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Does Soil Drying in a Lab Affect Arsenic Speciation in Strongly Contaminated Soils?

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Abstract: This study examined the changes in extractability and fractionation of arsenic (As) that can be caused by the drying of strongly polluted anoxic soil samples. Two untreated and manure-amended soils were incubated for 7 and 21 days in flooded conditions. Thereafter, As water- and 1 M NH_4NO_3-extractability and As fractionation in a 5-step sequential extraction according to Wenzel were examined in fresh, oven-dried and air-dried samples. Soil treatment with manure considerably affected the results of the sequential extraction. Air-drying caused a significant decrease in As extractability with 1 M NH_4NO_3 and in As concentrations in the F1 fraction. The highest reduction of extractability (30–41%) was found in manure-treated soils. Oven-drying resulted in a smaller reduction (5–34%) of As extractability. These effects were explained by opposing processes of As mobilization and immobilization. Sequential extraction did not allow for balancing As redistribution due to drying, as As loss from the F1 fraction was smaller than the confidence intervals in the other fractions. The results showed that for the precise determination of As extractability in anoxic soils, fresh samples should be analyzed. However, oven-dried samples may be used for a rough assessment of environmental risk, As the order of magnitude of easily soluble As did not change due to drying.

Keywords: arsenic; soil; extractability; fractionation; tailings; Złoty Stok; manure

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1. Introduction

Arsenic belongs to the most toxic elements; therefore, its high concentrations in the environment are always a matter of special concern [1,2]. Particularly, the strong enrichment of soils in As usually occurs in the sites associated with its historical mining and processing. One of these such sites is Złoty Stok (formerly Reichenstein), a leading European producer of arsenic for over two centuries, until 1962 [3–6]. The tailings, periodically released from impoundments, were flooding the valley of the Trująca ("poisonous") stream within a distance of ca. 2 km, causing a strong enrichment of soils in As. Its concentrations in soils in the valley reached values of 8000 mg/kg.

There is no need to emphasize that it is not the total concentrations, but primarily the soluble forms of toxic elements that determine the environmental risk associated with soil pollution. The approach based on the assessment of environmental risk has recently gained an increasing importance in the evaluation of the state of soil pollution [7]. The easily soluble forms of elements are usually determined in the extractions with water or diluted solutions of neutral salts, for instance 0.01 M $CaCl_2$ [8,9] or 1 M NH_4NO_3 [8,10], the latter having the status of ISO standard [11]. Potentially soluble forms of elements are those that can be released As a result of changing soil conditions, such As acidification, decomposition, or dissolution of solid soil components crucial for the binding of particular elements, for instance, the reductive dissolution of Mn and Fe (hydr)oxides in the case of As, oxidation of organic matter, etc. Sequential extraction is a very useful tool for assessing the potential solubility of toxic elements under various changes of soil conditions. It allows for the determination of operationally defined fractions of elements that can be released from the solid phase in well-defined circumstances. Numerous procedures of sequential extraction have been developed [8,12,13], among which the method proposed by Wenzel et al. [14], further referred to As the method by Wenzel, is most commonly used to examine the speciation of metalloids, such As As, and to assess their potential solubility.

Determination of the solubility/extractability of toxic elements in soils should always be preceded by a sample pretreatment, aimed at protecting it against possible changes in properties, for instance, due to biological processes, and allowing the sample to be stored for a certain time, and if necessary, analyzed again using standardized methods. The best, most frequently used method of sample preservation is drying. Oven-drying at 40, 60, or 105 °C is usually recommended for soil samples, and the alternative methods are air-drying and, less common, freeze-drying [15,16]. Several researchers have asked whether the process of drying could distort the information about the solubility of toxic elements in soils. The question arises of whether the release of trace metals and metalloids, such As As, from dried soil samples is representative of field conditions [16].

