Radionuclide distribution in soils of the Corumbataí River Basin, São Paulo State, Brazil

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Resumo:

A utilização de fertilizantes fosfatados nas plantações de cana de açúcar é uma prática comum na agricultura brasileira e, conseqüentemente, a atividade concentração de ^{226}Ra, ^{232}Th e ^{40}K nos solos pode aumentar, tornando-se os radionuclídeos disponíveis para as plantas e transferindo-se para a cadeia alimentar humana. No sul da bacia do rio Corumbataí, Estado de São Paulo, Brasil, foi identificada a ocorrência de maiores valores da taxa de exposição radiométrica, que é uma área onde são aplicados fertilizantes fosfatados, corretivos e vinhaça nas plantações de cana de açúcar. Os radionuclídeos incorporados nos fertilizantes fosfatados e corretivos são adicionados anualmente nas plantações de cana de açúcar à taxa de 0,16, 0,17 e 6,33 Bqkg^{-1}, respectivamente, para ^{226}Ra, ^{232}Th e ^{40}K. Os valores de atividade concentração dos radionuclídeos e Raeq são mais elevados num perfil de solo sujeito à aplicação de fertilizantes fosfatados e corretivos. A concentração atividade de ^{232}Th e ^{226}Ra no açúcar foi inferior ao limite de detecção da técnica analítica utilizada neste trabalho e a ingestão de ^{40}K é inferior ao valor de referência proposto para este radionuclídeo.

Abstract

The use of phosphate fertilizers in sugar cane crops is a very common practice in Brazilian agriculture and, as a consequence, the ^{226}Ra, ^{232}Th and ^{40}K activity concentration in soils may increase and become readily available for plants and transferred to the human food chain. In the southern part of the Corumbataí River Basin, São Paulo State, Brazil, high values for radiometric exposure have been identified. It is a region where phosphate fertilizers, soil correctors and vinasse are applied to improve sugar cane crops. Radionuclides incorporated in phosphate fertilizers and amendments are annually added at a rate of 0.16, 0.17 and 6.33 Bqkg^{-1} of soil to ^{226}Ra, ^{232}Th and ^{40}K, respectively. The radionuclide activity concentration and Ra_{eq} values are higher in a soil profile with application of phosphate fertilizers and amendments. The ^{232}Th and ^{226}Ra activity concentration in sugar was lower than the detection limit of the analytical technique utilized in this work and the ^{40}K intake is lower than the guideline value for the daily ingestion of this radionuclide.

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Introduction

The application of phosphate fertilizers and amendments is a common practice in agriculture for improving soil properties. For instance, in Brazil, the annual production of phosphate concentrate in 1999-2000 was 4.3-4.5 million ton (DNPM, 2000, 2001). The phosphate rocks used as raw material for fertilizer production are enriched in uranium, thorium and their daughters deposited as calcium phosphate minerals by isomorphic substitution, since natural uranium can substitute calcium in the phosphate rock structure due to the similarity in ionic size between U^{4+} and Ca^{2+} (Guzman, 1992). The major industrialized products derived from phosphate rocks are SSP (simple superphosphate), TSP (triple superphosphate), MAP (monoammonium phosphate) and DAP (diammonium phosphate).

Since the first report in 1908 (Ring, 1977), various authors have described the behavior of radionuclides in fertilizers derived from phosphatic rocks elsewhere (Menzel, 1968; Pfister et al., 1976; Ring, 1977; Rothbaum et al., 1979; Mortvedt, 1986; Guimond, 1990; Guzman, 1992; Todorovsky & Kulev, 1993; Sam & Holm, 1995; Hull & Burnett, 1996; Alam et al., 1997; Ioannides et al., 1997; Ibrahim, 1998; Khan et al., 1998; Sam et al., 1999; Khater et al., 2001; Conceição & Bonotto, 2006). Various authors have also studied the behavior of radionuclides in phosphogypsum (Bolivar et al., 1995; Rutherford et al., 1995; Haridasan et al., 2002) and in phosphoric acid (Singh et al., 2001) that are by-products of the fertilizer industry. In Brazil, some studies have emphasized the presence of radionuclides in phosphate rocks and phosphogypsum (Paschoa et al., 1984; Pessenda et al., 1988; Godoy, 1989; Mazzilli & Saueia, 1997; Mazzilli et al., 2000).

The use of phosphate fertilizers in sugar cane crops is a frequent practice in Brazilian agriculture and the possibility of increasing the radionuclides activity concentration in these soils was investigated at one important hydrographic basin located in the middle-eastern part of São Paulo State; more precisely, the Corumbataí River Basin (Figure 1). This redistribution of radionuclides constitutes an additional source of radiation exposure for workers and members of the public and may become readily available for plants (principally in acid soils) and transferred to the human food chain. Thus, the purpose of this paper was to identify possible anomalies generated in the superficial soil horizon by long-continued application of phosphate fertilizers and amendments at the Basin. Three soil profiles were also investigated for the same radionuclides in order to determine the effect of long-continued application of phosphate fertilizers and amendments, and the radionuclides uptake by vegetation was also estimated.

