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The use of *in situ* Gamma-Ray Spectrometry to Assess the Environmental Impacts of Intensive Agriculture in terms of Geochemical Mobility in soil and waters

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Abstract

The concentration and mobility of metals in the lithosphere and hydrosphere are led by many physical-chemical parameters and processes from natural and anthropogenic origins, the last one resulting in impacts over many ecosystems around the World, including wetlands. These transitional zones, often characterized by the presence of hydric soils, adapted vegetation, and seasonal or permanent presence of surface water, are commonly under human pressure in terms of land use conversion and contamination, notably in agricultural production areas, where excess of nutrients/organic matter, pesticides, salts, sediments, heavy metals and radionuclides (originated from inorganic fertilizers) can substantially alter the ecological balance of those ecosystems. Thus, this study aimed to evaluate the agricultural impact over a tropical geographically isolated wetland in the Brazilian Cerrado by the analysis of geochemical mobility and interaction between surface and groundwater through in situ gamma-ray spectrometry and hydraulic conductivity measurements. The results demonstrated that the margins of this diabase-derived soil wetland are one of the most important and critical compartments due to its capacity of metal immobilization and surface water infiltration, indicated especially by uranium concentrations. Thorium, in turn, was most related to colluvial transport from slopes to the center of wetland. It was also corroborated by low hydraulic conductivity zones as a result of soil compaction due to heavy agricultural machinery and increase in runoff fluxes. Thus, this methodology could be used as an initial fast screening method in wetlands under other climatic and geological/pedological contexts to evaluate the local hydrogeochemical dynamics and impacts of agriculture.

Key words: uranium, thorium, hydrology, wetland, contamination, hydraulic conductivity.

Resumen

La concentración y movilidad de metales en la litosfera y la hidrosfera están influenciadas por muchos parámetros físico-químicos y procesos de origen natural y antropogénico, siendo este último responsable de impactos en muchos ecosistemas alrededor del mundo, incluyendo los humedales. Estas zonas de transición, a menudo caracterizadas por la presencia de suelos hídricos, vegetación adaptada y presencia estacional o permanente de agua superficial, suelen estar bajo presión humana en términos de conversión de uso del suelo y contaminación, especialmente en áreas de producción agrícola, donde el exceso de nutrientes/materia orgánica, pesticidas, sales, sedimentos, metales pesados y radionúclidos (provenientes de fertilizantes inorgánicos) pueden alterar sustancialmente el equilibrio ecológico de estos ecosistemas. Por lo tanto, este estudio tuvo como objetivo evaluar el impacto agrícola en un humedal tropical geográficamente aislado en el Cerrado brasileño mediante el análisis de la movilidad geoquímica e interacción entre agua superficial y subterránea a través de espectrometría de rayos gamma in situ y mediciones de conductividad hidráulica. Los resultados demostraron que los márgenes de este humedal, con suelos derivados de diabasa, son uno de los compartimentos más importantes y críticos debido a su capacidad tanto de inmovilización de metales como de infiltración de agua superficial, indicado especialmente por las concentraciones de uranio. El torio, por su parte, se relacionó principalmente con el transporte coluvial desde las pendientes hacia el centro del humedal, corroborado también por zonas de baja conductividad hidráulica como resultado de la compactación del suelo debido al uso de maquinaria agrícola pesada y aumento del flujo de escorrentía. Por lo tanto, la metodología aplicada podría utilizarse como un método inicial de detección rápida en humedales bajo otros contextos climáticos, geológicos y edafológicos, con el fin de evaluar la dinámica hidrogeoquímica local y los impactos de la agricultura.

Palabras clave: uranio, torio, hidrología, humedal, contaminación, conductividad hidráulica.

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1. Introduction

The mobility and accumulation of certain chemical elements in geological and hydrogeological environments are fundamental aspects in studies of mineral exploration and soil and environmental sciences (Boyle, 1982; Ridley, 2013; Kesler & Simon, 2015). The influence of natural and anthropogenic processes occurring in the critical zone determine the mobilization and segregation of certain chemical species over others. Such mechanisms have been active since the beginning of the planet's evolutionary history, demonstrated by the chemical heterogeneity of the Earth, where the diversity of lithotypes, soils, and occurrence of mineral deposits are some of its most notable products.

Within the context of environmental studies, specific patterns in the spatial distribution of some chemical elements or compounds in water, air, soil, and sediment often demonstrate the direct or indirect influence of human activities on the environment (Calabrese *et al.*, 2005), which have the power to trigger profound impacts on ecosystem equilibrium at various scales.

In the case of agriculture and livestock farming, both activities have the capacity to drastically alter the integrity of soils and hydrological systems through the release of pesticides, nutrients, salts, sediments, organic matter, pathogens, and metals/heavy metals into the environment (Mateo-Sagasta *et al.*, 2018). Thereby, the complexity of mobility of an specific element is given by physical-chemical conditions of soils and waters, whose values of pH, presence of clay minerals (texture), organic compounds, microorganisms, and the concentrations of other chemical species, play a profound role in the geochemical behavior of metals through the mechanisms of sorption/desorption, complexation, reaction and precipitation (Iaea, 1973; Becegato & Ferreira, 2005; Souza & Ferreira, 2005; Conceição & Bonotto, 2006a; Hussain & Hussain, 2011; Mazzilli *et al.*, 2013).

Additionally, natural environmental radioactivity can also be disturbed by the addition of radionuclides originated from the decay series of ^{232}U, ^{235}U, and ^{232}Th present in mineral fertilizers (NPK), where the main raw material for the production of phosphate concentrates, with P_2O_5 concentrations ranging from 32% to 38%, are phosphate-rich minerals rocks, especially the apatite group (Ulbrich *et al.*, 2009). According to Isherwood (2000), besides U and Th, other elements such as Cd, also contained in small amounts in phosphate minerals, are also present in fertilizers due to the inefficiency of industrial processes to totally remove them. This fact occurs due to the crystal structure of apatite, where Ca^{2+} can also be partially replaced by other elements, such as Pb and the rare earth group (ETR) members, in addition to the exchange of the PO_4^{3-} by other radicals such as UO_4^{2-}, AsO_4^{2-}, or SiO_4^{4-} (Loureiro *et al.*, 2005). In the case of Brazil, igneous rocks such as carbonatites account for approximately 95% of the raw material for apatite concentrate production in the country (Loureiro *et al.*, 2005), where the application and management of agrochemicals are a growing concern as the country takes one of the highest positions in food production in the world.

Due to its extensive territory, Brazil is also the custodian of some of the world's most biodiverse tropical biomes, while also being an important worldwide recognized agricultural hub. As a result, land use and management associated with environmental preservation practices on local and regional scales constitute actions of global interest, both in terms of ensuring the supply of agricultural goods such as food, fuel, and fibers, preserving the integrity of the environment and the quality of water and biological resources.

This issue is even more critical in specific environments, such as wetlands, where the interaction between surface water and groundwater is even more active and direct, especially when considering the regional influence of an entire group of wetlands (Maltby, 1988; Mclaughlin *et al.*, 2014; Hayashi *et al.*, 2016; Rains *et al.*, 2016). Wetlands cover 6% of Earth`s surface, and the agriculture is the main factor to wetlands degradation, such as pollution and eutrophication (Guo & Yang, 2016). Pollutants are retained through precipitation and/or adsorption processes in clay minerals and organic matter or released to water (Luko-Sulato *et al.*, 2012). Their role on water quality, storage, and aquifer recharge can be extremely important for the management of water resources and environmental protection, however those ecosystems are often excluded from environmental politics and social interest. Thus, understanding the hydrogeochemical dynamics of those ecosystems is an important factor in soil, water and agriculture management.

The present study aims to evaluate the impact of agricultural activities based on the mobility of radionuclides and in situ hydraulic conductivity in a small isolated wetland originally developed in the Brazilian Cerrado. The relevance of the study relies on the location, like much of the state, which is mainly dedicated to the cultivation of sugarcane and soybeans, one of the most important sectors of Brazilian agribusiness

2. Study area

The study area is located in the rural zone of the municipality of Cordeirópolis, at an altitude of 653 m and defined by the coordinates -22º 29' 22'' S and -47º 29' 14'' W, part of the Limeira Microrregion and Piracicaba Mesoregion, central portion of the state of São Paulo, Brazil (Figure 1).

