

Review

Not peer-reviewed version

# Study Progress on Technogenic Magnetic Particles (TMPs) and Their Future Research in Continental Shelf Seas

Yong-Hong Wang\*, Meng-Yao Liang, Chun-Hui Xiao

Posted Date: 11 January 2024

doi: 10.20944/preprints202401.0902.v1

Keywords: Technogenic magnetic particles (TMPs); Characteristics; Distribution pattern; Sedimentary effects.; Continental shelf seas



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Disclaimer/Publisher's Note: The statements, opinions, and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions, or products referred to in the content.

Remiero

# Progress on the Characteristics of Technogenic Magnetic Particles (TMPs) and Its Future Study in Continental Shelf Seas

Wang Yong-Hong 1,2,\*, Liang Meng-Yao 1 and Xiao Chun-Hui 1

- Key Lab of Submarine Geosciences and Prospecting Techniques, MOE and College of Marine Geosciences, Ocean University of China, Qingdao 266100, China
- <sup>2</sup> Laboratory of Marine Geology and Environment, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China
- \* Correspondence: yonghongw@ouc.edu.cn

Abstract: With the increase of global human activities, a large number of technogenic magnetic particles (TMPs) generated by industrial activities such as coal combustion, traffic and so on enter sediments on continental shelves. However, there is currently a lack of understanding of the spatiotemporal distribution of TMPs on continental shelves, as well as the sedimentary effects they cause. This review work comprehensively analyzes the source, morphology, composition, and spatiotemporal distribution characteristics of TMPs. Then it elucidates their magnetic contribution to sedimentary environments in continental shelf seas, as well as the influence of heavy metals and active iron. At the same time, the existing problems and future development directions of TMPs on continental shelves are summarized.

**Keywords:** continental shelf and sea; technogenic magnetic particles (tmps); characteristics; distribution pattern; sedimentary effects

### 1. Introduction

Magnetic particles have both natural and anthropogenic sources. Natural magnetic particles come from the universe, wildfires, volcanic eruptions, or lighting sources, while anthropogenic sources are generally referred to as technical magnetic particles (TMPs). TMPs mainly come from a large amount of coal-fired fly ash formed by thermal power plants during high-temperature coal combustion and traffic (fuel consumption and exhaust emission) (Doyle et al., 1976; Lu et al., 2016; Shetye et al., 2019; Vasiliev et al., 2020; Wang et al., 2022).

The proportion of TMPs in the fly ash is about 2-15%, and the particle size is mostly 5-150  $\mu$  m. It appears spherical or nearly spherical, with a portion of it being iron containing oxides that are magnetic (Grimley et al., 2017; Zhu Lei et al., 2004). TMPs are discharged from source areas such as thermal power plants and are an important component of atmospheric PM2.5. When they enter the human alveoli, they cause damage to the respiratory system, and when they enter the human brain, they can lead to cardiovascular and cerebrovascular diseases (Tian et al., 2019). They also have been found on dung emitted by cow grazing in the surroundings of an iron smelter, which prove that TMPs enter ecosystems compartments and food chains (Ayrault et al., 2016).

Most of the coarse TMPs settle on land or lakes near source areas such as thermal power plants, causing enhanced soil or sediment magnetism and heavy metal pollution in these areas. Therefore, there are relatively rich research results on TMPs in soil and sediment in the land domain (Magiera et al., 2011; Sarkar et al., 2015; Lu et al., 2016; Tan et al., 2018; Grimley et al., 2021). Generally, magnetic particles from different sources can be distinguished by their morphology and composition (Tang et al., 2010). Additionally, it is widely believed that the number of TMPs in the near surface land and coastal zones is much greater than that of other natural sources, indicating that magnetic particles in modern sediments are essentially products of human activity (Tang et al., 2010; Kelepertzis et al., 2021).

TMPs in the land can also be washed into rivers by rainwater and eventually enter the sea. In addition, relatively fine particles move with the atmosphere and directly enter the continental shelf sea and settle to the seabed (Figure 1). For example, sediments along the southwestern coast of Taiwan in China contain a large amount of TMPs, mainly from coastal thermal power plants (Horng et al., 2009). However, overall, there is still a lack of understanding of the characteristics of TMPs entering the shelf sea and their impact on the sedimentary environment of the shelf sea.

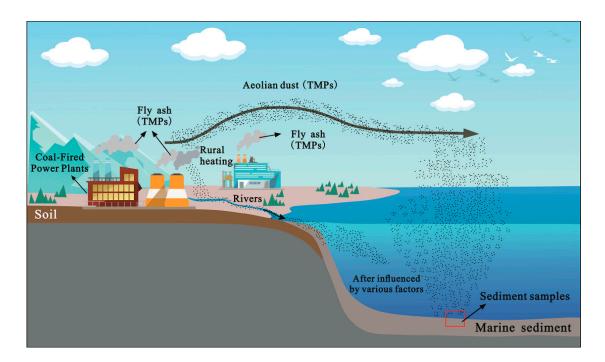


Figure 1. Schematic diagram of the TMPs aggregation process in the continental shelf sea.

# 2. Discovery of TMPs

In 1976, scientists discovered a large number of black iron magnetic spherules in the surface water of the eastern Gulf of Mexico. The study found that these magnetic spherules mainly come from coal-fired power plants on the eastern border of the Gulf. According to the collection experiments on the deck, it is estimated that approximately 650000 tons of black magnetic particles fall from the atmosphere each year. This number is several orders of magnitude higher than the amount of iron meteorite material falling on the entire Earth. This is the first report on TMPs formed by industrial activities such as coastal coal burning. It was formerly believed that magnetic spherules originated from extraterrestrial (cosmic) or volcanic eruptions on Earth (Murray and Renard, 1891; Del Monte, et al., 1975). The results of this work were published in the journal of "Science" that year (Doyle et al., 1976).

