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MOBILITY OF CERIUM DIOXIDE NANOPARTICLES IN SOILS AT DIFFERENT EXPOSURE SCENARIOS

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Nowadays, widespread application of engineered nanoparticles (ENPs) inevitably leads to their release into the environment. Soils are regarded as the ultimate sink for ENPs. The study on the mobility of ENPs in soils is important in the assessment of potential risks related to their toxicity. The behavior of ENPs depends not only on the parameters of soil, but also on the exposure scenarios, namely, the amount of ENPs trapped in soil. We studied the mobility of cerium dioxide nanoparticles ($n\mathrm{CeO_2}$) in soils at different exposure scenarios. The relationship between the mobility of $n\mathrm{CeO_2}$ and their concentration in the soil within the range 1 – 1000 µg/g is evaluated. It is shown that the mobility of $n\mathrm{CeO_2}$ decreases with a decrease in their concentration in the soil and attains the minimum value when the concentration of $n\mathrm{CeO_2}$ goes below 10 µg/g. In relative units, only about 0.1 – 0.2% of $n\mathrm{CeO_2}$ (in aforementioned concentration range) exhibit mobility and can migrate in the soil profile under saturated conditions. The lion's share of $n\mathrm{CeO_2}$ (about 99.8%) remains immobile in the soil. Evidently, the vertical transport of $n\mathrm{CeO_2}$ in soil profile should depend on the volume of released suspensions. In the case of small or moderate wet deposition, nanoparticles will accumulate in upper soil horizons characterized with the highest biological activity and thus can affect the soil inhabitants (plant roots, earthworms, insects, microorganisms, etc.).

Keywords: nanoparticles; cerium dioxide; soil; mobility; transport; exposure scenarios; microcolumn; ICP-MS.

Introduction

Nowadays, engineered nanoparticles (ENPs) are used in various fields of science and technology, e.g., in industry [1], medicine [2], agriculture [3], analytical chemistry [4], etc. A widespread application of ENPs inevitably leads to their release into the environment. The residence time of ENPs in solids dominated media (i.e. soils) is significantly higher than in aquatic systems. Therefore, considering different environmental compartments, soils are to be regarded as the ultimate sink for ENPs [5].

It is known that ENPs can be especially toxic and negatively affect the living organisms [6, 7]. Therefore, the risks associated with the presence of ENPs in soil should be assessed. These risks are strongly dependent on the mobility and bioavailability of ENPs. In turn, the mobility and bioavailability of ENPs in soil depend on their transformations, such as homo- and heteroaggregation, dissolution, chemical transformations, interactions with soil organic matter, etc. [8, 9]. It should be noted that mobility of ENPs is an important parameter, which determines their bioavailability and uptake by potential recipient. The probability that living organisms or plants can avoid exposure to poorly mobile ENPs spread in soil is relatively high [5]. The behavior of ENPs in soils is a very complicated phenomenon, which depends on different parameters of soil, such as type of soil [10, 11], clay content [12, 13], content of organic matter [14, 15], salinity [11, 16], etc. However, the fate of ENPs in soils is also dependent on exposure scenarios, namely the amount of ENPs released into the soil [5]. The amount of ENPs released into the soil can affect the homo- and heteroaggregation processes and hence the mobility as well as bioavailability of ENPs. There are two extreme exposure scenarios: (I) unintentional dispersed release of ENPs into the environment (e.g., wet and dry deposition) or (II) intentional localized release of large amounts of ENPs (e.g., the use of nanofertilizers, nanopesticides, etc.).

Cerium dioxide nanoparticles ($n\mathrm{CeO}_2$) are among the top-10 ENPs produced in the world [17]. Therefore, the release of $n\mathrm{CeO}_2$ into the environment is unavoidable. It was estimated that in 2010, the global production of $n\mathrm{CeO}_2$ reached 10000 tons, of which 1400 tons ended in soil [17]. Along with the application of $n\mathrm{CeO}_2$ in auto-industry, electronics, and optics, $n\mathrm{CeO}_2$ are also proposed to be used as nanofertilizers [18 – 21]. The release of $n\mathrm{CeO}_2$ into the soil can occur according to exposure scenarios mentioned above: (I) as a dispersed release via vehicle emissions, because $n\mathrm{CeO}_2$ are used as diesel fuel additives [22], and (II) as a concentrated deposition via use of, for example, $n\mathrm{CeO}_2$-based nanofertilizers.

