Available online at www.sciencedirect.com
ScienceDirect
C. R. Chimie 12 (2009) 850–853
COMPTES RENDUS CHIMIE
http://france.elsevier.com/direct/CRAS2C/

Full paper / Mémoire

# First measurements of anthropogenic and natural radionuclides in surface soils (10 cm) of Côte d'Ivoire

A. Koua [a], H. Michel [b,*], J. Alabdullah [b], V. Barci [b], H.K. Aka [c], G. Barci-Funel [b], G. Ardisson [b]

[a] *Laboratoire de physique nucléaire et radioprotection, UFR sciences des structures de la matière et de la technologie, Université de Cocody, 22 BP 582 Abidjan 22, Côte d'Ivoire*
[b] *Laboratoire de radiochimie, sciences analytiques et environnement, Université de Nice Sophia-Antipolis, 06108 Nice cedex, France*
[c] *Laboratoire de chimie-physique, UFR sciences des structures de la matière et de la technologie, Université de Cocody, 22 BP 582 Abidjan 22, Côte d'Ivoire*

Received 9 May 2008; accepted after revision 19 November 2008
Available online 23 May 2009

**Abstract**

$^{239-240}$Pu and $^{137}$Cs activities in soil samples were measured in two sites of the littoral part of Côte d'Ivoire: Abidjan and the classified forest of ''la Comoé''. Two areas were chosen: a forest and a clearing. The aim of this work is to establish a starting point for nuclear contamination data of a non-nuclear country. Measured soil cores were of 10 cm depth. $^{137}$Cs and $^{239-240}$Pu activities, mainly due to weapon nuclear tests in the 1960s, were in the range 0.37–2.3 and 0.023–0.125 Bq kg$^{-1}$ respectively. $^{239-240}$Pu/$^{137}$Cs values were found to be about 0.024–0.19 in agreement with the expected value for nuclear tests. ***To cite this article: A. Koua et al., C. R. Chimie 12 (2009).***


*Keywords:* $^{239-240}$Pu; $^{137}$Cs; Côte d'Ivoire; Soil

## 1. Introduction

The study of radionuclide spreading into the environment is of great interest. The long and medium half-life radionuclides were deposited in the world owing to the intensive testing of nuclear weapons in the atmosphere in the 1960s, adding their radioactivity to that of natural series of uranium, thorium and to the natural radionuclide $^{40}$K [1,2]. Moreover, the major accident of Chernobyl in 1986 spread many fission products, mainly in the northern hemisphere. Very few measurements of fission products and transuranium element activity have been made in West Africa. A recent accident (2006 December–2007 January) concerning the discharge of toxic wastes in the Abidjan laguna, for which we have few elements to judge the presence of radioactivity, but which points out the need for radioecological survey in the country, reinforces the interest to carry out the first measurements of anthropogenic radioactivity in soil samples.

* Corresponding author.
*E-mail address:* hmichel@unice.fr (H. Michel).

1631-0748/$ - see front matter © 2009 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crci.2008.11.012

## 2. Experimental

### 2.1. Sample collection

The samples were soil cores collected in the Abidjan city (site 1) and the classified forest of "la Comoé" (site 2), which is a protected primary forest located at about 100 km of Abidjan (the economic capital) between the Grand Bassam and Alépé departments. The sites are situated in the south-east of Côte d'Ivoire, the big rainfall region, at about 5° N latitude, 4° W longitude (Fig. 1). The sampling was carried out in two different areas: under tree canopy (sample A), and in a clearing site (sample B). Core samples were extracted with an iron cylinder of 7 cm diameter and 10 cm length. Each core was sliced into three sections (Table 1).

Soils are coming from parent rocks, which are essentially constituted of granites, migmatic and schist. The profile of these tropical soils is constituted by 2 horizons: the first horizon is rich in litter, due to the biogeochemical cycles and the second horizon is called the sand accumulation horizon. Its thickness is about 1 m. These soils are considered as ferrallitic forest soils [3,4].

### 2.2. Radiochemical separation

All reagents were of ACS grade: 65% $HNO_3$, 37% HCl, 30% $NH_3$. Dilutions were made with deionised water.

