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Pyrogenic carbon in soils dominated in mine-energy regions of Bulgaria

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Abstract

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Pyrogenic carbon (PyC) is a temperature forcing agent, air pollutant and dangerous to human health, but its functions in soils are still under discussion. There is a huge knowledge gap in Bulgaria on PyC distribution in soils especially in those located in mine-energy regions where the PyC major source are concentrated. Therefore, the present study aims to propose a method for determination of PyC content and to present its 3D-distribution in soils located in the oldest mine-energy regions of Bulgaria.

The method described in this article is a modification of the method developed by Lim and Cachier and uses a dichromate mixture for isolation of PyC fraction. It is experimented with Vertisols which are considered PyC-containing soils. The method is also applicable to soils strongly enriched with coal fragments that are usually located in mine-energy regions of Bulgaria.

According to the results obtained a strong variation of PyC content was established in studied soils from Maritsa-iztok and Pernik mine-energy regions (0.10% – 19.07%). A higher content (max 19.07%, average 4.30%) was registered in the region of Pernik, where weakly transformed organic artefacts (soot and coal) increased weather-resistant pyromorphic carbon forms.

According to the developed evaluative scale, the medium content of PyC prevails in Bulgarian soils – from 0.29% to 0.51%. The factors influencing this distribution are: paleo- and present fires, the content of coal impurities, and deposition of PyC-enriched aerosols emitted from coal operating thermal-electric power plants, domestic heating with coal, coal mining and transport.

Keywords: pyrogenic carbon; mine-energy regions; dichromate oxidation; Vertisol; Technosol

Introduction

Pyrogenic carbon, also called black carbon, is formed during the incomplete combustion of fossil fuels and vegetation. In nature, combustion is never complete (complete combustion converts all carbon into carbon dioxide) and therefore, in addition to CO_2, carbon monoxide (CO), volatile organic compounds, amorphous and crystalline carbon particles are also produced. Pyrogenic carbon is defined as a highly condensed carbon residue that includes a wide range of compounds with diverse reactivity – from lightly charred material to highly condensed soot and microcrystalline graphite (Preston & Schmidt, 2006). Two main fractions of this continuum (soot and charcoal) could explain to some extent the complex nature of PyC – to be highly resistant to degradation and hence persistent over millions of years (Smith et al., 1973) but also prone to disintegration in a very short time (Cheng et al., 2006; Bird et al., 1999; Bond et al., 2013; Zhou et al., 2019). Charcoal is formed at low combustion temperatures (< 400°C), has a large particle size and relatively short-chain aromatic structures (< 7 rings), while soot are ultrafine particles (< 2.5 pm) of highly condensed, long-chain aromatic compounds (>

19), which are fine aerosols at a temperature of about 700°C but crystallize to micrographite at higher temperatures (McBeath et al., 2011). Ultrafine particles of PyC ($PM_{2.5}$) are very common in the atmosphere (Andreae & Merlet, 2001; Duarte et al., 2005). They are highly volatile and can be transported over long distances (Lee et al., 2008; Louchouarn et al., 2009; Engling et al., 2017).

Worldwide approximately 8.4 Tg PyC were released into the atmosphere in 2000 (US EPA, 2012). Preston & Schmidt (2006) reviewed the PyC levels a few years later and estimated that they can reach 5.98 Tg y^{-1} from biomass combustion and 7.96 Tg y^{-1} from fossil fuels. In many regions, PyC emissions are entirely due to coal-fired thermal-electric power plants (Shekar & Venkataraman, 2002; Parashar et al., 2005; Sahu et al., 2008; Singh et al., 2013). According to author's estimates, more than 80% of PyC enters the soil, where it can age preserving particulate form or react and mineralize for approx. 2000 years (Kuzyakov et al., 2009; Bird et al., 2015; Pignatello et al., 2015; Santin et al., 2015; Lucheta et al., 2017). In the fine soil fractions (< 53 pm) PyC content can vary between 1.8 and 13.6 g kg^{-1} and can form up to 35% of the soil organic carbon (Skjemstad et al., 2002).

Pyrogenic carbon is a forcing agent of climate change, air pollutant and dangerous to human health (U.N.E.P./W.M.O., 2011; U.S. EPA, 2012; Arctic Council, 2013), but its functions in soils are still under discussion and provoke a constant interest.

Nowadays, there are four basic methods for PyC determination (Schmidt & Noack, 2000; Schmidt et al., 2001): a) Optical; b) Thermal; c) Chemical and d) Chemical-thermal. These analytical techniques identify three forms of carbon: inorganic carbonates, thermally unaltered organic carbon (such as humic substances or plant material) and PyC. They are based on the hypothesis that after removal of all reactive (soluble, extractable and oxidizable) and volatile carbon compounds, only PyC will remain in the samples.

Optical methods recognize the physical and structural differences between carbon compounds. They rely on a visual distinction of charred plant particles (i.e. blacker), which are traditionally considered charcoal, although some of them cannot presumably meet the Van Krevelen's criteria (Van Krevelen, 1950). Optical methods are fast, reliable and non-destructive, but not applicable to large batches of samples.