The wetland itself is classified as geographically isolated due to its lack of superficial connection with nearby drainages and streams (Leibowitz, 2015; Tiner, 2003; Hayashi *et al.*, 2016; Furlan *et al.*, 2023). Its circular shape resembles a roman amphitheater, with the center (flooded during a certain period of the year) at a lower level compared to the slopes, where the land was converted to agriculture in this specific case. Thus, the local hydrological connection occurs only through groundwater fluxes, probably recharging deep aquifers and nearby streams during most of the year (Casagrande *et al.*, 2021).

Due to the heavy agricultural machinery traffic in the area, unpaved roads were built around the entire perimeter of the area, as well as an area designated for high voltage power transmission lines that intercepts the study area in the approximate N-S direction, which corresponds exactly to the soybean cultivation zone (Figure 2).

The local climate is classified as "Cwa" (Köppen & Geiger, 1928), characterized by warm humid summer (from September to April) and dry mild winter (from May to August) with an average temperature of 21.1°C. In geological terms, the wetland is developed on a diabase sill of the Serra Geral Formation, a unit belonging to the Paraná Basin and associated with fissure magmatism caused by the breakup of the Gondwana megacontinent during the Cretaceous and the consequent evolution of the South Atlantic ocean (Milani *et al.*, 2007). This dike lies above the Perminan sedimentary rocks of Corumbataí Formation, whose maximum local thickness is about 130 m and predominantly composed of dark gray argillites and siltstones at its basal portion, while the top is described as reddish-purple argillites, shales, and siltstones with intercalations of carbonate banks and fine sandstones (Schneider *et al.*, 1974).

3. Environmental radioactivity

Radioactivity can be defined as the spontaneous decay of chemical elements, with the emission of alpha particles (positively charged as a helium nucleus) and beta particles (negatively or positively charged as electrons or positrons, respectively), and

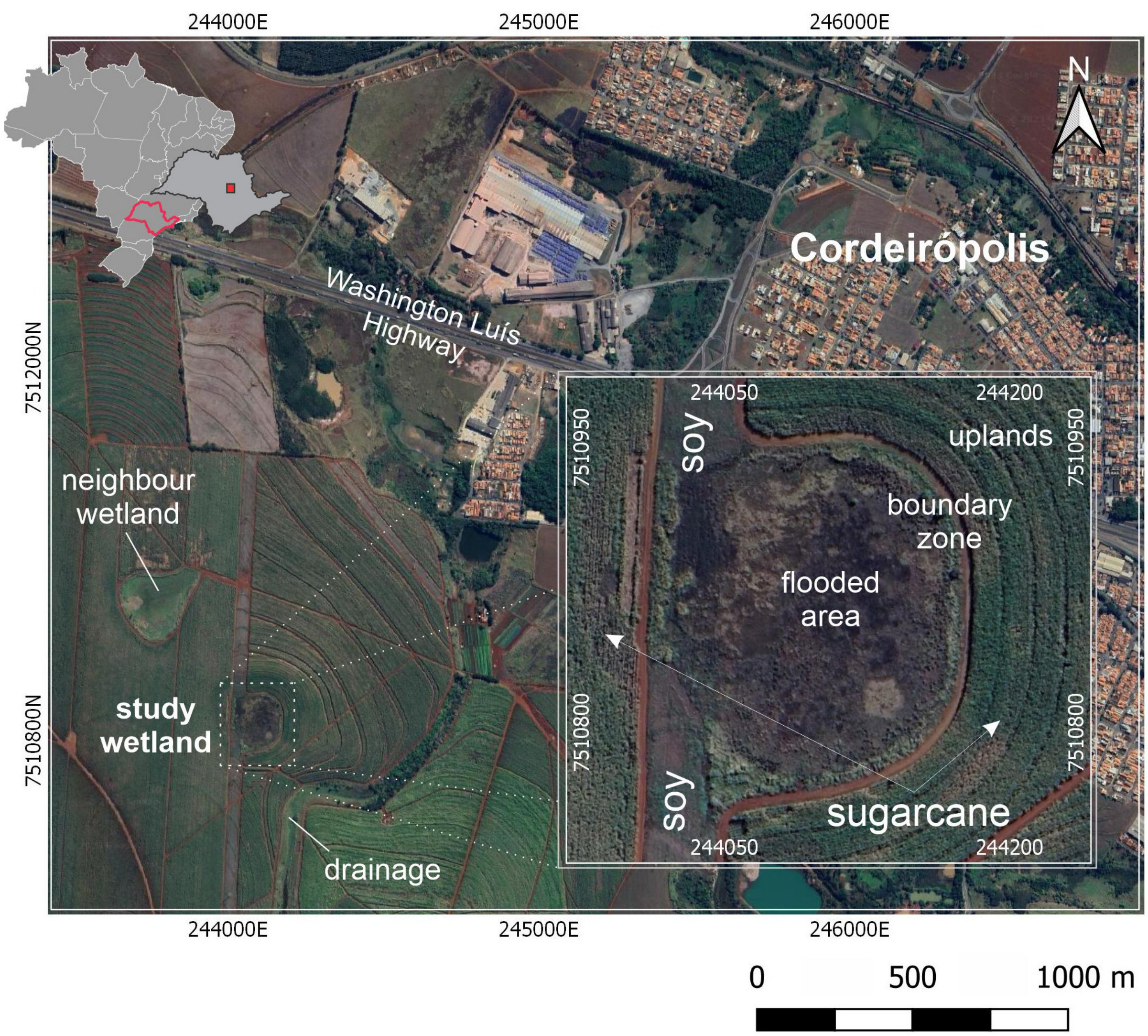

Figure 1. Location of the study area, with the indication of Cordeirópolis, access roads and highways.

Figure 2. North view of the wetland area (flat and lower terrain in the middle of the picture), with soybean (under the high voltage power transmission) and sugarcane cultivation. The yellow circle indicates the presence of surface water on the access road as a direct result of land conversion to agriculture.

the eventual release of energy in the form of gamma photons, which are highly penetrative. In the electromagnetic spectrum, gamma rays have the highest frequency (>1019 Hz) and the shortest wavelength (< 10-11 m).

Radionuclides tend to undergo spontaneous decay, where the atomic nucleus emits a radioactive particle or a gamma ray and ends up in a lower energy level and, therefore, relatively more stable. The decay of a number N of nuclei of any decaying radioactive element can be expressed by the general equation:

$$N=N_0e^{-\lambda t} \tag{1}$$

where N corresponds to the number of radionuclides at time t; N_0 is the initial number of radionuclides; and λ represents the decay constant.

Natural occurring radionuclides come from both cosmogenic (such as ^{14}C and ^{3}H) and lithospheric sources (such as ^{235}U, ^{238}U, ^{232}Th and ^{40}K) (Unscear, 2008), with the latter group being the most important source of environmental radioactivity, surface exposure, and mobilization into the hydrosphere and atmosphere, along with their associated radionuclides (Eisenbud & Gesell, 1997; Casagrande & Bonotto, 2018).

Unlike ^{40}K, which decays directly to stable nuclides such as ^{40}Ca through β- emission (89.3%) and to ^{40}Ar (10.7%) through the phenomenon of electron capture plus gamma emission of 1.46 MeV, the radioisotopes ^{238}U, ^{235}U, and ^{232}Th constitute primordial nuclides of the so-called decay series. In the case of uranium, its most abundant isotope is ^{238}U (93.3%), whose decay series includes 15 daughter radioisotopes with significantly shorter half-lives until its end as stable ^{206}Pb (Chu *et al.*, 1999). On the other hand, ^{235}U, of great interest in the nuclear industry for energy and military purposes, has a proportion of only 0.7% and its series, composed of 12 radioisotopic species, ends with the stable ^{207}Pb (Chu *et al.*, 1999; Unscear, 2008). Finally, ^{232}Th represents almost all the natural thorium (99.98%) and decays in a series down to ^{208}Pb (Chu *et al.*, 1999).

In terms of abundance, potassium is by far the most common element compared to uranium and thorium, commonly measured in parts per million (ppm). The first constitutes about 2.3% of the Earth's crust and is a major element in various rock-forming minerals, unlike the two other metals that have concentrations of approximately 2.4 ppm and 12 ppm, respectively, and are often found as minority elements associated with various resistate minerals (Emsley, 1998).

The three elements are unknown in natural settings as free metals and the most common oxidation states for uranium are U^{4+} and U^{6+}, whereas thorium often exhibits a 4+ oxidation state in nature. Both uranium and thorium are commonly associated with Zr, Hf, rare earth, Nb, and Ta in terms of geochemical aspects and mobility (Ulbrich *et al.*, 2009).