Various researchers have demonstrated that the drying of soil samples may increase the extractability of Fe, Cu, and Ni [17–20], i.e., the cationic elements, that have a high affinity to soil organic matter. Accelerated mineralization of organic matter [17,19,20] and an increase in the content of dissolved organic carbon [18,19,21] were most often reported As the main factors responsible for this effect. Hojdová et al. [22] also proved that soil drying influenced the total concentrations of Hg in soils. At this date, few studies have examined the extractability of As in soils, depending on the sample pretreatment. Huang et al. [23], Száková et al. [24], and Li et al. [25] investigated the impact of air-, oven-, and freeze-drying on the fractionation of As in spiked and moderately polluted soils, and indicated freeze-drying As the best method to minimize the effects on As extractability. However, so far, no studies have been carried out on anoxic soils highly enriched in As. It seems that the radical changes in As speciation due to drying can be expected in such soils, because of the strong susceptibility of soil As to the changes of redox potential. Under anoxic conditions, As can be released from the solid phase in effect of reductive dissolution of iron oxides and associated microbial transformations [1,2,5,26]. Soil treatment with organic matter, such As pig slurry, manure, sewage sludge, various organic waste materials, for instance compost and biochar, or forest litter may further contribute to the release of As from the soil solid phase [1,5,6,27–31]. Conversely, the drying process of anoxic samples may lead to the oxidation of As(III) and Fe(II) and their co-precipitation and crystallization, which may reduce As extractability. Numerous studies have analyzed the effects of alternate wetting and drying of rice paddy soils [32–35], but they did not provide a clear picture of how such processes affect As speciation and extractability.

The aim of this study was to examine the effects of two different drying methods on the extractability of As, and on its fractionation in soils heavily contaminated with tailings that were amended with an organic fertilizer and subjected to reducing conditions due to waterlogging.

2. Materials and Methods

2.1. Experimental Design

This research was carried out As a mini-incubation experiment with two kinds of soils collected from the area affected by the spills of As-rich tailings. Untreated soils and soils amended with manure (10 g per kg) were incubated for 7 days and 21 days in flooded conditions. More precisely, 400 g of each soil was placed in a 0.5 L container, mixed with distilled water to obtain a saturated paste, covered with an additional dose of water to make a 5 mm water layer on the soil surface, and tightly closed. After the incubation period, As extractability in 1 M NH_4NO_3 and in water, as well as As speciation determined by sequential extraction (SE) according to Wenzel [14], were examined:

- immediately, in fresh samples (F);

- in oven-dried samples (O);
- and in air-dried samples (A).

The analyses of wet samples were preceded by the determination of their water content, and the volumes and concentrations of extracting reagents were modified appropriately. Oven-drying was performed with a standard method, at 105 °C for 24 h, and air-drying was carried out in the dryer room at 25 ± 3 °C to the constant weight, which was obtained in all the samples after 8 days. Analogous extractions were also carried out at the start of incubation, after mixing air-dry soil samples with the appropriate doses of manure (the results of these analyzes were marked with the symbol 0). The experiment was carried out in three replicates. Additionally, a parallel experiment was run in the same conditions, in which pore water was collected to measure a redox potential Eh.

2.2. Soil Material

Two kinds of soil material flooded in the past by As-rich tailings were collected from the top soil layers (0–20 cm) in two grassland sites: a floodplain meadow—soil 1 (Fluvic Phaeozem), and a dry meadow—soil 2 (Spolic Technosol). More details about the sites from which these samples were collected have been described elsewhere [6]. The soil material was crushed and sieved to <5 mm on site, and then transported to the laboratory, air-dried, and homogenized. Table 1 presents the basic properties of the two soils. Soil 1 had a texture of sandy loam (6% of clay fraction) and neutral pH, whereas soil 2 was poorer in clay (3%) and classified As loamy sand, with alkaline pH. Soil 1 was much richer in organic carbon compared to soil 2 (2.45% vs. 0.55%). Total concentrations of As in soils were very high: 4620 and 7950 mg/kg, respectively. Despite such high total As concentrations in soils, As extractability in 1 M NH_4NO_3 and in water was, in general, very low (19–29 mg/kg), i.e., not higher than 0.5% of total As.

Table 1. Basic soil properties.

