# INFLUENCE OF THE SOIL ORGANIC MATTER CONTENT ON VOLTAMMETRIC DETERMINATION OF DERIVATISED GLYPHOSATE IN HERBICIDE CONTAMINATED SOILS

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*Dedicated to Dr. Lubomír Pospíšil on the occasion of his 70th birthday.*

The method for monitoring of Glyphosate (GP) in soil samples containing different organic matter content based on differential pulse voltammetry at a hanging mercury drop electrode was developed to reach higher sample preparation efficiency, its repeatability and sufficient limits of detection. The soil samples with three different organic matter contents (evaluated as total organic carbon contents 30.7, 13.0 and 6.3 g $kg^{-1}$) were tested. The decreasing content of organic matter resulted in a decreasing recoveries (86, 78 and 68%, respectively), with RSD around 10%. The GP derivatised to *N*-nitrosoglyphosate (NO-GP) can be determined using the adopted method with limits of detection around 2 ppm in the soil samples. This method might be further utilized for routine monitoring of the GP in soil samples during investigation of its effect on the soil biota.

**Keywords**: Voltammetry; Environmental chemistry; Mercury; Electrochemistry; Glyphosate; Hanging mercury drop electrode; *N*-nitrosoglyphosate; Pesticide; Soil.

The Glyphosate (GP; *N*-(phosphonomethyl)glycine) was firstly synthesized by Henri Martin in 1950. Its herbicidal function was discovered and patented by John E. Franz from Monsanto Company (Saint-Louis, MO, USA) in 1970. Due to its anionic character, it is produced as a sodium or isopropylamine salt. These GPs are the main parts of commercially available nonselective broadspectrum herbicides such as Roundup, Rodeo, Touchdown, etc. These GP herbicides are widely used for both agricultural and non-



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agricultural purposes (forestry, aquatic systems, outdoor usage, etc.). They are the only herbicides that target 5-enolpyruvylshikimate-3-phosphate synthase, an enzyme absent in animals and essential to the synthesis of aromatic amino acids in plants[1,2]. These facts make GP unique, highly effective and relatively toxicologically and environmentally safe. Its highest production "explosion" began with a development of transgenic Glyphosate resistant crops, such as soybean, maize, canola and cotton, since 1996. These crops nowadays dominate in many countries (e.g. Argentina, Brazil, USA, Canada) and the GP became a "number one" herbicide in its production and/or consumption in the world[3,4].

At the beginning, the GP herbicides were declared as toxicologically and environmentally safe. However, its increasing consumption and modern methodological approaches bring new information about environmental mobility, biodegradation processes, toxicological behavior to various plant and animal species, potential environmental risks and possible global impact[5,6]. The composition of GP herbicides also involves other substances (co-formulants). One of the most common used is the surfactant polyoxyethyleneamine (POEA). The POEA and GP metabolite aminomethylphosphonic acid (AMPA) must also be considered in the evaluation of GP herbicides toxicity[7]. It was already confirmed that GP herbicide (Roundup) has negative effects stronger than GP itself[8]. Metabolic processes at different plant species treated with GP herbicides were observed and AMPA and Shikimate, an accumulating indicator of plant sensitivity to GP, were determined in all tested plant species[9]. The impact of GP, AMPA and POEA to humans was reviewed and apparently, these substances do not pose a serious health risk for humans[10]. On the other hand, it was found that the GP herbicides have a strong affinity for the interaction with DNA and other cellular components, finally resulting in stable and covalent modifications of their structure[11]. Roundup, GP, POEA and AMPA were also found to have an influence on human cells and proprietary mixtures available on the market may cause cell damages[12]. Higher negative impacts of the GP herbicides are observed in aquatic ecosystem and its biodiversity[11–15]. An acute toxicity and impact of the GP, its co-formulant POEA and metabolite AMPA were also observed on amphibians, its tadpoles and embryos, and *Algae* organisms all around the world[7,16–22]. Studies in earthworms (*Eisenia fetida*) report a negative influence on their reproduction and significant morphological alterations on those specimens exposed to GP [23].