Thermal methods, such as chemo-thermal oxidation (CTO) differentiate the thermal stability of PyC and other carbon compounds. The soil combustion at 340–375°C for 24 h is the standard protocol to remove volatile and uncharred organic matter (Gustafsson et al., 1996; 2001; Gelinas et al., 2001; Kuhlbusch, 2002). This method includes a decarbonization step, which may precede (Gustafsson et al., 1996) or follow the thermal treatment (Gustafsson et al., 2001; Bucheli et al., 2004).

Chemical methods use differences in chemical stability between PyC and other forms of carbon. They include dichromate-acidic oxidation of soils ($K_2Cr_2O_7 + H_2SO_4$, HNO_3) to remove uncharred carbon substances (Wolbach & Anders, 1989; Lim & Cachier, 1996; Winkler, 2017), alkaline oxidation with KOH, NaOH or H_2O_2 (Griffin & Goldberg, 2003), extraction with organic solvents (benzene, methanol, methyl/isobutyl ketone) (Wolbach & Anders, 1989) or identification of molecular markers concomitant with the formation of PyC, such as benzene polycarboxylic acids (BPCA) (Glaser et al., 1998) or levoglucosan derived from heating of cellulose and therefor applicable only for detection of PyC derived from biomass burning (Elias et al., 2001). The main criticism of the BPCA method is that it detects only larger aromatic carbon chains resulting in lower PyC values and thus gives lower results (Preston & Schmidt, 2006). The dichromate-acidic oxidation also has disadvantages – it is destructive and a very time consuming chemical procedure, but very accurate and applicable to a large number of samples.

A review of international experience shows that the amount of PyC can differ by up to two orders of magnitude depending on the method used (Preston & Schmidt, 2006; Schmidt et al., 2001). The occurrence of PyC artefacts, removal of PyC during pre-treatment, and errors in the final assessment are discussed by Nguyen et al. (2004) as reasons for high differences between the results obtained. Depending on their selectivity, different methods probably isolate different fractions of PyC. However, it has been shown that thermal oxidation of labile organic carbon (OC) leads to the formation of artefacts (charred organic matter), and thus leads to an overestimation of the actual PyC content. At the same time, this method can underestimate the actual PyC content. Gelinas et al. (2001), compared thermal oxidation without any soil pre-treatment, after demineralization (HCl/HF) and subsequent acid hydrolysis (TFA/HCl). The PyC content in these samples correlates significantly with OC only when the heat treatment is applied alone, while thermal oxidation after demineralization and hydrolysis decreases PyC content by 15–20%.

The current lack of standardization in definition, identification, and analytical techniques is the reason for the slow accumulation of knowledge about the existence, behaviour and functions of PyC in soils and adjacent ecosystems. This problem is more complicated in Bulgaria because there are no studies on PyC content especially in mine-energy regions which are the major source of PyC. Therefore, the present study aims to propose a method for determination of pyrogenic carbon content and to present its 3D-distribution in soils located in the oldest mine-energy regions of Bulgaria.

Materials and Methods

Soil study and sampling techniques

Soils in the two oldest and highly industrialized regions of Bulgaria were studies – the mining and energy complex Maritsa-iztok, shown on Figure 1 and the mining and energy complex Pernik, shown on Figure 2. The sources of pyrogenic carbon in both regions are the aerosol emissions from: domestic heating with coal (in residential areas), the electricity production in nearby thermal-electric power plants (TPP "Maritsa-iztok 2", Figure 1 to the right of ellipsoid and TPP "Republika", Figure 2), coal mining (in the "Maritza-iztok" mines to the left of the ellipsoid and many mines in Pernik) and transport. Studied soils in both regions are vulnerable to PyC enrichment because are located in the direction of prevailing winds and close to PyC sources.

Soil research and sampling was designed in accordance with classical pedological methods and monitoring approach (BIS, 2019a; 2019b; 2019c). For the purposes of this study a monitoring network with a density of 50×50 m was applied in the selected area of Maritza-iztok region (marked with ellipsoid). The main part of soil profiles and the sampling points in Maritza-iztok complex are located in the monitoring network area (Figure 1). Four soil types (№ 2–5) falling into the ellipsoid are selected for study on the basis of their location – two of them are located at the ellipsoid edges /close to the "Maritsa-iztok" mines in the western part and close to the coal-operating thermal-electric power plant "Maritsa Iztok 2" in the eastern part) and two in between (Table 1). One profile (trial pit) and several digs are excavated in each

