# Journal Pre-proof


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PII: S0013-9351(23)00637-0

DOI: https://doi.org/10.1016/j.envres.2023.115845

Reference: YENRS 115845

To appear in: *Environmental Research*

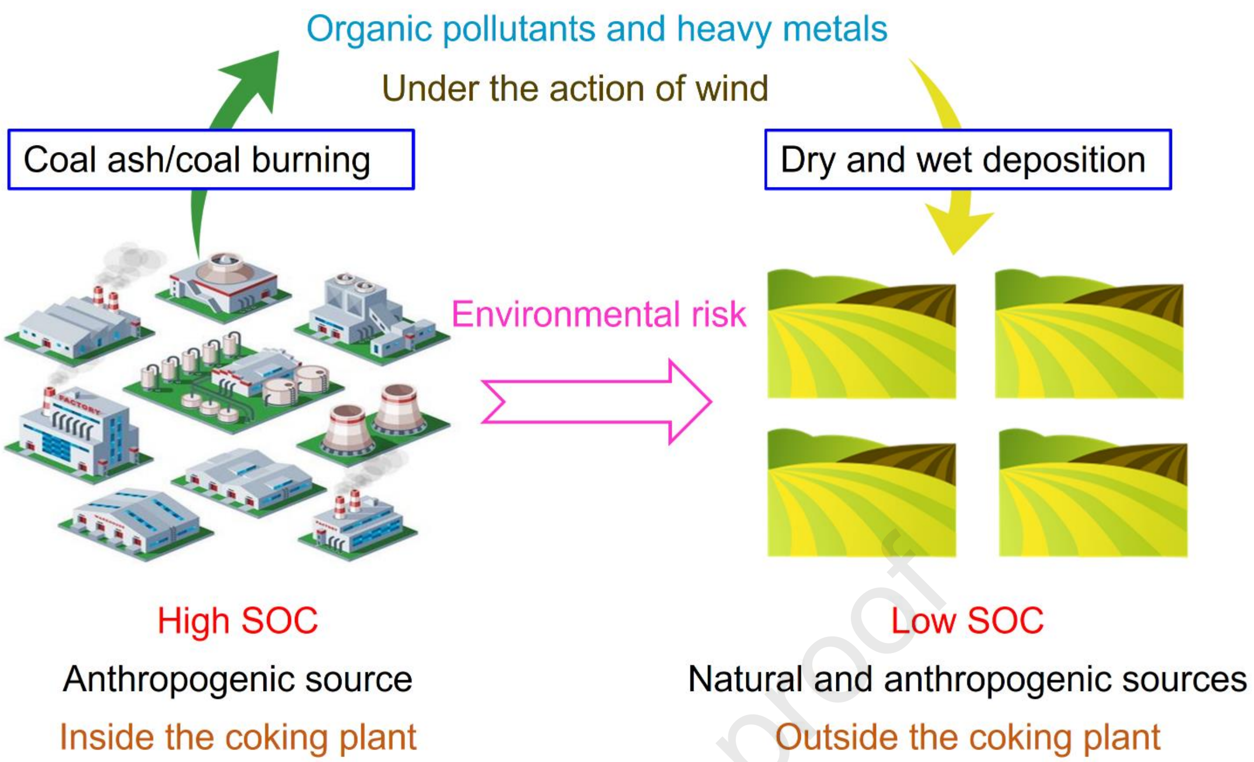
Received Date: 13 February 2023

Revised Date: 29 March 2023

Accepted Date: 3 April 2023

## Credit Author Statement

**Peng Wang**: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing; **Jian Hu**: Conceptualization, Project administration, Methodology, Investigation, Writing – original draft, Writing – review & editing; **Guilin Han**: Methodology, Writing – review & editing; **Tingyi Liu**: Writing – review & editing; **Wen-min Ma**: Writing – review & editing; **Jun Li**, Writing – review & editing.


Organic pollutants and heavy metals
Under the action of wind
Coal ash/coal burning
Dry and wet deposition
Environmental risk
High SOC
Anthropogenic source
Inside the coking plant
Low SOC
Natural and anthropogenic sources
Outside the coking plant

# Preliminary investigation of soil organic carbon distribution and turnover patterns, and potential pollution sources in and around a typical coking plant in North China

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**Abstract**: The variation characteristics of soil organic carbon (SOC) in and around the coking plant area are still unclear. In this work, the concentration and stable carbon isotope composition of SOC in coke plant soils were investigated to preliminarily identify the sources of SOC in and around the plant area, and to characterize soil carbon turnover. Meanwhile, the carbon isotopic technique was used to initially identify the soil pollution processes and sources in and around the coking plant area. The results demonstrate that the SOC content (12.76 mg $g^{-1}$) of the surface soil in the coking plant is about 6 times higher than that outside the coking plant (2.05 mg $g^{-1}$), and the variation range of $\delta^{13}C$ value of the surface soil in the plant (-24.63～-18.55‰) is larger than that

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of the soil outside the plant (-24.92～-20.22‰). The SOC concentration decreases gradually from the center of the plant outward with increasing distance, and the $\delta^{13}C$ in the middle and north of the plant tends to be positive compared with the $\delta^{13}C$ in the west and southeast of the plant. As the increase of soil depth, the SOC content and $\delta^{13}C$ value in the plant increases. On the contrary, $\delta^{13}C$ value and SOC content outside the plant decreases, with a minor variation. Based on the carbon isotope method, the SOC in and around the coking plant area is mainly from industrial activities (e.g., coal burning and coking), and partly from C3 plants. Notably, organic waste gases containing heavy hydrocarbons, light oils, and organic compounds accumulated in the northern and northeastern areas outside the plant due to south and southwest winds, which may pose an environmental health risk.