From the pedological point of view, the GP increases a microbial activity which fasten its degradation processes in soil with no significant effect on an organic carbon and nitrogen content[24,25]. Degradation of GP and other

selected pesticides by lygnolitic enzymes, such as lignin peroxidase, manganese peroxidase and laccase, were observed[26]. GP, AMPA and POEA induce variable absorption effect on the selected soil segments in dependence on pedological factors: Soil pH, phosphate, humic acids, copper and amorphous iron contents. The AMPA and POEA afford much higher mobility in soil than GP with strong adsorption and chelating effects[27–29]. Humic extracts from the soil adsorb GP even more than clay minerals. Such adsorption is explained by the multiple hydrogen bonding which can occur between the various acidic and oxygen-containing groups of both molecules[30]. It is obvious from the results mentioned above that co-formulants and AMPA have high negative impact on the soil organisms and aquatic biodiversity (due to their higher mobility and toxicity) than GP.

Many analytical methods for determination of GP, single co-formulants and/or metabolites of common GP herbicides were developed. Chromatographic techniques usually require previous derivatisation. The methods for extraction, derivatisation and sensitive determination of the GP herbicides and GP metabolites in water and soil samples by GC-MS [31,32] and LC-MS/MS [33] were already presented and reviewed[34]. Their high purchase and operational costs challenge electrochemists to develop sensitive and inexpensive electroanalytical methods. Several electroanalytical methods are based on direct voltammetric and/or amperometric determination of GP and AMPA using (i) electrooxidation at nickel and copper electrodes[35–37], (ii) complexation effect of Cu(II)[38] and/or Ni(II)[39], (iii) copper phthalocyanine/multiwalled carbon nanotube film-modified glassy carbon electrode[40], (iv) sensor based on $Ni_{1-x}Al_x(OH)_2NO_{3x}\cdot nH_2O$ layered double hydroxide prepared by co-precipitation or by electrodeposition at the Pt electrode surface[41], (v) polymer modified carbon paste electrode[42] and (vi) nanobiosensor prepared by electrostatical immobilization of the horseradish peroxidase enzyme onto the surface of a rotating gold disk[43].

Even though there is a tendency to substitute mercury electrodes by modern non-toxic electrode materials[44], mercury still remains the best electrode material[45] for the determination of broad spectrum of compounds in environment[46], including pesticides[47], and becomes a very useful tool in booming field of development of sensors and detectors for DNA and protein analysis in the 21st century[48]. Polarographic determination of GP, after its derivatisation to *N*-nitrosoglyphosate (NO-GP), was published in 1976 [49]. Nitroso compounds provide electrochemical signal thanks to a two-electron reduction of the nitroso group to hydroxylamine group in acidic media[50–52]. This approach was later utilized for determination of GP using square wave voltammetry[53] and differential pulse voltammetry (DPV)[54]

in water, soil and vegetable samples at a hanging mercury drop electrode (HMDE). However, the presence of organic matter in soil samples can influence the obtained results. Therefore, the main aim of this work is to determine the influence of the soil organic mater over the voltammetric response and develop a procedure for extraction of the GP from contaminated soil samples and for its preconcentration and derivatisation.

## EXPERIMENTAL

### Reagents

The Glyphosate (analytical standard, 99.7%, Pestanal®, Riedel-de Haen, Germany) was used in this work. Utilized solutions of potassium hydroxide (KOH p.a., Sigma–Aldrich, Brazil), hydrochloric acid (HCl p.a., 37%, Sigma–Aldrich, Brazil), sodium nitrite ($NaNO_2$ p.a., 99.0%, Merck, Germany) and ammonium sulfamate (p.a., >98%, Vetec Química Fina, Brazil) were prepared using deionized water (Simplicity UV, Millipore, USA). All the solutions were stored at ambient temperature in dark, except $NaNO_2$ solution which was freshly prepared every day. Activated charcoal (Sigma, Germany) was used for sample clearance. Before each voltammetric measurement, oxygen was removed from the measured solutions by 5 min bubbling with nitrogen 4.0 purity (Linde Gases, Brazil).

