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Effect of redox potential on heavy metals and As behavior in dredged sediments

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ABSTRACT

The effect of redox changes with respect to mobility of Cr, Cu, Pb, Zn, and As in five dredged sediments originating from disposal sites in the Netherlands was studied in the paper. An extraction procedure with a neutral unbuffered salt solution (0.01 M $CaCl_2$) was used to investigate the behavior of heavy metals and As in laboratory-based batch experiments conducted under oxidized and reduced redox conditions and carried out for 21 d. An increase in the redox potential (above +400 mV up to +503 mV) resulted in a rise of solubility of heavy metals in all sediments. However, at low redox potentials, an increase in As concentration was observed in the highly As-contaminated sediment. Mass balances were performed to follow the use of oxygen and the production of CO_2, NO_3^-, SO_4^{2-} and PO_4^{3-}. An increase in redox potential has a large effect (40–80%) on the oxidation of reduced sulfur compounds to SO_4^{2-}. Such increase in redox potential led to a solubilization of only about 1% of Cr, Cu, Pb, and Zn. Still, such low solubilization of these heavy metals leads to an increase of significance of the issue concerning ground and surface water quality.

Keywords: Heavy metals; As; Sulfur forms; Redox potential; Dredged sediments; Risk assessment

1. Introduction

Sediments are often polluted with a so-called "cocktail" of heavy metals and organic micropollutants. In the coming 25 years, 350 million m^3 fresh water sediments will have to be dredged in the Netherlands of which 75 million m^3 are heavily contaminated (class 3 and 4) [1]. Temporary storage of polluted dredging can be an option to partial or even complete remediation as this is an extensive, low-cost technique. It has to be taken into account that several physical, chemical, and biological processes occur during temporary storage [2]. Oxygenation as the main factor in a temporary disposal site is desirable for aerobic degradation of organic pollutants (polycyclic aromatic hydrocarbons and mineral oil). However, oxygenation and therefore redox changes affect the mobility of heavy metals and As. In reduced state, sediments redox potential is as low as −250 to −300 mV whereas, in aerated conditions,

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redox potentials can reach the range from +400 to +700 mV [3]. Most recently, research emphasis has been on the behavior of heavy metals and As under changing redox conditions. Exposure of sediments to aerobic conditions results in a sequence of oxidative reactions, leading to a decrease in pH, an increase in redox potential, an increase in sulfate levels in the water, and solubilization of the most cationic metals. Redox conditions as well as the pH are considered to be of prime importance in determining the mobility of trace metals from sediments [4–8]. These parameters affect processes related to metal binding, such as sorption and desorption to soil particles, formation and dissolution of carbonate bound metals, formation and decomposition of soluble and insoluble metal organic complex compounds, formation and dissolution of hydroxides and oxyhydrates, sorption and co-precipitation of metals by Fe/Mn-oxides, particularly in oxidic environments at neutral pH, precipitation of metal sulfides in strong reducing environments, and dissolution as sulfates under oxic conditions [9–12].

As metal sulfides are often present in anoxic sediments, the sulfur cycle is expected to play an important role to control the mobility of toxic metals [13]. Various sulfur compounds occur in sediments depending on oxygen conditions [14]. Under the anoxic state, solid compounds of heavy metals are usually stable. In particular, the sulphidic forms mainly consisting as (FeS) and pyrite (FeS_2) have low solubility products and elementary sulfur (S) may be present, too [15]. In aerobic conditions, most of the inorganic sulfur normally occurs as sulfate (SO_4^{2-})[16], which are rather soluble, except for $PbSO_4$. It is believed that redox potential defines conditions for mobility and (bio)availability of metals [17]. Dissolved or weakly adsorbed metals may be easily available to plants and aquatic organisms and therefore lead to health risks of these organisms [18–23].

Several methods are developed to mimic the concentration of metals that can be taken up by plants like $CaCl_2$ (0.01 M) extraction [24–26]. In this paper, the effect of redox changes is studied in relation to the mobility of heavy metals and As using the 0.01 M $CaCl_2$ as a medium.

2. Material and methods

2.1. Samples

Five sediments studied in this paper originated from three dredged sediment disposal sites in the Netherlands, namely Den Helder (DDHCr, DDHZn, WHAZn), Nieuw Vennep (HMAs), and Arnhem (MBHMe) (Fig. 1).