Therefore, people have also begun to pay attention to the need to distinguish between the natural and artificial sources of magnetic spherules in sediments. The methods of differentiation generally include (1) distinguishing their sources on a time scale, for example, the amount of TMPs is several orders of magnitude higher than the estimated falling speed of iron meteorite materials on the entire Earth (Doyle et al., 1976), and much higher in quantity and frequency than volcanic eruptions. Therefore, within the modern century scale, it is generally believed that a large number of magnetic spherules come from industrial emissions; (2) Its source can be distinguished by morphology, chemical and mineral composition.

#### 3. Characteristics of magnetic spherules from different sources

TMPs generated by industrial emissions such as coal combustion and road traffic are commonly found in the atmosphere, land, lakes, estuaries, and nearshore waters of densely populated and

3

industrialized regions (Horng et al., 2009; Fomenko et al., 2021; Grimley et al., 2021). Magnetic spherules of cosmic or volcanic origin are generally found in formations with slower sedimentation rates (Yin et al., 2006; Zhang et al., 2014). For example, magnetic spherules discovered at the boundary between the Neogene and Quaternary in China's terrestrial loess, dating back approximately 2.43-2.50 Ma, were formed when an extraterrestrial object collided with the Earth (Yin et al., 2006).

#### 3.1. Morphological features

TMPs produced by coal burning or road traffic in land areas may have different particle sizes, but their particle size composition mainly ranges from 10 to 50  $\mu$ m, accounting for 63% to 72%; particle sizes range from 5~10 $\mu$ m and < 5  $\mu$ m account for 13%~23% and 5-15%, respectively (Zhu et al., 2004; Kim et al., 2008; Catinon et al., 2014). The magnetic spherules produced by the universe and volcanoes are relatively large, generally ranging 5 $\mu$ m~2mm and mainly being 100~600  $\mu$ m (Yu et al., 1984; Zhang, 2007).

The TMPs has hardly undergone complex erosion, and various forms of microspheres have been well preserved. Although all magnetic spherules from different sources undergoes quenching processes, TMPs contains more crystalline components and complex surface decorations. This is because TMPs undergo longer periods of high temperature, allowing them enough time to form these crystals and decorations. The brain like flow pattern structure, grid like crystal pattern structure, pore structure, nodular protrusion, melting point surface, and mat like structure on the surface of spherical particles can be observed (Lu et al., 2009; Lu et al., 2016; Teller et al., 2020). The interior of industrial coal-fired magnetic spherules has solid or cavity structures, but the latter are more common (Grimley and Arruda, 2007; Tang Liling et al., 2010; Magiera et al., 2011).

Magnetic spherules of cosmic origin often exhibit surface U and V-shaped grooves and cupshaped structures formed by impacts (Szr et al., 2001). Magnetic spherules of volcanic origin are more likely to exhibit elongated or droplet like shapes due to the splashing of low viscosity magma during the eruption process (Glass et al., 2004). In addition to single-layer structures, some cross-sections of cosmic origin show two types of structures: single-layer and double-layer. The double-layer structure has a Ni-Fe core with a high density and forms an eccentric core. Magnetic spherules of volcanic origin are usually solid (Del Monte et al., 1975).

## 3.2. Chemical composition

Usually there are higher Ti (>7%) and Fe element content in TMPs. Meanwhile, the most obvious feature of TMPs is also contain other heavy metal elements such as Hg, Cd, Cr, Zn, Pb, Ni, etc. which are brought by coal combustion (Lu et al., 2009). Some of these heavy metal elements adsorb on the surface of TMPs, and some are incorporated into the lattice structure of TMPs (Magiera et al., 2011; Lu et al., 2016). When honeycomb coal is burned openly, its fly ash containing TMPs has a higher content of Zn and Pb, but the Ni content is higher when honeycomb coal is smoldered (Yan et al., 2018).

The chemical composition of magnetic spherules of cosmic origin has the following characteristics: 1) The proportion of Fe, Ni, and Co is similar to that of iron meteorites; 2) Containing Ni and Fe; 3) Containing wustite; 4) The abundance of elements that are rare in the cosmic, such as Mn, Ti, Cr, etc., is lower. For example, the Ti content is relative lower (0.001~0.5%) in magnetic spherules of cosmic origin (Xiao and Ouyang, 1984). On the other hand, the difference in the ratio of elements can also be used to determine the cosmic origin, for example, their Ni/Cu, Cu/Co, and Ni/Fe ratios need to be within the range of meteorites (Xiao and Ouyang, 1984). However, there are higher Ti contents (5% to 10%) and magnatic elements (Si, Al, Ca, Ti, Cr) and Mn in magnetic spherules of volcanic origin (Andronikov et al., 2016).

#### 3.3. Mineral composition

The mineral composition characteristics are one of the important criteria for determining the origins of magnetic spherules (Sun et al., 2005). The mineral combination of TMPs is commonly found

in magnetite and magnetite hematite, and may also contain very small amounts of mullite, calcite, gypsum, quartz, feldspar, amorphous substances, etc. If TMPs are formed after the combustion of brown coal, the mineral composition is mostly antiferromagnetic hematite and magnetic hematite due to the lower combustion temperature. The combustion of coke is more likely to produce magnetite (Magiera et al., 2011; Szuszkiewicz et al., 2015; Bourliva et a., 2017).

The mineral composition of magnetic spherules of cosmic origin is relatively simple, such as the combination of magnetite and hematite (Zhang et al., 1992), or the combination of magnetite pyrrhotite meteorite pyrite and hematite (Xiao and Ouyang, 1984). The high content of hematite is an important indicator of cosmic origin (Zhang Baomin et al., 1992). The main components of cosmic magnetic spherules in South China Sea boreholes are magnetite and magnetite hematite (Yu et al., 1984). The most common mineral components of volcanic magnetic spherules are magnetite and silicates, followed by metallic elements, lacking hematite and  $\alpha$ - Fe minerals (Iyer et al., 2007). The most abundant Fe oxides in technogenic soils (with TMPs) were (i) magnetite with (ii) a few percent of hematite admixture (both minerals mainly inherited from fresh ash and partly neoformed), and (iii) low-coercivity maghemite (B1/2 ~ 15–20 mT) which most likely formed by the surface oxidation of fine magnetite grains inherited from the parent material (Uzarowicz et al., 2021).