### Apparatus

A drying oven (ED 53, Binder, USA), 2 mm stainless steel sieve, analytical balances (MC 1, Sartorius, Germany), ultrasonic bath (model 3510, Branson, USA), Centrifuge 5804R (Eppendorf, Germany), 50 ml glass burettes with Teflon stopcocks, filled by strong anion exchange resin (anex) Dowex 1-X8 (mesh 100, chloride form, Sigma–Aldrich, Brazil) in hydroxyl form, glass wool zones, Teflon tubes (i.d. 1 mm), an eight channel peristaltic pump (Miniplus 3, Gilson, USA) and common filter paper were utilized in sample preparation procedure.

Voltammetric measurements were done with Autolab potentiostat (EcoChemie, Netherlands) connected to 663VA Stand (Metrohm, Swiss) operated by software GPES Ver. 4.9 (EcoChemie, Netherlands) working under operation system Windows 98 (Microsoft, USA). Three electrode system: Working electrode – HMDE (drop size 3, corresponding to drop area 0.55 $mm^2$), auxiliary electrode – platinum plate electrode and reference electrode – silver chloride electrode (Ag|AgCl, 3 mol $l^{-1}$) were used for differential pulse voltammetry (DPV; step potential 10 mV (scan rate 20 mV $s^{-1}$), pulse amplitude 175 mV and pulse time 100 ms, these parameters were taken from ref.[54]). DP voltammograms were measured in –0.1 to –1.0 V range.

### Procedures

*Soil sample preparation*: The soil samples were collected from three different places on the selected location in Mato Grosso State, Brazil. Two kilograms of dark brown (A), grey (B) and red (C) soils were collected from 5–30 cm depth, dried 2 h at 50 °C and 6 h at 105 °C in drying oven and finally sieved through 2 mm stainless steel sieve. The contents of organic

matter in these soils samples were evaluated as total organic carbon content (TOC) performed by the Embrapa National Soil Laboratory, Brazil.

*Extraction step*: 12.5 g of the selected soil sample was weighted four times (50.0 g totally) directly to four 50 ml centrifuge tubes, giving four soil sub-samples. Each of the four soil sub-samples was extracted by addition of 30 ml KOH solution (0.2 mol $l^{-1}$), 15 min sonicated and centrifuged for 40 min at 5000 rpm at 23 °C. The supernatants were transferred to the same 250 ml volumetric flask. The extraction procedure was repeated once more and supernatants were also collected in the same volumetric flask which was finally filled by 0.2 mol $l^{-1}$ KOH solution to the mark. Extraction and centrifugation was done in the same centrifuge tubes to minimize losses and cross contamination and to achieve higher sample preparation precision.

The procedure was applied to non-spiked soil samples to obtain blanks where concentration dependencies were measured. For evaluation of recovery, the 200 g dried and sieved soil samples were spiked by 1.0 ml GP stock solution (5000 ppm) to obtain model soil sample containing 25 ppm of added GP. The soil samples were left to dry overnight at ambient laboratory temperature and further properly mixed by glass rod. The procedure was repeated three times with each soil sample.

*Isolation step*: The anex (Dowex 1-X8) purchased at chloride form had to be first converted to the hydroxyl form by keeping in 1 mol $l^{-1}$ KOH solution overnight and then washing by deionized water until the eluent was neutral. The anex in the hydroxyl form was kept in water for further use. The 50 ml glass burettes, connected by Teflon tubes to the peristaltic pump controlling required constant flow rate, were filled with water, stopped by glass wool zone on the bottom, filled by 20 ml of the anex in hydroxyl form and stopped again by glass wool zone on the top of the anex batch to avoid bubble forming and resin swirling. The water over the resin was finally emptied just to the upper glass wool zone before sample percolation.

We have found that it is convenient to degas the extracted samples and all other solutions for 15 min in ultrasonic bath to avoid or minimize bubbles forming during final elution. The degassed samples were percolated through the resin at flow rate 1.5 ml $min^{-1}$. The columns were then washed by 50 ml of 0.25 mol $l^{-1}$ KOH and 50 ml deionized water, both previously degassed 15 min. The GP captured by the anex was eluted by 80 ml of 1.0 mol $l^{-1}$ HCl (degassed 15 min) in three fractions: 20 (F1), 40 (F2) and 20 ml (F3), respectively, at a flow rate 1.0 ml $min^{-1}$. The used anex batches were discarded due to strongly adsorbed humic acids contained in the soil extracts.