Feature	Unit	Soil 1	Soil 2
Textural group (USDA)	-	Sandy loam	Loamy sand
<0.002 mm	%	6 ± 1	3 ± 1
Corg	g/kg	26.5 ± 0.4	5.8 ± 0.3
DOC	g/kg	0.69 ± 0.10	0.24 ± 0.03
pH (1 M KCl)	-	6.30 ± 0.05	7.55 ± 0.10
$CaCO_3$	%	absent	2.0 ± 0.3
As total	mg/kg	4620 ± 180	7950 ± 140
Water-extractable As	mg/kg	24 ± 4	29 ± 5
1 M NH_4NO_3-extractable As	mg/kg	19 ± 1	21 ± 1
0.43 M HNO_3-extractable As	mg/kg	2950 ± 120	3250 ± 110

2.3. Manure

Dry, granulated cattle manure (M) was applied to soils at the rate 10 g/kg, which corresponds to ca. 45 Mg/ha, expressed As a fresh mass. The manure contained 360 g/kg Corg (dry mass) and had a neutral reaction (pH = 7.3). The concentration of soluble organic matter in the manure, determined As the cold- and hot-water-extractable Corg. according to the procedure by Gregorich et al. [6,36], was 38.2 and 75.3 g/kg d.m., respectively. Total concentration of As in the manure was 10.7 mg/kg d.m.

2.4. Single and Sequential Extractions

Both nonamended and manure-treated soil samples were subjected to single and sequential extractions. Fresh and variously dried samples were shaken overhead with 1 M NH_4NO_3 solution (1:5 m:v, 2 h) in accordance with a modified ISO procedure for the determination of readily soluble forms of trace elements [11], and with distilled water (1:5 m:v, 2 h). The As concentrations in extracts were determined using ICP-AES on an iCAP 7400 (Thermo Scientific, Waltham, MA, USA). The analytical correctness of the As determination in extracts, due to the unavailability of relevant CRMs, was verified using the method of standard addition. Additionally, in parallel experiments carried out under the same conditions, pore water was collected with MacroRhizon suction samplers, and its redox potential was measured immediately with a platinum electrode InLab Redox Micro (Mettler Toledo, Columbus, OH, USA), As it was described elsewhere [37].

Operationally defined As forms were determined in soil samples before and after incubation by sequential extraction (SE) according to Wenzel [14]. This method was considered by many authors As the most suitable procedure for the speciation of metalloids, including arsenic, in the soil solid phase. The procedure involved five extraction steps, additional washing that followed steps 3 and 4 (Table 2), and 15 min centrifuging at 1700× *g* after each extraction step and washing. The supernatants were filtered through a 0.45 µm cellulose acetate filter paper and immediately analyzed by ICP-AES, on iCAP 7400, Thermo Scientific, for the concentrations of As. Blanks were subjected to the same procedure As soil samples. All the extractions were performed in triplicate. The recovery of As in the SE, calculated As the difference between total soil As (determined after microwave digestion in aqua regia) and the sum of all fractions F1–F5, was in the range between 95 and 104%, which was assessed As satisfactory.

Table 2. Scheme of sequential extraction procedure according to Wenzel et al. [14].

Fraction	**Extractant**	**Extraction Conditions**	**Soil: Solution Ratio (m:v)**	**Washing Step**
F1 *	0.05 M $(NH_4)_2SO_4$	4 h shaking, 20 °C	1:25	-
F2	0.05 M $(NH_4)H_2PO_4$	16 h shaking, 20 °C	1:25	-
F3	0.2 M NH_4-oxalate buffer; pH 3.25	4 h shaking in the dark, 20 °C	1:25	0.2 M NH_4-oxalate, pH 3.25: m:v 1:12.5; 10 min shaking in the dark
F4	0.2 M NH_4-oxalate buffer + 0.1 M ascorbic acid; pH 3.25	30 min in a water bath, 96 ± 3 °C, in the light	1:25	0.2 M NH_4-oxalate, pH 3.25: m:v 1:12.5; 10 min shaking in the dark
F5	HCl:HNO3 (3:1)	Microwave digestion	1:50	-

* Operationally defined As fractions (species): F1 nonspecifically-bound (easily soluble), F2 specifically-bound, F3 amorphous (hydr)oxide-bound, F4 crystalline (hydr)oxide-bound, F5 residual.

2.5. Statistics

The significance of differences between the extractability of As in fresh (F) and variously dried (O, A) samples and between various incubation periods (0, 7, 21 days) was assessed with Fisher's least significant differences test at a significance level $p < 0.05$. Confidence intervals were determined based on calculated standard deviation values, at $p = 0.95$. Each soil (1 and 2) was evaluated separately. Statistical analyses were performed using a software Statistica, v13.0 (Dell Inc. Round Rock, TX, USA).