**Keywords**: coking plant; soil organic carbon; carbon isotope; distribution and turnover

## 1. Introduction

Soil carbon pools play a crucial role in soil fertility and ecosystem balance, and their faint changes can severely affect the dynamics and distribution of carbon (Chen et al., 2005; Jobbágy and Jackson, 2000; Raich and Potter, 1994). The primary sources of soil organic carbon (SOC) are natural and anthropogenic processes (Fennell and Bentley, 1998). In contrast, perturbations to the soil carbon pool caused by different forms of organic matter produced by human activities cannot be neglected (Guo et al., 2013; Guo et al., 2017). It is therefore imperative to identify the source of SOC and to assess the disturbance of soil carbon pools caused by human activities. Nonetheless, due to the influence of complex environmental factors and the lack of relevant research methods, previous studies have mainly focused on the determination of SOC content and state, making it difficult to accurately grasp the origin and dynamics of carbon. For example, ambient temperature, soil moisture, soil texture, C/N ratio, pH, and electrical conductivity can indirectly influence the carbon decomposition process by affecting the enzymatic activity of soil microorganisms, thus altering the input and distribution of SOC (Bird et al., 2003; Guggenberger et al., 1994; O'leary, 1981; Zhu and Liu, 2008). Besides, the shift of land use pattern will also alter the source and process of SOC, which brings difficulties in understanding the fate of SOC (Han et al., 2020; Liu et al., 2020).

The advent of stable carbon isotope technology has enabled qualitative and quantitative analysis of the source, turnover, mobility, stability and decomposition of SOC (Canadell et al., 2000; Ehleringer et al., 2000; Freeman et al., 1990; Guo et al., 2013; Lao et al., 2018; Liu et al., 2020; Malhi et al., 1999; Han et al., 2015; Natelhoffer and Fry, 1988; Weihmann et al., 2007; Zou et al., 2020). Among them, the dynamic fractionation effect of photosynthesis leads to an enrichment of light isotopes in biogenic carbon, resulting in differences in the isotopic composition of carbon between organisms and atmospheric $CO_2$ in terrestrial ecosystems (Bai et al., 2012). In general, SOC in natural soils is mainly derived from terrestrial higher plants. The carbon isotopic fractionation during SOC decomposition is negligible compared to that of plant photosynthesis, thereby resulting in that the SOC is consistent with the $\delta^{13}C$ of planted plants on this soil (Crow et al., 2006; Fernandez et al., 2003). Besides, the mineralization and humification of SOC and the influence of human activities (e.g., coal combustion) are accompanied by isotopic fractionation, and the isotopic composition of SOC from different sources is vastly different (Zou et al., 2020; Guo et al., 2013; Guo et al., 2017). From this, different sources of SOC can be accurately distinguished according to different isotopic compositions and the carbon conversion processes in the soil can then be integrated, thus providing an indication for the study of soil carbon turnover (Ehleringer et al., 2000; Gregory et al., 1999; O'leary, 1981; Sun et al., 2003).

Notably, coking plant, as a typical industrial area, the pollutants (e.g., benzene series, polycyclic aromatic hydrocarbons and heavy metals) generated from its production process will be directly discharged into the atmosphere, and finally accumulate and diffuse in the soil through wet and dry deposition (Hu et al., 2022; Mu et al., 2014; Yuan et al., 2013). And, during the process of coking, gas purification, and tar product recovery, the leakage of raw materials containing additional organic matter can also have a serious impact on the soil (Mu et al., 2013; Mu et al., 2014; Tsai et al., 2007). It can be seen that the prolonged operation of the coking production may inevitably affect the SOC turnover pattern (Guo et al., 2017; Nie et al., 2021; Zou et al., 2020). Previous studies on stable carbon isotopes mainly focused on agricultural soils. Nevertheless, the distribution and variation of $\delta^{13}C$ and SOC the industrial areas affected by human disturbance are not clearly identified. Therefore, it is necessary to study the distribution and turnover of soil organic carbon inside and outside the coking plant. Based on the hypothesis that isotope methods can sensitively reveal the interference and restoration processes of the soil carbon cycle, carbon isotopes may preliminarily identify the environmental pollution and sources from industrial activities. Therefore, a coking plant in Tangshan City was selected as the study area and carbon isotope tracing technique was used to understand the response of the coking industrial production process to the carbon turnover patterns inside and outside plant and preliminarily identify the soil pollution processes and sources in the coking plant area.

## 2. Materials and Methods

### 2.1. Study area

Tangshan is one of the most prominent industrial cities in Hebei province, located between 117°31'～119°19' E and 38°55'～40°28' N. It is a continental monsoon climate with an average annual temperature of 12.5 ℃ and an average annual precipitation of about 500~700 mm. The coking plant in this study is located in the eastern part of Tangshan City and was established in 2004 with an area of approximately 68 $hm^2$. The topography of the plant is flat and the surface is covered by quaternary strata. The plant located in the core industrial zone of eastern Hebei province, integrates coking, power generation, sintering and iron and steel production and has complex pollution sources. The waste, solid waste and particulate pollutants produced by the plant could have a potential impact on the environment of surrounding areas and even Hebei province. It mainly produces coke, tar, natural gas, and crude benzene, has been listed by the government as a key enterprise for environmental protection supervision.