#### 3.4. Comprehensive discrimination indicators

From the above discrimination criteria, comprehensive indicators are needed to determine origins of magnetic spherules. For example, TMPs can be considered. (1) The particle size of the spherules is generally less than 50  $\mu$ m; (2) High Ti (>7%) content and enrichment of multiple heavy metal elements (Hg, Cd, Cr, Zn, Pb, Ni, etc.); (3) The combination of mineral components is relatively complex; (4) It is common and extremely abundant in areas with high human activity.

Everyone agrees that magnetic spherules of cosmic origin need to meet the following criteria: (1) The ratio of Fe, Ni, and Co needs to be within the range of iron meteorites; (2) Core of spherules contain Ni and Fe; (3) Containing hematite; (4) Elements that are not abundant in the universe, such as Mn, Ti, and Cr, have extremely low abundance (Genge et al., 2008; Zhang, 2007).

Magnetic spherules of volcanic origin need to meet the following criteria: (1) The sphere is solid; (2) High Ti (5-10%) content, enriched in magmatic elements (Si, Al, Ca, Cr) and Mn; (3) Lack of wustite and  $\alpha$ -Fe minerals (Huang et al., 2012).

# 3.5. Time discrimination indicators

In summary, if there are no extreme natural events, TMPs are often orders of magnitude larger than natural sources. Therefore, on a time scale of nearly a century, by excluding geological events, magnetic spherules are generally considered to be sources of human activity. Therefore, by combining the above indicators and considering the occurrence strata and regions of magnetic spherules, it is possible to identify the magnetic spherules caused by coal combustion and belongs to TMPs.

#### 4. Distribution pattern of TMPs

# 4.1. Surface distribution

The research results of TMPs mainly focus on terrestrial environments. In the study of soil with severe heavy metal pollution in 13 central cities and their surrounding areas in China, it was found that the closer the soil samples were to coal-fired factories, the more TMPs there were (Tang Liling et al., 2010). In some cities, there is a pattern where the content of TMPs is higher in industrial areas than in residential areas, higher in central urban areas than in suburban areas, and higher in old urban areas than in new urban areas (Tang et al., 2010; Magiera et al., 2016). A study on TMPs in the surface soil of Luoyang urban area in northwest China found that the closer the area is to power plants and thermal power plants, the higher the number of TMPs (Lu et al., 2016).

Dust in the streets of Loudi City in China contains TMPs, which have diameter of 40-170  $\mu m$  and different surface structures. The TMPs in street dust mainly come from iron smelters, which are

significantly higher than those in agricultural samples (Zhang et al., 2012). In the central region of Upper Silesia in southern Poland, there are more TMPs in the soil near the thermal power plant. As the distance from the thermal power plant increases, the content of TMPs gradually decreases (Rachwal et al., 2015). This also occurs in the other areas of Poland, for example, areas close to power and cement plants (Magiera et al., 2013) and iron mine and a nickel smelter (Magiera et al., 2018) have higher TMPs contents.

There is limited research on the migration and distribution of TMPs in continental shelf seas. Surface water samples were taken every 1000 meters in the eastern waters of the Gulf of Mexico, and it was found that a large number of TMPs were mainly from coal-fired power plants on the eastern border of the Gulf (Doyle et al., 1976). The sediment along the southwestern coast of Taiwan in China contains TMPs, mainly related to thermal power plants along the coast (Horng et al., 2009). In the Yellow and Bohai shelf seas, research on aerosols in the eastern shelf seas has found that the total iron content decreases from north to south, in the order of Bohai>Yellow Sea>East China Sea (Qiu, 2015), reflecting the transport of source materials to the sea under the influence of the East Asian winter monsoon. Although there have been no published research results on TMPs in this area, the changes in total iron content may indirectly reflect the distribution characteristics of TMPs.

#### 4.2. Vertical distribution

The magnetic spherules in ancient sedimentary layers can reflect volcanic eruptions, cosmic events, etc.. Meanwhile, the change trend of the number of TMPs in shallow sediment layers over time can indirectly reflect changes in human activities such as industrial development (Sarkar et al., 2015; Ma et al., 2015; Szuszkiewicz et al., 2016; Magiera et al., 2021). There have also been studies using this characteristic to determine the sedimentary layers since the Industrial Revolution.

A 6 m sediment core was taken from Lake Crummock in the northwest of the UK, and research found that TMPs in lake sediments increased from about 30 particles per gram to about 2000 particles per gram before and after the Industrial Revolution, clarifying the time limit of 1900 in sediment (McLean, 1991). In the sediment of Michigan Lake, it was found that the content of TMPs in the upper few centimeters of sediment could even reach 50%, while in the sediment at a depth of 20 cm, which was 1800 years ago, there were almost no TMPs (Locke and Bertine, 1986).

The changes in the number of TMPs in lake sediment can be traced back to different stages of the Industrial Revolution in the UK since 1850, such as the steam engine era (1850-1950s), the coal-fired power plant era (1900-1970s), and the coal burning records of the household coal-fired era, where the peak coal consumption corresponds to the peak TMPs content. The content of TMPs rapidly decreased after 1960, mainly due to the enactment of laws to control coal combustion and the use of other alternative energy sources at that time. This example also illustrates that the distribution of TMPs is influenced by coal consumption and policies (Locke and Bertine, 1986).

In the soil profile of Baoshan area of Shanghai in China, it was found that the upper 20 cm of soil contains a large number of TMPs (40-125  $\mu$ m), but soil samples below 20 cm have fewer TMPs (Wang et al., 2013). TMPs produced by coal combustion have also been found in coastal sediments, such as in sediments along the southwestern coast of Taiwan, where the vertical contents of TMPs in sediment core change, documenting the rapid development of the coal-fired industry near southwestern Taiwan (Horng et al., 2009).