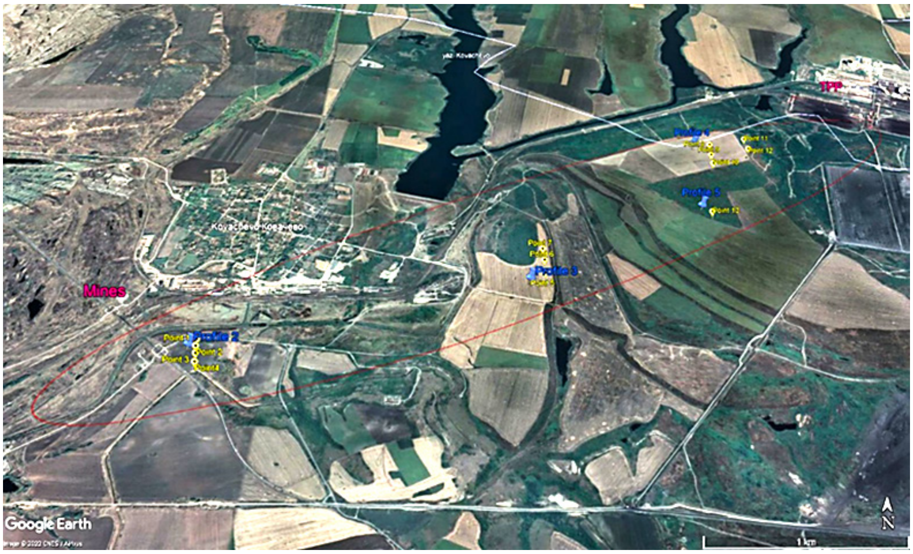

Fig. 1. Location of soil profiles and sampling points in the studied area of Maritsa-iztok industrial complex

Fig. 2. Location of soil profiles in Pernik region

soil type as the number of digs (maximum 5) depends on the landscape homogeneity and the degree of its anthropogenic modification. The referent soil (profile 1) is situated far from the studied region in order to present the PyC content in no affected soils (42°16′29.10″ N; 26°15′38.87″ E).

Four soil types (№ 6-10) have been studied in the mining and energy region "Pernik" (Figure 2, Table 1).

Soil classifications and GIS

Soils are studied and classified in accord with principals of FAO (2006), WRB (IUSS, Working Group, WRB, 2014) and Bulgarian classification (Koinov et al., 1968). Software ArcGIS for Desktop 10.6 was used for mapping of soils and sampling points. GPS Trimble JUNO and ArcPad Mobile GIS Software were used for Field Mapping Applications.

Labor methods

Samples from A-horizons (Ahp and Ah3) of slightly leached Smolnitsa (profile 2), located in Maritsa-iztok region were used to test and verify the methods for PyC determination. The Smolnitsa is the most appropriate for this analysis because is the major soil type in the region and is a PyC-containing soil (Gehring et al., 1997; Skjemstad et al., 1996). The profile view is shown in Table 2.

Two methods for determination of PyC content in Bulgarian soils were applied in the present study:

1. Thermal analysis (original muffle furnace method) according to the method described by Gustafsson et al. (2001). Briefly, the method includes: the removal of carbonates with 3 M HCl followed by sample heating at 375°C in a muffle furnace for 18 h. Due to the possibility of incomplete oxidation or artefacts production, we investigated the temperature regime. For this purpose, DTA-TG analysis was performed with a Setsys Evolution 2500 SETARAM apparatus at a heating temperature of 25°C – 500°C in a static air atmosphere, duration – 1 h, heating rate 10°C/ min and 30 min cooling (sample weight between 12–15 mg in corundum crucibles). An OmniStar mass spectrometer for gas phase analysis was connected to the device.

2. Dichromate-acidic oxidation method proposed by Lim & Cachier (1996). Elemental automatic analyzer EuroEA 3000 was used for subsequent determination of carbon content. The method was initially modified by several procedures to specify the pretreatment of soil samples for analysis:

- Pre-treatment of samples with organic solvents to remove waxes and resins, which may hinder and prolong the time for PyC analysis. The extraction was performed with two solvents – a mixture of benzene and ethanol, and toluene following Morrison-Bick method (Morrison & Bick, 1967) in modification: 50 g of the air-dry sample (fraction < 2 mm) was extracted continuously for 20 h with 150 ml of a mixture of benzene and ethanol (2: 1 by volume) in a glass Soxhlet extractor (with a 250 ml round-bottomed flask) or with 150 ml of toluene. The solvent was evaporated at 70°C in a rotary evaporator to dryness and the solid residue was determined by weight. The soil sample was dried at 50°C in a rotary evap-