*Derivatisation step*: Three fractions F1, F2 and F3 were captured into three 50 ml centrifuge tubes, 2.0, 4.0 and 2.0 ml of concentrated HCl and 0.25, 0.50 and 0.25 g, respectively of activated charcoal were added. Single fractions were 5 min shaken (for adsorption of eventual impurities by charcoal), filtrated through a common filter paper to 25, 50 and 25 ml volumetric flasks and derivatised by addition of 1.25, 2.50 and 1.25 ml, respectively, of 10 g $l^{-1}$ $NaNO_2$ solution excess. After 15 min, 1.25, 2.50 and 1.25 ml of 100 g $l^{-1}$ ammonium sulfamate solution was added to remove the nitrite excess (attention, the nitrogen is liberated during the reaction). Finally, the volumetric flasks were filled with deionized water to the mark and prepared for voltammetric measurements. The GP is present only in the second 40 ml fraction (F2). First and third 20 ml fractions are collected and measured only as the control ones.

The stock solution of the GP (5000 ppm) was prepared by dissolution of 125 mg of the GP in 25 ml of deionized water. Standard solution of electrochemically reducible NO-GP

(1000 ppm) was prepared by derivatisation of 5 ml of the GP stock solution (5000 ppm) in 25 ml volumetric flask by addition of 2.0 ml concentrated HCl for acidification and 5.0 ml of $NaNO_2$ solution (10 g $l^{-1}$) for the nitrosation. After 15 min, 5.0 ml of ammonium sulfamate (100 g $l^{-1}$) were added to remove remaining nitrites (beware of nitrogen liberation). This 1000 ppm NO-GP stock solution was used for construction of calibration curves using the standard addition method. This stock solution was stored in dark at 4 °C in refrigerator and it was stable for at least one month, checked by DPV, with expected recovery of the derivatisation close to 100%.

*Voltammetric measurements*: 10.0 ml of the derivatised sample were transferred to the voltammetric cell, 5 min bubbled by nitrogen to remove dissolved oxygen and DP voltammograms were registered from –0.1 to –1.0 V. Each voltammogram was measured five times. The third fraction was used for comparison (as baseline) with DP voltammograms of second fraction containing electrochemically active NO-GP.

*Calibration dependences*: Blank samples were obtained by the above described procedure using non-spiked soil samples. DP voltammograms of the 10.0 ml of the second fraction not containing GP after additions of exact volumes of NO-GP standard solution (1000 ppm) were registered and calibration curves constructed. Limits of detection ($L_D$) were evaluated as a signal to noise ratio equal to 3 ($S/N$ = 3). DP voltammograms of the first and third fractions were also measured as control measurements.

*Recovery*: Recovery was evaluated using soil samples spiked with GP. DP voltammograms of the 10.0 ml second fraction containing theoretically 25 ppm of NO-GP and selected additions of NO-GP standard solution 1000 ppm corresponding to 5, 10, 15, 20 and 25 ppm of NO-GP were registered and the recoveries were calculated using parameters of calibration curves.

## RESULTS AND DISCUSSION

### *Sample Preparation*

Analysis of GP in soil by DPV has been already published[54]. However, the use of the published method for determination of GP in soils containing different amounts of organic matter has shown great influence on obtained results.

The organic matter contents were evaluated for all three soil samples A (non-cultivated forest soil), B (shortly cultivated forest soil) and C (long time cultivated forest soil) as a total organic carbon content 30.7, 13.0 and 6.3 g $kg^{-1}$, respectively.

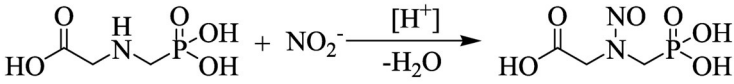
In general, the sample preparation is the most critical part of the real sample analysis because the soil samples are the most complex ones. Therefore, the extraction and preconcentration steps in this work were designed with minimal required manipulation steps to avoid losses and to achieve high precision. These changes and modifications were implemented in our procedure:

(i) The extraction step in four centrifuge tubes with four aliquots of soil samples, 4 × 12.5 g (50 g totally) in two extraction steps using ultrasonic bath was utilized instead of the two step extraction of 50 g soil by 125 ml KOH solution using shaker in one Erlenmeyer flask and further impractical decantation to centrifuge tubes. Deionized water, 0.1 mol $l^{-1}$ potassium chloride and 0.1 mol $l^{-1}$ phosphoric acid solutions were also tested for GP extraction from the soil B, but recoveries did not exceed 30%,