3. Results and Discussion

3.1. Arsenic Released in Single Extractions from Nonamended Soils

As mentioned above, despite the high total As concentrations in soils of several thousand mg/kg, the amounts of easily soluble As forms (released from soils in the extractions with 1 M NH_4NO_3 and water) remained low, ≤29 mg/kg. The slightly higher As extractability with water compared to that with 1 M NH_4NO_3 (Table 1) can be explained by the fact that aqueous soil extracts also contained, apart from the truly dissolved As forms, those associated with highly dispersed, colloidal iron (hydr)oxides with a particle size of 0.05–0.45 µm. Such an effect is a typical feature of water extracts acquired from the soils at neutral pH [1,38]. Some of the water extracts were, indeed, not perfectly transparent, which makes the interpretation of the results more complex. Therefore, the further analysis will be based mainly on the results of soil extraction with 1 M NH_4NO_3.

After the 7- and 21-day incubation under flooding, the extractability of As in the samples increased significantly (Figure 1).

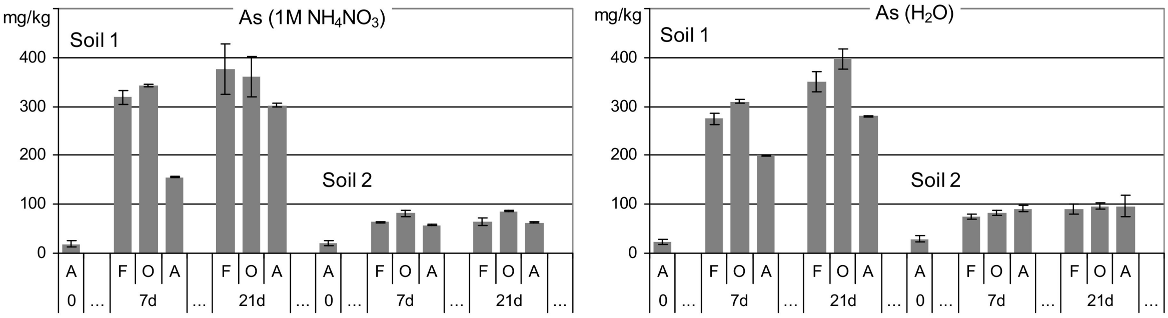

Figure 1. Arsenic extractability with 1 M NH_4NO_3 and with water (H_2O) in untreated soils 1 and 2, determined before incubation (0) and after 7 and 21 days of incubation, in fresh soil samples (F) and variously dried samples (A—air dried, O—oven dried). The data are mean values of 3 replicates. Error bars stand for confidence intervals, $p = 0.95$.

In soil 1, there was also a clear, statistically significant effect of air drying (A) on As extractability, both with 1 M NH_4NO_3 and with water. In this soil, air drying caused a significant decrease in the concentrations of easily soluble As. Undoubtedly, this effect was caused by chemical and biochemical processes opposite to those that led to the reduction and release of As under flooding. Although in this experiment, the concentrations of As (III) and As (V) in the extracts were not determined, it seems obvious that during the slow drying, reduced forms of As were oxidized to the pentavalent forms and re-adsorbed. The processes of such oxidation of As, in the soils that were previously subjected to waterlogging, have been described by many authors, e.g., those who examined alternate wetting and drying rice systems [32–35]. Many studies proved that these processes were mainly microbiologically driven [39,40], and their dynamics were highly dependent on the properties of soils, the kinds of microbial communities, and the availability of carbon sources. Consequently, the oxidation of the entire As(III) present in soil upon contact with air can last from several dozen hours [39] to many weeks [39–41]. In soil 2, the decrease in As solubility due to air drying of the samples was practically not observed. Huang et al. [41], who carried out the similar studies, emphasized that the share of soluble As in soils subjected to air drying was governed by the equilibrium of As mobilization (triggered by the oxidation of arsenopyrite and the decomposition of organic matter) and immobilization due to the so-called aging process.

Oven-drying (O) of nonamended soils resulted in a slight, although sometimes statistically significant, increase in As extractability with 1 M NH_4NO_3, which was not easy to clearly interpret. Though similar effects were observed by some authors who explained them analogously to air-drying, i.e., by overlapping of opposite processes of As mobilization caused by the oxidation of arsenopyrite and the decomposition of organic matter and immobilization induced by the high temperature, which increases the sorption capacity of clay minerals and can cause the diffusion of As into their micropores [23].

