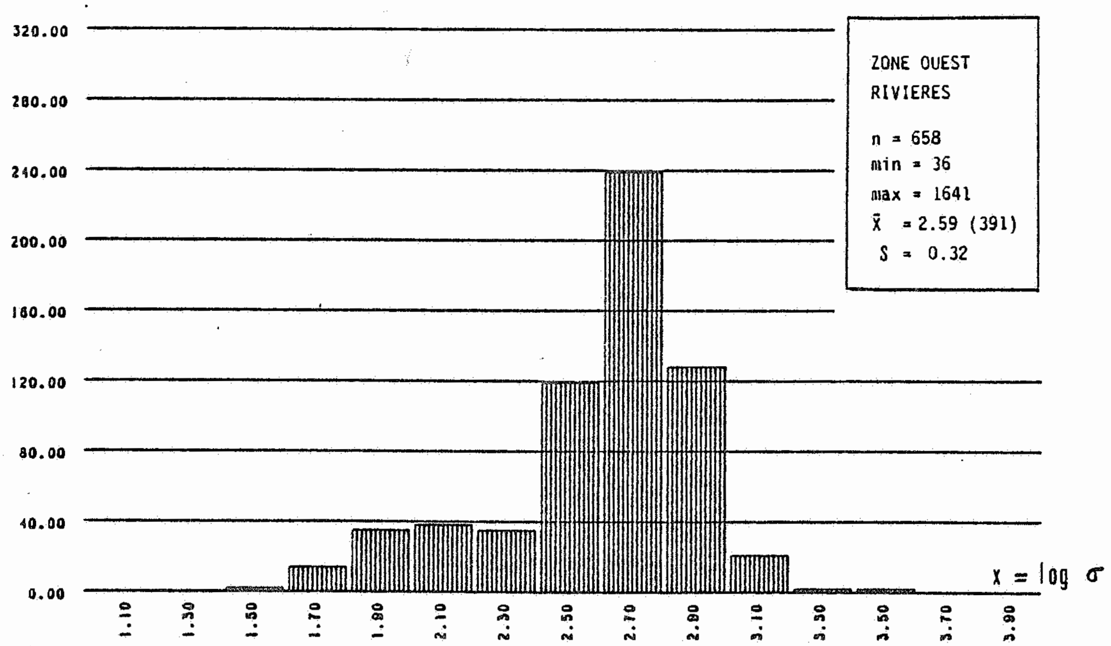


FIG. 37 LOG CONDUCTIVITE (μs/cm)

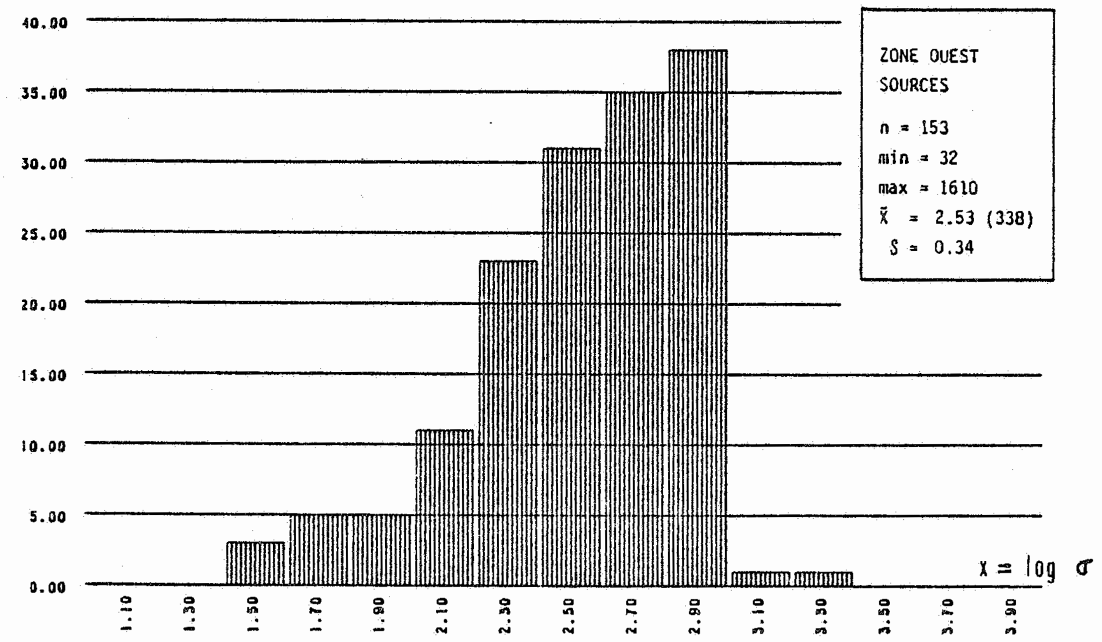


FIG. 38 LOG CONDUCTIVITE (μs/cm)

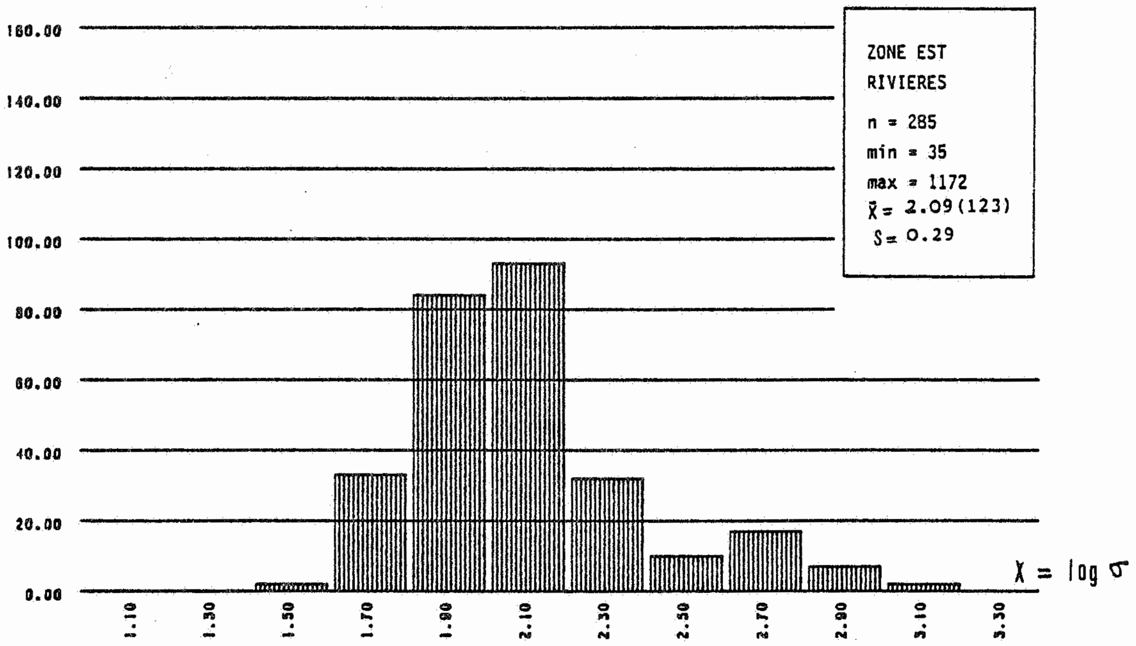


FIG. 39 LOG CONDUCTIVITE (μs/cm)

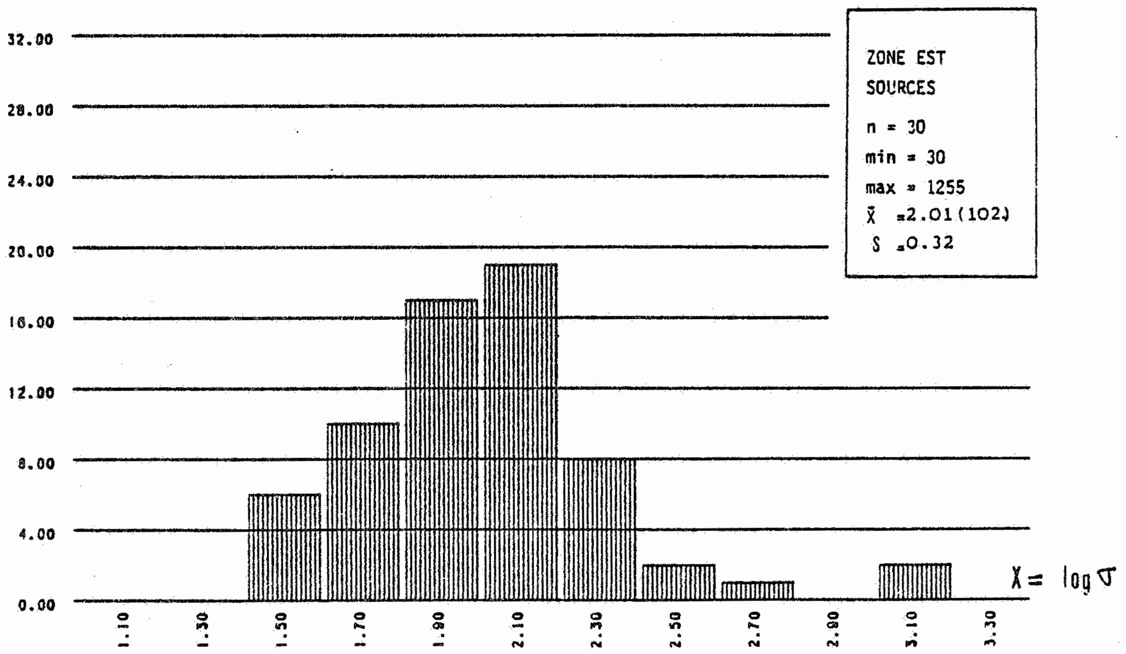


FIG. 40 LOG CONDUCTIVITE (μs/cm)

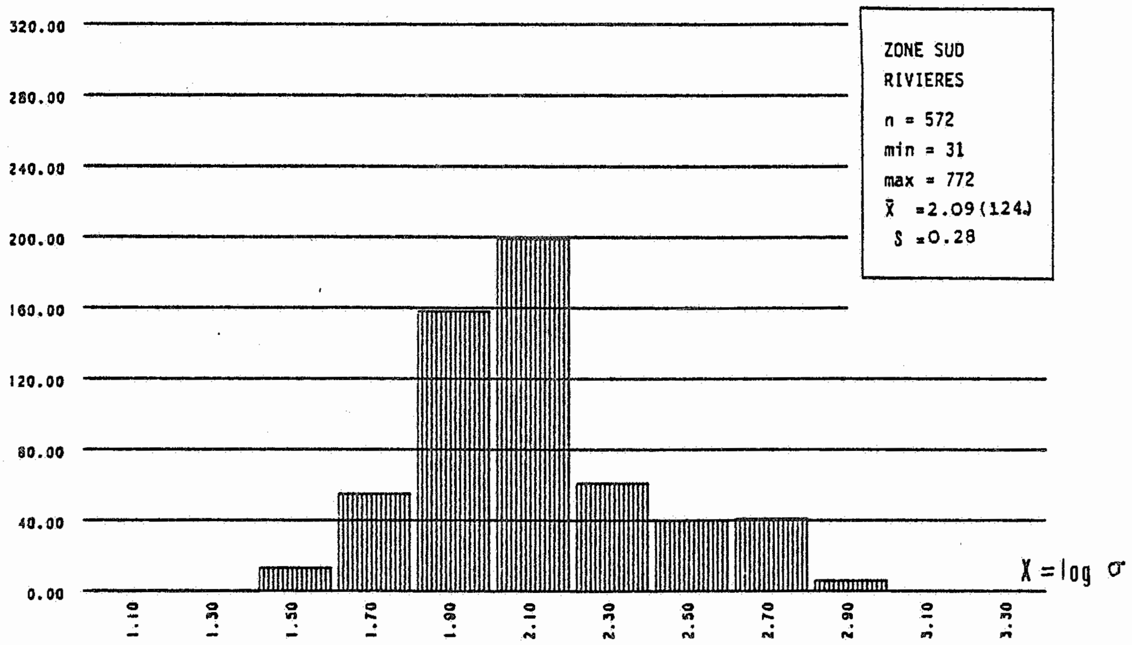


FIG. 41 LOG CONDUCTIVITE (µs/cm)

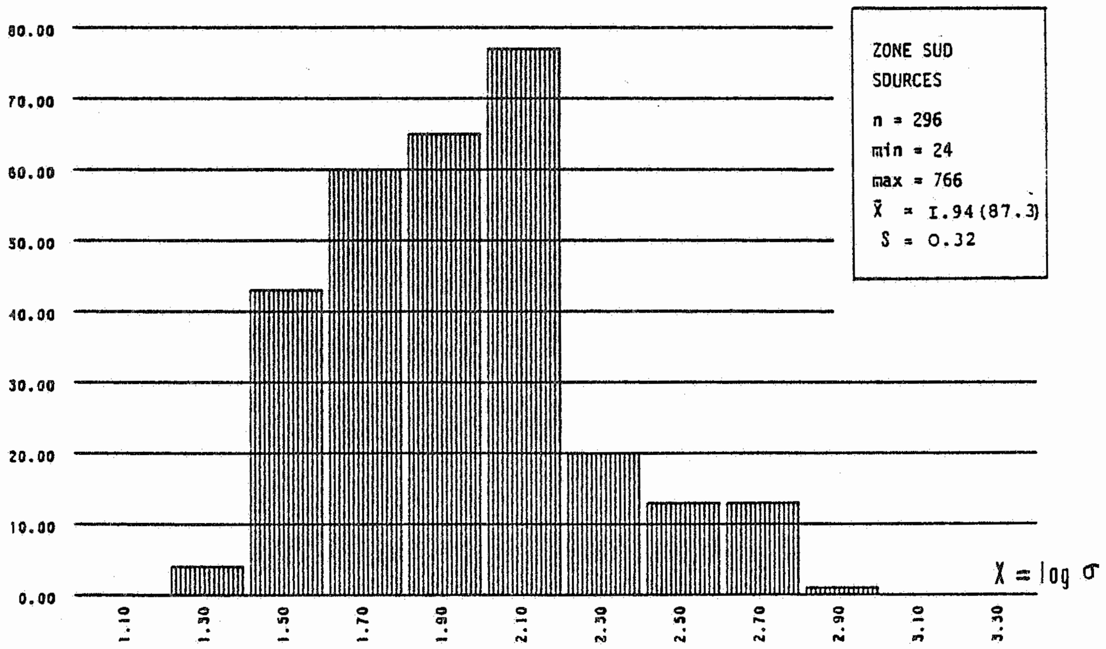


FIG. 42 LOG CONDUCTIVITE (µs/cm)

