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Assessment of the Impact of War on Concentrations of Pollutants and Heavy Metals and Their Seasonal Variations in Water and Sediments of the Tigris River in Mosul/Iraq

Zena Altahaan [1,*] and Daniel Dobslaw [2,*]

[1] Institute of Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart, D-70569 Stuttgart, Germany
[2] Department of Biological Waste Air Purification, Institute of Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart, Bandtäle 2, D-70569 Stuttgart, Germany
* Correspondence: zenafahkrey@yahoo.com (Z.A.); daniel.dobslaw@iswa.uni-stuttgart.de (D.D.)

Abstract: The war-related contamination of water and sediment of the Tigris River within the urban area of Mosul leads to seasonally independent exceedances of the WHO limit values for Cd, Pb, Cr, and Ni in water and sediments. Furthermore, exceedances consistently occur for conductivity, PO_4^{3-}, and SO_4^{2-}, as well as sporadically for salinity and COD in water samples, and consistently for salinity in sediment samples, highlighting the direct impact of war (ammunition, ignition of sulfur fields), as well as indirect effects (destroyed wastewater infrastructure). Conflict-related emissions from the former conflict zone (S5–S7) are highlighted by the sudden increases in load from S4 to S5, although partially masked by the discharge of highly polluted water from the Khosr River (between S3 and S4). Due to the sorption of sediments and the presumed wind-borne discharge of highly polluted particles into the Tigris River, sediments at S10 on the southern edge of Mosul showed the highest pollutant loads. Significant statistical differences were observed through T-test analyses for E.C., TDS, salinity, COD, PO_4^{3-}, NO_3^-, SO_4^{2-}, Cd, Pb, Zn, Cr, and Ni for water samples, as well as salinity, Cd, Pb, Zn, and Cr for the sediment samples for seasonal comparison. Since the percentage difference of water samples at S4–S7 is smaller than upstream and downstream, contaminant input is not limited to rainwater but also occurs via the year-round infiltration of highly polluted wastewater from the surrounding valleys or suburban areas, as well as presumably polluted groundwater or windblown particulate input.

Keywords: war impact; heavy metals; WHO limit values; contamination; Tigris River; Mosul

Citation: Altahaan, Z.; Dobslaw, D. Assessment of the Impact of War on Concentrations of Pollutants and Heavy Metals and Their Seasonal Variations in Water and Sediments of the Tigris River in Mosul/Iraq. *Environments* **2024**, *11*, 10. https://doi.org/10.3390/environments11010010

Academic Editors: Athanasia Tolkou and George Z. Kyzas

Received: 5 October 2023
Revised: 14 November 2023
Accepted: 17 November 2023
Published: 3 January 2024

1. Introduction

Over the centuries, wars have always brought disasters to humans and the environment, but the environment remains the silent victim [1]. Such environmental damage and destruction can be divided into three categories.

Environmental damage is caused by pre-war activities to extract resources for direct warfare or to finance the conflicts, e.g., oil, sulfur, mineral resources, or timber [2]. Low-tech processing methods are often used by competing armed groups to minimize investment costs and the need for skilled labor. As a result of low-tech processing, heavy metals such as mercury, lead, or cadmium can be released into the environment and pollute water bodies [3].

Environmental damage occurs due to direct acts of war, such as the destruction of agricultural land and specialty crops, as well as the fate of destroyed weapons and munitions remnants in the environment [2].

Anarchic conditions, or the proclamation of martial law, result in a reduced control and monitoring function of state environmental authorities, leading to private companies operating in conflict zones being subject to minimal environmental oversight [4].

In terms of population and area, Mosul is the second largest city in Iraq after Baghdad. The Tigris River is one of the most important rivers in the region, as it is the main source of water for drinking, industry, agriculture, entertainment, and public purposes in the city [5].

ISIS held the city from June 2014 to July 2017. The liberation battles, which lasted from October 2016 to July 2017, resulted in more than 40,000 casualties and the complete destruction of 9518 buildings (of which approximately 80% were residential), according to UN reports. The resulting debris in Mosul is estimated at 11 million tons. This mass is equivalent to three times the Great Pyramid of Giza or four times the Eiffel Tower [6,7].

The most severe pollution in the urban area, in addition to the direct use of weapons and resulting explosions, was caused by the burning of both 18 oil wells by ISIS in Qarrayah and their nine-month fire (soot) and 50,000 tons of pure sulfur in the Mishraq complex (SO_2, SO_3) [8].The release of these contaminants had a direct impact on water, groundwater, soil, and air and led to an accumulation of these contaminants over time. The consequences are clearly evident today in the quality of water and sediment of the Tigris River [5,9], especially in direct comparison with pre-war studies.

In the pre-war years, the water quality of the Tigris River met the limits set by Iraq and the World Health Organization (WHO) for drinking water and domestic use, although a wide variety of tributaries and activities resulted in the discharge of pollutants. For example, the drainage of many valleys to Lake Mosul, the discharges of the tributaries of the Al-Mur Valley, the Northern Aljazeera Irrigation Project, and the sulfur springs of the Badoosh Dam Project led to increased eutrophication and discharge of sulfur compounds. Furthermore, discharges of hazardous industrial wastes (e.g., cement industry), solid buffalo wastes (min 10 tons dry matter/day) in the Badoosh area, and car maintenance, car washing, livestock washing, and livestock treatment facilities located on both sides of the river bank resulted in degradation of the water quality of the Tigris River in terms of the parameters of hardness, salinity, nutrients, organic loads, and algal growth [10].

In 2012, a study [11] investigated the variations in pollutant concentrations in the Tigris River within the Mosul urban area. The water qualities determined were, on average, equivalent to that of clean water, with 17% of the test samples classified as being polluted. Although the river experienced pollutant discharges from many sources such as households, industry, and agriculture, the dilution and self-purification potential of the river was sufficiently high, especially at high flow rates, to sustain good water quality in the Tigris. The WQI average was 83% (good water quality). In a later study by [12], the authors addressed the water quality of the Tigris River upstream and downstream of Mosul city to elucidate the impact of wastewater discharges in Mosul during the period from 2002 to 2012. The detected nutrient and salinity loads were harmless to the growth and reproduction of all aquatic hydrophyte species. However, the organic loads, as well as the rotting of aquatic plants enhanced by eutrophication, resulted in an increased odor, a change in color and taste, and a significant increase in salinity.

Ref. [13] conducted an assessment of the water quality of the Tigris River in the urban area of Mosul for drinking water and domestic use using the CCME WQI based on fieldwork from 2008 to 2014. For the ten selected parameters, namely pH, turbidity, and concentrations of calcium, dissolved oxygen, dissolved solids, nitrate, chloride, phosphate, and sulfate, the Tigris showed water quality during the study period ranging from 66.3 to 93.7%, i.e., from moderate to good.

A study conducted in 2011–2012 by [14] of heavy metal concentrations in water and sediments within the Mosul urban area showed that heavy metal concentrations in both compartments were within the normal concentration ranges of Iraq, with concentrations in sediments always being higher than in water. The concentrations in water followed the descending order of Zn > Cu > Pb > Cd, while in sediment, a concentration order of Cu > Pb > Zn > Cd was observed. The results revealed a significant increase in the concentration of these heavy metals in both the aqueous phase and sediments in the area of Al-Busaif south of Mosul compared with the control in Al-Mushirfa area in the northwestern part of Mosul.

The importance of heavy metal pollution, besides acute toxicity, lies particularly in its ability to exhibit bioaccumulation in living organisms [15]), even though heavy metals and other contaminants lead to a deterioration in water quality and thus in the health status of the population.

The previous study indicated that there is no comprehensive overview of scientific evidence on the impact of armed conflicts on water resources and their management [16], therefore, aimed to quantify the effect of heavy metal inputs resulting from the war on the water and sediment of the Tigris River within the urban area of Mosul, taking into account seasonal variations (test series winter and spring vs. summer and fall) and comparing measurement points upstream and downstream of Mosul, and to compare them with existing global limits. A comparison of the measured values was made considering the percentage difference as well as the *T*-test approach.

2. Materials and Methods

2.1. Investigation Area

The Tigris River basin is located in the city of Mosul between northwest Mosul at Al Kuba and southeast Mosul at Hammam Al leel within the investigation area, with sampling points as shown in Table 1. The total length of the Tigris River in Mosul is about 214 Km, the width is between 50 and 200 m, the depth is around 50 m, and the river gradient is 1:2000. The basin area is 375,000 km^2. The Tigris River annually discharges 250–400 m^3/s. According to [17], the river bed consists of two layers: a surface layer of gravel with an average diameter of 32 mm and a subsurface layer of gravel and sand with an average diameter of 13 mm. The disc shape is dominant among the gravel grains, followed by flat and spherical [18].

Table 1. Coordinates and description of all study sites on the Tigris River in Mosul.

Site No.	Location Names	Latitude N	Longitude E	Describtion
S1	AlKuba	36.398501	43.074622	Residentioal area
S2	Alrashidia	36.39606	43.114278	Agricultural area
S3	Third bridge	36.363435	43.114976	Recreation area
S4	Finfth bridge	36.35485	43.12616	Recreation Area
S5	Old bridge	36.345667	43.136953	Commercial + Residential
S6	Aljumhoria bridge	36.340904	43.145025	Residential area
S7	Fourth bridge	36.332283	43.152415	Residential area
S8	Jarimjah	36.298735	43.176358	Agricultural area
S9	Albosaef	36.277681	43.163921	Agricultural area
S10	Hammam Al aleel	36.160292	43.263505	Residential area

2.2. Sampling Procedure

Thirty water and sediment samples were each taken at ten points on the Tigris (see Table 1) in triplicate during the two test series (series 1: January to March 2022; series 2: July to September 2022) using clean polyethylene bottles with a capacity of 250 mL, resulting in a total sample volume of 120 samples. The sample temperatures during sampling were 0–10 °C during the first test series, and they were between 35–45 °C in the second test series. The water flow rate during the period of the study was about 250–300 m^3/s.

Each sample was directly stored in a refrigerated container at −4 °C after sampling, transported directly to the laboratory, and further analyzed for 13 parameters: pH, electric conductivity (E.C.), % salinity, total dissolved solids (TDS), chemical oxygen demand (COD), SO_4^{2-}, PO_4^{3-}, NO_3^-, Pb, Zn, Cd, Cr, and Ni. The collection and analysis of the samples in the environmental laboratory was carried out according to standard methods [19].

Water samples were taken according to DIN EN ISO 5667-6. During sampling from the river bank, special attention was paid to ensure that sampling was performed from the homogeneous layer of the water body without picking up surface films, dead water, or swirling bottom sediments. Sampling was performed at mid-height between the riverbed and the surface as shown in Figure 1.

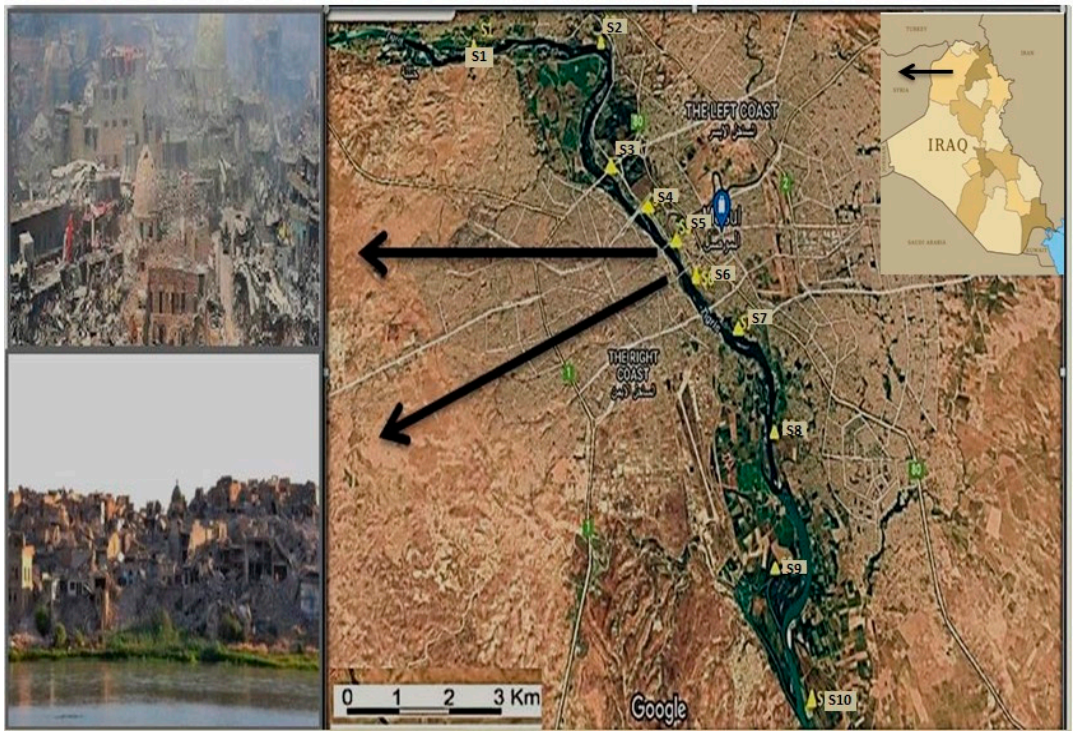

Figure 1. Map of lighted sampling locations.

Sediment samples were taken according to DIN ISO 5667-12 from the upper river sediment layer from a sediment depth of about 0–30 cm with a clean plastic scoop and placed in plastic bags. Sampling took place at the same 10 locations along the river as sampling for water samples.

2.3. Sediment Sample Preparation

Water samples were directly analyzed according to standard methods after membrane filtration. The sediment samples were dried, and their heavy metal concentrations were determined according to the method described in Jackson [20] in which 0.5 g of dry soil was placed in a glass flask and 5 mL of the digestion solution, consisting of concentrated sulfuric acid (H_2SO_4), concentrated nitric acid (HNO_3), and perchloric acid ($HClO_4$), was added at a ratio of 3:1:1. The samples were then heated on a heater at 90 °C in a hood for two hours. After the samples cooled down, they were diluted to 25 mL through the addition of distilled water, and the respective heavy metal concentrations were quantified in mg/kg dry weight of the soil using an atomic absorption spectrometer.

2.4. Field Measurement Parameters

Temperature, pH value, E.C., TDS, and % salinity of water samples were directly analyzed on-site using an Oumefar 5-in-1 digital water quality monitor analyzer of type UPC 886108495111.

2.5. Laboratory Measurement Parameters

The parameters described in Section 2.4 were measured for sediment samples by mixing the sample with distilled water (about 10–15 g of sample in 25 mL of distilled water).

After 2 to 3 min, until the soil was well loosened, the pH, E.C., and salinity of the solution were measured electrometrically with the Oumefar 5-in-1 analyzer. All of the following parameters were analyzed according to [19].

Phosphate PO_4^{3-} (in mg/L) was photometrical analyzed without digestion at 690 nm as phosphorus molybdenum blue using ammonium molybdate solution according to DIN EN 1189.

Nitrate NO_3^- (in mg/L) was also photometrically analyzed at 324 nm after acidification with HCl of the pre-diluted samples using a colorimetric reaction of nitrate with 2,6-dimethylphenole to 4-nitro-2,6-dimethylphenole according to DIN 38405-D9-2.

Sulfate SO_4^{2-} (in mg/L) was quantified through precipitation from acetic acid solution with barium chloride crystals as barium sulfate according to DIN 38405-D5. The intensity of the turbidity of the final suspension was measured at 420 nm using a turbidity meter.

The COD (in mg O_2/L) was determined according to DIN 38409-H41. Abundant potassium dichromate was titrated with iron(II) ammonium sulfate and ferrous as an indicator until the color changed from blue-green to red-brown.

Heavy metals (Cd, Cr, Ni, Pb, Zn) were analyzed after acidic digestion and were analyzed using a Phoenix-986AAS atomic absorption spectrometer. Absorbance levels were converted into concentrations in ppm through calibrations for each compound.

3. Result and Discussion

3.1. Water Samples

3.1.1. pH Value

The pH analysis at all sampling points revealed pH values between 6.84 and 7.53 (test series 1) and between 6.71 and 7.28 (test series 2), which were within the WHO guidelines [21] Along the flow route of the Tigris River, the pH decreased to 6.8–6.9 within the city passage compared to unpolluted conditions (test site 1; 7.28–7.53) due to the discharge of organic pollutant loads and the biodegradation of these contaminants [22], causing partial acidification due to oxygen-limiting conditions. Due to a combination of higher water temperature and thus lower oxygen solubility, higher biodegradation activity, and lower water flow velocity because of low river levels during dry months, oxygen limitation is more prominent in summer months. However, the drop did not exceed 0.69 pH units because the carbonate hardness of the river water resulted in a high buffering capacity [22] This is consistent with the fact that, if this buffering capacity was not present, a significant fluctuation in pH would be expected with implications for aquatic life [23] especially as lead levels are strongly affected by the presence of both orthophosphate (also a typical wartime contaminant) and organic contaminants in a pH range of 7.2–7.8 [24].

3.1.2. Electric Conductivity, Total Dissolved Solids and Salinity

Electrical conductivity of surface waters is highly regional and can range from 50 to 1500 µS/cm [25]. Studies of US inland fresh waters indicate that streams supporting good mixed fisheries have a range between 150 and 500 µS/cm [25]. Conductivity outside this range may indicate non-suitable water for certain species of fish or bugs. High conductivity of up to 10 µS/cm in inland surface water strongly indicates water contamination by industry or crises. The WHO suggests mid-range conductivity (200 to 1000 µS/cm), and maximal conductivity (1400 µS/cm) is the normal background for most major rivers [26]. Measurements in the Tigris River were within the WHO's target value in both test series, and the values are also within the range of electrical conductivities of North American streams, so this parameter is not an exclusion criterion for the use of Tigris water. However, it can be seen over the flow length that the conductivity increases over all 10 measuring points from originally 444.3 µS/cm to 884.3 µS/cm (test series 1) from 418.3 µS/cm to 623 µS/cm (test series 2). Thus, there is a discharge of saline wastewater or contaminated surface runoff through the urban area. Also, infiltration of saline series water cannot be excluded, since the hydrogeological Aljazeera area is part of the Tigris hydrogeological basin in which water flow converges towards the River Tigris [27–29]. Correspondingly,

the detected TDS curve correlates with the electrical conductivity, which also increases continuously between the measuring points S1 to S6 (series 1: 405 mg/L to 787 mg/L; series 2 from 292.3 mg/L to 621 mg/L; mean values in each case) and drops by approximately 10% to S7 in both series and then remains nearly unchanged. The TDS concentrations remain below the WHO specifications, whereby high TDS values are not fundamentally harmful to humans. However, the consumption of water with high TDS values can have an increased negative effect on people with kidney and heart diseases in particular. In general, this water may also have an increased laxative but also constipating effect [30,31].

The same effect was observed for the salinity content, which increased from 0.31% (series 1) or 0.39% (series 2) at the reference point S1 to the measuring point S7 and dropped by 35–71% and decreased by about 15–36% to S10. The WHO limit value was just met at S7 during wintertime. Comparing both series shows that an inconsistent picture is drawn for these three parameters. Due to the lack of precipitation during the summer period, and thus lower levels in the Tigris, an increase in electrical conductivity, TDS value, and salinity due to anthropogenic discharges would be expected. However, a direct comparison of Tables 2 and 3 shows that electrical conductivity outside the urban area remained almost unchanged, while that within the urban area remained 30% lower than during wintertime (series 1).

Table 2. Mean and standard deviation values for the concentration of pollutants and heavy metals for all study sites in the river water (series 1).

S1 Water		pH	E.C. µS/cm	TDS mg/L	Sal. %	COD mg/L	PO_4 mg/L	NO_3 mg/L	SO_4 mg/L	Cd µg/L	Pb µg/L	Zn µg/L	Cr µg/L	Ni µg/L
WHO Std.		**6.5–8.5**	**1400**	**1000**	**1%**	**100**	**0.4**	**50**	**250**	**5**	**10**	**5000**	**50**	**20**
S1	Mean	7.53	444.33	405.00	0.31	29.00	0.28	2.62	90.3	5.1367	30.236	338.2	27.8	26.66
	±Sd	0.31	29.3	21.39	0.09	3.06	0.02	0.62	28.10	1.5	14	19	3	7
S2	Mean	7.51	544.33	488.67	0.59	43.33	0.55	3.00	124.7	9.1333	96.47	292.13	37.98	28.33
	±Sd	0.26	12.10	52.32	0.10	5.51	0.11	0.58	6.24	1.2	18	20	6	7
S3	Mean	6.84	693.67	611.33	0.75	44.67	0.72	3.02	189.3	11.3333	130.53	246.50	56.47	46.67
	±Sd	0.16	22.11	34.59	0.06	4.51	0.05	0.60	24.21	4.5	16	34	13	11
S4	Mean	6.90	702.00	711.00	0.97	96.33	0.88	3.74	307	16.1333	138.73	923.33	57.00	56.67
	±Sd	0.09	19.55	34.59	0.04	7.77	0.06	0.10	6.56	4.7	23	37	12	18
S5	Mean	6.87	812.00	776.00	0.70	112.33	0.98	4.65	385.0	18.3333	143.73	973.33	59.00	69.67
	±Sd	0.22	17.62	48.17	0.07	8.08	0.08	0.06	32.19	5.8	34	52	27	21
S6	Mean	6.86	884.33	787.00	0.40	102.67	0.91	2.67	385.0	28.3667	163.80	1496.33	73.15	94.07
	±Sd	0.21	39.04	63.52	0.06	5.29	0.11	0.45	26.85	8	26	29	29	19
S7	Mean	6.98	829.67	717.00	1.07	90.67	0.94	4.03	493.0	26.0000	159.20	1284.00	78.57	92.33
	±Sd	0.15	53.59	45.65	0.07	9.61	0.06	0.50	130.66	7	32	55	14	17
S8	Mean	7.04	711.00	737.67	0.78	82.33	0.75	3.00	410.0	24.6333	169.00	1087.00	64.11	90.33
	±Sd	0.22	26.69	44.84	0.03	6.56	0.11	0.73	26.91	6	22	58	12	15
S9	Mean	7.20	660.67	748.00	0.49	92.00	0.59	3.04	383.7	18.8333	163.33	1165.33	66.23	85.27
	±Sd	0.23	36.01	71.15	0.09	5.03	0.03	0.45	62.66	4	14	37	16	17
S10	Mean	7.13	616	734	0.68	89	0.522	3.071	334.3	18.3333	148	1811.814	61.51333	83
	±Sd	0.25	28.21	28.75	0.04	5.00	0.06	0.78	51.59	7	12	52	13	18
		Zone 1				Zone 2			Zone 3				Zone 4	

In the case of the TDS values, there was an increase from 0.48% (series 1) or 0.52% (series 2) at reference point S1 to measuring point S5 or S7, which dropped by 6–17% to S10. The WHO limit value is just met at S7 during wintertime, with summer levels also being 35–40% lower. The situation is similar to that of salinity, which is also about 30% lower in summer than in winter but rises by 48% (winter) or 25% (summer) over the city passage. It temporarily increases by a factor of 2–3 within the urban area. The most likely explanation for this scenario is that due to the lack of precipitation in summer and thus the lack of surface runoff, a significantly lower pollutant load is flushed into the Tigris. In addition to anthropogenic discharges, the increase in contaminants in the urban area is due

to the presence of valleys loaded with contaminated water that flows from both sides of the river into the Tigris [22,27–29,32].

Table 3. Mean and standard deviation values for the concentration of pollutants and heavy metals for all study sites in the river water (series 2).

S2 Water		pH	E.C. µS/cm	TDS mg/L	Sal. %	COD mg/L	PO_4 mg/L	NO_3 mg/L	SO_4 mg/L	Cd µg/L	Pb µg/L	Zn µg/L	Cr µg/L	Ni µg/L
WHO Std.		**6.5–8.5**	**1000**	**1000**	**1%**	**100**	**0.4**	**50**	**250**	**5**	**10**	**5000**	**50**	**20**
S1	Mean	7.48	418.33	292.33	0.39	24.67	0.32	1.82	57.7	3.901	15.85	178.53	16.67	16.67
	±Sd	0.306	29.297	21.385	0.090	3.055	0.020	0.616	28.095	0.54	4.5	18	3.2	5.2
S2	Mean	7.300	524.33	315.33	0.34	28.67	0.31	1.999	107.0	6.98	66.67	196.53	24.40	13.31
	±Sd	0.265	12.097	52.320	0.104	5.508	0.111	0.578	6.245	1.8	11	20	5.7	3..5
S3	Mean	7.163	558.00	381.67	0.51	32.67	0.38	2.055	140.3	8.33	98.75	146.50	37.44	23.33
	±Sd	0.158	22.113	34.588	0.064	4.509	0.051	0.602	24.214	2.1	18	15	14	8
S4	Mean	7.093	498.33	401.33	0.47	51.67	0.51	2.487	147.0	14.76	122.40	848.17	50.00	57.67
	±Sd	0.090	19.553	34.588	0.038	7.767	0.064	0.100	6.557	1.8	34	37	16	13
S5	Mean	6.980	597.67	469.67	0.58	74.33	0.70	2.766	315.3	23.25	152.20	1391.07	60.47	83.33
	±Sd	0.220	17.616	48.170	0.068	8.083	0.080	0.056	32.192	3.6	31	134	23	19
S6	Mean	6.810	596.00	554.67	0.52	63.00	0.74	2.167	289.0	23.60	138.80	1266.80	63.93	81.
	±Sd	0.209	39.038	63.516	0.061	5.292	0.109	0.452	26.851	8	22	288	19	17
S7	Mean	6.993	610.00	557.00	0.60	65.30	0.81	2.477	232.5	22.53	130.20	1183.	67.53	68.33
	±Sd	0.148	53.594	45.654	0.070	9.609	0.063	0.503	130.664	8.8	35	242	23	18
S8	Mean	7.017	623.00	621.	0.40	59.00	0.56	2.228	293.0	20.04	99.42	853.67	49.67	60.47
	±Sd	0.222	26.690	44.837	0.025	6.557	0.106	0.730	26.907	6.5	21	95	19	17
S9	Mean	7.087	583.00	516.60	0.49	50.33	0.59	2.370	318.3	15.10	88.25	885.60	46.67	56.17
	±Sd	0.228	36.014	71.150	0.093	5.033	0.030	0.450	62.660	4.5	16	167	15	16
S10	Mean	6.833333	593.00	510.33	0.51	58.00	0.52	2.111	320.7	13.84	57.75	1208.03	47.42	55.63
	±Sd	0.254	28.213	28.746	0.040	5.0	0.055	0.776	51.588	4.80	21	214	13	14
		Zone 1			Zone 2				Zone 3			Zone 4		

3.1.3. Chemical Oxygen Demand COD

The thesis of increased infiltration of contaminated water can be confirmed using COD data. In both series, an increase in the COD value (about 73 mg O_2/L in series 1 and about 50 mg/L in series 2), respectively, occurred across the urban area. Within the city, even higher COD values of 112.3mg O_2/L (S5, series 1) and 74.33 mg O_2/L (S5, series 2) were temporarily achieved, detectable at nearly identical levels at S10 during the winter period, while a decrease of about 35% due to biodegradation processes was observed during the summer period, because of the discharge of polluted wastewater or contaminated surface runoff through the urban area to the river during the winter season and the infiltration of polluter groundwater, and from the valleys that, loaded with pollution, flowed into the river [10,33]. The increased direct or indirect discharge of sanitary wastewater and thus increased organic loads into the river due to war-related damages to the sewage system have been previously described [5].

3.1.4. Nitrate, Phosphate, and Sulfate

There are a variety of potential emission sources for nitrate, phosphate, and sulfate. For example, these anions can be released during the exploration of minerals, the agricultural use of fertilizer, industrial effluents, and general leakages in the destroyed municipal sewage network, but also through the direct use of weapons and ammunition. In the latter case, nitrate is directly used in munitions as ammonium nitrate.

Conflict-related phosphate emissions in the urban area of Mosul are particularly known from the use of phosphorus bombs during the liberation in the summer of 2017 [34]. However, this type of bomb was also used by U.S. forces during the second Gulf War [35]. Sulfate emissions can result from the combustion of antimony sulfides when munitions are fired [36,37]. However, in the case of Mosul, the burning of the Mishraq industrial

complex (SO_2, SO_3) [8,38], 45 km south of Mosul in October 2016, in particular, played a substantial role, where the resulting gases entered the river through wet deposition into the soil and surface drainage [5], and the sulfur springs extend from Mosul in the north to Qayara in the south for 60 km along the Tigris River, where the River Tigris is also a zone of discharge [27].

Accordingly, the analyses of the water samples for phosphate and sulfate, apart from S1 as the most northwestern measuring point, showed, in some cases, significant exceedance of the WHO limits. Thus, phosphate concentrations increased by a factor of 1.8–1.9 through the urban passage in both series, regardless of the season. In some cases, detected phosphate levels of 0.81 mg P/L (series 2) and 0.94 mg P/L (series 1) exceeded the WHO limit by a factor of 2–3 within the urban region. Phosphate levels exceeded limits from S2 to S10 in series 1 and from S4 to S10 in series 2.

Sulfate levels exceeded limits from S2 to S10 in series 1 and from S5 to S10 in series 2, at the highest value of 495 mg/L (S7 in Series 1). Again, a key aspect of lower sulfate levels, but also other anion levels, was the lack of surface drainage in combination with valleys contaminated with water infiltration to Tigris. However, biodegradation represents a second, possibly even dominant factor, where both sulfate and nitrate may be used as electron acceptors instead of oxygen. This aspect could be easily verified due to the severe odor emissions of H_2S gas near the valleys. Direct drainage into the river has been described previously [22,32,39]. In addition to the above factors, the detected sulfate levels were further increased by the dissolution of gypsum rock due to the impoundment of Tigris water in Mosul Lake [11].

In the case of nitrate, the course over the river flow showed only a small increase at S7, which is mainly due to agriculture upstream but remains at an almost constant level over the course of the river. As microbiological H_2S formation, and thus inevitably microbiological nitrate respiration as a sink of nitrate, occurred, a continuous discharge of nitrate over the urban area took place. The discharge was caused by defects in the sewage system and infiltration processes as a consequence. Nitrate concentration was clearly below the WHO limit value at all locations, irrespective of the season.

3.1.5. Heavy Metals

Due to international contracts prohibiting the use of expanding bullets, as well as the higher cost of hollow-point ammunition, full metal jacket bullets are the most used cartridges by soldiers as well as militias [40]. They consist of a soft core, usually lead, and a harder jacket metal alloy such as gilding metal (CuZn), CuNi, or steel encasing the core [36]. The purpose of this design is to provide improved trajectory as well as greater penetration of the projectiles into soft tissue [40,41]. Supplementary galvanic cadmium coatings are applied to improve some properties like corrosion resistance, improved tribological properties, and chemical stability [37]. Chromatic layers are applied as supplementary passivation [37]. Therefore, the use of weapons in conflict zones leads to an increase in heavy metal concentrations.

Concentrations of Cd, Pb, Cr, and Ni exceeded WHO limits even before entering the city (S1), while increasing further, especially through the Old City passage as a direct conflict zone (S5–S7) in both series.as shown in Figure 2.

The maximum concentrations (in µg/L) were 28.37 Cd, 169 Pb, 78.5Cr, and 94 Ni in series 1 and 23.6 Cd, 152.2 Pb, 67.5 Cr, and 83.3 Ni in series 2, and the WHO limits were exceeded here in part by a factor of 4.7 for Cd and 32 for Pb and 5.6 for Cr and 14.8 for Ni, as follows: Pb > Ni >> Cr > Cd > Zn. For Zn, a comparable concentration pattern occurred over the urban passage, but with maximum values of 1811.8 µg/L (series 1) and 1391 µg/L (series 2), the limits were not exceeded.

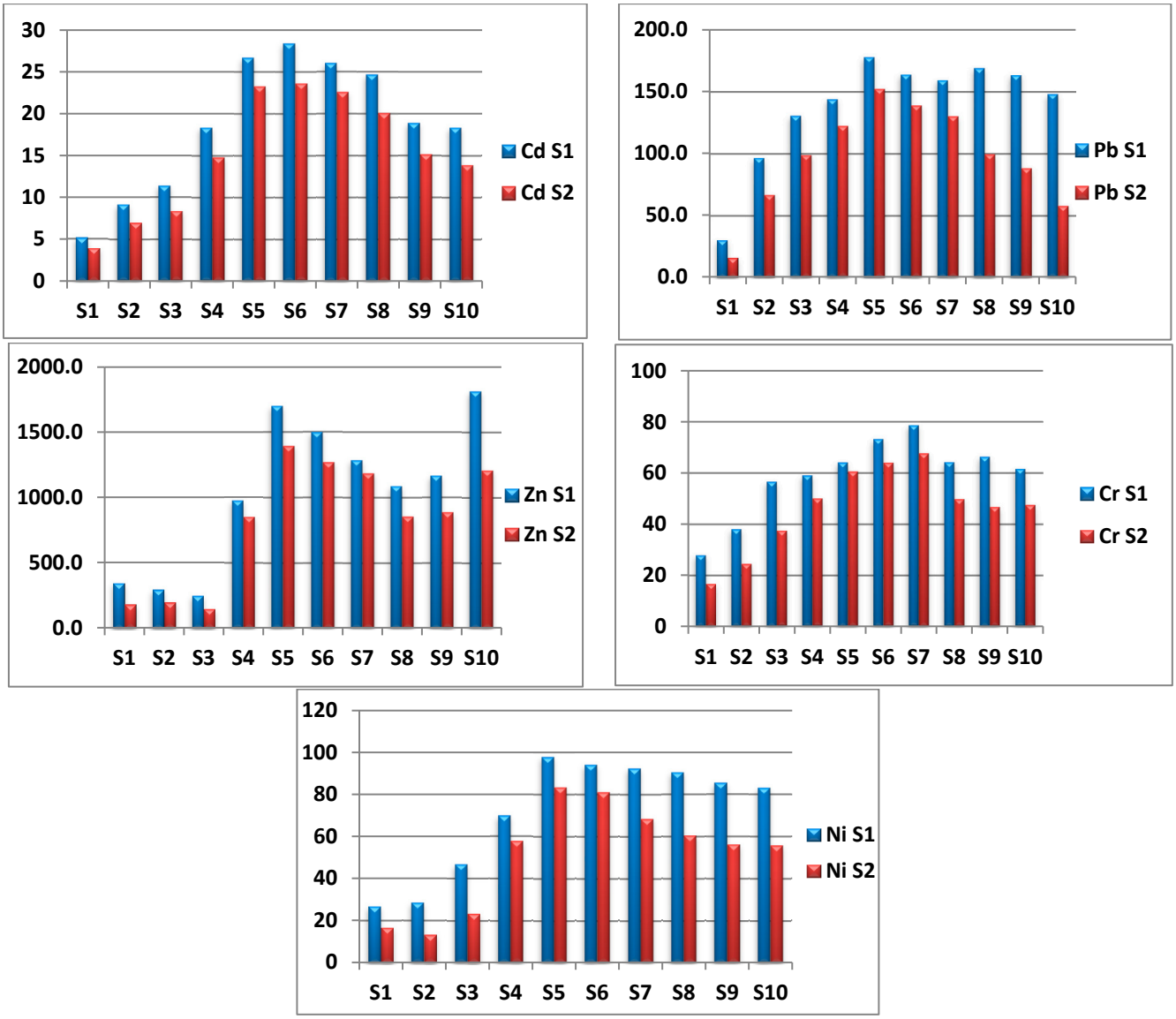

Figure 2. Average values of heavy metal concentration in the first and second series in river water in all sites.

3.1.6. Comparison of Water Samples in Conflict Zone vs. Urban Zone

The pollution of the Tigris River can be divided into four zones over its flow length in the urban area. Zone 1 (S1), as a reference before entering the densely populated urban area, illustrates the back pollution of the river. Zone 2 (S2–S4) essentially represents contamination from agricultural drainage. Since the zone is otherwise characterized by recreation areas, the influence of municipal drains is still low there. Between sampling points S4 and S5, the Al Khosr valley drains into the Tigris, which carries a heavy pollutant load on its flow route from the northeastern valleys through densely populated areas [42] and therefore leads to a strong increase in the parameters E.C., TDS, salinity, COD, nitrate, phosphate, and sulfate at S5.

The military operations to liberate Mosul focused on the Old City of Mosul, where sampling points S5–S7 (zone 3) are located. Therefore, within this zone, an increase in heavy metal concentrations is expected and has been observed as an indicator. Th destruction of the drainage infrastructure also leads to a further increase in the above parameters. zone 4, represented by S8–S10, again represents an area with strong agricultural use and residential development outside the direct conflict zone, so the discharge situation here is limited to

agricultural and municipal parameters, and the heavy metals decrease in concentration due to (bio)chemical processes such as adsorption, precipitation, uptake in tissues, and dilution effects.

The differences in concentration between summer and winter periods caused by the lack of surface drains and existing groundwater infiltration have already been pointed out. In addition, the role of entrained sediments should be mentioned, which will be further discussed in Section 3.2.

3.1.7. Comparison of Water Samples in Current Study with Previous Study

The comparison of the annual average values of heavy metals (Cd, Pb, and Zn) in zone 1, zone 3, and zone 4 in the current study in 2022 with a previous study of [14] which was conducted before the occupation and liberation of the city between 2011 and 2012, showed that, in S1, the values of Cd increased by a factor of 4.0, in zone 3 by a factor of 6.25, and in zone 4 by a factor of 3.69 and Pb values increased in zone 1 by a factor of 4.75, in zone 3 by a factor of 6.14, and in zone 4 by a factor of 3.17. Furthermore, the values of Zn in zone 1 decreased by a factor of −1.45, in zone 3 increased by a factor of −1.15, and decreased by a factor of −1.23 in zone 4 as shown in Table 4.

Table 4. Comparison of annual values of heavy metal values in water samples in the current study with previous study [14].

Sites	Element	2013	2022	Factor
Zone 1	Cd	1	4.0	4.0
	Pb	4	19	4.75
	Zn	469	258.4	−1.45
	Cr	ND	22.2	ND
	Ni	ND	21.7	ND
Zone 3	Cd	4	25.0	6.25
	Pb	27	165.1	6.14
	Zn	1339	1544.5	1.15
	Cr	ND	62.2	ND
	Ni	ND	90.5	ND
Zone 4	Cd	5	18.46	4.0
	Pb	33	102.9	3.17
	Zn	1961	1509.9	−1.23
	Cr	ND	54.5	ND
	Ni	ND	69.3	ND

The results indicated that zone 3 represents the most polluted site, especially with Cd and Pb. The increase was significant compared with the previous year, while the variant between the two studies in Zn values was not significant, as shown in Table 4. Even so, a significant increase in zinc concentration was observed within the present study compared to the previous year, and no significant differences were observed in comparison with the study by [14]. Sampling within zone 2 was not carried out by the latter.

3.1.8. Statistical Analysis

An adequate approach for the statistical analysis of deviations in analytical data and their significance is the *t*-test. The results for E.C., TDS, COD, nitrate, phosphate, sulfate, Cd, Pb, Zn, Cr, and Ni showed levels below the critical value ($p < 0.05$), which is why they are considered statistically significant differences. Thus, based on the null hypothesis that the sample mean and population mean are statistically different at the 0.05 significance

level due to the time lag between the two analytical series, a significant statistical difference results between these two series ($p < 0.05$, see Table 5).

Table 5. *t*-test value between first and second series for all sites in river water.

Parameters	*t*-Test	Df *	*p*	Status $p < 0.05$
PH	1.745881	18	0.048938	1
EC	2.648184	18	0.008176	1
TDS	3.868649	18	0.000563	1
Salinity%	2.669917	18	0.007808	1
COD	2.586038	18	0.009319	1
PO_4	1.826824	18	0.042179	1
NO_3	5.394127	18	1.99×10^{-5}	1
SO_4	1.813528	18	0.021327	1
Cd	1.798236	18	0.021757	1
Pb	2.008098	18	0.029941	1
Zn	1.668797	18	0.025606	1
Cr	1.6898	18	0.054156	1
Ni	1.484068	18	0.077546	1

* Df: degree of freedom.

The percentage difference in heavy metal analyses between the two series, S1 and S2, at all sites showed that the values of Cd, Pb, Zn, Cr, and Ni in S1, S2, S3, S8, S9, and S10 were higher than the values in S4, S5, S6, and S7, although the concentrations of pollutants in these sites were higher compared to other sites, which is due to the fact that the pollutants at these sites (S4, S5, S6, and S7) is discharged throughout the year via the drains from the valleys and is not only discharged via rainwater. Rather, surface drains from rainwater additionally enter the Tigris in addition to existing drains, which significantly increases the percent of pollution in the river at these sites, especially in winter. According to the topography and the slopes of the Old City, the passage of the water of the runways and their movement from the highest areas and their flow to the low area that represent the highest levels of drainage systems, or the main valleys, that eventually flow into the Tigris River [43].

The lowest percentage differences between both runs were seen at S5 and S6 for Cd (12.8% vs. 16.8%), Pb (14.5% vs. 18.2%), Ni (13.9% vs. 26%), Zn (7.8% vs. 18.2%), and Cr (5.5% vs. 14%), as shown in Table 6 and Figure 3. Differences at other locations (S1, S2, S3, S8, S9, S10) were higher in this case since the main pollution source of the Tigris River is the winter rainwater drain; therefore, the difference in heavy metal concentrations between both series is even more evident.

Table 6. The percentage of difference between the first and second series in all water sites.

Sites	Cd %	Pb %	Zn %	Cr %	Ni %
S1	24.0	47.6	47.2	40.0	37.5
S2	23.6	30.9	32.7	35.8	53.0
S3	26.5	24.3	40.6	33.7	50.0
S4	19.5	14.8	12.9	15.3	17.2
S5	12.8	14.5	18.1	5.5	14.7
S6	16.8	15.3	15.3	12.6	13.9
S7	13.3	18.2	7.8	14.1	26.0
S8	18.6	41.2	21.5	22.5	33.1
S9	19.8	46.0	24.0	29.5	34.1
S10	24.5	61.0	33.3	22.9	33.0

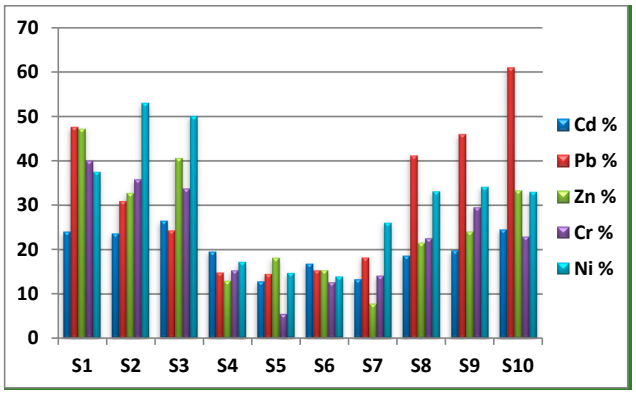

Figure 3. Percentage of difference of concentrations between the first and second series for heavy metals in all sites.

Table 7 and Figure 4 show that the ranking in the percent differences in site contaminants between upstream S1 and downstream S10 in both runs was as follows: Zn > Pb > Cd > Ni > Cr and for other parameters SO_4 > COD > Salinity > TDS >> PO_4 > >E.C. > NO_3. Except for pH values, the percentage increase in all parameters between upstream and downstream was higher in (series 1) (winter, spring) than in (series 2) (summer, Autumn) because the increased biodegradation of organics in summer combined with oxygen limitation led to an enhanced decrease in pH, which is also indicated by [44].

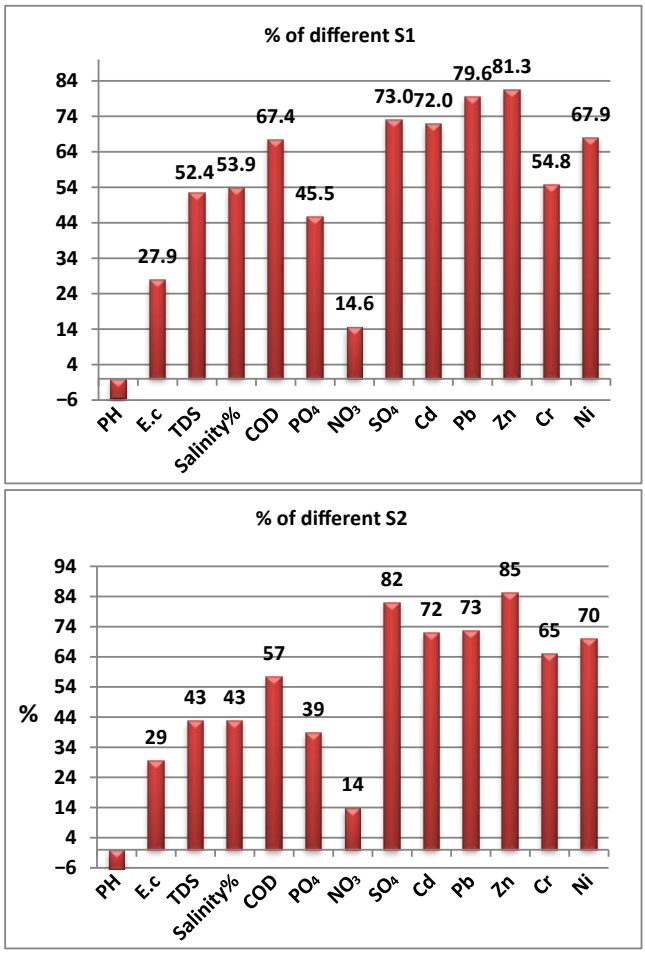

Figure 4. Percentage of difference of concentrations between Upstream (S1) and Downstream (S10) in both.

Table 7. Percentage of difference of concentrations between Upstream (S1) and Downstream (S10) in both.

	Series 1				Series 2			
	Upstream	**Downstream**	**Df**	**% DF**	**Upstream**	**Downstream**	**Df**	**%Df**
PH	7.5	7.1	−0.4	−5.6	7.18	6.73	−0.45	−6.63
E.C.	444.3	616.0	171.7	27.9	418.33	593.00	174.67	29.45
TDS	405.0	850.0	445.0	52.4	292.33	510.33	218.00	42.72
Salinity%	0.3	0.7	0.4	53.9	0.29	0.51	0.22	42.76
COD	29.0	89.0	60.0	67.4	24.67	58.00	33.33	57.47
PO_4	0.3	0.5	0.2	45.5	0.32	0.52	0.20	38.70
NO_3	2.6	3.1	0.4	14.6	1.82	2.11	0.29	13.78
SO_4	90.3	334.3	244.0	73.0	57.67	320.67	263.00	82.02
Cd	5.1	18.3	13.2	72.0	3.90	13.85	9.95	71.83
Pb	30.2	148.0	117.8	79.6	15.85	57.75	41.90	72.55
Zn	338.2	1811.8	1473.6	81.3	178.53	1208.03	1029.49	85.22
Cr	27.8	61.5	33.7	54.8	16.67	47.42	30.75	64.85
Ni	26.7	83.0	56.3	67.9	16.67	55.63	38.97	70.04

3.2. Sediment Samples

3.2.1. Chemical Parameters and Heavy Metals

Sediments are an important sink for pollutants, but they can also lead to the contamination of the water body through descriptive processes. In particular, if the sediment is primarily of a mineral nature, ions (e.g., heavy metals) may be adsorbed [45]. However, the interaction strength of heavy metals and geochemical fractions of sediments strongly depends on exchangeable, reducible, oxidizable, and residual fractions of the sediment [46,47]. The exchangeable and, therefore, weakly bound geochemical sediment fractions include the fixation of heavy metals to the solid surface via weak electrostatic interactions [48,49]. Hence, changes in environmental parameters like pH, E.C., or salinity can promote the desorption of heavy metals via the breakdown of these weak electrostatic interactions [47,50,51]. If the sediment is primarily of organic nature, organic contaminants (e.g., pharmaceuticals, flame retardants) may be adsorbed [52,53]. In addition to the complexity of the sediment composition, the interpretation of occurring distribution equilibrium between the sediment phase and the liquid phase is particularly complicated by the downstream transport of sediment or small-particle and thus suspended silt fractions. Hence, it is to be expected that even outside the direct conflict zone or the urban area, increased pollutant concentrations may occur in the water phase, as well as in the river sediment, due to sediment transport and subsequent desorption.

In fact, the sediment analysis confirmed a continuous increase in heavy metal concentrations over the flow distance, with the highest concentrations occurring at the southern urban border (S10) due to hydrogeological formation and slope of the Tigris River's bed. A similar result was already presented by [14]. The detected heavy metal concentrations had a mean of 6.30 ppm Cd, 45.33 ppm Pb, 21.33 ppm Zn, 81.33 ppm Cr, 64.00 ppm Ni (series 1), 9200 ppm Cd, 62,800 ppm Pb, 30 ppm Zn, 123,6 ppm Cr, and 78 ppm Ni (series 2). WHO limits were permanently exceeded at all locations except that of Zn. In the case of S10, the limit values for Cd, Pb, Cr, and Ni were exceeded by a factor of 3.1, 1.3, 3.3, and 3.2 (series 1) and by a factor of 4.6, 1.8, 4.9, and 4.0 (series 2). For zinc, the limits were met despite an increase in concentration over the urban passage (see Tables 8 and 9). However, due to the interaction between dissolved heavy metals in the water phase and sorbed heavy metals in the solid phase, severe local variations in concentration, in contrast to the water phase, were not detectable.

In the case of the parameters pH, E.C., and salinity, no significant change occurred for the pH value during the winter series. During the summer series, however, a moderate decrease in the pH value by 0.77 units in absolute terms was observed over the urban area. This decrease is related to the increased degradation of organic pollutants induced by higher temperatures, with partial oxidation of the components. The pH drop turns out to be comparatively small, since both the morphological sediment composition and

the existing lime–carbonic-acid equilibrium in the water phase, as well as the sediment phase, lead to a pH buffering [54].This pH buffering prevents the enhanced pH-induced mobilization of heavy metal ions. This effect has already been described for Cr, Ni, and Zn [46]. The mobility of heavy metals is further influenced by E.C., as well as salinity, with enhanced mobilization at increasing E.C. and decreasing salinity, respectively. Both parameters increased by a factor of 1.6–2.4 over the urban passage and just exceeded the WHO limits by a factor of 6.4 for E.C. and by a factor of 3.3 for salinity in the summer measurement, while in the winter period, only salinity exceeded the WHO limit by a factor of 1.8.

Table 8. Average and standard deviation values for the concentration of pollutants and heavy metals for all study sites in sediment (Series 1).

S1		pH	E.C.	Sal.%	Cd	Pb	Zn	Cr	Ni
WHO Std. Limits		**6.5–8.5**	**1000 µS/cm**	**1%**	**2 PPM**	**35 PPM**	**90 PPM**	**25 PPM**	**20 PPM**
S1	Mean	7.44	710	0.86	2.78	25	12	28.20	27
	±Sd	0.31	50	0.07	0.26	2.33	1.00	6.01	2.00
S2	Mean	7.78	680	0.88	2.87	24.70	10.33	36.00	32.67
	±Sd	0.43	20	0.28	0.32	1.12	1.53	7.94	6.51
S3	Mean	7.57	750	1.34	3.50	29.80	14.67	41.67	32.33
	±Sd	0.29	40	0.17	0.96	0.35	3.51	4.16	7.02
S4	Mean	7.80	800	1.50	4.44	33.70	11.67	40.67	37.00
	±Sd	0.10	40	0.00	0.30	0.30	2.07	8.50	2.65
S5	Mean	7.55	1150	1.17	5.63	35.40	16.50	73.67	49.00
	±Sd	0.19	240	0.12	0.83	1.26	3.97	3.51	6.24
S6	Mean	7.53	1640	1.44	5.48	38.20	18.67	80.00	52.00
	±Sd	0.40	710	0.23	0.30	1.53	3.06	1.00	4.36
S7	Mean	7.64	50	1.34	5.87	38.67	19.33	78.67	57.00
	±Sd	0.49	680	0.13	0.35	3.06	3.51	4.51	6.56
S8	Mean	7.93	20	1.03	6.30	40.00	17.83	77.67	59.67
	±Sd	0.05	750	0.12	0.60	1.00	5.11	6.51	4.16
S9	Mean	7.86	40	1.10	5.47	44.33	20.67	80.33	63.67
	±Sd	0.40	800	0.64	0.21	4.51	6.11	3.06	8.50
S10	Mean	7.17	40	1.82	6.23	45.33	21.33	81.33	64.00
	±Sd	0.32	1150	1.05	0.55	2.50	2.50	7.50	8.14
Zone 1			Zone 2		Zone 3			Zone 4	

Table 9. Average and standard deviation values for the concentration of pollutants and heavy metals for all study sites in sediment (Series 2).

S2		pH	E.C.	Sal.%	Cd	Pb	Zn	Cr	Ni
WHO Std. Limits		**6.5–8.5**	**1400**	**1%**	**2 PPM**	**35 PPM**	**90 PPM**	**25 PPM**	**20 PPM**
S1	Mean	7.62	611	1.387	3.3	31.3	10.16	32.0	30
	±Sd	0.19	88	0.528	0.6	7.87	0.76	9.5	3.0
S2	Mean	7.79	777	1.617	3.3	33.66	12.6	50.3	37.6
	±Sd	0.39	110	0.458	0.8	4.51	1.87	11.4	5.6
S3	Mean	7.27	807	1.343	4.28	35.6	15.1	50.6	39.3
	±Sd	0.26	90	0.151	0.7	3.7	2.9	10.4	6.8
S4	Mean	7.80	920	1.667	5.8	40	17.0	42.66	46.0
	±Sd	0.08	42	0.204	0.8	2.3	3.8	12.3	5.8
S5	Mean	7.35	1146	1.517	6.9	43.1	20.3	79.0	58.3
	±Sd	0.19	215	0.264	0.78	2.7	3.52	11.1	6.9
S6	Mean	7.28	1105	1.650	7.37	46.33	22.0	89.0	58.3
	±Sd	0.30	297	0.310	0.88	4.40	3.5	5.0	9.22
S7	Mean	7.13	1267	1.377	7.79	47.6	25.33	92.3	64.80
	±Sd	0.41	367.5	0.6194	0.87	4.41	9.83	9.35	0.41
S8	Mean	7.03	1062	1.600	7.76	51.6	21.6	97.0	67.90
	±Sd	0.53	36	0.431	0.46	7.67	4.7	11.7	3.34
S9	Mean	6.97	1365	1.857	7.86	49.6	24.3	96.0	71.2
	±Sd	0.55	143	0.478	1.20	6.06	5.9	13.1	6.43
S10	Mean	6.86	1445	3.292	9.20	62.8	30.	123.60	79.0
	±Sd	0.45	112	0.340	0.86	4.44	2.8	16.1	5.6
Zone 1			Zone 2			Zone 3		Zone 4	

3.2.2. Comparison of Sediment Samples in Urban Zone between Both Series

The direct comparison of these parameters between both series showed, with the exception of the pH value (see above) and the E.C. (almost unchanged), significant increases of 1.6–1.8 (salinity), 1.2–1.5 (Cd), 1.2–1.4 (Pb), 1.4 (Zn), 1.2–1.5 (Cr), and 1.1–1.2 (Ni) in the summer period (series 2, see Tables 8 and 9). This increase during dry weather is probably related to the presence of valleys that flow into the Tigris River during the summer as well, which are loaded with polluted water from the residential and agricultural areas it passes through [8], the combination of low flow velocity of the Tigris during the dry weather phase, and thus also an increased deposition of small particles, which either infiltrated directly into the Tigris from the conflict zones or were lifted up by wind and settled down above the water surface, as well as an increased particle-bound heavy metal input during the precipitation phase in winter and spring (series 1; These particles, some even forming conglomerates, are slowly transported downstream as sediment mixtures, resulting in the high concentrations detected throughout the entire sampling stretch of the river (see Figure 5).

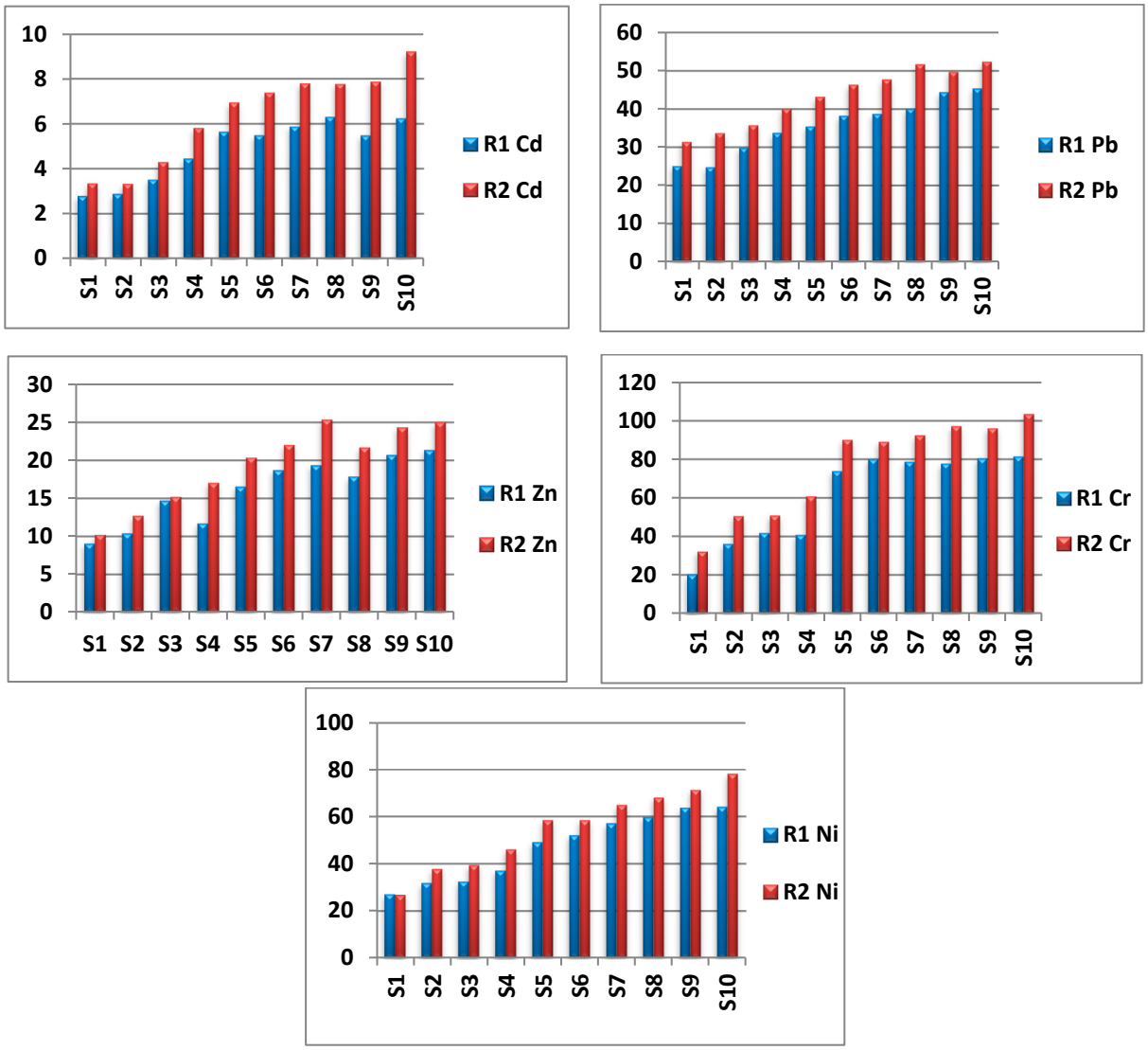

Figure 5. Average values of heavy metal concentration (ppm) between the first and second series in sediment sites.

3.2.3. Comparison of Sediment Samples in the Conflict Zone vs. the Urban Zone

The pollution of the Tigris via the city passage of Mosul can be divided into four zones, whereby zone 1 represents the upstream area before entering the densely populated area and thus serves as a reference, zone 2 describes a predominantly intensively agricultural area, zone 3 comprises the actual conflict zone, and zone 4 includes the southern suburbs of the city. Compared to the reference sampling at S1, the heavy metal concentrations in the sediment increased sharply upon entering Zone 3 and further through the urban area, by a factor of 2.14 (S5) and 2.3 (S10) for cadmium, by a factor of 1.52 (S5) and 1.81 (S10) for lead, and by a factor of 1.3 (S5) and 1.7 (S10) for zinc. The chromium concentrations increased in parallel by a factor of 2.6 (S5) and 2.9 (S10), and the nickel levels increased by a factor of 1.8 (S5) and 2.3 (S10). In the fourth zone in particular, there was a sharp increase in sediment contamination due to the hydrogeological conditions in the river.

The direct comparison of these parameters between both series showed, with the exception of the pH value (see above) and the E.C. (almost unchanged), a significant increase of 1.6–1.8 (salinity), 1.2–1.5 (Cd), 1.2–1.4 (Pb), 1.4 (Zn), 1.2–1.5 (Cr), and 1.1–1.2 (Ni) in the summer period (series 2; see Tables 7 and 8). This increase during dry weather is probably related to a combination of low flow velocity of the Tigris during the dry weather phase and thus also an increased deposition of small particles, which either infiltrated directly into the Tigris from the conflict zones or were lifted up by wind and settled down above the water surface, as well as an increased particle-bound heavy metal input during the precipitation phase in winter and spring (series 1; see Figure 5). These particles, some even forming conglomerates, are slowly transported downstream as sediment mixtures, resulting in the high concentrations detected throughout the entire sampling stretch of the river (see Figure 5).

3.2.4. Comparison of Sediment Samples in Current Study vs. Previous Study

The comparison of the annual average values of heavy metals (Cd, Pb, Zn) in zone1, zone3, and zone4 in the current study 2022 with a previous study by [14] showed that, in zone 1, the values of Cd increased by a factor of 30.5, in zone 3 by a factor of 32.1, and in zone 4 by a factor of 32.1. Furthermore, Pb values increased in zone 1 by a factor of 1.35, in zone 3 by a factor of 1.62, and in zone 4 by a factor of 1.5. The values of Zn in zone 1 increased by a factor of 1.43, in zone 3 increased by a factor of 1.52, and increased by a factor of 1.55 in zone 4. The result indicated that the values of Cd, Pb, and Zn increased in all sites compared with the previous study, and the highest values were in zone 10 due to hydrogeological formation and slope of the Tigris River's bed, as previously mentioned; see Table 10. The highest pollution level was significant in Cd.

Table 10. Comparison of annual values of heavy metal values in sediment samples for the current study with the previous study [14].

Sites	Element	2013	2022	Factor
Zone 1	Pb	14.89	20	1.35
	Cd	0.1	3.05	30.57
	Zn	6.72	9.583	1.43
	Cr	ND	30	-
	Ni	ND	27.8	-
Zone 3	Pb	24.28	39.28	1.62
	Cd	0.197	6.28	32.10
	Zn	12.15	18.42	1.52
	Cr	ND	76.33	-
	Ni	ND	53.6	-

Table 10. *Cont.*

Sites	Element	2013	2022	Factor
Zone 4	Pb	32.45	48.83	1.50
	Cd	0.242	7.72	32.17
	Zn	14.97	23.17	1.55
	Cr	ND	102	-
	Ni	ND	71	-

3.2.5. Statistical Analysis

The percentage difference in sediment analysis data between the locations of both series indicated that there is no regular variation between sites, as the rates of variation between both series were different in all sites, depending on the specific element. This is due to differences in the river's flow rate and the movement of sediments in the river, as well as the different sources of pollution. The highest percent difference in heavy metals was as follows: Cr in S1 (36.8%) > Cd in S10 (32.2%) > Pb in S2 (26.6%) > Zn in S7 (23.6%) > Ni in S1 (23%) (see Table 11).

Table 11. Percentage of the differences in concentration between the first and second series in all sediment sites.

Sites	Cd %	Pb %	Zn %	Cr %	Ni %
S1	16.60	20.12	14.2	36.88	23
S2	13.39	26.63	18.42	28.48	15.93
S3	18.29	16.45	3.08	17.76	17.80
S4	23.51	15.75	31.37	32.97	19.57
S5	18.75	17.99	18.85	18.15	16.00
S6	25.76	17.55	15.15	10.11	10.81
S7	24.69	18.88	23.68	14.80	12.04
S8	18.85	22.58	17.69	19.93	12.13
S9	30.49	10.74	15.07	16.32	10.58
S10	32.25	13.38	14.67	21.29	17.95

There was a general increase in contaminant concentrations between upstream S1 and downstream S10 in both test series, with the highest percentage increase as follows: Cr > Cd > Pb > Zn > Ni > E.C. > salinity (See Table 12).

Table 12. Percentage of difference of concentrations between upstream (S1) and downstream (S10) in sediment in both series.

	S1				S2			
	Upstream	**Downstream**	**Df**	**% DF**	**Upstream**	**Downstream**	**Df**	**%Df**
pH	7.4	7.2	−0.3	−3.8	7.6	6.9	−0.8	−11.2
E.C.	0.7	1.2	0.5	41.4	0.6	1.4	0.8	57.7
Salinity%	0.9	1.8	1.0	52.5	1.4	3.3	1.9	57.9
Cd	2.8	6.2	3.5	55.4	3.3	9.2	5.9	63.8
Pb	25.0	45.3	20.3	44.9	21.3	62.8	41.5	66.0
Zn	9.0	21.3	12.3	57.8	10.2	30.0	19.8	66.1
Cr	28.0	81.3	53.3	65.6	32.0	123.6	91.6	74.1
Ni	27.0	64.0	37.0	57.8	30.0	79.9	49.9	62.5

The statistical T-test analysis shows that the T-test values for salinity, Cd, Pb, Zn, and Cr were below the critical value of $p < 0.05$. This means that there was a significant statistical difference between series 1 and series 2 ($p < 0.05$). Conversely, the numerical

values of Ni and E.C. were greater than 0.05 ($p > 0.05$), which means that there was no significant statistical difference between series 1 and series 2 for these two parameters. This indicates different pollution sources or input sources of nickel to the sediments, while the T-test values for pH were significant, such that the p-value was <0.05 (see Table 13).

The reason for the high concentration of chromium in the sediments at a higher rate than other minerals is due to the waste of the tanning factory, which has been operating since the years before the war, and whose wastewater is thrown into the river, which contains a high percentage of chromium, and accumulated in the sediments over time [14]. However, high levels of cadmium, zinc, lead, and nickel may be mainly caused by military activities. In the case of pH, an enhanced decrease was observed during summer tests (series 2) due to present biodegradation (see Figure 6).

Table 13. *t*-test value between first and second series for all sites in river sediment.

Parameter	*t*-Test	Df *	*p*	Status $p < 0.05$
Ph	2.453	18	0.012	1
E.C.	−0.03433	18	0.486495	0
Salinity	−2.36597	18	0.014703	1
Cd	−2.02299	18	0.02909	1
Pb	−1.79197	18	0.04498	1
Zn	−1.81791	18	0.04392	1
Cr	−1.61075	18	0.04339	1
Ni	−1.17174	18	0.12829	0

* Df: degree of freedom.

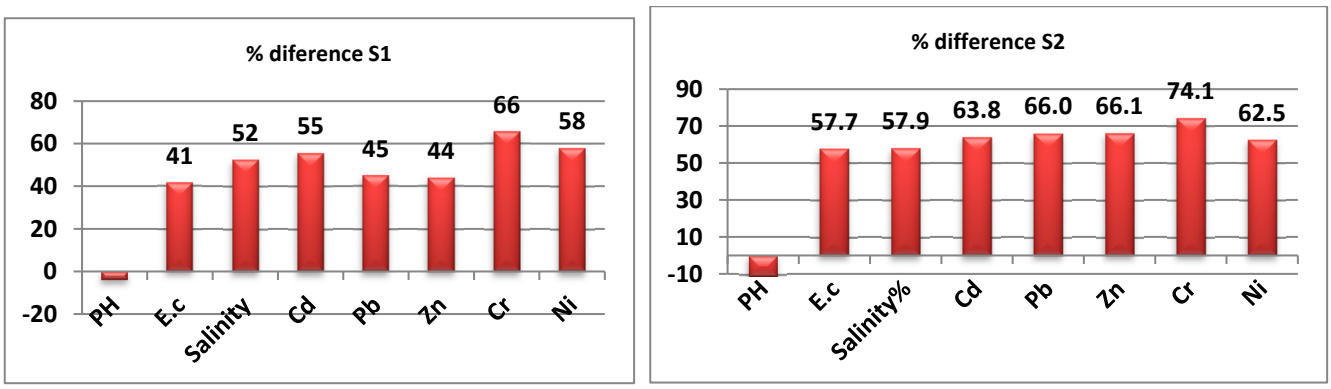

Figure 6. Percentage difference of concentrations between upstream (S1) and downstream (S10) in sediment in both series.

4. Conclusions

The impact of the war was evident due to high contamination levels in water and sediment samples from the Tigris River within the urban area of Mosul. With the exception of Zn, heavy metal loads exceeded WHO limits in a way that was seasonally independent, in both water and sediment. Further exceedances occurred in the water samples for conductivity, phosphate, and sulfate and in individual samples for salinity and COD, regardless of season and location. Salinity was exceeded almost consistently in sediments, while, in contrast, pH, TDS, COD, nitrate, and Zn were (almost) within the limits for all water samples and pH, E.C., and Zn met limits for all sediment samples. The very high loads of heavy metals, but also the exceedances for sulfate, indicated the direct effects of war (ammunition and ignition of sulfur fields). The increased loads of phosphate, but also of COD and TDS, within the urban area indicated indirect effects of war in the form of destroyed wastewater infrastructure. The direct impact of war within the Old City of Mosul as a former conflict zone (S5, S6, S7) is particularly evident in the form of the sudden increase in pollution from S4 to S5. Already between S3 and S4, a clear increase in load

occurred due to the discharge of the Khousr valley. The highest load in sediments occurred at S10, which can be attributed to the transport and deposition of polluted sediment due to hydrogeological conditions.

A seasonal comparison showed a decrease in pollutant concentrations in the water samples during the dry season (summer/fall) compared to the wet season (winter/spring), while the pollutant concentration in the sediments increased in contrast during the summer. This effect was caused in the water body by the lack of infiltration of highly contaminated surface drains into the Tigris River and the simultaneous existing infiltration of less contaminated groundwater during the dry season. The increase in pollutants in sediments over the flow distance may have been caused by the deposition of wind-borne, highly contaminated particles and their deposition in the sediment or by low water flow supporting the enhanced deposition of particles transported during the dry season. The hydrogeological conditions of Mosul support the latter scenario.

Apart from pH, the T-test analysis for both series indicated a significant statistical difference between both series for all other parameters in the water samples ($p < 0.05$). For the sediment samples, corresponding significant statistical differences were identified for salinity, Cd, Pb, Zn, and Cr. Since the percentage difference in water samples at S4–S7 is smaller than upstream and downstream, the contaminants are introduced not only via rainwater but also via the year-round infiltration of highly polluted wastewater from the surrounding valleys draining into the river or suburban areas.

It is worth noting that in addition to warfare, a secondary but also relevant source of pollution occurred during the war. This is the use of the river as a disposal system by Mosul's citizens, which was due to the lack and enforcement of environmental laws during and immediately after the war.

A critical comparison of the present data on the water body and the sediment of the Tigris River with studies before the outbreak of the war clearly showed that the water quality deteriorated significantly. Even though the water quality at the entrance to Mosul at an earlier time complied with the WHO limits, the pollution of the river increased sharply during the city passage, and the Tigris required a natural regeneration distance of 40 km to regain acceptable water quality [6]. Due to the effects of the war, as well as the wild discharges by the habitants, the water quality of the river is even more significantly impaired, such that downstream cities such as Hammam Al aleel are still affected by the low water quality.

Author Contributions: Z.A.: Sampling, material preparation, data collection and analysis, writing, literature research. D.D.: Study conception, sampling plan, literature screening, writing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We are very grateful for the support of the consulting office for laboratory tests in the College of Agriculture and Forestry/Mosul University for analytical support.

Conflicts of Interest: The authors declare no conflict of interest.

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