The samples DDHCr and DDHZn were in depot for about 2 years, whereas WHAZn was freshly dredged sediment from a canal near Amsterdam with a deep black appearance. The sediment HMAs originated from a dredging in the Haarlemmermeer and was converted into soil during a one-year storage in depot and had a light brown appearance. The MBHMe sample originated from the Malburger-haven in Arnhem. After sampling, the sediments were homogenized for 24 h at 20˚C in 27-l barrels with a roller bank and stored at 4˚C until analyzed.

2.2. Sediment characteristics

The physic-chemical properties are presented in Table 1. All sediments approximated a neutral pH (pH 6.8–7.6). All sediments were in a reduced state (Eh +55 +146 mV) and had a wide range of dry matter contents (24.1–74.9%). Due to storage at dry conditions, the dry matter content of the sediment HMAs (74.9%) was rather high. Sediments varied in organic matter content from 6.2 to 27.6%. Organic matter may play an important role as metals can be sorbed to organic matter [27,28]. The highest heavy metal concentrations in each sediment were as mg metal per kilogram of dry sediment (mg/kg of dm): DDHCr 1,014 mg Cr/kg dm, DDHZn 1,109 mg Zn/kg dm, HMAs 486 mg As/kg dm, MBHMe 1,294 mg Zn/kg dm and WHAZn 1,281 mg Zn/kg dm, respectively.

Besides, most values for other metals were above the Dutch intervention values for heavy metals in soils: As 55 mg/kg dm, Cr 380 mg/kg dm, Cu 190 mg/kg dm, Pb 530 mg/kg dm and Zn 720 mg/kg dm [29]. Regard-

Fig. 1. Location of sampling points DDHCr, DDHZn, WHAZn (1), HMAs (2), MBHMe (3).

Table 1
Characteristic of sediments[a]

	DDHCr		DDHZn		HMAs		MBHMe		WHAZn	
	Value	Std.	Value	Std.	Value	Std.	Value	Std.	Value	Std.
pH	6.80	0.01	7.40	0.03	7.6	0.1	7.10	0.01	7.00	0.01
Eh(mV)	55	22	93	8	146	23	73	3	62	15
	56.3	0.3	38.9	0.5	74.9	0.7	27.7	0.1	24.1	0.4
OM (%)	10.5	0.1	21.6	0.4	6.2	0.3	14.8	0.2	27.6	0.3
Total contents (mg/kg dm)										
As	13.1	0.3	27	0.4	486	8.5	62	0.7	174	8.6
Cr	1,014	22	481	1.9	25	0.3	166	2.4	64	1.6
Cu	148	4.7	206	1.4	16	0.8	119	2.3	190	1.4
Pb	366	8.3	137	1.4	29	2.3	781	14	551	33
Zn	770	28	1,110	5	75	1.0	1,290	80	1,280	66
Ca	12,536	48	26,650	287	39,701	897	70,341	1,625	26,758	2,571
Fe	7,345	122	38,272	402	35,345	766	37,659	573	29,369	4,683
Mg	1866	39	5,138	232	5,296	61	44,115	160	6,580	1,130
P	693	50	4,609	46	1906	32	2,626	56	1926	307
S	4,644	46	8,162	42	3,283	18	3,262	394	22,211	3,168

[a] All values represent the mean of three subsamples.

ing Polish soil quality legislation [30] for area B (up to 0.3 m depth) including, among others, soil cultivation, the values for heavy metals are as follows: As 20 mg/kg dm, Cr 150 mg/kg dm, Cu 150 mg/kg dm, Pb 100 mg/kg dm and Zn 300 mg/kg dm. In the case of depth greater than 15 m, the concentrations are the same as for Dutch intervention values except Cu 200 mg/kg dm and Pb 200 mg/kg dm. To characterize sediments further, a selection of macroelements was also analyzed. High concentrations of calcium (Ca) (4,650–70,341 mg/kg of dm) and magnesium (Mg) (1,119–44,115 mg/kg of dm) determined for some sediments may lead to metals' binding with organic matter. Iron (Fe) was also determined (7,345–35,345 mg/kg of dm) since different forms of Fe can be found depending on redox conditions. In all sediments, the total concentration of phosphorus (P) (1906–7,201 mg/kg of dm) is expected not to limit biological conversion. The total sulfur (S) was also determined (3,283- 22,211 mg/kg of dm) since, as mentioned before, different sulfur compounds can be formed depending on aerobic and anaerobic environments.