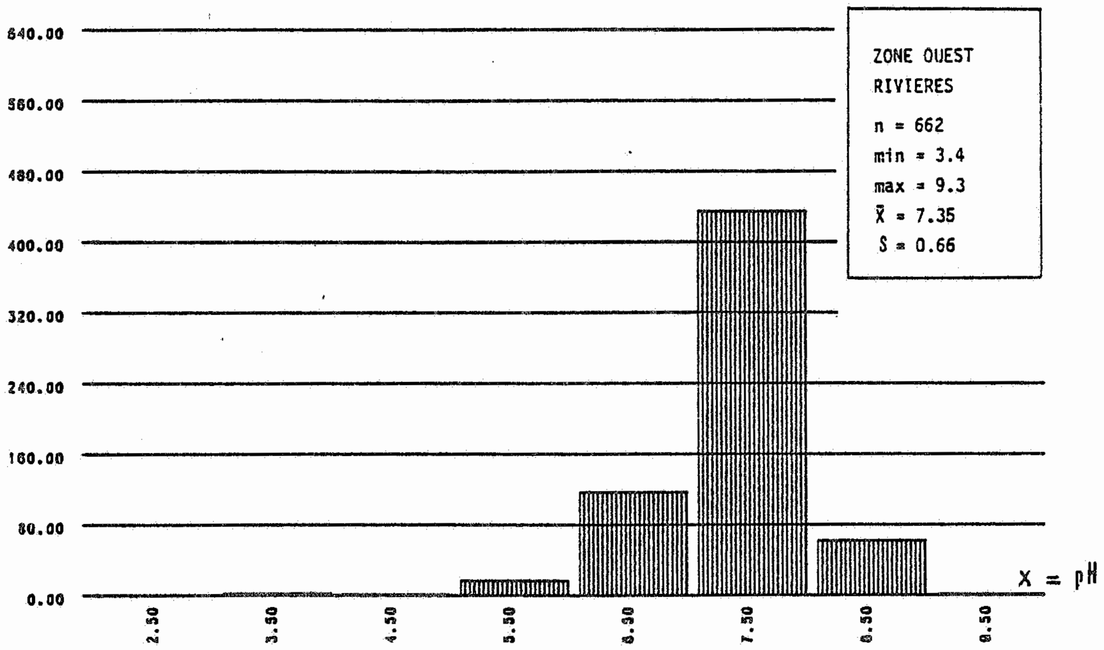


FIG. 43 pH

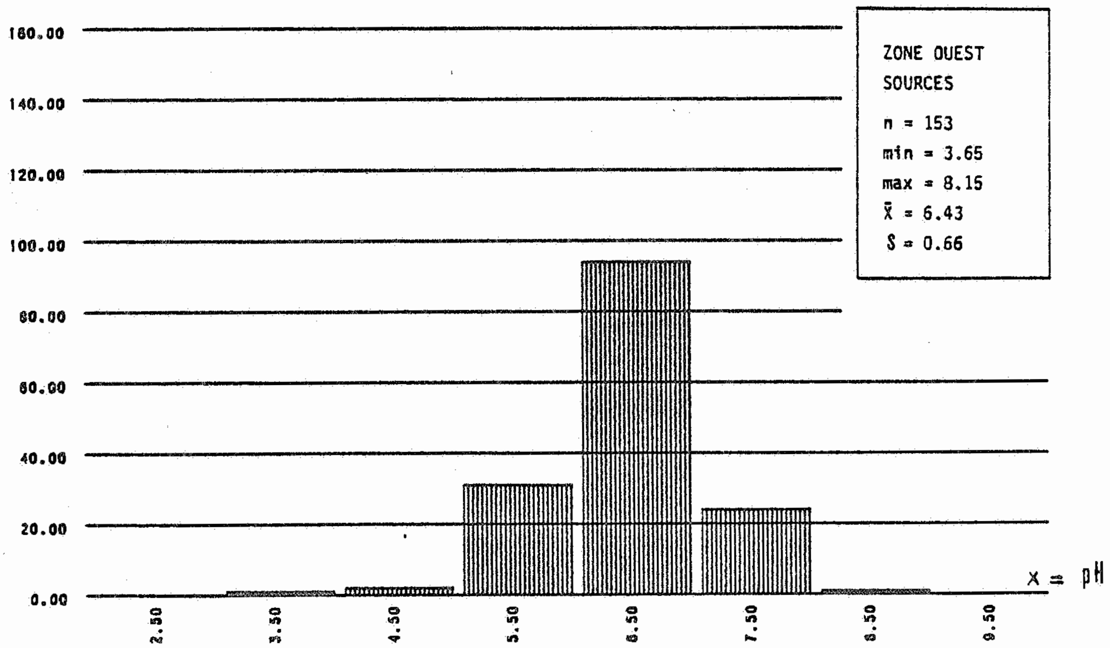


FIG. 44 pH

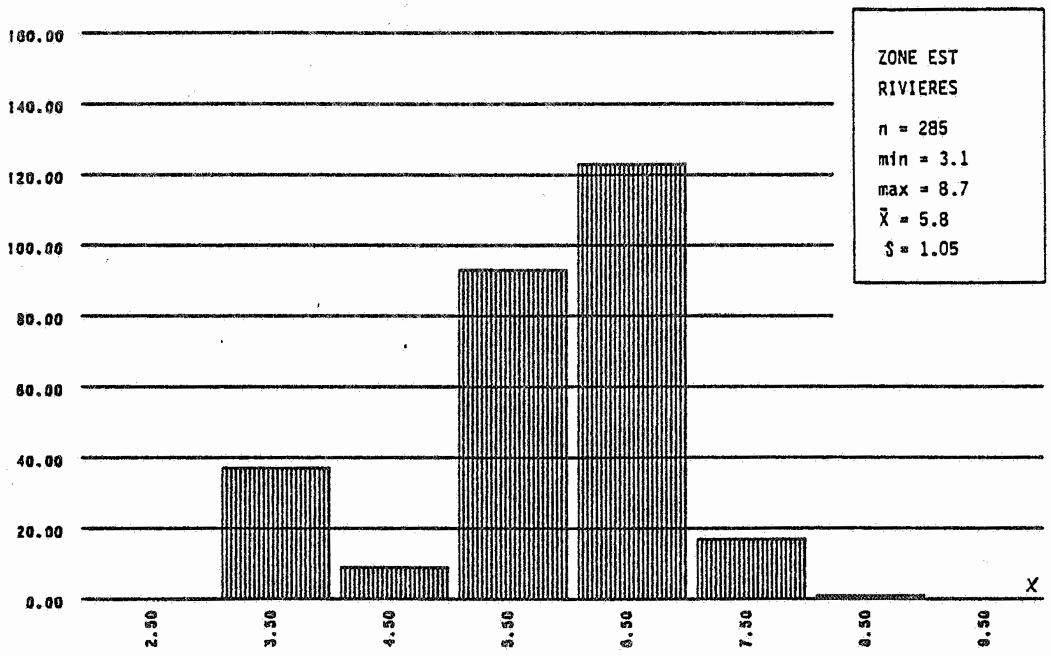


FIG. 45 pH

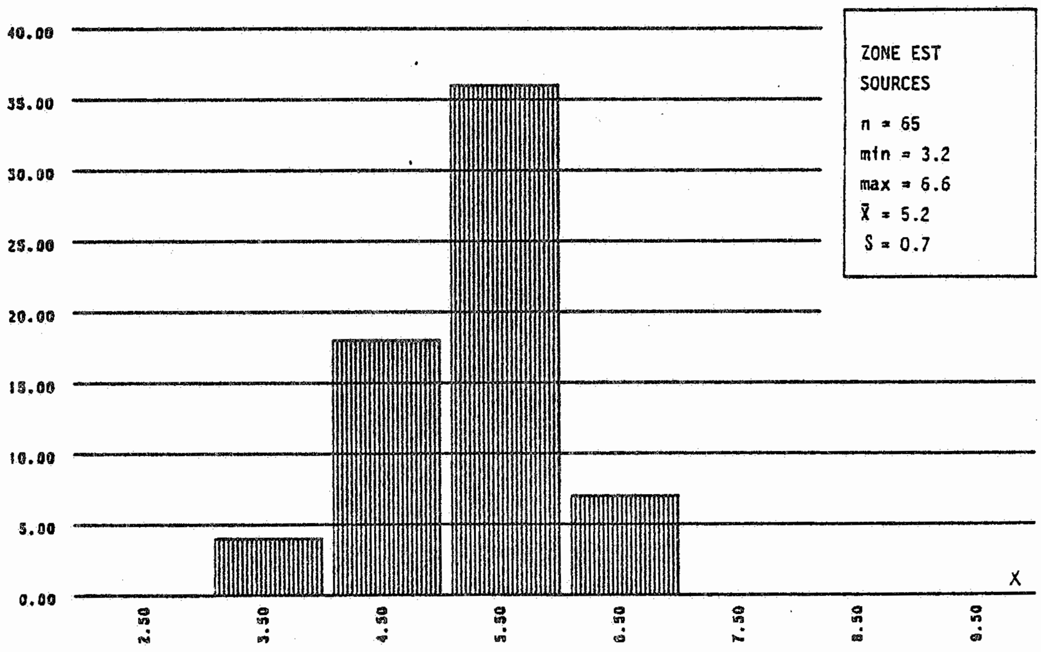


FIG. 46 pH

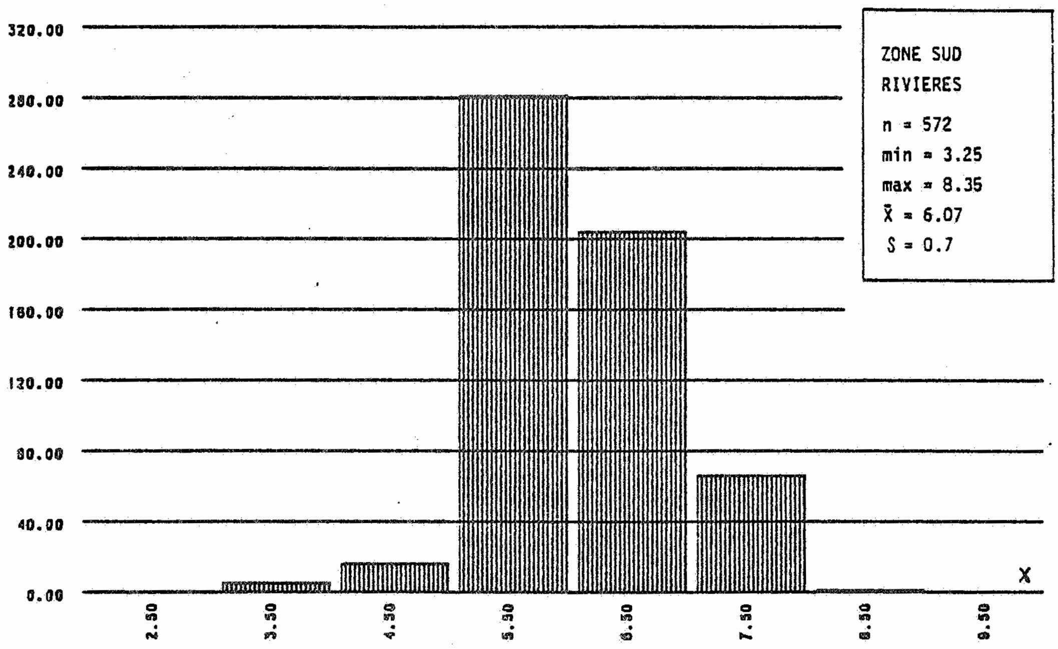


FIG. 47 pH

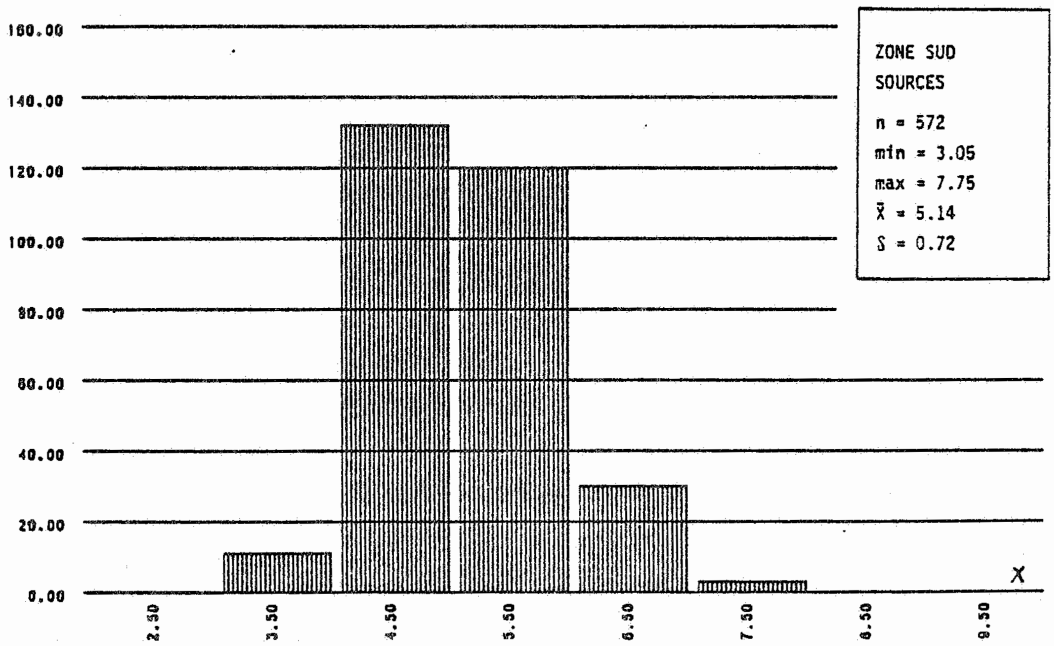


FIG.48 pH

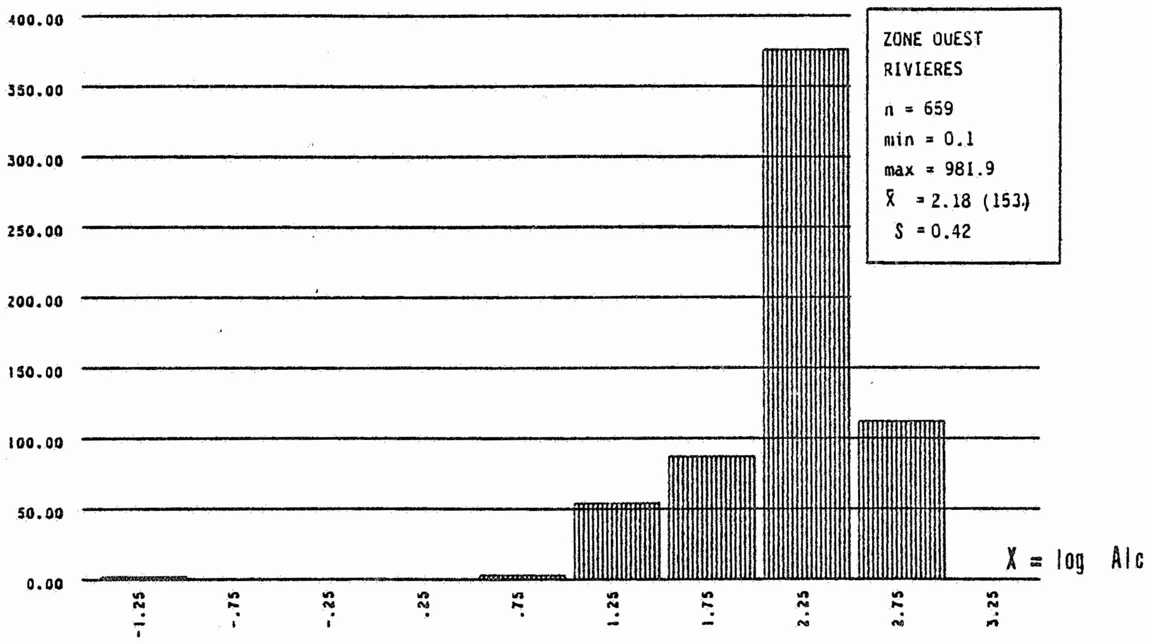


FIG. 49 LOG ALCALINITE (mg/L)

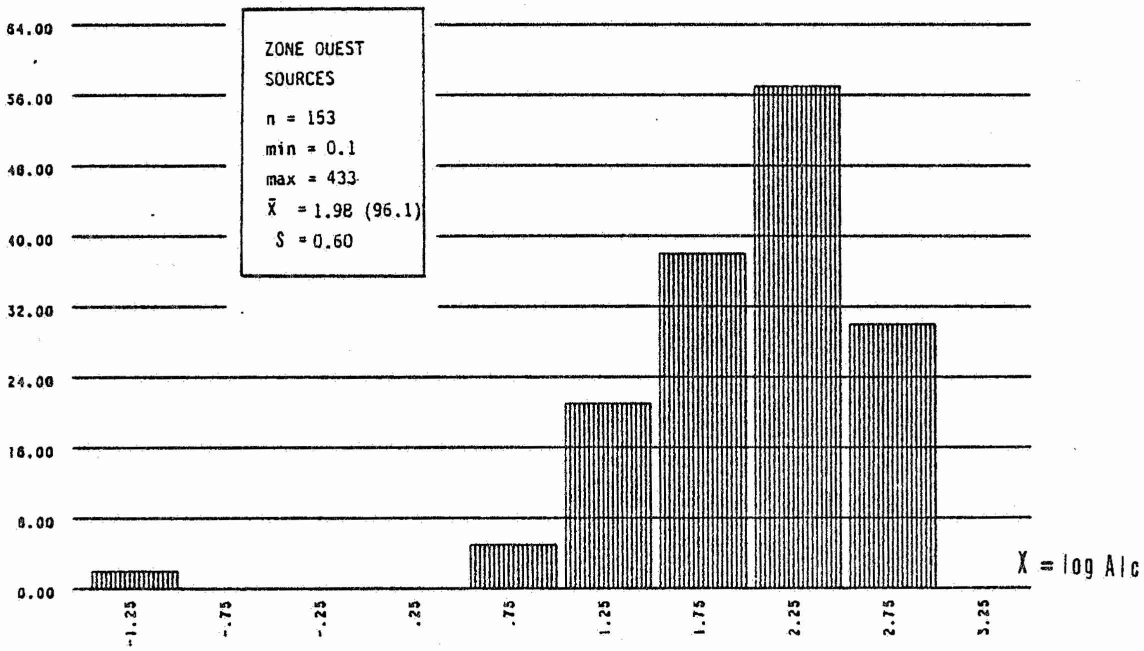


FIG. 50 LOG ALCALINITE (mg/L)

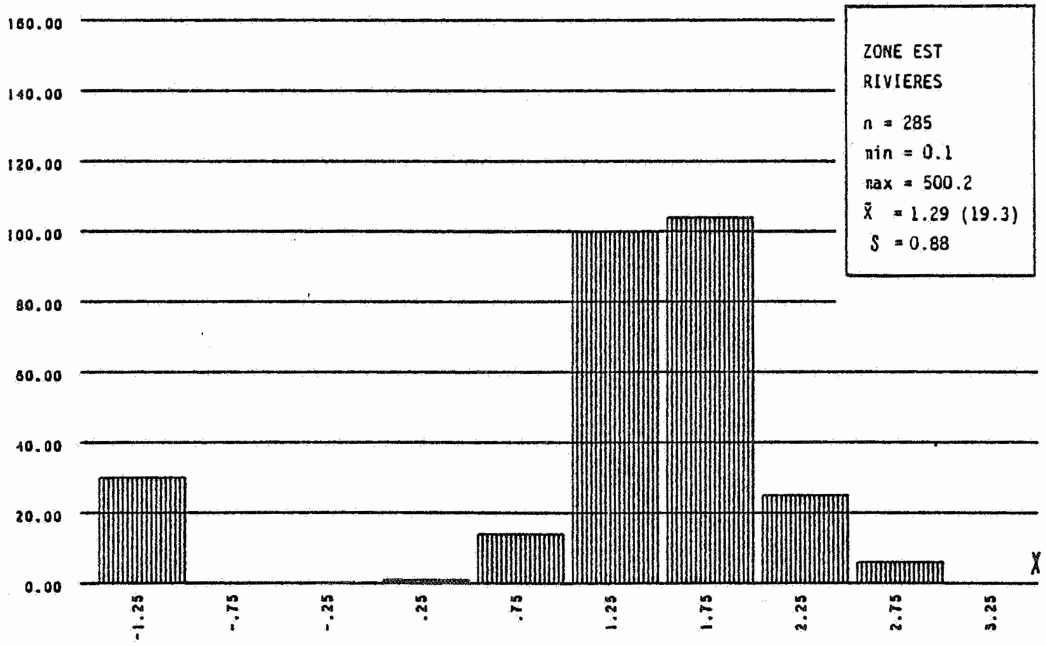


FIG. 51 LOG ALCALINITE (mg/L)

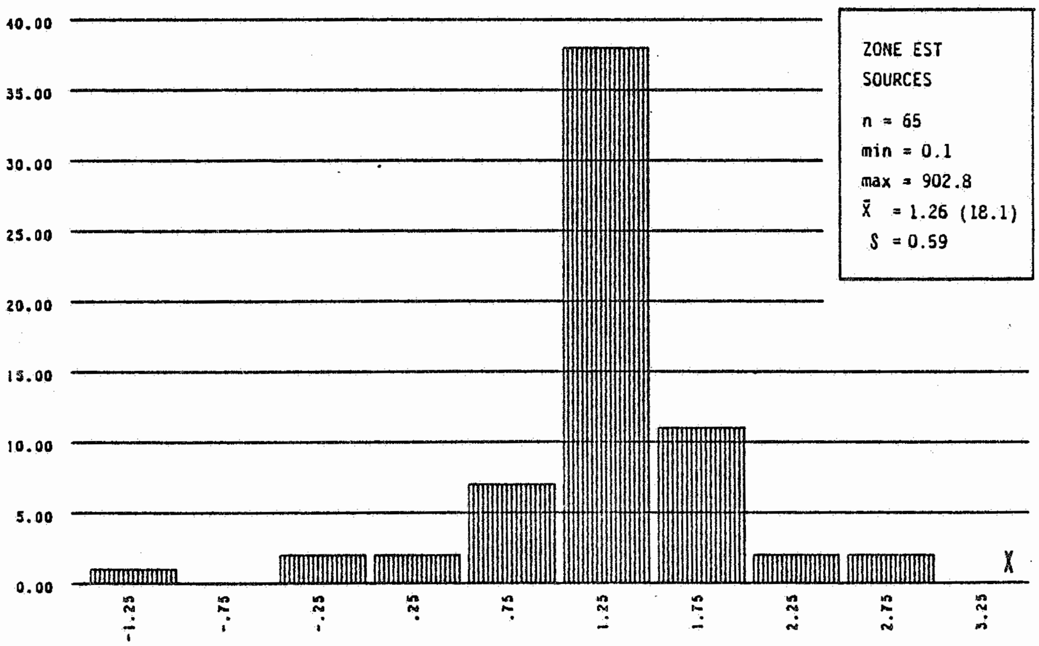


FIG.52 LOG ALCALINITE (mg/L)

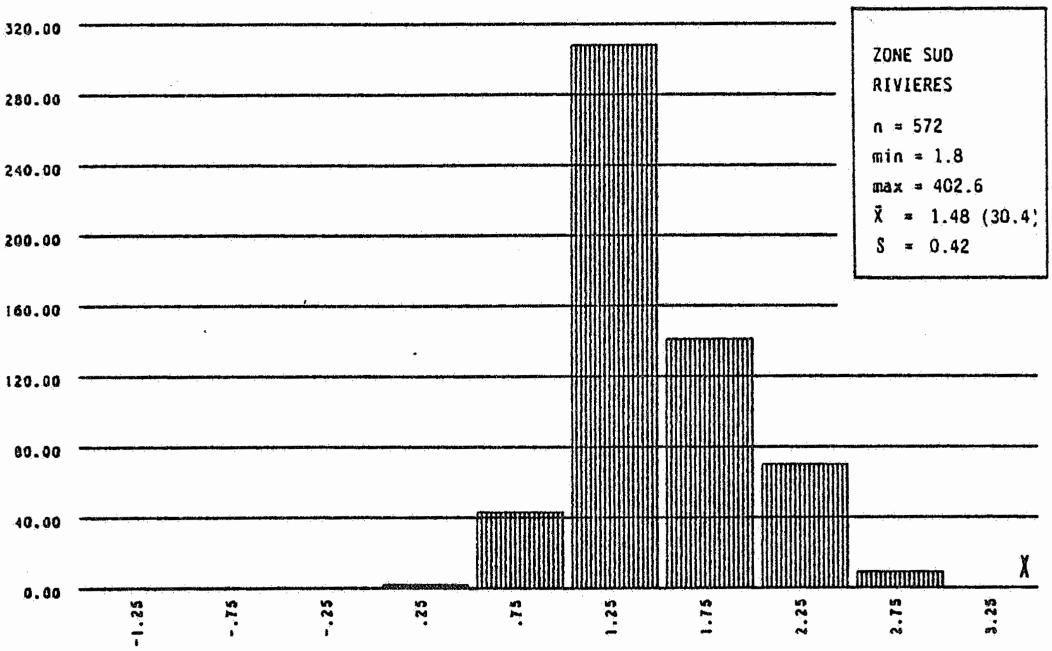


FIG. 53 LOG ALCALINITE (mg/L)

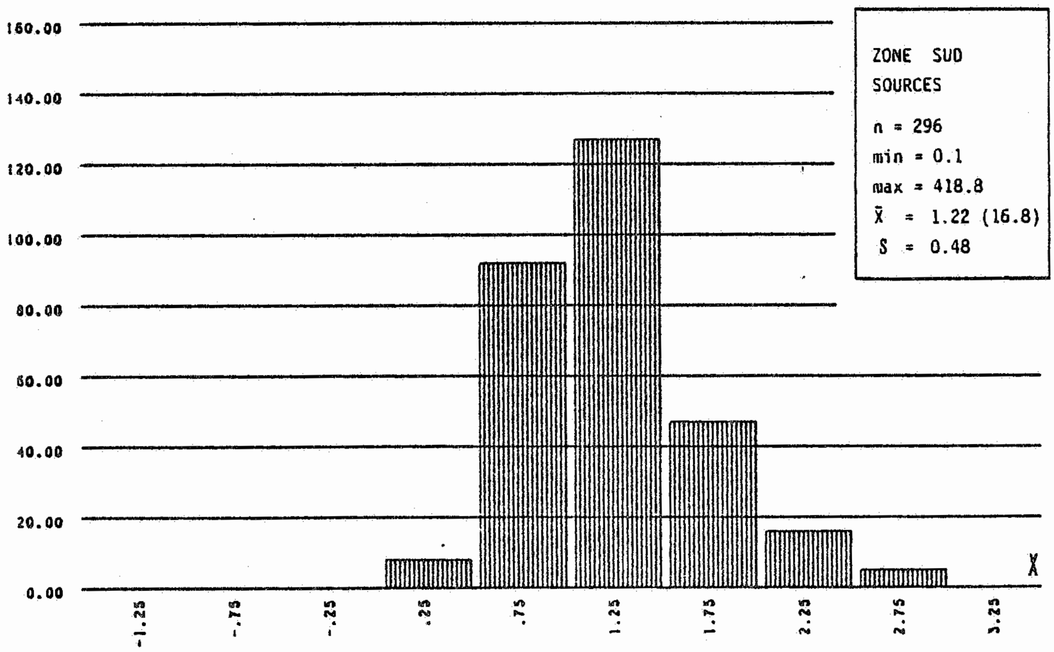


FIG. 54 LOG ALCALINITE (mg/L)

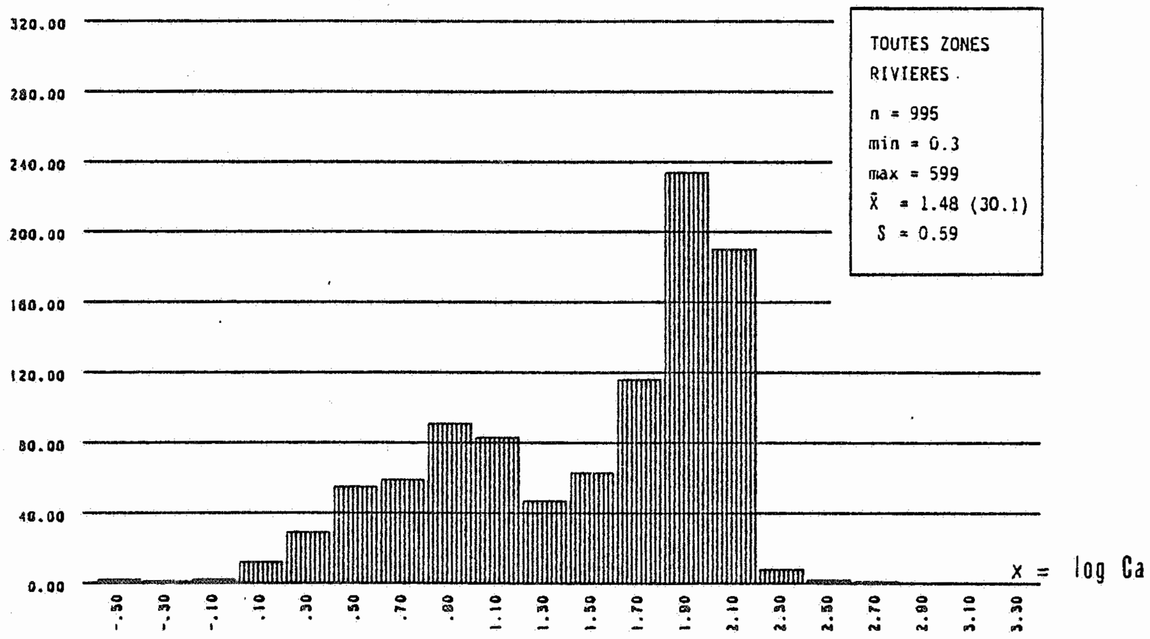


FIG. 55 LOG CALCIUM (ppm)

CA-RIVIERES

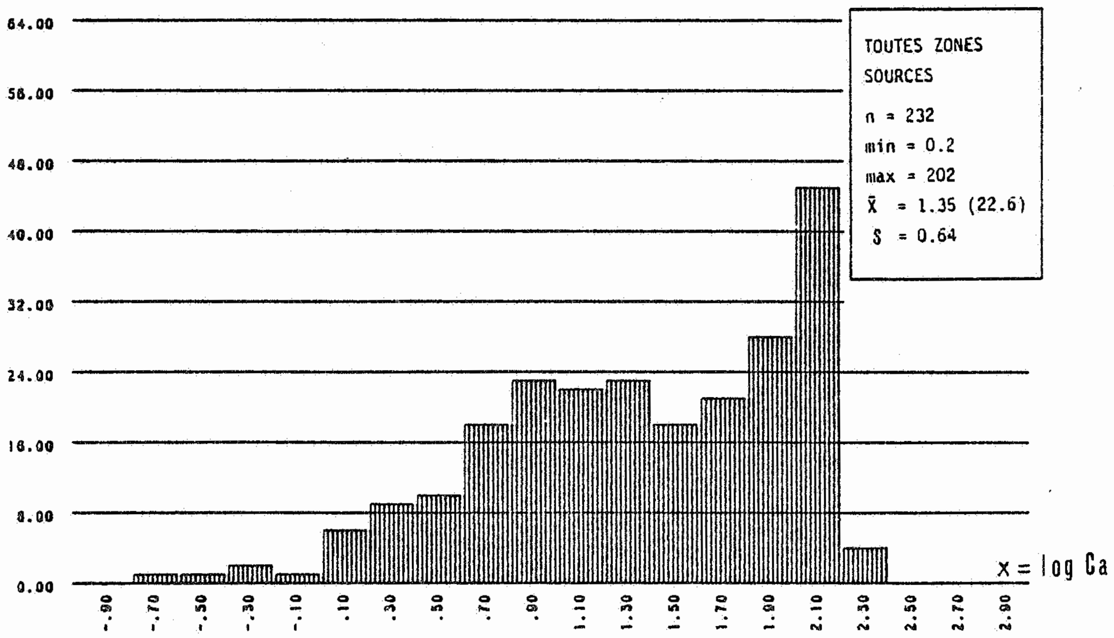


FIG. 56 LOG CALCIUM (ppm)

CA-SOURCES

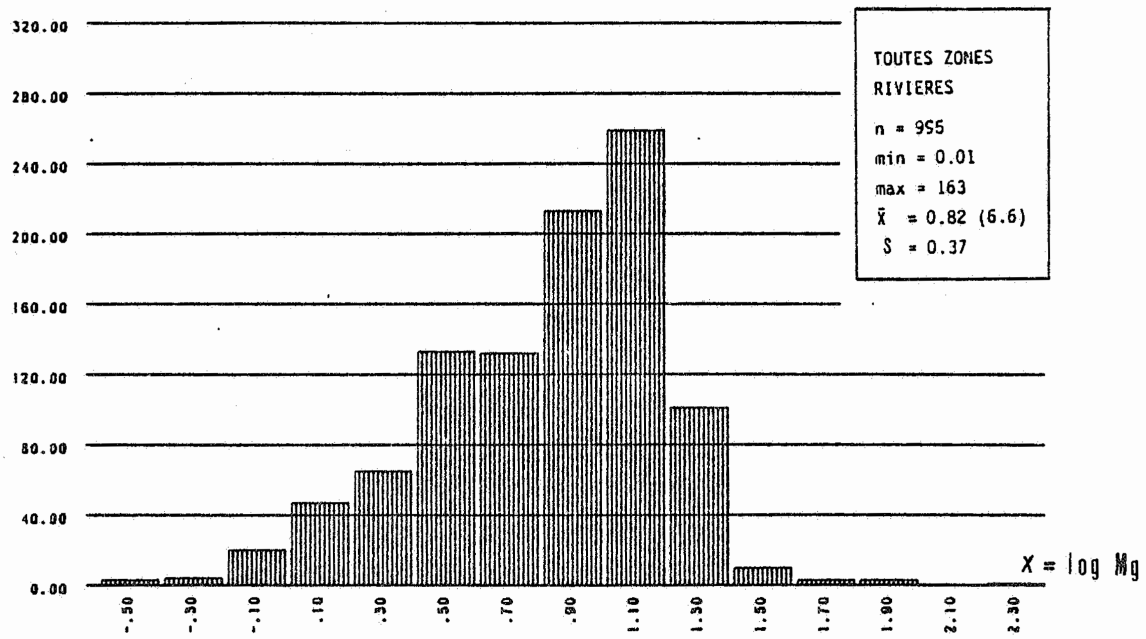


FIG. 57 LOG MAGNESIUM (ppm)

MG-RIVIERES

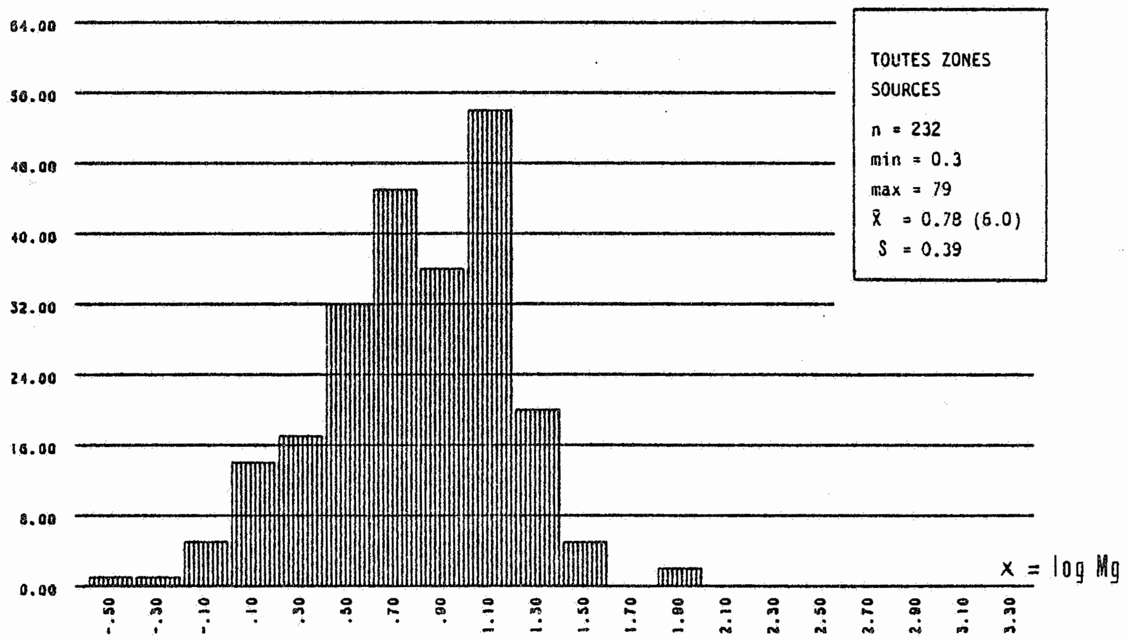


FIG. 58 LOG MAGNESIUM (ppm)