3.2. Arsenic Released in Single Extractions from Manure-Amended Soils

Soil treatment with manure caused a clear increase in As solubility in both soils, observed immediately, before the incubation started. The extractability of As in soil samples treated with manure continued to increase during incubation, so that in the samples examined fresh, i.e., without drying (F), after 7 d- and 21 d-incubation period, it was several times higher compared to the samples without manure (0), As shown in Figure 2. This effect corresponds to the knowledge of the influence of organic matter and reducing conditions on the solubility of As in soils [1,27–30]. In particular, a longer incubation (21 d) resulted in strengthening of anoxic conditions, so that the redox potential Eh of soil pore water collected from the manure-treated soils 1 and 2 decreased to −160 mV and −134 mV, respectively (Table 3).

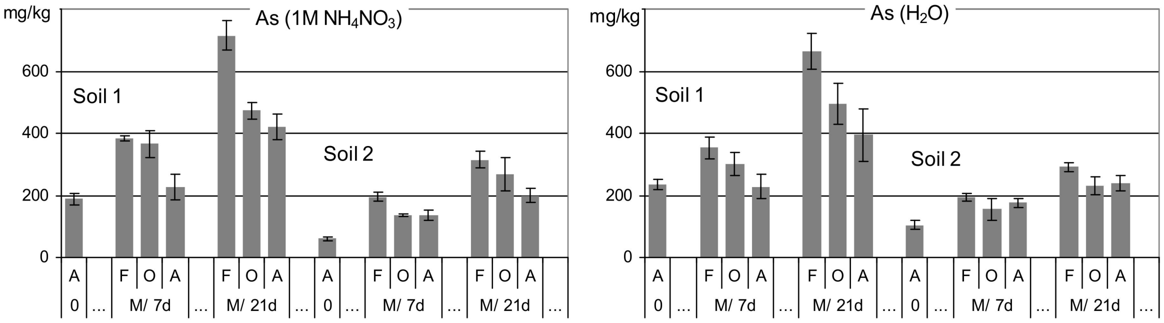

Figure 2. Arsenic extractability with 1 M NH_4NO_3 and with water (H_2O) in manure-amended soils 1 and 2, determined before incubation (0) and after 7 and 21 days of incubation (M/7 d and M/21 d, respectively), in fresh soil samples (F) and variously dried samples (A—air dried, O—oven dried). The data are mean values of 3 replicates. Error bars stand for confidence intervals, $p = 0.95$.

Table 3. Redox potential measured in the samples after incubation.

Incubation Time	Redox Potential, Eh, mV			
	Soil 1 (0)	**Soil 1 (M)**	**Soil 2 (0)**	**Soil 2 (M)**
7 d	95 ± 10	−36 ± 8	165 ± 7	−7 ± 6
21 d	−53 ± 12	−160 ± 21	−97 ± 13	−134 ± 18

Drying of those manure-treated and waterlogged samples had a clear impact on the concentrations of easily soluble As in soils, particularly in the case of soil 1. The highest amounts of As were extracted from the fresh samples (F), and unambiguously the lowest, from air-dried samples (A). Oven-drying (O) also resulted in the reduction in As extractability compared to fresh samples (F), but this effect was statistically significant only in soil 1, subjected to a prolonged incubation for 21 d (Figure 2).

To summarize the effects of drying on As extractability, it should be stated that both types of drying (O,A) reduced the amounts of As extractable with 1 M NH_4NO_3, the decrease being greater in the case of slow air-drying (A). The differences between the results obtained for fresh (F) and air-dried (A) samples were the highest (reduction by 30–41%) in long-incubated, manure-treated soils that had a particularly low redox potential (Table 4).

Table 4. Decrease in As extractability in manure-treated, oven (O)- and air (A)-dried samples, compared to fresh (F) soil samples (mean values of three replicates).