#### 5. The impact of TMPs on the marine sedimentary environment

#### 5.1. Impact on magnetic signals of marine sediments

The mechanism of residual magnetism acquisition in marine sediments and the disturbance changes of magnetic recording signals are important foundations for environmental magnetic research. Due to the presence of various magnetic minerals from different sources in marine sediments and the influence of physical and chemical processes, complex changes in sediment magnetic records can occur. Especially in the marine sedimentary layers affected by human activities, the influence of TMPs on sediment magnetic signals has been less considered. In fact, due to the

presence of a large amount of iron oxide (Fe<sub>3</sub>O<sub>4</sub>) in TMPs, TMPs themselves have strong magnetism. If the amount of TMPs is large, it will have a significant impact on the magnetic signal of sediments (Locke and Bertine, 1986; Tang et al., 2010 Magiera et al., 2023).

In terrestrial environments, studies have found that wind dust, soil, and sediment rich in magnetic spherules generally have high magnetic susceptibility, so magnetic susceptibility is often used to represent the content of magnetic spherules. For example, in the suburbs of Luoyang of China, the magnetic susceptibility of soil rich in TMPs ( (400-3500) × 10-8 m³kg-1) is about 5-10 times the magnetic susceptibility of general soil (average 118.6 × 10-8 m³kg-1) (Lu et al., 2016). The white grass and wood ash generated by high-temperature combustion has a high magnetic susceptibility of about 200×10-8 m³kg-1 due to the existence of TMPs formed during combustion. Meanwhile, the black grass and wood ash formed by low-temperature combustion does not contain TMPs, with a magnetic susceptibility of about (20-40) × 10-8 m³kg-1 (Menshikova et al., 2020). Kim et al. (2008) found that outdoor building roof samples collected in Seoul, South Korea had higher magnetic susceptibility and more magnetic components than the Chinese loess samples, which were thought the source of roof samples. They believed that this was the result of wind dust mixing into a large amount of TMPs during transportation through industrial areas.

In the sediment of Lake Michigan in the United States, it was found that the content of TMPs was high in the upper several centimeters of sediment. However, below a depth of 20 cm, which was 1800 years ago, there were almost no TMPs in the sediment. This resulted an increase in magnetic properties in shallow sediments and a decrease in magnetic properties in lower sediments (Locke and Bertine, 1986). A study on the vertical magnetic profile of soil in Baoshan area of Shanghai found that the upper 20 cm of soil contains a large number of TMPs, but soil samples below 20 cm have fewer magnetic spherical particles, with an average magnetization of about  $120 \times 10^{-8} \, \text{m}^3 \text{kg}^{-1}$  from the upper section to approximately  $12 \times 10^{-8} \, \text{m}^3 \text{kg}^{-1}$  of the lower section (Wang et al., 2013). Within a sediment thickness of about 50 cm in the soil layer near urban thermal power plants, magnetism decreases from the surface layer downwards, which is related to the lower content of TMPs in the lower layer (Tang et al., 2010).

In nearshore sedimentary areas, such as the southwestern sea area of Taiwan, researchers found TMPs in four core samples (around 30cm each core), with the maximum number of TMPs corresponding to their peak magnetic parameters. Researchers believe that the number of TMPs is mainly controlled by the atmospheric emissions from heavy industry production in southwestern Taiwan (Horng et al., 2009).

The magnetic susceptibility of sediment ( $\chi$ ) can reflect the number of TMPs and the ratio parameter  $\chi_{ARM}/\chi$  can also reflect the particle size of TMPs, with smaller values indicating larger particle sizes (Jordanova et al., 2006; Horng et al., 2009). The Hard Isothermal Residual Magnetism (HIRM) indicates the content of hematite in TMPs. For example, in southwestern Taiwan, before the large-scale outbreak of industrial production, the magnetic minerals in sediments entering nearby shallow waters were mainly magnetite and pyrrhotite. However, after the large-scale industrial production began, the magnetic minerals were mainly spherical magnetite and hematite caused by coal combustion (Horng et al., 2009).

During the study of the topsoil samples in the vicinity of 4 European iron- and steelworks (Poland, Norway, and Czech Republic), it is found that the TMP produced by the iron and steel metallurgy had relatively narrow ranges of magnetic parameters (saturation ratio Mrs/Ms, <0.15, coercivity ratio Bcr/Bc 2.5–6.0 and saturation to susceptibility ratio Mrs/ $\chi$  3.5–15). These magnetic parameters may be indicative for TMPs and helpful in the study of pollution sources in topsoil in urban and post-industrial areas (Magiera et al., 2021).

#### 5.2. Impact on heavy metal enrichment in sediments

When the TMPs are discharged into the air, a portion of them settle on land and merge into rivers into the continental shelf and sea, and part of them enter the continental shelf and sea directly through wind transport in the atmosphere. The heavy metal elements carried during the formation process of these TMPs can be incorporated into the lattice structure of magnetic particles or adsorbed

onto their surfaces (Lu et al., 2016; Kelepertzis et al., 2019), causing an enrichment of heavy metal content in sediment in the settling zone. TMPs can also lose stability under extreme conditions, releasing heavy metals and polluting the sedimentary environment, thus also having a significant impact on the marine ecological environment here (Lu et al., 2009).