### 2.2. Collection and testing of soil samples

Soil samples were collected according to the classification of different functional zones (Fig. 1). Specifically, 36 sampling points were set inside and outside the coking plant, including 14 inside and 22 outside samples (Fig. 1). Soil samples at different depths (0～10 cm, 10～20 cm, and 20～40 cm) were collected in June 2019. The plants, roots, leaves, and other organic residues as well as rocks in the samples were removed using tweezers and then air-dried. Subsequently, the soil sample is ground, sifted, and transferred to a brown grinding flask for later use. The samples passed through the 100-mesh sieve were used to detect the total organic carbon (TOC). Samples passed through a 20-mesh sieve were used to determine pH (Hu et al., 2022). In addition, soil physicochemical parameters, including organic carbon, electrical conductivity, total nitrogen, and grain size distribution, also were measured. The specific detection and analysis procedures are detailed in the supplementary text.

**2.3. Carbon isotope analysis**

About 2 mg of soil sample wrapped in tin cups (organic carbon content > 1%, pure carbon content > 20 ug) was placed in an autosampler and then into a combustion furnace. Among them, helium was used as the carrier gas and the flow rate was controlled to about 100 mL $min^{-1}$. Oxygen was used as the supporting gas for combustion and the flow rate was controlled at 175 mL $min^{-1}$ for a duration of three seconds. The furnace temperature was set at 1050 °C. Subsequently, the $CO_2$ from the high-temperature burning of the organic carbon was dehydrated and dried with magnesium perchlorate, and then separated from other impurities by gas chromatography. Finally, the carbon isotopic composition of the obtained pure $CO_2$ gas was determined using an isotope mass spectrometer (MAT253).

International reference material for stable isotope analysis of $\delta^{13}C$, namely Vienna Pee Dee Belemnite (VPDB). The carbon isotopic composition is described by $\delta^{13}C$, which is defined as:

$$\delta^{13}C\ (‰) = [R_{sample}/R_{standard} - 1] \times 1000$$

IAEA600 (Caffeine, carbon isotope value -27.771 ‰) was used to calibrate the sample. The $\delta^{13}C$ value was measured repeatedly throughout the study with an accuracy of 0.2 ‰.

## 2.4. Data Processing

The map of the sampling sites was drawn using ArcGIS 10.7, and the other figures were drawn by Origin 2021. The inverse distance weight analysis function included in ArcGIS is used to characterize the spatial variability properties of certain parameters in the studied region. Pearson correlation analysis was also performed in Origin 2021 to investigate the relationship between carbon isotopic composition and SOC.

# 3. Results and discussion

## 3.1 Physical and chemical properties of soil

The distribution of physical and chemical properties of the soil is shown in Table S1. Except for pH and SOC concentrations, the coefficients of variation (CV) of electrical conductivity (EC), total nitrogen (TN), organic matter (OM), $CaCO_3$, and soil particle composition (SPC%) data are all above 15%, indicating strong natural and anthropogenic disturbance (Table S1) (Hu et al., 2022). Moreover, the soil inside the coke plant is alkaline with an average pH of 8.3, while the soil outside the plant is neutral with an average pH of 7.4 (Fig. 2-A). The soil in the plant is composed mainly of sand particles, loam particles, and clay particles, with an average ratio of 60.79%, 20.0%, and 19.5%, respectively. The average proportions of loam particles (14.0%) and sand particles (55.0%) in the outside plant was not significantly different from that in the inside plant, but there are more clay particles (30.7%). Besides, the average values of EC (0.75 ms $cm^{-1}$), OM (75.4 g $mg^{-1}$), and $CaCO_3$ (43.4 g $mg^{-1}$) in the inside soils of plant are higher than that of EC (0.2 mS $cm^{-1}$), OM (25.6 g $mg^{-1}$), and $CaCO_3$ (15.1 g $mg^{-1}$) in the outside soils, respectively. The difference is that the TN content of the inside soil (0.6 g $mg^{-1}$) is lower than that of the outside soil (0.8 g $mg^{-1}$).

**3.2 Distribution characteristics of carbon isotopes and SOC**

**3.2.1 Horizontal variation characteristics**

The overall $\delta^{13}C$ value of soil organic carbon in the coking plant area varies from -24.92‰ to -18.55‰ (Fig. 2-B). The variation range of $\delta^{13}C$ in the soil inside the plant (-24.63～18.55 ‰) is higher than that in the soil outside the plant (-24.92～20.22 ‰). The $\delta^{13}C$ values of in-site soils with an average value of -22.42‰ are more positive compared to those of off-site soils (-23.26‰) (Fig. 2-B), which may be caused by the high $CaCO_3$ content of soil in the plant (Table S1) (Boeckx et al., 2006). Meanwhile, the SOC content of the soil inside the plant (12.81 mg $g^{-1}$) is about 6 times higher than that of the soil outside the plant (2.05 mg $g^{-1}$) (Fig. 2-B). After removing these two outliers, the organic matter content (5.3 mg $g^{-1}$) of the soil inside the plant remained higher than that of the soil outside the plant (2.05 mg $g^{-1}$).