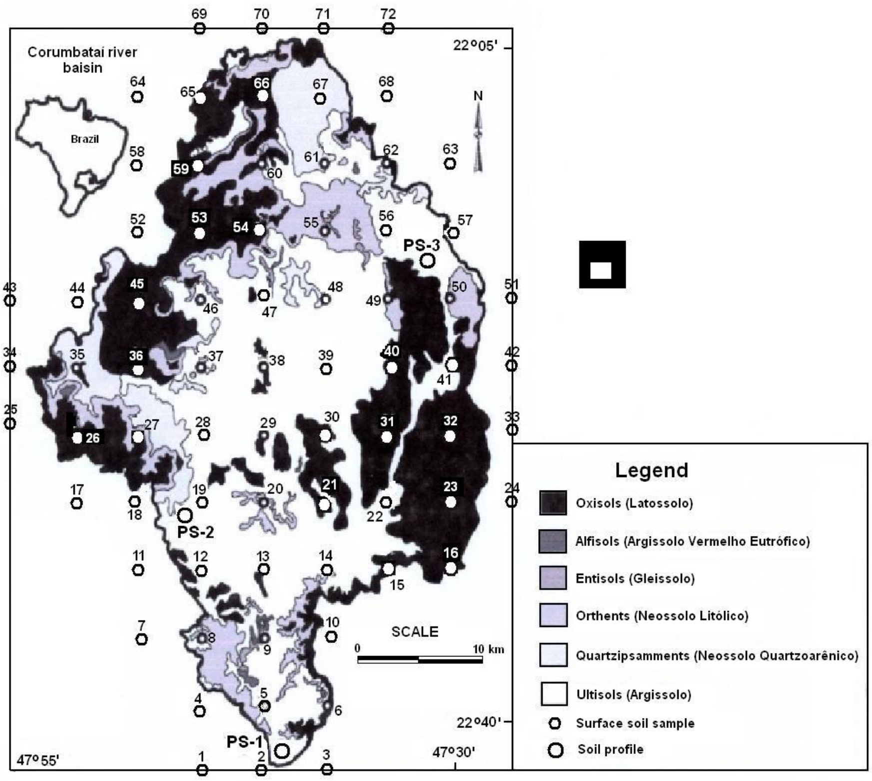


Figure 1. The major soil types at the Corumbataí River basin and the sampling points for radiometric analysis.

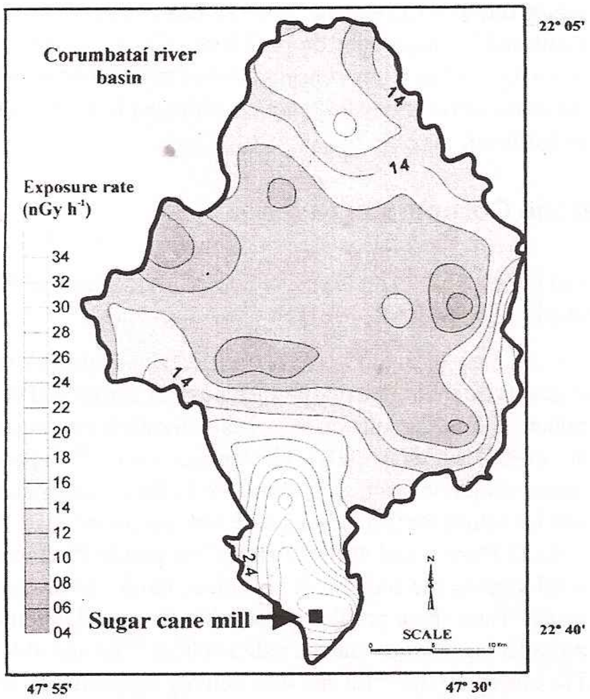
General features of the area studied

The Corumbataí River Basin extends over an area of about 1,710 km² in the middle-eastern part of the São Paulo State, and its altitude ranges from 470 to 800 m (Figure 1). It occurs as an eroded belt in the cuestas zone of the Depressão Periférica geomorphological province (Penteado, 1976). This province delimits the northeastern edge of the basaltic flows in the Paraná sedimentary basin and the crystalline plateau, and was submitted to smoothing processes during the past geological times.

The city of Rio Claro is the most important municipality in the basin, with about 170,000 inhabitants. Land use in the area is mainly for sugar cane crops (55%) and pasture (28%), among other purposes (Figure 2). Monthly measurements of discharge between 1973 and 1999 indicated an average monthly flow of 26.4 m^3s^{-1} (Conceição, 2000). The tropical climate of the region is characterized by a wet summer (October through March) and dry winter (April through September) (Inácio & Santos, 1988), with the mean annual rainfall corresponding to 1,572 mm (Conceição, 2000). The Corumbataí River Basin comprises several stratigraphic units of the giant Paraná sedimentary basin (Paleozoic – Cenozoic) (IPT, 1981): the Tubarão Group (Itararé Subgroup and Tatuí Formation), Passa Dois Group (Irati Formation and Corumbataí Formation), São Bento Group (Pirambóia Formation, Botucatu Formation, Serra Geral Formation and related basic intrusives) and different types of Cenozoic covers like the recent deposits, terrace sediments and the Rio Claro Formation.

According to USDA (1999) and EMBRAPA (1999) nomenclatures, the major soil types occurring in the Basin are Ultisols (argissolos) and Oxisols (latossolos), which cover about 65% of the basin area (Köffler, 1993) (Figure 1). The Typic Rhodiudults (terra roxa estruturada), Kandiudults (argissolo vermelho distrófico) and Rhodic Kandiudults (argissolo vermelho escuro) are mineral soils with a textural B horizon and low CEC (cation exchange capacity). The Oxisols are sub-divided into three different types: Rhodic Kandiudox (latossolo vermelho distrófico) - mineral soil derived from basic rocks, with oxic B horizon and considerably high Fe_2O_3 content (18-40%), clay loam and clay; Xanthic Kandiudox (latossolo vermelho escuro) - mineral soil with oxic B horizon, presence of Fe_2O_3 (18%), clayey (usually lower than 8%); Humic Hapludox (latossolo vermelho amarelo) - mineral soil with oxic B horizon, presence of Fe_2O_3 between 7 and 11%.

Oliveira et al. (1982) also presented other soil types at the Basin: Alfisols (*argissolo vermelho eutrófico*) - mineral soil derived from basic rocks, with relatively high Fe_2O_3 content (minimum 15%) and 1.5% of TiO_2, clay loam and clay; Lithic Udorthents (neossolo litólico distrófico/eutrófico) - soil normally thinner than 30 cm with A-R horizons; Humaqueptic Endoaquents (*gleissolo melânico distrófico*) - hydromorphic lower than 120 cm depth; Quartzipsamment (*neossolo quartzoarênico*) - deep (more than 2 m below ground surface), very friable soil with sandy grain size along the profile.



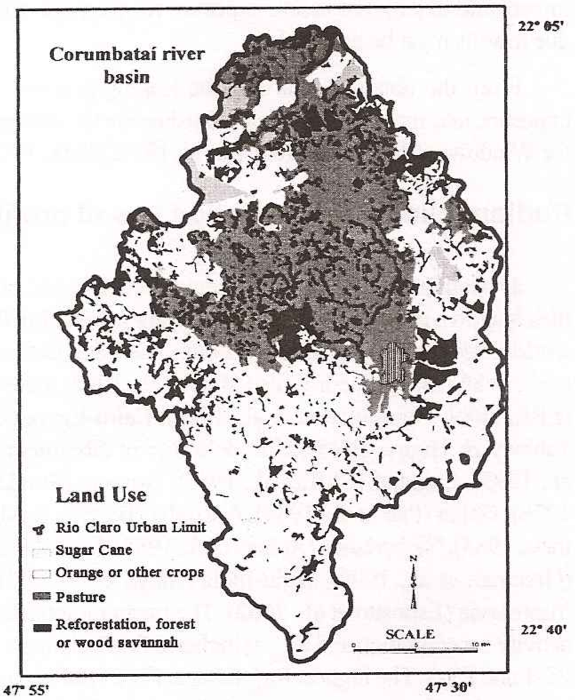


Figure 2. Map of exposure rate (nGyh⁻¹) in air 1 m above the ground and map of the land use at the Corumbataí River basin.