In the area of Brynica River basin of the southern Poland, historical TMPs resulting from exploitation, processing, and smelting of iron, silver, and lead ores were accumulated in the soil layer at the depth 10 to 25 cm, which also show the magnetic peak. Thus the magnetic peak is consistent with the presence of charcoal and pollution from heavy metals, such as Ag, Cd, Cu, Fe, Pb, or Sn (Magiera et al., 2016)

In the study of soil, road, and house dust in heavy industrial areas of Greece, it was found that there are many TMPs in the samples, usually containing certain amounts of Cr, Cu, Mn, Pb, and Zn, which may come from emissions from steel plants. A study on dust from 43 houses in the most populous city of Athens, Greece, also found the widespread presence of TMPs. The EF values of Cd, Cu, Zn, and Pb in the samples are all higher than 5, indicating a correlation with human activities (Kelepertzis et al., 2019; 2021). In the study of road sediments in Indiana, the presence of TMPs was found, with most particles containing high concentrations of Ca, Si, Fe, and Mn. The geological accumulation indexes of Cr, Mn, and Zn in the samples are all >1, and the enrichment factor is >4, indicating the generation of anthropogenic pollution sources. The concentration of Mn is particularly high, with a hazard index >1, which may have an impact on the growth of children in the region (Dietrich et al., 2019).

In the study of the characteristics of street dust in typical rapidly developing industrial cities in Loudi City, Hunan Province of China, it was found that the dust samples contained TMPs, mainly from iron smelting plants. There is a significant positive correlation between contents of Co. Fe. Mo and magnetic parameters (Ms, SIRM,  $\chi$ ), which indicate that Co, Fe, Mo and TMPs are homologous. Meanwhile, the pollution levels of heavy metals Fe, Pb, Zn, Cu, V, Mo, Cd, Ni, Co, Be, and Cr are high and moderate (Zhang et al., 2012). In the surface soil of Delhi, India, it is found that the concentration of TMPs not only reflects the degree of magnetic pollutants in cities, but also reflects the concentration of heavy metals in cities (Meena et al., 2011).

#### 5.3. Contribution to active iron

The TMPs not only carry heavy metals but also iron oxides into the ocean. Therefore, after TMPs enter the ocean, a portion of them will enter the early diagenesis process driven by organic matter degradation as sediment accumulates. The divalent iron ions (Fe (II), a part of active iron, Mortimer et al., 1999) produced by the reduction of iron oxides by organic matter will migrate upwards and downwards, often stimulating algal blooms and leading to negative ocean carbon emissions (Zhao et al., 2018; Vosteen et al., 2022).

Research has found that Fe (II) is commonly present in estuarine and shelf surface sediments. In studies of active iron in multiple marginal seas, it was found that 25-62% of highly active organic complex Fe (III) enters shelf sediments through flocculation or precipitation and is rapidly reduced to Fe (II), which is four times higher than that of deep-sea sediments (Barber et al., 2017; Xiao et al., 2019). The surface sediments of the South Yellow Sea and the southern Bohai Sea in China are both highly active iron zones (Tao et al., 2017; Song Jinming and Li Pengcheng, 1996). TMPs also distributed in the shallow surface of sediments, contain a large amount of iron oxides, and their contribution to the active iron content here needs further research.

#### 6. Existing problems and future development

In summary, although a lot of work has been done on the properties and environmental pollution of TMPs in terrestrial environments, research on the characteristics and distribution of TMPs in continental shelf seas, as well as sedimentary environmental effects, is still weak. There is still a lack of understanding of the impact of TMPs on the magnetic signals, heavy metals, and active iron content of sediments after entering continental shelf seas. Therefore, for the study of TMPs in continental shelf seas, attention should be paid to the following aspects:

8

Firstly, due to the long-distance transportation of magnetic particles reaching the continental shelf sea, their morphological characteristics should be different from the land environment near thermal power plants. For example, the size of TMPs should smaller than those in the terrestrial environments due to the long distance transportation. Therefore, it is necessary to understand the basic characteristics and distribution pattern of TMPs in the continental shelf sea;

Secondly, due to the fact that the TMPs in modern sediments mainly come from industrial coal combustion and are typical artificial products, the sedimentary layers and boundaries since the Industrial Revolution can be well determined in the vertical distribution of continental shelf seas. Therefore, TMPs can be combined with other dating methods to determine the history of human activities on continental shelf seas;

The third is the impact of TMPs in continental shelf and marine sediments on the sedimentary environment, including their contribution to the magnetic properties of the sediment, the impact of heavy metal pollution, and the contribution of active iron.

Overall, the study of the characteristics of TMPs in shelf seas and their impact on the environment will provide a new perspective to understand the impact of human activities on the sedimentary environment of shelf seas, and provide targeted theoretical support for the improvement and management of offshore environment.

**CRediT authorship contribution statement:** Wang Yong-Hong: Conceptualization, Writing, Revision, Supervision, Funding acquisition. Liang Meng-yao: Material collection, Writing. Xiao Chun-Hui: Material collection, Figure.

**Acknowledgments:** This research was funded jointly by the General Program of National Natural Science Foundation of China (42376163), the Shandong Provincial Natural Science Foundation, China (ZR2022MD109), the Special Survey of Basic Scientific and Technological Resources (2022FY202402), and National Key Research and Development Program (2016YFC0402602).