2.3. Experiments

Aerobic experiments were performed in closed batches (1,000 ml) with a sufficiently large headspace $O_2/N_2 21/79$ (v/v %) to avoid anoxic conditions. Anaerobic experiments were performed in 120 ml bottles with N_2/CO_2 80/20 (v/v %) by a gas change device (five gas volume changes). All batch experiments were carried out for 21 d. The sediment samples (5 g dm) were suspended in a medium of a liquid/solid ratio 10:1 (w/w). The medium had the final $CaCl_2$ concentration of 0.01 M as extractant [31,32]. Samples were shaken by end-over-end shaker at 20°C (22 rpm). Gas composition, heavy metals, and ions in supernatants were analyzed every two or three days. Sediment characteristics are presented in Table 1. Eh, pH, dry and organic matter content, total heavy metals, macroelements, and total sulfur concentration in sediments were determined at the beginning and at the end of the experiment, respectively.

2.4. Chemical analyses

The pH of sediments was measured potentiometrically in a 5:1 liquid/solid suspension of the sediments in distilled water [33]. Redox potentials were measured by inserting platinum electrode (Pt-AgCl/Ag) in the sediment paste until stable reading [34]. Dry matter (DM) was determined by drying in an oven at 105°C for 24 h. Organic matter (OM) was estimated by heating during 3 h at 550°C. The total metal concentration and macroelements in the samples as (mg/kg of dm) were determined after microwave destruction (CEM 2,100, Matthews, USA) of pre-dried samples (40°C), subjected to digestion with aqua regia (HCl/

HNO_3, 3:1 v/v) according to [35]. After digestion, the samples were paper filtered (Schleicher & Schuell 589, Germany) and diluted to the volume of 100 ml. The supernatant liquid was acidified by HNO_3 to pH 2, stored at 4°C and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP - MS, Elan 6,000, Perkin–Elmer, detection limit 0.1–2,000 µg/L). The amount of metal in the liquid phase of supernatants of batch experiments was determined by centrifugation (15,000 rpm over 10 min). The supernatant liquid was acidified by HNO_3 to pH 2, stored at 4°C, and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Elan 6000, Perkin–Elmer). The following ions: Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, were analyzed using Ion Chromatograph (DIONEX DX 600). The total sulfur concentration was determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Spectra-Flame, Spectro—detection limit 0.1 mg/L–100 µg/L). The gas composition—O_2, CO_2, and N_2 was measured by Gas Chromatograph TCD MFC 800, Fisons. The nitrogen compounds: NH_4^+, total NO_2^-, and NO_3^- and PO_4^{3-} were determined using Segmented Flow Analysis (SFA).

3. Results and discussion

3.1. Redox potential and metal and As concentrations in liquid

Oxygenation of anoxic sediments by continuous mixing of 50 ml sediment slurry (L/S = 10) with air in 1 l bottles led to an increase from initially +55 to +146 mV to above +435 mV for DDHCr up to a redox potential of +503 mV for WHAZn sediment (Fig. 2) [36].

In moderately altered conditions, the experiment with low redox potential applied decreased from +116 mV for DDHCr to +39 mV for WHAZn, respectively.

The increase in the redox potential resulted in the release of heavy metals to the liquid phase from all five sediments (Fig. 3(A–E)); however, the absolute increase in solubilized metals is relatively small (<1%) compared to the initial metal concentrations.

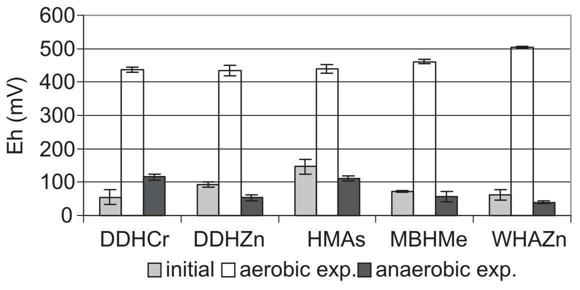

Fig. 2. Redox potential Eh (mV) in sediments after 21 d.

Aerobic conditions in sediment DDHCr resulted in mobility of all five metals (Fig. 3(A)). The highest Zn concentration was observed after 12 d 33,070 µg/L. In the case of Cr, the highest mobility occurred at the beginning of the experiment 377 µg/L.