The ecological risks of $n\mathrm{CeO}_2$ should be assessed. $n\mathrm{CeO}_2$ in soil can affect its inhabitants, such as plants, earthworms, microorganisms, etc. For example, the toxic effects from the exposure of soybean plants [23] and *Arabidopsis thaliana* [24] to $n\mathrm{CeO}_2$ were demonstrated. It should be noted that $n\mathrm{CeO}_2$ can stimulate plant growth at low concentrations, and can be toxic at high ones [24]. As a whole, results of use of $n\mathrm{CeO}_2$ as nanofertilizers are often ambiguous, and toxic effects of $n\mathrm{CeO}_2$ are observed.

Earthworms are in intimate contact with the soil and have a high potential for exposure to ENPs released into the soil. It is reported that the exposure of *Caenorhabditis elegans* to $n\mathrm{CeO}_2$ leads to their decreased survival [25, 26]. Furthermore, at environmentally relevant concentrations, exposure to $n\mathrm{CeO}_2$ was found to induce reactive oxygen species accumulation and oxidative damage in *C. elegans* [27]. Another study shows that exposure of *Eisenia fetida* to $n\mathrm{CeO}_2$ leads to histological changes that could indicate possible deleterious effects over long-term exposure [28]. In addition to invertebrates, $n\mathrm{CeO}_2$ can also affect the soil microbial communities; it is shown that $n\mathrm{CeO}_2$ increase the metabolic quotient ($q\mathrm{CO}_2$), probably due to microbial stress and changes in the composition of microbial communities inhabiting soil [29].

The aim of the present work is to study the mobility of ENPs in soils at different exposure scenarios, i.e., depending on their concentration. The study is performed using $n\mathrm{CeO}_2$ and chernozem soil samples. At present, chernozem soils are poorly studied in terms of mobility of ENPs [8]. Moreover, due to high fertility chernozem soils are often used in agriculture. Therefore, the study on the mobility of $n\mathrm{CeO}_2$ in chernozem is interesting for assessing the risks of their use as nanofertilizers.

Experimental

Samples and reagents. Cerium dioxide nanoparticles (Sigma Aldrich) with certified particle size distribution <50 nm were used. The study was performed using three chernozem soil samples collected during fieldwork in June – July 2017. The soil samples were stored at room temperature and humidity. Prior to study, the soil sample was sieved through 1 mm screen.

Deionized water with resistivity 18.2 MΩ · cm (Millipore) was used on all stages of the research.

Characterization of NPs and soil samples. Size distributions of NPs under study were measured by laser diffraction method (Shimadzu SALD-7500nano). The size and morphology of NPs were also characterized by scanning electron microscopy (JEOL JSM-6700F).

The elemental composition of soil samples before and after spiking with NPs was studied by inductively coupled plasma atomic emission spectrometry (ICP-AES, iCAP 6500 Duo, Thermo Scientific) and mass spectrometry (ICP-MS, XSeries, Thermo Scientific) after acid digestion. The digestion of soil was performed in an open beaker using a combination of three acids ($\mathrm{HClO_4}$, HF, $\mathrm{HNO_3}$). Geological certified reference material (Gabbro, GSO 521-84P, Russian CRM) was used to control the completeness of digestion. The digestion procedure was described in detail earlier [30, 31]. According to the procedure used the relative standard deviation (RSD) for the determination of low concentrations of elements (less than 5 × LOD, where LOD is the limit of detection) does not exceed 0.2. For higher concentrations of elements (greater than 5 × LOD), RSD does not exceed 0.1.

The content of total organic carbon in soils was determined using CNS analyzer (Elementar Vario EL III). Soil pH was measured in soil:water solution (1:2.5 wt.) by Hanna Instruments pH-meter.

Spiking soils with $n\mathrm{CeO}_2$. The soil samples were spiked with $n\mathrm{CeO}_2$ to reach the total concentration of $n\mathrm{CeO}_2$ in soil 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000 µg/g. $n\mathrm{CeO}_2$ were added to soil samples as water suspensions prepared using ultrasound treatment (60 W during 10 min). The volume of the suspensions was chosen to reach complete wetting of soil sample (saturation of pore volume), but to avoid the formation of supernatant. The weight ratio of $n\mathrm{CeO}_2$ suspension to soil sample was 0.75 – 1.