**Declaration of competing interest:** The authors declare no conflict of interest.

#### References

- Andronikov, A.V., Andronikova, I.E., Loehn, C.W., Lafuente, B., Ballenger, J., Crawford, G.T., 2016. Implications from chemical, structural and mineralogical studies of magnetic microspherules from around the lower younger dryas boundary (New Mexico, USA). Geografiska Annaler 98(1), 39-59.
- 2. Ayrault, S., Catinon, M., Boudouma. M., Bordier, L., Agnello, G., Reynaud, S., Tissut, M., 2016. Metal exposure in cows grazing pasture contaminated by iron industry: Insights from magnetic particles used as tracers. Environmental Pollution 212: 565-573
- 3. Barber, A., Brandes, J., Leri, A., Lalonde, K., Balind, K., Wirick, S., Wang, J., Gélinas, Y., 2017. Preservation of organic matter in marine sediments by inner-sphere interactions with reactive iron. Science Report, 7, 366
- 4. Bourliva, A., Papadopoulou L., Aidona, E., Giouri, K., Simeonidis, K., Vourlias, G., 2017. Characterization and geochemistry of technogenic magnetic particles (TMPs) in contaminated industrial soils: Assessing health risk via ingestion. Geoderma 295: 86–97
- 5. Catinon, M., Ayrault, S., Boudouma O., Bordier L., Agnello, G., Reynaud S., Tissut, M., 2014. Isolation of technogenic magnetic particles. Science of the Total Environment 475: 39–47
- 6. Del Monte, M., Nanni, T., Tagliazucca, M., 1975. Ferromagnetic volcanic particulate matter and black magnetic spherules: a comparative study. Journal of Geophysical Research, 80(14), 1880-1884.
- 7. Dietrich, M., Wolfe, A., Burke, M., Krekeler, M.P.S., 2019. The first pollution investigation of road sediment in gary, indiana: anthropogenic metals and possible health implications for a socioeconomically disadvantaged area sciencedirect. Environment International, 128, 175-192.
- 8. Doyle, L.J., Hopkins, T.L., Betzer, P.R., 1976. Black magnetic spherule fallout in the eastern gulf of Mexico. Science, 194(4270): 1157-1159.
- 9. Fomenko, E.V., Anshits, N.N., Solovyov, L.A., Knyazev, Y.V., Semenov, S.V., Bayukov, O.A., Alexander G. Anshits, G.A., 2021. Magnetic fractions of pm 2.5, pm 2.5–10, and pm 10 from coal fly ash as environmental pollutants. ACS Omega. 6, 30: 20076–20085
- 10. Genge, M.J., Engrand, C., Gounelle, M., Taylor, S., 2008. The classification of micrometeorites. Meteoritics & Planetary Science, 43(3), 497-515.
- 11. Glass, B.P., Huber, H., Koeberl, C., 2004. Geochemistry of Cenozoic microtektites and clinopyroxene bearing spherules. Geochimica et Cosmochimica Acta 68(19): 3971-4006.

- 12. Grimley, D.A., Arruda, N.K., 2007. Observations of magnetite dissolution in poorly drained soils. Soil Science, 172: 968–982.
- 13. Grimley, D.A., Anders, A.M., Bettis, E.A., Bates, B.L., Wang, J.J., Butler, S.K., Huot, S., 2017. Using magnetic fly ash to identify post-settlement alluvium and its record of atmospheric pollution, central USA. Anthropocene 17: 84-98.
- 14. Grimley, D.A., Lynn, A.S., Brown, C.W., Blair, N.E., 2021. Magnetic fly ash as a chronological marker in post-settlement alluvial and lacustrine sediment: examples from North Carolina and Illinois. Minerals 11(5): 476.
- 15. Horng, C.S., Huh, C.A., Chen, K.H., Huang, P.R., Hsiung, K.H., Lin, H.L., 2009. Air pollution history elucidated from anthropogenic spherules and their magnetic signatures in marine sediments offshore of Southwestern Taiwan. Journal of Marine Systems 76(4): 468-478.
- 16. Hu, L.M., Wang, P., Zhang, G.S., Liu, G.S., Li, Y., Shen, T.Y., Crittenden, J.C., 2020. Enhanced persulfate oxidation of organic pollutants and removal of total organic carbons using natural magnetite and microwave irradiation. Chemical Engineering Journal 3831: 123-140.
- 17. Huang, C., Xu, R., Gong, Y.M., 2012. Microspherules: important information carriers bridging microscopic and cosmicoscopic worlds, Earth science Journal of China University of Geosciences 37(S2): 97-116. (in Chinese with an English abstract)
- 18. Iyer, S.D., Mascarenhas-Pereira, M.B.L., Nath, B.N., 2007. Native aluminium (spherules and particles) in the Central Indian basin sediments: implications on the occurrence of hydrothermal events. Marine Geology 240(1-4): 177-184.
- 19. Jordanova, V.K., Miyoshi, Y.S., Zaharia, S., Thomsen, M.F., Reeves, G.D., Evans, D.S., 2006. Kinetic simulations of ring current evolution during the geospace environment modeling challenge events. Journal of Geophysical Research Space Physics 111(A11).
- 20. Kelepertzis, E., Argyraki, A., Botsou, F., Aidona, E., Szabóet, Á., Szabo, C., 2019. Tracking the occurrence of anthropogenic magnetic particles and potentially toxic elements (PTEs) in house dust using magnetic and geochemical analyses. Environmental Pollution 245: 909-920.
- 21. Kelepertzis, E., Chrastný, V., Botsou, F., Sigala, E., Kypritidou, Z., Komárek, M., Skordas, K., Argyraki, A., 2021. Tracing the sources of bioaccessible metal(loid)s in urban environments: A multidisciplinary approach. Science of the Total Environment 77: 144827.
- 22. Kim, W., Doh, S.J., Yu, Y., Lee, M., 2008. Role of Chinese wind-blown dust in enhancing environmental pollution in Metropolitan Seoul. Environmental Pollution 153(2): 333-341.
- 23. Locke, F., Bertine, K.K., 1986. Magnetite in sediments as an indicator of coal combustion. Applied Geochemistry 1: 345-356.
- 24. Lu, S.G., Chen, Y.Y., Shan, H.D., Bai, S.Q., 2009. Mineralogy and heavy metal leachability of magnetic fractions separated from some Chinese coal fly ashes. Journal of Hazardous Materials 169(1-3): 246-255.
- 25. Lu, S., Yu, X., Chen, Y., 2016. Magnetic properties, microstructure and mineralogical phases of technogenic magnetic particles (TMPs) in urban soils: Their source identification and environmental implications. Science of the Total Environment 543: 239-247.
- 26. Ma, M.M., Hu, S.Y., Cao, L.W., Appel, E., Wang, L.S., 2015. Atmospheric pollution history at Linfen (China) uncovered by magnetic and chemical parameters of sediments from a water reservoir. Environmental Pollution 204: 161-172.
- 27. Menshikova, E., Osovetsky, B., Blinov, S., Belkin, P., 2020. Mineral Formation under the Influence of Mine Waters (The Kizel Coal Basin, Russia). Minerals 10(4): 364.
- 28. Magiera, T., Jablońska, M., Strzyszcz, Z., Rachwal, M., 2011. Morphological and mineralogical forms of technogenic magnetic particles in industrial dusts. Atmospheric Environment 45(25): 4281-4290.
- Magiera, T., Parzentny, H., Łukasik, A., Leokadia Róg, L., Chybiorz, R., Wawer, M., 2015. Spatial variation
  of soil magnetic susceptibility in relation to different emission sources in southern Poland Geoderma (255
   256): 94–103
- 30. Magiera, T., Gołuchowska, B., Jabłońska, M., 2013. Technogenic magnetic particles in alkaline dusts from power and cement plants. Water Air Soil Polluting 224 (1): 1389.
- 31. Magiera, T., Parzentny, H., Łukasik, A., 2016. The influence of the wind direction and plants on the variability of topsoil magnetic susceptibility in industrial and urban areas of southern Poland. Environ. Earth Sci 75 (3): 1–11.
- 32. Magiera, T., Mendakiewicz, M., Szuszkiewicz, M., Jabłońska, M., Chróst, L., 2016. Technogenic magnetic particles in soils as evidence of historical mining and smelting activity: A case of the Brynica River Valley, Poland. Science of the Total Environment 566–567: 536–551.
- 33. Magiera, T., Zawadzki, J., Szuszkiewicz, M., Fabijańczyk, P., Steinnes, E., Fabian, K., Miszczak, E., 2018. Impact of an iron mine and a nickel smelter at the Norwegian/Russian border close to the Barents Sea on surface soil magnetic susceptibility and content of potentially toxic elements. Chemosphere 195: 48–62.