MG-SOURCES

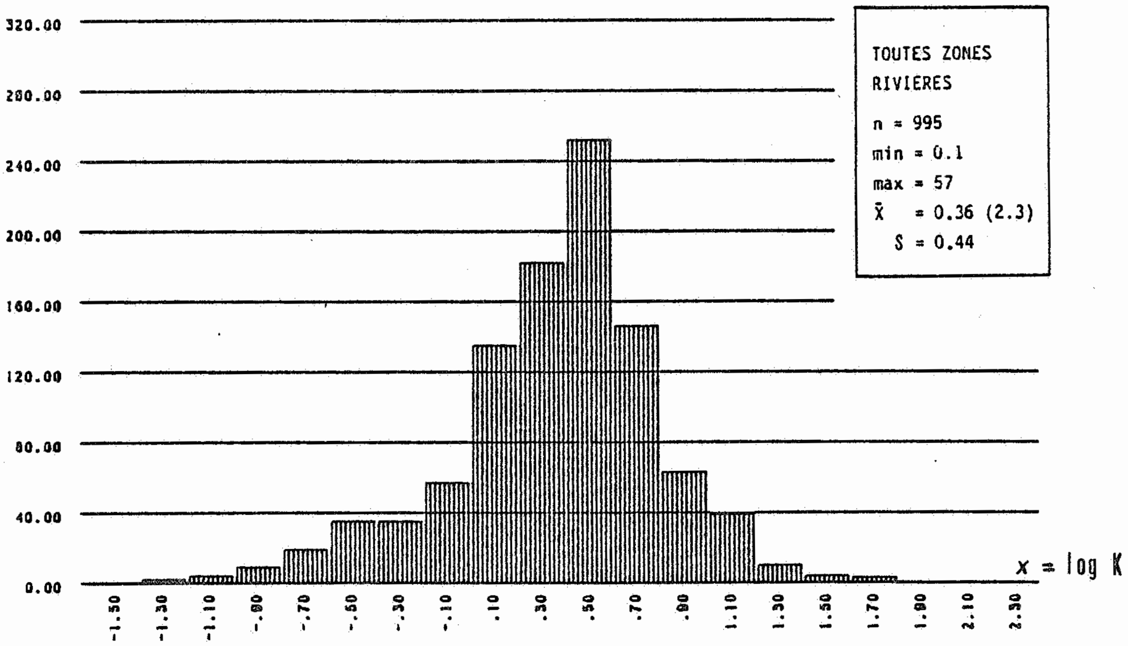


FIG. 59 LOG POTASSIUM (ppm)

K-RIVIERES

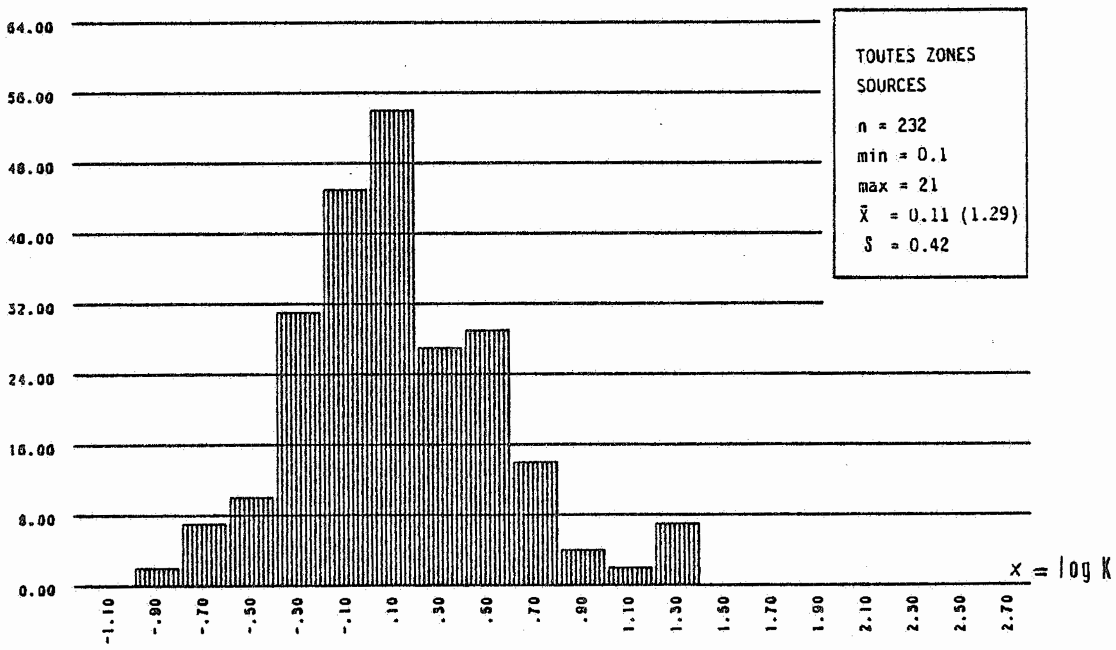


FIG. 60 LOG POTASSIUM (ppm)

K-SOURCES

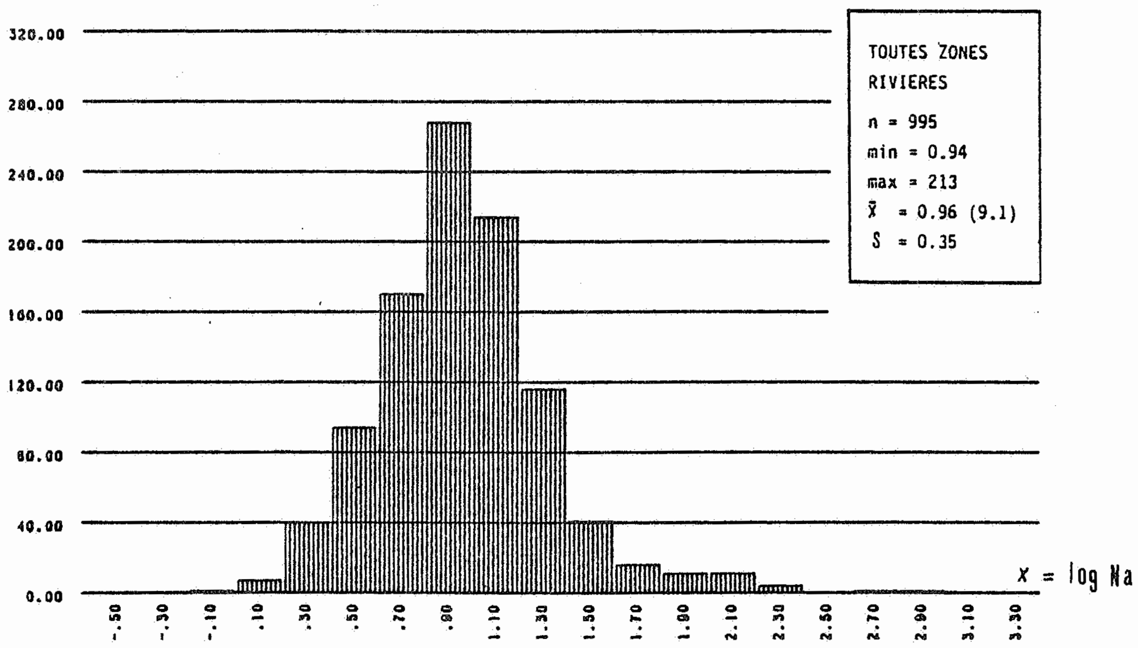


FIG. 61. LOG SODIUM (ppm)

NA-RIVIERES

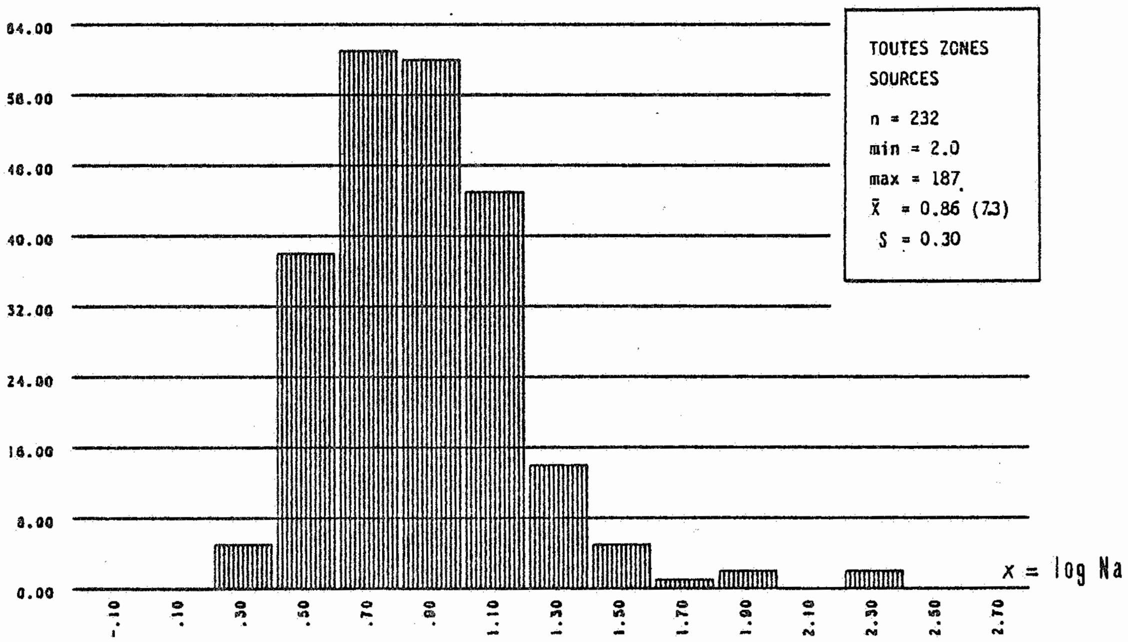


FIG. 62 LOG SODIUM (ppm)

NA-SOURCES

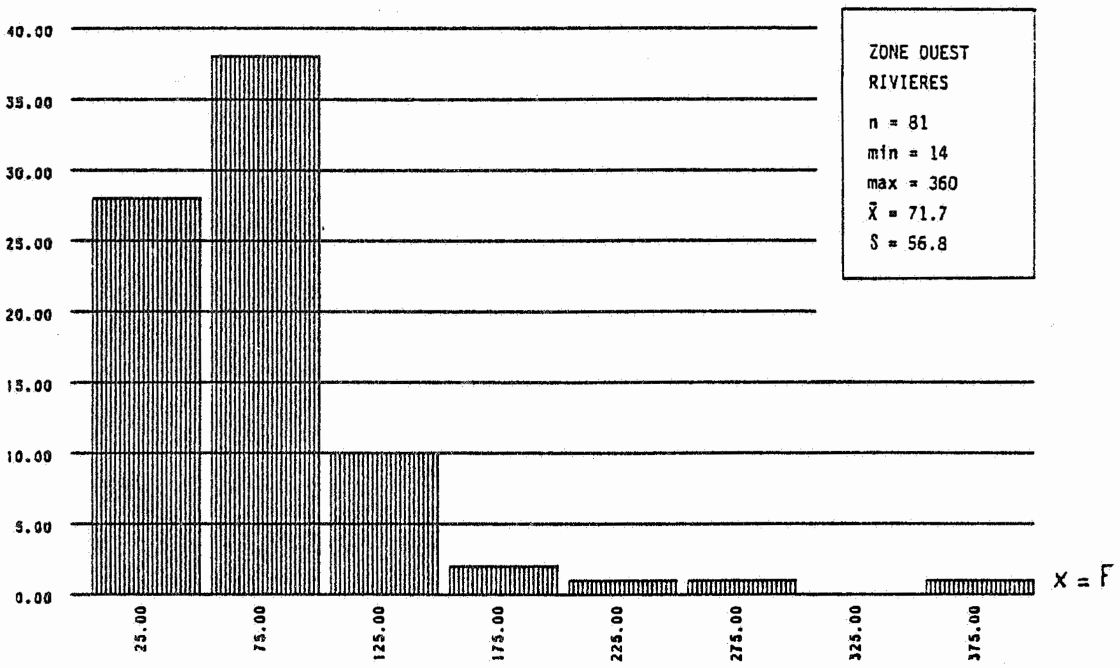


FIG. 63 FLUOR (ppb)

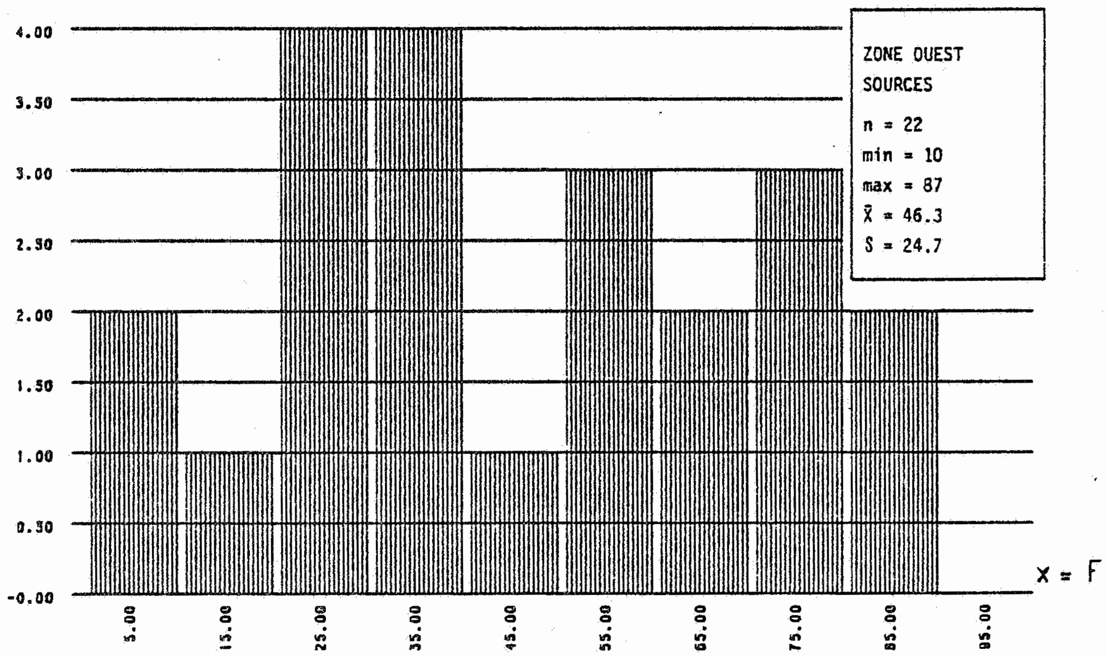


FIG. 64 FLUOR (ppb)

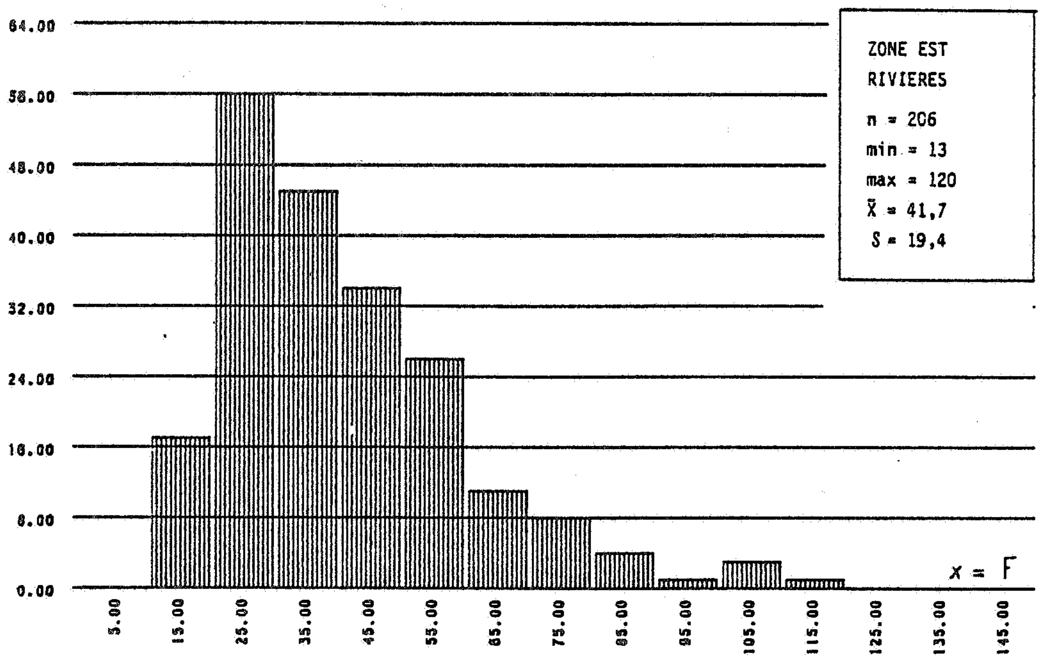


FIG. 65 FLUOR (ppb)

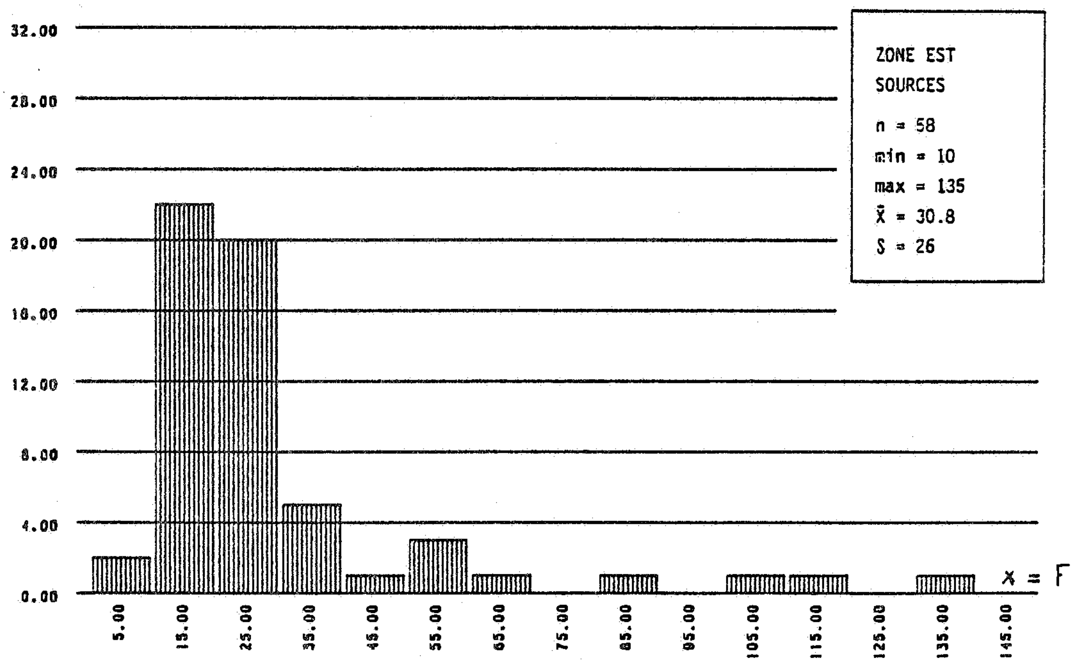


FIG. 66 FLUOR (ppb)

III. 7. PRELIMINARY INTERPRETATION

Strictly speaking, the results of the hydrogeochemical prospection of the Belgian Paleozoic as presented in the previous chapter must be interpreted in conjunction with those of the stream sediment geochemical prospection and of the carborne scintillometric prospection (cf. Chapter V).

This does not rule out the possibility of making, at this stage, a certain number of essentially descriptive preliminary interpretations.

III. 7. 1. *Mean uranium contents of the waters*

From the histograms of the samples analysed for uranium by neutron activation (fig. 29 and 30), it is clear that the arithmetic mean is below the detection limit of 2 ppb ($\bar{x}$ springs = 1.02 ppb; $\bar{x}$ rivers = 1.30 ppb; meaningless values since in 9 cases out of 10, they are calculated from random numbers). This is even more true for the geometric mean which gives a better estimate of the median tendency for distributions with such a distinct skewness towards the left (cf. histograms of logarithmic values, fig. 31 to 34).

The same goes for histograms of the samples analysed by fluorimetry (fig. 35 and 36), although in this case the detection limit is ten times lower (0.20 ppb).

These histograms also show that the mean uranium contents of the stream and river waters are not significantly different from one another.

Taking into account the probable underestimation of the values for the samples analysed by fluorimetry (problem of loss, cf. III.3.3.b), it may be considered that the mean uranium contents of the river and spring waters from the Belgian Paleozoic are between 0.2 and 2 ppb, and most likely closer to 0.2 ppb.

This conclusion is in perfect agreement with data from the literature for "normal" river waters whose contents in uranium fall between 0.1 and 1 ppb (39, 48).

III. 7. 2. *Anomalous uranium values of the waters*

Although the notions of background and anomaly in the geochemistry of waters are difficult to define rigorously, and have only a relative meaning (40), we could, basing ourselves on the discussions in the previous paragraph, consider values greater than 2 ppb to be certainly anomalous.

It seems, however, that in the region analysed by fluorimetry (central zone, fig. 28), it would be of interest to take a much lower anomaly threshold, considering the greater sensitivity of the analytical method.

Temporarily considered as anomalous are :

- values greater than 2 ppb for results obtained by neutron activation;
- values greater than 1 ppb for results obtained by fluorimetry.

From the histograms of the distribution of uranium, it can be seen that, taking into account the adopted thresholds, the number of samples with anomalous values in uranium is clearly higher for the analysis by activation than for that by fluorimetry : 10 % of the samples have values that exceed 2 ppb, whereas for fluorimetry, only 1.2 % of the samples exceed 1 ppb.

This difference could be attributed to the geology, but it seems more realistic to attribute it to a bad choice of the anomaly threshold for the results of the fluorimetric analyses. The value would rather be around 0.5 ppb, which was used in the preparation of the summary map (map VII).

This summary map gives the geographical repartition of all the anomalous values as previously defined (thresholds of 2 ppb or 0.5 ppb depending on the zone), as well as contour-lines corresponding to 2 and 5 ppb. This latter presentation, whose validity is questionable, owing to the lack of homogeneity in the analytical methods, has the sole aim of better accentuating the anomalous zones. Moreover, from the size of the points, two classes of anomalous values can be distinguished :

- values from fluorimetry and neutron activation greater than 2 ppb;
- values from fluorimetry greater than 0.5 ppb.

This summary map thus enables the differentiation at first sight of the morphology and intensity of the anomalous zones.

III. 7. 3. *Description of the anomalous zones*

In the eastern zone analysed by activation, four anomalous zones can be distinguished :

- anomalous zone A : straddling the eastern margin of the massive of Stavelot, this zone of about 100 km^2 contains 35 samples with 2-5 ppb and 4 samples with 5-10 ppb of uranium. It is constituted of Devonian (Gd, Si, Em) and Cambro-Ordovician (Revinian, Salmian) terranes.
- anomalous zone B : situated at the south-east of the massive of Stavelot at the edge of the German border, this zone, which is more restricted, contains two samples with 10 ppb, 9 samples with 5-10 ppb and 4 samples with 2-5 ppb. It is the highest anomaly encountered and occurs within the Gedinnian and the Siegenian.
- anomalous zone C : is situated at the south of the massive of Stavelot, a short distance from anomalous zone B, with which it is likely associated. It occurs in the Siegenian.
- anomalous zone D : situated at the north-west margin of the massive of Stavelot ("fenêtre de Theux"), this restricted zone contains 8 samples with 2-5 ppb and 4 samples with 5-10 ppb, which represents a high density of anomalies. The anomaly is remarkably centered around a Salmian syncline.

These four zones can clearly be seen in map VII.

In the western zone, also analysed by activation, the Entre-Sambre-et-Meuse is characterised by a very low density of anomalies except in its northern part :

- anomalous zone E : situated along the Sambre from the French border as far as Namur and then to the north of the Meuse (valley of the Mehaigne), this rather large zone is poorly defined. The anomalies are dispersed and of low intensity. It likely corresponds to the Carboniferous terranes of the synclinorium of Namur.
- anomalous zone F : situated east of the projection of Givet, this diffuse zone contains 4 samples with 5-10 ppb and 6 samples with 2-5 ppb. It consists in fact of several small anomalies in Lower and Middle Devonian terranes (Siegenian to Famennian).