Metal concentrations released to the water phase from sediments exceeded the permissible values of ground and surface water quality taking into consideration Dutch [37] and Polish Legislation [38,39].

In DDHZn sediment (Fig. 3(B)), Zn was released to 33,070 µg/L, which is above allowable groundwater level and surface water. In HMAs sediment (Fig. 3(C)), again Zn was the most mobile metal reaching 678 µg/L that is above allowable surface water concentration for Holland and above groundwater values for Poland. In the MBHMe sediment (Fig. 3(D)), again Zn released in the high concentration 3,950 µg/L exceeding permissible groundwater values. In the WHAZn sediment (Fig. 3(E)) also, Zn was the most mobile metal and reached the value of 3,225 µg/L after 12 d. However, for sediments HMAs, MBHMe, and WHAZn, it was found that Cr concentration after 12 and 21 d was below detection limit (<0.1 µg/L). In the case of sediment DDHZn, Cr concentration below detection limit was observed after 12 d.

Looking at Cu and Pb behavior in DDHDr sediment, it can be noted that the highest released of Cu observed after 12 d reached the value of 104.7 µg/L exceeding allowable surface water concentrations. The highest release of Pb to the water phase took place after 21 d with the amount of 82.5 µg/L and was also above surface water concentrations. In DDHZn sediment, highly contaminated with Cu, the highest Cu concentration exceeding permissible surface water concentrations was observed after 12 d with the amount of 64.6 µg/L. In MBHMe sediment, the maximal Pb release was obtained after 2 d, 55.8 µg/L. In WHAZn sediment, Pb released in the highest concentration after 21 d with the amount of 31.3 µg/L. In both sediments, extracted Pb values exceeded allowable surface water concentrations.

Calmano et al. [40] and Zoumis [8] showed that oxidation resulted in mobilization of some heavy metals. Zn was released significantly higher in all sediments due to its weaker binding properties [12,41]. Mobilization of metals in the presence of oxidation was also confirmed in other studies [42–44]. Pb and Cu generally are less mobile elements in the environment [45]. Kerner and Wallman [46] conducted a laboratory study simulating periods of aerobic and anaerobic conditions of sand flat sediment and followed the mobilization of Zn. Zn was believed to be released from the sediment solid phase during aerobic cycles attributed to mineralization of organic