Method of Drying	Incubation Time	Reduction of As Extractability, %					
		Soil 1			Soil 2		
		1 M NH_4NO_3	**H_2O**	**0.05 M $(NH_4)_2SO_4$ (F1 in SE)**	**1 M NH_4NO_3**	**H_2O**	**0.05 M $(NH_4)_2SO_4$ (F1 in SE)**
Oven	7 d	5	14	7	30	19	16
	21 d	34	26	21	15	21	10
Air	7 d	41	36	27	30	9	23
	21 d	41	41	22	37	18	23

The extractability of As with 1 M NH_4NO_3 in the oven-dried samples (O) was also significantly lower (by an average of 5–34%) than in the fresh samples (F), although the differences here were smaller and not always statistically significant. In both cases (O,A), these differences resulted undoubtedly from the overlapping of opposing processes that favored mobilization of As (as a result of organic matter decomposition), and its immobilization due to As oxidation and re-sorption, oxidation of Fe(II), precipitation and crystallization of

Fe (hydr)oxides, and possible diffusion of As into micropores. We can guess that under the air-drying conditions (A), these processes were, to a larger extent, driven microbiologically.

3.3. The Effects of Soil Amendment with Manure and Drying on As Fractionation in SE

The results of SE performed before incubation (0) and after the 21-day incubation of nonamended soils and soils treated with manure, analyzed fresh (F), without drying of the samples, are shown in the diagram (Figure 3). The dominant As fraction in both soils was F3, the fraction extracted with NH_4-oxalate buffer, considered to consist of the species associated mainly with amorphous Fe (hydr)oxides [14]. It has been documented by numerous authors that amorphous Fe (hydr)oxides are the main soil hosting phase for arsenates and arsenites [1,3,14,41–43], although the sorption of As(III) is poorer compared to As(V). In soil 2, that was developed of almost pure tailings, there was also a considerable share of residual fraction, F5, strongly associated with the solid phase of the soil, and irreducible. In this fraction, As remains either in primary minerals, such As arsenopyrite, which is common in mine-affected soils and tailings, or in organically-bound forms, that are not distinguished in the SE procedure according to Wenzel [14]. The amounts of organically bound As forms—when determined separately—turn out to widely differ in highly enriched soils and mining sediments. Several studies reported their small share [14,44], but some other research proved that they can constitute up to several dozen percent of the total As [45,46]. In our experiment, the long-term incubation of both soils, especially those treated with manure, resulted in a considerable increase in the shares of the most mobile fractions (F1 and F2) and a decrease in the residual fraction F5 (Figure 3), which probably should be attributed to the decomposition of organic matter and the release of organically-bound As.

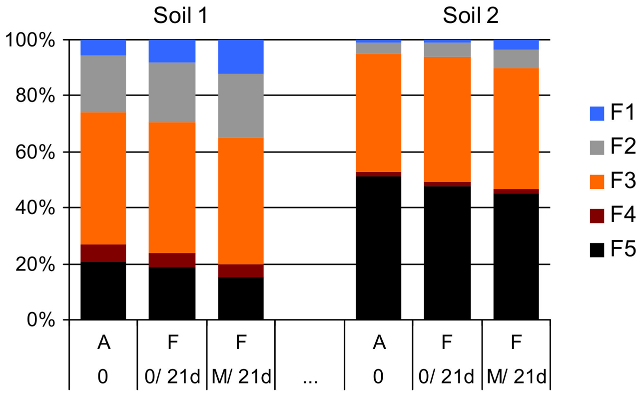

Figure 3. Fractionation of arsenic in soils 1 and 2, according to Wenzel et al. [14], determined in air-dried soil samples before incubation (A, 0) and in fresh soils (F) after 21 days of incubation without manure (0/21 d) and with manure (M/21 d). The data are mean values of 3 replicates.

More detailed data on the changes in the amounts of As extracted in the most mobile fractions F1 and F2, As well As in the F3 fraction that could be expected to partially decompose during incubation, are presented in the diagrams (Figure 4). This figure also illustrates the changes in fractionation caused by oven- and air-drying of the samples.