In the central zone analysed by fluorimetry, three anomalous zones can be observed from north to south :

- anomalous zone G : situated at the west and the north-west of Liège, this anomaly is very intense : 14 samples with values greater than 2 ppb. It corresponds to the terranes with Cretaceous overburden.
- anomalous zone H : this zone forms a large band of north-east/ south-west direction that extends from the north-east of Liège towards Dinant but does not continue into the Entre-Sambre-et-Meuse. It yields 50 samples with 1-2 ppb and a greater number of samples with 0.5-1 ppb. It disappears towards the west beyond the Meuse where the analyses were carried out by activation (lack of sensitivity ?). This is the largest of the anomalous zones encountered and corresponds to the central part of the synclinorium of Dinant and of the Vesdre-Herve massifs.
- anomalous zone I : is situated at the extreme south of the prospected zone and corresponds to the Upper Triassic overburden in the south of Belgium.

III. 7. 4. *Fluorine*

Halfway through the campaign, and in view of the first results showing zones anomalous in uranium in the eastern part of the country, it was decided to carry out analyses for fluorine for trial purposes. Two geologically different zones were chosen for these trials (fig. 67) :

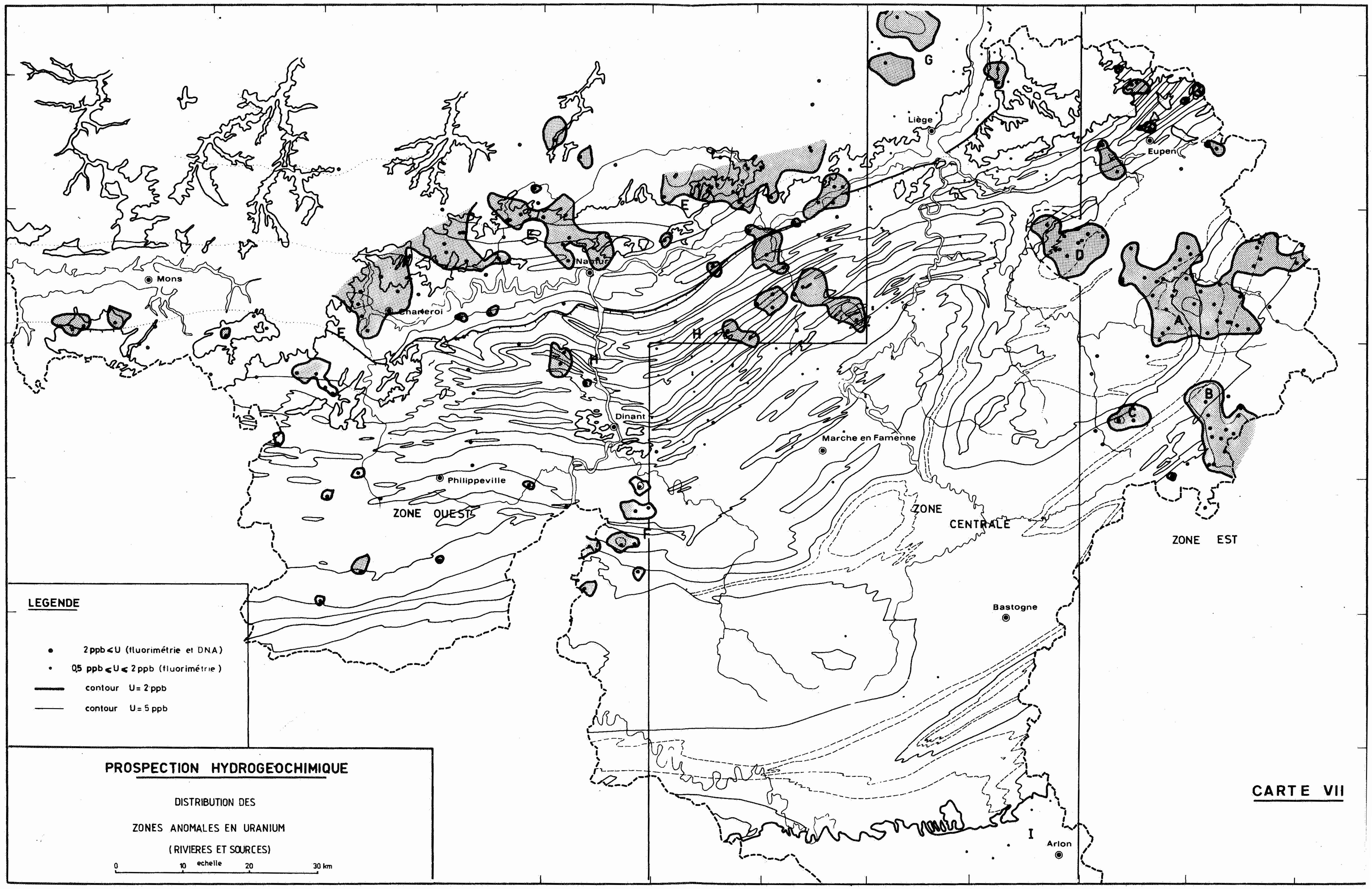
- the massive of Stavelot with an essentially silicate lithology and presenting some anomalies in uranium;
- the southern margin of the synclinorium of Dinant with an essentially carbonate lithology and a low geochemical background in uranium.

The first zone contains 244 samples and the second 103.

Comparison of the histograms for fluorine (fig. 63 to 66), despite their polymodal shape, shows that samples from the calcareous zone are richer in fluorine ($\bar{x}$ = 50-70 ppb) than those from the silicate zone ($\bar{x}$ = 40-50 ppb).

The calculation of Bravais-Pearson coefficients of correlation shows that there is no significant relationship between F and U in the silicate zone ($r = 0.1$). In the carbonate zone, on the contrary, fluorine shows a clear positive correlation with Ca (0.56) and with Mg (0.57). This is not surprising considering the presence of some fluorine mineralisations in the region of Givet.

In such a sedimentary environment as characterises Belgium, fluorine is not an interesting element in the prospection for uranium. On the other hand, it seems interesting in the search for Pb-Zn-Ba ores which are often accompanied by some fluorine.



CARTE VII

PROSPECTION HYDROGEOCHIMIQUE

DISTRIBUTION DES

ZONES ANOMALES EN URANIUM

(RIVIERES ET SOURCES)

LEGENDE

- ● 2 ppb < U (fluorimétrie et DNA)
- • 0,5 ppb ≤ U ≤ 2 ppb (fluorimétrie)
- ━ contour U = 2 ppb
- ─ contour U = 5 ppb

BIBLIOGRAPHY OF CHAPTER III

34) BENSON, L.V. and LEACH, D.L., 1978

Uranium transport in the Walker river basin, california and Nevada.

Journ. Geoch. Expl., 11, 227-248.

35) BERTHOLLET, P., 1968

Méthodes d'analyses utilisées par la section de géochimie : Uranium, Radon, Radium.

Rapport CEA-R-3557, 49 p.

36) BROXTON, D.E., 1978

Uranium Hydrogeochemical and Stream Sediment Reconnaissance in Southwestern Montana.

Los Alamos Scientific Laboratory LA-6981, 94 p.

37) CHARLET, J.M.; DUPUIS, C.; QUINIF, Y., 1977

Perspectives de la prospection de l'uranium à l'échelle nationale.

Annales des Mines de Belgique, 5e livraison, 522-532.

38) DALL'AGLIO, M., 1972

Planning and interpretation criteria in hydrogeochemical prospecting for uranium.

Uranium Prospecting Handbook, 121-133.
The Institution of Mining and Metallurgy, 346 p.

39) FLEICHER, M., 1963

Data of geochemistry.

Geol. Survey Prof. Papers, 440-G.

40) GRANIER, Cl., 1973

Introduction à la prospection géochimique des gîtes métallifères.

Mason et Cie, 143 p.

41) GRIMBERT, A., 1972

Use of geochemical techniques in uranium prospecting.

Uranium Prospecting Handbook, 110-119.
The Institution of Mining and Metallurgy, 346 p.

42) HERBOSCH, A.; DE WITTE, S-M.; PREAT, A., 1979

Recherches sur les indices de minéralisations uranifères dans la région de Visé.

Prof. Paper n° 162, 90 p.

43) HOSTLE, D.; COLEMAN, R-F.; and BALL, T.K., 1972

Neutron activation analysis as an aid to geochemical prospecting for uranium.

Uranium Prospecting Handbook, 95-107.
The Institution of Mining and Metallurgy, 346 p.

44) LANGMUIR, D., 1978

Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits.

Geochimica et Cosmochimica Acta, 42, 547-569.

45) LORRAIN, 1974

Contribution à l'étude des glaces basales du glacier d'Argentière - Approche d'un problème géomorphologique par des méthodes chimiques.

Thèse de doctorat inédite, Université Libre de Bruxelles, 185 p.

46) PRICE, V. and JONES, P.L., 1979

Training manual for water and sediment geochemical reconnaissance.

Savannah River Laboratory NURE program DPST-79-219, 103 p.

47) WENRICH-VERBEEK, K.J., 1977

Uranium and coexisting elements behaviour in surface waters and associated sediements with varied sampling techniques used for uranium exploration.

Journal Geoch. Expl., 8, 337-355.

48) WEDEPOHL, K.H., 1972

Handbook of Geochemistry (Chapitre sur l'uranium).

CHAPTER IV

RADIOMETRY

IV. 1. INTRODUCTION

The radiometric survey started effectively in June 1979, after a preparatory phase that lasted six months, and went on with a number of interruptions (due to various technical incidents) until the end of March 1981.

Two university graduates and a driver-technician were employed full-time during the period of the operations. During the first six months, their work consisted in preparing road maps, installing and controlling the calibration stations, participating in mounting and calibrating the instruments on the vehicle.

At the end of this period, the personnel under contract carried out the following two main tasks :

- prospection in the field following the road maps prepared during the first semester of 1979 (a university graduate plus a driver-technician), which were completed as the work progressed;
- data processing and interpretation (a university graduate).

The general services, the workshops and the Centre of Instrumentation of the Polytechnic Faculty of Mons actively participated in this work by helping with the installation of the calibration stations and by providing the electronic maintenance and the repairs.

IV. 2. TECHNIQUES USED

IV. 2. 1. *Carborne instrumentation*

The equipment used, of the mark GEOMETRICS, was hired from UNION MINIERE and mounted onto a vehicle Land Cruiser TOYOTA, bought specially for the purposes of the contract (fig. 70). It consists of :

- an NaI (Tl) crystal detector, model NAL 110, diameter : 6", thickness : 4", volume : 1853 cm^3;
- a spectrometer analyser DRGS 1002;
- a pen recorder MARS 6;
- a mileage recorder with a numerical display and conversion from km to cm (DMI : Distance Measuring Instrument).

Two supplementary devices were mounted by the technicians of the Polytechnic Faculty in order to facilitate the reading and processing of the recordings :

- a pen linked with the DMI indicates blips on the paper after every 100 m of route covered;
- a second pen controlled by a manual switch to note the presence of constructions along the routes by traits ("indicator of events").

The equipment used carries a device which automatically corrects the count rate for contributions from secondary radiations associated with rays of the highest energy level, thus allowing a 100% discrimination between the three radioelements U, K, Th.

It is also fitted with an automatic spectral stabilisation device which prevents the energy drift due to variations in temperature.

The following working conditions were adopted :

- energy threshold on the total count : 1 MeV
- energy levels for the three elements (MeV) : K_{40} : 1.4 to 1.62

Bi_{214} : 1.69 to 1.95

Tl_{208} : 2.58 to 2.84

IV. 2. 2. *The calibration stations*

To calibrate the carborne spectrometer, calibration stations consisting of cylindrical concrete slabs were constructed, relying on data from the literature (52, 56), advice from experts at the meeting of the AEN-OCDE (Paris), and on the internal reports of the University of Prague (53).

The first two slabs, with a diameter of 2 m and a thickness of 0.65 m, were respectively doped in U and Th, while the third, left undoped, served as a reference for the background noise (fig. 68).

For the doping of the slab "uranium", a mineral from the Hoggar whose radioactive equilibrium had been verified was used. The slab "thorium" was doped with an essentially thorium-rich monazite.

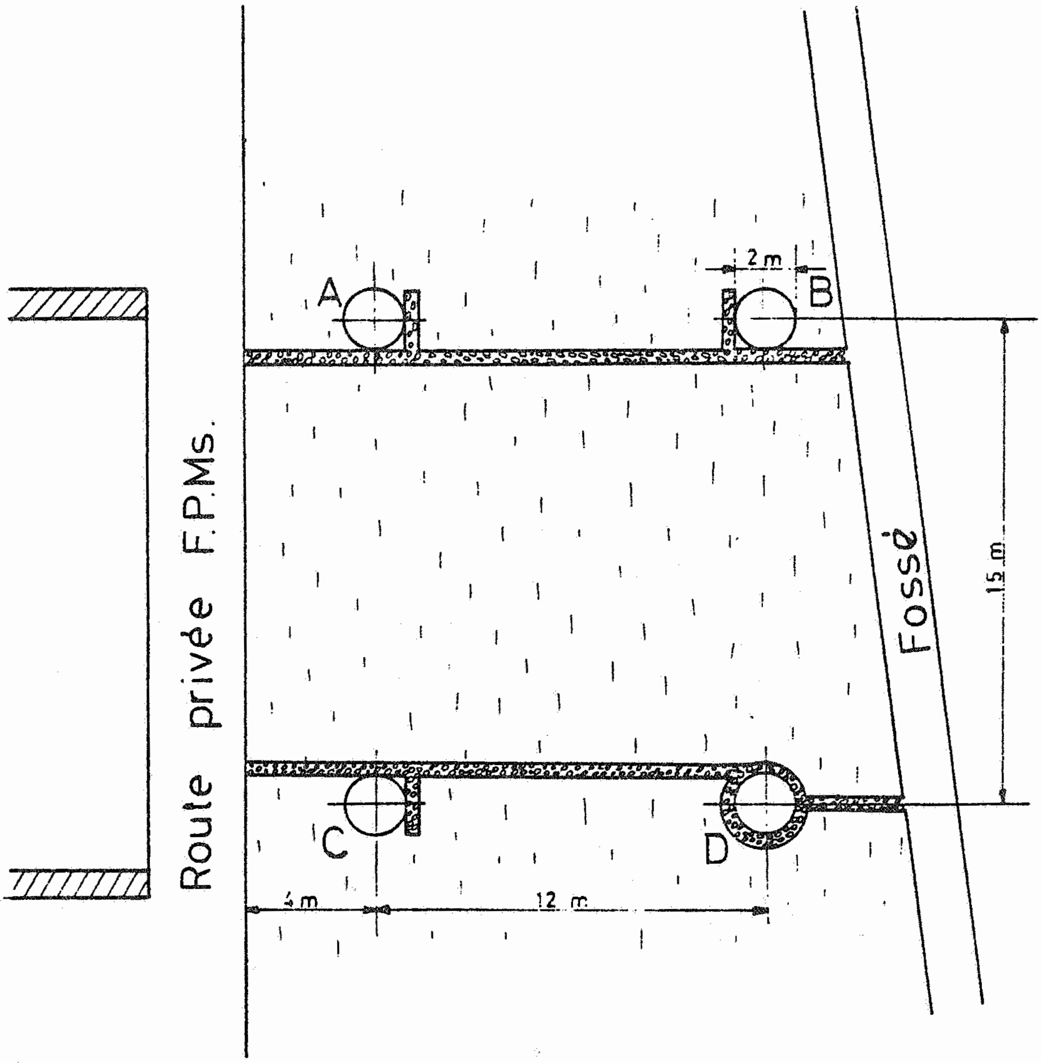
For the fourth slab ("potassium"), the concrete was replaced with non-radioactive sand mixed with KCl. Thus was avoided the addition of large quantities of K_2O to the concrete, which would have made it difficult to set. This last slab was protected by an aluminium cover.

Drains for the evacuation of water were installed along the slabs, and the entire structure was completely enclosed.

The homogeneity of the slabs, both on the surface and in depth, was carefully controlled (notably by coring) and considered satisfactory. For the uranium slab, however, a certain vertical heterogeneity had to be reckoned with, and a mean value had to be calculated for the zone that influenced the detector (fig. 69).

From these calculations and after deduction of the values for the undoped slab, the corrected values of thorium, uranium and potassium were as follows :

- Th flagstone (ppm) : 102
- U flagstone (ppm) : 36
- K flagstone (% K_2O) : 8.19.



A : STATION DU BRUIT DE FOND

B: STATION URANIUM

C: STATION THORIUM

D: STATION POTASSIUM

FIG 68 : THE CALIBRATION STATIONS.

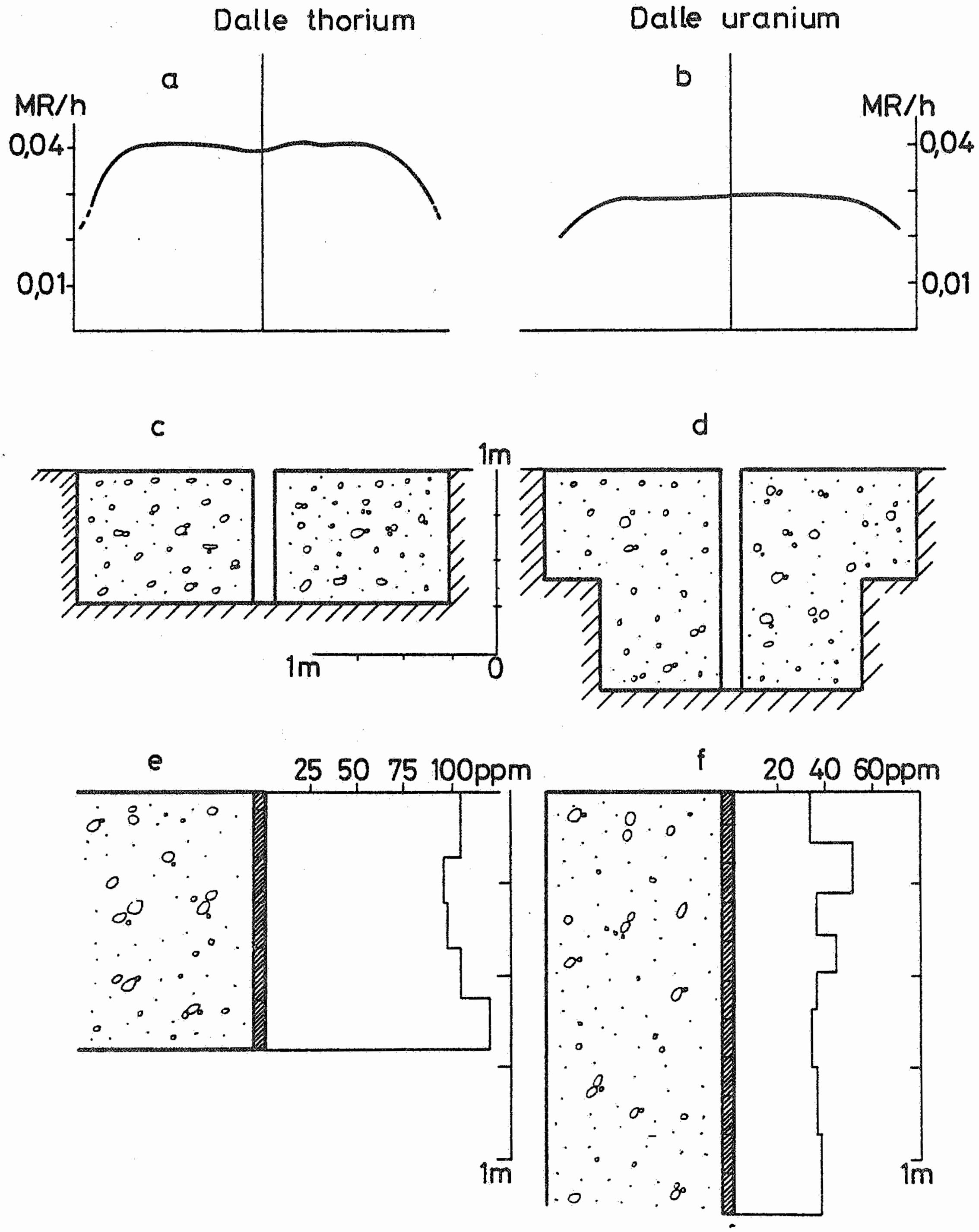


FIG. 69 : Distribution of the radioelements through the 'uranium' and 'thorium' stations.

IV. 3. WORKING OUT OF ITINERARIES

Working in a forest region under very humid climatic conditions posed certain problems. The forest roads are generally in a very bad state, mainly due to the utilisation of tractors in the exploitation of timber. On many occasions, the vehicle got stuck in deep mud-filled pot holes and had to be removed by a winch. Thus a considerable amount of time was needed when some of the forest roads were to be followed.

The most serious problem encountered at the beginning of the prospection concerned the disposition of the detector on the vehicle. Indeed, it soon became apparent that the coating of some of the roads gave rise to high peaks for thorium and weaker peaks for potassium and uranium. In order to reduce the contribution from the road coating, the detector was initially mounted along the right side of the vehicle, 1 m above the ground and at a 45° inclination towards the exterior. However, the resulting lateral bulkiness soon proved to be a hindrance to the driving and to the speed of the vehicle. In 1979, the detector was involved in two accidents along narrow forest roads leading to interruptions of the prospection.

For this reason, the detector was finally mounted at the back of the vehicle, in the space occupied by the spare wheel, always inclined at 45° but this time 1 m 20 above the ground (fig. 70).

With this configuration, the vehicle no longer acts as a screen to the radiations coming from the road coating. However, it is possible to keep close to the right hand side of the road, the effect of the coating not being more important than before.

From the experience thus acquired, it follows that considering the nature of the ground (routes in forest areas), the most appropriate place for mounting the detector is at the back of the vehicle (but not beyond the roof).

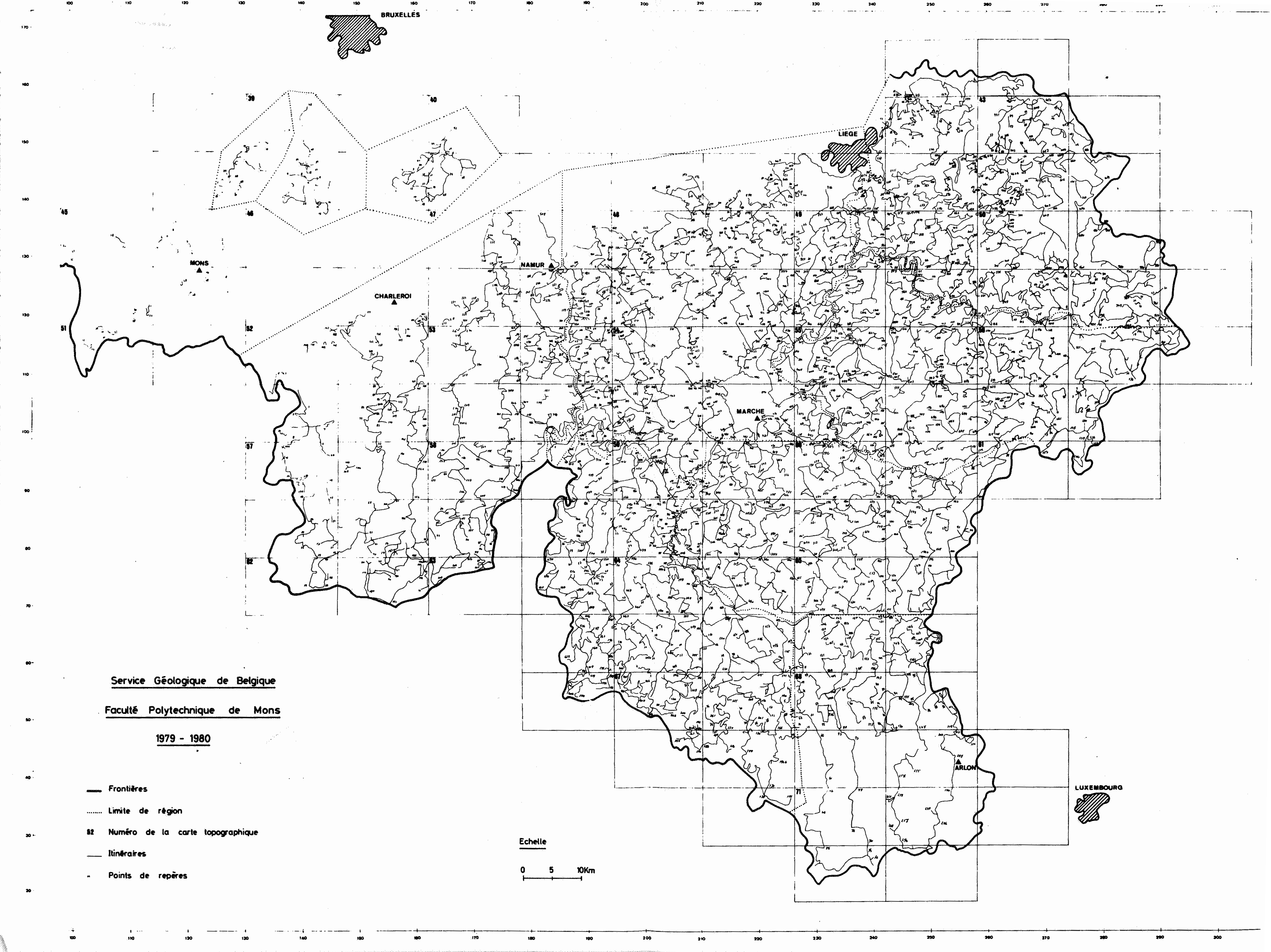
With this disposition, and under favourable conditions, 100 km of route were covered per day.