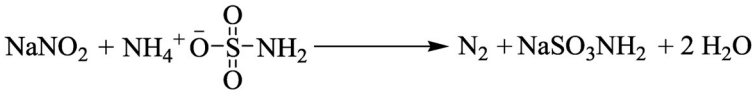
(ii) the dark suspension obtained after the soil extraction with high organic matter content had to be centrifuged at higher speed and for a longer time due to high content of small soil particles which finally clogged the anex column during the sample percolation. Speed 5000 rpm and 40 min were used instead of 4000 rpm and 20 min leading to better sedimentation even of the smallest particles and the dark coloured but transparent supernatant, resulting in no clogged columns, constant flow rate and higher recovery, and

(iii) 15 min degassing of all eluents by ultrasonic bath was found to be convenient to minimize the air liberation during final sample elution. Otherwise the compact batch of resin can be interrupted by releasing air bubbles producing uncontinual (variable) flow rate of the eluent (1.0 mol $l^{-1}$ HCl at flow rate 1.0 ml $min^{-1}$).

GP derivatisation step proceeds in acidic medium according to reaction (*1*) and the nitrite excess is removed by ammonium sulfamate with intense nitrogen liberation (reaction (*2*)).




(*1*)

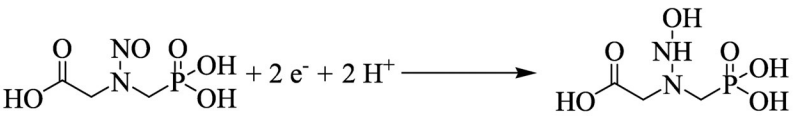



(*2*)

Whole sample preparation procedure was theoretically designed to determine the same GP concentration as it was contained in the soil sample in the case of 100% recovery.

*Voltammetric Determination of Derivatised GP*

GP derivatised to NO-GP is electrochemically reducible in acidic medium according to reaction (*3*).




(*3*)

DPV peak corresponding to this two-electron reduction appears around –800 mV (vs Ag|AgCl) at HMDE in 1 mol $l^{-1}$ HCl solution. It is about 100 mV more positive than hydrogen reduction wave in this medium. This fact makes impossible to utilize a mercury meniscus modified silver solid amalgam electrode[55–57] which was also tested for this purpose. The NO-GP reduction signal was not observed due to narrower potential window of this electrode.

Using unspiked (blank) and spiked (25 ppm of GP) soil samples A, B and C, the individual fractions (F1, F2 and F3) of the individual soil samples were compared to confirm the presence of the GP only in the second fraction (F2) and to observed their voltammetric behavior. For illustration, DP voltammograms of all three fractions obtained from unspiked and spiked (25 ppm GP) soil sample B are shown in Fig. 1. DP voltammograms of the second fractions of all three spiked and unspiked soil samples are depicted in Fig. 2.

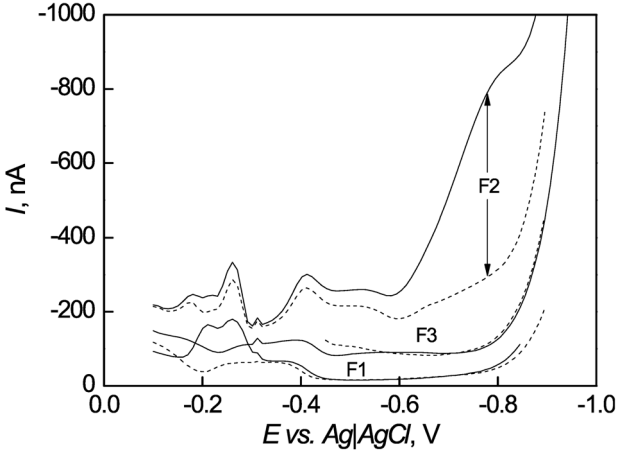



FIG. 1

DP voltammograms of first (F1) and third (F3) control fractions and second fraction (F2) containing: 0 ppm (blank, dash lines) and 25 ppm (solid lines) of GP in soil sample A; HMDE, DPV (scan rate 20 mV $s^{-1}$)