In soils, U and Th comprises concentrations as low as 1 ppm and 5 ppm in average, respectively, with a deep increase in soils derived from granitic, gneissic and alkalic igneous rocks (BOYLE, 1982). Otherwise, most mafic and ultramafic rocks generally exhibit low U and Th concentrations but in soils the A horizon is usually the richest in U, whereas C horizon is generally the most enriched just in vicinity of uraniferous deposits (Musset & Khan, 2000). The differential solubility of uranium and thorium can influence their mobility in natural environments as U^{6+} presents higher solubility, which can favor its release, for example, through liquid soil phase in oxidizing mediums (Boyle, 1982), allowing its migration. However, uranyl ion can be retained by neoformed substances, including colloids of organic origin.

Th^{4+}, in turn, has the opposite behavior compared to U^{6+}

under same environmental conditions (Ulbrich *et al.*, 2009). However, when released, thorium will certainly be immobilized with some ease, through its retention in secondary substances.

4. Materials and methods

Gamma detectors are widely used in geosciences due to the relative ease of detection and high penetrability of gamma emissions, as well as their ability to provide quantitative and qualitative information on radioactive elements in mineral samples, soils, and water. As such, their applicability, especially in portable or airborne equipment, includes research on undifferentiated intrusions and impact craters, mineral prospecting, oil exploration, aiding in the determination of geological boundaries and large structures (Hoff *et al.*, 2004; Vasconcelos *et al.*, 2012; Fianco *et al.*, 2014; Ferronsky, 2015), as well as in the environmental field, with applications in controlling areas impacted by radioactive leakage, medical geology, and studying the influence of fertilizer compounds in water systems and soils (Umisedo, 2007; Schuler *et al.*, 2011).

This tool is incorporated in geophysics as a passive, non-invasive radiometric method that involves detecting gamma emissions from various natural radioisotopes, including those from the decay series of ^{235}U, ^{238}U, ^{232}Th, and ^{40}K. In gamma spectrometry, it is common the use of photopeaks generated by daughter radionuclides in order to determine their respective initial decay series components, where energies of 1461 keV (^{40}K), 1765 keV (^{214}Bi), and 2615 keV (^{208}Tl) are used to estimate the concentrations of K, U, and Th, respectively (Erdi-Krausz *et al.*, 2003). However, this condition is theoretically valid only with the consideration of secular equilibrium in the sample or investigated medium (Ferronsky, 2015; Casagrande & Bonotto, 2018).

In order to determine the coefficient of soil hydraulic conductivity in the field and make a correlation with gamma signals distribution, a Guelph Permeameter was utilized (Reynolds *et al.*, 1983). The method is based on the measurement of saturated hydraulic conductivity in situ, by excavating boreholes up to a depth of 50 cm, where the equipment is set. When a constant hydraulic load is established inside the borehole, a "bulb" of water saturation is generated into the soil. The calculation of the hydraulic conductivity in situ is only possible after the stabilization of the water column, where graduate marks on the equipment and a chronometer are used in order to determine water infiltration rates (R1 and R2), followed by the equations of the double head method (Soil Moisture Corp., 2012):

$$K_{fs} = [(0.0041)(X)(R2) - (0.0054)(X)(R_1)] \tag{2}$$

$$K_{fs} = [(0.0041)(Y)(R2) - (0.0054)(Y)(R_1)] \tag{3}$$

where K_{fs} comprises the hydraulic conductivity (cm.$^{s-1}$); X and Y stand for the area of the reservoir tube section (35.22 cm^2 or 2,16 cm^2); R1 and R2 are the stabilized infiltration rates corresponding to H_1 (5 cm) and H_2 (10 cm), respectively, in cm.s^{-1}. Taking into account the physical properties of the study area, the dimensionless values of 0,0041 and 0,0054 are based on some important parameters such as soil type (texture-structure category related to the local clay and agricultural soils), water height in borehole, soil matric flux potential and borehole radius (Zhang *et al.*, 1998; Soil Moisture, 2012).

5. Data aquisition

In the study area, 507 surface reading points were obtained, covering all segments of the wetland, including its center and slopes (Figure 3). The focus of the analysis was on K, Th, and U elements, with a predefined acquisition time of 180 seconds, analogous to other studies (see Šimíček *et al.*, 2012; Nardy *et al.*, 2014). The conversion of counts per second in the energy windows defined for ^{40}K, ^{214}Bi, and ^{208}Tl to concentration units was automatically performed by the RS-332 gamma spectrometer model from Canadian Radiation Solutions, associated with a BGO scintillation crystal of 104 cm^3 and FWHM resolution less than 11.5%.

The analysis period was concentrated in the dry season, specifically in two field campaigns in August 2020, in order to minimize the effect of gamma signal attenuation in excessively wet soils, as expected for the central zone of the wetland. A second field campaign was carried out after one year, shortly after a fire of unknown causes consumed the entire area. The purpose of the new survey was to analyze possible temporal variations in K, Th, and U in the soil, as well as to serve as a qualitative comparative in determining the degree of gamma signal absorption caused by the natural substrate moisture, which was very low after the fire. Thus, the focus of the new acquisition stage was concentrated only inside the wetland, which included 157 reading points with the usual acquisition time of 180 seconds.

For data quality analysis, the coefficient of variation (CV) (Becegato *et al.*, 2008; Mikami *et al.*, 2015) of the obtained values was calculated, according to equation 4:

$$CV = (\sigma.100\%) / \mu \tag{4}$$

where μ represents the arithmetic mean of the values obtained at each analysis point and σ represents the associated standard deviation. The generation of maps of eU, eTh, Ke, and eU/eTh distribution was performed through the Oasis Montaj (Geosoft) platform, where the data were interpolated using the kriging method, followed by the minimum curvature for central value smoothing over the edges.

The hydraulic conductivity tests, on the other hand, comprised 70 uniformly distributed points throughout the study area, both inside and on the slopes of the wetland (Figure 3). Data acquisition was performed over a period of 2 years (2020-2021) and was carried out only during the dry season due to the impossibility of conducting hydraulic conductivity tests in fully saturated soils, which occurs annually in the study area during the rainy period. Subsequently, the spatial data were interpolated to generate a hydraulic conductivity map of the area using the kriging method through Oasis Montaj (Geosoft) software.

6. Results and discussions

The results indicate that the concentrations of K varied from 0.03 to 0.2%, with a mean of 0.082% and a median of 0.078%. Approximately 8% of the analysis points resulted in values below the detection limit of the equipment (0.02%). On the other hand, eU and eTh did not present values below the detection limit, ranging from 1.28 pmm to 2.83 ppm and 6.94 ppm to 11.43 ppm, respectively. In this case, eU resulted in an average value of 2.02 ppm and a median of 2.01 ppm, while eTh indicated mean and median values of 9.55 ppm and 9.57 ppm, respectively. For comparison, in agriculture soil managed with phosphate fertilizer Souza Souza e Ferreira (2005) found average concentrations for eU as high as 6,87 ppm, whereas eTh showed lower values of around 4,3 ppm.