- 34. Magiera, T., Górka-Kostrubiec, B., Szumiata, T., Wawer, M., 2021. Technogenic magnetic particles from steel metallurgy and iron mining in topsoil: Indicative characteristic by magnetic parameters and Mössbauer spectra. Science of the Total Environment 775: 145605.
- 35. Magiera, T., Górka-Kostrubiec, B., Szumiata, T., Bućko, S.M., 2023. Technogenic magnetic particles in topsoil: Characteristic features for different emission sources. Science of the Total Environment 865: 161186
- 36. McLean, D., 1991. Magnetic spherules in recent lake sediments. Hydrobiologia 214: 91-97.
- 37. Meena, N.K., Maiti, S., Shrivastava, A., 2011. Discrimination between anthropogenic (Pollution) and lithogenic magnetic fraction in urban soils (Delhi, India) using environmental magnetism. Journal of Applied Geophysics 73(2): 121-129.
- 38. Mortimer, R.J.G., Davey, J.T., Krom, M.D., 1999. The effect of macrofauna on porewater profiles and nutrient fluxes in the intertidal zone of the Humber Estuary. Estuarine, Coastal and Shelf Science, 48(6), 683-699.
- 39. Murray, J., Renard, A., 1891. Deep sea deposits. In Challenger Reports. Longman, London, 525p.
- 40. Qiu, S., 2015. Solubility of iron in atmospheric aerosols and related factors in Marginal Seas, China. Qingdao: Ocean University of China. (in Chinese with an English abstract)
- 41. Rachwal, M., Magieral, T., Wawer, M., 2015. Coke industry and steel metallurgy as the source of soil contamination by technogenic magnetic particles, heavy metals and polycyclic aromatic hydrocarbons. Chemosphere, 138, 863-873.
- 42. Sarkar, S., Ahmed, T., Swami, K., Judd, C.D., Bari, A., Dutkiewicz, V.A., Husain, L., 2015. History of atmospheric deposition of trace elements in lake sediments, ~1880 to 2007. Journal of Geophysical Research: Atmospheres, 120, 5658-5669.
- 43. Shetye, S.S., Rudraswami, N.G., Nandakumar, K., Manjrekar, S., 2019. Anthropogenic spherules in Zuari estuary, south west coast of India. Marine Pollutin Bulletin. 143, 1-5.
- 44. Song, J.M., Li, P.C., 1996. Active iron and redox envieonment of sediments in the Southeren Bohai sea. Marine science, 1, 32-36. (in Chinese with an English abstract)
- 45. Sun, J.M., Yao, Q., Liu, H.Y., Xu, X.C., 2005. Microstructure and mineral characteristics of ferruginous sphere in fly ash. Journal of Fuel chemistry and Technology, 33(3), 264-266. (in Chinese with an English abstract)
- 46. Szr, G., Elekes, Z., Rózsa, P., Uzonyi, I., Kiss, Z., 2001. Magnetic spherules: cosmic dust or markers of a meteoritic impact. Nuclear Instruments & Methods in Physics Research, 181(1-4), 557-562.
- 47. Szuszkiewicz, M., Magiera, T., Kapička, A., Petrovský, E., Grison, H., Gołuchowska, B., 2015. Magnetic characteristics of industrial dust from different sources of emission: A case study of Poland. Journal of Applied Geophysics 116: 84–92
- 48. Szuszkiewicz, M., Lukasik, A., Magiera, T., Mendakiewicz, M., 2016. Combination of geo- pedo- and technogenic magnetic and geochemical signals in soil profiles Diversification and its interpretation: A new approach. Environmental Pollution 214: 464-477
- 49. Tan, Z., Lu, S., Zhao, H., Xiao, K., Peng, J.X., Myat Sandar, W., Yu, S., Yonemochi, S., Wang, Q.Y., 2018. Magnetic, geochemical characterization and health risk assessment of road dust in Xuanwei and Fuyuan, China. Environmental Geochemistry and Health, 40, 1541-1555.
- 50. Tang., L.L., Wang, Z.F., Ma, S.M., 2010. Environmental characteristics of magnetic micro—particles derived from coal combustion in soil of peripheral areas of cities. Acta Petrologica et Mineralogica, 29(3):319-324. (in Chinese with an English abstract)
- 51. Tao., J., Ma, W.W., Li, W.J., Li, T., Zhu, M.X., 2017. Organicarbon preservation by reactive iron oxides in South Yellow Sea sediments, Haiyang Xuebao, 39(8):16-24. (in Chinese with an English abstract)
- 52. Tian, Y.H., Liu, H., Wu, Y.Q., Si, Y.Q., Song, J., Cao, Y.Y., Li, M., Wu, Y., Wang, X.W., Chen, L.B., Wei, C., Gao, P., Hu, Y.H., 2019. Association between ambient fine particulate pollution and hospital admissions for cause specific cardiovascular disease: time series study in 184 major Chinese cities. British Medical Journal, 367, 16572.
- 53. Teller, J., Boyd, M., LeCompte, M., Kennett, J., West, A., Telka, A., Diaz, A., Adedej, V., Batchelor, D., Mooney, C., Garcia, R., 2020. A multi-proxy study of changing environmental conditions in a Younger Dryas sequence in southwestern Manitoba, Canada, and evidence for an extraterrestrial event. Quaternary Research, 93(1), 60-87.
- 54. Uzarowicz, L., Gorka-Kostrubiec, B., Dudzisz, K., Rachwal, M., Zagorski, Z., 2021. Magnetic characterization and iron oxide transformations in Technosols developed from thermal power station ash. Catena 202: 105292
- 55. Vassilev, S.V., Menendez, R., Borrego, A.G., Diaz-Somoano, M., Rosa Martinez-Tarazona, M., 2004. Phase mineral and chemical composition of coal fly ashes as a basis for their multi-component utilization. Characterization of magnetic and char concentrates. Fuel, 83(11-12), 1563-1583.
- 56. Vasiliev, A., Gorokhova, S., Razinsky, M., 2020. Technogenic magnetic particles in soils and ecological-geochemical assessment of the soil cover of an industrial city in the ural, Russia. Geosciences. 10(11), 443...