To determine the plutonium activity, a radiochemical separation is needed (Fig. 2). The samples were weighted and dried in a furnace at 600 °C during 24 h in order to destroy the organic matter. $^{242}$Pu (100 µl, 0.07368 ± 0.00066 Bq/g) yield tracer was added to the samples; afterwards they were leached twice with 8 M

Table 1
Sample collection information.

| Site | Area | Depth (cm) |
|---|---|---|
| *1* Abidjan city | *A* Under the tree canopy | 0–3 |
| | | 3–6 |
| | | 6–10 |
| | *B* Clearing area | 0–3 |
| | | 3–6 |
| | | 6–10 |
| *2* The classified forest of "la Comoé" | *A* Under the tree canopy | 0–4 |
| | | 4–7.2 |
| | | 7.2–10 |
| | *B* Clearing area | 0–3.6 |
| | | 3.6–6.8 |
| | | 6.8–10 |

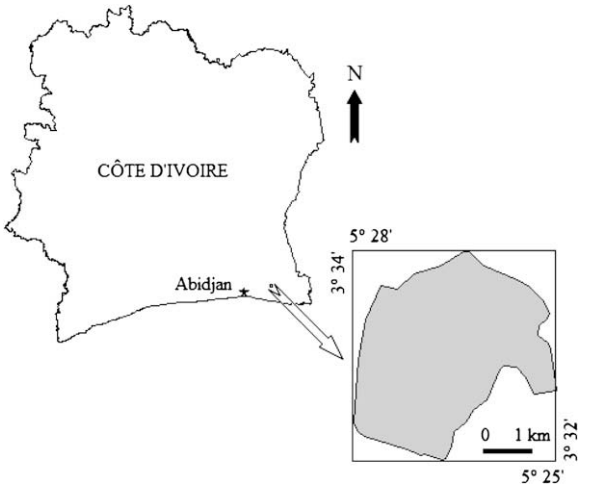


Fig. 1. Location of Abidjan city and of the classified "la Comoé" Forest.

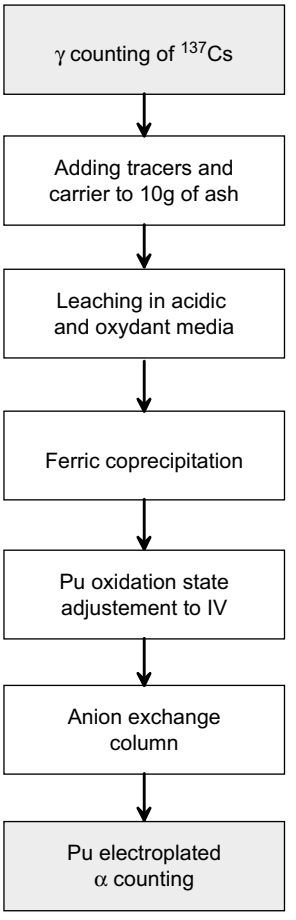


Fig. 2. Synoptic scheme of the radiochemical separation.

$HNO_3$ during 4 h each. A few 30% $H_2O_2$ drops were also added each hour. The supernatant (≈200 ml) was centrifuged and evaporated to 25 ml. The solution was diluted to 150 ml with deionised water in order to get a higher pH.

Transuranium elements were then co-precipitated with ferric hydroxide in ammonia medium until pH 8–9. The precipitate was washed with 1% $HNO_3$, centrifuged twice, dried at 50 °C, and finally dissolved with 50 ml 8 M $HNO_3$.

The sample solution was filtered and percolated through anionic exchange column Dowex 1X8 (100–200 mesh; diameter = 10 mm, length = 100 mm) pre-conditioned with 100 ml 8 M $HNO_3$ solution. The column was then washed with 100 ml 8 M $HNO_3$ to remove mainly Am, Cm and with 100 ml 10 M HCl to desorb Th. Finally, Pu was stripped off the resin with 100 ml 0.1 M $NH_4I$–10 M HCl [5,6]. The eluate was evaporated to dryness; a few drops of $H_2O_2$ were added to eliminate iodide.

Pu isotopes were then electroplated in sulphuric acid–ammonia medium at pH = 2.4 on a stainless steel disk with a current of 1 A during 1 h [7].