Sampling and analytical methods

Soil samples (72) were collected at the Basin and adjacent areas (Figure 1), with the sampling being realized at the most superficial soil horizon (first 20 cm). Three soil profiles in Ultisols were sampled in the basin: PS-1, PS-2 and PS-3 (Figure 1). The PS-1 and PS-2 profiles are located in areas with sugar cane crops, where the application of vinasse and phosphate fertilizers/amendments occur. The PS-3 profile was collected in native forest vegetation without anthropogenic interferences, allowing the data comparison in terms of land use; that is, the radionuclide accumulation caused by the continuous application of phosphate fertilizers for at least 35 years. Two samples of sugar, alcohol, filter cake (sugar cane sub product) and vinasse (alcohol sub product) representing the industrialized products of a sugar cane mill located at the Basin were also collected and analyzed.

The gamma spectrometry was utilized to measure the ^{226}Ra, ^{23}2Th and ^{40}K activity concentration in all samples. The methodology has been described by Duarte & Bonotto (2000). The Ra_{eq} of each sample was calculated by the equation (Berekta & Mathew, 1985):

$$Ra_{eq}=A_{Ra}+1.43A_{Th}+0.077A_{K} \qquad (1)$$

where: A_{Ra}, A_{Th} and A_{K} are the specific activities of ^{226}Ra, ^{232}Th and ^{40}K in $Bqkg^{-1}$, respectively. The exposure rate, radiation effects in the air above 1m of the area (UNSCEAR, 1993), was estimated using the following dose-rate conversion factors (DRCF): 0.0414, 0.623 and 0.461 nGy h^{-1} per $Bqkg^{-1}$ for ^{40}K, ^{232}Th and ^{226}Ra, respectively.

Results and discussion

Radionuclide activity concentration in surface soils

The radionuclides activity concentration in the analyzed surface soil samples is given in Table 1. The 226Ra, 232Th and 40K activity concentration ranged from 5 to 33 Bqkg-1 (mean = 12.2 Bqkg-1), 4 to 13 Bqkg-1 (mean = 7.8 Bqkg-1) and 13 to 894 (mean = 121.2 Bqkg-1), respectively. The mean exposure rate of 14.8 nGyh-1 associated with the soils analyzed represents 27% of the world's outdoor average exposure due to terrestrial gamma radiation (55 $nGyh^{-1}$, according to UNSCEAR, 1993). Thus, the radioactive impact and external radiation exposure for the population due to soils must be minimal.

From the obtained data and the kriging process, an exposure rate map was constructed using Surfer software for Windows (Matheron, 1962; David, 1977; Clark, 1979; Landim, 1998). This map (Figure 2) indicates the highest exposure rate (values above 29 $nGyh^{-1}$) in the southern portion of the Basin, close to the confluence of the Corumbataí and Piracicaba rivers. In this area, the application of phosphate fertilizers, amendments and vinasse is used for the sugar cane crops that are extensively cultivated by industries producing alcohol and sugar (Figure 2). Ferreira et al. (1997) also reported radiometric anomalies (^{238}U, ^{232}Th and ^{40}K) in soils developed on basic rocks (diabase sills) in the Araras region (close to Corumbataí River basin), which is heavily cultivated by sugar cane crops. These soils are known to normally contain a low concentration of radionuclides and the radiometric anomalies may be attributed to impurities in fertilizers.

Radionuclides accumulation in soil profiles at the Corumbataí River

The radionuclide activity concentration in the soil profiles is shown in Table 2. The reported values are within the world range for soils, for instance, Louisiana-USA (Delaune et al., 1986), Bangladesh-India (Miah et al., 1998), Greece (ERL, 1989; Papastefanou et al., 1983), Cairo-Egypt (El-Tahawy & Higgy, 1995), Nile delta-Egypt (Ibrahiem et al., 1993), England (Cliff.et al., 1985), Norway (Straden, 1976), China (Pan et al., 1984), Australia (Berekta & Mathew, 1985), Netherlands (Ackers et al., 1985), East of USA (Greeman et al., 1999), Kulu-India (Singh et al., 2001), Yugoslavia (Esposito et al., 2002). The mean radionuclide activity concentration and Ra_{eq} is higher at PS-2 relatively to PS-1 and PS-3. The highest Ra_{eq} value at PS-2 (124 $Bqkg^{-1}$) is lower than the maximum annual allowable of 544 $Bqkg^{-1}$ that corresponds to an exposure rate of 2.4 $mSvyr^{1}$ (or 55 $nGyh^{-1}$) (UNSCEAR, 1993).

Mathematical models have been utilized worldwide to characterize environmental problems as they can predict the radionuclide accumulation in agricultural soils (Greeman et al., 1999; Hakanson, 2004). The comparison of ^{232}Th data (mean values) in profiles PS-2 and PS-3 (Table 2) indicates similar values for this radionuclide whereas an increase of ^{226}Ra (5 $Bqkg^{-1}$) and 40K (23 $Bqkg^{-1}$) in profile PS-2 that is affected by the addition of phosphate fertilizers/amendments. Thus, these profiles are suitable for modeling purposes taking into account the radionuclides ^{226}Ra and 40K. The change of the ^{226}Ra and 40K activity concentration in a soil system may be written as:

Table 1. Activity concentration of ^{226}Ra, ^{232}Th, ^{40}K, Raeq (in $Bqkg^{-1}$) and exposure rate (in $nGyh^{-1}$) in surface soils of the Corumbataí River basin.