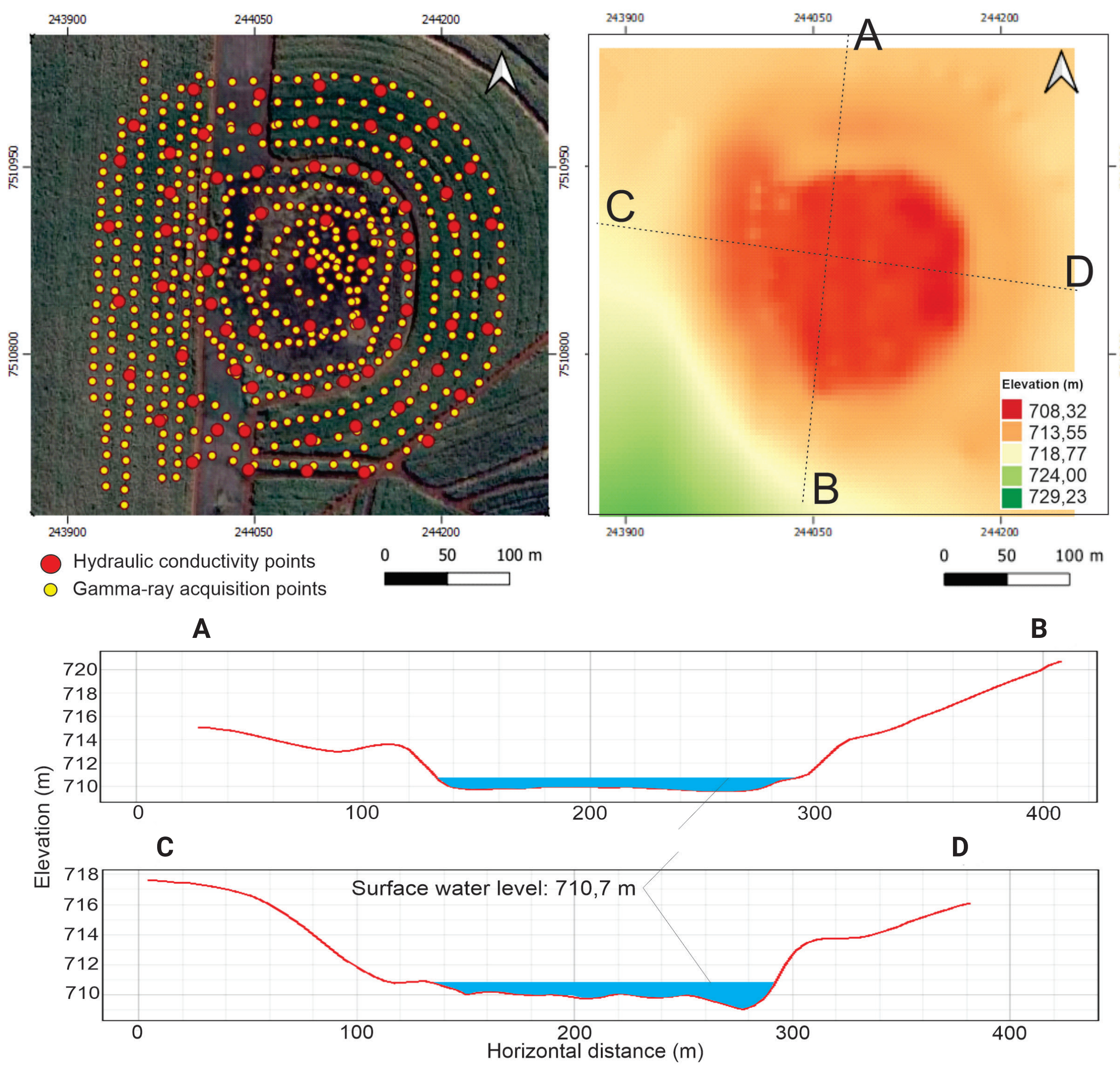

Figure 3. Distribution of hydraulic conductivity and gamma-ray acquisition points, covering all segments of the study wetland. The Digital Elevation Model (DEM) of the area was generated by multiple high precision GPS acquisitions, giving an idea of the local topography in terms of slopes around the wet center (geographically isolated wetland).

Although the use of coefficient of variation CV as a way of evaluating data dispersion in terms of precision and accuracy, its value is subjective and a maximum value of 10% was established for eU and eTh during the interpolation stage. Only five points exceeded this limit for eU (all of them discarded) and the boxplot diagrams (Figure 4) indicated extremely high CV values related to K, with minimum and maximum values of 14% and 100%, respectively.

Soils generated by the alteration of the Serra Geral Formation diabases are generally characterized by low concentrations of radionuclides (Conceição & Bonotto, 2006a), although several studies have pointed to the existence of radiometric anomalies in associated soils generated by the use of phosphate fertilizers in agriculture, especially for sugarcane (Souza & Ferreira, 2005; Conceição & Bonotto, 2006b). This fact may be related to the radiometric interest zones found in the study region, where presence of diabase-derived clay-rich soils and the occurrence of organic matter might lead to a geochemical sink for many elements and compounds, including radionuclides belonging to U and Th decay series originated from mineral fertilizers (Souza & Ferreira, 2005). However, Olivie Lauquet *et al.* (2001) emphysises that the dissolved organic carbon (DOC) concentrations play an important role in a wetland's behavior as a sink or source of trace elements and their transfer to water systems.

The spatial distribution of the element K showed strong heterogeneity throughout the study area, as observed in the map of Figure 5, where warmer shades correspond to higher concentration values (%) and cooler colors indicate relatively depleted regions in the element. The map allowed for the identification of anomalous concentration zones characterized by values close to 0.19 ppm, particularly in the northwest and southwest portions of the map, which correlate with areas of the slope covered with sugarcane. It is noteworthy that the SW-NE orientation of the anomaly located in the southwest region of the map is associated with the roads and the alongated soy plantation area, with visible propagation into the interior of the humid area.

Likewise, a large anomaly of relatively high concentration was identified along the northern and northeastern edges of the wetland, which also appears to follow the same orientation as the rural access road that borders the center of the humid area. In this case, the tendency of the anomaly to propagate into the central region of the study area is equally notable.

By comparing the maps of potassium CV distribution and K gamma-ray (Figure 5), it was possible to verify a clear correlation between low K anomalies and regions characterized by higher CV values, theoretically indicating low reliable data. In theory, this issue would be solved if longer acquisition times were applied, but according to tests performed in the field the chosen acquisition time of 300 seconds was the best option compared to other tests (600 and 900 seconds) where the slightly difference in results (less tha 10%) did not justify the large increment of acquisition time.

Methodologically, this relationship would point to a very low concentration of ^{40}K at the site, combined with the "short" acquisition time that is usually adopted in terrestrial gamma-ray acquisitions. However, in qualitative terms, such areas should not be disregarded because they represent potassium depleted zones. Thus, it was possible to indicate the presence of at least four low-K zones in Figure 5, especially along the soy plantation located in the east of the study area. The soil derived from weathering of diabase and constituted by low-activity clays. Thus, it is expected that K contents variation is mainly related to plant uptake or leaching losses of mobile K via fertilizers (Reinhardt and Herrmann, 2018).

On the other hand, the eU distribution map indicated a high contrast in the element concentration between the interior of the

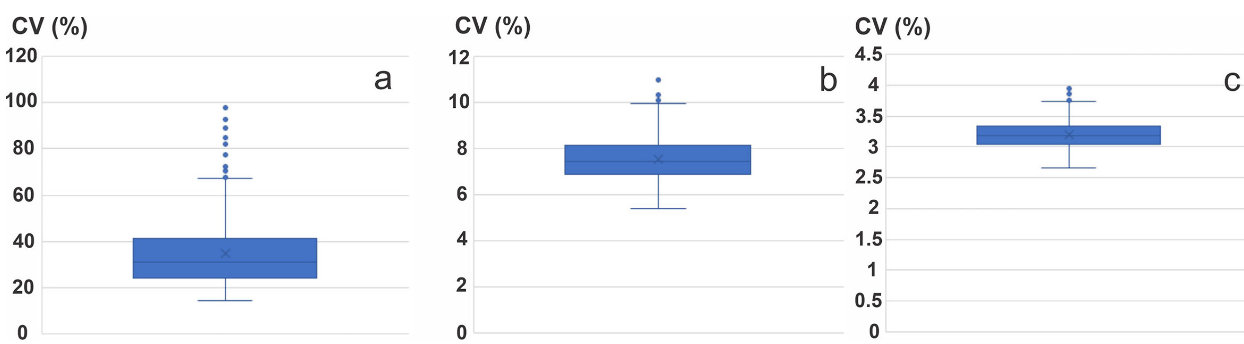

Figure 4. Boxplot diagrams for coefficient of variation related to K (a), U (b) and Th (c) data.

study area and its slopes, with its center anomalously depleted in U (~1.5 ppm) and its outer edges enriched in the metal (~2.8 ppm). From the perspective of the slopes, the northern portion is characterized by moderate eU values (~2 ppm), while further south there are zones of higher concentrations correlated with agriculture (~2.8 ppm).

In a less defined way, the variation in eTh concentration throughout the study area followed, to some extent, the same behavior observed for eU, but with a center that was not completely depleted in the element in question (Figure 5). There, eTh concentrations varied from 6.95 ppm to values greater than 11.40 ppm, mainly in the northeast and southeast edges of the central area.

It is worth noting the presence of a high concentration anomaly correlating to the point of water accumulation in the N-S oriented rural access road, where high eU values are also observed, as well as the southeastern portion of the study area already in agricultural land.

In this case, the eU/eTh ratio was used for mapping and examining patterns of uranium mobility relative to thorium, due to the observed average ratio of 0.21 between the two metals in the in the study area and the relatively immobile nature of Th compared to U. Therefore, lower eU values relative to eTh would indicate depletion, while higher values would indicate enrichment. The map shows warmer colors concentrated along the edges of the central area of the study region, suggesting relative enrichment of uranium in these zones. In contrast, the green and yellow shades distributed along the slopes and northwestern portions of the study region approach the obtained average value of 0.21, being also close to the average of approximately 0.25 discribed for the lithosphere. In addition, the study area shows several anomalies of high eU/eTh ratio (possibly due to accumulation of leached U) (BOYLE, 1982).