### 2.3. Alpha spectrometry

Alpha-spectra were measured with a 450 $mm^2$ active area boron implanted silicon detector. The energy resolution (FWHM), measured on the 5.47 MeV alpha group of $^{241}Am$, was 20.0 keV. The α-spectrometer was a dual vacuum chamber EG&G Ortec 576A; the output pulses were analyzed with a multichannel buffer analyzer (spectrum master Ortec 919).

### 2.4. Gamma spectrometry measurements

$^{137}Cs$ activity measurements were carried out without radiochemical separations. Soil samples were oven dried at 100 °C, homogenised and packed in thin plastic containers in a well-defined geometry.

The γ-spectrometer consisted of a 17% relative efficiency HPGe detector with an energy resolution (FWHM) of 1.90 keV on the 1.33 MeV photo peak of $^{60}Co$. The relative photo peak efficiency was determined using standard activity sources of $^{152}Eu$, $^{137}Cs$ and $^{133}Ba$. The background contribution was reduced by surrounding the detector and source assembly with a 5 cm thick lead castle internally covered by copper sheets of 2 mm thickness. Four counting runs of about 100,000 s were carried out for each sample in order to obtain good statistics on the unique photo peak of 661.6 keV of $^{137}Cs$.

## 3. Results and discussion

Table 2 presents the organic matter content of the samples after calcinations at 600 °C. For the forest and the clearing area in the two sites, the values are respectively in the range of 8.25–4.21% and 6.61–3.21%. The trees' impact on the soil composition is shown by an organic matter content more important in the forest area than in the clearing area. But globally the studied soils are poor in organic substance.

The activity concentrations (Bq $kg^{-1}$ of dried matter) of $^{137}Cs$ and of the $^{239-240}Pu$, measured in soil (0–10 cm) are reported in Table 2. For comparison, natural uranium and thorium series and $^{40}K$ are also presented.

The general trend for the anthropogenic radionuclides $^{137}Cs$ and $^{239-240}Pu$ is: (i) specific activity increase with depth due to the leaching and migration of elements by the rainfalls; (ii) activity is more important in area B than A due to the biomass transfer of elements by the vegetation. The trees have the capacity by the roots to pump elements up to the surface layers. The observed trend suggests that soil layers deeper than 10 cm most likely contain more plutonium and cesium, part of sixties' plutonium and cesium having migrated to the depth.

The 2007 isotopic ratio $^{239-240}Pu/^{137}Cs$ (Table 2) ranges from 0.024 to 0.186. The ratio stays, after the decay correction, in agreement with the weapon testing fallout ratio [8] for the 1960s.

For the two areas the ratio increases with depth. Forest trees are particularly effective in enhancing radiocaesium recycling [9,10]. An explanation for the current relative enrichment of forest surface soils in radiocaesium compared to plutonium may be the capacity of trees with high fine root biomass in the lower soil profiles to pump radiocaesium up to the surface layers through uptake and further litterfall and to promote overall radiocaesium circulation in the system.

The depositions of $^{137}Cs$ and $^{239-240}Pu$ from Chernobyl fallout in 1986 in general Côte d'Ivoire and West Africa were in very small amounts.

For the natural radionuclides, $^{40}K$ soil activity is very low and perturbed. It could be due to the high solubility of this element and to the washing by the abundant rains in this region of the country. It can be stated that the quantity of potassium recycled annually is high in comparison with the stocks in the vegetation and in the soil. The ecosystem of the forests is efficient for potassium retention. The site affects greatly the importance of the quantities put into circulation. The natural uranium and thorium

Table 2
Organic matter content, radionuclide activity concentration and Pu/Cs ratio results for studied soil samples.