In practice however, the daily average was far below this figure, considering the difficulties mentioned above, due to the vehicle often getting bogged.

PROSPECTION RADIOMETRIQUE AUTOPORTEE

CARTE VIII :

Itinéraires parcourus



Service Géologique de Belgique

Faculté Polytechnique de Mons

1979 - 1980

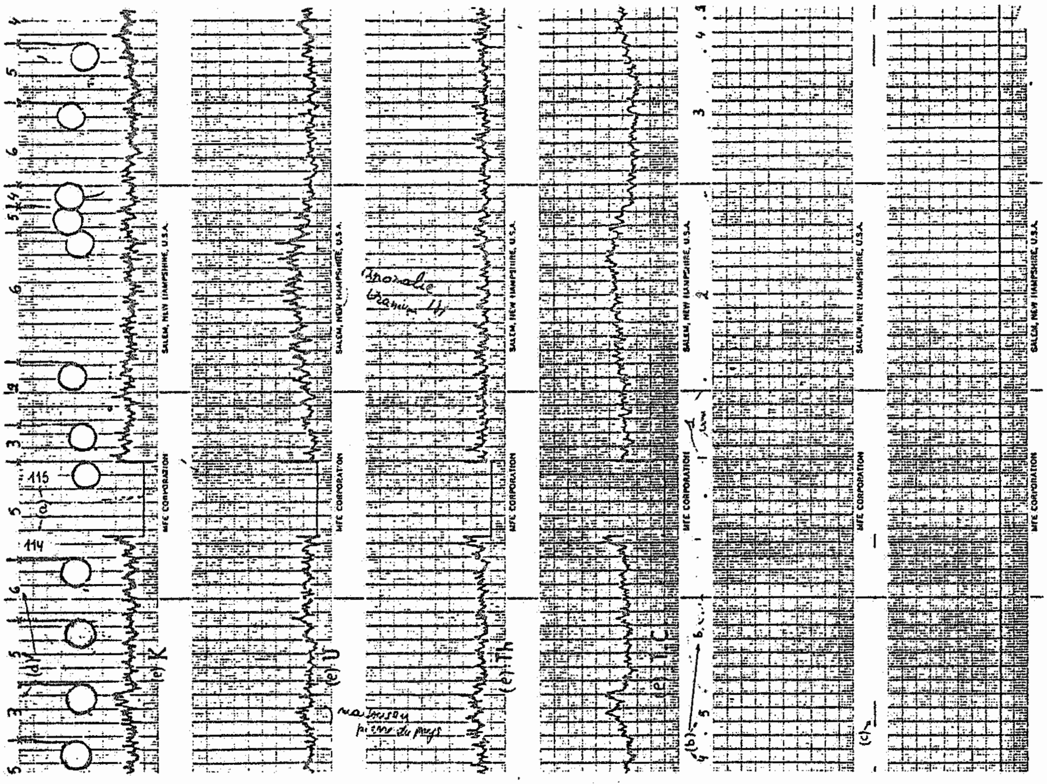
FIG 70: BACK VIEW OF THE VEHICLE, SHOWING THE INCLINED DETECTOR.

Other problems, mainly of a technical nature such as failures of the DMI and the spectrometer analyser led to a number of interruptions of the work. The latter instrument even had to be replaced in July 1980.

An "indicator of events" (cf. IV.2.1) was used to signal the effects of entropic factors on the readings : the presence of inhabited zones (buildings, bridges etc...) was indicated by linear traits with the help of the fifth pen of the MARS 6 recorder controlled by a manual switch.

Topographic or geometrical effects were indicated by sticking on the recording paper reference points with appropriate colours (fig. 71). Thus the various possible lies of the road relative to the normal ground level were codified as follows :

- roads at ground level : black
- embanked road : yellow
- slope : blue
- small outcrop : white
- large outcrop : red.



PAGE N°: 1 E.M.O.L. II 15/12/80 Carte 49/1-2

(a)	(b)	(c)	(d)	(e)				(f)		(g)	(h)	(i)		(j)		(k)
POINT	STEP	HABITAT.	C.G	K	U	Th	T.c	A	N°	Pl.c	Km	corr U	corr Th	N° du POINT	COMMENTAIRES	REPORT
	4		5	9	8	8	18	a	7	10		5	5	449017		O.K.
		5													maison en pierres du pays	
	6	}	5	9	8	8	18	a	7		1					
		}	6	9	9	8	19	A	7			5	5	449018		O.K.
114		Zéro :		5	5	5	5									
115		Zéro :		5	5	5	5									
	1		2	10	8	7	19									
	2		6	9	13	7	23	A	7			5	5	449019	Anomalie Uranium	O.K.
	3		6	9	7	8	16	A	7			5	5	449020		O.K.
		407								10						

Fig 71 : - Dépouillement d'un enregistrement.

- Processing of a recording

IV. 4. DETERMINATION OF COEFFICIENTS OF CALIBRATION

From the count-rates regularly read at the calibration stations, and expressed in counts /second, the mean corrected count rate for the background noise over a period starting from the 25th June to the 7th November 1980 was determined :

Table XIV : *Mean count rate of the calibration slabs (corrected for values of the undoped slab) in counts /second*

	slab K	slab U	slab Th
K way	127.2	- 0.46	0.41
U way	0.26	47.9	1.05
Th way	0.04	1.23	77.3
"Total Count"	256.1	275.76	388.72

Taking into account the corrected values of U, Th and K in each slab, the sensitivity of the spectrometer for the chosen energy levels (s_U, s_{Th}, s_K) as well as the coefficients in "total count" (a_U, a_{Th}, a_K) were determined.

These coefficients are such that the total count rate is given by the formula :

$$[1] \quad \text{Total count} = a_U U + a_{Th} Th + a_K K$$

For the count rate in "total count", the unit adopted is that recommended by the IAEA (56) and by the recent meeting of a joint group of AEN-AIEA experts on the 13th and 14th of November 1980.

It is the "unit of concentration in radioelements" represented by the symbol Ur(*).

Taking into account the global count rate on the slab "uranium", and under our working conditions, the Ur corresponds to 7.66 counts/sec. The values of the coefficents of calibration are given in table XV.

Table XV : *Coefficients of calibration*

s_K str/sec / % K	15.53	a_K str/sec / % K	31.27
s_U str/sec /ppm U	1.33	a_U str/sec /ppm U	7.66
s_{Th} str/sec /ppm Th	0.758	a_{Th} str/sec /ppm Th	3.81

It is interesting to compare these values with those given in the literature (57) for a crystal of sodium iodide of the same volume:

Table XVI : *Comparison of coefficients of calibration*

	s_K	s_U	s_{Th}
MONS	15.53	1.33	0.758
IAEA(°)	12.97	1.20	1.24

(°) cf. bibliogr. No. 57

(*) A geological formation with one Ur unit gives the same response as an identical source containing 1 ppm of U in radioactive equilibrium.

IV. 5. PROCESSING OF RECORDINGS

IV. 5. 1. *Correction and conversion of data*

The rolls of recordings are not easy to handle and access to the information they contain is relatively slow. Each channel was digitally processed at intervals of 100 m on leaflets that could easily be referred to.

Because of the digital processing of the recordings, the count rate of the different channels could be expressed in mm's of deflection on the paper.

After a series of measurements, the correspondence between the counts per second (read on the spectrometer dial) and the mm's transcribed by the pens on paper, were established. They are expressed by linear relationships of the form :

[2] $x = a_1 y + a_2$ y in mm
x in counts/second

Table XVII : *Correlations between deflections (mm) and count rate (counts/second)*

	K channel	U channel	Th channel	"Total Count" channel
$x =$	$3.208\ y + 1.46$	$2.01\ y + 0.42$	$1.33\ y + 2.16$	$10.22\ y$
Correlation coefficient	0.9985	0.9982	0.9992	1

The variable y(mm) must be corrected for drift before application of the formulae. The corrections must take into account :

- erratic displacements of the paper on its support
- unpredictable movements of the pens in their canal
- differential dilatation of the pens.

These corrections can have appreciable effects on the values which expressed in mm on the paper are generally around 0-15 mm on K, 1-4 mm on U, 1-6 mm on Th, 8-16 mm on "total count". Belgium is not a country with a high uranium background !...

As it is, the accuracy of reading, taking into account statistical fluctuations (2 to 5 mm), is about 1 mm. The corrections mentioned above vary between 0 and 4 mm and are thus of the same order of magnitude as the normal reading on the U channel. This means that the corrections cannot be considered negligible.

In order to correct for the movements of the paper, one of the unused pens was fixed, serving somehow as a base line.

Concerning the drift of the pens, experience proved that it was subject to slow and regular variations. This was corrected by disconnecting the spectrometer at regular intervals. The rate of one measurement every 5 km proved sufficient to obtain a relatively exact estimate. On the average, for every meter of recording (10 km in the field), the correction to be applied was about 1 mm.

Once these corrections have been carried out, the linear correlations previously referred to can be used to obtain the count rate in counts /second.

Before converting the count rate into values of radioelements, one further important correction must be applied : that of the background represented by cosmic rays and by the descendants of the radon fixed into the atmospheric dust (airborne radon daughters).

This background was estimated in two ways :

a) by comparing for each channel, the count rate measured on the undoped concrete slab to the count rate calculated from the actual contents in radioelements for the same slab. The contribution of the background is obtained by substraction;

b) by placing the probe on a boat 12 meters from the edge of a stretch of water situated near Mons (water stretch of the "Grand Large").

The results of these two methods are very comparable :

Table XVIII : *Measurement of background*

	K Channel cts/sec	U Channel cts/sec	Th Channel cts/sec	TC Channel cts/sec
Slab	7.37	0.98	3.94	72.9
Boat	7	0.75	> 4	73

It seems that the value on the Th channel has been influenced by pollution in thorium on the boat.

Once the correction for the background is taken into account, the calculation of the contents in the radioelements can at last be made using the coefficients of calibration s_K, s_U and s_{Th} determined at the stations (table XV).

If the different corrections enumerated above are introduced into the conversion formulae [2], global formulae enabling the direct translation from mm to values of radioelements are obtained. Their general form is given below :

$$[3] \quad \text{value} = [(a_1 y + a_2) - b] \cdot \frac{1}{s} \cdot d$$

y = deflection in mm

a_1, a_2 = coefficients of formula [2]

b = background

s = coefficient of calibration (cf. IV.4)

d = correction for geometric effect (cf. IV.5.2).

Applied to the three elements U, Th, K and to the total count, these formulae become :

$$U\ (ppm) = [\ (2.01\ y_U + 0.42) - 0.98\ ]\ .\ \frac{1.19}{1.33}$$

$$Th\ (ppm) = [\ (1.33\ y_{Th} + 2.16) - 3.94\ ]\ .\ \frac{1.16}{0.758}$$

$$K\ (\%) = [\ (3.208\ y_K + 1.46) - 7.37\ ]\ .\ \frac{1.20}{15.53}$$

$$n = \text{Total Count (Ur)} = [\ (10.22\ y_{TC} - 72.9)]\ .\ \frac{1.22}{7.66}$$

The validity of the results obtained can be verified by calculating the global count rate (in counts /second) from formula [1] of § IV. 4 :

$$n' = a_K K + a_U U + a_{Th} Th$$

and by comparing this value to the total count n (in counts /second) measured directly on the TC channel of the spectrometer.

The ratio between n and n' should be around 1. Significant fluctuations in this rate can be due to a local heterogeneity in the distribution of the radioelements.

Two examples are given of measurements carried out on a supposedly homogeneous and infinite source, the detector being placed in the same geometric position as adopted during the field prospection (table XIX) :

Table XIX

a) *Phosphatic chalk of Ciply*

	K	U	Th	TC
Deflections (mm)	3	23	2.5	32.5
Values	0.24 %	33.7 ppm	2.04 ppm	33.41 Ur

Calculated total count n' (in Ur) $= \dfrac{7.5 + 25 + 7.77}{7.76} = 35.2$

b) Farmland on silt (Harmignies)

	K	U	Th	TC
Deflections (mm)	7	2.5	4.5	15.5
Values	1.07 %	2.73 ppm	5.55 ppm	11.02 Ur

$$\text{Calculated total count (in Ur)} = \frac{33.46 + 20.84 + 21.15}{7.76} = 9.72$$

It can be noted that the calculated total counts are very close to the actual measured values. The formulae [3] established for the processing of the recordings thus seem to give full satisfaction.

IV. 5. 2. *Field of influence of the detector and geometrical effect*

The field of influence of the detector was calculated for a horizontal and homogeneous formation by introducing the following function into the microcomputer of the Polytechnic Faculty of Mons prospection team :

$$I = I_o h/2\, \pi \iint_s e^{-\mu 2} r^{-3} ds .$$

The curve showing I/I_o as a function of the radius (a) of the field of influence was calculated, taking into account the following conditions :

- infinite horizontal and homogeneous source (geometry 2 π)
- height of detector above the ground : 1 m 30 (prospection condition)
- density ρ of air : 1.293 mg/cm^3
- coefficient of attenuation $\mu /_{\rho}\, x^{\rho}$ for the uranium ray : 0.007.

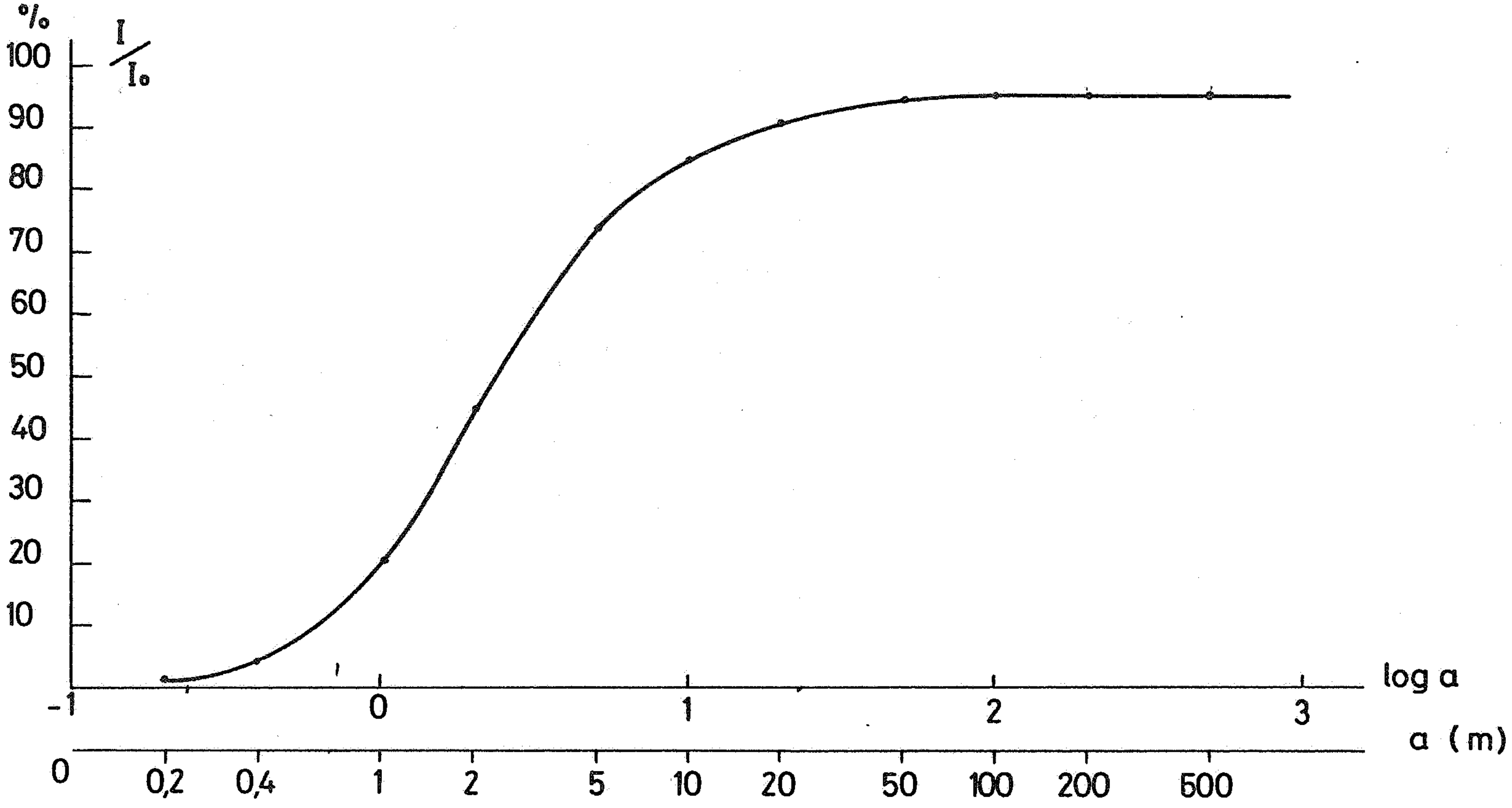


FIG. 72 : THEORETICAL CURVE FOR THE ASSESSMENT OF THE RADIUS (a) OF THE DETECTION FIELD.

Figure 72 shows that :

- the effect of the density of air is practically negligible (I/I_o = 0.95 - 0.96 for an infinite source);
- 50 % of the radiation originates from a source with a radius of 2.4 m around the detector and 90 % from a source with an 18 m radius.

It must however be noted that the field of influence varies with geometrical effects (rough ground, slope...). The concentrations can be overestimated by about 50 % at the foot of an escarpment.

However, considering the position of the detector on the vehicle, the calculated curve (fig. 72) gives an order of magnitude of the zone investigated by the carborne prospection.

In order to verify the influence of the position of the detector and of the length of the cables on the calculated values, measurements were carried out under different conditions on the silty lands situated at the summit of the quarry of Harmignies that constitute a homogeneous source (table XX) :

Table XX

	K (%)	eU (ppm)	Th (ppm)	TC (Ur)	TC (Ur) calculated
1	1.07	2.73	5.55	11.02	9.72
2	1.29	3.33	6.42	13.43	11.54

1. detector in the same geometrical position as adopted during the field prospection
2. detector placed on the ground.

It can be seen that with the detector on the ground, the values are slightly higher. In consequence, the values will have to be corrected for geometrical effects (absorption of the background by the vehicle itself, absorption in air...).

IV. 5. 3. *Influence of the size of outcrops on the calculation of values and of the total count*

In order to verify the effects of the size of outcrops on the calculation of concentrations and of the total count, we took as an example the mean values obtained from the coded information on the geometry of the outcrops (cf. IV.3), and this for the Lower Devonian.

Table XXI shows that the values obtained from formulae [3] are systematically higher for the large outcrops. Nevertheless, the values of the ratios Th/U and U/K_2O are rather close to each other and are thus characteristic of a given formation.

Table XXI : *Influence of the geometry of outcrops*

6 = big outcrops
5 = small outcrops

TC_1 = total count measured
TC_2 = total count calculated

	K_2O	eU	Th	Th/U	U/K_2O	TC_1	TC_2	Variation TC_1-TC_2 (%)
Emsian 6	3.54	3.78	12.54	3.32	1.07	25.75	21.79	+ 16.6
Emsian 5	2.45	3.01	9.96	3.31	1.23	19.21	16.08	+ 17.7
Siegenian 6	3.20	3.26	11.1	3.40	1.02	23.48	19.41	+ 19
Siegenian 5	2.36	2.42	8.8	3.64	1.02	18.42	14.62	+ 23
Gedinnian 6	3.21	4.03	10.65	2.64	1.25	23.40	20.00	+ 15.7
Gedinnian 5	2.28	3.24	9.21	2.84	1.42	17.51	15.39	+ 13

IV. 6. PRESENTATION OF RESULTS

IV. 6. 1. *Constitution of the file*

For the constitution of the data bank, the plan was to introduce the following data for all the points characterized by their geographical co-ordinates :

- values of the intensities of the radiations on the four channels (converted into concentrations using formula [3]);
- coded information on the nature of the geological formations.

The interval retained for digital processing was 100 m, and with about 10 000 km of routes covered, it would have meant the introduction of at least 100 000 points into the computer file ! This was practically impossible, so a choice had to be made : priority was given to outcrops, outstanding pinpoint anomalies and a certain number of measurements in superficial formations.

In any case, the number of points was limited to 999 per 1:50 000 map.

The lists prepared after processing of the recordings, and which constitute the basic documents for the data bank, indicate the following information (fig. 71) :

a) the number of points on the 1:25 000 road maps

b) the sampling interval

c) the localisation of inhabited zones

d) information on the geometric conditions using the following code : 2 - road at ground level, 3 - embanked road, 4 - slope, 5 - small outcrop, 6 - large outcrop

e) the uncorrected values (in mm) on the U, Th, K and TC channels

f) the presence of an outcrop and its attribution to a particular geological formation, using the code given in Table XXII. When the point does not correspond to an outcrop, the code number of the superficial formation is used

g) the position of the fixed pen on the paper

h) the number of kilometers recorded

i) the corrected values on the U-Th channels

j) the number of the point, consisting of six figures : a first figure "3" (code for the radiometric prospection) followed by five figures designating the number of the point according to the rule defined in § I.

In principle, as already stated, the number of points per 1:50 000 map was strictly limited to 999. For certain maps, however, this number was exceeded. These points in excess, which carry numbers already assigned, were distinguished by replacing the first number "3" with the number "4". In the computer file, these points were indexed under a fictitious map number (actual map number + 30).

Example : the points in excess on map 49 are to be found in the file on the fictitious map no. 79.

Table XXII : *Numerical code used to designate the geological formations*

No	Formations	Lithology	No	Formations	Lithology
1	superficial		21	Gedinnian	sandstone
2	Tertiary	clay	22	Silurian	
3	Tertiary	sand	23	Salmian	slate
4	Cretaceous		24	Salmian	quartz-phyllites
5	Westphalian		25	Revinian	slate
6	Namurian		26	Revinian	quartzite
7	Visean		27	Devillian	slate
8	Tournaisian		28	Devillian	quartzite
9	Famennian	shale	29		eruptive rocks
10	Famennian	sandstone	50	Famennian	✻
11	Frasnian	shale	51	Frasnian	✻
12	Frasnian	limestone	52	Couvinian	✻
13	Givetian		53	Emsian	✻
14	Couvinian	shale	54	Siegenian	✻
15	Couvinian	limestone	55	Gedinnian	✻
16	Emsian	sandstone	57	Salmian	✻
17	Emsian	shale	58	Revinian	✻
18	Siegenian	sandstone	59	Devillian	✻
19	Siegenian	shale	40	Permian	✻
20	Gedinnian	shale			

✻ unspecified.

IV. 6. 2. *Descriptive statistics*

a) Treatment of measurements on outcrops by geological formation

Contrarily to the geochemical prospections which are based on the analysis of the elements dispersed in the superficial transporting agents (alluvia, surface waters), the carborne prospection involved the measurement "in situ" of the radioactivity of the outcropping geological formations.

It is thus possible, in principle, to estimate the contents in radioelements of the different geological formations provided an adequate calibration of the carborne probe is made.

As stressed in § IV.5, the accuracy of these measurements is influenced by factors of geometry (size of outcrops, presence of escarpments, etc...) and eventually a radioactive desequilibrium in the case of measurements on the uranium channel.

During the preparation of the "RADIO" file, each point of measurement was characterised by numerical coded information on the geometry on the one hand, and on the geological age of the formations on the other hand.

It was thus easy, using the computer terminal, to effect all the possible selections corresponding to combinations of these two criteria.

Table XXIII shows the statistical parameters (arithmetic means and standard deviations) of all the measurements on outcrops for the main formations of the Belgian Paleozoic.

The histograms of frequencies in fig. **73** to **92** coincide with certain groups of formations corresponding to some relatively homogeneous series (Lower Paleozoic, Lower Devonian, Devonian calcareous rocks, Dinantian calcareous rocks). The parameters analysed in each case are : uranium, thorium, potassium and the total count.

On examination of all the data, a certain number of observations can be made :

1°) concerning the detrital formations, the prospected area is characterised by a rather marked uniformity in the repartition of the three radioelements U, Th and K.