Signals observed between –0.1 and –0.6 V supposedly correspond to metal complexes of organic compounds, such as humic acids contained in the soil, or to other electrochemically active anionic compounds which were also retained by anex and further eluted. Similarities between the

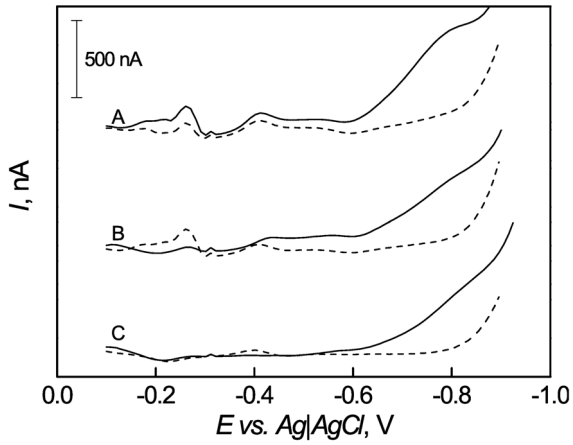



FIG. 2
DP voltammograms of second fractions (F2) containing 0 ppm (dash lines) and 25 ppm (solid lines) of GP in soil samples A, B and C; HMDE, DPV (scan rate 20 mV $s^{-1}$)

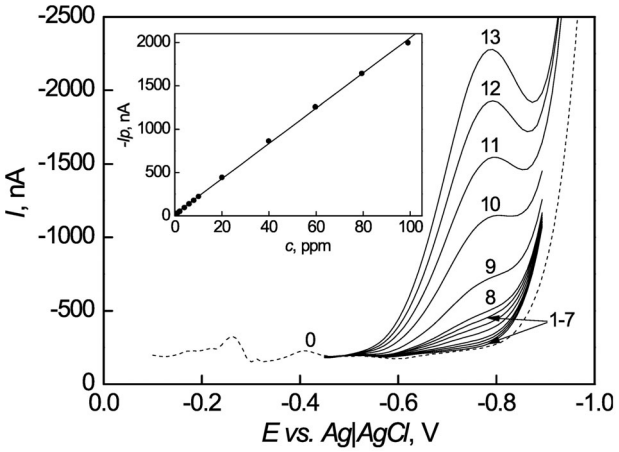



FIG. 3
DP voltammograms of NO-GP as a function of its concentration (in ppm) in soil sample B: *0* blank F3, *1* 0 (blank F2), *2* 0.5, *3* 1.0, *4* 2.0, *5* 4.0, *6* 6.0, *7* 7.9, *8* 9.9, *9* 19.6, *10* 38.5, *11* 56.6, *12* 74.1 and *13* 90.9; HMDE, DPV (scan rate 20 mV $s^{-1}$); inserted calibration straight line

voltammetric curves of the second fractions should indicate similar origin of all three soil samples. Fortunately, no signals coincided with the signal of NO-GP.

Calibration dependences of NO-GP were measured by DPV at HMDE using standard additions of the NO-GP stock solution (1000 ppm) in concentration range 0.5–100 ppm into the second fractions of unspiked soil samples. DP voltammograms as a function of NO-GP concentration were registered and concentration straight lines evaluated. Figure 3 shows an example obtained with soil sample B. The recoveries were determined using standard additions to the second fraction of spiked soil samples (25 ppm of GP) and then calculated from the intercepts and slopes of obtained straight lines (0–25 ppm of added NO-GP). An example obtained at soil sample B is depicted in Fig. 4. All parameters of evaluated concentration straight lines with corresponding limits of detection and recoveries of individual soil samples are summarized in Table I.