Another and more plausible possibility relies on the mobility of Th, and consequently its daughter radionuclides, through colluvial transport (Pickup & Marks, 2000; Ulbrich *et al.*, 2009). As long as Th can be adsorbed by solid fractions of soil (clay minerals, Fe-Mn-Al-Ti oxi-hydroxides, and organic compounds), the element might act as a good indicator of erosional and sediment accumulation processes, which are of profund interest in water and soil management. Thus, the spacial variability of Th over the study area follows almost the same pattern as observed for U, exept by the presence of a high-Th narrow elongated segment from the wet margins to the center of the wetland (NW-SE) where no fertilizer is directly applied, indicating an apport of sediments from the nearby slopes (Figure 5). Thus, the relationship between U and Th might be an complex influence of both processes: the geochemical lixiviation of U in relation to Th and the mobility of adsorbed Th by fine soil particles.

Another interesting characteristic relyes on the fact that the high-Th zones forming a ring around the wetland margin have some continuity into the flooded area, including the west portion along the N-S road and soy plantation, which might facilitate the input os sediments from higher levels to the lower zone, especially when the natural margin vegetation is impacted. Figure 2 shows the accumulation of water and sediments in the already mentioned pound formed along the unpaved road, right the same place where high values of eTh (and, in this case, eU as well) were observed (>11,40 ppm), a zone where a significative edge of the original wetland soil was converted into the access road and agriculture, as indicated by the elevation model and aerial imagery. Additionaly, K shows low concentration values in this exactly same spot probably due to plant uptake or leaching to groundwater.

The differences in the mobility of Th^{+4} and U^{+6} under an oxidizing environment may be the explanation of the existence of a well-defined uranium-rich ring over wetland margins in contrast to a similar less defined high-Th aureole.

All this complexity of geochemical mobilization of metals is especially because its different phases act through different retention and liberation mechanisms as a function of very specific physical-chemical paramethers that occur in the environment (Strawn *et al.*, 2020). From an ecological point of view, the fluxes between solid and liquid phases of soil are one of the basis of the maintenance of life on Earth, providing the disponibility of nutrients for primmary producers. Those mechanisms, however, might also act in the fixation of contaminnats of natural and human origins and are applied in many environemental projects (Uddin, 2017; Han *et al.*, 2019; Arif *et al.*, 2021), where the sorption mechanism work in the immobilization of ion on mineral surfaces, especially clay minerals, whose electrostatic behavior is controlled by chemical and cristalographical particularities.

After the fire in the following year, the K concentration values obtained were practically the same, while the spatial distribution of K in the center of the humid area showed certain changes, especially due to the absence of the elongated southwest anomaly that extended into its interior (Figure 6). In the case of eU, the range of values obtained during the second campaign was slightly lower, with the center of the study area still contrasting with its surroundings characterized by greater gamma response, but with values not as low as those observed during the acquisition prior to the fire. The eTh, in turn, also presented relatively higher concentration values in the second campaign, in addition to the extension of the high concentration anomaly (~11.3 ppm) from the northeastern edge to the center of the study area. As a result, the eU/eTh ratio was also affected in the same trend, although the contrast between the outer part and the edges of the study area persisted after the fire.

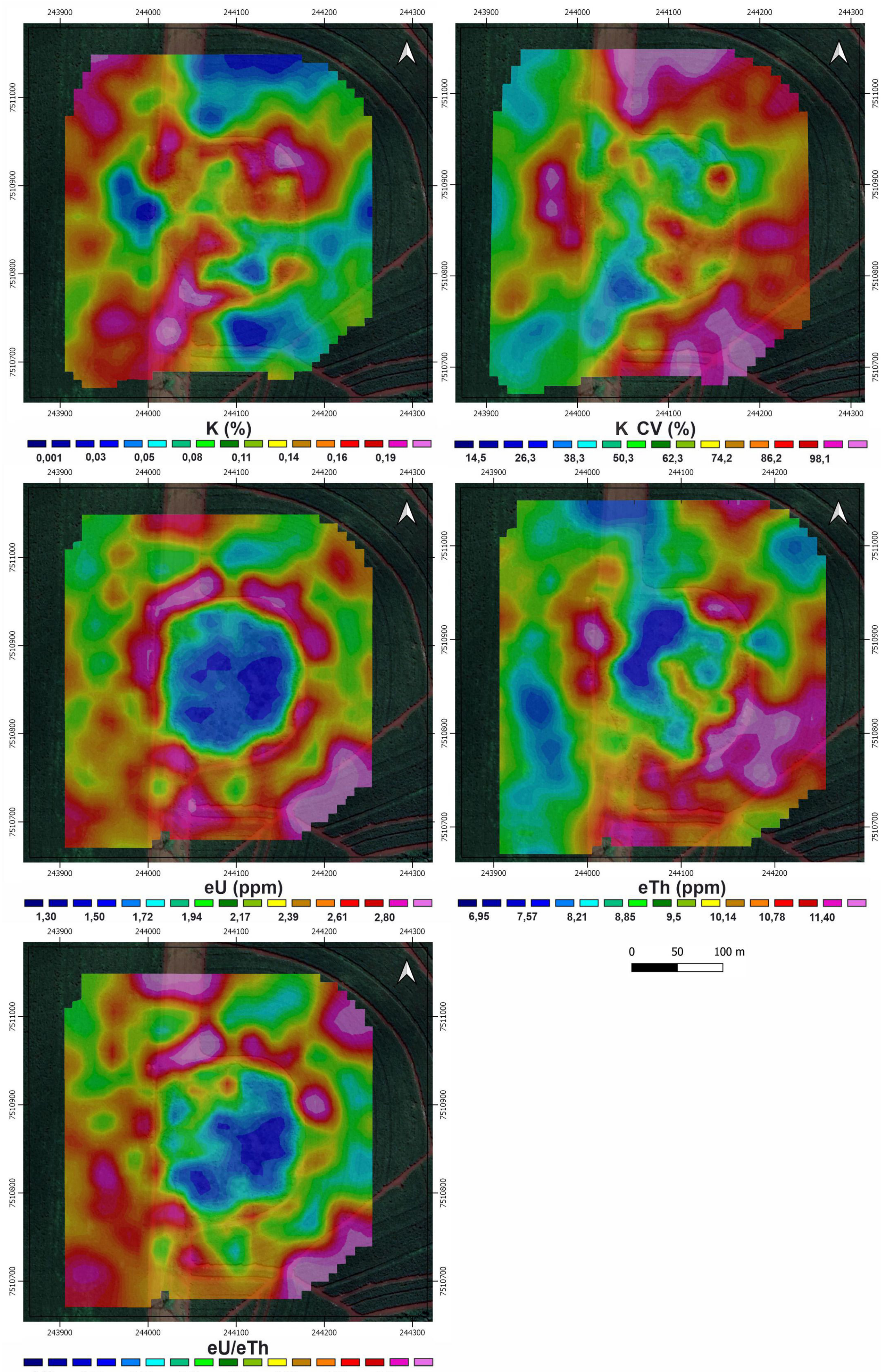

Figure 5. Maps of K (%), CV (K) (%), eU (ppm), eTh (ppm), and eU/eTh distribution obtained by gamma-ray acquisitions.

The slight variation in gamma response after one year is probably attributed to the reduction of the natural absorption effect due to low soil moisture and reduction of superficial organic matter in the weeks following the fire (Reinhardt & Hermann, 2018), when no precipitation was recorded in the area. However, the soil absorption effect was not intense enough to impair the qualitative evaluation of the spatial distribution of K, eU and eTh in the area, especially since the relative concentrations basically followed the same overall trend, particularly the contrast between the interior of the study area and its wet margins.

Other factors such as variations in fertilizer application over time and the presence of large amounts of mineral matter in the soil (ashes) can also have a subordinate influence on the surficial variability of the gamma response obtained after the fire. However, a more profound evaluation of element mobility from the soil to the water system must consider associated factors related to seasonal variations of hydrological and biochemical cycles, especially seasonal parameters such as temperature and water-table fluctuation over the year, which directly influences reducing conditions and organic matter decomposition (Olivie Lauquet *et al.*, 2001).