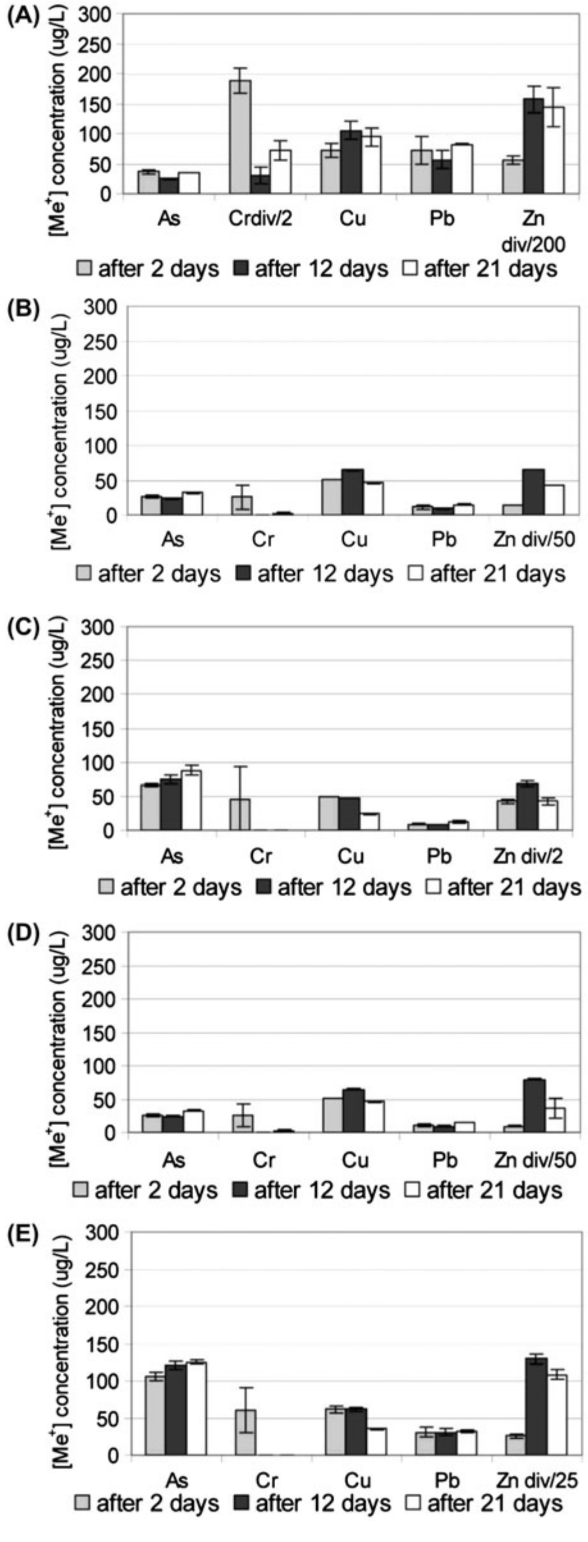

Fig. 3. Solubilized metal concentrations after 2, 12, 21 d in aerobic leaching conditions for DDHCr (A), DDHZn (B), HMAs (C), MBHMe (D), and WHAZn (E).

matter and sulfide oxidation. They also simulated periods of anaerobic conditions of sand flat sediment and it turned out that the mobilization of Zn had occurred. Sulfide precipitation caused the removal of Zn from pore water during anaerobic cycles.

Kelderman et al. [47] investigated different binding forms of Cu, Zn, and Pb onto sediments under changing redox conditions. They found that oxidation of heavy metals sulfides had occurred leading to heavy metal release from the sediments.

The low redox potentials resulted in lower release of heavy metals from sediments to the liquid phase (Fig. 4(A–E)).

It should be stated that despite Cu and Pb released in lower amounts in anaerobic conditions rather than in an aerobic experiment, the concentrations are still above allowable surface and ground water concentrations. The highest Cu released from DDHZn sediment after 21 d with the value of 37.3 μg/L. Pb was the most mobile metal in sediment MBHMe at day 0 with the amount of 23.8 μg/L, whereas the highest concentration of Pb was found in the sediment WHAZn after 21 d with the value of 32.8 μg/L.

Anaerobic conditions affected the mobility of As with the following highest amounts exceeding both the maximum allowable groundwater and surface values: 157 μg/L of As in sediment HMAs (Fig. 4(C)), 71 μg/L of As in MBHMe sediment (Fig. 4(D)), and 538 μg/L of As in the WHAZn sediment (Fig. 4(E)) released at day 0, respectively.

With respect to the literary data under anaerobic sediments, acid volatile sulfide (AVS) controls the behavior of some divalent cationic metals, usually present naturally [48,49]. In the anaerobic sediment, AVS is bound with iron as solid monosulphide (FeS), crystalline mackinawite (FeS), pyrrohotite (FeS), greigite (Fe_3S_4), or exists as free sulfide. However, if Cu, Cr, Pb, and Zn are present, the iron and iron sulfide are displaced and one of the aforementioned metals rapidly bind to AVS with strong affinity.

Aqueous sulfide (H_2S or HS^-) is a strong reductant and frequently occurs at appreciable concentrations in reduced systems, and consequently it may play an integral part in arsenic redox chemistry [35,50,51]. In other studies, As mobility in overbank sediments was also investigated [52]. It was found that leaching of As was only significant in sediments from which P was also released. This phenomenon was explained by the effect of competition between arsenate and phosphate or by the fact that studied samples contained Ca_3PO_4 particles enriched in As. Another explanation was competition between dissolved organic matter and arsenate.