It is obvious that recovery depends on composition of the soil. Changes of resin from yellow to a dark brown after sample percolation were obviously caused by strongly adsorbed humic acids. Increasing humic acid content could affect decreasing recovery, but this influence was rejected by our experiment with variable organic matter content of the soil samples. The highest recovery was obtained with the soil sample A (dark brown, unculti-

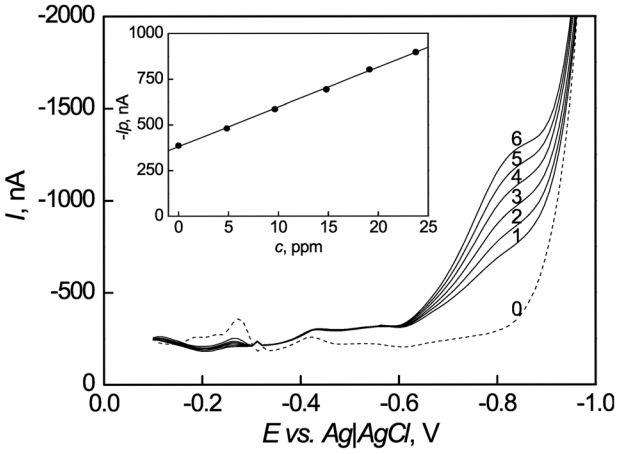



FIG. 4

DP voltammograms of NO-GP as a function of its concentration (in ppm) in soil sample B: *0* blank F3, *1* 25 (GP spiked soil sample), *2* 25+5, *3* 25+10, *4* 25+15, *5* 25+20, *6* 25+25; HMDE, DPV (scan rate 20 mV $s^{-1}$); inserted calibration straight line

vated forest soil) with the highest content of organic matter and, to the contrary, the lowest preparation efficiency was obtained with the soil sample C (red, long time cultivated forest soil) with the lowest organic matter content. It is obvious that the organic matter content decrease during cultivation. This can be confirmed by the soil color and other soil parameters such as contents of copper, iron, clay, sand, etc. The color change during cultivation from dark brown (soil A) to the red (soil C) can be caused by higher content of iron and/or copper, typical elements in the place of origin (Mato Grosso State, Brazil). Higher clay and/or sand contents are also evident. The metal cations can form complexes with GP, which is not further retained by anex and/or GP can be adsorbed by clay or sand and remains in the solid phase during extraction. Despite of all these facts, obtained recoveries were relatively high, 86 ± 11%, 76 ± 9% and 68 ± 10% for A (dark brown, uncultivated), B (grey, short time cultivated) and C (red, long time cultivated) tropical forest soils, respectively, and their low RSD proved high repeatability of proposed procedure providing the limits of detection around 2 ppm.

TABLE I
Calibration straight line parameters and evaluated recoveries for DPV determination of GP in soil samples (A, B, C) containing different contents of organic matter (TOC)

| Soil | TOC g $kg^{-1}$ | $c_{Range}$ ppm | Slope nA $ppm^{-1}$ | Intercept nA | $R^2$ | Recovery % | $L_D$ ppm |
|---|---|---|---|---|---|---|---|
| A | 30.7 | 0.5–100 | 24.0 ± 0.5 | 8.0 ± 6.7 | 0.9997 | 86 ± 11 | 1 |
| | | 0–25 | 23.4 ± 1.3 | 501 ± 18 | 0.9990 | | |
| B | 13.0 | 0.5–100 | 20.3 ± 0.6 | 10.4 ± 7.6 | 0.9997 | 76 ± 9 | 2 |
| | | 0–25 | 21.7 ± 1.1 | 411 ± 15 | 0.9985 | | |
| C | 6.3 | 0.5–100 | 23.4 ± 0.4 | 11.3 ± 8.5 | 0.9996 | 68 ± 10 | 2 |
| | | 0–25 | 21.3 ± 1.2 | 362 ± 17 | 0.9972 | | |

## CONCLUSION

Procedure for a routine DPV determination of GP herbicides in soil samples was developed. Using three soil samples with different contents of organic matter (A, B, C), the high influence of organic matter content on soil sample recovery was confirmed. Apparently, higher content of organic matter facilitates the recovery of the GP from soil, suggesting being easier to remove GP associate with organics than adsorbed in inorganic soil matter. In

fact, the content of iron oxide in the red soil (sample C) is higher than in samples A and B. Following soil parameters ion exchange capability, the composition of the inorganic fraction and even the characteristics of the organic matter are factors influencing GP adsorption in the soil and they should be objects for further investigation. Soil sample is very complex matrix and there are many factors affecting predictable, but also unpredictable behavior of the soil parameters in connection with behavior of investigated analytes.

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