To determine the spatial variation characteristics of SOC concentration and $\delta^{13}C$ value in the study area, ArcGIS was used to perform inverse distance weight analysis on SOC concentration and $\delta^{13}C$ value (Fig. 3). The results display that the SOC concentration in the surface soil of the inside plant (especially in the raw material area and the dust area of the road) is relatively high, and SOC concentrations decrease from southwest to northeast and decreases with increasing distance from the center of the coking plant, suggesting that the SOC outside plant is mainly from industrial activities (Fig. 3-A) (Guo et al., 2017). Nevertheless, the $\delta^{13}C$ values of top-soils located in the central and northern parts of the study area are more positive than those of other areas (Fig. 3-B). Significantly, stack emissions (fly ash) and unorganized emissions (poor containment) are the main emission patterns of coking-generated emissions (Mu et al., 2014). Among these, gases consisting of heavy hydrocarbons, light oils and additional organic compounds (including POPs, VOCs, and PAHs), and coal ash (containing heavy metal) are continuously releases into the atmosphere, and then enter the soil through wet and dry deposition (Deng et al., 2014; Mu et al., 2013; Norra et al., 2005). Moreover, the wind direction in Tangshan City is mainly south and southwest, leading to a high SOC concentration in the surface soil of the inside plant, and gradually decreases with the increase of the distance from the center of the plant (from the center to the outside). Simultaneously, coal dust deposition caused by coal storage can enrich the soil with $\delta^{13}C$ (Norra et al., 2005). Wind force causes $\delta^{13}C$-rich exhaust gas and particulate matter to migrate and accumulate in the northern part of the plant, which is also the key to the significant difference in $\delta^{13}C$ distribution characteristics outside the plant ($\delta^{13}C$ values in the middle and north of the plant tend to be positive compared with those in the west and southeast).

### 3.2.2 Vertical variation characteristics

Variations in the organic carbon isotope and organic matter content were investigated at different depths. As the soil depth increases from 0～10 cm to 20～40 cm, regions with large variation in $\delta^{13}C$ values include coke oven area (S1), waste water pond (S2), ammonium sulfide area (S4), tank area (S6), and gas tank area (S8) (Fig. S1-B), indicating that SOC in those areas are degraded naturally by microorganisms in its profile (Chen et al., 2005). Conversely, the $\delta^{13}C$ values in the gas tank area (S13), coke oven area (S11), and coke quenching area (S10) have a slight variation range (Fig. S1-B). The reason for this can be concluded by the fact that coal slag enters and enriches in the soil, which influences the SOC fractionation induced by soil microorganisms (Zou et al., 2020). With the increase of soil in the outside plant depth from 0～10cm to 20～40cm (e.g., S15, S18, S20, S24, S27, S29, S33, and S35), the variation of $\delta^{13}C$ value is tiny (Fig. S2-B), while the regions with large variation of SOC content include ammonium sulfide zone (S4), tank zone (S6), coke quenching zone (S10), and the soil outside plant (S15 and S18) (Fig. S1-A and Fig. S2-A), which are mainly affected by the spatial distribution of leaf and root litter. On the contrary, the variation range of SOC content in the coke oven area (S1), waste water pool (S2), gas tank area (S8 and S13), coke oven area (S11), and the soil outside plant (e.g., S20, S24, S27, S29, S33, and S35) is small (Fig. S1-A and Fig. S2-A). This may be due to various pollutants produced in industrial processes affect the microbial activity, which is detrimental to the sequestration of SOC.

Owing to the restriction of some functional areas in the coking plant, only soil samples with a depth of 0～20 cm were collected from most of the sample sites (Table S2). Based on this, we discuss the vertical variation of SOC and $\delta^{13}C$ values in the shallow soil of the plant from 0 cm to 20 cm. On the whole, the average SOC content at different soil depths inside the plant is 4.9 mg $g^{-1}$ (0～10 cm) and 5.5 mg $g^{-1}$ (10～20 cm), respectively, showing an increasing trend with the increase of depth (Fig. 4-A). And the $\delta^{13}C$ values of the inside plant also show a similar trend (from -22.39‰ to -20.56‰) (Fig. 4-A). The coking plant is dominated by coal burning and coking, which makes abundant organic matter accumulate in the soil inside the plant (Guo et al., 2017). Differently, the SOC content outside plant decreases with the increase of soil depth (from 1.96 mg $g^{-1}$ to 1.89 mg $g^{-1}$) (Fig. 4-B). When the soil depth increases from 0～10 cm to 10～20 cm, the average $\delta^{13}C$ value decreases from -22.26‰ to -22.35‰ (Fig. 4-B). In contrast to natural soil profiles, the soil inside and outside the plant tend to decrease in SOC concentration with increasing depth, but the change is not significant enough (Liu et al., 2021; Zhu et al., 2008).

### 3.3 Source identification of SOC

#### 3.3.1 Pearson correlation analysis

Pearson correlation analysis was used to investigate the relationship between organic carbon isotopes and SOC content in the soil. It can be seen that there is a positive correlation between SOC concentration and $\delta^{13}C$ inside the coking plant ($R^2 = 0.171$) (Fig. S3-A). The SOC content is enriched by the accumulation of organic feedstock in the coking coal producing areas. Meanwhile, dust generated from coal accumulation and transportation tends to be enriched in $\delta^{13}C$ (Lopez-Veneroni, 2009). Besides, the soil inside the plant is rich in $CaCO_3$ and alkaline, which is typical of saline-alkali soils (Table S1). In the process of soil salinization, the carbonate in the soil accumulates $\delta^{13}C$, which can increase the value of $\delta^{13}C$ (Boeckx et al., 2006). Interestingly, there is a negative correlation between SOC concentration and $\delta^{13}C$ outside the plant ($R^2$ = -0.0999) (Fig. S3-A), indicating that the decomposition degree of SOC outside the plant is low. This may be due to complex isotopic fractionation caused by microbial and animal respiration during the conversion of plant residues to organic carbon (Bai et al., 2012; Fujiyoshi et al., 2011).