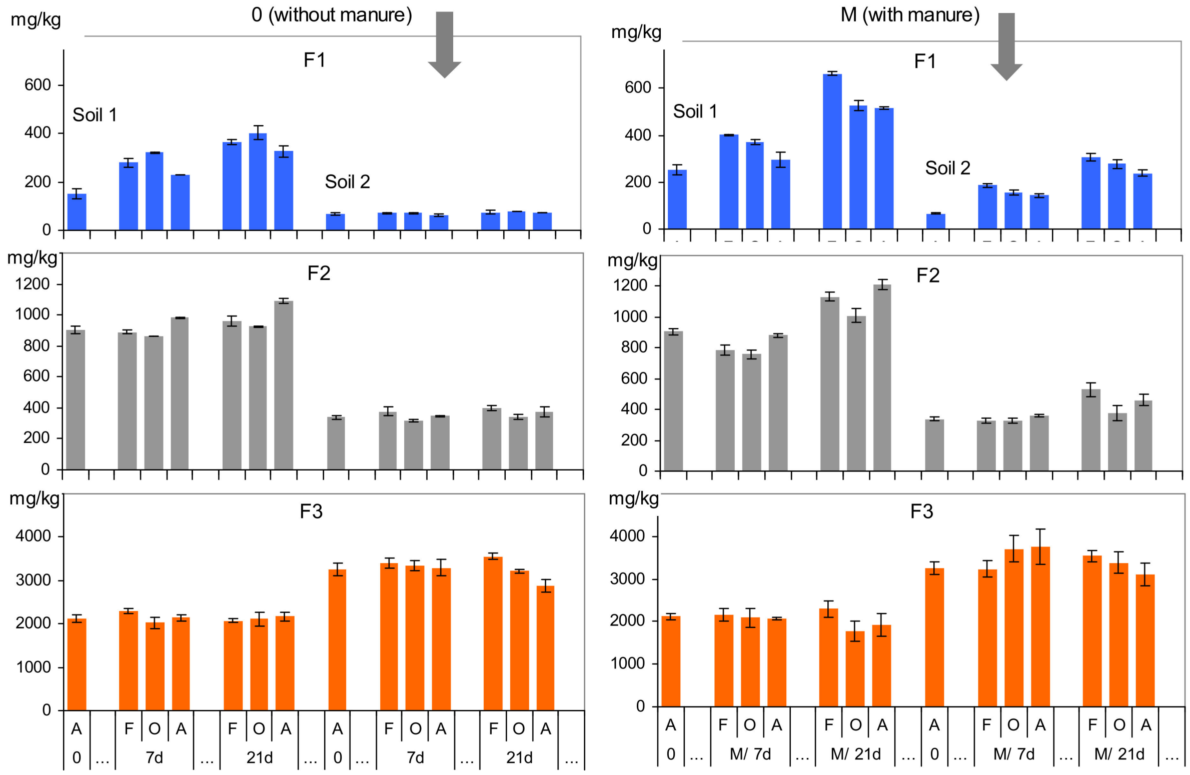

Figure 4. Fractions F1, F2, and F3 of arsenic, determined according to Wenzel et al. [14], in untreated (0) and manure-amended (M) soils 1 and 2 after 7 and 21 days of incubation. The soils were examined As fresh (F), and variously dried samples (A—air dried, O—oven dried). The data are mean values of 3 replicates. Error bars stand for confidence intervals, $p = 0.95$.

Air drying (A) resulted in a partial depletion of the readily soluble F1 fraction, extracted with 0.05 M $(NH_4)_2SO_4$, especially in all the samples of soil 1 and in the manure-treated soil 2. In the case of manure-treated soils, the amounts of As extracted As F1 from air-dried samples were by 22–27% lower compared to fresh samples (Table 4). At the same time, air drying (A) caused a slight, but statistically significant, increase in the content of the F2 fraction in soil 1, whereas in soil 2, such an effect did not occur. Regrettably, it was not possible to balance the transformation of particular As fractions into the other that apparently resulted from air-drying, since the changes in the absolute amounts of As in the F1 fraction remained smaller than the confidence intervals of As determined in fractions F2, and particularly in F3, that contained much more As. The results of SE (Figure 4) also show that in the long-incubated soil 2 treated with manure, the share of As in the F3 fraction decreased due to air-drying (A) compared to freshly examined samples (F), but it was not possible to balance this loss, As an increase of As in F4 and F5 fractions was not statistically confirmed. Relatively large values of standard deviation SD in the results of SE, and related wide confidence intervals of As concentrations in particular fractions, were caused both by the heterogeneity of the samples, especially those treated with manure, and the complexity of the SE procedure, in which certain losses of the analyzed elements, As well As analytical errors, are possible at many stages [12–14]. Therefore, the recovery of elements in SE within the range 90–110% is usually considered highly satisfactory.