- 58. Wang, G., Chen, Y.Y., Zhang, W.G., Ren, F.F., Fang, A.D., Chen, J., Mzuza, M.K., 2022. Magnetic response of urban topsoil to land use type in Shanghai and its relationship with city gross domestic product. Applied Geophysics. 200, 104623.
- 59. Wang, Y.H., Oguchi, T., Ridd, P.V., Shen, H.T., 2013. Anthropogenic influence on sedimentation during the last 100 years inferred from magnetic properties in the Changjiang Estuary, China. Environmental Earth Sciences, 70, 1671-1680.
- 60. Xiao, X.Y., Ouyang, Z.Y., 1984. A Study on the Chemical Composition of Cosmic Dust Samples. Geology and geochemistry, 3, 28-34. (in Chinese with an English abstract)
- 61. Xiao, L., Wang, Di, Ma, W.W., 2019. Kinetic characterization of reactivity of iron dissolution and phosphorus release in surface sediments of the Changjiang (Yangtze) River Estuary and the adjacent East China Sea. Haiyang Xuebao, 41(12): 1-13 (in Chinese with an English abstract)
- 62. Xu, W.X., Sun, J.Q., Liu, Y.X., Xiao, Y., Tian, Y.Z., Zhao, B.X., Zhang, X.Q., 2019. Spatiotemporal variation and socioeconomic drivers of air pollution in China during 2005–2016. Journal of Environmental Management, 245, 66-75.
- 63. Yan, Q., Kong, S.F., Liu, H.B., Wang W., Wu, J., Zheng M..M., Zheng, S.R., Yang, G.W., Wu, F.Q., 2018. Emission factors of heavy metals in size-resolved particles emitted from residential coal combustion. Environmental Science, 39(04), 1502-1511. (in Chinese with an English abstract)
- 64. Yin, Y.H., Chen, Z.X., Sun J.S.. 2006. The discovery and the significance of the rich layer of magnetis miron pellets in Holocene in the central part of southern Huanghai Sea. Acta oceanologica Sinica. 4, 153-158. (in Chinese with an English abstract)
- 65. Yu, Z., Peng H.C., Zhuang, S.J.. 1984. A Study on Magnetic Microspheres in Drilling Cores from the South China Sea. Geological Science, 1, 98-104. (in Chinese with an English abstract)
- 66. Zhang, C.X., Qiao, Q.Q., Appel, E., Huang, B.C., 2012. Discriminating sources of anthropogenic heavy metals in urban street dusts using magnetic and chemical methods. Journal of Geochemical Exploration, (119-120): 60-75
- 67. Zhang B.M., Li R.Q., You C.J., Jia T.F.. 1993. A Study on Black Magnetic Spheroids in the Soil Layer of Dongling Mountain. Science Bulletin, 12, 1113-1117.
- 68. Zhang H., 2007. Microspherules in the geologic record. Journal of Stratigraphy. 31(2), 7.110-116
- 69. Zhang, H., Shen, S.Z., Cao, C.Q., Zheng, Q.F., 2014. Origins of microspherules from the Permian riassic boundary event layers in South China. Lithos, 204(3), 246-257.
- 70. Zhao, B., Yao, P., Bianchi, T.S., Shields, M.R., Cui, X.Q., Zhang, X.W., 2018. The role of reactive Iron in the preservation of terrestrial organic carbon in estuarine sediments. Journal of Geophysical Research: Biogeosciences, 123, 3556–3569.
- Zhao, B., Yao, P., Bianchi, T.S., Yu, Z.G., 2021. Controls on organic carbon burial in the Eastern China Marginal Seas: A regional synthesis. Global Biogeochemical Cycles, 35, e2020GB006608.
   Zhu L., Lu, S.G., He, L.P.. 2004. Mineralogy, Morphology and Physical Properties of Fly Ashes. Bulletin of Science and Technology, 4, 359-362. (in Chinese with an English abstract).

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.