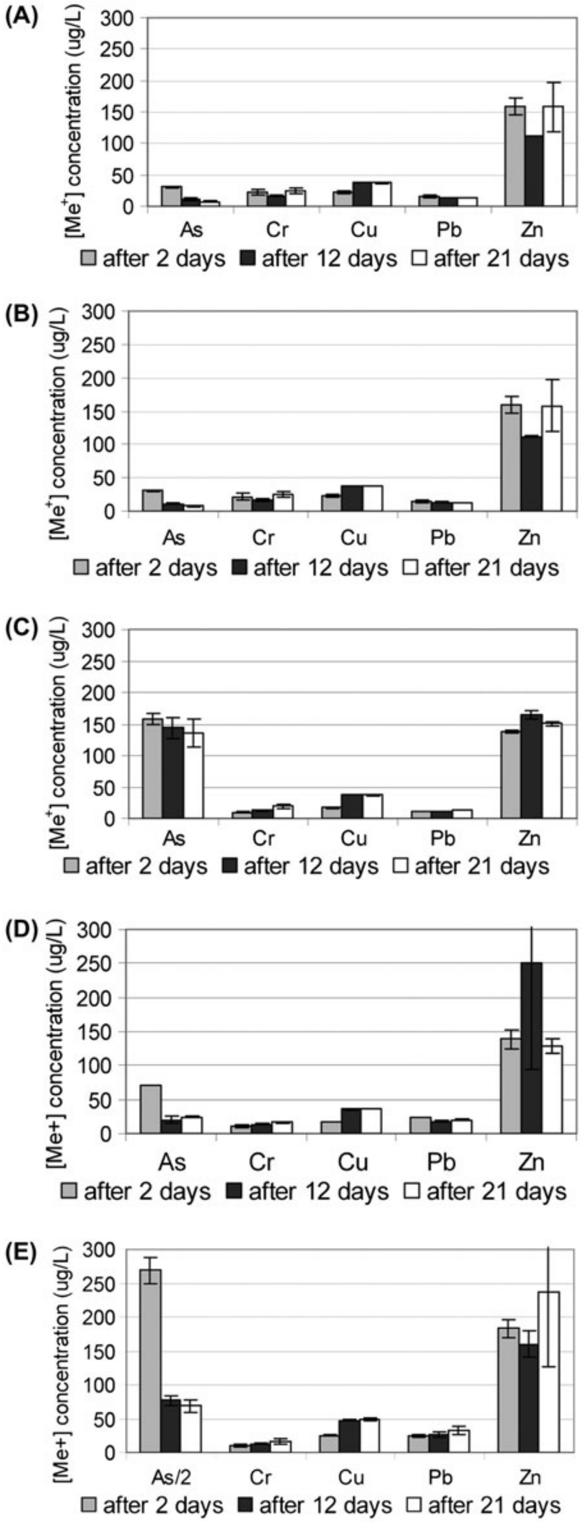

Fig. 4. Solubilized metal concentrations after 2, 12, 21 d in anaerobic leaching conditions for DDHCr (A), DDHZn (B), HMAs (C), MBHMe (D), and WHAZn (E).

Another study confirms that under oxidizing conditions, As, Zn, and Cr behavior was governed by redox chemistry of Fe(III) and Mn(IV) oxides [53]. When sediment redox potential increased, the affinity between Fe(III) and Mn(IV) oxides and As, Cd, Cr, and Zn increased, too. When sediment redox potential decreased, the affinity between insoluble sulfides, large molecular humic matter, and As, Cd, Cr, and Zn increased; the soluble Cd and Zn decreased; the soluble As and Cr remained constant.

Masscheleyn et al. [54] investigated the effect of redox potential and pH on As speciation and solubility in contaminated soil. They concluded that under moderately reduced conditions (0–100 mV), As solubility was controlled by the dissolution of iron oxyhydroxides and released upon their solubilization.

Zn release concentrations in studied sediments were lower in comparison with aerobic conditions. However, in the case of DDHZn, MBHMe, and WHAZn sediments polluted with this metal, Zn released to the water phase in the concentrations exceeding permissible surface water concentrations in the amounts: 196.4 μg/L at day 0, 251 μg/L after 12 d, and 236.8 μg/L, respectively.

3.2. Mass balances

Consumption of O_2 in DDHCr after 21 d reached 0.234 mmol O_2/g dm (Fig. 5(A)). The measured products CO_2, NO_3^-, SO_4^{2-}, PO_4^{3-} used 69% of oxygen consumed after 21 d. It can be seen that 31% of oxygen was not found in O_2-containing products. The major product for O_2 consumption was sulfate 0.149 mmol O_2/g dm. The highest O_2 consumption 0.339 mmol O_2/g dm after 21 d took place in DDHZn (Fig. 5(B)). In this sediment, CO_2 NO_3^- SO_4^{2-} PO_4^{3-} used 77.8% of oxygen consumed at the end of the experiment and 0.225 mmolO_2/g dm was consumed for sulfate production. The lowest oxygen consumption after 21 d was observed in the sediment HMAs (Fig. 5(C)), the products CO_2, NO_3^-, SO_4^{2-}, PO_4^{3-} used 55.2% of oxygen consumed after 21 d and 0.155 mmol O_2/g dm was consumed by sulfate. Fig. 5(D) shows the consumption of 0.181 mmol O_2/g dm in the sediment MBHMe after 21 d. The products CO_2, NO_3^-, SO_4^{2-}, PO_4^{3-} used 86.55% of the oxygen consumed after 21 d, whereas 0.118 mmol O_2/g dm was consumed for sulfate production. The consumption of O_2 in WHAZn after 21 d reached 0.208 mmol O_2/g dm (Fig. 5(E)). CO_2, NO_3^-, SO_4^{2-}, PO_4^3 used 83.8% of the oxygen that was consumed after 21 d. The major product for O_2 consumption was again sulfate 128 mmol O_2/g dm.