Sample	^{226}Ra	^{232}Th	^{40}K	Ra_{eq}	ER¹	Sample	^{226}Ra	^{232}Th	^{40}K	Ra_{eq}	ER¹
1	28	4	56	38	17	37	8	8	62	24	11
2	23	7	115	42	19	38	10	8	80	27	12
3	18	9	92	38	17	39	11	7	51	25	11
4	5	4	311	34	16	40	11	10	65	30	13
5	10	4	689	69	31	41	5	4	42	14	6
6	5	4	894	80	36	42	29	11	128	55	25
7	8	4	13	15	7	43	9	4	131	25	11
8	17	4	86	19	19	44	10	11	42	29	13
9	24	4	508	69	31	45	5	4	48	14	6
10	17	4	101	20	19	46	5	8	38	19	9
11	5	8	282	38	17	47	9	8	74	26	12
12	17	7	130	36	16	48	8	8	42	23	11
13	33	12	193	65	29	49	13	5	54	24	11
14	15	7	174	37	17	50	14	4	47	23	11
15	28	6	140	43	19	51	12	8	89	29	13
16	16	8	202	43	19	52	5	5	95	20	9
17	7	7	65	22	10	53	10	10	68	30	13
18	16	10	124	39	18	54	6	5	77	20	9
19	17	11	159	44	20	55	10	8	123	30	13
20	19	10	118	42	19	56	8	4	196	27	12
21	17	9	192	43	18	57	12	10	104	34	15
22	8	4	47	23	11	58	10	11	92	33	15
23	7	4	101	21	9	59	10	12	74	33	15
24	32	6	83	47	21	60	6	10	75	26	12
25	9	7	59	23	11	61	19	10	125	30	13
26	11	4	101	23	11	62	10	10	68	43	19
27	5	10	172	33	15	63	11	10	139	36	16
28	5	7	45	19	9	64	11	12	62	33	15
29	8	6	42	20	9	65	10	12	74	33	15
30	11	4	56	21	10	66	12	10	160	39	18
31	5	11	53	25	11	67	11	12	101	36	16
32	13	13	26	34	15	68	7	10	53	25	11
33	27	4	178	46	21	69	10	10	57	29	13
34	5	4	36	14	6	70	12	10	61	31	14
35	10	9	44	26	12	71	12	12	98	37	17
36	5	10	86	26	12	72	10	11	59	30	13

Analytical uncertainty ±10% (1σ standard deviation)

¹Exposure rate evaluated by DRCF = 0.0414, 0.623 and 0.461 $nGyh^{-1}$ per Bq/kg of ^{40}K, ^{232}Th and ^{226}Ra, respectively (UNSCEAR, 1993).

$$dm/dt = G_{in} - G_{out} + I - D \quad (2)$$

where: m = radionuclide activity concentration (equivalent to mass) in the soil; t = time; G_{in} = radionuclide flux into the system, G_{out} = radionuclide flux out of the system; I = radioactive ingrowth; D = radioactive decay.

The ^{226}Ra ingrowth from its radioactive ^{230}Th parent should be small (Greeman et al., 1999) and because $\lambda_K = 0.6\times10^{-10}$ yr^{-1} and $\lambda_{Ra} = 0.433\times10^{-3}$ yr^{-1}, then, it is possible to disregard the ^{40}K radioactive decay for the modeling purposes. The G_{in} represents the radionuclide flux due to the application of phosphate fertilizers and amendments. The G_{out} corresponds to the radionuclide loss in the soil system due to a combination of the lixiviation to rivers/groundwater and of the uptake from the superficial horizon by vegetation. To simplify, it may be assumed that the loss is proportional to the amount retained in soil, that is:

$$G_{out} = 1/k' m_{(t)} \quad (3)$$

where: k = 1/k', is a constant. Thus, substituting D by $\lambda_{Ra}[Ra]$, G_{out} by $km_{(t)}$ and eliminating I in both cases, the general equation (2) applied to ^{40}K and ^{226}Ra, respectively, can be re-written as:

$$dm_{(t)}/dt = G_{in} - km_{(t)} \quad (4)$$

Table 2. Radionuclides activity concentration ($Bqkg^{-1}$), Ra_{eq} ($Bqkg^{-1}$) and exposure rate ($nGyh^{-1}$) in soil profiles at the Corumbataí River basin.

Horizon	Depth (cm)	Sample	^{226}Ra	^{232}Th	^{40}K	Ra_{eq}	ER³
PS-1 Ultisols¹ (Neossolo Flúvico Argilúvico Vértico²)							
Ap	20	PS-11	21	15	49	46	21
2Bt1	30	PS-12	18	20	51	51	23
Bt2 (high)	40	PS-13	18	19	60	50	23
Bt2 (low)	65	PS-14	18	20	65	51	23
3Bt3 (high)	80	PS-15	21	23	65	59	27
Bt3 (low)	120	PS-16	24	25	76	66	30
Bt4	140	PS-17	26	25	78	68	31
Mean			21	21	63	56	25
PS-2 Ultisols¹ (Neossolo Flúvico Argilúvico²)							
A	20	PS-21	39	20	122	77	35
A/B	30	PS-22	34	25	115	79	36
Bt1 (high)	40	PS-23	51	31	133	106	48
Bt1 (low)	80	PS-24	59	31	140	114	52
2Bt2 (high)	100	PS-25	57	31	148	113	51
2 Bt2 (low)	130	PS-26	57	36	153	121	55
Bt3	140	PS-27	61	36	149	124	56
Mean			51	30	137	105	48
PS-3 Ultisols¹ (Neossolo Flúvico Nítico-Argilúvico Latossólico²)							
A1	20	PS-31	49	31	110	102	46
2Btw	30	PS-32	44	36	108	104	47
Btw2 (high)	40	PS-33	48	31	117	101	46
Btw2 (low)	50	PS-34	46	31	117	99	45
Btw3 (high)	80	PS-35	46	31	115	99	45
Btw3 (low)	100	PS-36	43	25	120	88	40
Mean			46	30	114	99	45

Analytical uncertainly ±10% (1σ standard deviation)
¹USDA (1999) nomenclature; ²Brazilian classification (EMBRAPA, 1999)
³Exposure rate evaluated by DRCF = 0.0414, 0.623 and 0.461 $nGyh^{-1}$ per Bq/kg of ^{40}K, ^{232}Th and ^{226}Ra, respectively (UNSCEAR, 1993).

$$dm_{(t)}/dt = G_{in} - (km_{(t)} + \lambda_{Ra} m_{(t)}) = G_{in} - (k+\lambda_{Ra}) m_{(t)} \quad (5)$$

Because soil absorption capacity is expected to decrease with time the solution of equations (4) and (5) is, respectively:

$$m_{(t)} = G_{in}/k + e^{-kt}(m_0 - G_{in}/k) \quad (6)$$

$$m_{(t)} = (G_{in}/k + \lambda_{R}a) + e^{-(k+\lambda_{Ra})t}\,[m_0 - (G_{in}/k + \lambda_{Ra})] \quad (7)$$

where: m_0 is the initial activity concentration.