Oven-drying (O) of soil samples did not cause any consistent, statistically significant changes in As fractionation. A slightly higher As concentration was found in fraction F1 in the oven-dried samples (O), As compared to the fresh samples (F) of nonamended soil 1. This effect was similar to the results of single extractions with 1 M NH_4NO_3 and water. On the contrary, in the case of manure-treated soils, oven-drying caused a reduction of F1 compared to the freshly extracted soil. As already mentioned, such differences were probably due to overlapping of opposing processes that affected the most mobile fraction of As. The changes in the fraction F1 caused by oven-drying were not associated with statistically significant changes in As in the other fractions because the absolute amounts of As redistributed from F1 were in fact smaller than the analytical uncertainty in determining F2, F3, and F5. Similar studies carried out by various authors also reported inconsistent conclusions As to the effects of oven-drying on the species of trace elements in contaminated soils. Numerous authors stressed that oven-drying may cause the thermal decomposition of organic matter [12,17–21] and an increase in the concentrations of mobile species of metals and metalloids; however, Huang et al. [23] emphasized that the adsorption capacity of As onto Fe and Al (hydr)oxides is usually strengthened during oven-drying at a high temperature and should result in the immobilization of As and its transition from F1 and F2 fractions to those Fe (hydr)oxide-bound and residual (F3, F4 or F5). The accelerated diffusion of As from an inner-sphere surface into micropores of clay minerals and the speed up of the conversion of amorphous iron hydroxides to more crystalline forms additionally contributed to such transition. Probably, the balance of the processes that favor the release of As from organic matter during oven-drying and its immobilization due to thermal transformations of minerals depends on the share of organically-bound As in soil, which, in our study, was not distinguished, As its separate determination is not provided for by the SE according to Wenzel.

4. Conclusions

This study proved that soil sample pretreatment, i.e., drying, can significantly affect the extractability and fractionation of As in strongly polluted soils incubated under flooded conditions. There were differences in the amounts of extractable As and its operationally defined fractionation between the fresh and oven- and air-dried soils, particularly in those amended with manure. In brief, the greatest differences in comparison to fresh samples were caused by air-drying, which in all tested samples resulted in a significant decrease in the 1 M NH_4NO_3-extractability of As and in the amounts considered easily soluble (F1 fraction in SE). The differences in NH_4NO_3-extractable As between the fresh and air-dried samples were the largest (reduction by 30–41%) in the case of manure-treated soils subjected to strongly anoxic conditions. These differences can be explained by the redistribution of arsenic fractions during air-drying due to the oxidation of As(III) to stronger adsorbed As(V) and the re-precipitation and crystallization of Fe (hydr)oxides. Oven-drying resulted in a smaller reduction of easily extractable As compared to fresh samples (by 5–34%), which was only in some cases statistically significant. This effect was a resultant of increased mobility of As due to the decomposition of organic matter during oven-drying and As immobilization due to the precipitation and crystallization of Fe (hydr)oxides, As well As a possible diffusion of As into micropores. Sequential extraction (SE) has not proved to be a good tool to illustrate how As was redistributed, mainly because the absolute loss of As from the F1 fraction remained smaller than the confidence intervals determined in the extraction of all other fractions that contained much more As.

The research shows that in order to precisely assess the extractability of As in anoxic soils, it is advisable to carry out the analyses on fresh samples, without their drying. Though, if for any reasons the samples require drying, a relatively rapid oven-drying at 105 °C should be preferred over slow air-drying. On the other hand, it is worth emphasizing that the differences in NH_4NO_3-extractability of As between the fresh and dried samples were not dramatically large, As they did not exceed 41%, which means that the order of magnitude of extractable As did not change radically due to drying, in particular, to oven-drying. Therefore, it can be concluded that anoxic soil samples strongly enriched in As may be subjected to oven-drying prior to extraction, which should not radically distort the picture of what is the order of the magnitude of As solubility. Related results may be used for a rough assessment of environmental risks. In order to generalize these conclusions, however, several other soils with different properties subjected to anoxic conditions for a longer time should additionally be examined.

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