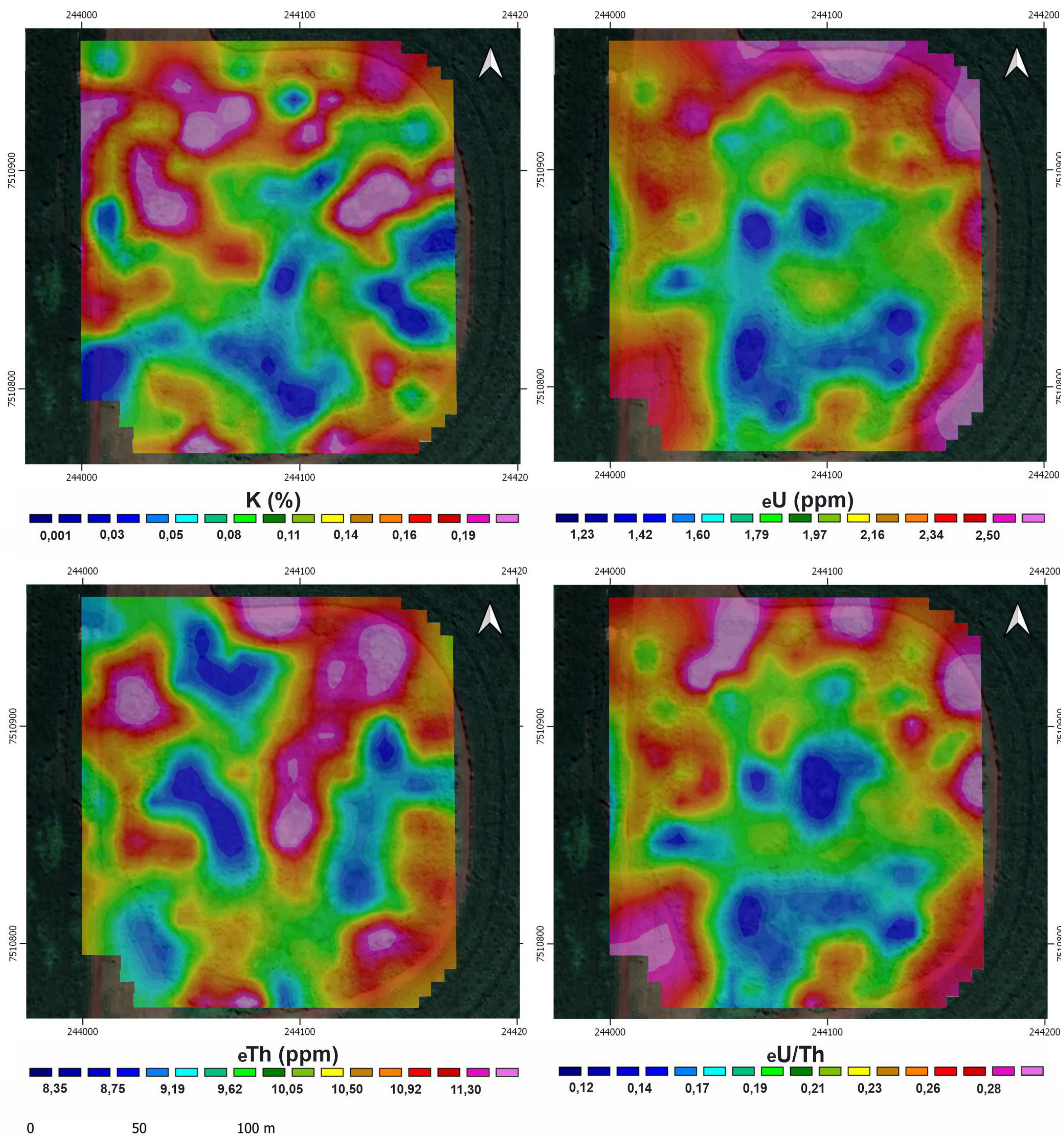

Figure 6. Maps of K (%), eU (ppm), eTh (ppm), and eU/eTh distribution obtained by gamma-ray acquisitions. (after the fire).

The hydraulic conductivity data acquired though Guelph Permeameter configure a shallow method to quantify the ability of water (or a given fluid) to pass through the pores and fractures in the geological environment. Thus, these surficial results can be compared with the spatial variability of K, U, and Th in order to describe the link between geochemical mobility and the local hydrogeological dynamics in terms of mass transfer. The relationship between soil and hydrosphere plays an important role in the geochemical dynamics of the system, since many reactions and ion mobility occur in aqueous medium.

The values of hydraulic conductivity were deeply variable, with a range in the order from 10^{-3} cm/s to 10^{-6} cm/s (Figure 7). The contrast between the center and the slopes around the wetland is very clear, specially by the low hydraulic conductivity values at its center (<10^{-5} cm/s) and the variable, but frequently higher, values at the agriculture zones (>10^{-4} cm/s). Some exceptions are observed as low conductivity zones over the slopes (blue areas, especially the one N-S oriented), which might be explained by the near surface soil compaction due to heavy machinery applied in the sugarcane plantation (Horn & Peth, 2011).

The reduction of pore space in the soil can impact not only the natural geochemical and biological dynamics, but also soil productivity in terms of food production (Tubeileh *et al.*, 2003; Blum, 2013). In addition, the increase of surface water flux resulted by the compaction of uppermost part of soils is often accompanied by a gain of erosion rates and consequent sedimentation, thereby causing the loss of arable land and soil nutrients, reduction of surface water quality, and siltation. Thus, this phenomenon might be a key factor for the occurrence the already mentioned high eTh concentration zones at the wetland center associated with colluvial transport, also evidenced by the same N-S alignment as observed for the long low conductivity zone in the slopes. This factor might be allied to the suppression of the natural margin vegetation, which acts as a natural barrier against solid particles (Mitsch & Gosselink, 2015)

Again, the wetland margins seem to be a very critical natural buffering zone, especially for its capacity to drain runoff water as a result of medium to high hydraulic conductivity values (~10^{-4} cm/s) compared to the center portion. This same compartment is also the responsible for the accumulation of U, probably by a combination of factors such as immobility as a result of a reduction front (at least during the surface water accumulation season), low hydraulic conductivity towards the central region of the wetland, and adsorption/complexation mechanisms in the fine textured diabase-derived soil.

During the dry season, it is possible that an alternation to aerobic conditions occur by the lowering of water-table level and the input of occasional oxygen-rich waters in the presence of electrons acceptors (Mn^{4+}, Fe^{3+} and NO^{3-}), which might lead to the mobilization of trace elements, in addition to a more efficient decomposition of organic matter (especially with medium to high temperatures even during winter), resulting in a higher DOC

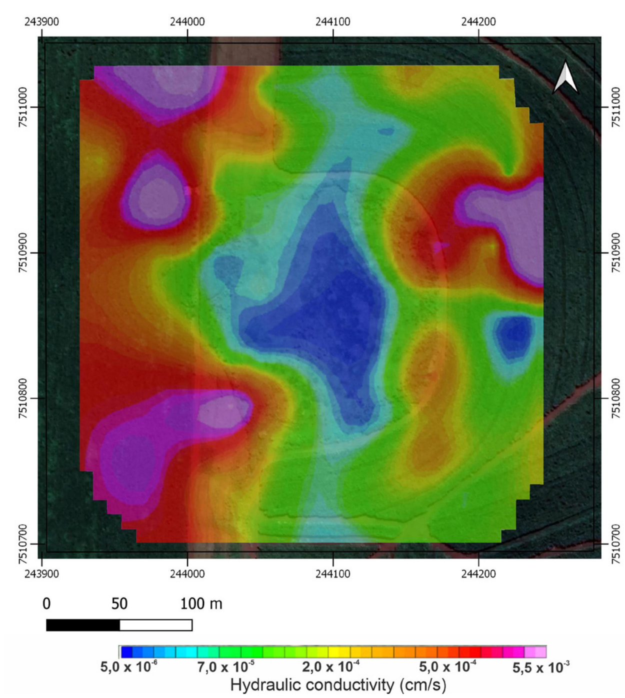

Figure 7. Hydraulic conductivity map acquired using a Guelph Permeameter.

concentration in waters (Strawn *et al.*, 2020; Olivie Lauquet *et al.*, 2001). Hence, the local wetland system might act as a source of chemical species for a short period of the year.

7. Conclusions

Based on gamma ray data and the hydraulic conductivity map, it was possible to assume the existence of a 20 meters wide strip zone around the wetland (from external and internal sides of the margins) where geochemical processes and hydrogeological factors play important role in the uptake, concentration, and immobilization of certain chemical elements, allied to the protection of wetlands's interior against heavy sedimentation uptake and surface water flow. Thus, the well-defined eU and eTh rings around wet margins represent clear evidences of the significance of wetlands as attenuation zones in the protection of surface and groudwater quality.