The ^{226}Ra, ^{232}Th and ^{40}K activity concentration, Ra_{eq} and exposure rate to phosphate fertilizers NPK and amendments utilized in sugar cane crops at the Basin were reported by Conceição & Bonotto (2005) who estimated that the maximum average annual addition of radionuclides distributed per unit arable land corresponds to 25, 26 and 969 Bqm^{-2} for ^{226}Ra, ^{232}Th and ^{40}K, respectively. These values are lower than those reported in many parts of the world where untreated ground phosphate rocks have been used as plant fertilizers (Makweba & Holm, 1993; Sam et al., 1999; Khater et al., 2001). Conceição & Bonotto (2005) calculated a maximum annual increase in 0.16, 0.17 and 6.33 $Bqkg^{-1}$ of soil for ^{226}Ra, ^{232}Th and ^{40}K, respectively (Table 3). Consequently, the external radiation exposure caused by phosphate fertilizers NPK and amendments used in sugar cane crops at the Basin corresponded to 0.89 $nGyh^{-1}$ at 1 m above the ground level (Conceição & Bonotto, 2005), that is a value only representing 1.6% of the world average outdoor exposure due to terrestrial gamma radiation.

The constant k in equations (6) and (7) may be evaluated from data given in Table 3, permits expressions of $m_{(t)}$ according to the curves shown in Figure 3. Therefore, the mathematical modeling indicates that soil saturation could occur after about 120 and 14,000 years for ^{40}K and ^{226}Ra, respectively.

Parameter	Description	^{40}K (unit)	^{226}Ra (unit)	^{232}Th (unit)
t_0	Initial time (the time period without application of phosphate fertilizers and amendments)	0 (year)	0 (year)	0 (year)
m_0	Initial mass (equivalent to the mean activity concentration found in the natural profile, PS-3)	114 ($Bqkg^{-1}$)	46 ($Bqkg^{-1}$)	30 ($Bqkg^{-1}$)
t	Time for the application of phosphate fertilizers and amendments	35 (years)	35 (years)	35 (years)
m	Final mass (equivalent to the mean activity concentration found in the profile with application of phosphate fertilizers and amendments, PS-2)	137 ($Bqkg^{-1}$)	51 ($Bqkg^{-1}$)	30 ($Bqkg^{-1}$)
	Radionuclides annual flux due to the use of phosphate fertilizers and amendments[1]	6.33 ($Bqkg^{-1}$)	0.16 ($Bqkg^{-1}$)	0.17 ($Bqkg^{-1}$)

[1] Conceição & Bonotto (2005)

Table 3. Parameters utilized for the mathematical modeling adopted in this study.

Radionuclides in sugar cane crops and their ingestion through sugar consumption

The radionuclide activity concentration in vegetation is often measured in its ash, because after decomposition the non-organic fraction remains in soils. The results in Table 4 indicate that there is significant transfer of ^{226}Ra to the filter cake, non-detectable incorporation of ^{232}Th in any fraction, and detectable ^{40}K presence in sugar, filter cake and vinasse. Each 1000 kg of sugar cane crop produces, in a sugar cane mill, 110 kg of sugar, 8 kg of alcohol, 40 kg of filter cake and 15 kg of vinasse (Zotelli, 2004). The following mass-balance equation allows estimation of the ^{226}Ra and ^{40}K related to the sugar cane crops in the area studied:

$$1000\ R_c = 110\ R_s + 8\ R_a + 40\ R_t + 15\ R_v \qquad (8)$$

where: R_c, R_s, R_a, R_t and R_v is the radionuclide activity concentration ($Bqkg^{-1}$) in the sugar cane crop, sugar, alcohol, filter cake and vinasse, respectively. Thus, the weighted mean associated to the sugar cane crop is 0.27 $Bqkg^{-1}$ (^{226}Ra) and 12.3 $Bqkg^{-1}$ (^{40}K).

If an annual sugar cane production corresponding to 80 ton/ha is considered (Zotelli, 2004), then, such values imply on 2.16 and 98.4 $Bqm^{-2}yr^{-1}$ for ^{226}Ra and ^{40}K, respectively. These are consistent with the calculation performed by Conceição & Bonotto (2005) for the average annual addition of radionuclides distributed per unit of arable land that corresponded to 25 and 969 Bqm^{-2} for ^{226}Ra and ^{40}K, respectively.

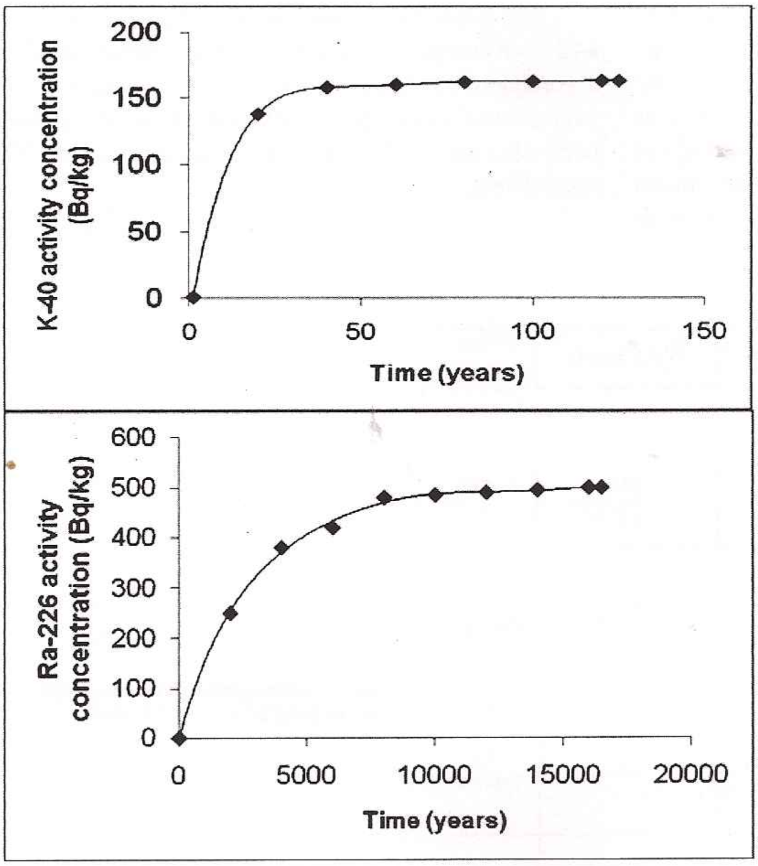


Figure 3. Variation of 40K and 226Ra activity concentration (in Bqkg-1) with time.