The suspensions $n\mathrm{CeO}_2$ were carefully poured to soil samples (2 g each) preliminarily placed in glass beakers. Then, the samples were left for 1 week for drying at room temperature and humidity. After drying soil samples were gently crushed with a spatula to initial state and scrupulously mixed for homogenization. Thus, ten soil samples with concentration of $n\mathrm{CeO}_2$ in the range 1 – 1000 µg/g were obtained for each soil under study.

Studying mobility of $nCeO_2$ in soils. The mobility of nCeO$_2$ in soils was studied using leaching experiments in microcolumn, constructed by the authors of present paper. Earlier, the similar microcolumn were used for the fractionation of toxic metals and metalloids in soils, sludge, and sediments [32]. Leaching of nCeO$_2$ from soil was performed using PTFE microcolumn with the following parameters: diameter — 7 mm, length — 28 mm, volume — 1 mL. The principal scheme of the column is presented in Fig. 1. Soil sample (0.2 g) was placed into the column, where it was held by cellulose membrane filters (Sartorius) with pore size 0.45 µm. The eluent (water) was pumped through the column at flow rate 1 mL/min. The direction of flow was “from bottom to top” to achieve complete saturation of soil column. The leachates (20 mL) were collected at the outlet of the column for further analysis by ICP-MS. It has been previously determined that 20 mL of eluent is sufficient to complete leaching of nCeO$_2$ [33]. All the leaching experiments were made in triplicate.

Analysis of leachates. The leachates were immediately analyzed by ICP-MS (Agilent 7900). The internal standard (Rh, 10 µg/L) was used during the analysis. The concentrations of Ce in leachates were determined at the following parameters: a RF generator power of 1550 W; a MicroMist nebulizer; a plasma-forming Ar flow rate of 15 L/min; an Ar flow rate into the nebulizer of 1.05 L/min; an analyzed sample flow rate of 1.0 mL/min. The standard solutions (High-Purity Standards) were used for calibration.

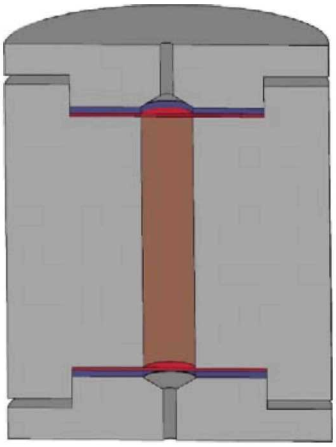

Fig. 1. Cross-section of microcolumn: PTFE column with screw caps (gray); silicone spacers (blue); membrane filters (red), soil sample (brown)

