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Selma Ünlü, Bedri Alpar

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An Evaluation of Vanadium Enrichment in the Eastern Shelf Sediments of the Turkish Black Sea

Selma Ünlü[1,*] and Bedri Alpar[2]

[1] İstanbul University, Institute of Marine Sciences and Management, Department of Marine Biology and Physical Oceanography, 34134 Vefa Fatih Istanbul,TR
[2] İstanbul University, Institute of Marine Sciences and Management, Department of Marine Geology and Geophysics 34134 Vefa Fatih Istanbul,TR

*Corresponding author
Tel : +90 212 440 0000
E-mail : su@istanbul.edu.tr

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Abstract
This paper presents an evaluation of the spatial distribution of vanadium level, its enrichment and possible sources in the bottom sediment along the shelf of the Turkish Black Sea. In April 2006, vanadium concentrations were measured along the measurement profiles (20, 50 and 100 m) using ICP-MS. The vanadium levels ranged from 40 to 315 µg g^{-1}, usually within the range of typical and background values (*Cf<1*), except the one offshore the Yeşilırmak River (315.2 µg g^{-1}), revealing significant riverine inputs and geographical conditions (*Cf>3*). The concentrations decrease gradually with water depth, implying the dominance of anthropogenic sources such as industrial wastes, agricultural effluents, sewage discharge, and port activities. The vanadium levels had not significant correlations with the physicochemical parameters (sediment texture, water content, TOC) and TPH level in the sediment. At the eastern basin, a serious vanadium enrichment (Cf>6-9) was observed in November 2010, implying some important regional and seasonal contributions; which may be natural or anthropogenic. Biogeochemical processes, eutrophication, wave-based erosion, abnormal current circulations, bottom morphology and influence of other substances in the environment may be other regulating factors to this enrichment. Continuous monitoring and further studies are required for a detailed description of vanadium mobility and for assessment of the main controlling processes associated with vanadium enrichment in the eastern Black Sea basin.
Keywords: Vanadium, Petroleum Hydrocarbon, Marine Sediment, Contamination Factor, Black Sea

Introduction

Vanadium (V) is a transition metal and one of the lightest members of the first row transition elements. It is a relatively abundant element in the earth's crust (0.019%), ranking 22nd in abundance with a mean concentration 150 mg kg^{-1} (Rehder, 2008). Clay may contain appreciable amounts of vanadium (>200 mg kg^{-1}). The transportation and partitioning of vanadium is influenced by the presence of particulate matter (Moore, 1991). Vanadium is an essential nutrient in trace amounts, but toxic when concentrations increased (Tomlison et al., 1994). Although the amounts of vanadium used are small, combustion of fossil fuels, coal and waste, steel alloy productions, insecticides, dumping of sewage sludge, discharge of domestic wastewater and vessels make significant contributions to environmental contamination (Wann and Jiang, 1997). The enrichment of vanadium in bottom sediments depends on oil contamination, as well as its biodegradation (Ramondetta and Harris, 1976).

The Black Sea, the largest natural anoxic water basin in the world, is ranked among the most ecologically threatened water bodies (Yüce and Gazioğlu, 2006). It has a surface area of more than 436,000 square kilometers, 5 times larger than its drainage area (Ross and Degens, 1974; Zaitsev et al., 1997). It has a large river system, providing the main part of freshwater, sediment and pollutants. The annual sediment load of Turkish rivers is 28 million tons; corresponding to 20% of the total (Hay, 1994). The highest annual discharges of the rivers of Yeşilırmak, Kızılırmak, Sakarya and Filyos are 10.3, 7.4, 6.0 and 3.2 km^3, respectively (Algan, et al., 1999, 2000; Atlas and Büyükgüngör, 2007). The maximum depth of the Black Sea is more than 2212 m, with an average of 1250 m.

The water exchange with other seas is small and occurs only along the shallow Turkish Straits. Below 100-150 m water depth, high concentrations of hydrogen sulphide and sulphate-reducing bacteria make this intercontinental sea virtually dead (Murray et al., 1991).

In April 2006, vanadium concentrations have been measured in the shelf sediments recovered from the Turkish Black Sea. The concentrations were within the toxicity limits except a near-shore station at the mouth of the Yeşilırmak River. Although these were the first vanadium data measured along the Turkish Black Sea shelf, they were not published anywhere as the background results, except the elevated concentrations observed on a three-station transect offshore the Yeşilırmak River delta (Ünlü and Alpar, 2009).

Recently, Sur et al. (2012) published a research paper about the enrichment and distribution of some selected metals (Al, Cd, Cu, Pb, Hg and V), using the sediment samples recovered in November 2010. Most of their sampling sediments were taken exactly from the same near-shore stations (20 m water depth) used in this study. The authors reported that the contamination factor *Cf* for vanadium was bigger than 6 for the most of the eastern stations; Yeşilırmak > Çayeli > Hopa > Yeşilırmak-SK1 > Ordu > Yeşilırmak-SK2 > Akçaabat > Trabzon > Pazar.

Therefore, in addition to present the vanadium levels and spatial distribution along the Turkish Black Sea shelf, the main scopes of this study are to explain anomalous differences between the surveys carried out in April 2006 and November 2010, to determine their correlations with physicochemical parameters and TPH, and finally to assess ecological risk due to sediment contamination.

Materials and Methods

Sampling procedure

In April 2006, the sea bottom sediment samples were recovered from some selected transects, perpendicular to coast (20, 50 and 100 m water depth) along the Turkish Black Sea shelf, using a grab sampler (Figure 1). The water depths at the stations were between 9 and 103 m. The topmost 3 cm parts of the grab samples were removed carefully using clean stainless steel spatula. Samples were frozen until analysis at the laboratory. The sediment samples for vanadium analysis were dried and kept in plastic bags.

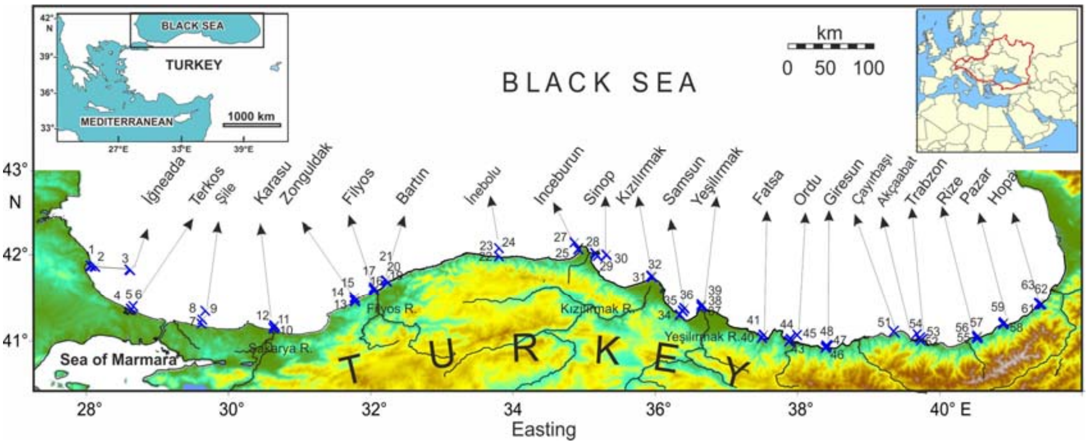

Fig 1. Sediment sampling stations along the Turkish Black Sea shelf. Insets show the study region and the drainage area of the Black Sea basin.

Sample preparation for chemical analysis

Approximately 10 g wet weight of sediments was placed in a labeled precombusted jar for chemical drying with anhydrous sodium sulfate until the sample was dry, free-flowing, and homogeneous, then automatic Soxhlet-extracted with dichloromethane (100 ml) for 8h with activated copper. Two grams of anhydrous sodium sulfate were added to remove water.

The combined extracts were dried with anhydrous sodium sulphate, and the volume was reduced to 2 ml by rotary evaporation.

The samples were also prepared for textural analyses, moisture content, total organic carbon (TOC) and total petroleum hydrocarbon (TPH).

Vanadium Analyses

The vanadium concentrations in samples were determined using ICP-MS (Thermo Elemental X7) at MERLAB Central Research Laboratory of Istanbul University, and validated according to polluted marine sediment IAEA Soil 7 and IAEA 405 reference materials. Each sample was measured in triplicate; mean, standard deviation and percentage of relative standard deviations (RSD%) were calculated (Table 1). Performance and validation parameters of the analytical methodology for analysis of vanadium are summarized in Table 1. The precision of the results were evaluated by percentage relative standard deviation of the results of three samples. In this study, the values of relative standard deviation and the average recoveries were lower than 2% and 98–101%, respectively.

Other analyses in the sediment samples

The changes in the particle grain size (PGS) fractions can influence the chemical compositions of the sediments significantly. Mud fraction, for example, is the most reactive fraction of the total sediment for hydrocarbon adsorption and/or organic-inorganic complex formation (Romankevich, 1984). PGS analysis is broken down into several steps dealing first with the coarse fraction (sand and gravel) and then with the fine fraction (silt and clay). It was performed using petrographic procedures described by GERG SOP-8908.

The total organic carbon content of sediment samples were measured by a Thermo Finnigan FLASH EA 1112 model CHN analyzer at the Advanced Analyses Laboratories, Istanbul, after removing the inorganic carbonate fractions, and were replicated within runs and over time with a confidence interval of 0.1%. TOC were measured by means of the Walkley-Black method (Loring and Rantala, 1992). The analytical precision of analysis was better than ±4% at 95% significance level from five replicates.
The total concentration of petroleum hydrocarbons in the extracts measure using a luminescence spectrometer (Jasco-6300 Shimadzu) and were given in detail by Ünlü et al. (2009).

Statistical Analyses

Pearson’s correlation coefficients calculated the strength of relationships between the vanadium and TPH concentrations, and principal component analysis (PCA) quantified spatial/temporal variability of vanadium sources for Turkish Black Sea coast sediment samples. The first few components explain the inherent variances to largest possible extent (Varmuza and Filzmoser, 2008). In the present study, PCA was conducted with varimax rotation. The first three eigenvalues retained were greater than one; as 2.1, 1.2 and 1.0 (n=55).

Results

Textural characteristics of sediment

The southern shelves of the Black Sea extend northwards until a shelf break at about 100-130 m water depth. The sediment samples usually stay within the oxygenated surface layer of the Black Sea, which is 50-100 m thick (Table 1). They are composed of various size-grained sediments, mud is dominant. Even though the main controlling parameter is depth, the sea floor morphology of the Black Sea intersected with canyons (Algan et al., 2002) and biogeochemical processes in sediment and water column (Inglet et al., 2008; Bat et al., 2015; Bat and Özkan, 2015) are also important on the granulometric distribution of the surface sediments.

Table 1. Sampling depth, sediment texture (shell, pebble, sand, silt and clay %), sediment water content (swc %), organic carbon (TOC%), concentrations of total petroleum hydrocarbon (TPH) and vanadium (µg g^{-1} dry weight) in the sediment samples.

Region	Station	Depth	Shell	Pebble	Sand	Silt	Clay	swc	TOC	TPH	V	V-StDev	V-%RSD
Igneada	S1	23	27,4	0,0	99,9	0,1	0	14,4	0,5	64	44,0	0,2	0,2
	S2	50	0,0	0,5	7,4	50,6	42	57,8	1,5	63	95,6	0,8	0,5
	S3	100	9,4	6,3	9,4	37,1	47	47,4	2,4	17	103,8	0,1	0,0
Terkos	S4	21	39,3	24,8	72,1	3,1	0,0	16,5	1,2	2	40,5	0,6	0,8
	S6	94	0,0	0,5	4,6	62,6	32,2	59,6	2,5	27	53,0	0,9	1,0
Şile	S7	28	0,0	16,7	80,9	1,3	1,1	21,2	1,3	33	51,6	1,0	1,1
	S8	51	47,7	37,0	45,1	7,8	10,1	27,8	1,6	13	60,1	1,1	1,0
	S9	103	22,1	18,8	30,1	23,5	27,6	36,9	1,8	6	52,2	0,8	0,8
Karasu	S10	21	45,2	8,9	87,1	2,3	1,8	27,7	1,1	7	99,3	0,4	0,2
	S12	98	0,0	0,0	0,0	52,6	47,4	59,3	2,7	14	124,9	0,7	0,3
Zonguldak	S13	23	0,0	0,0	12,7	41,6	45,6	25,7	3,2	5497	111,2	0,8	0,4
	S14	51	18,0	6,2	29,8	42,5	21,5	38,2	2,1	3939	121,3	0,5	0,2
	S15	103	0,0	12,9	27,8	34,7	24,6	43,5	1,4	257	95,4	0,2	0,1
Filyos	S16	21	0,0	0,5	8,2	67,7	23,6	21,3	1	53	104,5	0,4	0,2
	S17	50	20,5	10,6	3,9	62,1	23,5	36,0	2,1	205	98,6	0,8	0,5
Bartın	S19	21	0,0	1,7	54,3	28,1	15,9	29,5	0,7	121	87,2	0,6	0,4
	S20	54	0,0	2,1	5,5	50,7	41,8	40,5	1,2	143	106,0	1,2	0,6
	S21	103	0,0	0,0	0,0	56,7	43,3	45,1	1,3	220	117,5	1,4	0,9
Inebolu	S22	23	63,4	4,4	62,9	25,3	7,3	26,7	0,5	27	64,3	0,9	0,8
	S23	48	12,7	0,1	21,0	53,0	26,0	51,7	1,2	18	66,4	0,9	0,7
	S24	100	6,4	0,8	4,9	53,5	40,8	51,9	1,7	41	80,0	0,2	0,1
Inceburun	S25	21	12,7	0,0	98,1	1,9	0,0	20,1	0,8	8	59,2	0,6	0,6
	S27	101	23,5	0,0	30,4	35,4	34,2	46,9	1,5	25	114,6	0,9	0,4
Sinop	S28	21	28,9	26,4	37,4	18,7	17,5	32,7	1	321	101,6	1,6	0,9
	S29	49	2,4	1,5	0,9	47,4	50,2	53,8	1,6	18	136,5	0,8	0,3
	S30	97	19,4	4,7	14,4	45,3	35,7	43,9	1,6	21	110,2	0,6	0,3
Kızılırmak	S31	25	0,8	0,0	1,5	67,8	30,7	32,1	0,7	9	111,0	1,4	0,7
	S32	38	0,0	0,3	13,9	65,4	20,5	37,1	0,8	37	113,5	1,5	0,8
	S33	103	2,5	0,0	3,2	62,4	34,4	45,0	1,3	23	79,1	0,7	0,5
Samsun	S34	13	0,0	0,0	1,4	54,1	44,5	8,9	2	297	129,3	1,2	0,5
	S35	51	0,0	0,0	0,0	54,6	45,4	46,1	0,9	18	119,0	0,7	0,3
	S36	103	11,5	1,3	7,4	45,9	45,5	50,4	1,7	25	125,7	1,3	0,6
Yeşilırmak	S37	12	46,0	0,0	98,2	0,8	1,0	17,3	0,8	5	315,2	1,4	0,3
	S38	51	5,6	2,4	5,0	55,6	37,0	46,1	1,3	6	151,2	1,4	0,5
	S39	103	0,0	0,0	3,5	42,5	53,9	47,3	1,3	25	127,3	1,8	0,8
Fatsa	S40	21	0,0	0,0	36,3	29,1	34,5	43,1	0,7	22	151,1	1,0	0,4
	S41	51	0,0	0,5	4,0	62,3	33,2	44,3	1,6	45	148,3	0,5	0,2
Ordu	S43	9	45,3	1,7	55,7	35,8	6,9	23,7	0,7	8	141,5	2,0	0,8
	S44	53	0,0	3,7	3,4	60,9	32,0	45,2	3,2	52	140,2	1,0	0,4
	S45	100	8,2	3,3	6,6	41,6	48,5	55,5	1,9	13	134,9	1,9	0,8
Giresun	S46	21	14,4	20,4	79,0	0,7	0,0	20,8	0,7	471	104,8	0,7	0,4
	S47	53	8,9	2,3	12,8	64,8	20,1	48,1	1,7	37	133,5	1,2	0,5
	S48	98	10,0	0,7	24,2	51,0	24,1	44,8	2,1	9	130,1	0,3	0,1
Çarşıbaşı	S51	95	11,8	0,4	37,2	41,3	21,1	53,8	1,2	36	71,4	0,0	0,0
Trabzon	S52	10	0,0	0,0	6,5	70,7	22,9	38,4	0,9	52	119,0	0,8	0,4
	S53	52	0,0	0,2	9,8	58,5	31,5	50,6	1,7	65	110,3	0,5	0,3
Akçaabat	S54	93	3,8	1,5	11,4	54,6	32,5	40,8	1,4	33	120,5	0,8	0,4
Rize	S55	21	1,6	0,0	71,1	25,3	3,6	28,8	1,1	48	111,8	2,4	1,2
	S56	53	0,0	0,2	12,2	69,0	18,5	53,2	2,1	49	116,3	0,8	0,4
	S57	113	0,0	0,0	2,6	70,3	27,1	48,6	1,9	41	109,9	0,4	0,2
Pazar	S58	21	41,9	15,8	58,9	18,2	7,1	11,5	1,4	19	106,6	0,2	0,1
	S59	52	21,1	10,8	29,6	41,0	18,5	45,8	2,4	49	127,7	1,0	0,5
Hopa	S61	22	1,6	0,0	98,5	1,5	0,0	17,5	1,3	35	141,4	0,5	0,2
	S62	52	0,0	0,8	11,1	65,4	22,7	47,4	2,6	38	133,6	0,7	0,3
	S63	101	0,0	1,5	19,2	55,9	23,4	47,4	2,3	853	131,0	0,4	0,2
	MIN	9,0	0,0	0,0	0,0	0,1	0,0	8,9	0,5	2	40,5	0,0	0,0
	MAX	113,0	63,4	37,0	99,9	70,7	53,9	59,6	3,2	5497	315,2	2,4	1,2
	MEAN	55,7	11,5	4,6	28,6	41,3	25,5	38,5	1,5	247	110,1	0,9	0,5

TOC and TPH Distributions

The TOC content in the sediments ranges from 0.5 to 3.2% with an average of 1.5±0.7% (n=55) (Table 1). The highest values of TOC content were recorded offshore the harbours of Zonguldak and Ordu (3.2%), possibly due to coal production and port activities.

The levels of total hydrocarbon are scattered in a wide range from 2 to 5497 µg g^{-1} (dry weight) (Table 1). The high values (>100 µg g^{-1} dw) confirm chronic oil pollution, especially those measured near the Zonguldak port (257-5497 µg g^{-1}), Hopa (853 µg g^{-1}), Giresun (471µg g^{-1}), Sinop (321 µg g^{-1}), Samsun (297 µg g^{-1}), Bartın and Filyos (205-220 µg g^{-1}). According to Readman et al. (2002) the concentrations higher than 100 µg g^{-1} dw are mainly related with port activities or riverine (terrestrial) inputs.

Vanadium levels in sediment samples

Results indicated that the levels of vanadium in the sediment ranged from 40 to 315 µg g^{-1}, with a mean value of 110 µg g^{-1} (Table 1). Almost all of these concentrations are within the range of typical and background values (20- 150 µg g^{-1}) recorded for sediment by Moore (1991), except S37, which had the extreme value of vanadium (315.2 µg g^{-1}).

Table 2. Comparison of vanadium levels in the sediments from the Mediterranean region.

Region	Sampling Year	V (µg g^{-1})	References
Near shores, Kuwait	1995	25 - 179	Metwally et al., 1997
Suez Bay, Egypt	2004	4 - 168	El-Moselhy, 2006
Red Sea, Egypt	2004	8 - 214	El-Moselhy, 2006
Western Black Sea,Turkey	2010	10 - 152	Sur et al., 2012
Eastern Black Sea, Turkey	2010	40 - 1215	Sur et al., 2012
Eastern Mediterranean Sea, Egypt	2008	25 - 575	Abdel Ghani et al., 2013
Western Black Sea, Turkey	2006	40 - 125	This study
Eastern Black Sea, Turkey	2006	71 - 315	This study

The sediment sample S37 was recovered from a water depth of -12 m nearshore the Yeşilırmak River delta that receives huge amount of wastewater effluents. Such kind of sediments offshore lowland areas are likely to host the higher amount of vanadium coming from river particulates (McLennan and Murray, 1999). On the other hand, the lowest concentration (40.5 µg g^{-1}) was observed at station S4, at the western side and offshore a fresh water lake (Terkos). For an overall assessment, the vanadium concentrations from the survey carried out in April 2006 was in the range of other data recorded from other parts of the Mediterranean region (Table 2).
The samples at the eastern part of the study area have higher vanadium concentrations. In other words, the mean of the stations remained to the east of 34°E (126±39 µg g^{-1}) was significantly higher than the mean of western stations (85±27 µg g^{-1}). In the eastern side, the concentration levels also decrease gradually with the depth of water (Figure 2).

Comparison with November 2010 survey data

In fact, they were the first vanadium data measured systematically along the Turkish Black Sea shelf, and they could only be used as background data for future monitoring. The vanadium levels were low, except the maximum at S37 and the slight elevation of concentrations at the eastern basin. Recently, Sur et al. (2012) published a research paper indicating metal contaminations (Al, Cd, Cu, Pb, Hg and V) along the Black Sea coast; using the sediment samples exactly taken from the same near-shore stations given above. The authors reported that the contamination factor C*f* was bigger than 6 for the nearshore stations at Hopa, Ordu, Çayeli, Trabzon, Yeşilırmak, Akçaabat and Pazar (Sur et al., 2012). They found vanadium was enriched very much (C*f*>6) in most of the eastern stations; Yeşilırmak > Çayeli > Hopa > Yeşilırmak SK1 > Ordu > Yeşilırmak SK2 > Akçaabat > Tabzon > Pazar.

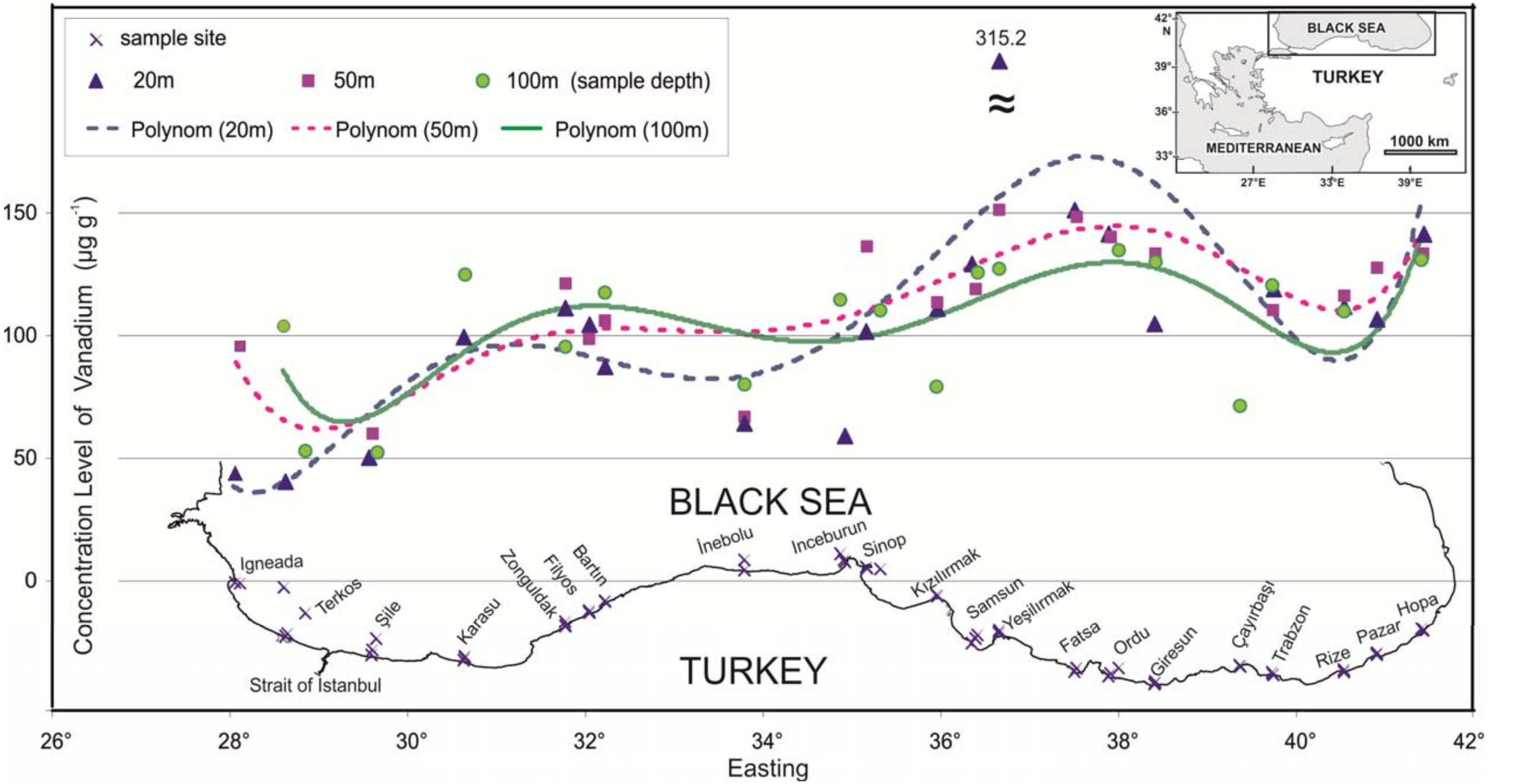

Fig 2. Distribution of vanadium levels in sediment along the narrow Turkish Black Sea shelf. The concentration levels and their polynomial fits for 20, 50 and 100 m water depths are slightly different.

The contamination factor (C*f*, Håkanson, 1980) is a kind of normalization according to a background value. The average crustal abundances (background) of vanadium is 130 µg g^{-1} for (Turekian and Wedepohl 1961; Taylor 1972). A comparison of C*f* data for April 2006 and November 2010 surveys reveal an important enrichment at the eastern basin that must be explained (Figure 3).

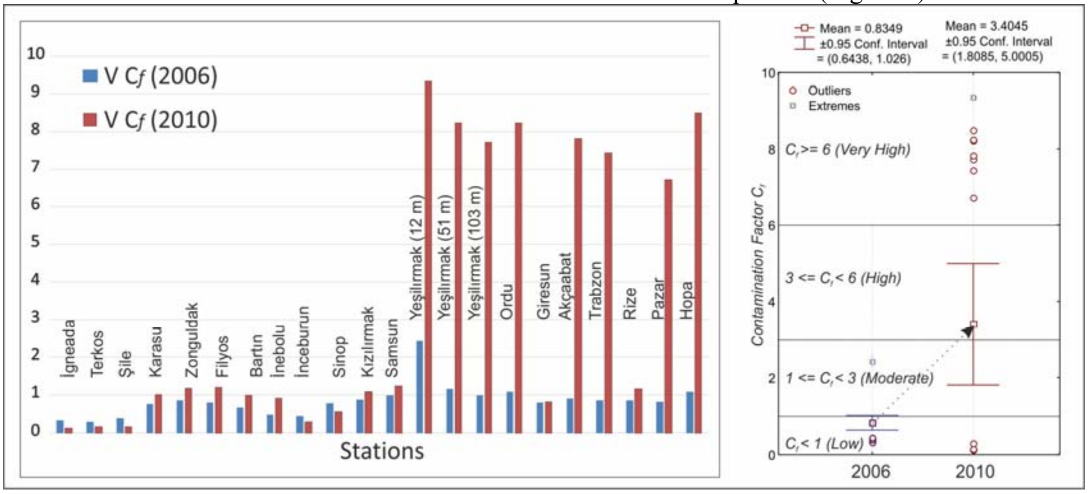

Fig 3. Comparison of contamination factors (C*f*) of vanadium levels for 2006 (April) and 2010 (November) surveys and their box and Whisker plots. The C*f* values less than unity 1 refer to low contamination, while 1≤C*f*<3 means moderate contamination, 3≤C*f*<6 considerable contamination, and finally C*f*≥6 indicates very high contamination.

Statistical relationships between parameters

The regression analysis revealed the relationships between the concentration of vanadium, percentage of grain size, sediment water content, TOC and total petroleum hydrocarbon levels (Table 2). The TOC concentrations increase slightly with the increasing depth and finer grain size (i.e. silt and clay). The finer grained sediments have much ability to carry and store pollutants than coarse-grained sandy sediments. Therefore, the samples with higher TOC values are mostly made up of fine-grained sediments.

The regression analysis shows no significant correlations among the vanadium concentrations, other physicochemical parameters and TPH level (Table 2). Large accidental spills generally cause significant vanadium contamination in sediment. However, there was not any meaningful relationship between the levels of vanadium and TPH for the samples. In that case, the enrichment of vanadium observed at the eastern Black Sea stations may be associated with the reasons given below;

a) natural release to sediment because of weathering of rocks,

b) dominant current regime of the eastern basin,

c) wet and dry deposition vanadium-containing particulates during combustion of coal and residual fuel oils,

d) transportation of sediment, including mineral matter, chemicals, pollutants and organic matter via the rivers.

Source identification of the vanadium pollution

Principal component analysis (PCA) is a useful statistical tool to define if relevant relationships exist between the cases. Three principal components were retrieved for the Black Sea shelf sediments (Eigen values >1). Including the loadings of vanadium, TPH, and the physicochemical parameters, the variance loadings of the first three factors were 44.3, 24.4 and 19.8% of the total variability respectively (accumulative variance 86.5%, n=55). The first two factors used to identify the source categories and the loadings are shown in Figures 4a and b.

Factor 1. Accounting for 42.3 of total variance, this factor exhibits higher loadings for the percentages of mud, sediment water content and TOC.

Factor 2. This factor show 24.4% of total variance (Figure 4a). This factor predominantly composed by TPH pollution solely, coming from point sources. They were observed at the stations close to the coast; i.e. Zonguldak and Samsun (S13, S14 and S34). At these sampling points, TPH levels were greater than 100µg g^{-1}, implying occurrence of oil spill or leakage pollution caused by vessels, possible discharges from municipal and industrial wastewater or occasional surficial runoff.

Factor 3. The third factor is responsible for 19.8% of the total variance. This factor exhibits higher loadings of vanadium (Figure 4b). The highest concentration was observed at the station S3 at the mouth of the Yeşilırmak. The positive values of the third factor correspond to the vanadium levels smaller than 90 µg g^{-1} dw.

Table 2. Pearson-coefficient correlation matrix (r) between the concentrations of vanadium and other parameters in the sediment samples (n = 55).

	Depth	Silt	Clay	Mud	swc	TOC	TPH	V
Depth	1.00							
Silt	.386**	1.00						
Clay	.574**	.540**	1.00					
Mud	.511**	.936*	.870**	1.00				
swc	.714**	.637**	.663**	.713**	1.00			
TOC	.433**	.391**	.428**	.447**	.425**	1.00		
TPH	-.110	.008	.115	.058	-.119	.373**	1.00	
V	-.098	.127	.134	.143	.034	.070	.029	1.00

** Correlation is significant at the 0.01 level (2-tailed).

Discussion and Conclusion

The vanadium levels in the sediment of the Turkish Black Sea shelf indicated low range spectra, usually below the background values (20 - 150 µg g^{-1}), except an accumulation (315.2 µg g^{-1}) nearshore the Yeşilırmak. This indicated that the subaqueous part of the Yeşilırmak River delta receives significant amount of vanadium from riverine particulates. Sur et al. (2012) suggested that these anomalous accumulations were related with sulfuric acid production in the region. In addition, the vanadium concentrations indicated elevated levels at the eastern margin, implying that geographical variations from both anthropogenic (e.g. riverine inputs, dumping of sewage sludge, discharge of domestic wastewater and atmospheric emissions) and natural sources (e.g. mineralogical backgrounds, eutrophication under anaerobic conditions, bioturbation and organic-rich shales) were important. In general, the levels decrease with water depth gradually, possibly due to decreasing effects of industrial discharges, other terrestrial inputs and natural weathering processes.

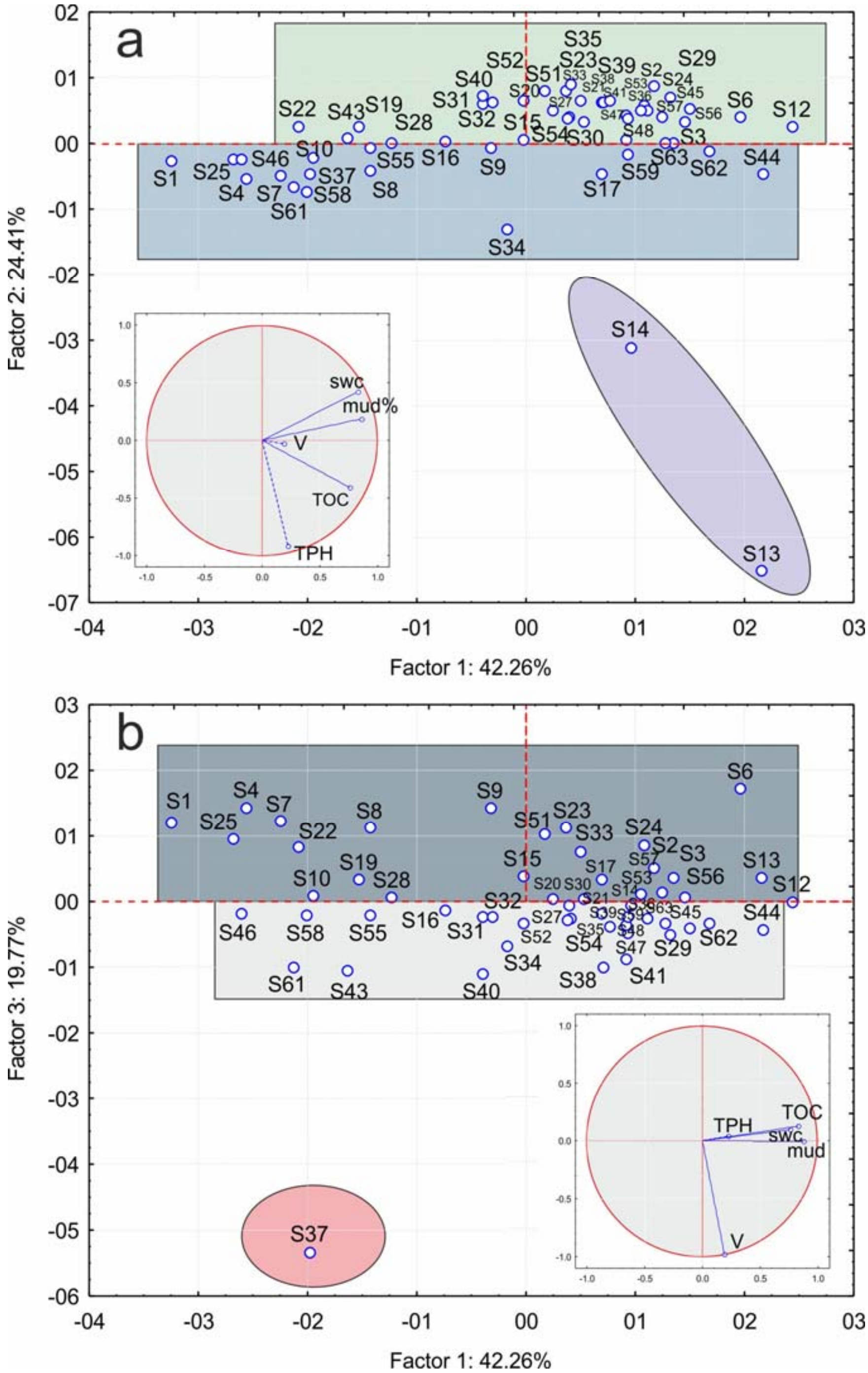

Fig 4. The projection of the variables and cases on the factor plains of a) 1x2 and b) 1x3 for the Turkish Black Sea shelf sediments.

Anomalous increment of vanadium concentrations was observed at the eastern basin sediment recovered in November 2010. A six-to-nine times increment of *Cf* index indicates that vanadium has been elevated due to some seasonal influences of the Turkish rivers or primary production of organic matter. The counterclockwise gyres and longshore currents, partly controlled by the sea bottom morphology, and wave-based erosion caused by waves may have been contributed to this enrichment as well. Moreover, the concentration levels may become variable under the control of various substances (e.g. fulvic and humic acids) presented in the environment.

Several planned and continuous monitoring studies are needed such as a) to explain of vanadium variations in sediment and its mobility, b) to determine the correlations between vanadium and organic matters, c) to define exchange of vanadium between sediment and seawater with direct flux measurements, etc. Similar studies will provide a basis for environmental impact assessment and control.

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References

Abdel Ghani, S.A., Shobier, A.H. Shreadah, M.A. (2013). Assessment of arsenic and vanadium pollution in surface sediments of the Egyptian Mediterranean coast. International Journal of Environmental Technology and Management, 16(1/2), 82-101.

Algan O, Gazioğlu C, Çağatay N, Yücel ZY., Gönençgil B. (1999). Sediment and water influxes into the Black Sea by Anatolian rivers. Zeitschrift für Geomorphologie 43,61–79.

Algan O., Gazioğlu C., Yücel Z., Çağatay N., Gönençgil B. (2000). Sediment and Freshwater Discharges of the Anatolian River into the Black Sea, IOC-BSRC Workshop «Black Sea Fluxes», Workshop Report No. 145. Paris: UNESCO, 38–50.

Algan, O., Gökaşan, E., Gazioğlu, C., Yücel, Z Alpar, B., Güneysu, C., Kırcı, E., Demirel, S., Sarı, E., Ongan, D. (2002). A high resolution seismic study in Sakarya Delta and Submarine canyon, southern Black Sea. Continental Shelf Research, 22(10), 1511–1527.

Atlas, L. and Büyükgüngör, H. (2007). Heavy metal pollution in the Black Sea shore and offshore of Turkey. Environmental Geology, 52, 469–476.

Bat, L. and Özkan, E.Y. (2015). Chapter 13. Heavy metal levels in sediment of the Turkish Black Sea coast. In: Bikarska I, Raykov V, Nikolov N. (Eds.) Progressive Engineering Practices in Marine Resource Management. IGI Global book series Advances in Environmental Engineering and Green Technologies (AEEGT) (ISSN: 2326-9162; eISSN: 2326-9170) USA, pp. 399-419.

Bat, L., Özkan E.Y. and Öztekin, H.C. (2015). The contamination status of trace metals in Sinop coast of the Black Sea, Turkey. Caspian Journal of Environmental Sciences, 13 (1), 1-10.

El-Moselhy, Kh. M. (2006). Distribution of vanadium in bottom sediments from the marine coastal area of the Egyptian Seas. Egyptian Journal of Aquatic Research, 32(1), 12-21.

Håkanson, L. (1980). An ecological risk index for aquatic pollution control: A sedimentological approach. Water Research, 14, 975–1001.

Hay, B. J. (1994). Sediment and water discharge rates of Turkish Black Sea rivers before and after hydropower dam construction. Environmental Geology, 23, 276-283.

Inglett, P.W., Inglett, K.S. and Reddy, K.R. (2008). Biogeochemical processes and implications for nutrient cycling. In: Brown, M.T., Reiss, K.C., Cohen, M.J., Evans, J.M., Inglett, P.W., Inglett, K.S., Reddy, K.R., Frazer, T.K., Jacoby, C.A., Phlips, E.J., Knight, R,L., Notestein, S.K., Hamann, R.G., McKee, K.A. (Eds.), Summary and Synthesis of the Available Literature on the Effects of Nutrients on Spring Organisms and Systems. University of Florida Water Institute, 570 Weil Hall, Gainesville, FL 32611-6601.

Loring, D.H. and Rantala, R.T.T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth-Science Reviews, 32(4), 235–283.

McLennan, S.M. and Murray, R.W. (1999). Geochemistry of sediments. In: Marshall, C.P., Fairbridge, R.W. (Eds.), Encyclopedia of Geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 282-292.

Metwally, M.E.S., Al-Muzaini, S., Jacob, P.G., Bahloul, M., Urushigawa, Y., Sato, S. and Matsmura, A. (1997). Petroleum hydrocarbons and related heavy metals in the near-shore marine sediments of Kuwait. Environment International, 3(1), 115–121.

Moore, J.W. (1991). Inorganic contaminants of surface water: research and monitoring priorities. Springer-Verlag, New York Inc. 334.

Murray, J.W., Top, Z. and Özsoy, E. (1991). Hydrographic properties and ventilation of the Black Sea. Deep-Sea Research, 38(Suppl.2A), S663–690.

Ramondetta, P.J. and Harris, W.H. (1976). Heavy metal distribution in Jamaica Bay sediments. Environmental Geology, 2, 145-149.

Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.-P., Catinni, C. and Mee, L.D. (2002). Petroleum and PAH contamination of the Black Sea. Marine Pollution Bulletin, 44, 48–62.

Rehder, D. (2008). Bioinorganic Vanadium Chemistry (1st ed.). Hamburg, Germany: John Wiley and Sons, Ltd. 5, 9–10.

Romankevich, E.A. (1984). Geochemistry of organic matter in the ocean. Berlin, Heidelberg, New York: Springer and Verlag.

Ross, D.A. and Degens, E.T. (1974). Recent sediments of the Black Sea. In: Degens, E.T., Ross, D.A. (Eds.), The Black Sea - Geology, Chemistry, and Biology, The American Association of Petroleum Geologists, Memoir 20, Tulsa, Oklahama, 183–189.

Sur, M., Sur, H.İ., Apak, R. and Erçağ, E. (2012). The pollution status of bottom surface sediments along the Turkish coast of the Black Sea. Turkish Journal of Fisheries and Aquatic Sciences, 12, 453-460.

Taylor, S.R. (1972). Abundance of chemical elements in the continental crust: a new table. Geochemica Cosmochim Acta, 28, 1273–1286.

Tomlison, M.J., Wang, J. and Caruso, J.A. (1994). Speciation of toxicologically important transition metals using ion chromatography with inductively coupled plasma mass spectrometric detection. Journal of Analytical Atmospheric Spectrometry, 9, 957-964.

Turekian, K. K. and Wedepohl, K.H. (1961). Distribution of the elements in some major units of the Earth's crust. Bulletin Geological Society of America, 72, 175-192.

Ünlü, S. and Alpar, B. (2009). Hydrocarbon contamination in sediment offshore Yeşilırmak River, Black Sea, Turkey, In: E. Özhan (Ed.), Proceedings of the Ninth International Conference on the Mediterranean Coastal Environment, MEDCOAST 09, 2, 689–699.

Ünlü, S., Alpar, B. and Aydın, Ş. (2009). Spectrofluorometric characterization of aromatic hydrocarbon contamination in the sediment from the Zonguldak Industrial Region, Black Sea, Turkey. Fresenius Environmental Bulletin, 18, 474–480.

Varmuza, K. and Filzmoser, P. (2008). Introduction to multivariate statistical analysis in chemometrics. CRC Press, Taylor and Francis Group, Boca Raton, FL.

Wann, C. and Jiang, S. (1997). Determination of vanadium species in water samples by liquid chromatography-inductively coupled plasma mass spectrometry. Analytica Chimical Acta, 357 211-218.

Zaitsev Yu, Mamaev VO. (1997). Biological diversity in the Black Sea: A study of change and decline, Black Sea Environmental Series, Vol. 3, United Nations Publishing, New York, 208 pages.