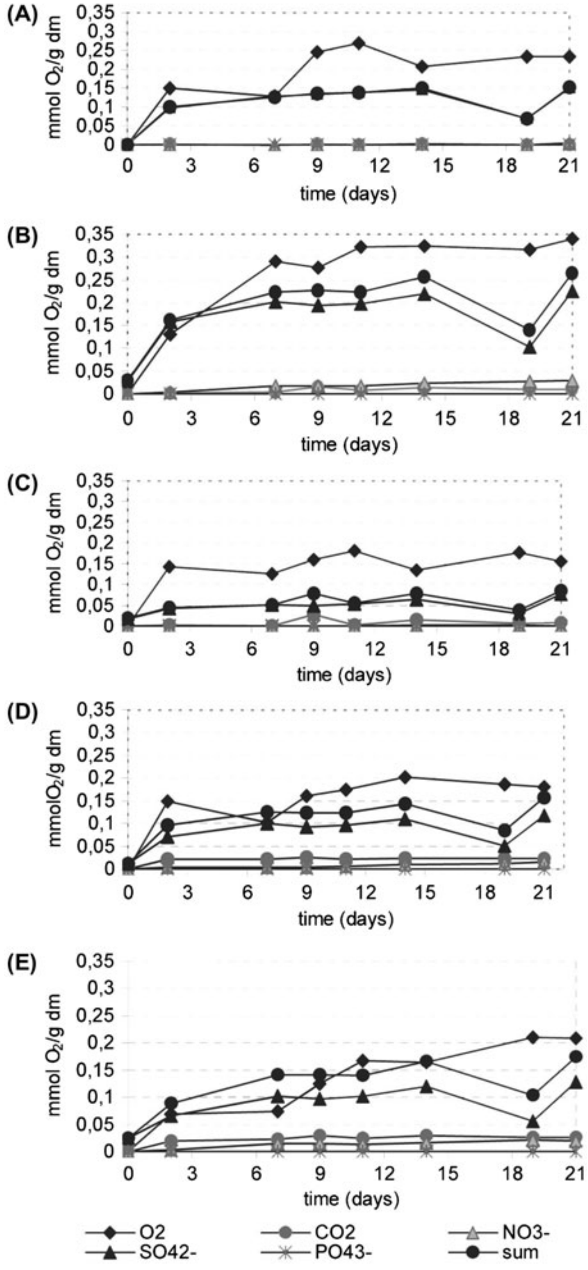

Fig. 5. The use of oxygen consumption (diamonds) and the production of SO_4^{2-} (black triangles), CO_2 (gray cicrles), NO_3^- (gray triangle), and PO_4^{3-} (star) for DDHCr (A), DDHZn (B), HMAs (C), MBHMe (D), and WHAZn (E) Sum—O_2 present in products $(CO_2 + NO_3^- + SO_4^{2-} + PO_4^{3-})$ (black circles).

The results show that it is quite likely that not all of O_2 consumed can be found in O_2-containing products. It is probably caused by binding of O_2 to carbon in the solid matrix [55]. It was concluded that most of O_2 is used for oxidation of sulfur compounds as sulfate for all sediments was the major product for the O_2 consumption. Therefore, attention was also paid to sulfur balance (Fig. 6).