Therefore, the proportion of radionuclides absorbed by the sugar cane crops relatively to their application of phosphate fertilizers/amendments is 8.6% for ^{226}Ra and 10.2% for ^{40}K.

The radionuclides data (mean values) in profiles PS-2 and PS-3 (Table 2) indicated an increase of ^{226}Ra (5 Bqkg^{-1}) and ^{40}K (23 Bqkg^{-1}) in profile PS-2 affected by the addition of phosphate fertilizers/amendments. Thus, the accumulation of ^{226}Ra and ^{40}K in soils with sugar cane crops at the Corumbataí River Basin over the last 35 years may be estimated to occur at annual rates corresponding to 0.14 Bqkg^{-1} (^{226}Ra) and 0.66 Bqkg^{-1} (^{40}K). The higher rate related to ^{40}K implies a shorter time for the soils to reach saturation, also confirmed by the mathematical modeling (Figure 3).

The sugar consumption rate of 25 kgyr^{-1} expected for adults in Brazil (IBGE, 1998) signifies an estimate of ^{40}K intake of 4.86 Bqday^{-1} which is lower than the proposed limit of 115.3 Bqday^{-1} (Akinloye et al., 1999) for daily ingestion of this radionuclide. The radionuclide activity concentration in sugar is lower than that in vegetables, cereals, potatoes, eggs, milk, fruits, meats and poultries analyzed worldwide (England - Smith-Brigges & Bradley, 1984; USA - Fisenne et al., 1987; Japan - Shiraishi et al., 1992; Ukraine - Shiraishi et al., 1997; Taiwan - Kuo et al., 1997; Nigeria - Akinloye et al., 1999; Canadian - van Netten et al., 2000; Poland - Pietrzak-Flis et al., 2001; India - Singh et al., 2001; Brazil - Santos et al., 2002). Because Raeq=544 Bqkg^{-1} corresponds to an annual dose rate of 2.4 mSvyr^{-1} (UNSCEAR, 1993), the value of Ra_{eq} = 6 Bqkg^{-1} in sugar (Table 4) allows for an estimate of 26 μSv as the annual dose due to its ingestion,. This represents 11.5% of the world mean annual effective dose (0.23 mSv) due to the intake of radionuclides through food ingestion (UNSCEAR, 1993).

Conclusion

The exposure rate in soils is higher towards the south of the Corumbataí River Basin, where phosphate fertilizers, amendments and vinasse are applied to sugar cane crops. The 226Ra and 40K activity concentration is higher in the soil profile where phosphate fertilizers and amendments have been added at the rates of 0.16, 0.17 and 6.33 Bq/kg of soil for ^{226}Ra, ^{232}Th and ^{40}K, respectively. The mathematical modeling indicated soil saturation occurring after 120 and 14,000 years for ^{40}K and ^{226}Ra, respectively. The percentage of radionuclides absorbed by the sugar cane crops relative to the addition of phosphate fertilizers/amendments is 8.6% for ^{226}Ra and 10.2% for ^{40}K. The radionuclides activity

Sample	^{226}Ra	^{232}Th	^{40}K	Ra_{eq}
Sugar	<1	<1	71	6
Sugar	<1	<1	71	6
Filter cake	4	<1	107	12
Filter cake	4	<1	115	13
Alcohol[1]	<0.01	<1	<0.10	-
Alcohol[1]	<0.01	<1	<0.10	-
Vinasse[1]	<0.01	<1	0.79	0.1
Vinasse[1]	<0.01	<1	0.85	0.1

[1]in Bq/L

Table 4. Radionuclides activity concentration and Raeq (Bqkg-1) in samples recovered/released by a sugar cane mill.

concentration in sugar is lower than in vegetables, cereals, potatoes, eggs, milk, fruits, meats and poultries analyzed worldwide. The 40K intake of 4.86 Bqday-1 is lower than the proposed limit of 115.3 Bqday-1 for its ingestion. Thus, there is little radionuclide transference from soils to sugar cane crops at the Corumbataí River Basin, and sugar consumption does not offer a hazard to human health in terms of radiometric aspects.

Acknowledgements

To Dr. Helder de Oliveira and one anonymous reviewer for helpful comments that improved the readability of the manuscript.