Table 1. Classification of studied soils

№ of profile, region	Soil type (Bulgarian classification)	Soil name (WRB classification)
Profile 1 (referent soils), Maritsa-iztok	Strongly leached smolnitsa, non-eroded, light clayey	Pellic Vertisol (Mollic, Bathyhumic, Hypereutric, Clayic)
Profile 2, Maritsa-iztok	Slightly leached smolnitsa, not eroded, heavy sandy-clayey, deep	Pellic Vertisol (Mollic, Amphihumic, Bathycalcaric, Hypereutric)
Profile 3, Maritsa-iztok	Reclaimed soils, black, calcaric, deep	Spolic Technosol (Transporto-Mollic, Clayic, Epihumic, Hypereutric)
Profile 4, Maritsa-iztok	Reclaimed soils, light olive, calcaric, shallow	Spolic Technosol (Amphiochric, Gleyic, Hypereutric, Clayic)
Profile 5, Maritsa-iztok	Reclaimed soils, dark gray, calcaric, deep	Spolic Technosol (Mollic, Profundihumic, Endocalcaric, Hypereutric, Siltic)
Profile 6, Pernik	Reclaimed soils, dark gray, heavy sandy-clayey, shallow	Pantogarbic Technosol (Eutric, Loamic, Gleyic, Endohyperartefactic, Endohyposulfidic)
Profile 7, Pernik	Smolnitsa-like cinnamon forest soils, super deep	Endocalcic Chernic Phaeozem (Bathyclayic, Profundihumic)
Profile 8, Pernik	Chernozemoid smolnitsa, moderately eroded	Calcic Vertisol (Mollic)
Profile 9, Pernik	Typical cinnamon forest soils, moderately eroded	Endorhodic Hypereutric Cambisol (Bathybrunic, Bathyclayic, Ochric, Endoprototechnic, Reductic)
Profile 10, Pernik	Typical cinnamon forest soils, moderately eroded	Rhodic Hypereutric Cambisol (Bathybrunic, Bathyclayic, Ochric, Epiprototechnic)

orator and PyC content in both soil samples was determined by the method of Lim and Cachier.

- The duration of the dichromate oxidation was parameterized by measuring the content of PyC in an interval of 30 h.
- Determination of suitable fraction size – several soil fractions were tested (Table 1). Fractions were separated by wet sieving through a sieve of the designated size.

The applicability of the developed modification has been tested on samples from reclaimed soils /Pantogarbic Technosol (Eutric, Clayic, Gleyic, Endohyperartefactic, Endohyposulfidic) located in the periphery of Pernik town (profile 6 on Figure 2). This soil contains a large number of coal fragments (up to 60-70%) mixed with slag produced in the "Republika" TPP (profile view is shown in Table 3). The surface horizon is slightly mixed with artefacts, but the prevailing content of weathered coal pieces is established in depth. The weathered coal fragments despite of their anthracite color and polished surfaces, are altered by incorporated between layers yellow and red clays, and sinters that bleach strata.

The preparation of samples for physico-chemical analysis follows BDS ISO 11464 (BIS, 2012). Soil organic carbon (SOC) was determined by the method of Kononova (1963).

Results and Discussion

Determination of PyC content

The results of adaptation of dichromate oxidation method are shown in Table 2. It is evident that mixed organic solvent (benzene and ethanol) extracts the waxy components, while toluene is ineffective – this solvent does not change its color during the extraction (unlike the combined extractant, which becomes yellowish-pale brown) and does not extract organic fractions that can be separated as a residue after drying. The analysis also shows that extraction does not accelerate

Table 2. Content of organic and pyrogenic carbon in the analyzed samples from Smolnitsa

Profile view	№	Horizon and fraction size	Depth	SOC, %	PyC, %
	1	Ahp (Fraction < 2 mm)	0–30 cm	1.72	0.52
	2	Ahp (Fraction < 2 mm agate grinded)	0–30 cm	1.75	0.53
	3	Ahp (Fraction < 0.125 mm)	0–30 cm	1.31	0.47
	4	Ahp (Fraction < 0.063 mm)	0–30 cm	1.47	0.24
	5	Ah3 (Fraction < 2 mm)	73–105 cm	1.03	0.50
	6	Ah3 (Fraction < 2 mm agate grinded)	73–105 cm	1.04	0.52
	7	Ah3 (Fraction < 0.125 mm)	73–105 cm	1.44	0.18
	8	Ah3 (Fraction < 0.063 mm)	73–105 cm	1.49	0.04
	9	Ahp after extraction with benzene and ethanol	0–30 cm	1.38	0.49
	10	Ahp after extraction with toluene	0–30 cm	1.71	0.52

Table 3. Content of PyC and organic carbon in reclaimed soils

Profile view	Horizons and depth	SOC	After 60 h treatment		After 30 h treatment	
			PyC	Over-estimation	PyC	Over-estimation
	cm	%	%			
	Cτeu (0-20)	8.69	14.10	62.26	14.54	67.32
	Cτu1 (20-40)	8.63	6.77	–	8.52	–
	Cτu2 (40-60)	11.32	15.07	33.13	14.40	27.21
	Cgρτu/ Ouτ (60-80)	20.11	9.60	–	22.12	10.00
	2OuτCgρ1 (80-100)	16.18	19.07	17.86	17.84	10.26
	2OuτCgρ2 (100-120)	15.81	18.94	19.80	19.07	20.62
	SD	±0.24	±0.32		±0.32	

the oxidation of kerogen and especially of its old forms and thence it is not rational to be included as an analytical step.