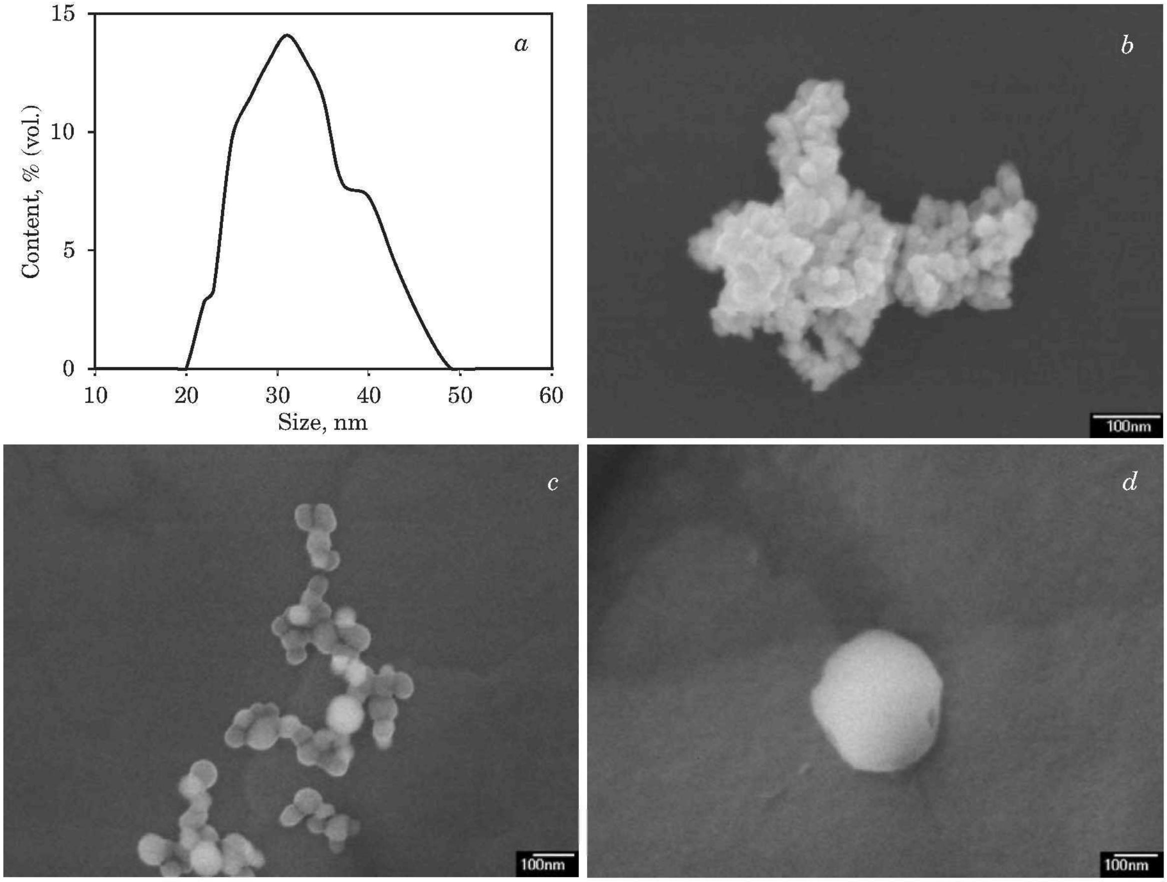

Fig. 2. Size distribution (*a*) and micrographs of nCeO$_2$ (*b* – *d*)