References

ACKERS, J.G.; DEN BOER, J.F.; DE JONG, P.; WOLSHRIJÏN, R.A. (1985) Radioactivity and radon exhalation rates of building materials in the Netherlands. Sci. Total Environ., 45: 151-156.
AKINLOYE, M.K.; OLOMO, J.B.; OLUBUNMI, P.A. (1999) Meat and poultry consumption contribution to the natural radionuclide intake of the inhabitants of the Obafemi Awolowo University, Ile-Ife, Nigeria. Nucl. Instrum. Meth. A, 422: 95-800.
ALAM, M.N; CHOWDHURY, M.; KAMAL, S.; GHOSE, S.; BANU, H.; CHAKRABORTY, D. (1997) Radioactivity in chemical fertilizers used in Bangladesh. Appl. Radiat. Isotopes, 8: 1165-1168.
BEREKTA, J.; MATHEW, P.J. (1985) Natural radioactivity of Australian building materials waste and by-products. Health Phys., 48: 87.
BOLÍVAR, J.P.; GARCÍA-TENÓRIO, R.; GARCÍA-LÉON, M. (1995) Enhancement of natural radioactivity in soils and sand-marshes surrounding a non-nuclear industrial complex. Sci. Total Environ., 173/174: 125-136.
CLARK, I. (1979) Practical geoestatistics. Applied Science Publ., London.
CLIFF, K.D.; GREEN, B.M.R.; MILES, J.C.H. (1985) The levels of radioactive materials in some UK building materials. Sci. Total Environ., 45: 181-186.
CONCEIÇÃO, F.T. (2000) O método do desequilíbrio isotópico do urânio aplicado no estudo do intemperismo na bacia do Rio Corumbataí (SP). MSc Dissertation, IGCE–UNESP, Rio Claro.
CONCEIÇÃO, F.T.; BONOTTO, D.M. (2005) Transferência de metais pesados, flúor e radionuclídeos para solos agrícolas na bacia do Rio Corumbataí (SP). Geociências, 24: 67-76.
CONCEIÇÃO, F.T.; BONOTTO, D.M. (2006) Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil, and their (by) products. Environ. Pollut., 139: 232-243.
DAVID, M. (1977) Geostatistical ore reserve estimation. Elsevier, Amsterdam.
DELAUNE, R.D.; JONES, G.L.; SMITH, C.J. (1986) Radionuclide concentration in Louisiana soils and sediments. Health Phys., 21: 239-244.
DNPM (Departamento Nacional de Produção Mineral) (2000) Mineral Summary. DNPM, Brasília.
DNPM (Departamento Nacional de Produção Mineral) (2001) Mineral Summary. DNPM, Brasília.
DUARTE, C.R.; BONOTTO, D.M. (2000) Calibração em energia e concentração de espectrômetro gama para análise de U, Th e K. Geociências, 19: 313-319.
EL-TAHAWY, M.D.; HIGGY, R.H. (1995) Natural radioactivity in different types of bricks fabricated and used in the Cairo region. Appl. Radiat. Isotopes, 46: 1401-1406.
EMBRAPA (Empresa Brasileira de Pesquisa Agropecuária) (1999) Sistema Brasileiro de Classificação de Solos. EMBRAPA, Brasília.
ERL (Environmental Radioactivity Laboratory) (1989) Environmental monitoring program of the country (data available). NCSR, Athens.
ESPOSITO, M.; POLIC, P.; BARTOLOMEI, P.; BENZI, V.; MARTELLINI, M.; CVETKOVIC, O.; DAMJANOV, V.; SIMIC, M.; ZUNIC, Z.; ZIVANCEVIC, B.; SIMIC, S.; JOVANOVIC, V. (2002) Survey of natural and anthropogenic radioactivity in environmental samples from Yugoslavia. J. Environ. Radioactiv., 61: 21-282.
FERREIRA, F.J.F.; SOUZA, J. L.; ROCHA, H.O.; MANTOVANI, L.E. (1997) Airborne gamma-ray spectrometry and remote sensing to map uranium accumulation in soils from long-continued application of fertilizers in Araras region, Brazil. In: XII Int. Conf. Applied Geologic Remote Sensing, Proceedings, v. 1, p: 323-330.

FISENNE, I.M.; PERRY, P.M.; DECKER, K.W.; KELLER, H.W. (1987) The daily intake of 234,235,238U, 228,230,232Th and 226,228Ra by New York City residents. Health Phys., 53: 35.

GODOY, J.M. (1989) Determination of 226Ra and 228Ra in gypsum. Ciência e Cultura, 41: 86-87.

GREEMAN, D.J.; ROSE, A.W.; WASHINGTON, J.W.; DOBOS, R.R.; CIOLKOSZ, E.J. (1999) Geochemistry of radium in soils of the Eastern United States. Appl. Geochem., 14: 365-385.

GUIMOND, R.J. (1990) Radium in fertilizers. In: Environmental behavior of radium, IAEA (International Atomic Energy Agency) (Ed.), Tech. Rep. 310, p: 113-128.

GUZMAN, E.T.R. (1992) Recovery of uranium in phosphate rocks and their products. Monograph (Bachelor in Chemistry), Universidad Autónoma del Estado de México.

HAKANSON, L. (2004) Modeling the transport of radionuclides from land to water. J. Environ. Radioactiv.,73: 267-287.

HARIDASAN, P.P.; MANIYAN, C.G.; PILLAI, P.M.B.; KHAN, A.H. (2002) Dissolution characteristics of 226Ra from phosphogypsum. J. Environ. Radioactiv., 62: 287-294.

HULL, C.D.; BURNETT, W.C. (1996) Radiochemistry of Florida phosphogypsum. J. Environ. Radioactiv., 32: 213-238.

IBGE (Instituto Brasileiro de Geografia e Estatística) (1998) Consumo alimentar per capita. Pesquisa de orçamento familiar, 1995-1996. IBGE, Rio de Janeiro, v. 2.

IBRAHIEM, N.M.; ABD EL GHANI, A.H.; SHAWKY, S.M.; ASHRAF, E.M.; FAROUK, M.A. (1993) Measurement of radioactivity levels in soils in the Nile Delta and Middle Egypt. Health Phys., 64: 620-627.

IBRAHIM, N. (1998) Determination of natural radioactivity in fertilizers by gamma ray spectroscopy. Radiat. Phys. Chem. 51: 62.

INÁCIO, A.; SANTOS, M.J.Z. (1998) Características climáticas de Rio Claro. Bol. Geografia Teorética, 18: 87-104.

IOANNIDES, K.G.; MERTZIMEKIS, T.J.; PAPACHRISTODOULOU, C.A.; TZIALLA, C.E. (1997) Measurements of natural radioactivity in phosphate fertilizers. Sci. Total Environ., 196: 63-67.

IPT (Instituto de Pesquisas Tecnológicas do Estado de São Paulo) (1981) Mapa Geológico do Estado de São Paulo. Monografias, São Paulo, IPT.

KHAN, K.; KHAN, H.M.; TUFAIL, M.; KHATIBEH, A.J.A.H.; AHMAD, N. (1998) Radiometric analysis of Hazara phosphate rock and fertilizers in Pakistan. J. Environ. Radioactiv., 38: 7-84.

KHATER, A.E.M.; HIGGY, R.H.; PIMPL, M. (2001) Radiological impacts of natural radioactivity in Abu-Tartor phosphate deposits, Egypt. J. Environ. Radioactiv., 55: 255-260.

KÖFFLER, N.F. (1993) Diagnósticos do uso agrícola das terras da Bacia do Rio Corumbataí - SP. Tech. Rep., Instituto de Geociências e Ciências Exatas/UNESP, Rio Claro, 102 p.

KUO, C.; LAI, Y.; HUANG, C.; LIN, M. (1997) Activity concentrations and population dose from Radium-226 in food and drinking water in Taiwan. Appl. Radiat. Isotopes, 48: 1245-1249.

LANDIM, P.M.B. (1998) Análise estatística de dados geológicos. Editora UNESP, São Paulo. MAKWEBA, M.M.; HOLM, E. (1993) The natural radioactivity of the rock phosphate, phosphatic products and their environmental implications. Sci. Total Environ., 133: 99-110.