**3.3.2 Natural and anthropogenic sources**

Carbon isotopic composition is commonly used to distinguish the natural and anthropogenic contributions of carbon in soils (e.g., coal, rocks, and plants (C3 and C4 plants) (Ehleringer et al., 2000). The previous results showed that the $\delta^{13}C$ values of plant samples from steel industrial areas vary -15.4～-15.1‰ and -30.0～-26.7‰ (Guo et al, 2013 and 2017). And the isotopic composition of C3 plants ranges from -30‰ to -20‰, while that of C4 plants ranges from -17‰ to -8‰ (Lin et al., 2013). As mentioned above, topsoil $\delta^{13}C$ values inside and outside the coking plant range from -24.63 to -18.55‰ and -24.92 to -20.22‰, respectively. Comparative studies have found that natural sources of SOC inside and outside coking plant should be dominated by C3 plants, with limited sources from C4 plants.

Compared with the $\delta^{13}C$ value of the surface soil of the industrial area in Beijing (-24.7 ± 0.5‰), the $\delta^{13}C$ value of the surface soil in the coking plant is more positive (-22.4 ± 1.56‰) (Fig. 5). Besides, the $\delta^{13}C$ values of several typical production areas in

Beijing (23.8 ± 0.5‰ (sintering plant), 23.71 ± 0.3‰ (rolling section), 23.6 ± 0.2‰ (coke production), 24.7 ± 0.5‰ (top-soil in industrial area), and 24.3±0.6‰ (coal)) are also related to the average $\delta^{13}C$ value (-23.2 ± 0.8‰) of the coking production areas (including raw material area, solid waste accumulation area, gas tank area, coke quenching area, and coke oven area) is similar (Fig. 5). Therefore, SOC in the coking plants mainly comes from industrial production activities and the accumulation of raw materials and wastes (Guo et al., 2013). Besides, the $\delta^{13}C$ value of soil outside the coking plant (-22.4 ± 1.06‰) is mostly consistent with the $\delta^{13}C$ value of surface soil of non-industrial area in Beijing (-21.9 ± 1.5‰) (Fig. 5), suggesting that SOC in the two regions has similar sources (Guo et al., 2017). The $\delta^{13}C$ value and SOC difference of coking production areas are analyzed emphatically, and the results are shown in Fig. S4. Undoubtedly, SOC in the raw material area and road ash accumulation area is significantly higher than that in other sampling areas, which is mainly generated in the process of coal accumulation and burning (Mu et al., 2013 and 2014). SOC contents of solid waste accumulation area, gas tank area, coke quenching area, and coke oven area are not significantly different from $\delta^{13}C$. On the whole, the $\delta^{13}C$ values of the soil in the coking plant and its surrounding areas are -24.63～-18.55‰ and -24.92～-20.22‰, respectively, which are consistent with the isotopic compositions of the fly ash collected by blast furnace during coking (-23.84‰～-23.32‰). It can be seen that coal/coal burning has a great contribution to soil organic carbon in and around the plant (Guo et al., 2013; Mu et al., 2013; Zou et al., 2020).

Previous research has found that there are some differences in carbon isotope composition and SOC content between industrial, surrounding industrial and non-industrial areas (Fig. S5) (Guo et al., 2017). Specifically, the soil SOC concentration level showed an obvious change (i.e., industrial area > surrounding industrial area > non-industrial area) (Fig. S5-A). As far as the variation of $\delta^{13}C$ is concerned, the non-industrial area is larger than that of the industrial area and the surrounding area (Fig. S5-B). Besides, the region with stable $\delta^{13}C$ value and relatively elevated SOC is mainly influenced by industrial activities, and the area with large variation of $\delta^{13}C$ value and low SOC concentration is mainly affected by microbial turnover of SOC in the surface layer (Guo et al., 2017). However, in this study, the variation of $\delta^{13}C$ values of SOC in and out of the plant are fundamentally the same, which may be due to the lack of significant isotope fractionation in the coking industrial production process and the consistent source of SOC in and outside plants (Fig. 6) (Norra et al., 2005). Furthermore, the soil in the coking plant has a steep SOC content, further indicating that coking production activity is the main source of SOC. Compared with the soil inside plant, the SOC content outside the plant is lower, and the isotopic composition of SOC is relatively positive, indicating that the SOC outside plant mainly comes from dead branches and defoliations (mainly C3 plants).

## 4. Conclusions

Stable carbon isotope method is used to explore organic carbon turnover patterns and preliminarily identify the soil pollution processes and sources in and around the coking plant area. The main conclusions are as follows: (1) the physical and chemical properties of the soil inside and outside the plant are significantly different, and are heavily disturbed by industrial activities and fluctuate considerably; (2) the SOC concentration in the study area increases from southwest to northeast, and decreases with the increase of the distance from the center of the coking plant. The $\delta^{13}C$ of topsoil located in the middle and north of the study area is more positive than that of other areas; (3) with the increase of soil depth, the average SOC content of different soil depths in the plant shows an increasing trend, while the SOC content of outside soil haves a decreasing trend; (4) the main sources of SOC of the coking plant primarily include industrial sources (e.g., coal burning and coking) and natural sources (C3 plants). It is worth noting that exhaust gases (heavy metals and organic pollutants) from the coking plant accumulate downwind of the plant due to the action of wind. Therefore, the severe environmental risk on the downwind areas of the coking plant should be given extra attention.