The removal of sand fractions allows more homogeneous oxidation of the samples, but produces data below the limit of accuracy (< 0.2%, Table 2) and cannot be used for accurate quantification of PyC.

The performed thermal analysis showed that mainly endothermic reactions (dehydration) take place up to 250°C, after which the oxidation of the organic component (exothermic reactions) begins, as CO_2 curve reveals (Figures 3& 4). This is a long process that continues after 500°C, but the temperature at the inflection point of CO_2 is 383°C for sample 1 (Ahp, fraction < 2 mm) and 393°C for sample 5 (Ah3, fraction < 2 mm).

Thermograms also show that the composition of organic matter differs in the two samples, because at the 383°C nitrogen and sulfur dioxide are released from the surface horizon (Ahp), while the sample from the sub horizon (Ah3) does not release sulfur dioxide within this temperature range. In general, the results show that the heat treatment at 375°C does not imply optimal temperature conditions. For this reason, we performed the treatment at 390°C and the PyC content after the described subsequent treatments was 0.49% in both samples. The need of a more detailed study of temperature conditions and the possibility they could be specific to different soil types and soil horizons makes this procedure inapplicable as a standard method.

The described experiments and results allowed us to de-

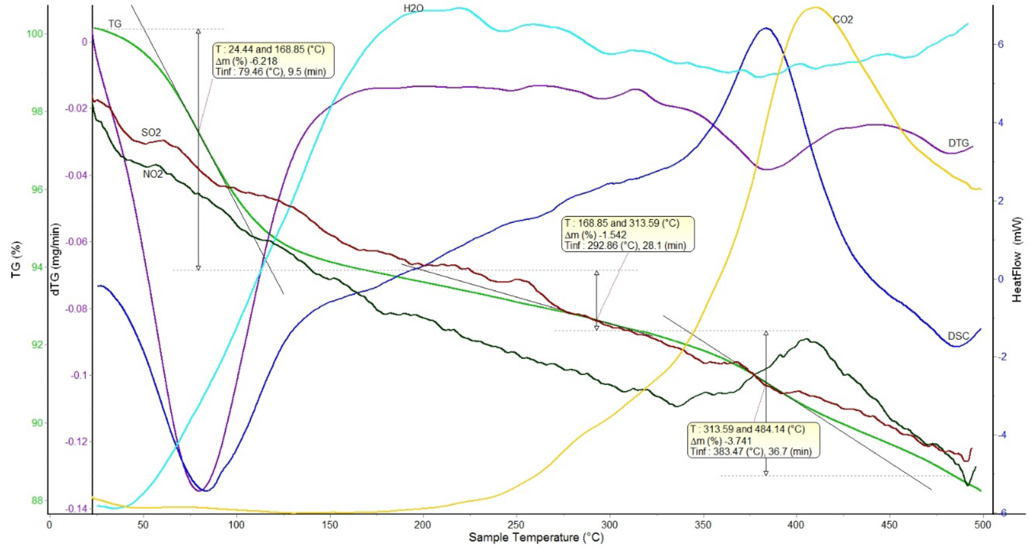

Fig. 3. Differential thermal analysis (TG-DTA-DTG) of sample 1 (Ahp)

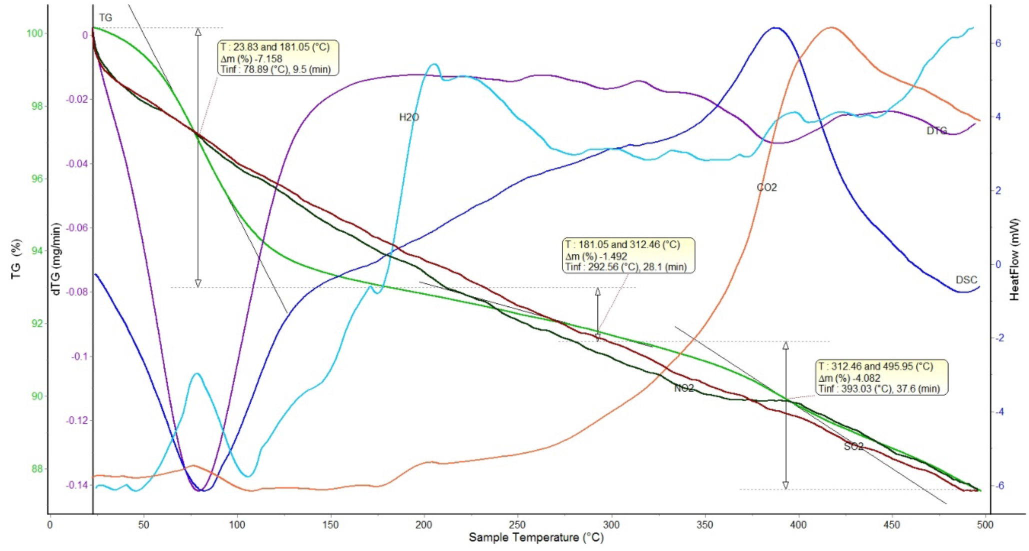

Fig. 4. Differential thermal analysis (TG-DTA-DTG) of sample 5 (Ah3)

velop a modification of Lim and Cachier method, which includes the following analytical steps:

The representative sample for analysis is taken from the whole air-dry sample ground to 2 mm (original method used fraction <0.1 mm) in the amount of 1.5 g (± 0.01 g). It is placed in a polypropylene centrifuge tube (100 ml) and treated with 15 cm^3 of 3 M HCl for 24 h to remove carbonates. When effervescence lulls, the sample is stirred periodically for better contact with the reagent. After rinsing 5 times with deionized water and centrifugation, another 15 cm^3 of the acid mixture 10 M HF/1 M HCl are added. The reagents are left for another 24 h. The purpose of this procedure is to dissolve the more stable carbonates. The sample is washed again 5 times with deionized water and the supernatant is removed by centrifugation. This is followed by the last 24-hour treatment with 10 M HCl, washing and centrifugation. To prevent the formation of analytical artefacts during dichromate oxidation, the sample is dried at 60°C to constant weight. One gram (±0.01) of the prepared sample (original method used 0.5 g) is weighed and placed in a centrifuge tube, where it is treated with 10 cm^3 dichromate mixture (0.1 M $K_2Cr_2O_7$/2 M H_2SO_4) for 60 h in a water bath at 55 (± 1)°C and periodic stirring. The ratio between solution and sample is maintained constant during the reaction by adding a new solution (not deionized water in contrast to the original method). This step is followed by cooling of the sample, centrifugation, washing 5 times with deionized water and drying at 60°C to constant weight. Finally, the PyC content is determined on an elemental automatic analyzer.

In order to determine the range of PyC values that can be determined with developed modification, reclaimed soils with high content of PyC (originated from coal) were studied. The content of organic and PyC in reclaimed soils is shown in Table 3.

The reclaimed soils built in the coal-mining regions of Bulgaria are of great interest in view of organic carbon specific and possible greenhouse gas emissions. The most distinguish feature of reclaimed soils is the high content of organic carbon due to the constant presence of coal impurities (Tsolova et al., 2011; 2014). Data in Table 3 show that carbon in coal is not entirely chemically inert and resistant to oxidation but appears mostly as PyC. It is obvious that the shorter extraction time leads to a greater overestimation of the content in horizons that are plenty of PyC, although the uneven distribution of coal along the profile significantly increases the fluctuation of data.

3D-distribution of PyC in studied soils

The content of pyrogenic carbon varies from 0.22% to 0.76% in the surface horizons of the studied soils from the region of Maritsa-iztok and gradually decreases in deeper horizons to 0.14% (Figure 5, Table 4). In the Pernik region, the range is even greater – from 0.39% to 14.1% in the topsoil and up to 0.1% in depth.

The wide range of data as well as the high coefficients of variation (V > 32% in both regions) show inhomogeneity in PyC distribution.

Table 4. Descriptive statistics of PyC values in studied soils

Parameter	Values	
	Maritsa-iztok	Pernik
Mean	0.40	4.30
Standard Error	0.02	1.20
Median	0.42	0.42
Standard Deviation	0.15	6.33
Sample Variance	0.02	40.06
Kurtosis	-0.28	0.26
Skewness	0.03	1.29
Range	0.62	18.97
Minimum	0.14	0.10
Maximum	0.76	19.07
Count	40	28
Confidence Level (95.0%)	0.05	2.45

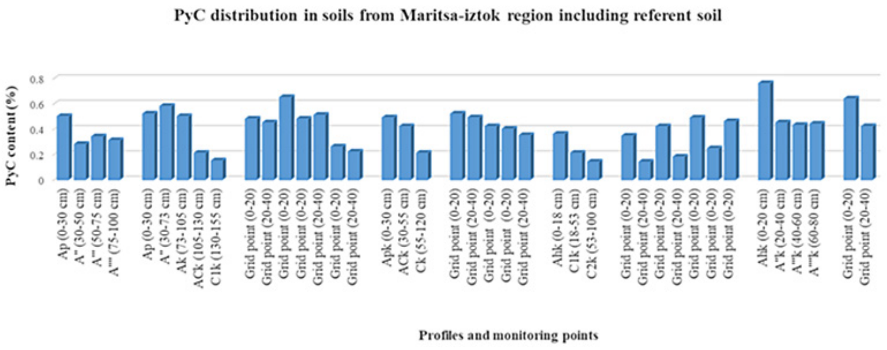

Fig. 5. PyC distribution in soils from Maritsa-iztok region including referent soil

From the beginning of axes: profile 1, profile 2, samples from monitoring grid in soil 2, profile 3, samples from monitoring grid in soil 3, profile 4, samples from monitoring grid in soil 4, profile 5, samples from monitoring grid in soil 5