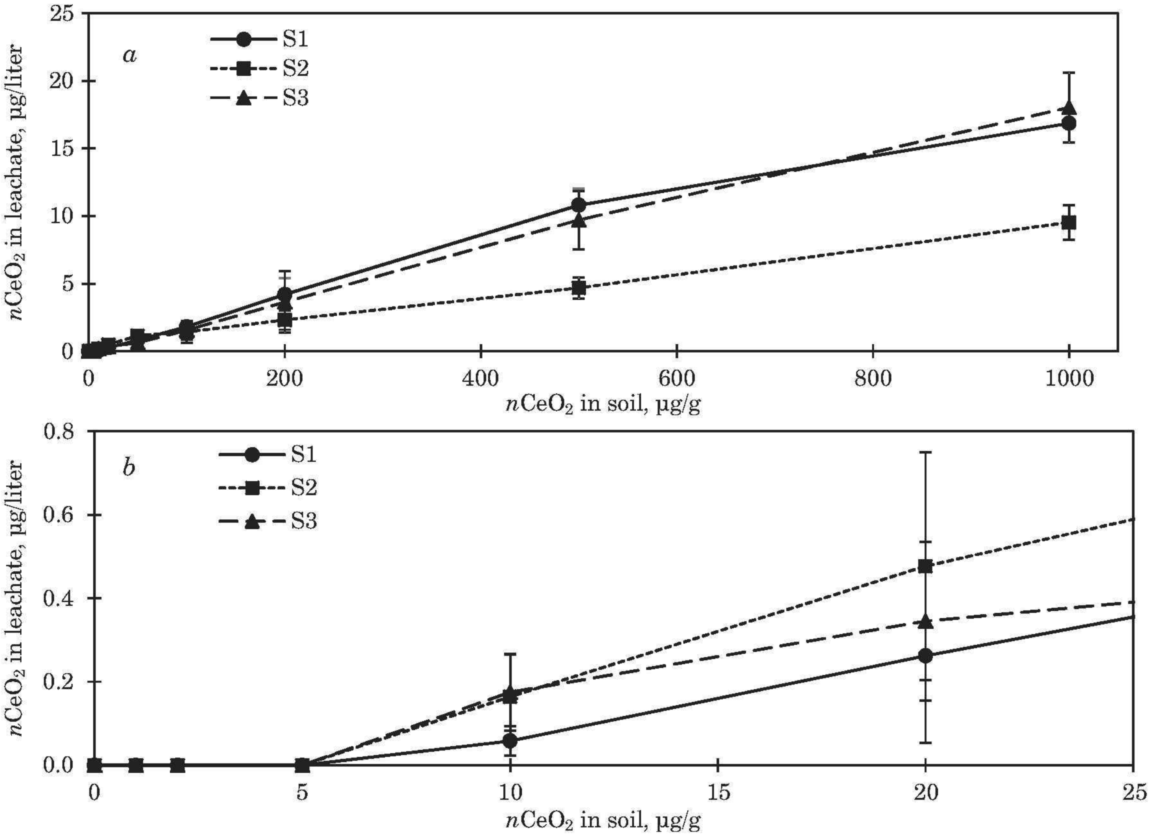

Fig. 3. Relationship between concentration of $n\mathrm{CeO_2}$ in soil and leachates as obtained by ICP-MS: *a* — full range of concentrations; *b* — low concentrations area (error bars indicate standard deviation)

Control experiments. The leaching experiments with soil without added $n\mathrm{CeO_2}$ were used as control ones. All the control experiments were made in triplicate.

Results and discussion

Characterization of $n\mathrm{CeO_2}$ and soils. Before commencing the study, the size distribution of $n\mathrm{CeO_2}$ was measured. The size distribution of $n\mathrm{CeO_2}$ is presented in Fig. 2, *a*. The median diameter of $n\mathrm{CeO_2}$ is 30 nm. The size and morphology of $n\mathrm{CeO_2}$ were also studied by scanning electron microscopy; the micrographs are presented in Fig. 2, *b* – *d*. In general, the size of $n\mathrm{CeO_2}$ (see Fig. 2, *b*) is in good agreement with obtained size distribution; however, particles up to about 300 nm in size are also presented in small amounts (see Fig. 2, *c*, *d*).

The physicochemical properties of soils are presented in the table below.

The mobility of $n\mathrm{CeO_2}$ in soils. On the basis of the results of analysis of leachates, the graphs representing the concentration of $n\mathrm{CeO_2}$ in leachates as a function of their concentration in soil have been obtained (Fig. 3). Nearly linear relationship between mobility of $n\mathrm{CeO_2}$ and their concentration in soil in the range 10 – 1000 µg/g has been found (see Fig. 3, *a*). As for soils with concentration of $n\mathrm{CeO_2}$ in the range 1 – 10 µg/g, the determined concentrations of Ce in leachates were the same as ones determined in control experiments (i.e., naturally occurring Ce in soil nanoparticles). Hence, it has been demonstrated that mobility of $n\mathrm{CeO_2}$ in soil decreases sharply with decreasing their concentration in soil below 10 µg/g (see Fig. 3, *b*). It can be assumed that soil has certain “retention capacity” for ENPs, so ENPs can be nearly completely immobilized at their low concentration in soil. It should be noted that $n\mathrm{CeO_2}$ may be leached at low concentration in soil (e.g., <10 µg/g); in this case for their accurate identification in soil leachates, the application of single particle-ICP-MS is needed.

The mobility of $n\mathrm{CeO_2}$ in soil as a function of their concentration has been also evaluated in relative terms (Fig. 4). It is shown that only about 0.1 – 0.2 % of $n\mathrm{CeO_2}$ added to soil are mobile and can migrate within soil profile under saturated conditions. The relationship between mobility of $n\mathrm{CeO_2}$ and their concentration in soil varies for soil samples under study; this can be attributed to the different parameters of soils [8]. It should be noted that the mobile fraction of $n\mathrm{CeO_2}$ remains nearly the same at their concentration in soil within the