**Declaration of Interest Statement**

The authors declare that they have no competing financial interests or personal relationships.

## Acknowledgments

This work was financially supported by the National Key Research and Development Program of China (grant No 2019YFC1805805, 2018YFC1800306) and National Natural Science foundation of China (grant No 21307090).

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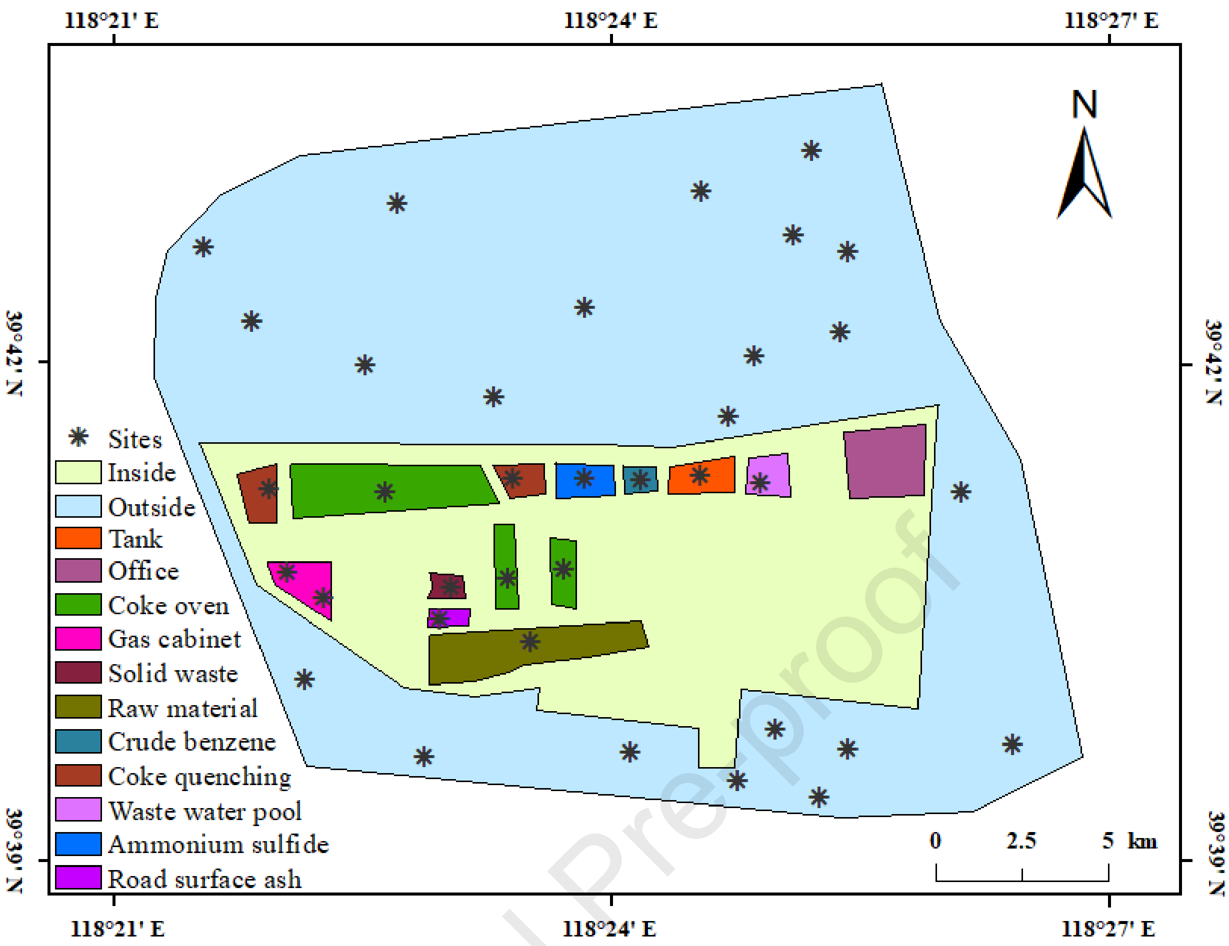