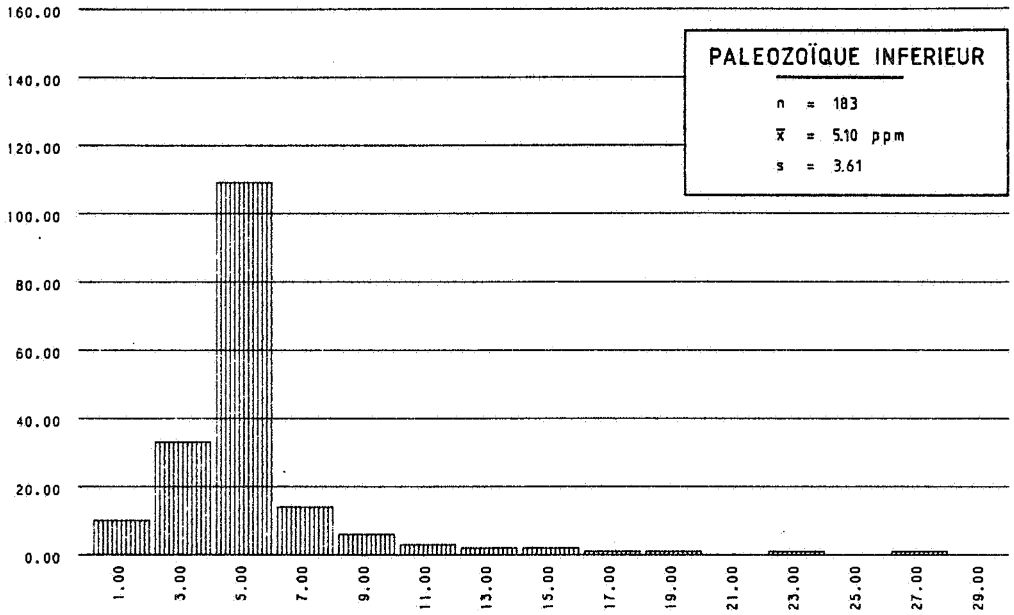


Fig. 73 : URANIUM (ppm)

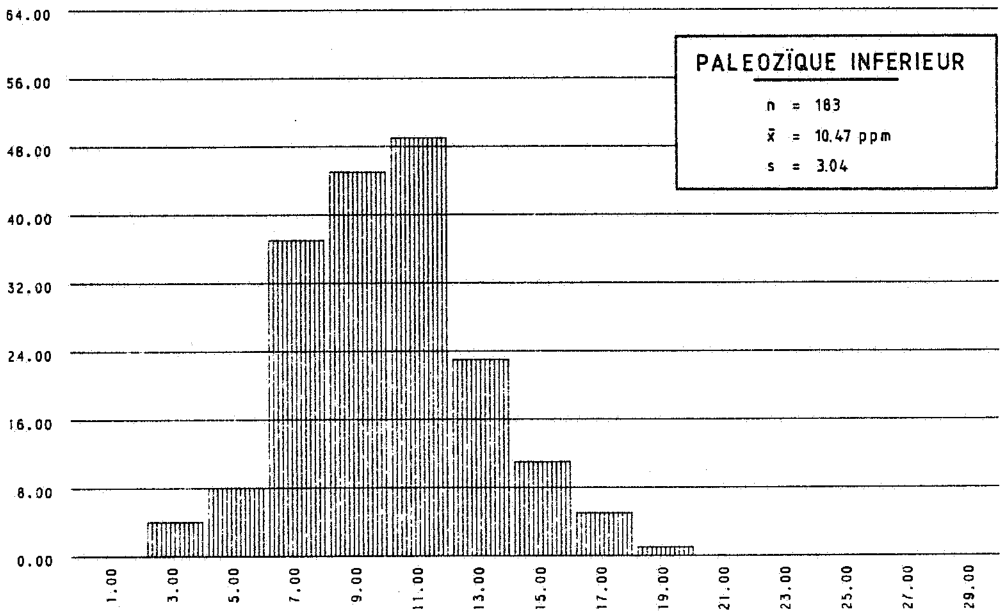


Fig. 74 : THORIUM (ppm)

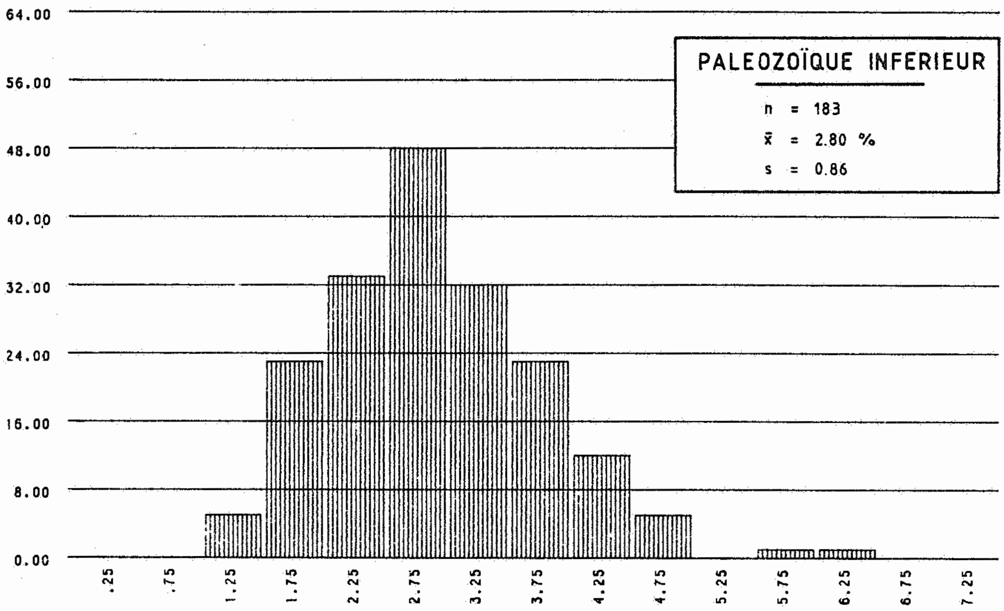


Fig. 75 POTASSIUM (%)

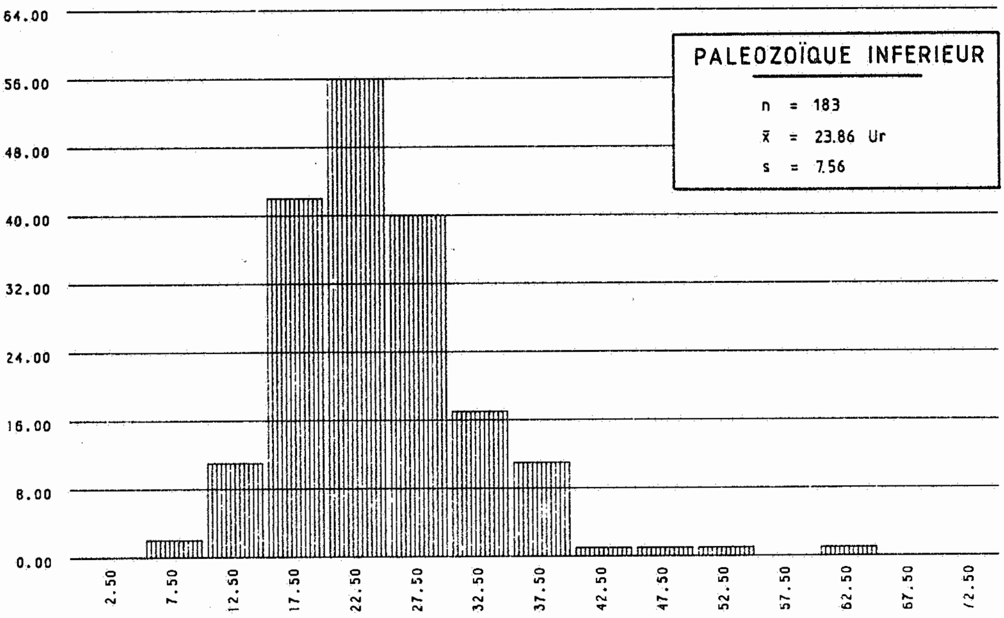


Fig. 76 : COMPTAGE TOTAL (Ur)

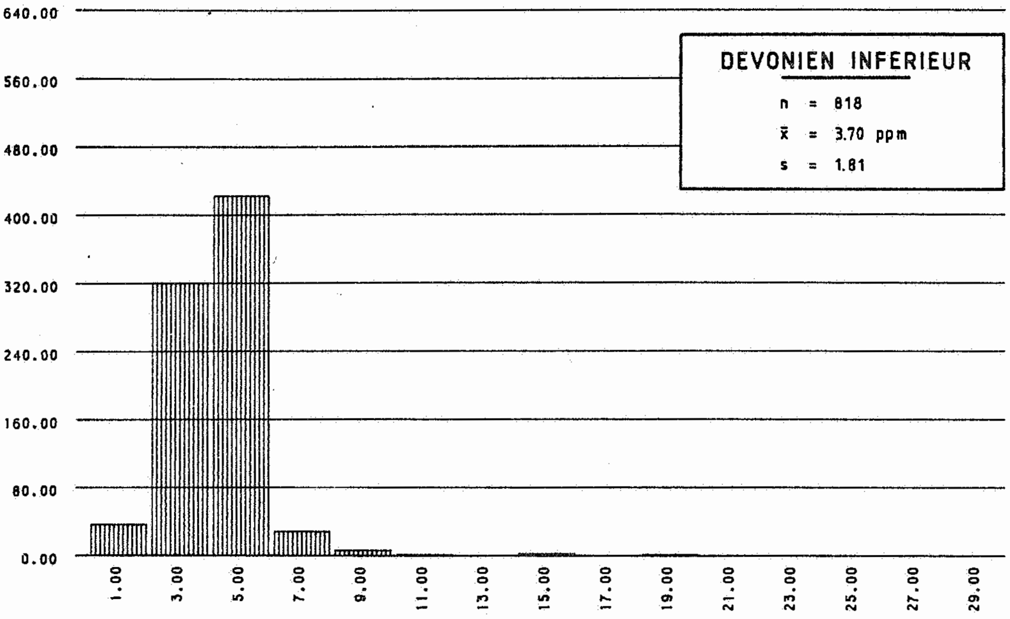


Fig. 77 : URANIUM (ppm)

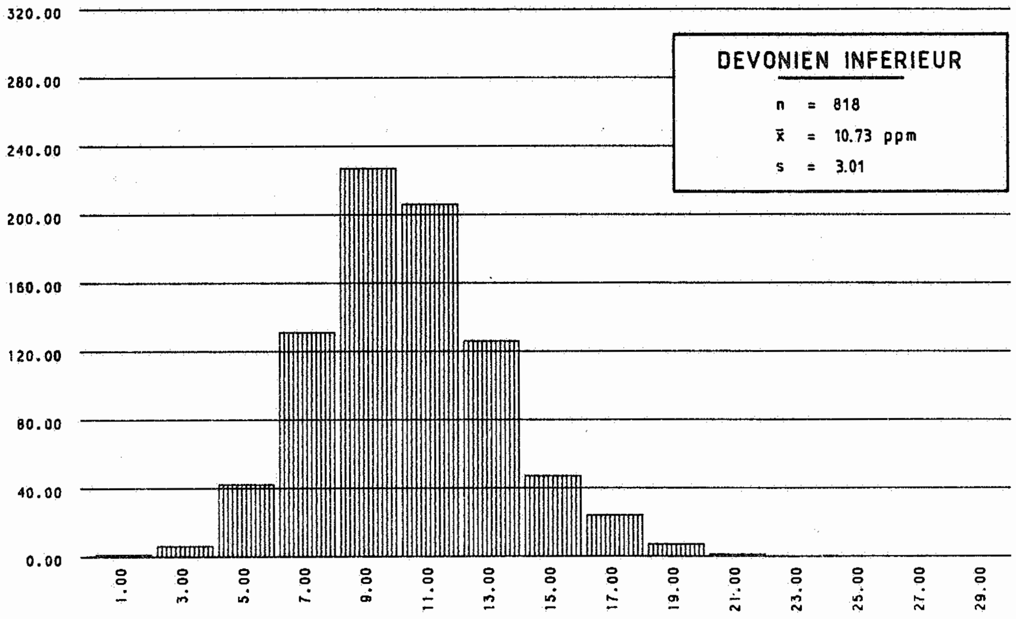


Fig. 78 : THORIUM (ppm)

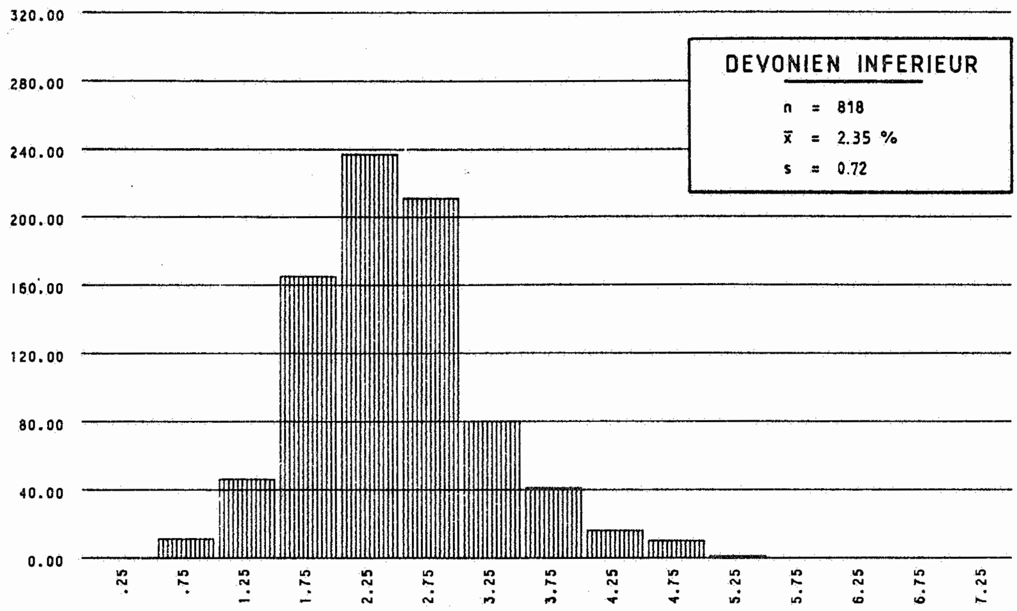


Fig. 79 : POTASSIUM (%)

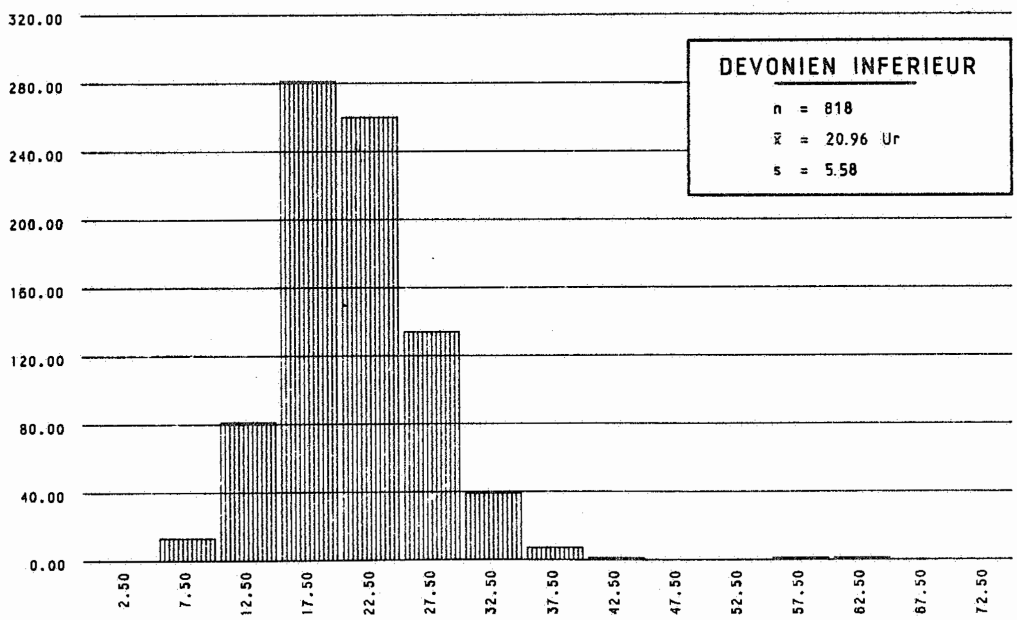


Fig. 80 : COMPTAGE TOTAL (Ur)

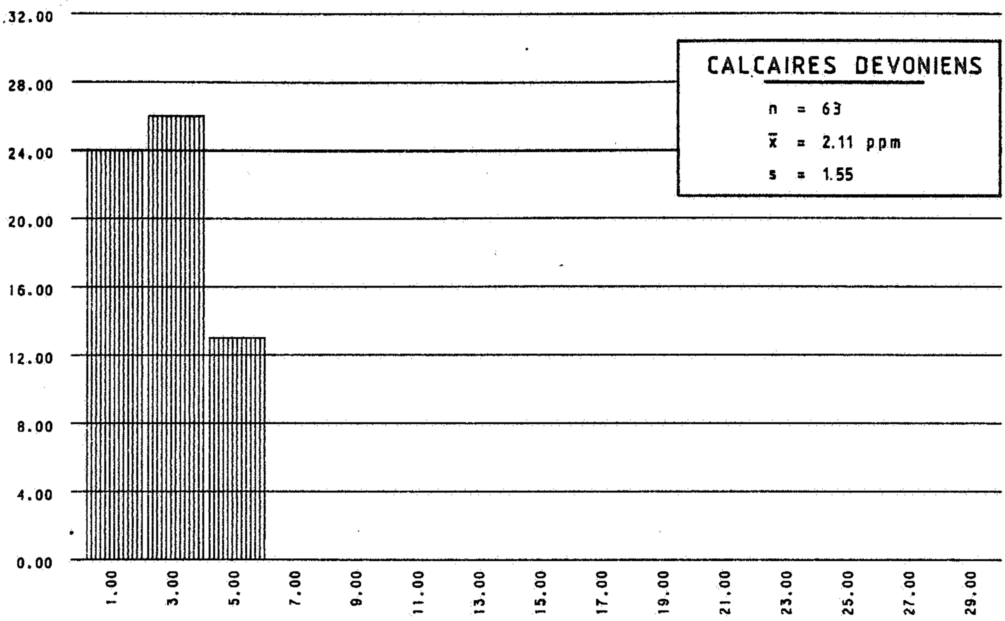


Fig. 81 : URANIUM (ppm)

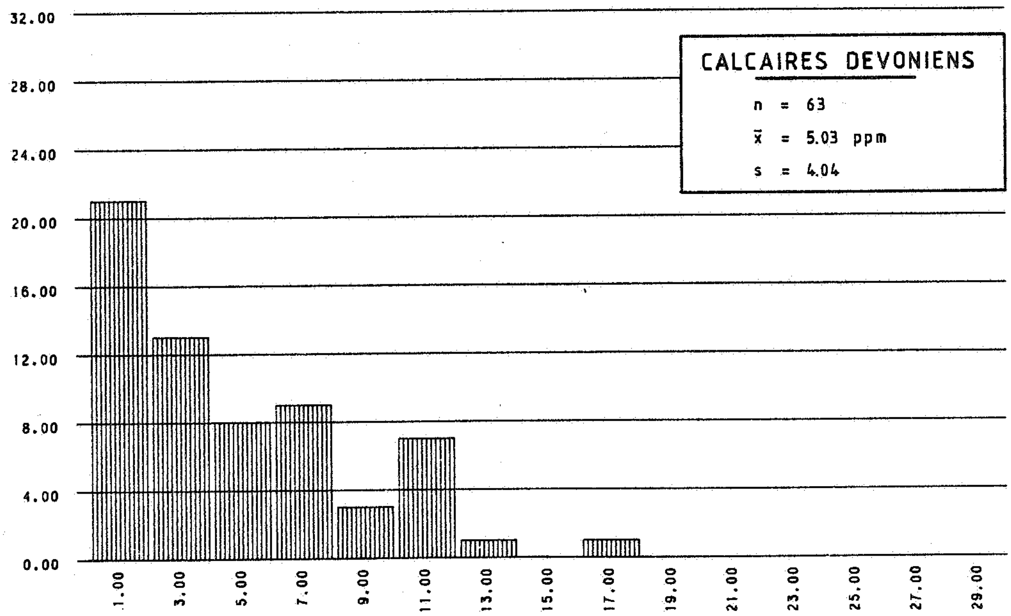


Fig. 82 : THORIUM (ppm)

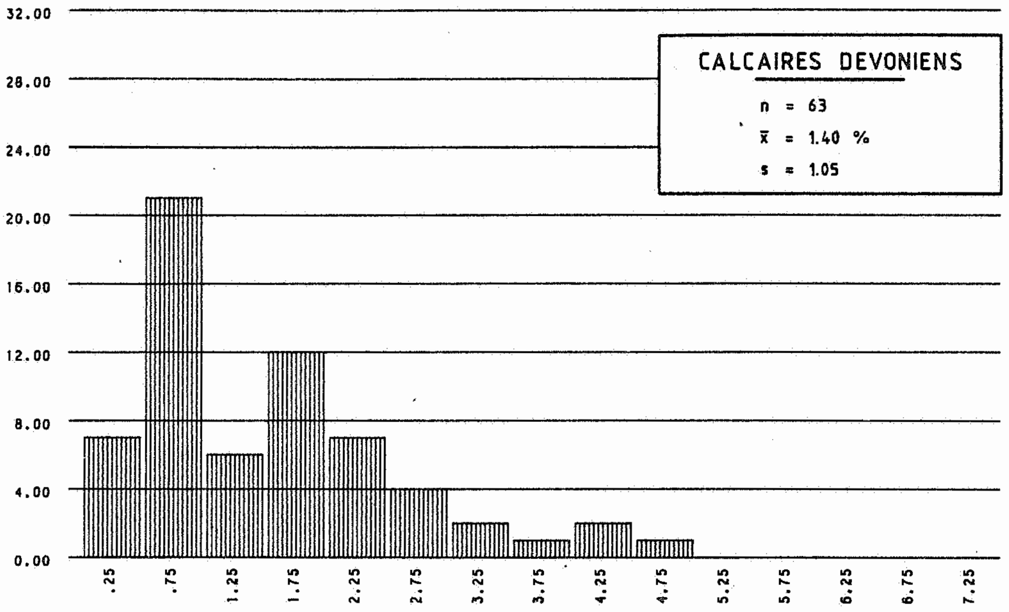


Fig. 83 : POTASSIUM (%)

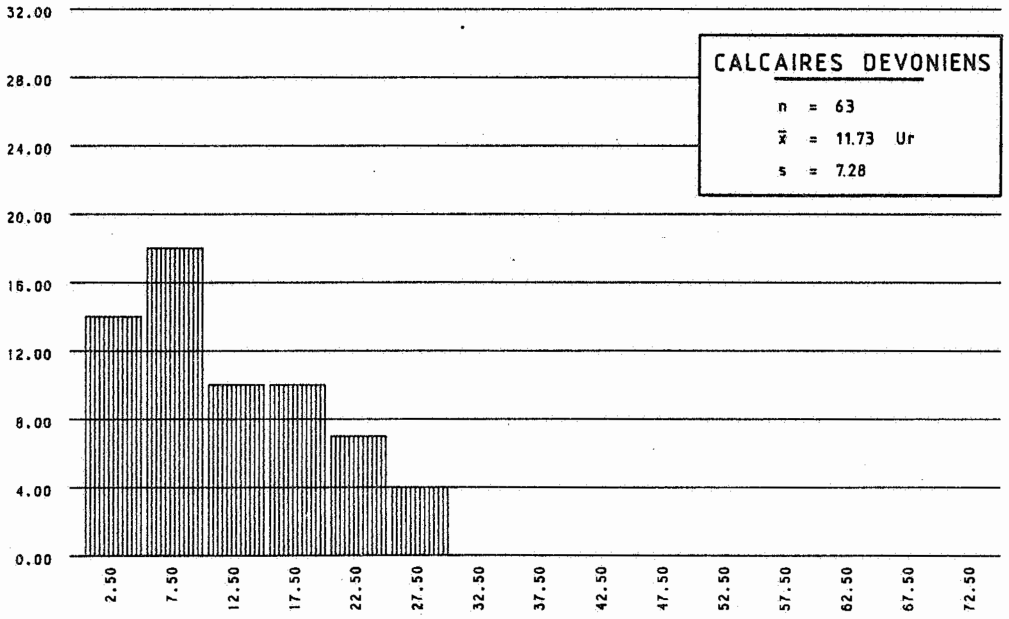


Fig. 84 : COMPTAGE TOTAL (Ur)

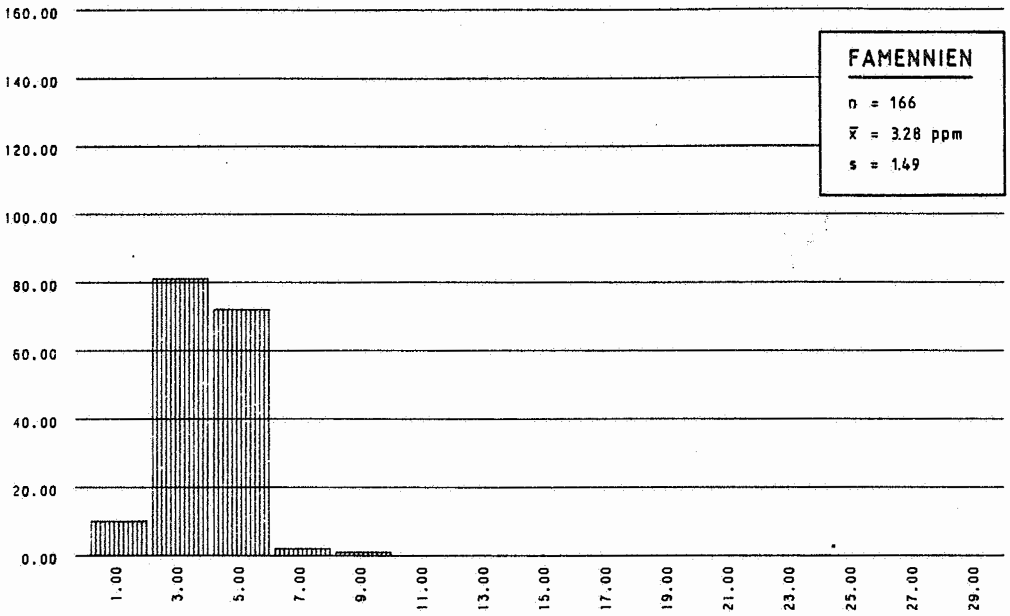


Fig. 85 : URANIUM (ppm)