It is important to mention that even the higher values of eTh and eU found do not necessarily configure a contaminated site. However, the spatial distribution analysis based on gamma spectrometry method showed to be a very useful tool in order to establish an initial geochemical model and the definition of target areas for soil sampling in a such complex environment in terms of metal mobility, even though each specific element has its own behavior under different environmental parameters (pH, Eh, temperature, etc.) so other methods could be applied for a more detailed assessment, which includes regular soil sampling and chemical analysis that could lead to more expenses and longer field acquisitions. Thus, given the large variability of Brazilian wetlands in terms of size, geology, climate, vegetation, geochemistry and pedology, the use of gamma ray spectrometry as an initial fast low-cost screening method for hydrogeological characterization, soil management and evaluation of human impacts could easily be combine to other methods and applied to other similar environments.

The results corroborate the fact that wetlands are very distinct and important ecosystems with many environmental functions that must be considered in governmental policies, water resources management and public discussions. Thus, the results aim to contribute to highlight wetland importance and its wet margin zone in in terms of water infiltration (aquifer recharge and storage) and fixation of certain chemical species as natural "geochemical sponges". However, even though the accumulation of trace elements was observed, a profound study focused on local water samples collected over the hydroperiods should be performed in order to stablish the possible release of those elements to groundwater during periods of change in the parameters of pH, redox potential, water-table fluctuation and temperature.

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9. Author contributions

MFSC and CAM: Conceptualization, planning, data acquisition, data processing, interpretation and writing. VR: Planning, acquisition, critical data analysis and writing. LMF: Critical data analysis, writing and review.

10. References

Arif, M., Liu, G., Yousaf, B., Ahmed, R., Irshad, S., Ashraf, A., Zia-Ur-Rehman, M., Rashid, MS. (2021). Syn.thesis, characteristics and mechanistic insight into the clays and clay minerals-biochar surface interactions for contaminants removal-a review. *J Clean Prod.*; 310:127548. **https://doi.org/10.1016/j.jclepro.2021.127548**

Becegato, V.A., Ferreira, F.J.F. (2005). Gamaespectrometria, resistividade elétrica e susceptibilidade magnética de solos agrícolas no noroeste do estado do Paraná. *Revista Brasileira de Geofísica.* 23(4): 371-405. **http://dx.doi.org/10.1590/S0102-261X2005000400004**

Becegato, V.A., Ferreira, F.J.F., Cabral, J.B.P., Rafaelli Neto, S.L. (2008). Gamma-ray Spectrometry Sensor and Geochemical Prospecting in an Area of Sugar Cane Plantation. *Braz. arch. biol. technol.* 51:1, 1-10. **http://dx.doi.org/10.1590/S1516-89132008000100001**

Blum, W.E.H. (2013). Soil and Land Resources for Agricultural Production: General Trends and Future Scenarios-A Worldwide Perspective. *International Soil and Water Conservation Research.* 1;3, 1-14. **https://doi.org/10.1016/S2095-6339(15)30026-5**

Boyle, R.W. (1982). *Geochemical prospecting for thorium and uranium deposits.* Elsevier Scientific Publishing Company, Amsterdam, 498 p.

Calabrese, E.J., Kostecki, P.T., Dragun, J. (2005). Contaminated Soils, Sediments and Water: *Science in the Real World.* Springer, Boston. 611 p.

Casagrande, M.F.S., Bonotto, D.M. (2018). The use of γ-rays analysis by HPGe detector to assess the gross alpha and beta activities in waters. *Appl Radiat. Isot.* 137:1–11. **https://doi.org/10.1016/j.apradiso.2018.02.027**

Casagrande, M.F.S., Furlan, L.M., Moreira, C.A., Rosa, F.T.G., Rosolen, V. (2021). Non-invasive methods in the identification of hydrological ecosystem services of a tropical isolated wetland (Brazilian study case). *Environ Chall.* 5:100233. https://doi.org/10.1016/j.envc.2021.100233

Chu, S.Y.F., Ekström, L.P., Firestone, R.B. (1999). *The Lund/LBNL Nuclear Data Search.* http://nucleardata.nuclear.lu.se/nucleardata/toi/index.asp

Conceição, F.T., Bonotto, D.M. (2006a). Dose de exposição radiométrica e composição das rochas sedimentares e ígneas na bacia do Rio Corumbataí. *Rev. Bras. Geof.* 24 (1), 37-48. https://doi.org/10.1590/S0102-261X2006000100003

Conceição, F.T., Bonotto, D.M. (2006b). Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil, and their industrial (by) products. *Environ. Pollut.* 139 (2): 232-243. https://doi.org/10.1016/j.envpol.2005.05.014

Eisenbud, M., Gesell, T. (1997). *Environmental Radioactivity from Natural*, Industrial, and Military Sources. 4th ed. Academic Press, San Diego, 688 p.

Emsley, J. (2001). *Nature's Building Blocks: An A-Z Guide to the Elements*. Oxford: Oxford University Press, 720p.

Erdi-Krausz, G., Matolin, M., Minty, B., Nicolet, J.P., Reford, W.S., Schetselaar, E.M. (2003). *Guidelines for radioelement mapping using gamma-ray spectrometry data*. International Atomic Energy Agency (IAEA),. 179p.

Ferronsky, V.I. (2015). Nuclear Geophysics: Applications in Hydrology, Hydrogeology, Engineering Geology. 1st ed. *Agriculture and Environmental Science*, 522p.

Fianco, C.B., Vidotti, R.M., Pires, A.C.B. (2014). Phosphorite porspection using ground gamma spectrometry in northeast Goiás state, Brazil. *Revista Brasileira de Geofísica*.; 32(4): 721-733. http://dx.doi.org/10.22564/rbgf.v32i4.540

Furlan, L.M., Ferreira, M.E., Moreira, C.A., Alencar, P.G., Casagrande, M.F.S., Rosolen, V. (2023). Satellite, UAV, and Geophysical Data to Identify Surface and Subsurface Hydrodynamics of Geographically Isolated Wetlands: Understanding an Undervalued Ecosystem at the *Atlantic Forest-Cerrado Interface of Brazil. Remote Sens*. 15, 1870. https://doi.org/10.3390/rs15071870

Guo, Y., Yang, S. (2016). Heavy metal enrichment in the Changjiang (Yangtze River) catchment and on the inner shelf of the East China Sea over the last 150 years. *The Science of the Total Environment*, 543 (Part A), 105-115. https://doi.org/10.1016/j.scitotenv.2015.11.012

Han, H., Rafiq, M.K., Zhou, T., Xu, R., Mašek, O., Li, X. (2019). A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. *Journal of Hazardous Materials*. 369, 780-796. https://doi.org/10.1016/j.jhazmat.2019.02.003

Hayashi, M., Van Der Kamp, G., Rosenberry, D.O. (2016). Hydrology of Prairie Wetlands: Understanding the Integrated Surface-Water and Groundwater Processes. *Wetlands.* 36, 237-254. https://doi.org/10.1007/s13157-016-0797-9

Hoff, R., Rolim, S.S.A., Bastos Neto, A.C. (2004). Mapeamento aerogamaespectrométrico da alteração hidrotermal associada à mineralização no distrito fluorítico de Santa Catarina, Brasil. *Revista Brasileira de Geofísica.* 22(1): 45-55. https://doi.org/10.1590/S0102-261X2004000100004

Horn, R., Peth, S. (2011). Mechanics of unsaturated soils for agricultural applications. In P. M. Huang, Y. Li & M. E. Sumner (Eds.), *Handbook of soil sciences*, 2nd. ed. (pp. 1-30). Boca Raton, FL; CRC Press.

Hussain RO, Hussain HH. (2011). Investigation the Natural Radioactivity in Local and Imported Chemical Fertilizers. *Braz. Arch. Biol. Technol.* 54(4): 777-782. https://doi.org/10.1590/S1516-89132011000400018

International Atomic Energy Agency. (1973). *Safe Handling of Radionuclides.* Safety Series. No.1. International Atomic Energy Agency, Viena.

Isherwood, K.E. (2000). *O uso de fertilizantes minerais e o meio ambiente*. IFA/UNEP/ANDA.

Kesler, S.E., Simon, A.C. (2015). *Mineral resources, economics and the environment*, 2nd. ed.: Cambridge, Cambridge University Press, 434 p.

Köppen W, Geiger R. (1928). *Klimate der Erde*. Gotha: Verlag Justus Perthes.