**Fig. 1.** Distribution of soil sample sites inside and outside the coking plant in Tangshan.

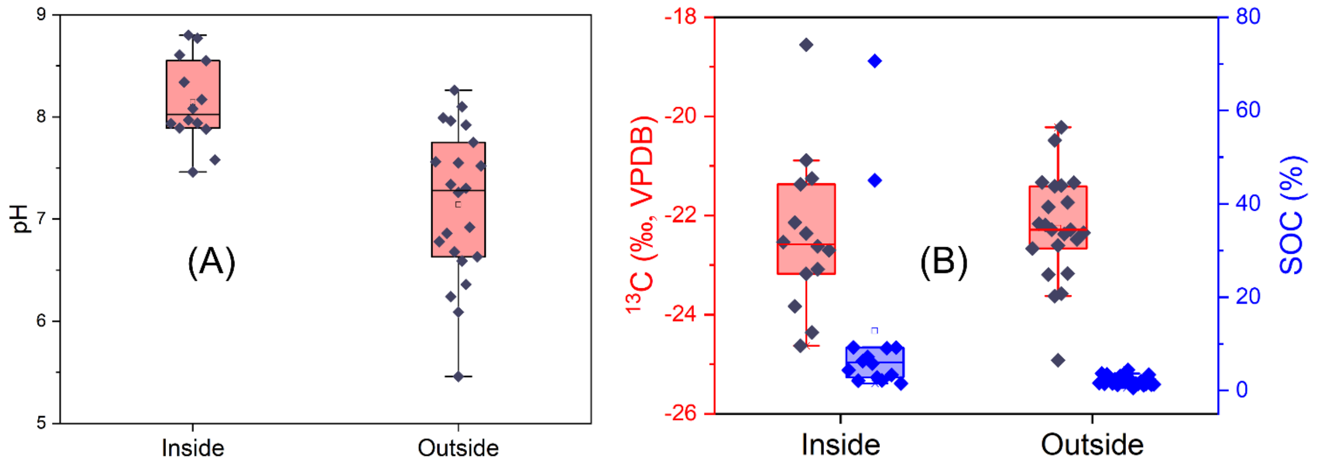


**Fig. 2.** Variation of pH, $\delta^{13}C$, and SOC in the surface soil (0～10 cm) inside and outside the coking plant.

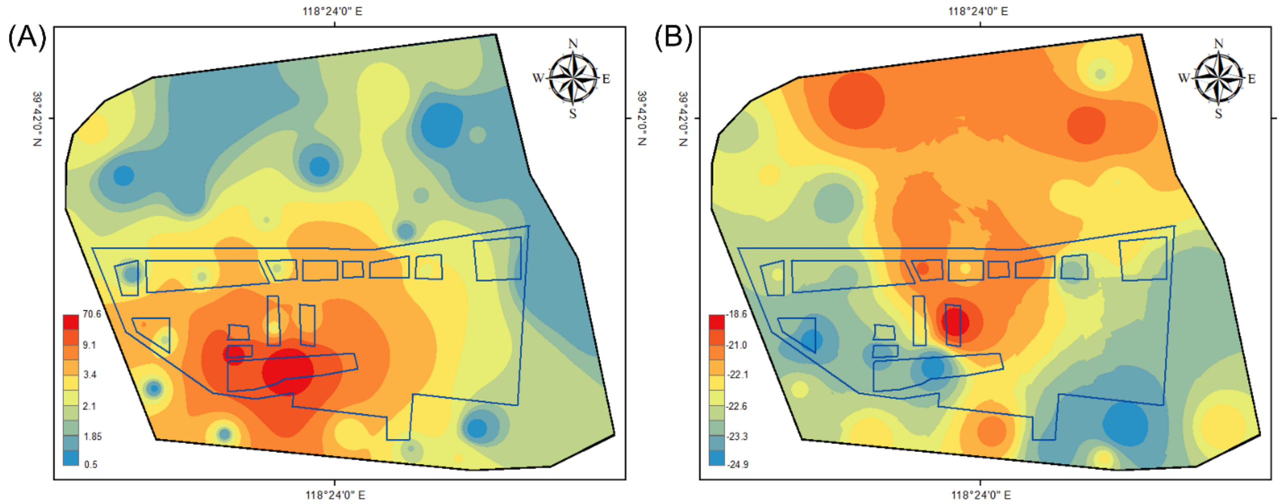


**Fig. 3.** Spatial distribution of SOC concentrations (A) and $\delta^{13}C$ (B) in topsoil (0～10 cm) of the study area.