Looking at the total sulfur concentration in sediments, it can be observed that the initial S_{total} concentration is nearly equal to the S_{total} final concentration both in aerobic and anaerobic conditions (Fig. 6(A)). In Fig. 6(B) SO_4^{2-} production at the end of the both oxidized and reduced experiments is shown. In the aerobic experiment, more SO_4^{2-} is found in all studied sediments in comparison with anaerobic experiment. The highest SO_4^{2-} concentration was found for DDHZn sediment 112.7 mmol/kg and the lowest one for HMAs 38.6 mmol/kg. It can be explained that SO_4^{2-} is converted to S^{2-} in reduced environment. This sulfide can react with Fe, leading to FeS or FeS_2 precipitation [55]. In the study, approximately 40% of all sulfur compounds were oxidized (Fig. 6(C)), whereas for sediment DDHCr even 80% was converted. From Fig. 6(C) showing the percentage of sulfur that was oxidized, it can be seen that not all S is converted to sulfate, which is also confirmed by other researchers [56]. It is due to the fact that amorphous FeS is rapidly oxidized, whereas crystalline FeS_2 is not [57].

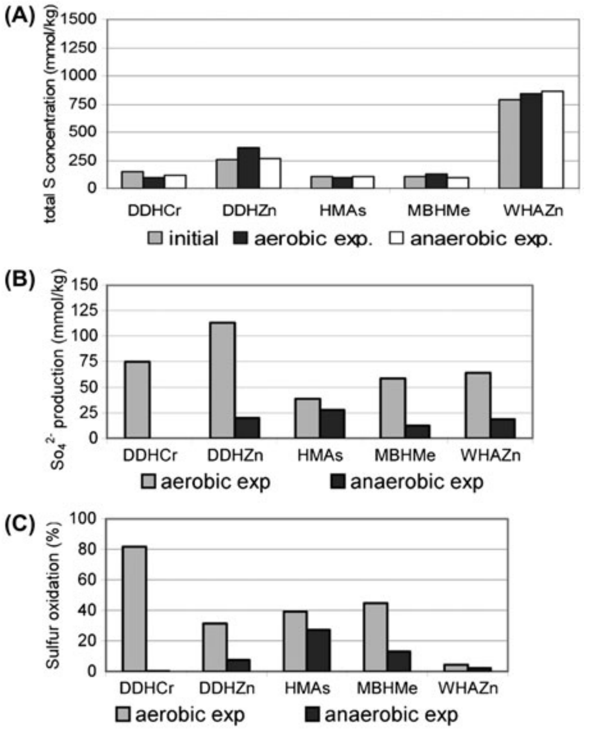

Fig. 6. Sulfur balance for S_{total} concentration (A), SO_4^{2-} production after 21 d (B), sulfur oxidation (C).

Table 2
Comparison of the moles of SO_4^{2-} produced per g dm with the moles of metal solubilized after 21 d at aerobic conditions

Sediment	Sum of mobilized metals (mmol/g dm)	SO_4^{2-} produced in 21 d (mmol/g dm)	Metals solubilized/ SO_4^{2-} produced (%)
DDHCr	0.00448	0.07405	6.04
DDHZn	0.00035	0.11274	0.31
HMAs	2.92E-05	0.03866	0.07
MBHMe	0.00029	0.05882	0.49
WHAZn	0.00044	0.06389	0.68

Analyzing the correlation between SO_4^{2-} produced and metal solubilized at aerobic conditions (Table 2), it can be stated that less than 6% of metals are dissolved compared to SO_4^{2-} formed.

Most probably, the solubility product plays here a role. The solubility product of FeS and ZnS are about equal, whereas CdS and CuS are much more stable.

4. Conclusions

The redox status is often reported as an important parameter while studying the mobilization and availability of heavy metals and As in sediments. Indeed, Cr, Cu, Pb, and Zn showed increased mobility after an increase in the redox potential. However, only up to 1% of the initial metal concentration could be mobilized. The amount of extracted metals that released to the water phase was only 6% of the sulfate formed by oxidation on molar basis. The most probable reason for this phenomenon is the low solubility products of the heavy metals as well as such processes as sorption, adsorption, and desorption. Although an increase in solubilized metals was only 1% compared to the initial metal concentration, still these concentrations are above the maximum allowable concentrations in groundwater and surface water taking into consideration Dutch and Polish legislation. Therefore, oxidation of sediment should be avoided.

On the other hand, the moderately reducing conditions resulted in the release of As from heavily polluted sediments indicating the environmental hazards since such redox changes occur rapidly in dredged sediments. That indicates the risk of re-entering of metals and As fixed in the sediments and the susceptibility of living organisms to them. Therefore, in the further studies, the necessity of remediation of sediments will be taken into account.

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