| Sample | Depth (cm) | % Organic matter | Activity concentration Bq kg$^{-1}$ with (error) in 2007 | | | | | 2007 ratio Pu/Cs |
|---|---|---|---|---|---|---|---|---|
| | | | $^{137}$Cs | $^{239-240}$Pu | $^{226}$Ra ($^{238}$U) | $^{228}$Ac ($^{232}$Th) | $^{40}$K | |
| 1A | 0–3 | 6.94 | 0.75 ± 0.20 | 0.023 ± 0.006 | 16.7 ± 0.4 | 15.0 ± 0.3 | Nd | 0.031 ± 0.012 |
| | 3–6 | 6.11 | Nd | 0.030 ± 0.006 | 19.2 ± 0.5 | 16.0 ± 0.3 | Nd | |
| | 6–10 | 4.21 | 0.37 ± 0.20 | 0.069 ± 0.007 | 14.7 ± 0.4 | 18.7 ± 0.4 | Nd | 0.19 ± 0.11 |
| 1B | 0–3 | 3.21 | 1.30 ± 0.15 | 0.031 ± 0.006 | 16.5 ± 0.5 | 14.6 ± 0.4 | Nd | 0.024 ± 0.006 |
| | 3–6 | 5.30 | 1.55 ± 0.14 | 0.047 ± 0.007 | 12.0 ± 0.4 | 15.6 ± 0.3 | 14.4 ± 0.4 | 0.030 ± 0.006 |
| | 6–10 | 6.61 | 2.24 ± 0.13 | 0.080 ± 0.008 | 18.9 ± 0.3 | 12.5 ± 0.3 | 2.69 ± 0.23 | 0.036 ± 0.005 |
| 2A | 0–4 | 8.25 | 1.2 ± 0.5 | 0.035 ± 0.007 | 7.68 ± 0.21 | 16.5 ± 0.3 | 78.6 ± 0.6 | 0.030 ± 0.014 |
| | 4–7.2 | 7.31 | 2.0 ± 0.4 | 0.079 ± 0.010 | 8.5 ± 0.3 | 14.5 ± 0.3 | 46.2 ± 0.4 | 0.039 ± 0.010 |
| | 7.2–10.1 | 6.97 | 1.7 ± 0.3 | 0.094 ± 0.008 | 9.08 ± 0.22 | 14.2 ± 0.5 | Nd | 0.054 ± 0.011 |
| 2B | 0–3.6 | 4.44 | 1.6 ± 0.4 | 0.062 ± 0.006 | 7.20 ± 0.24 | 12.19 ± 0.23 | Nd | 0.040 ± 0.011 |
| | 3.6–6.8 | 3.55 | 2.1 ± 0.4 | Nm | 8.7 ± 0.5 | 14.6 ± 0.4 | Nd | |
| | 6.8–10.3 | 4.11 | 1.5 ± 0.3 | 0.125 ± 0.006 | 10.4 ± 0.4 | 15.3 ± 0.3 | Nd | 0.086 ± 0.018 |

Nd: not detected (<detection limit); Nm: not measured.

activities are similar in the soils and in the world average.

## 4. Conclusion

The first measurements of plutonium and cesium radionuclides in surface soils (10 cm) of Côte d'Ivoire for a forest area and clearing area show very low radioactive contaminations from global nuclear fallout. The Chernobyl nuclear power plant accident in 1986 had no impact on this region. Vegetation and precipitations seem to affect the radionuclide vertical migration and redistribution to the soil. The maximum of the artificial radioactivity (plutonium and cesium from nuclear atmospheric test fallout) should be in layers deeper than 10 cm.

## References

[1] M.B. Gavini, Earth Planet. Sci. Lett. 41 (1978) 228.
[2] R.J. Pentreath, Appl. Radiat. Isot. 46 (1995) 1279.
[3] P. De Boissezon, Cath ORSTOM, ser. Pédol. 8 (1970).
[4] B. Dadin, Cath ORSTOM, ser. Pédol. 21 (1984–1985).
[5] H. Michel, G. Barci-Funel, J. Dalmasso, G. Ardisson, J. Radioanal. Nucl. Chem. 240 (1999) 467.
[6] H. Michel, J. Gasparro, G. Barci-Funel, J. Dalmasso, G. Ardisson, G. Sharovarov, Talanta 48 (1999) 821.
[7] N.A. Talvitie, Anal. Chem. 44 (1972) 280.
[8] J. Cizdziel, V. Hadge, S. Faller, Health Phys. 77 (1999) 67.
[9] F. Goor, Y. Thiry, Sci. Total Environ. 325 (2004) 163.
[10] B. Delvaux, N. Kruyts, E. Maes, E. Smolders, in: G.R. Gobran, W.W. Wenzel, E. Lombi (Eds.), Trace Elements in the Rhizosphere, CRC Press LLC, UK, 2001, p. 61.