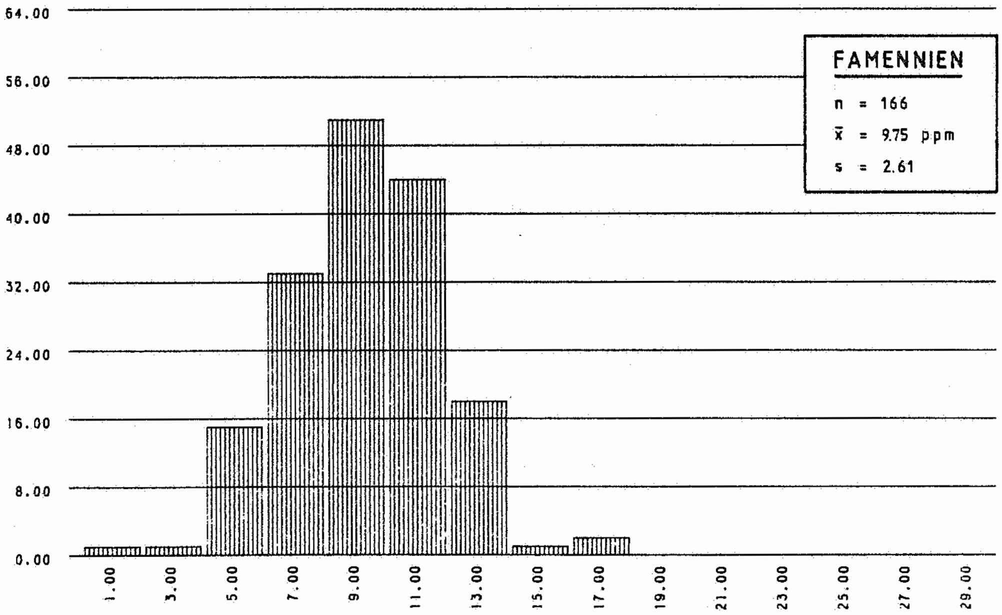


Fig. 86 : THORIUM (ppm)

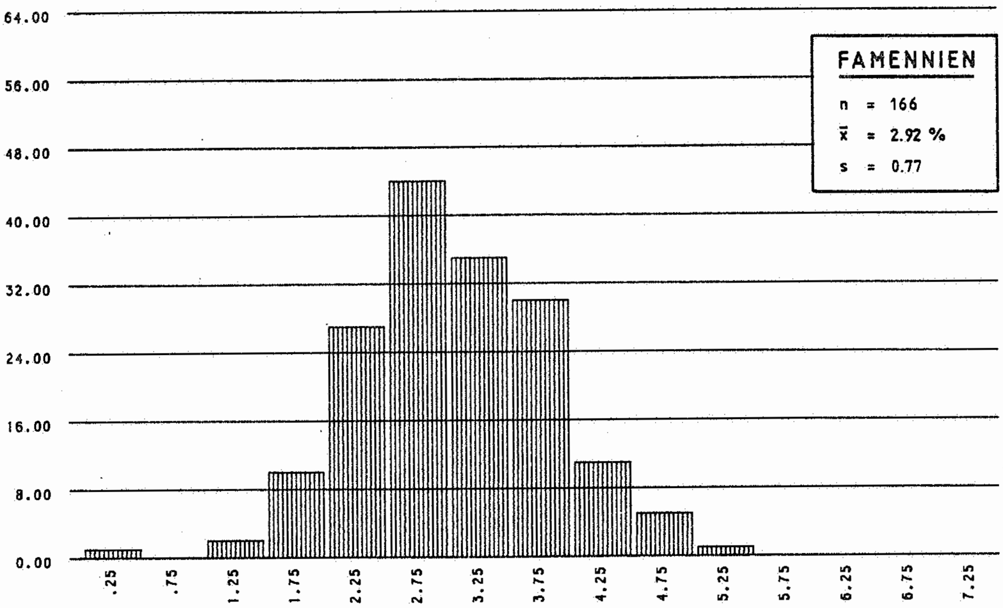


Fig. 87 : POTASSIUM (%)

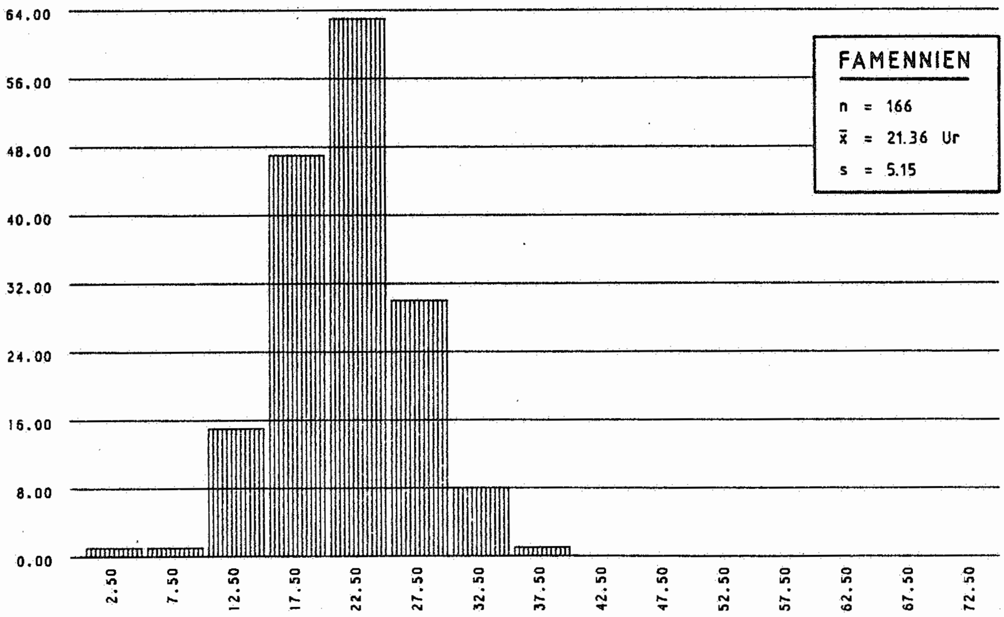


Fig. 88 : COMPTAGE TOTAL (Ur)

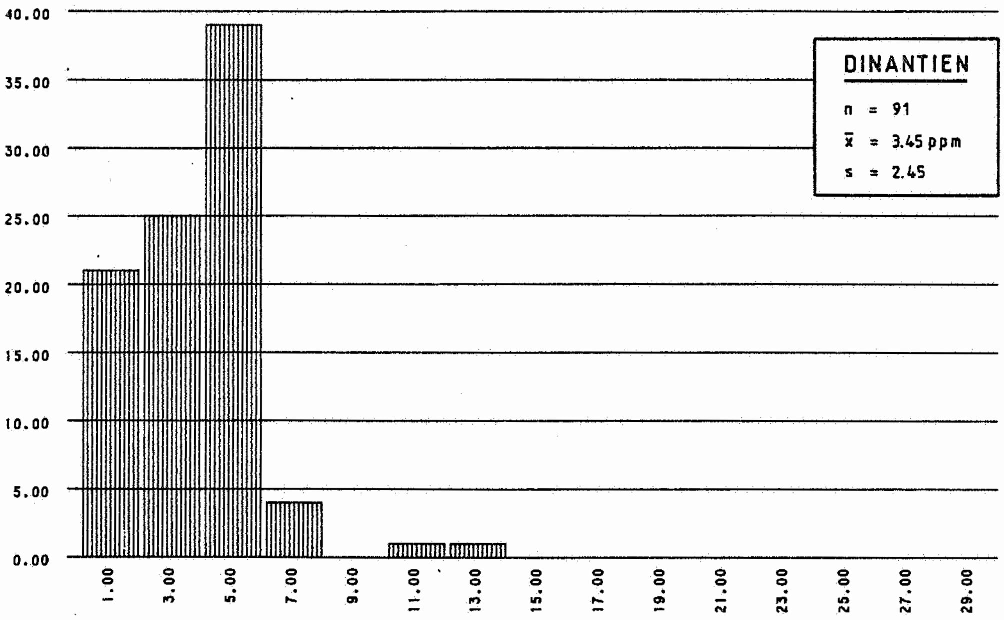


Fig. 89 : URANIUM (ppm)

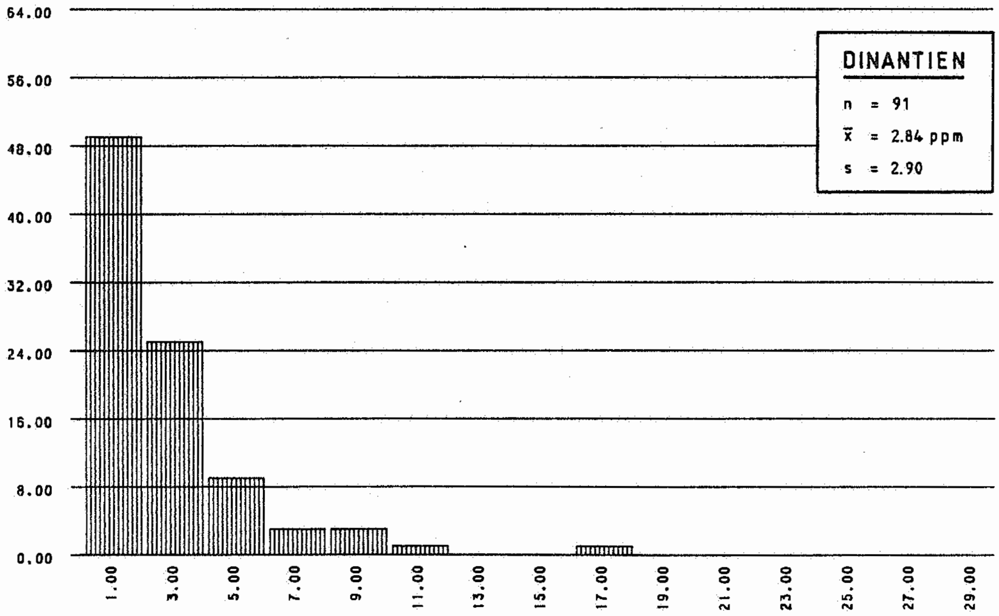


Fig. 90 : THORIUM (ppm)

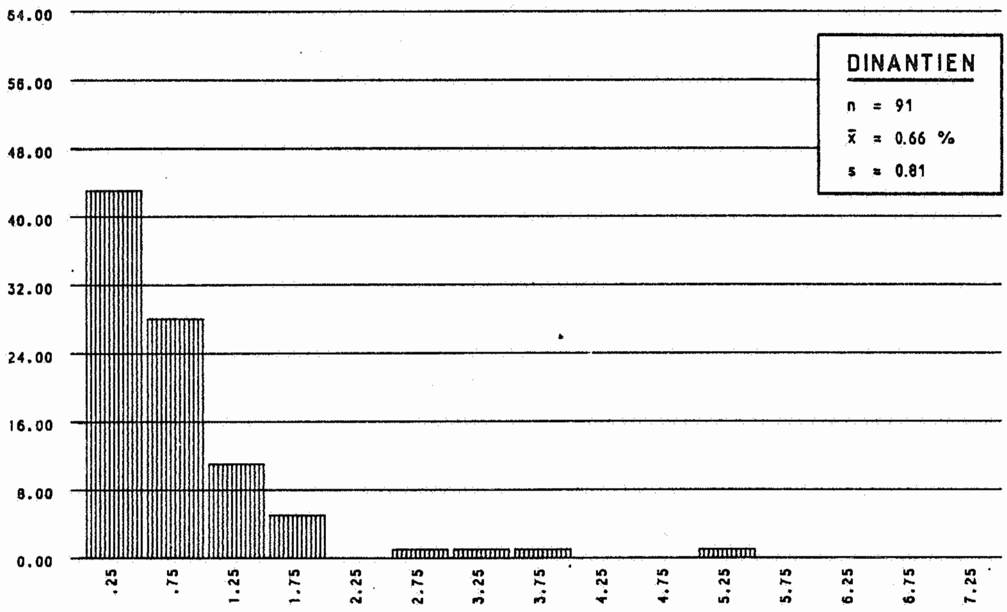


Fig. 91 : POTASSIUM (%)

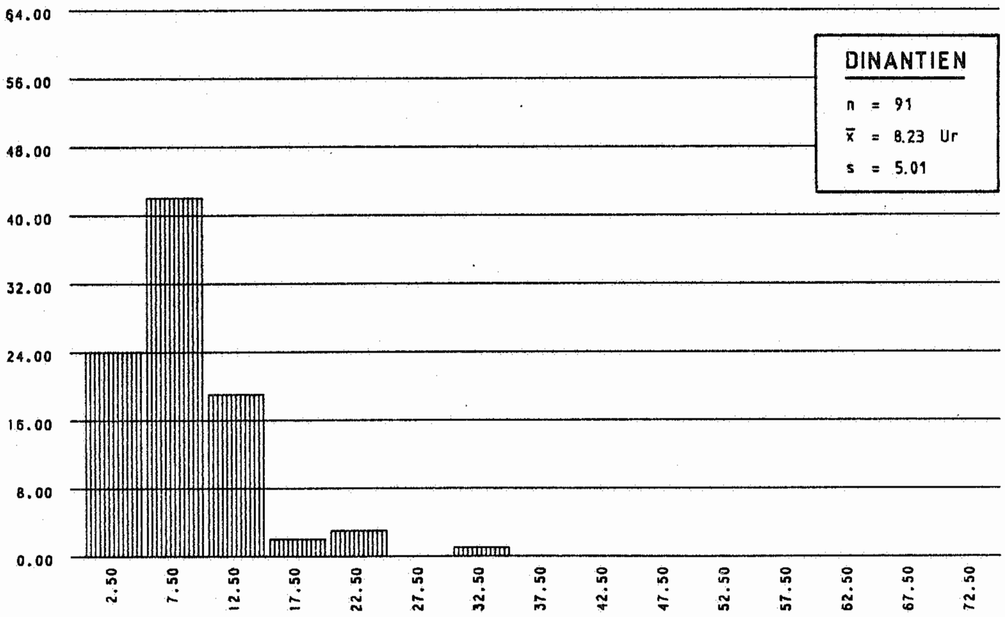


Fig. 92 : COMPTAGE TOTAL (Ur)

Table XXIII : *Statistical parameters showing the distribution of the radioelements and of the total count in various formations (totality of the outcrops)*

Formations			eU (ppm)	Th (ppm)	K (%)	TC (Ur)	Th/U
Lower Paleozoic	Revinian	$\bar{x}$	4.67	9.64	2.48	21.24	2.92
	n = 97	s	2.72	2.71	0.69	5.71	2.72
	Salmian	$\bar{x}$	5.67	11.50	3.17	26.93	3.14
	n = 84	s	4.40	3.10	0.91	8.35	3.14
	Lower Pal.	$\bar{x}$	5.10	10.47	2.80	23.86	3.02
	n = 183	s	3.61	3.04	0.86	7.56	2.96
Lower Devonian	Gedinnian	$\bar{x}$	3.35	9.83	2.16	18.59	4.23
	n = 150	s	1.52	2.99	0.72	5.37	7.98
	Siegenian	$\bar{x}$	3.79	10.63	2.27	20.89	3.63
	n = 309	s	2.18	3.16	0.65	5.83	2.92
	Emsian	$\bar{x}$	3.77	11.20	2.49	22.01	3.68
	n = 359	s	1.53	2.80	0.74	5.14	2.79
	Lower Dev.	$\bar{x}$	3.70	10.73	2.35	20.96	3.76
	n = 818	s	1.81	3.01	0.72	5.58	4.27
Meso- and Neo-Devonian	Devon.calc. rocks	$\bar{x}$	2.11	5.03	1.40	11.73	4.42
	n = 63	s	1.55	4.04	1.05	7.28	11.92
	Famennian (total)	$\bar{x}$	3.28	9.75	2.92	21.36	3.88
	n = 166	s	1.49	2.61	0.77	5.15	3.35
	Famennian (sandstone)	$\bar{x}$	3.49	10.19	2.96	21.15	4.05
	n = 41	s	1.92	2.43	0.68	4.04	3.72
	Dinantian calc.rocks	$\bar{x}$	3.45	2.84	0.66	8.23	1.65
	n = 91	s	2.45	2.90	0.81	5.01	2.42
	Silesian	$\bar{x}$	4.25	9.13	2.10	19.07	2.19
	n = 17	s	1.49	3.31	0.63	4.51	0.54

This observation comes true particularly in the Lower Devonian. From the Gedinnian to the Emsian, the averages of the measurements hardly vary : the values of uranium (eU) are about 3.5 ppm, thorium about 10 ppm and potassium about 2,3 %.

The same goes for the formations that constitute the Caledonian massives. However, here, the mean values of uranium are appreciably higher than in the Lower Devonian : between 4.7 and 5.7 ppm. The standard deviations which measure the dispersion of the values are also higher.

In the Upper Devonian, it can be seen that the Famennian shows values close to those of the Lower Devonian, with however a certain enrichment in K_2O.

Finally, on passing to the Carboniferous, the Silesian shows little difference comparatively to the lower series : the mean on the uranium channel is greater than 4 ppm, whereas the thorium and potassium channels give values comparable to those of the other detritic formations.

In all the quartzo-schistose formations, the mean values of the total counts, expressed in Ur, are between 19 Ur and 26 Ur, with standard deviations of 5 to 8 (a mean of about 20 Ur seems to be the norm.

2°) concerning the carbonate formations, it can be seen that the variations are relatively larger than in the detritic series.

Generally speaking, the contents in thorium and potassium of the calcareous rocks are always low with repercussions on the total count : about 10 Ur instead of 20 Ur in the schistose-sandstone rocks.

The values of uranium are somehow surprising : where Devonian calcareous rocks show rather low values, the Dinantian calcareous rocks on the contrary show equivalent values comparable to those of the lower Devonian : averaging 3.5 ppm.

b) Influence of the outcrops size on the measurements

The figures presented in table XXIII concern the totality of the outcrops encountered in each different formation. Table XXIV shows how these values vary when only special categories of outcrops (small outcrops, large outcrops), or, to be even more selective, quarries, are considered.

As already established in § IV.5 (table XXI), marked differences appear. In the measurements on small outcrops, count rates are influenced by the soil cover (silts, clays...) which occupy a part of the solid angle of detection. The result is a decrease in apparent values relatively to the measurements on large outcrops. Thus, measurements on large outcrops and on quarries should be viewed as more representative than measurements on small outcrops. However, as far as quarries are concerned, it should be borne in mind that the measurements are often effectued on a type of lithology which is not representative of the average geological formation (sandstones or quartzites exploited for road covering in the Lower Devonian, pure calcareous rocks exploited for lime preparing.)

c) Definition of a threshold of anomaly fo uranium

With the threshold of anomaly as defined in the precedent chapter by the formula :

$$t = \bar{x} + 2S$$

the values arrived at vary considerably depending on the type of formation (5 ppm eU for the Devonian calcareous rocks, 14 ppm for the Salmian).

In order to meet the needs of the cartographic representation, the minimal value of 6 ppm was retained (cf. map IX).

Out of the 13 000 points or thereabout on the file, only 421 show values greater than this value. The anomalous values are distributed as follows :

total : 421 points > 6 ppm
85 points > 10 ppm
16 points > 20 ppm.

Thus, less than 4 % of the values considered as anomalous are greater than 20 ppm.

Table XXIV : *Influence of the type of outcrop on the radiometric parameters*

Formation	Type(*) of out-crop	Arithmetical means						Number of points
		eU	Th	K	TC	Th/U	U/K	
Lower Paleozoic	5	4.18	9.30	2.37	21.05	2.89	1.82	65
	6	5.61	11.11	3.04	25.40	3.10	1.83	118
	7	–	–	–	–	–	–	–
Lower Devonian	5	3.25	10.01	2.05	19.00	4.06	1.66	350
	6	4.34	11.27	2.57	22.42	3.54	1.80	468
	7	3.36	11.74	3.27	23.57	3.68	1.20	25
Givetian	5	1.59	4.59	1.36	10.96	7.95	1.23	22
	6	1.88	3.95	1.35	10.68	2.27	0.74	27
	7	0.90	1.20	0.47	3.40	1.21	1.36	8
Visean	5	4.08	2.42	0.61	8.89	1.27	28.14	33
	6	3.49	1.43	0.26	5.79	0.80	38.25	30
	7	3.50	1.50	0.20	3.97	0.15	15.49	24

(*) 5 = small outcrops
6 = large outcrops
7 = quarries

IV. 6. 3. *Cartography of radiometric data*

a) Choice of a method of representation

The cartographic representation of the radiometric data set a particular problem, mainly due to the heterogeneous distribution of the points of measurement. This is well illustrated in fig. 93, which shows the network of points of measurement on a unit of the 1:50 000 map of Belgium. The density of measurements is very high along the routes followed by the vehicle, whilst the insides of itinerary loops are completely devoid of measurements. In areas where, for reasons of inaccessibility, a sufficiently dense coverage of the area could not be achieved, the consequent disposition of points along routes far apart from each other would render any tracing of iso-value contours haphazard.

Another type of cartography was therefore chosen : the area mapped was represented by juxtaposed unit square grids (dimension : 600 m) which were more or less obscured by hatchings. The value within each grid is taken as the weighted average of four measurements closest to the centre of the grid within a maximum distance of 2 kilometers. The output board of the computer hatches the grid according to a code representing three classes of values.

For uranium, the code is as follows :

- class 1 : eU values between 0 and 3 ppm.
  Only the limits of the grid are traced (no inside subdivisions).
- class 2 : eU values between 3 and 6 ppm.
  The grid is subdivided into four by two orthogonal hatches.
- class 3 : eU values greater than 6 ppm (*anomalies*).
  The grid is subdivided into sixteen by 3 x 2 orthogonal hatches.

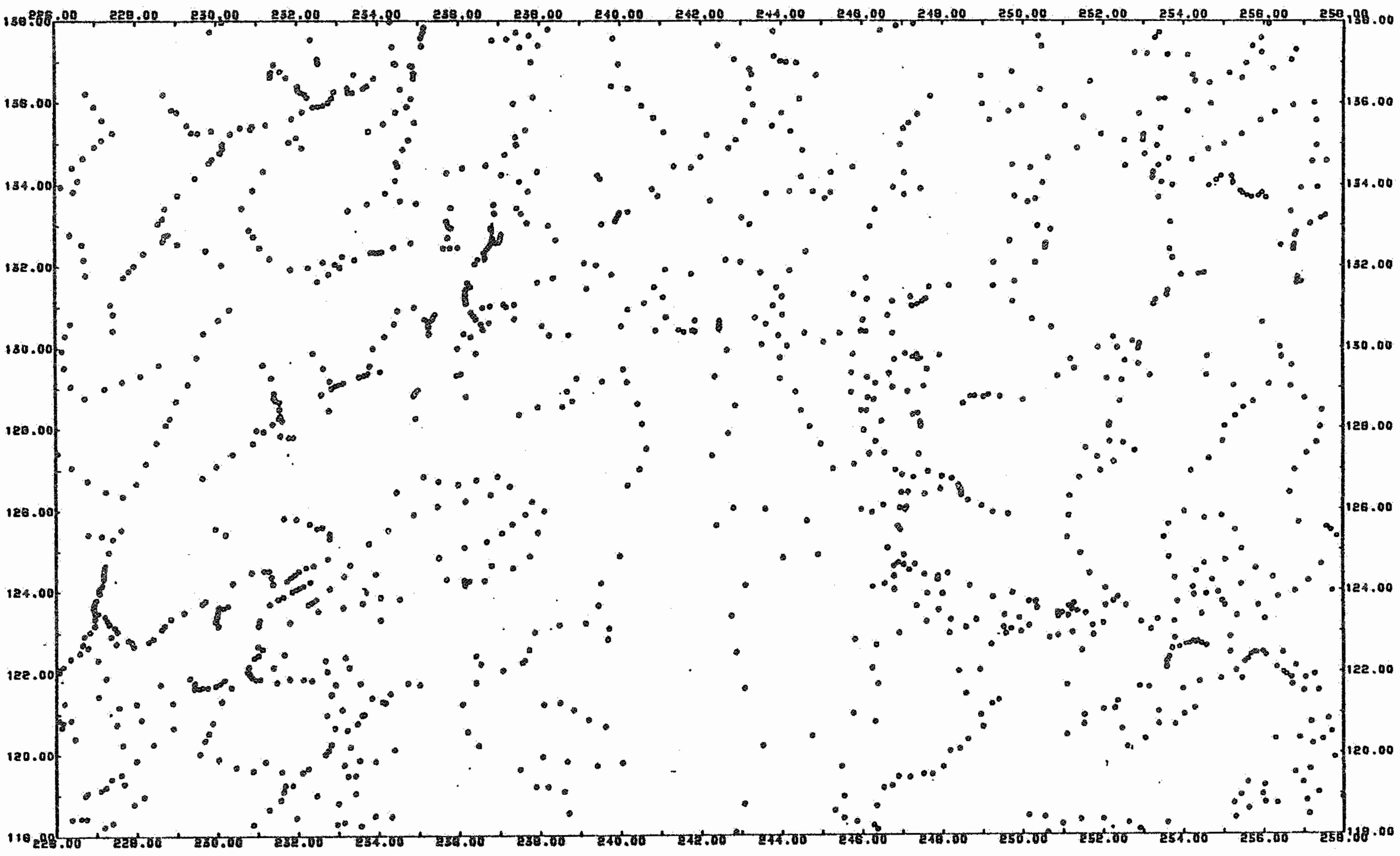


Fig. 93 : – Distribution spatiale des mesures radiométriques (carte 49)

– Distribution of the points of measurement on map 49.