Leibowitz, S.G. (2015). Geographically Isolated *Wetlands*: Why We Should Keep the Term, *Wetlands*. 2015; 35, 997-1003. https://doi.org/10.1007/s13157-015-0691-x

Loureiro, F.E.L., Monte, M.B.M. 2005 , Nascimento, M. Fosfato. In: *Rochas e minerais industriais: usos e especificações*. Rio de Janeiro, RJ, Brasil: Centro de Tecnologia Mineral-Ministério da Ciência e Tecnologia,.

Luko-Sulato, K., Rosa, V.A., Furlan, L.M., Rosolen, V. (2021). Concentration of essential and toxic elements as a function of the depth of the soil and the presence of fluvic acids in a wetland in Cerrado, Brazil. *Environ Monit Assess*, 193:157. https://doi.org/10.1007/s10661-021-08945-y

Maltby, E. (1988). Global *wetlands*-history, current status and future. In: Hook, D.D.; McKee, W.H.; Smith, H.K.; *et al. The Ecology and management of wetlands.* London: Croom Helm, v.1: 3-14.

Mateo-Sagasta, J., Marjani Zadeh, S., Turral, H. (2018). *More People, More Food, Worse Water? A Global Review of Water Pollution from Agriculture*. Roma: Food and Agriculture Organization of the United Nations.

Mazzilli, B.P., Máduar, M.F., Campos, M.P. (2013). *Radioatividade no meio ambiente e avaliação de impacto radiológico ambiental.* São Paulo: Instituto de Pesquisas Energéticas e Nucleares (IPEN).

Mckee, W.H., Smith, H.K., *et al.* (1988). *The Ecology and management of wetlands*. London: Croom Helm, v.1: 3-14.

Mclaughlin, D.L., Kaplan, D.A., Cohen, M.J. (2014). A significant nexus: geographically isolated wetlands influence landscape hydrology. *Water Resour. Res.* 50 (9), 7153-7166. https://doi.org/10.1002/2013WR015002

Mikami, S., Sato, S., Hoshide, Y., Sakamoto, R., Okuda, N., Saito, K. (2015). In Situ Gamma Spectrometry Intercomparison in Fukushima, Japan. Jpn. *J. Health Phys.*; 50 (3): 182-188. http://dx.doi.org/10.5453/jhps.50.182

Milani, E. J., Melo, J. H. G., Souza, P. A., Fernandes, L. A., França, A.

B. Bacia do Paraná. (2007). Bacia Parana Carta Estratigraf Simples. *Boletim de Geociências da Petrobras*, v. 15, n. 2, p 265-287.

Mitsch, W.J., Gosselink, G. (2015). *Wetlands.* 5th ed. pp 456.

Mussett, A.E.; Khan, M.A. Looking into the earth: an introduction to geological geophysics. *Nova Iorque:* Cambridge University Press, 2000, 470 p.

Nardy, A.J.R., Moreira, C.A., Machado, F.B., Luchetti, C.F., Hansen, M.A.F., Rossini, A.J., Barbosa Jr. (2014). Gamma-ray spectrometry signature of Paraná volcanic rocks: preliminar results. *Geociênc.,* [s.l.], 33, 216-227.

Olivie-Lauquet, G., Gruau, G., Dia, A., Riou, C., Jaffrezic, A., Henin, O. (2001). Release of trace elements in wetlands: role of seasonal variability. *Wat. Res.,* [s.l.], v. 35, n. 4, pp. 943-952. **https://doi.org/10.1016/S0043-1354(00)00328-6**

Pickup, G., Marks, A. (2000). Identifying large-scale erosion and deposit processes from airbone gamma radiometrics and digital elevation models in a weathered landscape. *Earth Surface Processes and Landforms*, v. 25, p. 535-557, **https://doi.org/10.1002/(SICI)1096-9837(200005)25:5%3C535::AID-ESP91%3E3.0.CO;2-N**

Rains, M.C., Leibowitz, S.G., Cohen, M.J., Creed, I.F., Golden, H.E., Jawitz, J.W., Kalla, P., Lane, C.R., Lang, M.W., Mclaughlin, D.L. (2016). Geographically isolated wetlands are part of the hydrological landscape. *Hydrol. Process*., [s.l.], 30, 153-160. **https://doi.org/10.1002/hyp.10610**

Reinhardt, N., Hermann, L. (2018). Gamma-ray spectrometry as versatile tool in soil science: A critical review. *J. Plant Nutr. Soil Sci.*, [s.l.], 1-19. 2018. **https://doi.org/10.1002/jpln.201700447**

Reynolds, W.D., Elrick D.E., Topp G.C. (1983). A reexamination of the constant head well permeameter method for measuring saturated hydraulic conductivity above the water table. Soil Sci., [s.l.], 136(4), 250–268.

Ridley, J. (2013). *Ore deposit geology*. 398 p. Cambridge University Press.

Schneider, R.L., Muhlmann, H., Tommasi, E., Medeiros, R. A., Daemon, R. F., Nogueira, A.A. (1974). Revisão estratigráfica da Bacia do Paraná. In: Congresso Brasileiro De Geologia, 28, Porto Alegre. Anais. Brazil, Porto Alegre: SBG, v. 1, p. 41-65.

Schuler, U., Erbe, P., Zarei, M., Rangubpit, W., Surinkum, A., Stahr, K., Herrmann, L. (2011). A gamma-ray spectrometry approach to field separation of illuviation-type WRB reference soil groups in northern Thailand. *Journal of Plant Nutrition and Soil Science*, [s.l.], 174, 536-544. **https://doi.org/10.1002/jpln.200800323**

Šimíček, D., Bábek, O., Leichmann, J. (2012). Outcrop gamma-ray logging of siliciclastic turbidites: Separating the detrital provenance signal from facies in the foreland-basin turbidites of the Moravo-Silesian basin, Czech Republic. *Sedimentary Geology,* [s.l.], v.261, 50-64,. **https://doi.org/10.1016/j.sedgeo.2012.03.003**

Soil Moisture Corp. (2012). Model 2800K1, *Guelph Permeameter: Operating Instructions*. Santa Bárbara, CA, 93105, 28p.

Souza, J.L., Ferreira, F.J.F. (2005). Anomalias aerogamaespectrométricas (K, eU e eTh) da quadrícula de Araras (SP) e suas relações com processos pedogenéticos e fertilizantes fosfatados. *Revista Brasileira de Geofísica*, [s.l.], 23(3): 251-274. **https://doi.org/10.1590/S0102-261X2005000300005**

Strawn, D.G., Bohn, H.L., O'connor, G.A. (2020). *Soil chemistry*. 5th ed. West Sussex, U.K.: John Wiley & Sons.

Tiner, R.W. (2003). Geographically isolated *wetlands* of the United States. Wetlands, [s.l.], 23, 494-516.

Tubeileh, A., Groleau-Renaud, V., Plantureux, S., Guckert, A. (2003). Effect of soil compaction on photosynthesis and carbon partitioning within a maize-soil system. *Soil Tillage Res.* 71:151-161.

Uddin, M.K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal*, vol. 308, pp. 438-462. **https://doi.org/10.1016/j.cej.2016.09.029**

Ulbrich, H.H.G.J., Ulbrich, M.N.C., Ferreira, F.J.F., Alves, L.S., Guimarães, G.B., Fruchting, A. (2009). Levantamentos gamaespectrométricos em granitos diferenciados. I*: revisão da metodologia e do comportamento geoquímico dos elementos K*, Th e U. Geologia USP, Série Científica, São Paulo, 9 (1), p. 33-53.

Umisedo, N.K. (2007). Dose de radiação ionizante decorrente do uso de fertilizantes agrícolas. [Tese de doutorado]. Faculdade de Saúde Pública da Universidade de São Paulo, São Paulo.

United Nations Scientific Committee on the Effects of Atomic Radiation. (2008). *Sources and effects of ionizing radiation*. UNSCEAR 2008 report. vol. 1. New York: United Nations Scientific Committee on the Effects of Atomic Radiation.

Vasconcelos, M.A.R., Leite, E.P., Crósta, A.P. (2012). Contributions of gamma-ray spectrometry to terrestrial impact crater studies: the example of Serra da Cangalha, northeastern Brazil. *Geophys. Res. Lett*., [s.l.], v. 39, L04306. **https://doi.org/10.1029/2011GL050525**

Zhang, Z.F., Groenevelt, P.H., Parkin, G.W. (1998). The well shape-factor for the measurement of soil hydraulic properties using the Guelph Permeameter. *Soil Tillage Res.*, [s.l.], 49:219-221.