These differences in PyC content are interpretative in view of the organic matter genesis and the variability of factors determining PyC distribution. Smolnitsas are known for deep humus horizons (50 cm and more), very dark color (10YR 2 (3)/1) and middle total organic carbon content (average 2.5%, Gurov & Artinova 2015). Schmidt et al. (1999) found a strong correlation between the color of dark soils and PyC content, which is a reason for authors to assume that fires in the past have played an important role in their genesis. This undoubtedly explains the content of PyC in referent soils (profile 1, Figure 5) – strongly leached Smolnitsa. In the referent profile (1) it has a different distribution curve compared to soil organic carbon (SOC), which content gradually decreases in depth (Figure 6). The sharp accumulation of PyC in the surface horizon is a reason to assume that additional deposition of PyC takes place. Furthermore, the correlation coefficient between PyC and SOC is the lowest in these soils (r = 0.85), which also reveals a possible new addition of PyC.

The natural soils, slightly leached Smolnitsa, located in the ellipsoid (profile 2 – Pellic Vertisol) are also arable soils with low values of SOC (1.23% – 1.45%). Here again, the PyC shows different distribution from SOC with a maximum in the sub-horizon and content of over 0.5% up to 1 m depth. This almost plateau-like content is an indicator of stability of PyC facilitated by clay texture and good homogenization with mineral ingredients due to the recommendable for Vertisols deep tillage.

Reclaimed soils in Maritsa-iztok region (profiles 3–5, Figure 6) in contrast show similar distribution of SOC and PyC which could be allied to the short period of their formation and use (10–15 years).

Reclaimed soils (profile 6) from the region of Pernik/Pantogarbic Technosol (Eutric, Clayic, Gleyic, Endohyperartefactic, Endohyposulfidic)/ are very specific case – they contain organic waste (slag produced in local TPP) and coal fragments, which are dominant in some horizons and form 70% of their volume. Organic impurities determine the extremely high content of PyC (19.07%, Figure 7), and the frequent coal self-ignition during the summer months (then the soil temperature reaches 80°C according to Kuzev et al., 2000) additionally increases the content of different in resistance components of pyrogenic continuum.

The natural soils in this region (profiles 7–10) also contain high amounts of PyC due to the soot which are well distinguishable and slightly altered by hypergenic processes (Figure 7).

Values similar to those found in profiles 9 and 10 were published by Wang et al. (2005) for different strata of the Loess Plateau in China affected by surrounding paleofires – 0.041% to 0.572%. This again shows high resilience of PyC and the prospects for its storage in soils.

The calculated percentiles, as well as the frequency of values allow us to introduce a scale for estimating the content of PyC in soils from industrial regions of Bulgaria (Table 5). As threshold values are choose (Figure 8): the minimum value of PyC content in all soils – 0.10%; the value of 25-percentile – 0.28%; the value of 75-percentile – 0.51% and the maximum content of PyC in the soils – 0.76% with the exception of reclaimed soils from the town of Pernik, which represent a specific case and fall into the last column.

According to the developed evaluative scale the average content of PyC prevails in the investigated soils – from 0.29% to 0.51%. High content (0.52–0.76%) was registered in Smolnitsas, which, as mentioned above, are enriched with PyC (genetically and anthropogenically), and very high con-

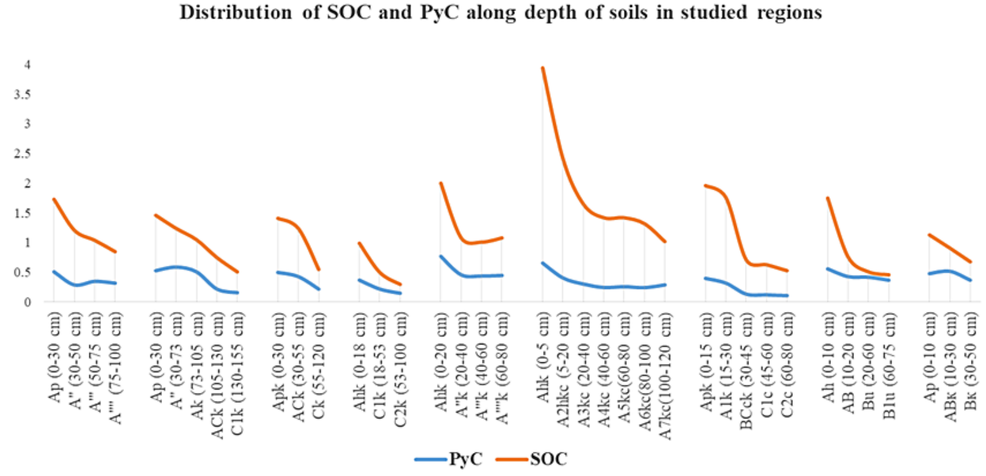

Fig. 6. Distribution of SOC and PyC along depth of soils in Maritsa-iztok (profiles 1, 2, 3, 4 and 5) and Pernik regions (profiles 6, 7, 8 and 9)