The same method of representation was adopted for the "total count", with the following class limits : 15 Ur and 25 Ur. (*)

b) Description of the map of uranium (map IX)

Even at its highest level, Belgium is poor in rock outcrops. The Ardenne is a plateau still largely covered with Quaternary deposits (loess, solifluction surfaces), the outcrops occurring most often along the flanks of valleys. Consequently, a vast majority of the radiometric measurements concern points listed under the caption "superficial formations". This explains why, on maps IX and X, low values (class 1 defined in (a) above) occupy the largest area.

The darker zones on the map, which correspond to the average and high values of the radiometric parameter (classes 2 and 3), are generally areas where the geological substratum outcrops most. They often show an elongated and sinuous morphology following the outlines of valleys of or certain routes rather than geological structures.

These considerations call for some caution in the interpretation of the maps. The scarcity of anomalies in certain regions could merely be due to a relative rarity of outcrops associated with an absence of relief (ancient planations).

This being said, it should be admitted that on the map for uranium, the visible anomalies, as in the case of the alluvial prospection, appear to occur in several large constellations, corresponding in all likelihood to particular geological environments.

Outstanding are :

1°) the massive of Stavelot

Within the rectangle defined by

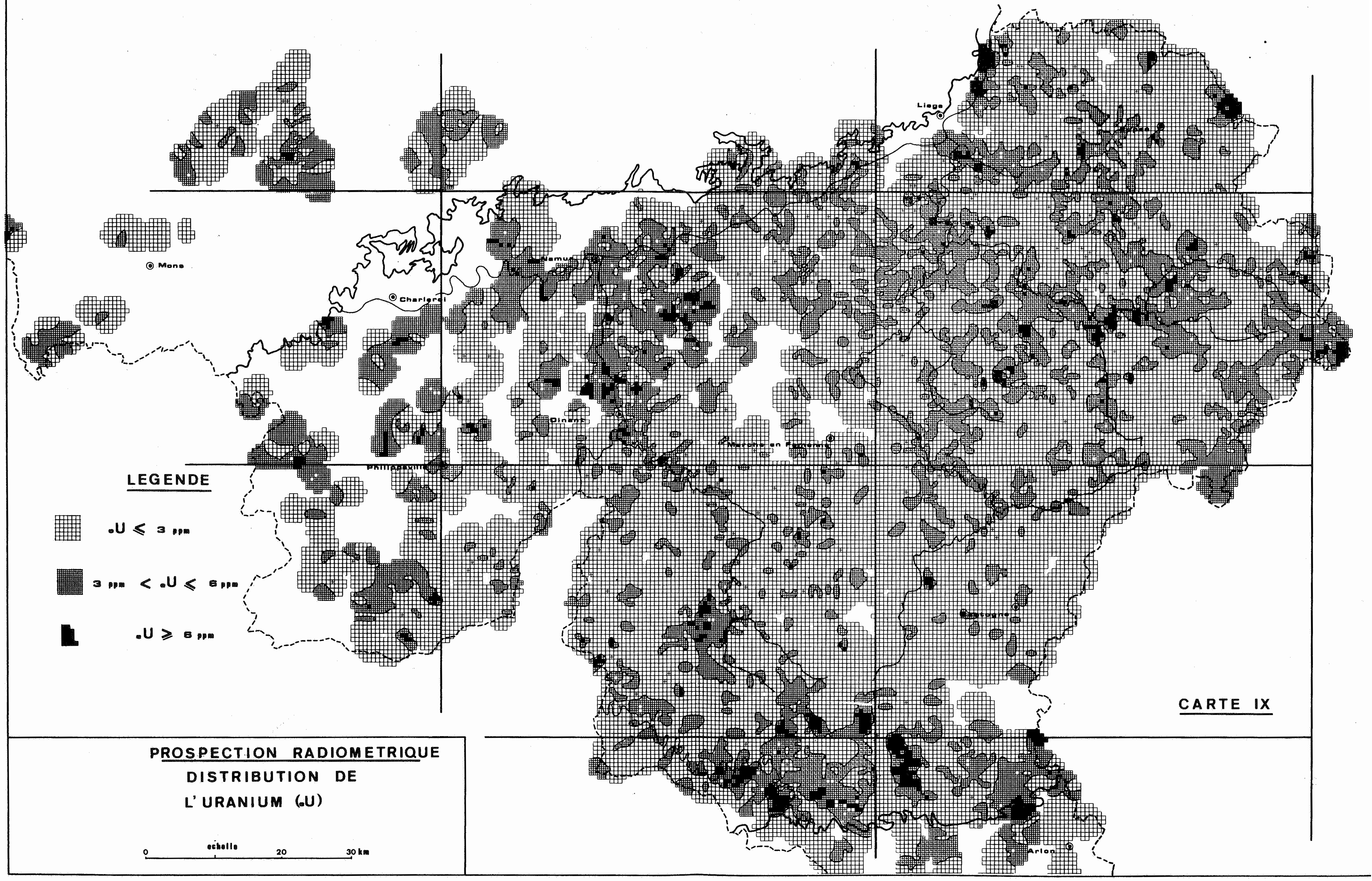
X = 242 to 300
Y = 98 to 138

there are 84 measurements greater than 6 ppm distributed into a certain number of anomalies. A few of these occur clearly along the Revinian-Salmian limit (localities : Lorcé, Chevron, Malmédy, Xhoffrai...). Other are rather localised at the central part of the Revinian massive (Trois-Ponts, Stavelot). Finally, a few belong to

---

(*) These limits, expressed in μR/h, correspond to 9 and 15 μR/h.

CARTE IX



PROSPECTION RADIOMETRIQUE

DISTRIBUTION DE

L'URANIUM (eU)

the Salmian (Bra, Vaux-Chavanne).

2°) the synclinorium of Dinant

Within the rectangle defined by

X = 146 to 210
Y = 98 to 125

98 values exceed 6 ppm (eU). These anomalies correspond to a type well-known in Belgium, that of the transition beds between the Visean and the Namurian.

Two anomalies are most conspicuous : one in the vicinity of the Meuse, near Yvoir (localities : Haut-le-Wastia, Anhée, Yvoir), and the other north of the N4 Namur-Marche highway, not far from Assesse (localities : Sorinne-la-Longue, Gesves).

3°) the meridional fringe of the Ardenne (synclinorium of Neufchâteau)

Within the rectangle defined by

X = 200 to 250
Y = 40 to 65

there are 88 points with eU values greater than 6 ppm.

This vast anomalous zone consists essentially of points situated within the different strata of the Siegenian (but mainly within the Lower Siegenian).

At the southern flank of the synclinorium of Neufchâteau, there is a string of anomalies aligned west-east in the forests of Bouillon, Muno, Herbeumont, Chiny and Rulles.

The anomaly in the forest of Muno runs over the Gedinnian of the anticline of Givonne. That in the forest of Rulles occupies the entire drainage basin of the Mellier from the Lower Siegenian to the Upper Siegenian.

At the northern flank of the synclinorium, three other anomalies are located between Bertrix and Neufchâteau within the Lower Siegenian.

4°) the anticlinal zone of the Ardenne

An anomalous zone, localised within the Gedinnian, but less extended than the other zones mentioned above, occupies part of the drainage basin of the upper Lesse, close to the localities of Gembes, Porcheresse and Daverdisse.

Other anomalies

Some dispersed anomalies can be seen on the map outside of the large zones previously defined. Without being exhaustive, let us cite the following localities close to which the anomalies were observed :

- Visé (known anomaly and studied long ago);
- Raeren (within the Revinian at the north-east extremity of the massive of Stavelot);
- Manderfeld (Emsian, synclinorium of Eifel).

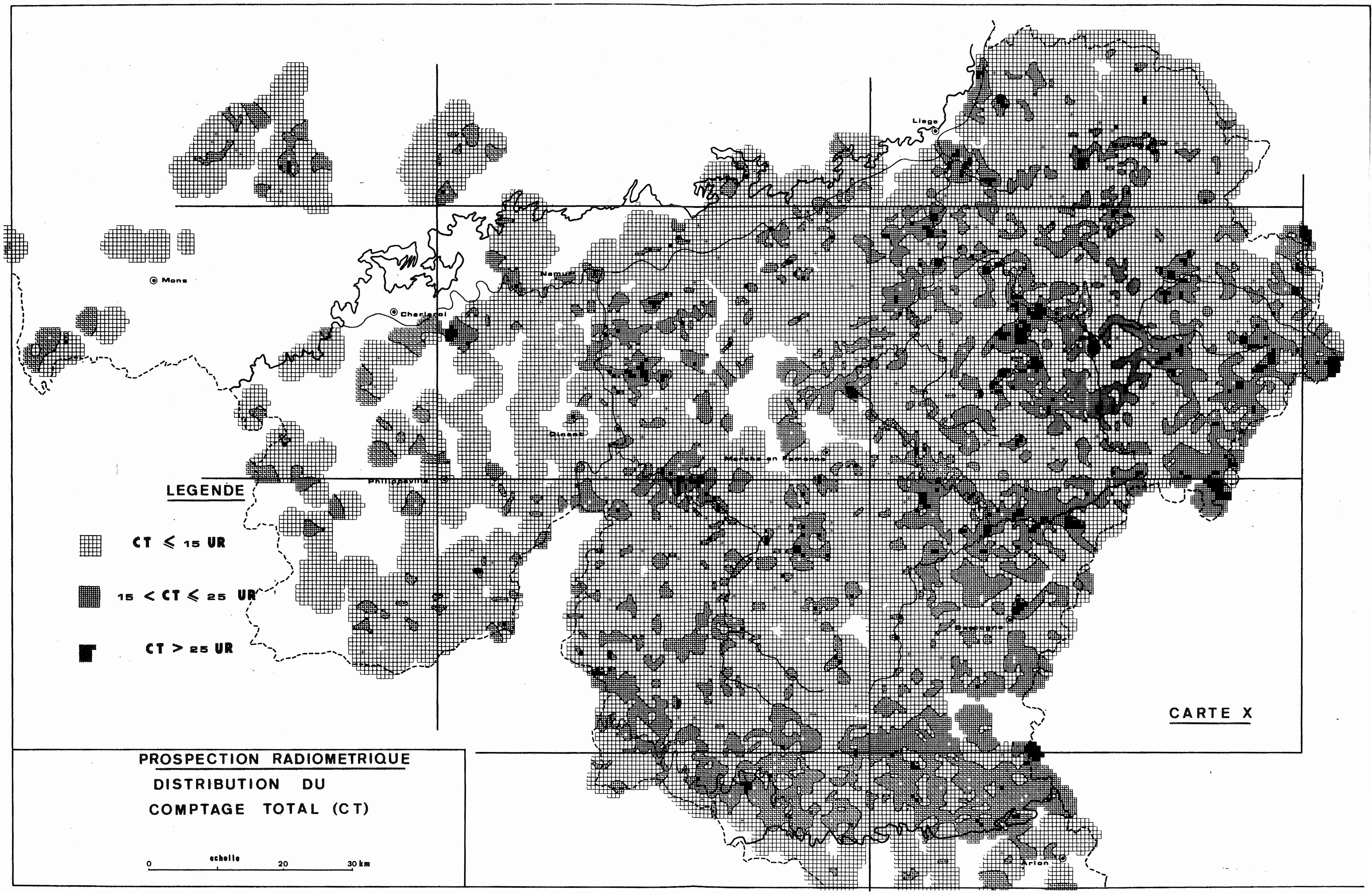
c) Description of the "Total count" map (map X)

The total count is much influenced by the thorium and potassium concentrations (as can be seen from the results for the Lower Devonian schists and the calcareous Dinantian, displaying similar eU values, in table XXII).

Much more than the uranium map, the "total count" map will give a picture of the regional lithology.

Table XXIII shows that, generally, the Visean limestones are characterised by values lower than 15 Ur, whereas the sandy-schistose facies of the Caledonian and of the Lower Devonian generally present higher values in the 15-25 Ur range. With regard to the Middle and Upper Devonian, the values are influenced by numerous schistose interstratifications (schists with calcareous nodules, calcshales) and the range of total count measurements can increase accordingly.

An anomaly in uranium can also increase the total count value. However, it should be noted that the weight of the uranium in the total count is relatively unimportant. For example, in the Lower Devonian, the incidence of an increase of the eU value from 3.57 ppm to 7.15 ppm ($\bar{x} + 2S$) on the total count measurement has been calculated : the total count value, initially 19.68 Ur, rises only to 23.26 Ur.



PROSPECTION RADIOMETRIQUE
DISTRIBUTION DU
COMPTAGE TOTAL (CT)

CARTE X

LEGENDE

- ▦ CT ⩽ 15 UR
- ▩ 15 < CT ⩽ 25 UR
- ■ CT > 25 UR

Finally, the "total count" map will reflect the presence of superficial formations, more than it was the case for the uranium (eU) map (great influence of thorium and potassium on the Ur values).

Consequently the "total count" map will reflect principally the lithological variations and the geometrical effects more than the eventual anomalies in uranium.

Taking these preliminary remarks into perspective, a few large units can be singled out :

- the massive of Stavelot

  The high "total count" values (more than 25 Ur) are in accordance with the anomalies in uranium. Here the "total count" maxima reflect both a particular lithology (black shales of the Upper Revinian and Salmian), and some uranium anomalies related to that stratigraphic level.

- the synclinorium of Dinant

  A series of rather high values (15-25 Ur) forms a more or less uninterrupted strip centred on maximum values higher than 25 Ur, and extending from S-SW (Givet) to N-NE (Durbuy) (axis Givet-Beauraing-Rochefort-Durbuy). It can be related to the schistose and sandstone facies of the Frasnian and Famennian (region of the Famenne). The anomalies in uranium of the Namurian and Visean, well marked on the "uranium" map, are here somewhat lessened (including the particularly strong anomalies of the Visean region). The strongest "total count" anomalies visible in the region of Condroz are actually related to the Famennian anticlines (the so-called "psammites" of Condroz).

- the Lower Devonian of the central and southern Ardenne

  The structures of the Neufchâteau synclinorium, and the Rocroi-Serpont-Bastogne anticline are quite apparent on the "total count" map. A zone characterised by strong Ur values (15-25 Ur with numerous values higher than 25 Ur) is spreading towards the south and the east of the Ardenne anticline; it corresponds to the slaty rocks of the Siegenian. In the axial part of the anticline, the lower Ur values (less than 15 Ur, with a few 15-25 Ur zones) correspond to the Gedinnian. It should also be observed, in this axial zone, that a few anomalous values correspond to high uranium values delimitating the eastern border of the massive of Rocroi.

- Finally, without aiming at completeness of description, we point out to a localised zone near Manderfeld, where a "total count" anomaly is superposed upon a uranium anomaly.

In short, the "total count" map can roughly speaking be considered as a representation of the lithology, the eventual coincidences between uranium and total count anomalies generally occurring in a few zones where the uranium is related to a particular slaty facies.

BIBLIOGRAPHY OF CHAPTER IV

49) BOWIE S.H.U., HALE F.M., OSTLE D., BEERK E., 1955

Radiometric surveying with a carborne counter.

Bull. Geol. Survey of Great Britain, n° 10, pp. 1-23.

50) GOSO H., SPOTURNO J., PRECIOZZI F., 1976

Metodologica de prospección autoportada - Primeros resultados obtenidos en la Cuenca del Nordeste (Uruguay).

In Exploration for Uranium Ore Deposits IAEA (Vienna).

51) LØVBORG L., 1973

Future Development in the use of gamma-ray spectrometry for uranium prospecting on the ground.

In Uranium Exploration Methods, pp. 141-153 (Proceedings of a panel, Vienna, 10-14 April 1972).

52) MATOLIN M., 1973

Artificial standards for calibration of airborne, field portable and logging gamma spectrometers.

In Uranium Exploration Methods, pp. 125-139 (Proceedings of a panel, Vienna, 10-14 April 1972).

53) MATOLIN M., DEDACEK K., 1971

Study for foundation of calibration base for field gamma-spectrometers.

In Czechoslovakia, Final Rep. of the Faculty of Science, Charles Univ., Prague (In Czech, 118 pages).

54) MILLER J.M., LOOSEMORE W.R., 1971

Instrumental techniques for uranium prospecting.

In Uranium prospecting handbook (London, Institution of Mining and Metallurgy), pp. 135-148.

55) NELSON J.M., 1953

Prospecting for Uranium with car-mounted equipment.

Geological Survey Bulletin (USA), 988-1, pp. 211-221.

56) Radiometric Reporting Methods and Calibration.

In Uranium Exploration, technical report series n° 174, 1976, IAEA (Vienna).

57) Gamma-ray Surveys.

In Uranium Exploration, technical reports series n° 186, 1979, IAEA (Vienna).

CHAPTER V

CONCLUSIONS

V. 1. PRELIMINARIES

Within the period allowed for the completion of the present program, we could not afford a complete scientific exploitation of the 100 000 data or so derived from the 10 200 stream sediment samples, 2 400 water samples and about 13 000 radiometric measurements collected.

It is beyond doubt that, in the future, a more elaborate statistical treatment of the files will allow to draw some new relationship which could not be inferred from the direct examination of the documents and maps presented here.

However, the main objective of this program, which was to carry out a preliminary prospection, appears to be largely achieved. A first picture of the geochemical distribution of uranium in the whole Belgian Paleozoic is already available and, from this moment, some detailed research could be undertaken in particular zones.

V. 2. A FEW METHODOLOGICAL LESSONS DRAWN FROM THE PROSPECTION

The joint utilisation of three different prospection methods allows, by a comparison of their results in the same region, to formulate interesting remarks about their relative adequacy and their fields of application.

So, as far as the stream sediment prospection is concerned, the methods of sampling and analysis chosen by the Louvain-la-Neuve team appeared to be well adapted to the purposes of a preliminary campaign, even in the calcareous terranes. The comparison with the results of the radiometric prospection is eloquent in that respect : the two methods have revealed numerous anomalies in the same regions, with, in a few cases, rather accurate superpositions.

The radiometric maps of chapter IV (maps IX and X) demonstrate that, in a country like Belgium (equipped with a particularly dense roads network), a carborne prospection achieves a rather complete and low-price covering of the field (if compared to an airborne program).

On the other hand, as far as the hydrogeochemical prospection is concerned, unfortunately we have to report some negative results owing to the fact that the Brussels team was obliged to send the water samples to two different laboratories successively.

Indeed, it can easily be stated from map VII that in the central and southern zone of the Ardennes, whose water samples were analysed by the French laboratory COGEMA (i.e. by a fluorimetric method), no significant anomaly is visible. The major surface in that zone corresponds to the Lower Devonian of the central and southern Ardennes and, partly,, to the Caledonian of the massive of Stavelot. Such a fact is rather amazing, more especially as a lot of uranium anomalies have been detected in the same region by the other two methods of prospection. Furthermore, in the eastern and western zones of map VII, where the uranium analyses were performed by the "delayed neutron" method, a lot of clear anomalies are visible above the threshold value of 2 ppb and some of them present a good correlation with the corresponding results of the other prospections (see the massive of Stavelot for instance).

We can only come to the conclusion that such a disparity between adjacent zones is to be attributed to the differences in the methods of analysis. It is likely that the samples which were analysed by COGEMA suffered losses (probably much more severe than it can be inferred from the study exposed in § III.3.3.)

V. 3. INVENTORY OF THE MAIN ANOMALOUS ZONES

The synthesis documents for uranium (map II for the stream sediments results and map IX for the radiometric results) bring out three main regions where the presence of numerous anomalies seem to reveal a more favourable geochemical or geological context.

1°) The massive of Stavelot as a whole

With a uranium background higher than in the rest of the country (5 to 6 ppm in rocks, 1.5 ppm in stream sediments), this region presents a series of anomalous areas whose spatial arrangement seems to confirm the existence of a more radioactive level at the top of the Revinian series (level attributed to the RV5; see results of the 1955 prospection, chapter I).

A few anomalous spots of maps II and IX can be superposed. They grossly correspond to the following localisations :

a) the drainage basin of the Lienne river (Chevron, Vaux-Chavanne);

b) the drainage basin of the Warche river (Malmédy, Xhoffrai);

c) the confluence between the Salm and the Amblève (Trois-Ponts, Stavelot).

The synthesis map for the hydrogeochemical results (map VII) also shows a halo of anomalous values in a sector between the Warche and Amblève rivers.

2°) The southern Ardenne

In this part of the country, no uranium anomaly had ever been reported before the present campaign.

The results of the stream sediments and radiometric prospections are concordant enough; they reveal a lot of anomalous spots which seem to be distributed in two distinct areas :

- the synclinorium of Neufchâteau
- the anticlinal axial zone of Gedinne-Paliseul.

In the first region, some anomalies are nearly coincident in the two prospections. The areas concerned are the forests of Muno, Herbeumont, Chiny and Neufchâteau. The geological basement belongs mainly to the Siegenian.

In the Gedinne-Paliseul region, the concordance is far from being obvious : while the stream sediments results reveal a string of localised anomalies along the Nafraiture-Paliseul axis, the radiometric prospection only shows a large anomalous area in the north of that zone (region of Porcheresse and Daverdisse). However that may be, the two prospections allow to believe that the Gedinnian is liable to conceal uranium anomalies in that particular zone, as is confirmed by the results of a detailed study on an anomalous outcrop near Daverdisse (see § V.4).

3°) The synclinorium of Dinant

The three prospections have revealed a lot of uranium anomalies in this vast tectonic unit where the Dinantian limestones largely outcrop.

The origin of those anomalies is to be sought, in most cases, in the intermediary shales between the Visean and the Namurian, but, in some instances, they originate in the calcareous Visean itself. It is one of the contributions of the present work to have pointed out to the rather high uranium background of the Visean limestones. The radiometric measurements in quarries have given eU values higher than 3 ppm and a number of values obtained on large Visean outcrops go beyond 10 ppm.

These results confirm some observations made by A. HERBOSCH *et al.* (42) in the massive of Visé.

V. 4. A PARTICULAR STUDY ON A RADIOMETRIC ANOMALY IN THE LOWER DEVONIAN AND ITS MINERALOGY

Follow-up work has been undertaken on the radiometric anomaly of Daverdisse (Haute-Lesse) discovered by the Mons prospecting crew.
A description of the physical features of the radiation as well as its geological trap and a preliminary investigation of the minerals associated have been published by L. Dejonghe *et al.* (58). Complementary mineralogical researches by J. Jedwab and L. Dejonghe (59) have increased the amount of minerals discovered at that place.

Situated in a fractured zone of rocks lying between the Upper Gedinnian and the Lower Siegenian, this very punctual anomaly displays, in its most active spot, eU values in the order of 2000 ppm. The thorium and potassium values are, on the other hand, quite normal.

Field observations show that the anomaly developed along an interface between a schistose layer and a sandstone block separated by a minor fault. At the hand specimen scale, the uranium appears concentrated in strongly altered limonitic veins.

Microprobe analyses, following an episcopic examination, revealed a complex mineralogical association, in which four groups have been distinguished by Dejonghe *et al.* (58).

- group 1 : lamellar uranyl phosphates.
- group 2 : lead, iron and aluminium phosphates with variable uranium content. Non lamellar.
- group 3 : iron oxides with a variable uranium content.
- group 4 : titanum oxides with a minor uranium content.

Reassessed by J. Jedwab and L. Dejonghe (59) with the help of several instrumental methods, the uraniferous occurence has yielded numerous new minerals.

Finally, more than 20 minerals, have been discovered among which : uraninite ; Ti - V - Fe oxides (uraniferous rutile and anatase, brannerite and an undetermined red compound) ; selenides and sulfides of Hg, Ag, Pb, Bi, Cu and Sb ; U, Bi or Zr bearing iron hydroxides ; iron sulfates ; uranium phosphates and xenotime.

From an economic point of view, although this particular anomaly does not present any real interest, the possibility of economically valuable concentrations in the Lower Devonian cannot be excluded as long as the uranium source has not been precised.

Indeed, the sedimentological features of the Lower Devonian are well suited for the formation of stratabound uranium concentrations.

Besides, if the Daverdisse anomaly presents a particular interest owing to its intensity and to the presence of minerals newly observed in Belgium, we have to stress that the carborne prospection led to the discovery of other uranium anomalies (in outcropping rocks) in the Lower Devonian of that part of the Ardenne. Most of them occurred in the Gedinnian (anticline of Serpont-Bastogne) and in the Siegenian (syncline of Neufchâteau), Daverdisse holding from this point of view the most septentrional position.

BIBLIOGRAPHY OF CHAPTER V

58) DEJONGHE L., CHARLET J.M., DUPUIS C., 1982
L'anomalie radioactive de Daverdisse et les minéraux uranifères associés.
Ann. Soc. géol. Belg., t. 105, pp. 177-193.

59) JEDWAB J., DEJONGHE L., 1983
Contribution à l'étude minéralogique de l'indice radiactif de Daverdisse.
Bull. Soc. belge Géol., t. 91, pp. 217-233.

PROFESSIONAL PAPER 1983/1 - N° 196