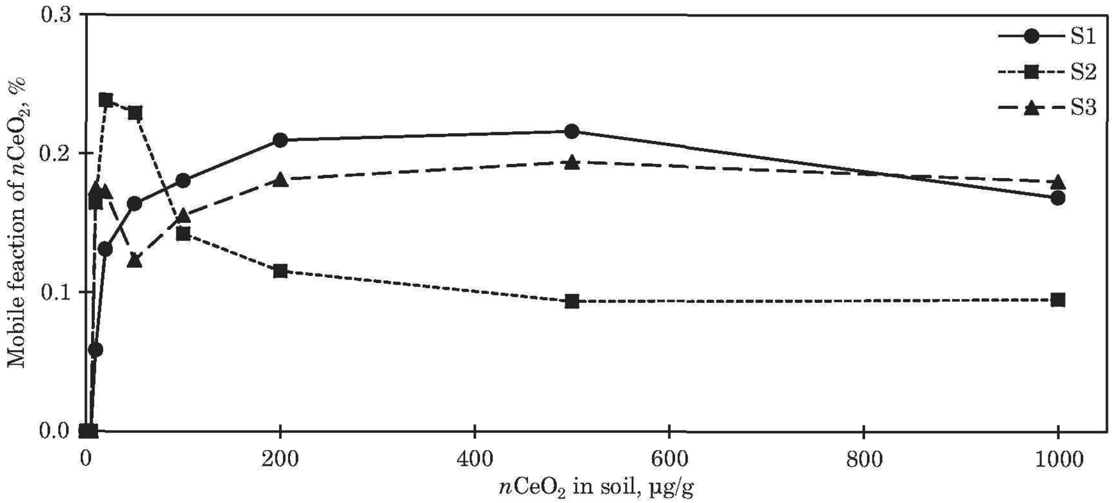

Fig. 4. Mobility of $nCeO_2$ in soil as a function of their concentration

range 100 – 1000 µg/g. The mobility of ENPs in soil is dependent largely on homo- and heteroaggregation processes. Homo- and heteroaggregation are defined as self-aggregation of ENPs and their aggregation with soil particles, correspondingly. Evidently, at high concentration of ENPs in soil the process of homoaggregation prevails. It can be assumed that highly concentrated deposition of $nCeO_2$ in soil leads to their homoaggregation. In the present work, the use of membrane (0.45 µm) at the outlet of soil column enables the leaching of large aggregates to be avoided. Therefore, the increase of mobile fraction of $nCeO_2$ with increasing their concentration in soil is not observed. It should be noted that removing the aggregates of ENPs from leachate is important in the assessment of mobility and environmental impact of nanoparticles (not their aggregates), which are of particular interest due to their toxicity.

Conclusion

In the present work, the mobility of $nCeO_2$ in soils at different exposure scenarios has been studied. The relationship between mobility of $nCeO_2$ and their concentration in soil in the range from 1 to 1000 µg/g is evaluated. It is shown that the mobility of $nCeO_2$ decreases with decreasing their concentration in soil. It should be noted that $nCeO_2$ nanoparticles remain immobilized in soil at their concentration below 10 µg/g. In relative terms, only about 0.1 – 0.2 % of $nCeO_2$ at their concentration in soil 10 – 1000 µg/g are mobile and can migrate within soil profile under saturated conditions. The major portion of $nCeO_2$ (about 99.8%) remains immobile in soil. Evidently, due to poor stability of $nCeO_2$ in water suspensions, their vertical transport in soil profile should depend on the volume of released suspensions. The greater the volume of suspension, the deeper $nCeO_2$ can infiltrate in soil profile. In the case of small volume of wet deposition, nanoparticles will accumulate in upper soil horizons, i.e., habitat for most plant roots, earthworms, insects, microorganisms, etc., where biological activity is highest. In this sense, such accumulation of ENPs in soil can have adverse effects for inhabitants.

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Description and physicochemical properties of soil samples

Parameter	Soil sample		
	S1	S2	S3
Sampling site	Kursk region, Russia (51.621417 °N 36.261667 °E)	Kursk region, Russia (51.330888 °N 35.511462 °E)	Lipetsk region, Russia (53.496117 °N 38.990066 °E)
Soil type	Typical chernozem	Typical chernozem	Leached chernozem
Horizon, cm	0 – 10	0 – 20	0 – 20
pH	7.80	5.62	5.31
Chemical composition, %			
Na_2O	0.82	0.78	0.73
MgO	1.1	0.9	1.3
Al_2O_3	10.3	9.2	11.7
P_2O_5	0.17	0.17	0.20
K_2O	2.3	2.3	2.3
CaO	1.7	1.2	1.5
TiO_2	0.58	0.52	0.59
MnO	0.09	0.07	0.09
Fe_2O_3	3.7	3.2	4.7
Organic carbon	2.93	3.56	4.35

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