MATHERON, G. (1962) Traité de geoestatistique appliqué. Technip, Paris.

MAZZILLI, B.; PALMIRO, V.; SAUEIA, C.; NISTI, M.B. (2000) Radiochemical characterization of Brazilian phosphogypsum. J. Environ. Radioactiv., 49: 113-122.

MAZZILLI, B.; SAUEIA, C. (1997) Implicações radiológicas da utilização de fosfogesso como material de construção. Ambiente Construído, 1: 17-22.

MENZEL, R.G. (1968) Uranium, radium, and thorium content in phosphate rocks and their possible radiation hazard. J. Agr. Food Chem., 16: 231-284.

MIAH, F.K.; ROY, S.; TOUHIDUZZAMAN, M.; ALAM, B. (1998) Distribution of radionuclides in soils samples in and around Dhakar city. Appl. Radiat. Isotopes, 49: 133-137.

MORTVEDT, J.J. (1986) Effects of calcium silicate slag application on radium-226 concentrations in plants tissues. Commun. Soil Sci. Plant Anal., 17: 75-84.

OLIVEIRA, J.B.; MENK, J R.F.; BARBIERI, C.L.; ROTTA, C.L.; TREMOCOLD, W. (1982) Levantamento pedológico semi-detalhado do Estado de São Paulo: Quadrícula Araras (1:100.000). Boletim Técnico do Instituto Agronômico de Campinas, 71: 1-183.

PAN, Z.; YANG, Y.; GUO, M. (1984) Natural radiation and radioactivity in China. Radiat. Prot. Dosim., 7: 235-238.

PAPASTEFANOU, C.; MANOLOPOULOU, M.; CHARAMLAMBOUS, S. (1983) Exposure from the radioactivity in building material. Health Phys., 45: 349-361.

PASCHOA, A.S.; MAFRA, O.Y.; CARDOSO, D.O.; ROCHA, A.C.S. (1984) Applications of SSNTD to the Brazilian phosphate fertilizer industry to determine uranium concentrations. Nucl. Tracks Rad. Meas., 8: 469-472.

PENTEADO, M.M. (1976) Geomorfologia do setor centro-ocidental da Depressão Periférica paulista. Série Teses e Monografias, 22, IGEOG/USP, São Paulo.

PESSENDA, L.C.R.; NASCIMENTO FILHO, V.F.; NADAI, E.A.; FERRAZ, E.S.B. (1988) Determinação de Ra-226 e Th-232 em amostras de fosfatos naturais, gessos industriais e solos superficiais por espectrometria gama. In: II Cong. Geral Energia Nuclear, Proceedings, p: 403-407.

PFISTER, R.J.; PHILLIP, G.; PAULY, H. (1976) Population dose from natural radionuclides in phosphate fertilizers. Radiat. Environ. Bioph., 13: 247-261.

PIETRZAK-FLIS, Z.; ROSIAK, L.; SUPLINSKA, M.M.; CHRZANOWSKI, E.; DEMBINSKA, S. (2001) Daily intakes of 238U, 234U, 232Th, 230Th, 228Th and 226Ra in the adult population of central Poland. Sci. Total Environ., 273: 163-169.

RING, R.J. (1977) Recovery of (by)product uranium from of manufacture of phosphate fertilizers. Atom. Energy, 12: 20.

ROTHBAUM, H.P.; McGAVESTON, D.A.; WALL, T.; JOHNSTON, A.E.; MATTINGLY, G.E.G. (1979) Uranium accumulation in soils from long-continued applications of superphosphate. J. Soil Sci., 30: 147-153.

RUTHERFORD, P.M.; DUDAS, M.J.; SAMEK, R.A. (1995) Environmental impacts of phosphogypsum. Sci. Total Environ., 149: 1-38.

SAM, A.K.; AHAMED, M.M.O.; KHANGI, F.A.; NIGUMI, Y.O.; HOLM, E. (1999) Radiological and chemical assessment of Uro and Kurun rock phosphate. J. Environ. Radioactiv., 42: 66-75.

SAM, A.K.; HOLM, E. (1995) The natural radioactivity in phosphate deposits from Sudan. Sci. Total Environ., 162: 173-178.

SANTOS, E.E.; LAURIA, D.C.; AMARAL, E.C.S.; ROCHEDO, E.R. (2002) Daily ingestion of 232Th, 238U, 226Ra, 228Ra and 210Pb in vegetables by inhabitants of Rio de Janeiro City. J. Environ. Radioactiv., 62: 5-86.

SHIRAISHI, K.; IGARASI, Y.; TAKAKU, Y. (1992) Daily intakes of 232Th and 238U in Japanese males. Health Phys., 63: 187-191.

SHIRAISHI, K.; TAGAMI, K.; BAN-NAI, T. (1997) Daily Intakes of 134Cs, 137Cs, 40K, 232Th and 238U in Ukrainian adults males. Health Phys., 73: 814-819.

SINGH, S.; MALHOTRA, R.; KUMAR, J.; SINGH, B.; SINGH, L. (2001) Uranium analysis of geological samples, water and plants from Kulu Area, Himachal Pradesh, India. Radiat. Meas., 34: 427-431.

SMITH-BRIGGES, J.L.; BRADLEY, E.J. (1984) Measurement of natural radionuclides in UK diet. Sci. Total Environ., 35: 431-440.

STRADEN, E. (1976) Some aspects on radioactivity of building materials. Phys. Norv., 8: 167-213.

TODOROVSKY, D.; KULEV, I. (1993) On the uranium content in some technogenic products potential environmental pollutants. J. Radioanal. Nucl. Chem., 5: 405-413.

UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation) (1993) Sources and effects of ionizing radiation. UNSCEAR, United Nations, New York.

USDA (United States Department of Agriculture) (1999) Soil Taxonomy - A basic system of soil classification for making and interpreting soils surveys. US Government Office, Washington.

VAN NETTEN, C.; HOPTION CANN, S.A.; MORLEY, D.R.; VAN NETTEN, J.P. (2000) Elemental and radioactive analysis of commercially available seaweed. Sci. Total Environ., 255: 169-175.

ZOTELLI, H.B. (2004) Informação técnica sobre a capacidade produtiva da cana-de-açúcar. Usina Costa Pinto S/A Açúcar e Álcool, Piracicaba.