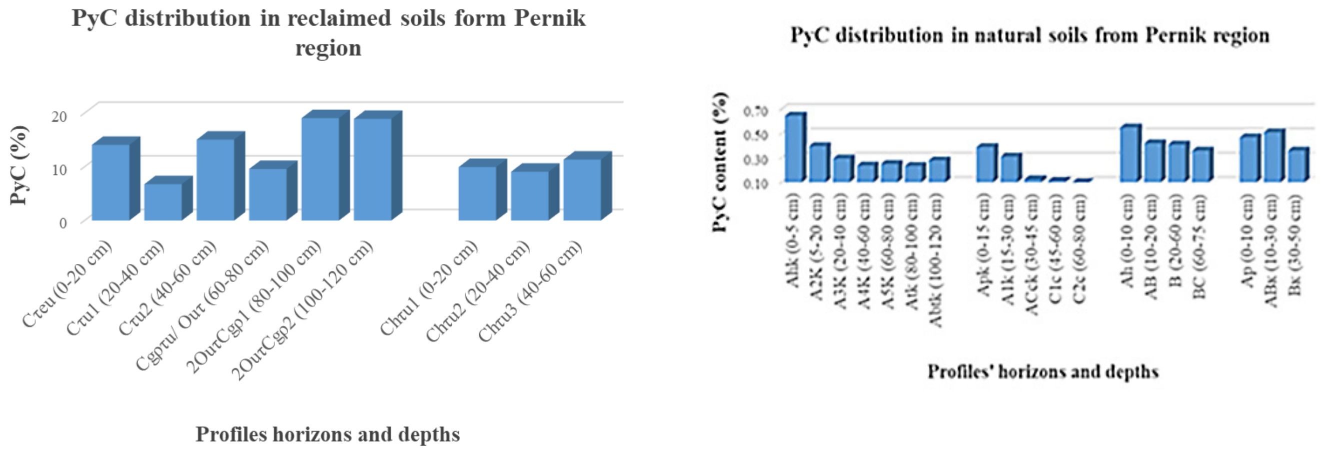

Fig. 7. Distribution of PyC in soils from the region of Pernik

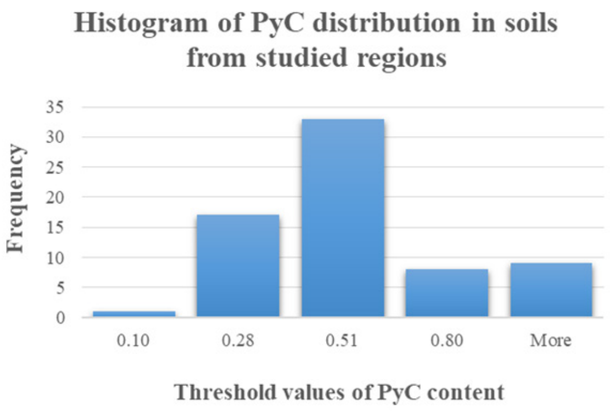

Fig. 8. Histogram of the distribution of PyC values in studied soils

Table 5. Scale for assessment of PyC content in Bulgarian soils

PyC content, %	Estimation
< 0.10	very low
0.11–0.28	low
0.29–0.51	medium
0.52–0.80	high
> 0.80	very high

tent – in reclaimed soils from the Pernik region, where the content of coal impurities dominates in most horizons.

Conclusion

The elaboration of analytical protocols with high reproducibility and accuracy is of paramount importance because increases the predictability of data and the reliability of simulation models. Analytical procedures included in the study show that thermally-assisted oxidation of soil samples with dichromate mixture is a time-consuming but accurate method for determining PyC content. The procedure is supplemented with prior triple treatments of soil samples to remove inorganic forms of carbon, followed by dichromate extraction of soluble and extractable organic substances to separate the fraction of chemically stable pyrogenic carbon. The method described in this article has been experimented with Smolnitsas which are considered PyC-containing soils. The method is also suitable for soils that are highly enriched with PyC (originated from abundant coal impurities) and are usually located in mine-energy regions of Bulgaria.

This first study of PyC in Bulgarian soils reveals its diverse content and distribution in two of the oldest and highly industrialized regions of Bulgaria – the mining and energy complexes Maritsa-iztok and Pernik. Data show that PyC content varies from 0.10% to 19.07%. A higher content (up to 19.07%, average 4.30%) was registered in the region of Pernik, where weakly transformed organic artefacts (soot and coal fragments) enriched soils with weather-resistant pyromorphic carbon forms. Here, in Technosols, PyC is a major ingredient of soil organic carbon and reaches 82% relative content.

According to the developed evaluative scale, the medium content of PyC prevails in the studied Bulgarian soils – from 0.29% to 0.51%. This result coincides with other published data on soils enriched with PyC. The factors influencing PyC distribution in studied soils are: paleo- and present fires, content of coal impurities, and deposition of PyC-dressed aerosols emitted from coal operating TPPs, domestic heating with coal, coal mining and transport.

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Data availability statement

The author confirms that data supporting the findings of this study are available within the article.

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