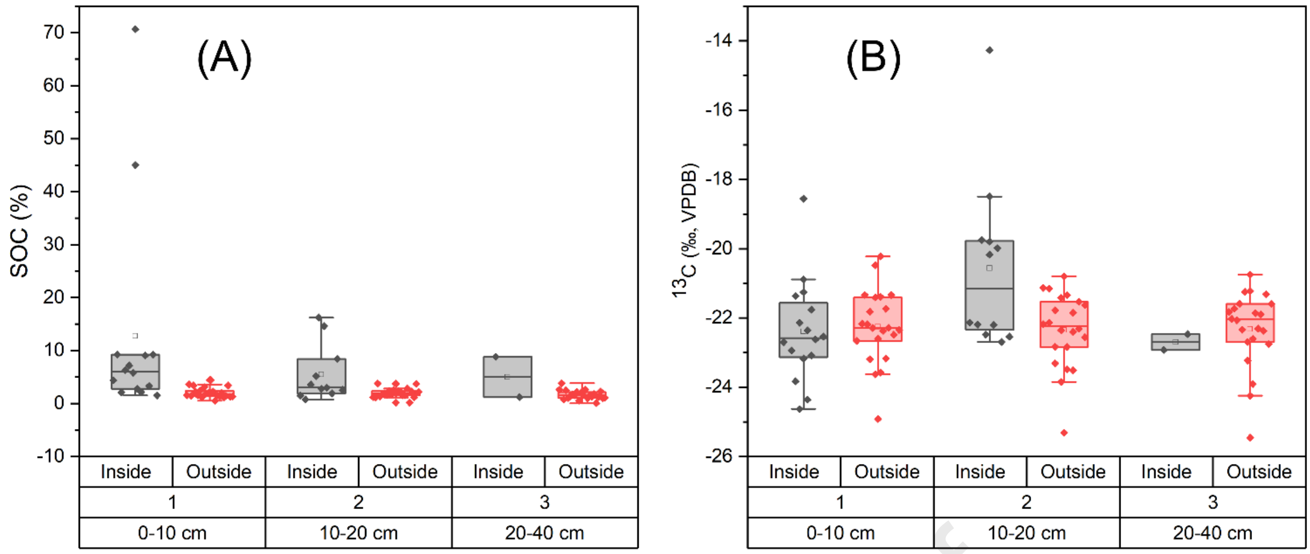


**Fig. 4.** Vertical variation of soil SOC and $\delta^{13}C$ inside and outside the coking plant.

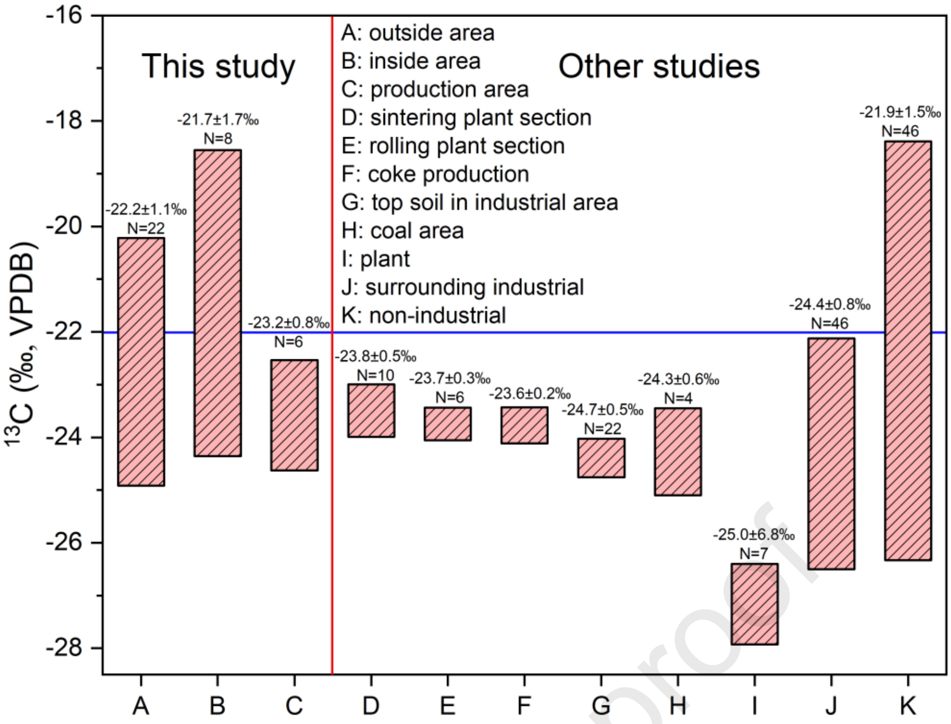


**Fig. 5.** Comparison of $\delta^{13}C$ values based on different sources (Guo et al., 2013; Guo et al., 2017; Mu et al., 2021).

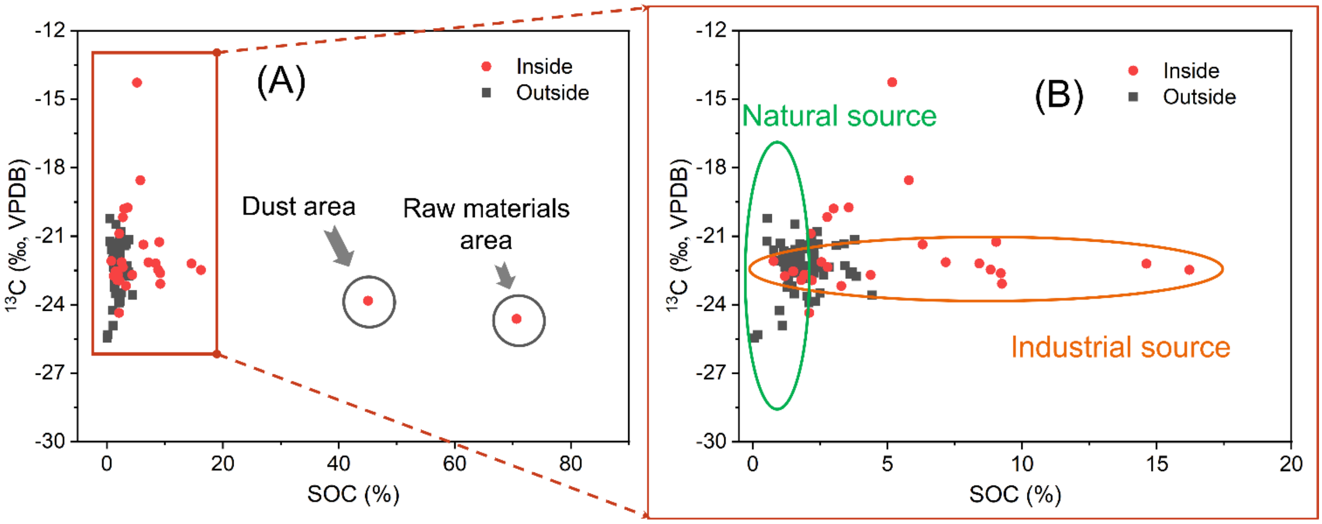


**Fig. 6.** Relationship between SOC and $\delta^{13}C$ composition (A); Relationship between SOC and $\delta^{13}C$ composition excluding dust in raw material area and dust area (B).

**Highlights**

- Soil properties inside and outside the plant vary significantly.
- Spatial and vertical differentiation of soil organic carbon and $\delta^{13}C$ are obvious.
- Carbon isotopic technique may identify the soil pollution processes and sources.
- There are environmental risks in the downwind area of the coking plant.

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: