Supporting information

Contributions of Atmospheric deposition to Pb concentration and isotopic composition in Seawater and Particulate Matters in the Gulf of Aqaba, Red Sea

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Text S1. Sample Pretreatments and Chemical Analyses

Details of salt removal and trace metals (Al, Mn, Co, Zn, Cd, and Pb) concentration from seawater is described in Chien et al. (2017). Briefly, seawater was passed through a Chelate-PA1 resin (HITACHI, Japan) for seawater matrix removal and trace metal pre-concentration[1] at the IUI clean lab. This method has been demonstrated to be efficient for [Pb] by analyses of GEOTRACES intercalibration seawater and accurate for isotopic composition by analyses of seawater spiked with NIST SRM-981.[2] To determine trace metal concentrations, around 60 mL of seawater was processed using the method described above. To assess recovery rates, trace metals free seawater was pretreated with the Chelate-PA1 resin, this seawater was then spiked with different amount of trace metal standards and processed as other samples for concentration calibrations. The recovery of Al, Mn, Co, Zn, Cd, and Pb was determined to be 92%, 97%, 96%, 99%, 97%, and 96%, based on comparison between the standard spiked seawater and standards of similar concentration prepared in 3% HNO_3. Average procedural blanks of Al, Mn, Co, Zn, Cd, and Pb concentration analyses were 1430, 16.5, 2.1, 67, 1.0 and 1.6 pmol kg^{-1}, respectively. 350 to 500 mL of seawater from each sample was processed with the same method for Pb isotopes analyses. Procedural blank of Pb isotopes extractions was 0.9 ± 0.3 pmol kg^{-1}. Different amounts of NIST SRM-981 were added to Pb free seawater and processed as unknowns to evaluate accuracy. The results showed that isotope fractionation and contamination was negligible (Table S2). For extracting the soluble Pb fraction of the TSP samples, half of the filter for each sample was placed in a 50 mL acid cleaned polypropylene vial (Bio-Rad) with 40 mL of trace metal free local seawater (prepared with the same resin mentioned above and pH was adjusted to 8 with optima grade ammonia hydroxide). The samples were placed on a shaker for one hour,[3] centrifuged and the seawater with the soluble fraction was transferred to another vial. The residual non-soluble fraction of the TSP was rinsed with 5 mL trace metal free seawater, centrifuged again, and the seawater was combined with the 40-mL soluble fraction. Pb in the TSP seawater soluble fraction was then extracted in the same way as other seawater samples mentioned above.

Suspended particles, sinking particles, surface sediment and the non-soluble fraction of the TSP were digested with a 3:1 mixture of double distilled concentrated nitric acid and hydrogen fluoride in tightly closed 15 mL Teflon beakers on a 150 ℃ hot plate for eight hours to obtain trace metal concentrations and Pb isotope ratios. Efficiency of the digestion was

verified by processing two SRM NIST 2709 standards with each batch of samples, average efficiency of four NIST 2709 shows >90% of the Pb was recovered. Two polycarbonate filters without sample were also digested together with the other samples to determine the overall procedural blanks which were 62 and 63 pg of Pb. Trace metal concentrations were analyzed by ICP-MS (Agilent 7500cx) at the Institute of Earth Sciences, Hebrew University of Jerusalem. 10 $\mu g\ L^{-1}$ of Indium was used as an internal standard during the analyses. Matrix effect from seawater were determined by preparing our calibration standards in trace metal free seawater, and standards were processed and analyzed in the same way as the samples.

For isotope analyses of particulate matters, Pb was separated from other elements using column chemistry. Briefly, digested samples were dried down and re-dissolved in 100 μL of concentrated HBr (Optima grade, Fisher Scientific) three times. Pb separation was carried out using AG1-X8 resin (procedure adapted from Kamber et al.[4]), the column was eluted with 1N HBr to remove interfering elements and the Pb fraction was eluted by 6N double distilled HNO_3. The Pb fraction was dried down and brought up with 3% HNO_3 to a concentration of at least 10 ppb of Pb for analyses. Seven 100 ng aliquots of NIST SRM-981 were treated similarly and did not show isotope fractionation (Table S2). Pb isotopic compositions were analyzed by a multi collector inductively coupled mass spectrometer (MC-ICP-MS Neptune) at the Institute of Earth Sciences, Hebrew University of Jerusalem. NIST SRM-997 Tl solution was added to correct for the mass fractionation with an exponential law correction. Typically, 10 ppb of NIST SRM-981 resulted in 1 V for ^{208}Pb. Based on 36 NIST SRM-981 analyses, average and one standard deviation of $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ are 16.9298 ± 0.0056, 1.0936 ± 0.0001 and 2.3684 ± 0.0002, respectively (Table S2).

Table S1. Seawater, suspended particle, sinking particle and TSP Pb isotope data from this study.

			Pb isotope			1 se		
	Date	Depth (m)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Seawater		0*	18.38	1.173	2.440	0.049	0.0001	0.0005
		20*	18.26	1.170	2.440	0.042	0.0004	0.0001
		60*	18.30	1.171	2.440	0.010	0.0001	0.0012
		100*	18.20	1.167	2.437	0.028	0.0012	0.0001
		140*	18.37	1.171	2.439	0.054	0.0008	0.0007
		200*	18.23	1.166	2.436	0.006	0.0002	0.0002
		300*	18.23	1.167	2.433	0.005	0.0003	0.0004
		400*	18.37	1.172	2.442	0.002	0.0001	0.0005
		500	18.20	1.167	2.435	0.018	0.0004	0.0004
		600	18.29	1.173	2.439	0.025	0.0002	0.0004
Suspended particle		20	18.31	1.173	2.437	0.013	0.0002	0.0003
		60	18.19	1.166	2.433	0.007	0.0001	0.0002
		100	18.26	1.170	2.435	0.009	0.0001	0.0002
		200	18.28	1.171	2.436	0.006	0.0003	0.0007
		400	18.33	1.174	2.440	0.016	0.0001	0.0002
		500	18.40	1.178	2.443	0.011	0.0002	0.0004
		600	18.49	1.184	2.447	0.017	0.0002	0.0003
		700	18.50	1.184	2.450	0.021	0.0002	0.0003
Sinking particle		124	18.33	1.173	2.441	0.001	0.0000	0.0001
		226	18.31	1.172	2.439	0.002	0.0001	0.0001
		347	18.40	1.177	2.445	0.001	0.0000	0.0001
		580	18.44	1.180	2.446	0.002	0.0000	0.0001
TSP soluble	July 21 - July 28		18.25	1.169	2.443	0.004	0.0001	0.0002
	July 28 - August 6		18.05	1.157	2.432	0.001	0.0000	0.0001
	August 6 - August 17		18.12	1.161	2.435	0.002	0.0001	0.0001
TSP non-soluble	July 28 - August 6		18.27	1.170	2.442	0.002	0.0001	0.0002
	August 6 - August 17		18.46	1.180	2.452	0.002	0.0001	0.0001

* Results from analyses of replicate extractions.

Table S2. Pb isotopes of NIST SRM-981: Mean value and one standard deviation of 36 analyses of NIST SRM-981 prepared in 3% HNO_3. Seawater: Analyses of Pb free seawater spiked with different amount of NIST SRM-981. Particle: Analyses of NIST SRM-981 processed with column chemistry used for particles.

	NIST SRM-981		Pb isotope			1 std		
			$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
3% HNO3	n=36		16.9298	1.0936	2.3684	0.0056	0.0001	0.0002
Seawater	concentration (pmol kg-1)	40	16.9356	1.0937	2.3689	0.0027	0.0001	0.0001
		80	16.9320	1.0935	2.3689	0.0065	0.0002	0.0002
		100	16.9289	1.0934	2.3687	0.0064	0.0005	0.0002
Particle	size (ng)	100	16.9310	1.0935	2.3687	0.0024	0.0001	0.0001
			16.9331	1.0934	2.3689	0.0025	0.0001	0.0002
			16.9334	1.0935	2.3688	0.0029	0.0001	0.0001
			16.9331	1.0934	2.3688	0.0025	0.0001	0.0001
			16.9322	1.0934	2.3687	0.0023	0.0001	0.0001
			16.9372	1.0936	2.3691	0.0019	0.0000	0.0001
			16.9327	1.0934	2.3688	0.0016	0.0000	0.0001

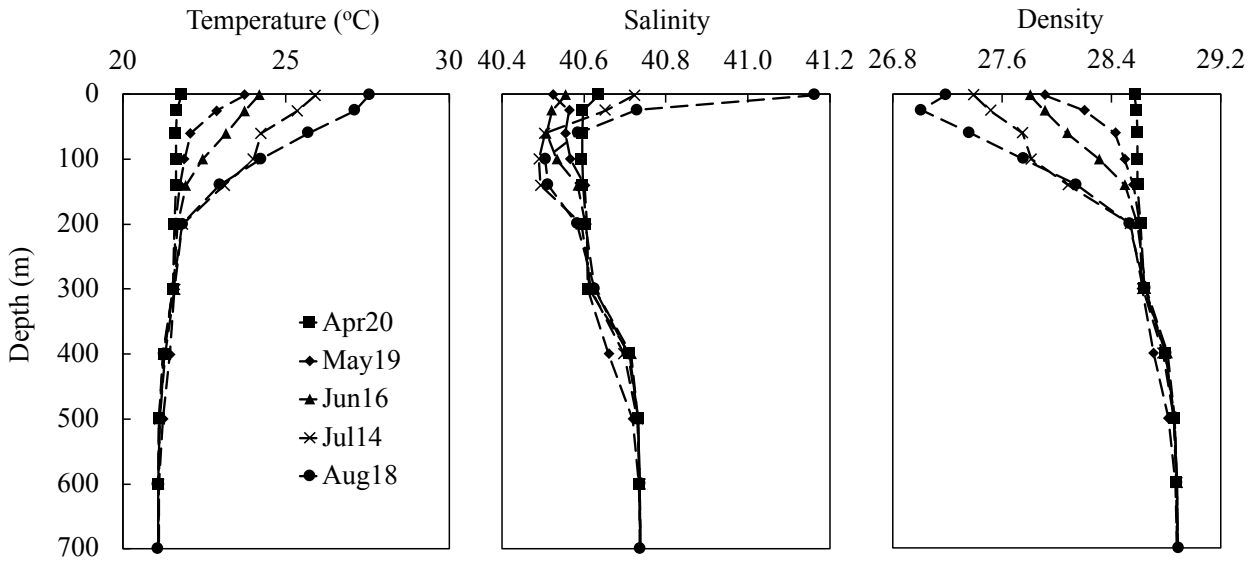
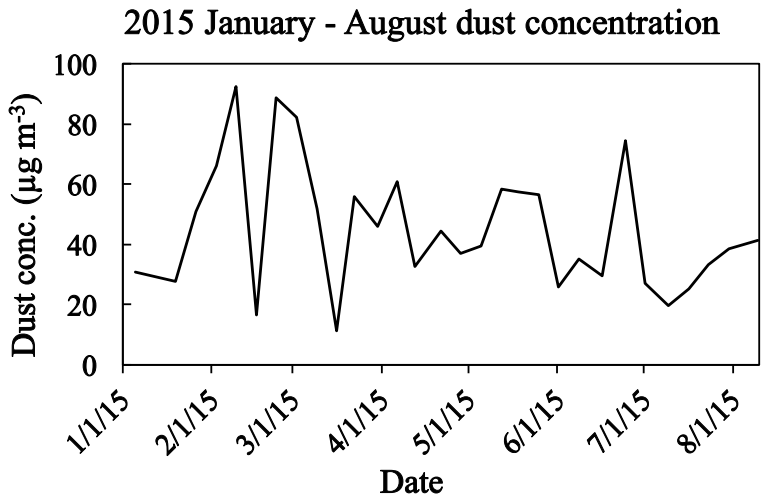


Figure S1. Temperature, salinity and density at Station A in the GOA from April to August 2015.



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94 Figure S2. TSP loads between January and August 2015. Data taken from Israel Ministry of

95 Environmental Protection (http://www.svivaaqm.net).[5]

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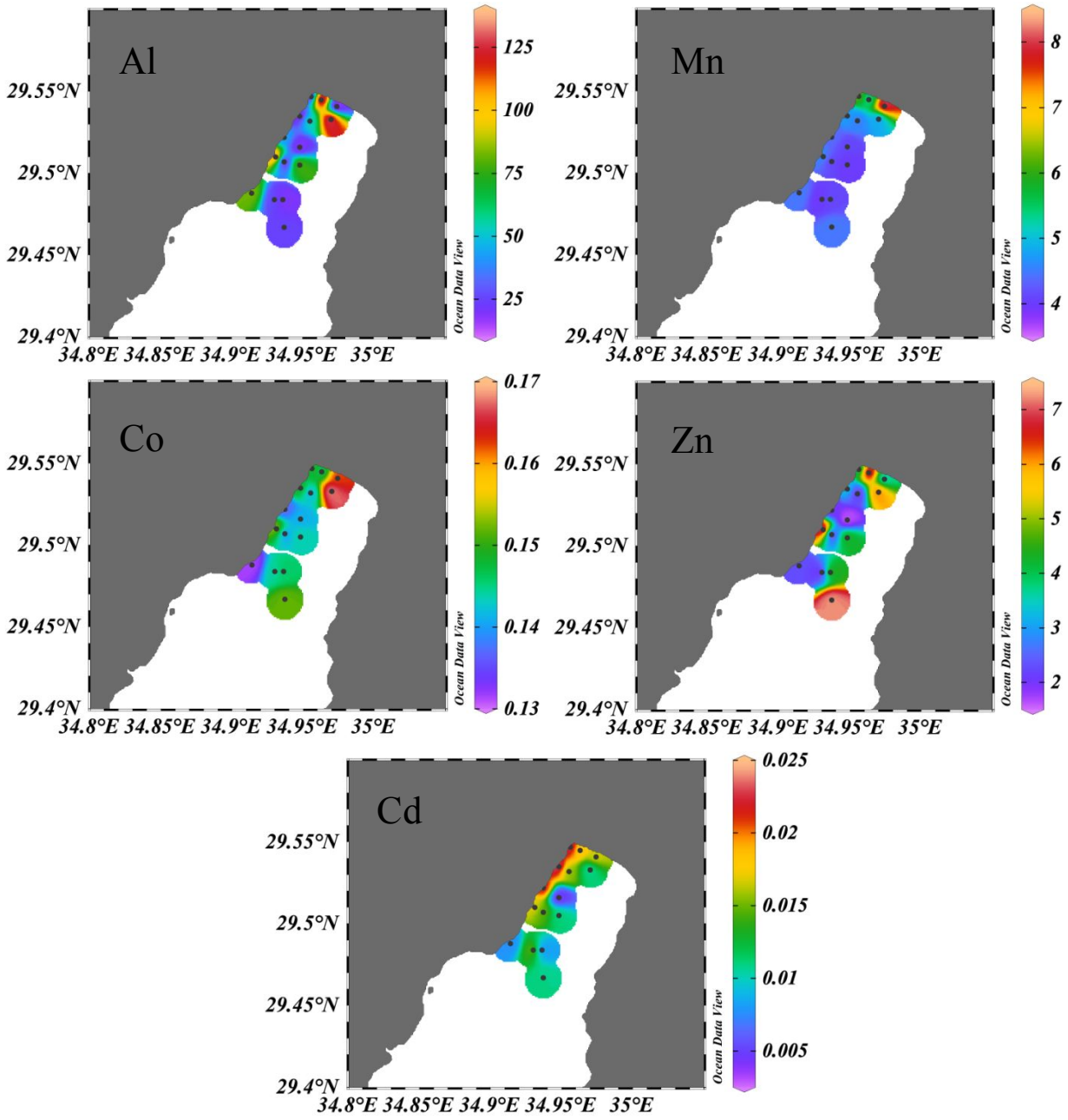

Figure S3. Trace metal (Al, Co, Mn, Zn and Cd) surface concentrations in the GOA in 2015

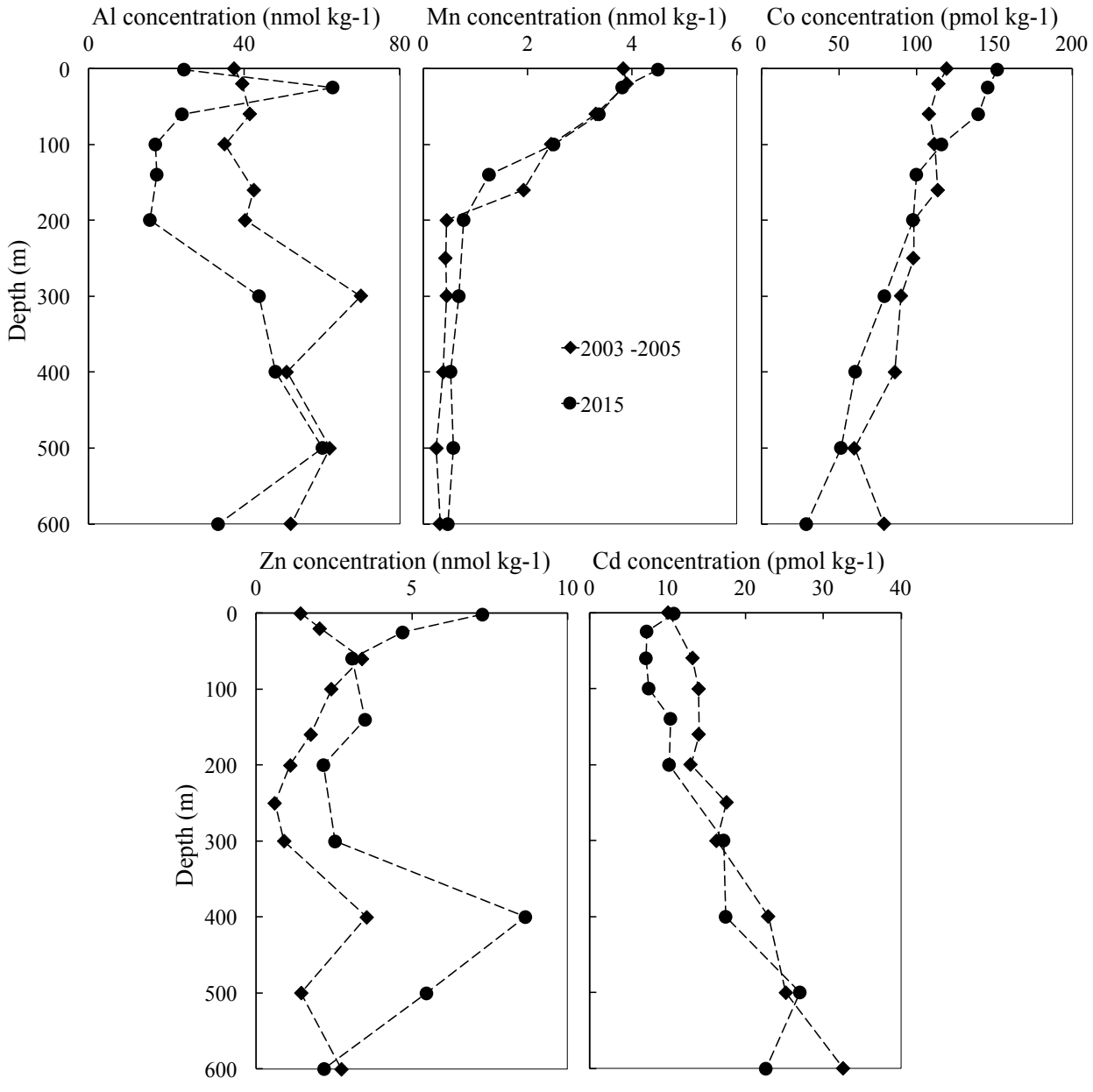

Figure S4. Trace metal (Al, Co, Mn, Zn and Cd) profiles at station A in GOA in 2015 (this study, circles) and averaged values between 2003 – 2005 (diamonds) from Chase et al.[6]

Supporting Information Reference

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